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Hydrocarbon potential of the Voltaian basin of Ghana, West African Craton: Implications based on organic geochemistry and clay mineralogy

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Abstract
A preliminary investigation of the hydrocarbon potential of the Voltaian basin of Ghana, based on sedimentology and organic geochemistry of outcrop samples. Unlike other Precambrian basins, the hydrocarbon potential of the Voltaian basin is still poorly known. Inorganic geochemistry proxies show the basin has good hydrocarbon potential although further work is required. This paper aims at providing additional information to the ongoing discussion on the basin's hydrocarbon. Based on sedimentary structures, the sediments were rapidly deposited in shallow-marine settings. The studied samples are largely poor in OM with TOC < 0.5 wt. % and S2 < 0.2 mg HC/g rock. They are of type II-III and type III kerogen in the Pendjari Formation and Mpraeso areas, respectively. The Pendjari Formation has indications of good source rock that is within the oil window, with Tmax (86 – 139°C) and HI (373 – 452 mg HC/g TOC) values, the Mpraeso (> 460°C and < 50 mg HC/g TOC) shales are overmature with dry gas potential. The calculated %Ro < 1.0 and > 1.1 also suggest mature source rock with oil-gas potential and post-mature source rock of dry gas generation potential for the Pendjari Formation and Mpraeso area, respectively. The clay mineralogy largely suggests immature organic matter in the shales, with the absence of illite. The grey shales of the Pendjari Formation probably form a thick sequence and their hydrocarbon potentials are worth further using drill core samples.

Keywords
Sedimentology; organic geochemistry; clay mineralogy; hydrocarbon potential; Voltaian basin; Ghana

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1. Introduction

Hydrocarbon exploration in Precambrian sedimentary basins has been given less attention compared to Phanerozoic sedimentary basins due to their overmatured organic matter (OM) coupled with long evolution history (Shi et al. 2020). However, following recent oil and gas discoveries with TOC content >1.0 wt.% in the Precambrian basins of Algeria, Australia, China, India, Oman, Libya, Namibia, Russia, and Pakistan, the search for hydrocarbons in Precambrian basins has been enhanced (Tang et al. 2019; Shi et al. 2020). The aforementioned discoveries have turned the focus of research on petroleum potential toward Precambrian petroleum systems globally (Chen et al. 2019; Wang et al. 2019; Wang et al. 2020). Notwithstanding the recent interest in the petroleum systems of Precambrian basins, the characterization of the source rocks of these basins remains uncertain to a large extent (Craig, Thurow, Whitham and Abutarruma, 2009; Craig, Grigo, Rebora, Serafni and Tebaldi, 2010; Chen et al., 2018; Yang, Zhou, Peng, Song and Kou, 2020; Shi et al. 2020).

The Voltaian basin of Ghana is one of the Precambrian basins of the West African Craton (WAC) (Affaton, Sougy and Trompette, 1980; Goodwin, 1996). For other sedimentary basins, Tindouf and Taoudeni of the WAC, hydrocarbon potential has been assessed and proven these two basins (Craig et al., 2010). The Voltaian basin in contrast has received very little effort toward understanding the basin's hydrocarbon potential. Early work by Abu, Ehinola, Adeleye, Asiedu and Nunoo (2022) suggested that the paleoredox conditions and sedimentation rates in the Voltaian basin could have favored preservation of organic matter in shales.

The standard and widely used method for the assessment of the hydrocarbon generation potential of probable source rocks in sedimentary basins is organic geochemical analysis. This technique provides information on organic matter type/kerogen type, thermal maturity, and organic matter quality of potential source rocks (Makeen et al., 2014; Luo, George, Xu and Zhong, 2016; Silva, Carlisle and Wach, 2017; Ordonez et al. 2019). Anoxic marine environments are commonly developed in the deeper parts of marine environments characterized by low-energy eddies, which are hence the areas for argillaceous material to settle (Turker, 2004). In these marine settings, there is limited to no oxygen to support the survival of zooplankton, which feeds on phytoplankton (source of OM) (Khan et al. 2022), hence the accumulation and preservation of OM in these environments. Subsequently, OM and clay minerals coexist in these marine settings (Jiang, 2012; Al-Juboury et al. 2020). For this reason, clay mineralogy of shales and carbonates has been widely used as a tracer of OM preservation in source rock evaluation over the years (Pollastro, 1993; Weaver, 2006; Srodon, 2009; Jiang, 2012; Al-Juboury et al. 2020).

This study is a result of the multidisciplinary approach to the preliminary investigation of the hydrocarbon potential of the Voltaian basin. This study integrates sedimentology, organic geochemistry, and mineralogy of outcrop samples of the Voltaian basin for the first time to assess the hydrocarbon potential of the basin.

2. Geological Setting

The Voltaian basin of Ghana (Figure 1) is largely a flat-lying sedimentary basin that covers most of the central part of Ghana extending over about 105,000 km2 of the total land area of the country (Anani, Abu, Kwayisi and Asiedu, 2017). The basin is generally accepted to contain three major groups of Kwahu-Bombouaka, Oti-Pendjari, and Tamale-Obosum groups (Carney et al. 2010).

The Kwahu-Bombouaka Group unconformably overlies the Paleoproterozoic Birimian crystalline rocks (Carney et al. 2010). The group consists of three formations. The Tossiegou Formation with a characteristic dominant ripple-marked sandstone basement crystalline rocks (Anani et al. 2017). On the top of the Tossiegou Formation is the Poubogou Formation, which contains shales, sandy shales, and some siltstones and mudstones. The observed black shales (Figure 3C; Table 1) in the southeastern part of the basin, which is reported herein for the first time, are believed to belong to this formation. The Panabako Formation is the uppermost formation of the group above the Poubogou Formation, with characteristic feldspathic and quartzitic sandstones (Affaton et al. 1980; Carney et al. 2010; Abu, 2018; Abu, Adeleye, Ehinola and Asiedu, 2021) (Table 1).

The Oti-Pendjari Group is divided into two formations, Kodjari and Pendjari. The Kodjari Formation is characterized by carbonates, cherts, mudstone/argillite in the Buipe and Fumbisi areas of the basin and the Pendjari Formation (in the Yendi and Sabari areas) consists of dark-grey and greenish-grey shales (Abu et al. 2022).

The uppermost Tamale – Obosum Group is undifferentiated with red sandstones (Tamale red beds; Affaton et al. 1980; Anani et al. 2017), sandstones, argillaceous materials, and conglomerates (conglomerates), being the main lithological components of the group (Carney et al. 2010).

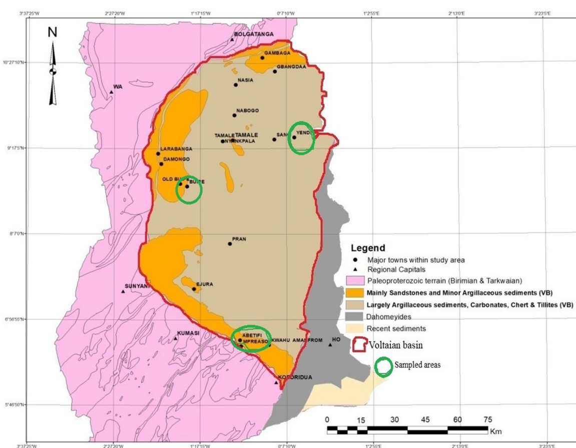

Figure 1. The Geological map of Ghana with the Voltaian basin and sampled areas shown.

Table 1. The lithostratigraphic sequence of the Voltaian basin with the sampled formations shown (modified after Abu et al. 2021).

GEOLOGICAL TIME		GROUP	FORMATION	LITHOLOGY	This Study	THICKNESS	
Paleozoic 450 – 320 Ma	Ordovician - Carboniferous	Tamale-Obosum		Sandstones, Conglomerates, shales, and mudstones	Not studied	∼ 400 m	∼5 – 7 km
	Unconformity; erosion or non-deposition or peneplanitization						
Neoproterozoic 675 – 600 Ma		Ediacaran	Oti-Pendjari	Pendjari	Shales and mudstones	Massive, greenish-grey and grey–dark–grey shales	∼ 1058 m
	Late Cryogenian		Kodjari	Carbonate, cherts, and tillites	Carbonates, argillaceous material (mudstone), cherts	∼ 40 m	
	Unconformity; erosion or non-deposition						
Late Mesoproterozoic 1100/ 1034/ 993 Ma		Kwahu/Bombouaka	Panabako	Sandstones	Sandstones	∼ 600 m	
			Poubogou	Sandy shales, shales, mudstones	black shales (Mpraeso-Ebetifi area), greenish and red shales (Ejura area)	∼ 260 m	
			Tossiegou	Sandstones	Not seen	∼ 500 m	
	Angular unconformity						
	Basement: Paleoproterozoic Birimian rocks						

3. Samples and Methods

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3.1 Sampling

Fieldwork was conducted in the Yendi-Sabari, Buipe, and Mpraeso areas (Figure 1). Observations based on field exposures are presented in Figure 2. The samples for the hydrocarbon potential assessment are outcrop samples of grey and black shales from the Pendjari Formation and the Kwahu Group of the Mpraeso area, respectively. Carbonate samples of the Kodjari (Buipe) Formation from the Buipe area were also included for analysis. 24 samples were initially submitted to the laboratory, initial visual assessment of the samples showed that they were poor in OM, some were greenish and greenish–grey in color. Generally, relatively fresh samples from the Pendjari Formation were collected by digging to a depth of about (0.5 m) below the surface using a chisel and geological hammer. Eight grey – greenish grey samples were collected from the formation. A road cut at the Mpraeso area exposes a black shale unit, and 2 relatively fresh samples were collected by chiseling off the exposed altered surface using a chisel and a geological hammer (Figure 3C). The 4 carbonate samples (Figure 3D) were collected from freshly exposed units within the Buipe area where the Savana cement factory is currently mining the carbonates for cement production. After physical assessment of the samples, 5 outcrop samples were submitted to GeoMark laboratory Ltd. in Texas, USA due to the generally poor TOC content of the samples.

3.2 Laboratory Analysis

Crushed and pulverized whole-rock samples were prepared and submitted for Source Rock Analysis and TOC content analysis to GeoMark laboratory Ltd. Source Rock Analysis was performed at GeoMark research using HAWK pyrolysis technique on samples AMM001, AMM003, AMY001, AMY011, and AMY006 using standard conditions; %TOC of these samples was determined by decarbonating the rock powders and analyzing on a LECO C230 instrument, following procedures described by Zumberge, Don and Gordon (2020). For all other samples, %TOC was determined by Elemental Analysis at the SIFIR laboratory at UCR. Sample powders were decarbonated with 6N HCl followed by repeated rinsing/centrifuging/decanting and then drying. The concentration of total organic carbon was measured using a CostechTM 4010 Elemental Analyzer (EA) coupled to a Thermo FinniganTM Delta V Advantage isotope-ratio mass-spectrometer via an open-split interface (ConFlo IV, Thermo FinniganTM). Two intra-laboratory standards (acetylene and glycine) were analyzed before, between, and after unknowns in each run. To monitor the quality of sample preparation and analysis performance, the international standard USGS Devonian Shale SDO-1 was treated and analyzed as an unknown. The potential yield (PY), production index (PI), migration index (MI), and vitrinite reflectance (%Ro) were estimated from equations shown as a footnote in Table 2, and %Ro from %Ro = $(0.0180 \times \text{Tmax}) - 7.16$ (Javie et al., 2001).

4. Results and Discussion

4.1 Depositional setting of the studied units

Sedimentary features that constrain sediment depositional process and environment were observed around the Yendi-Sabari (Figures 2A to 2D) and the Mpraeso-Ebetifi areas (Figure 2E). Thick (> 50 m), parallel laminated grey shales sequence and cross-laminated greenish-grey shales were observed at the Sabari (Figures 2A and B) area of the Pendjari Formation. Climbing ripples together with disrupted lamination and ripple marks were also observed at the outskirt of Yendi (Figure 2C). In the Kwahu areas, parallel laminations of black shales (Figure 2E) were observed in the Mpraeso-Ebetifi area.

The thick sequence of uninterrupted dark-grey shale at the Sabari area of the Pendjari Formation (Figure 2A) supports a continuous sediment supply from sediment-laden currents. This sedimentation process could have been possible in a low-energy marine environment, thus a possible fluviatile environment (Haruna, Dio, Maunde and Raji, 2013). The observable cross laminations facies of the greenish-grey shales (Figure 2B) are associated with thick dark-grey facies sequence, this suggests a fluvial environment for these argillaceous sediments (Abu, 2018). Shales with both cross laminations and ripple marks are indicative of a fluvial marine setting (Dorrik and Stow, 2005; Haruna et al. 2013). Climbing ripples according to Dorrik and Stow (2005), are proxies for rapid sedimentation of sediments from sediment-laden currents. The association of the disrupted laminations, which are indicative of the collapse of micro-ripples, with the climbing ripples in the Yendi area (Figure 2C), supports a rapid sedimentation process for these sediments. The ripple marks (Figure 2D) are also evidence of a shallow-marine environment with wave dominance during sedimentation. The parallel lamination of the black shales at the Mpraeso-Ebetifi area corroborates Abu's (2018) interpretation of the depositional environment of the shales and sandy shales of the Kwahu-Bombouaka Group equivalents in the northwestern part of the basin, the Gambaga-Nakpanduri areas.

The depositional environment of the argillaceous sediments observed in the Pendjari Formation and the Kwahu Group is that of a shallow-marine environment with wave action to that of a fluvial environment where the sedimentation process in these environments was rapid. This sedimentary, shallow-marine environment was most probably oxygenated where organic matter was efficiently oxidized or consumed by other zooplanktonic organisms, and hence not preserved. This setting may be the reason for the high oxygen index values (Table 2). The rapid sedimentation of the sediments in these environments could have favored the rapid burial of the supplied OM to these environments, and as such could have helped to preserve OM from remineralization by heterotrophs. This interpretation corroborates the inorganic geochemistry indication of a positive and significant correlation between TOC and paleodepth depositional environment proxy (Fe/Mn), and sedimentation rate proxy (Ce/Tm) (Abu et al. 2022).

Figure 2. Field photos from the Yendi-Sabari and Mpraeso areas of the Pendjari Formation and parts of the Kwahu Group

A, thick, black shale unit exposed at the Sabari area of the Oti river, B = cross laminations at the eastern outskirt of Sabari, C, climbing ripple (right of scale – in red lines) and disrupted lamination (left of scale – in green lines) exposed at Yendi area (pick-axe scale = 55 cm, human scale = 172 cm), D, ripple marks at the outskirt of Yendi towards Sabari and E, parallel-laminated black shales (within red lines) at Mpraeso-Ebetifi.

4.2 Organic Geochemistry

The results show that all the samples submitted for analysis have TOC (wt%) content < 0.5 wt% with the maximum TOC content being 0.32 wt% (Table 2). These values indicate that the samples (Figure 4) are poor in OM content and are hence not suitable for Rock-Eval pyrolysis evaluation. Despite this poor OM content, 5 samples with TOC content in the range of 0.07 – 0.32 wt%, which includes 3 samples of the Pendjari Formation and 2 samples of the Mpraeso area of the Kwahu Group were submitted for Rock-Eval pyrolysis, following the analytical procedure of Hamiki et al. (2018). The samples studied have TOC values within the range of 0.00 – 0.32 wt%, with S1 values between 0.05 – 0.13 mg HC/g rock and S2 values within the 0.07 – 0.10 range (Table 2). The S3, Tmax, HI, and OI values are within the ranges of 0.22 – 0.36 mg HC/g rock, 373 – 469oC, 31 – 138 mg HC/g TOC, and 111 – 542 mg HC/g TOC respectively (Table 2). The migration index (MI), PI, and PY are also within the ranges of 16 – 181, 0.33 – 0.57, and 0.12 – 0.15, respectively. The calculated vitrinite reflectance (%Ro) values are between 0.01 – 1.28 for the grey shales of the Pendjari Formation and the black shales of the Mpraeso area (Table 2).

Figure 3. Hand specimen of samples analyzed

A and B, are shales from the Sabari and Yendi areas, respectively, C, is the black shales of the Mpraeso area and D, the limestone of the Buipe area.

4.3 Source rock characterization

The TOC, S2, PY, and Tmax are the often-used parameters in characterizing source rock organic matter (OM) richness and quality with implications for hydrocarbon generation (Peters and Cassa, 1994; Hakimi et al., 2018). TOC of < 0.5 wt% is typical of source rocks with poor OM content (Tissot and Welte, 1984; Hunt, 1996), whereas source rocks with TOC content between 0.5 and 4 wt% or above are considered to be source rocks with fair to excellent OM content, with the potential of generating hydrocarbons under favorable conditions suitable for OM transformation (Tissot and Welte, 1984; Alizadeh, Sarafdokht, Rajabi, Opera and Janbaz, 2012; Al-Selwi and Joshi, 2015). The samples studied have TOC content that is < 0.5 wt%, with the TOC content within the range of 0.7 – 0.32 wt% (Table 2), meaning that the OM content of the outcrop samples is indicative of very poor to lean OM source rocks in the Pendjari Formation and Mpraeso area.

The S2 content is a proxy for source rock characterization with S2 < 2.5 mg HC/g rock, indicative of a source with poor OM matter content and poor hydrocarbon generation potential and > 4 mg HC/g rock indicative of good source rock with good prospects for hydrocarbon generation (Al-Selwi and Joshi, 2015). The samples of the Voltaian basin (Table 2) with S2 values < 0.2 mg HC/g

Table 2. Search strings used for the study (Search string combinations)

Sample ID	Group/ Formation	Type of Sample	TOC	S1	S2	S3	Tmax	%Ro	HI	OI	HR	MI	PI	PY
				Rock-Eval pyrolysis data										
AMM001	Kwahu	Black shale	0.32	0.05	0.10	0.22	462	1.16	31	69	0	16	0.33	0.15
AMM003	Kwahu	Black shale	0.21	0.05	0.09	0.23	469	1.28	43	111	0	24	0.36	0.14
AMY011	Pendjari	Grey shale	0.09	0.04	0.08	0.28	436	0.69	87	304	0	43	0.33	0.12
AMY001	Pendjari	Grey shale	0.07	0.13	0.10	0.39	373	0.01	139	542	0	181	0.57	0.23
AMY006	Pendjari	Grey shale	0.08	0.07	0.07	0.26	452	0.98	86	320	0	86	0.50	0.14
AMY002	Pendjari	Grey shale	0.04											
AMY003	Pendjari	Greenish-grey shale	0.08											
AMY005	Pendjari	Greenish-grey shale	0.03											
AMY007	Pendjari	Greenish-grey shale	0.02											
AMY008	Pendjari	Greenish-grey shale	0.03											
AMY009	Pendjari	Greenish-grey shale	0.05											
AMY010	Pendjari	Greenish-grey shale	0.04											
AMY011	Pendjari	Greenish-grey shale	0.06											
AMY012	Pendjari	Greenish-grey shale	0.04											
AMY013	Pendjari	Greenish-grey shale	0.02											
AMY014	Pendjari	Greenish-grey shale	0.02											
AMY015	Pendjari	Greenish-grey shale	0.05											
AMY016	Pendjari	Greenish-grey shale	0.02											
AMY019	Pendjari	Greenish-grey shale	0.01											
AMY020	Pendjari	Massive greenish-grey shale	0.01											
AMB016	Kodjari	Limestone	0.05											
AMB017	Kodjari	Limestone	0.03											
AMB025	Kodjari	Limestone	0.06											
AMB026	Kodjari	Limestone	0.06											

TOC = Total organic carbon content, wt% PY = Potential yield, S1+S2 (mg/g rock). S1 = Volume of hydrocarbon content, mg HC/g rock HR: Hydrogen richness, S2/S3 mg HC/mg CO2 S2 = Hydrocarbon generation potential remaining, mg HC/g rock MI: Migration index, S1/TOC S3 = Carbon dioxide yield, mg HC/g rock %Ro = Vitrinite reflectance Tmax = Temperature of S2 peak HI = Hydrogen index (S2 x 100/TOC), mg HC/g rock OI = oxygen index (S3 x 100/TOC), mg HC/g rock PI = Production index, S1/(S1+S2) rock indicate that the probable source rocks under consideration are of poor quality. The values of the oxygen index of the samples (Table 2) are high. This is indicative of probably oxidized source rocks in the shallow-marine settings as independently indicated by sedimentologic observations.

The bivariate discriminant plots for source rock characterization (Figure 4) show that the samples of the grey shales of the Pendjari Formation are indicative of poor to fair source rock with the potential of generating gas. The Mpraeso area black shale samples plot in the zone of fair to good source rocks with gas generation potential (Figures 4A and B). The outcrop samples generally show poor hydrocarbon generation potential from the PY versus TOC plot (Figure 4C).

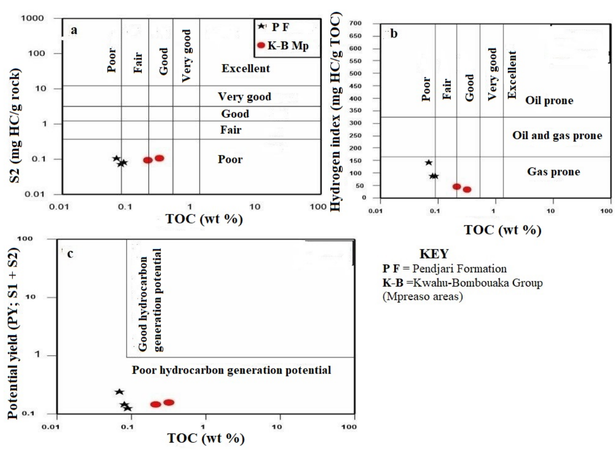

Figure 4. Bivariate plots characterizing the probable source rocks (A and B) of the Voltaian basin with hydrocarbon generation implication (C) using S2, TOC, HI, PY, and Tmax.

The effect of physical and chemical alteration processes on outcrops of potential source rocks has made the use of outcrop samples for hydrocarbon source rock evaluation a last resort (Emmings et al. 2017). However, the Voltaian basin is a frontier Neoproterozoic sedimentary basin without drill cores or trenches to explore its hydrocarbon potential; therefore, this pioneering work had to use outcrop samples, despite possible alteration effects on them, in assessing the basin's hydrocarbon potential. The poor to very lean OM content could be accounted for by physical and chemical alteration processes at the outcrop scale, which have the tendency of reducing the OM content in outcrop samples.

The depositional environment also plays a pivotal role in OM preservation within sedimentary basins. Shallow-marine, oxidized environments (as evidenced by high OI values in Table 2) and also from inorganic geochemical results (Abu et al. 2022), allow heterotrophs to thrive and feed on the supplied organic materials; hence, OM depletion in such environments. Thus, deposition in a shallow-marine, oxygenated environment could have also led to the low quantity of organic matter in these deposits. This interpretation corroborates the sedimentological observations (Figure 2) in the area. The results (Table 2) and the bivariate plots (Figure 4) show that the samples are generally poor in TOC content; however, it is too early to preclude the hydrocarbon potential of the Voltaian basin from this data. The Pendjari Formation with grey shales (Figure 3A) having a reasonable thickness (Figure 2A), is worth drilling so that drill core samples could be collected for further investigation.

4.4 Kerogen type

The type of kerogen determines the quality of the OM and the type of hydrocarbon, thus oil or gas generation potential from source rocks with a significant amount of OM content. The kerogen type also shows the source of the organic matter. The TOC, S2, OI, and HI have been used over the years to characterize the kerogen of OM (Hakimi and Abdullah, 2013; Makeen, Abdullah, Hakimi and Mustapha, 2014; Osli, Shalaby and Islam, 2018; Ordonez et al. 2019). Source rocks with HI $>$ 600 mg HC/g TOC, 300 – 600 mg HC/g TOC, 50 – 200 mg HC/g TOC, and $<$ 50 mg HC/g TOC indicate kerogen type I, II, III, and IV, respectively (Alizadeh et al., 2012). HI values for the grey shales of the Pendjari Formation are between 87 and 139 mg HC/g TOC, whereas those of the Mpraeso area range between 31 and 43 mg HC/g TOC. These results are indicative of kerogen type III and type IV for the Pendjari Formation and the Mpraeso area, respectively (Table 2). The bivariate plots of S2 versus TOC and HI versus O1 (Figure 5) indicate kerogen type II-III and type III for the grey and black shales, respectively (Figures 5A and B). The organic matter of these kerogen types might correspond to terrestrial organic matter according to McCarthy et al. (2011), however extensive and voluminous biosphere was lacking on landmasses in the Neoproterozoic.

4.5 Maturation

Hydrogen index (HI) together with Tmax and %Ro have been used as effective proxies for source rock maturity and hydrocarbon (oil/gas) generation potential. HI $<$ 200 with $>=$ 500 mg HC/g TOC and HI $>$ 200 with $<=$ 300 mg HC/g TOC are indicative of source rocks with gas and oil generation potential, respectively (Peters and Cassa, 1994; Alizadeh et al. 2012; Makeen et al. 2014; Mishra et al. 2016). Tmax values $<$ 435°C, 435 – 460oC, and $>$ 465°C are indicative of immature, mature with oil generation potential, and overmature without wet gas generation potential conditions, respectively. Vitrinite reflectance (%Ro) values of 0.8 – 1.1, 1.1 – 1.5, and $>$ 1.5 are suggestive of mature source rock with oil generation potential, mature source rock that is suitable for oil and gas generation, and overmature source rock with only dry gas, but without wet gas generation potential, respectively

(Jarvie, Claxton, Henk and Breyer, 2001; Mishra et al. 2016). The HI values of the Pendjari Formation are between 87 and 139 mg HC/g TOC (Table 2), which indicates those samples are immature for hydrocarbon generation. Those from the Mpraeso area have HI of 31 and 43 mg HC/g TOC, which are indicative of immature OM (Table 2). The Tmax values within the range of 373 – 452°C for the Pendjari Formation agree well with other indicators that the samples contain immature to mature OM. The samples of the Mpraeso area reached the post-maturation stage with Tmax values of 462 to 469°C (Table 2). The %Ro (calculated) values of the grey shales are < 1 with values between 0.01 and 0.98 pointing to samples within the oil-gas maturation window and > 1 %Ro values for the Mpraeso area (1.16 and 1.26). The < 1.5 %Ro of the black shale samples suggests their gas generation potential. The %Ro however needs further characterization with organic petrography. Hence, although the organic geochemistry data indicates oil and gas generation potential based on %Ro values, this may not be conclusive as a guide in a decision-making process. Dellisanti, Pini, Tateo and Baudin (2008), based on the PI, classified source rocks into mature and immature with < 0.1 and > 0.4 implying thermally immature and thermally mature source rocks, respectively. The outcrop samples of the Voltaian basin (Table 2) show thermally immature values for 3 samples (1 sample of the Pendjari Formation and 2 samples of the Mpraeso area) with PI < 0.4, whereas the other 2 grey-shale samples are thermally mature with PI > 0.4 (table 2).

The samples studied plot within the oil and condensate generation fields with an indication for a gradient from immature to increasing maturity for the Pendjari Formation shales (Figures 4C and D). The Mpraeso area black shales plot in the dry gas generation zone with much higher maturity implications (Figure 5D). This trend of the plots suggests that the Pendjari Formation shales are immature to mature and within the oil and wet gas generation window. The degree of preservation of the OM of this formation suggests that it is worth considering it for further studies since the OM is not overmature for effective hydrocarbon generation.

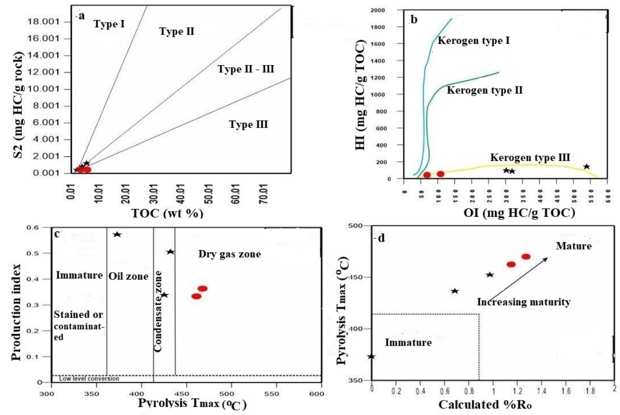

Figure 5. Kerogen types (A and B) and maturity of organic matter with implication for oil and gas generation (C and D) bivariate plots for the studied samples.

4.6 Hydrocarbon Potential

Although the TOC content of the basin is generally low, it is premature to preclude the basin's hydrocarbon potential. There are some indications that the basin has fair – good source rocks in the Pendjari Formation with the potential to generate oil and wet gas, although further work is required. Unlike the Mpraeso black shales, the Pendjari Formation grey shales plot within the maturation window with type II-III kerogen that could generate oil and gas. Migration index (MI) > 2 is indicative of the contribution of free hydrocarbons from other sources, probably from other geological units according to Alizadeh et al. (2012). The MI of the samples is between 16 and 181, with higher MI values > 50 recorded by the Pendjari Formation (Table 2). This suggests a possible migration of hydrocarbons from deeper levels within the grey shale formation upwards to the upper stratigraphical level of the outcrops at the surface. This assertion corroborates with Figure 5 showing that the OM source is the same type II-III (Figure 5A) without contamination (Figure 6A) from other, extraneous OM sources. This agrees with their high MI values (Table 2). Hence, drilling to obtain core samples from deeper levels of the formation will help provide a much better insight into the formation's hydrocarbon potential. Although much work needs to be carried out on the basin regarding its hydrocarbon potential, it can be inferred from this study that it is too early to preclude the hydrocarbon potential of the basin based on the data presented herein.

The production index (PI) of the source rock is considered to be good when the PI values are greater than 0.05 – 0.1, according to Hunt (1996) and Mishra et al. (2016). The analyzed outcrop samples have PI values in the range of 0.33 to 0.57 with the higher PI values recorded in the Pendjari Formation (Table 2). The PI values support the point that notwithstanding the low

TOC values, the hydrocarbon potential of the Voltaian basin is worth further exploring.

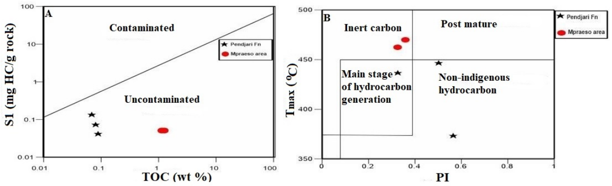

Figure 6. Bivariate plot indicating the effect of external input (A) on the existing OM and the source (B).

4.7 Clay mineralogy

The samples analyzed using the XRD method indicate the presence of albite, phengite, quartz, kaolinite, muscovite, and cronstedtite in the shales (Figures 7a – d), whereas the carbonate samples show the presence of dolomite, calcite, and quartz (Figures 7e and f). Clay minerals, like smectite, kaolinite, and illite, are a result of chemical alteration of feldspars; e.g., albite and microcline. Clay minerals and OM have been shown to positively correlate, and they coexist in marine settings (Jiang, 2012). The clay minerals: kaolinite, cronstedtite (kaolinite-serpentine group), and muscovite form the minority group of the sedimentary minerals in our samples (Figure 7), suggesting the low degree of chemical alteration of the feldspars e.g., albite and other potassium-bearing feldspars in the shales.

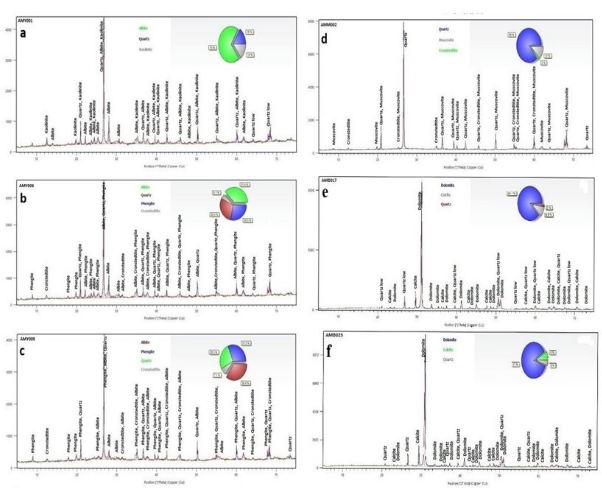

Figure 7. XRD mineralogical characterization of the studied shales and carbonates of the Voltaian basin; grey shales (a-c), black shales (d), and carbonates (e & f).

The process of smectite transformation to illite through the process of illitization correlates with OM maturation and migration, according to Pollastro (1993), Srondon (2009) and Jiang (2012). In the chemical alteration cycle of clays with K-felspar origin, kaolinite is formed before illite with an increasing degree of chemical alteration. The presence of kaolinite and cronstedtite and the absence of illite is an indication of a weaker alteration process of the kaolinite to have converted it into illite. The development of illite also marks the beginning of OM maturation (Pollastro, 1993; Al-Juboury et al. 2020), hence the absence of illite in the clay-mineral suite (Figure 7) could be attributed to immature OM due to insignificant heating, and thus limited hydrocarbon migration.

The mineralogical study suggests an immature OM of the shales, hence with suitable temperature conditions necessary for the OM transformation, the shales could generate some amount of hydrocarbons. This, however, is at variance with the inferences from the organic geochemistry.

The carbonates have very low clay mineral content; coupled with their low OM content this lithology is probably not suitable as a source rock in the Voltaian basin. Clay-mineral presence in the probable reservoir rocks, such as carbonates, could affect their effective porosity, hence the absence of clay minerals in the carbonates makes them more suitable as reservoir rocks. The organic geochemistry of the carbonate samples shows very low OM content, which is consistent with the absence of clay minerals in them.

5. Conclusion

The sedimentation in the study area of the Voltaian basin occurred rapidly from sediment-laden currents. The depositional environment was that of a dominant shallow-marine environment with the wave present and with a subordinate fluvial environment. Organic matter preservation was likely restricted by OM scavengers who thrived in this shallow-marine environment with dissolved oxygen. The organic geochemistry of outcrop samples from the Voltaian basin shows that the probable source rocks had low OM content with TOC content varying between 0.0 and 0.32 wt%. The Rock-Eval pyrolysis parameters, Tmax, HI, OI, and %Ro, indicate that the kerogen types are mainly type II-III and type III for the Pendjari Formation shales and the Mpraeso area black shales, respectively. The Pendjari Formation grey shales are generally fairly to well-mature source rocks with the potential of generating oil and wet gas. PI values suggest that the Voltaian basin is suitable for hydrocarbon generation. The Mpraeso black shales are at the post-mature stage of OM evolution with the potential of only generating dry gas. The MI values also suggest that the poor to lean hydrocarbon shows might have migrated from other geological units, with higher MI values recorded by the Pendjari Formation. The basin, based on this preliminary investigation, is not enough to conclude its hydrocarbon status and potential without further studies. Low content of clay minerals in the carbonates of the basin agrees with the low OM content of the carbonates, which lack clay minerals. For the shales, although further studies are required, their OM is largely immature and hence partially agrees with the organic geochemistry conclusions for some samples.

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References

[1] Abu, M. (2018). Sedimentary facies & depositional environments of the Neoproterozoic sediments of the Gambaga-Nakpanduri massifs, Volta basin. Journal of Geology and Mining Research, 10(5), 48–56.

[2] Abu, M., Adeleye, M. A., Ehinola, O. A. & Asiedu, D. K. (2021). The hydrocarbon prospectivity of the Mesoproterozoic–Paleozoic intracratonic Voltaian Basin, West African Craton, Ghana. Journal of Petroleum Exploration and Production Technology. https://doi.org/10.1007/s13202-020-01036-7

[3] Affaton, P., Sougy, J. & Trompette, R. (1980). The tectono-stratigraphic relationships between the upper Precambrian and lower Paleozoic Volta Basin and the Pan-African Dahomeyide orogenic belt West Africa. Am J of Sci 280:240–248

[4] Alizadeh, B., Sarafdokht, H., Rajabi, M., Opera, A. and Janbaz, M. (2012). Organic geochemistry and petrography of Kazhdumi (Albian–Cenomanian) and Pabdeh (Paleogene) potential source rocks in southern part of the Dezful Embayment, Iran. Organic Geochemistry 49: 36-46

[5] Al-Juboury, A.I., Howard, J., Thusu, B., Nicholsd, G., Vincent, S.J., Kayee, M.N.D & Vautravers, B. (2020). Mineralogy, geochemistry and source potential of shale in the Cambro-Ordovician Khabour Formation, Iraq. J. Afr. Earth Sci. 170, 103901. https://doi.org/10.1016/j.jafrearsci.2020.103901.

[6] Al-Selwi, A. & Joshi, M. (2015). Source Rock Evaluation using Total Organic Carbon (TOC) and the Loss-On-Ignition (LOI) Technique. Oil Gas Res 1: 105. doi: 10.4172/2472- 0518.1000105

[7] Anani, C. Y., Abu, M., Kwayisi, D. & Asiedu, D. K. (2017). Provenance of sandstones from the Neoproterozoic Bombouaka Group of the Volta Basin, northeastern Ghana. Arab. J. Geosci. 10:465. https://doi.org/10.1007/s12517-017-3243

[8] Carney, J. N., Jordan, C. J., Thomas, C. W., Condon, D. J., Kemp, S. J. & Duodo, J. A. (2010). Lithostratigraphy, sedimentation and evolution of the Volta Basin in Ghana. Precambr Res 18:701–724

[9] Craig, J., Thurow, J., Thusu, B., Whitham, A. & Abutarruma, Y. (2009). Global Neoproterozoic petroleum systems and the emerging potential in North Africa. In: Craig J, Thurow J, Whitham A, Abutarruma Y (eds) Global neoproterozoic petroleum systems: the Emerging Potential in North Africa. Geological Society, London, vol 326, pp 1–24

[10] Craig, J., Grigo, D., Rebora, A., Serafni, G. & Tebaldi, A. (2010). From Neoproterozoic to Early Tertiary: exploring the potential of older and deeper hydrocarbon plays across North Africa and the Middle East. In: Vining BA, Pickering SC (eds) Petroleum geology: from mature basins to new frontiers. Proceedings of the 7th petroleum geology conference, vol 7. Petroleum Geology Conference Series, pp 673–705

[11] Chen, Z.H., Simoneit, B.R., Wang, T.G., Ni, Z.Y., Yuan, G.H. & Chang, X.C. (2018). Molecular markers, carbon isotopes, and rare earth elements of highly mature reservoir pyrobitumens from Sichuan Basin, southwestern China: Implications for PreCambrian- Lower Cambrian petroleum systems. Precambr. Res. 317, 33–56. https://doi.org/10.1016/j.precamres.2018.08.005.

[12] Dellisanti, F., Pini, G. A., Tateo, F. & Baudin, F. (2008). The role of tectonic shear strain on the illitization mechanism of mixed-layers illite–smectite. A case study from a fault zone in the Northern Apennines, Italy. Int J Earth Sci (Geol Rundsch) 97:601–616

[13] Dorrik, A. & Stow, V. (2005). Sedimentary rocks in the field. A colour guide.73 Corringham Road, London NW11 7DL, UK.

[14] Emmings, J. F., Davies, S. J., Vane, C. H., Leng, M. J., Moss-Hayes, V., Stephenson, M. H. & Jenkin, G. R. (2017). Stream and slope weathering effects on organic-rich mudstone geochemistry and implications for hydrocarbon source rock assessment: A Bowland Shale case study. Chemical Geology (2017), http://dx.doi.org/10.1016/j.chemgeo.2017.09.012

[15] Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P. and Paulet, J. (1977). Methode rapide de caracterisation des roches meres, de leur potential petrolier et de leur degree d'evolution. Review of Institute Petroleum 32: 23–45.

[16] Fishman, N. S., Egenhoff, S. O., Lowers, H. A., Boehlke, A. R. and Ahlberg, P. (2019). Pyritization History in the Late Cambrian Alum Shale, Scania, Sweden: Evidence for Ongoing Diagenetic Processes. in W. Camp, K. Milliken, K. Taylor, N.

Fishman, P. Hackley, and J. Macquaker, eds., Mudstone diagenesis: Research perspectives for shale hydrocarbon reservoirs, seals, and source rocks: AAPG Memoir 120, p. 83–102.

[17] Goodwin, A. M. (1996). Principles of Precambrian geology. Academic Press, New York

[18] Hakimi, M.H. and Abdullah, W. H. (2013). Geochemical characteristics of some crude oils from Alif Field in the Marib-Shabowah Basin, and source-related types. Mar. Pet. Geol. 45, 304-314

[19] Hakimi, M. H. and Abdullah, W. H. (2015). Modelling petroleum generation of late Cretaceous Dabut Formation in the Jiza-Qamar basin, eastern Yemen. Mar. Petrol. Geol. 61, 1–13.

[20] Hakimi, M. H., Alaug, A. S., Ahmed, A. F., Yahya, M. M. A., El Nady, M. M. and Ismail, M. I. (2018). Simulating the timing of petroleum generation and expulsion from deltaic source rocks: Implications for Late Cretaceous petroleum system in the offshore Jiza-Qamar Basin, Eastern Yemen. Journal of Petroleum Science and Engineering 170: 620-642

[21] Haruna, I. V., Dio, C. J., Maunde, A. and Raji, A. S. (2013). Provenance and Paleoenvironmental Study of Bima Sandstone in the Upper Benue trough, N.E., Nigeria. Int. Res. J. Earth Sci. 2321-2527. 1(2):1-11.

Hunt, J. M. (1996). Petroleum Geochemistry and Geology. 2nd Edition, W.H. Freeman and Company, New York, 743p

[22] Jarvie, D. M., Claxton, B. L., Henk, F. and Breyer, J. T. (2001). Oil and shale gas from the Barnett Shale, Ft. Worth Basin, Texas. American Association of Petroleum Geologists Bulletin 85: A100 (No. 13 supplement)

[23] Jiang, S. (2012). Clay Minerals from the Perspective of Oil and Gas Exploration. http://dx.doi.org/10.5772/47790

[24] Khan, N., Ullah, W., Siyar, S. M., Wadood, B., Ayyub, T. and Ullah, T. (2022). Hydrocarbon source rock assessment of the shale and coal bearing horizons of the Early Paleocene Hangu Formation in Kala-Chitta Range, Northwest Pakistan. Journal of Petroleum Exploration and Production Technology https://doi.org/10.1007/s13202-021-01433-6

[25] Luo, Q., George, S. C., Xu, Y. and Zhong, N. (2016). Organic geochemical characteristics of the Mesoproterozoic Hongshuizhuang Formation from northern China: Implications for thermal maturity and biological sources. Organic Geochemistry 99: 23-37

[26] McCarthy, K., Rojas, K., Niemann, M., Palrnowski, D., Peters, K. and Stankiewicz, A. (2011). Basic petroleum geochemistry for source rock evaluation. Oilfield Review, 23(2), 32–43

[27] Makeen, Y. M., Abdullah, W. H., Hakimi, M. H. and Mustapha, K. A. (2014). Source rock characteristics of the Lower Cretaceous Abu Gabra Formation in the Muglad Basin, Sudan, and its relevance to oil generation studies. Marine and Petroleum Geology 59: 505 - 516

[28] Mishra, S., Mendhe, V. A., Kamble, A. D., Bannerjee, M., Varma, A. K., Singh, B. D. and Pandey, J. K. (2016). Prospects of shale gas exploitation in Lower Gondwana of Raniganj Coalfield (West Bengal), India. The Palaeobotanist 65: 31–46

[29] Ordoñez, L., Vogel, H., Adatte, T., Sebag, D., Ariztegui, D., Russell, J., Kallmeyer, J., Vuillemin, A., Bijaksana, S., Crowe, S. and Friese, A. (2019). Empowering conventional Rock-Eval pyrolysis for organic matter characterization of the siderite-rich sediments of Lake Towuti (Indonesia) using End-Member Analysis. https://doi.org/10.1016/j.orggeochem.2019.05.002

[30] Osli, L. N., Shalaby, M. R. and Islam, M. A. (2018). Characterization of Source Rocks and Depositional Environment, and Hydrocarbon Generation Modelling of the Cretaceous Hoiho Formation, Great South Basin, New Zealand. Pet Coal; 60(2): 255-275

[31] Pollastro, R.M. (1993). Considerations and applications of the illite/smectite geothermometer in a hydrocarbon-bearing rocks of Miocene in Mississippian age, Clays and Clay Minerals, 41: 119-133.

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

[33] Shi, C., Cao, J., Luo, B., Hu, W., Tan, X. and Tian, X. (2020). Major elements trace hydrocarbon sources in over-mature petroleum systems: Insights from the Sinian Sichuan Basin, China. Precambrian Research. 343: 105726

[34] Silva, R. L., Carlisle, C. A. M. and Wach, G. (2017). A new TOC, Rock-Eval, and carbon isotope record of Lower Jurassic source rocks from the Slyne Basin, offshore Ireland. Marine and Petroleum Geology86: 499-511

[35] Srodon, J. (2009). Quantification of illite and smectite and their layer charges in sandstones and shales from shallow burial depth. Clay minerals, 44, 421–434

[36] Tang, Y., Li, M., Zhu, Q., He, D., Jiang, X., Xiao, H., Shan, J., Kang, W., Leng, J. and Wang, W. (2019). Geochemical characteristics and

origin of hydrocarbons in the Mesoproterozoic reservoirs in the Liaoxi Depression, NE China. Energy Exploration and Exploitation 0(0) 1–15

[37] Tissot, B. P. and Welte, D. H. (1984). Petroleum Formation and Occurrence. Springer, pp. 160– 198.

[38] Tucker, E.M. (2004). Sedimentary rocks in the field. The geological field guide series, 3rd Edn. West SuSESx PO19 8SQ, England Wang, Y., Xu, S., Hao, F., Lu, Y., Shu, Z., Yan, D. and Lu, Y. (2019). Geochemical and petrographic characteristics of Wufeng-Longmaxi shales, Jiaoshiba area, southwest China: Implications for organic matter differential accumulation. Marine and Petroleum Geology 102: 138-154.

[39] Wang, H., Li, Z.W., Liu, S.G., Ran, B., Song, J.M., Li, J.X., Ye, Y.H. and Li, N. (2020). Ediacaran Extension along the Northern Margin of the Yangtze Platform, South China: Constraints from the lithofacies and geochemistry of the Doushantuo Formation. Mar. Pet. Geol. 112. https://doi.org/10.1016/j.marpetgeo.2019.104056. Weaver, C. E. (2006). Possible uses of Clay Minerals in the search for oil.

[40] Yang, F.L., Zhou, X.F., Peng, Y.X., Song, B.W. and Kou, X.H. (2020). Evolution of Neoproterozoic basins within the Yangtze Craton and its significance for oil and gas exploration in South China: An overview. Precambrian Res. 337. doi.org/10.1016/j.precamres.105563

[41] Zumberge, J. A., Don, R. and Gordon, D. L. (2020). "Free and Kerogen-Bound Biomarkers from Late Tonian Sedimentary Rocks Record Abundant Eukaryotes in Mid-Neoproterozoic Marine Communities." Geobiology 18: 326–47. https://doi.org/10.1111/gbi.12378.