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Contribution of Organic Geochemistry and Palynofacies to the Characterization of Organic Matter of Black Shales in Côte d'Ivoire Sedimentary Basin (Northern Gulf of Guinea)

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Abstract: The organic matter contained in the black shales of Cenomanian-Turonian series of Côte d'Ivoire was characterized from pyrolytic analysis at Rock-Eval 6 and palynofaciologic observations under Electron Microscope in transmitted and fluorescent light. The results indicate that black shales mainly contain organic matter of marine origin (type II), sometimes of lacustrine origin (type I) and rarely of mixed origin (type II / III). These organic matter is immature and very fluorescent (IPF = 5). In these rocks, TOCs reach 5% weight, HI is high and OI is low. The black shales of Cenomanian-Turonian series of Côte d'Ivoire are potential source rocks that oil potential reaches 15 mg HC / g of rock.

Keywords: Black shales, Cenomanian, Turonian, organic matter, palynofacies, Côte d'Ivoire

INTRODUCTION

Sedimentary basins today are of great interest because they are place of hydrocarbons accumulation. The anoxic events are the privileged moments of the accumulation of large amounts of organic matter and consequently of hydrocarbons during severe disturbances of certain physicochemical parameters of oceanological environment. Thus, since the 1970s, the anoxic oceanic event 2 (EAO2) Schlanger & Jenkyns[1] has attracted the continuous attention of researchers. According to the work of Thurow *et al.*[2], cited by Soua.[3], the EAO 2, subject of this study is known worldwide has well as demonstrated in Atlantic and Pacific regions but also on the West-Australian margin. During this anoxic event, Black

shales accumulated, under dark-grained fine-grained sediments with sedimentological, geochemical and paleo-ecological characteristics associated with deposits under dysoxic to anoxic Tyson[4].

In Côte d'Ivoire, very few studies were carried out on palaeo-ecological aspect (foraminifera) but also on the sedimentological distribution of black shales by Kouassi *et al.*[5], and Ouattara *et al.*[6], The geochemical aspect of the black shales of Côte d'Ivoire is still poorly understood, whereas according to the definition their geochemical content is also one of the key elements in determining this type of accumulation. The present work attempts to characterize the black shales in the basin, mainly those from the Cenomanian-Turonian interval of an oil well (BENO 2X) from the margin of Abidjan. It addresses the issues of total organic carbon (TOC) content, the type of organic matter (OM) that determines the quality of oil supplied, thermal maturity and oil potential.

MATERIAL AND METHODS

Two complementary methods have been used for the geochemical characterization of black shale organic matter; (i) Rock-Eval pyrolysis and (ii) palynofacies studies performed with the Axioscop 40 natural and fluorescent light optical microscope.

Pyrolysis Rock[7]-Eval 6: is a method for the global characterization of organic matter (M.O) contained in rock samples[4]. It allowed to evaluate the characteristics of the organic matter as well as the oil potential of drilling sample. Cuttings sample (20 g) were subjected to thermal cracking (pyrolysis) and the compounds derived there from were quantified. In the present study, four parameters were considered for the characterization of organic matter and the determination of depositional environment known from the literature [8,9]; namely Total Organic Carbon (TCO) expressed in% by weight, hydrogen Index (HI) expressed in mg HC / g TOC, maximum Temperature (Tmax) in ° C Table IV) and the petroleum potential (S2) in mg HC / g of rock.

NB: Tissot & Welte[10]describeas source-rocks carbonates which have a minimum TOC of 0.3% weight and a value of 0.5% weight for shales.

Palynofacies: The palynofacies Combaz[11] describes the microscopic components of organic matter. It is carried out under the electron microscope with transmitted light (M.E.T) and fluorescent on isolated organic matter. The organic matter of the mineral matrix is isolated by treatment with hydrochloric and hydrofluoric acids [12] followed by the assembly of the solution obtained between blade and lamella. Their study provides information on the conditions and the depositional palaeoenvironments. The petrography of the organic matter at M.E.T allows a qualitative and semi-quantitative estimation of the different macerae including leptinite, vitrinite and inertinites.

Organic matter fluorescence index: The fluorescence analysis of the organic matter was carried out under a fluorescent light microscope. This analysis consists in subjecting the organic matter to the ultraviolet light of the transmitted and fluorescent light microscopy of the AXIOSKOP 40 FL type in order to determine its fluorescence as a guarantee of good preservation. The qualitative scale of preservation of Tyson[4], was adopted in this work to estimate thermal maturity and preservation from fluorescence. The difference in fluorescence is indicative of the maturity level and of the preservation of the organic matter.

Spore coloring index (SCI): This method was used to determine the maturity of organic matter in sediments from staining of miospores under a transmitted light of electron microscope. The colors

(yellow to black, orange and brown) of the observed miospores were compared to those of the reference blades and then to the charter "FRL Spore Color Index (1-10)".

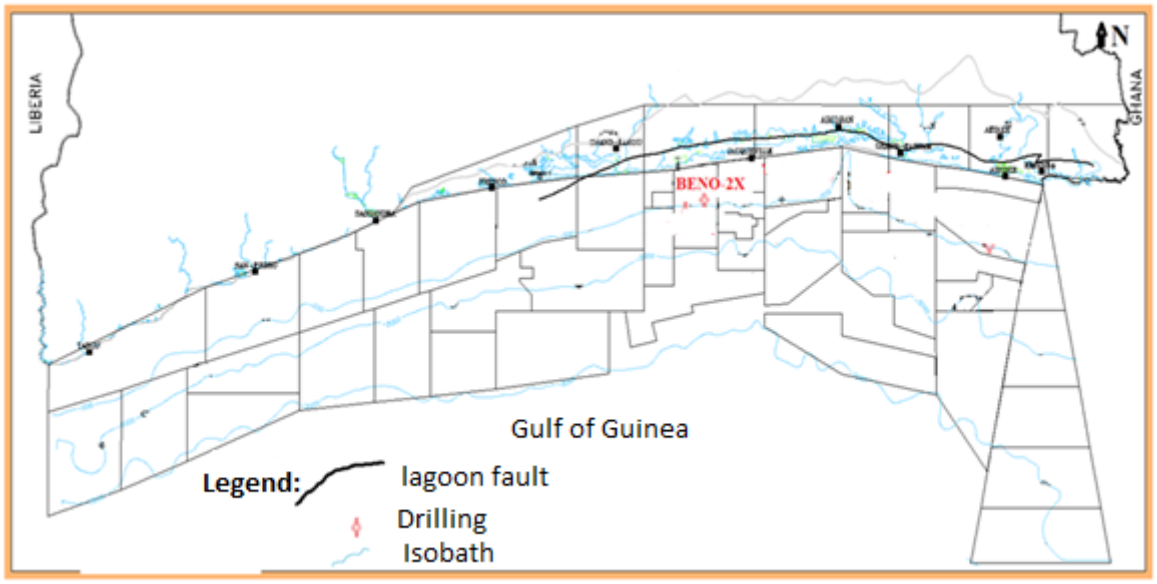

Figure 1: Location map of well BENO-2 studied

RESULTS

Results of Rock-Eval 6 and microscope analyzes of the sediments studied in BENO-2X well carried out on the black shales (medium gray-colored marly rocks) of the Turonian Cenomanian interval are recorded in **Table I**.

Table I: Summary of Rock Eval 6 parameters of the BENO-2X well studied

Depth (m)		**S2** (mg HC/ g de rock)	**Tmax** (°C)	**IH** (mg HC/g de TOC)	**TOC** (% weight)	**Comment**
TURONIAN	**MIN**	2,48	419	166	1,49	Good source rock containing a very good quantity of immature organic matter of type II which can generate oils
	MAX	21,88	431	529	4,14	
	AVERAGE	9,72	424,18	336,22	2,76	
	NB	27				
CENOMANIAN	**MIN**	10,96	417	456	1,98	Good source rock containing a very good quantity of immature organic matter of type II which can generate oils
	MAX	30,35	422	672	4,55	
	AVERAGE	16,78	419,75	585,5	2,83	
	NB	24				

1. *Cenomanian*

1.1. Rock Eval 6 parameters

The mean value of TOC given by the Rock Eval 6 is 2.83% weight **(Figure 2)** indicating the presence of very good amounts of organic matter. The HI values range from 456 to 672 mg HC / g TOC, with

an average of 585.5 mg HC / g COT (**Figure 3**, **Table I**) indicating an organic material type I (lacustrine origin) at maturity (**Figure 2**), will produce mostly oil with little gas. These results reflect a depositional environment from lake to sea. The mean value of Tmax (419.75 ° C) suggests an immature organic matter (**Figure 4)** while that of S2 (16.78 mg HC / g of rock, Table I) translates from very good to excellent -source-rocks within of black shales. In short, at the Cenomanian, the black shales of Côte d'Ivoire recorded good quantities of immature organic matter, type I and II of marine origin, within an excellent potential rock of marly nature.

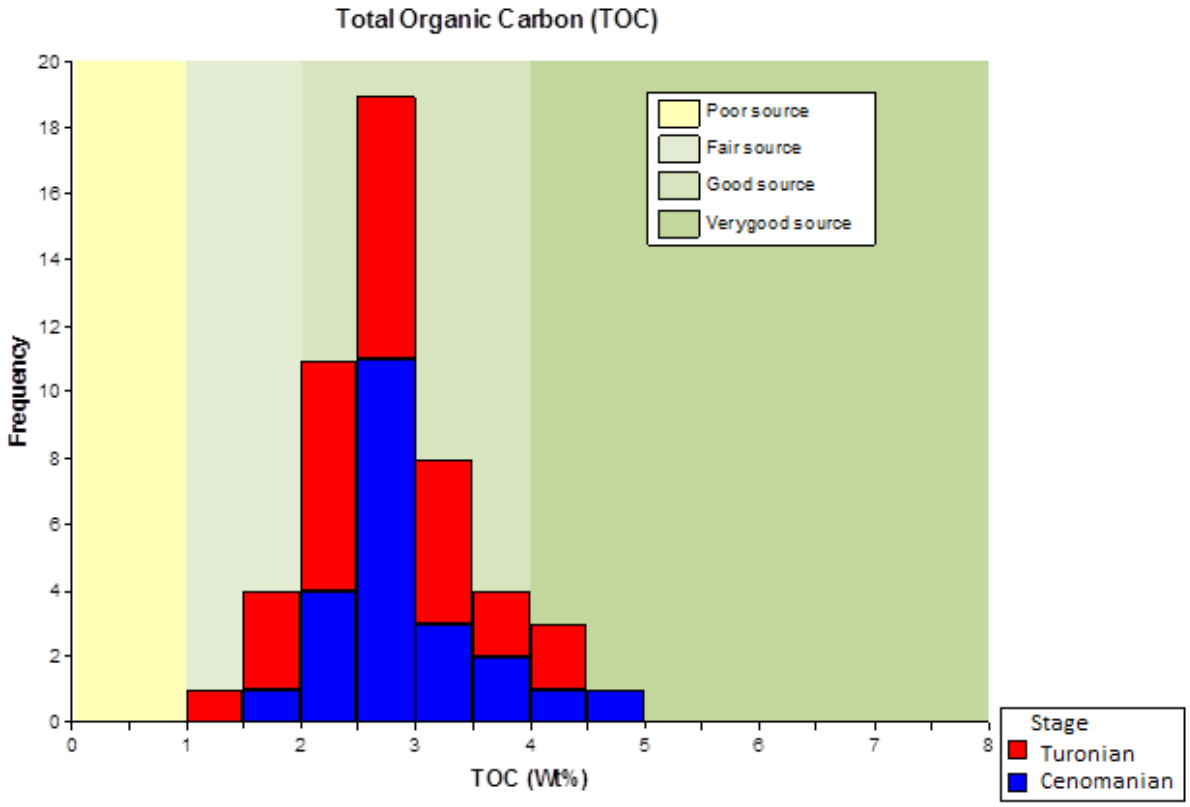

Figure 2: Sample frequency histogram as a function of the amount of organic matter in BENO-2X well.

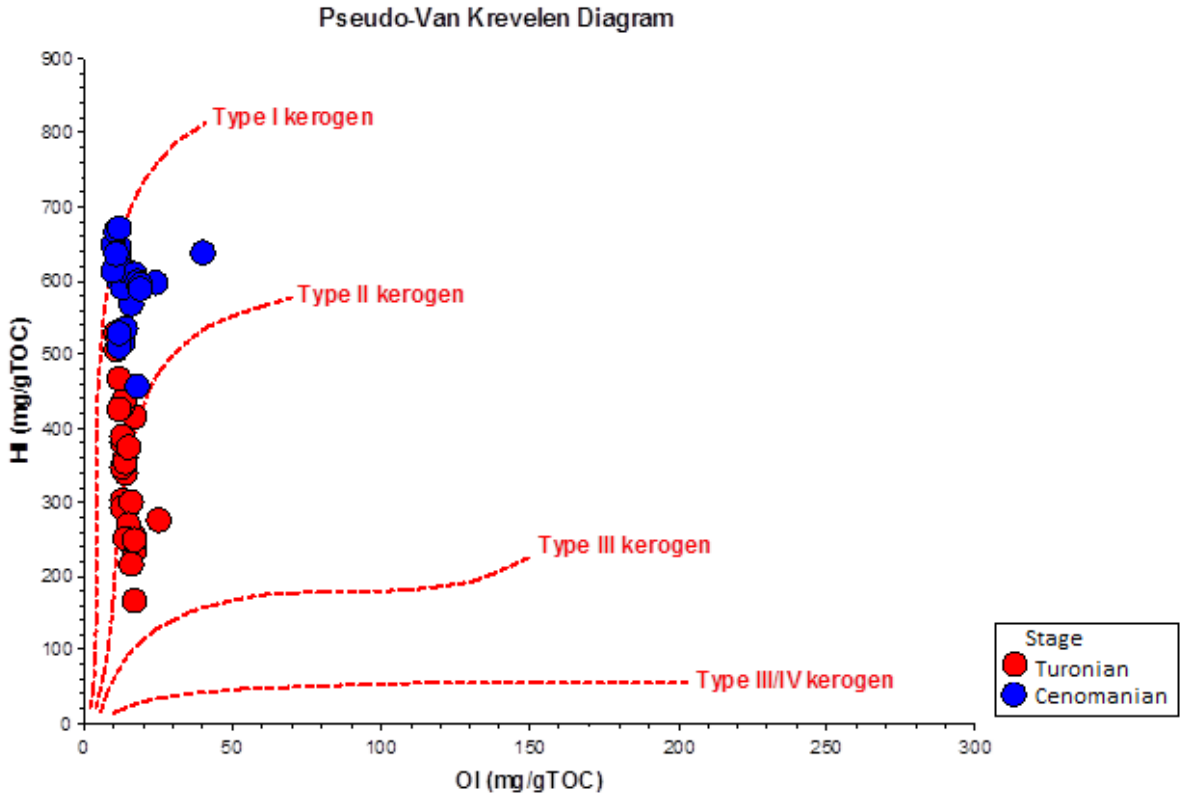

Figure 3: Pseudo Van Krevelen diagram showing evolution of the hydrogen index as a function of oxygen index in the BENO-2X well.

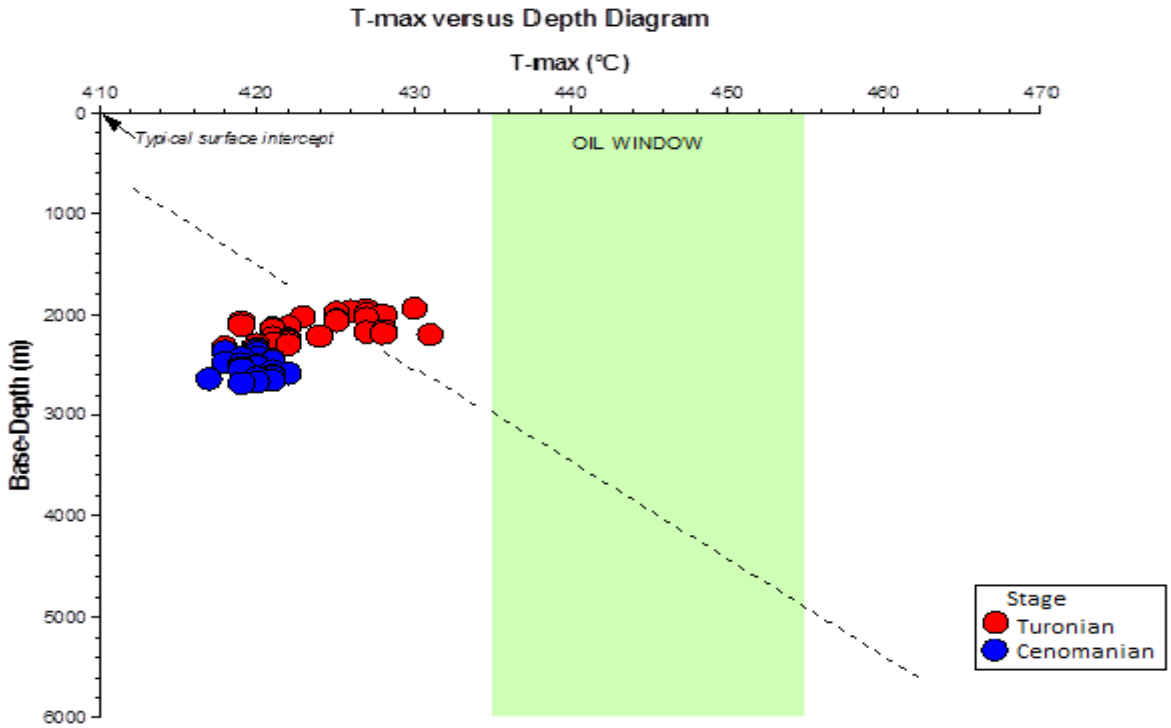

Figure 4: Geochemical diagram showing evolution of maximum Temperature as a function of the depth in BENO-2X well.

1.2. palynofacies

The palynological facies of **Fig. 5** is of sapropelic type characterized by an abundance of amorphous organic matter (AOM) (**Table II**) and orange (70 to 100%). The proportions of vitrinite and inertinite vary from 0 to 30%, characterizing a open marine depositional environment confirmed by the presence of very good quantities of well-preserved organic matter of marine origin.

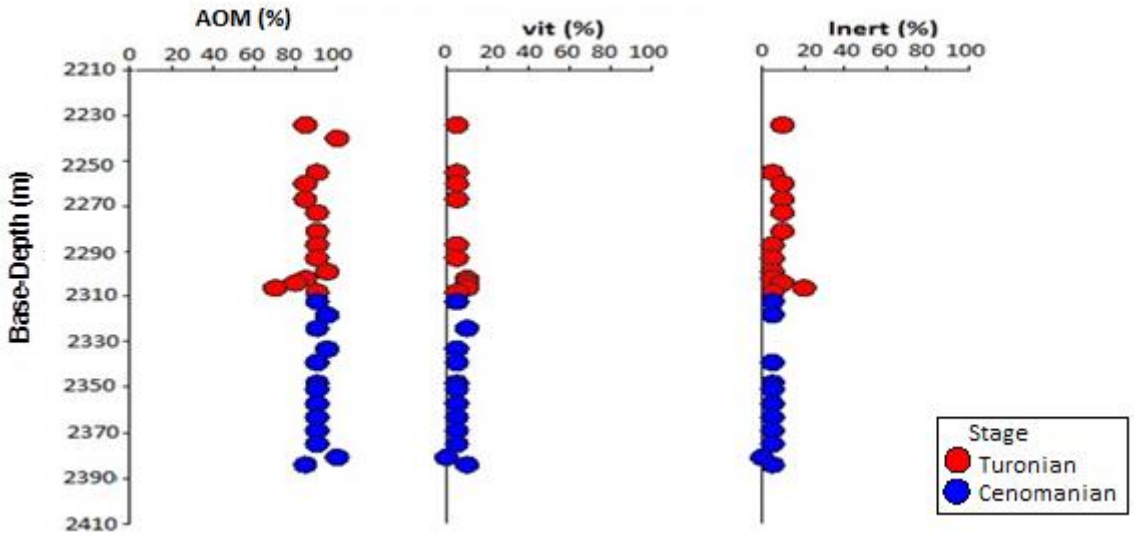

Figure 5: Percentage of Macerals as a function of depth in BENO-2X well.

Such homogeneity of marine organic matter in black shales is, according to the work of Tissot[13] and Nzoussi-Mbassani[14], induced by a marine transgression which would have caused a blockage of terrigenous deposits far from the oceanic sedimentary basins. It would thus have avoided a considerable dilution of organic matter by considerable inputs of continental components.

Table 2: Summary of Palynofacies and Rock Eval 6 parameters in BENO-2X well

AGE	DEPTH(ft)	% AOM	TOC (%weigth)	%VIT	%IN	SCI	Tmax (°C)	IH	TYPE	I F P
TURONIAN	2247	85	2,48	5	10	4,61	430	248	II/III	3
	2256	100	2, 41	0	0	4,33	426	253	II/III	3
	2262	90	3,56	5	5	4	427	347	II	3
	2268	85		5	10	4,5				3
	2273	85	4,14	5	10	3,75	419	529	II	3
	2278	90		0	10	4,5				3

REWORK ZONE	2285	90	2,39	0	10	5,3	427	252	II/III	3
	2290	90	1,49	5	5	4,86	431	166	III	3
	2295	90	3,23	5	5	5,16	421	390	II	3
	2300	95	1,87	0	5	4,2	422	374	II	3
	2305	85	2,58	10	5	4,7	422	434	II	3
	2310	80	2,77	10	10	3,5	421	431	II	3
	2315	70	2,9	10	20	4,37	420	440	II	3
	2320	90	3,05	5	5	4,43	422	426	II	3
CENOMA-NIAN	2325	90	2,34	5	5	4,22	418	468	II	3
	2330	95	2,63	0	5	4,5	420	515	II	4
	2335	90	2,35	10	0	3,88	420	536	II	4
	2340	95		5	0	4,25				4
	2345	90	2,51	5	5	4,5	421	597	II	4
	2350	90	2,3	5	5	3,8	419	568	II	4
	2355	90		5	5	4,65				4
	2360	90	2,15	5	5	4,5	419	600	I	4
	2365	90	1,98	5	5	4,5	422	589	II	4
	2370	90	4,24	5	5	4,5	421	647	I	4
	2377	90	3,29	5	5	3,66	417	672	I	4
	2385	100	3,61	0	0	4	420	637	I	4
	2390	85	2,62	10	5	4,27	419	456	I	4

It should also be noted that in the Ivorian basin, the western zone, which is richer in black shales, does not receive any major watercourse from the continent, making it less influenced by continental intakes. This isolation would have accentuated the confinement making this environment more anoxic as demonstrated by Ouattara *et al.*[6], by a relative abundance of pyrite. The figured organic matter in this range is made up of rare dinocysts with very little diversity and mainly represented by miospores suggesting a marine depositional environment with a weak continental influence. This organic matter and miospores are fluorescent (IPF = 4) (**pictures 1 and 2**) and evoke a good preservation linked to accumulation in an anoxic marine environment as suggested by Kouassi *et al.*[5] and Ouattara *et al.*[6].ICS values between 3.5 and 4.5 (**Figure 6**) with rare peaks up to 5 suggest an immature kerogen in agreement with the data obtained at Rock Eval.

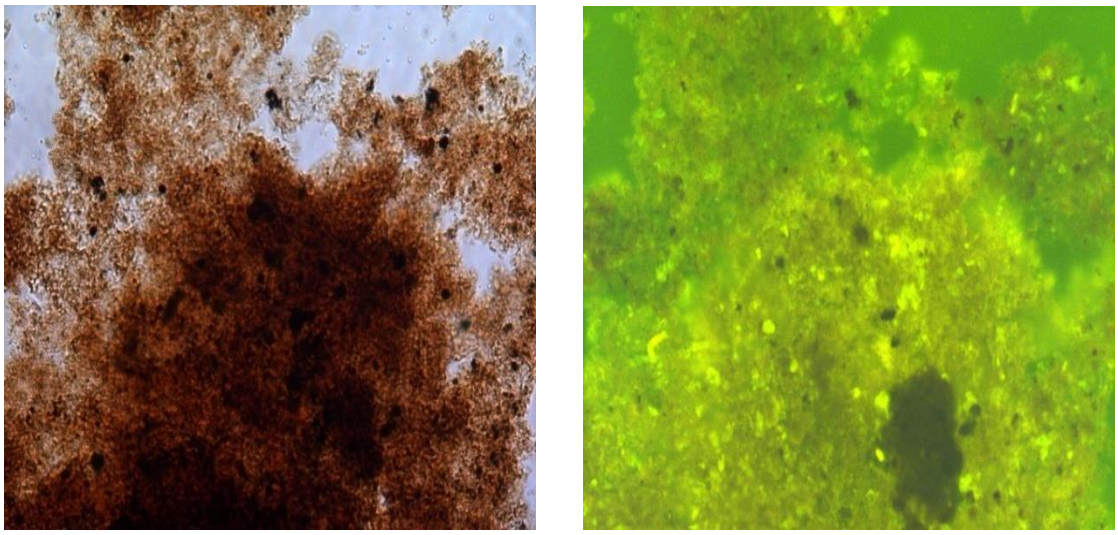

Photo 1: Palynofacies of the black shales of BENO-2X well of fluorescence 4 indicating a very good Conservation

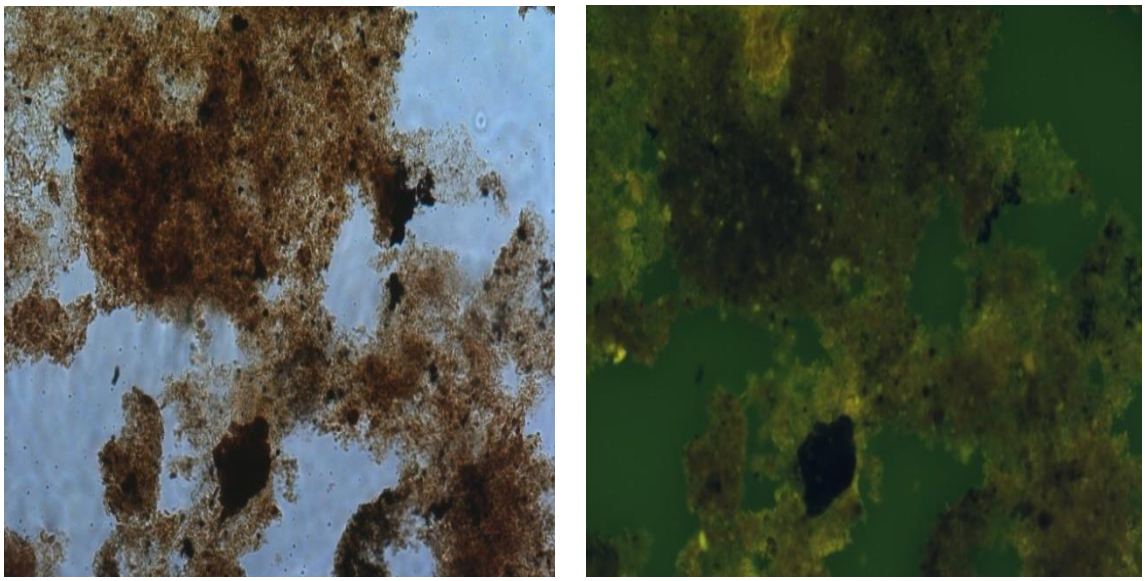

Photo 2: Palynofacies of the black shales of BENO-2X well of fluorescence 3 indicating a good conservation.

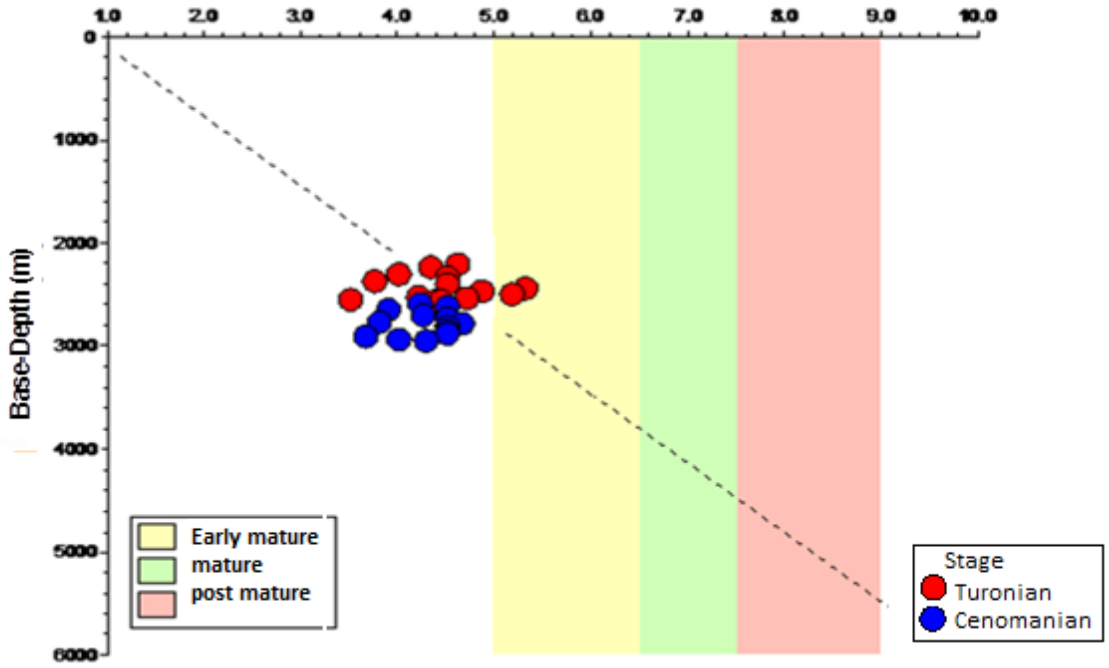

Figure 6: Diagram showing evolution of Coloration Index of Spores according depth of BENO-2X well.

2. *Turonian*

2.1. Rock Eval 6 parameters

The total organic carbon (TOC) values range from 1.49 to 4.14% weight indicating good to excellent amounts of organic matter.

The hydrogen average value is 336.22 mg HC / g TOC, characteizing a kerogen of type II (Table I) of marine planktonic and mixed origin. The latter is made up of a part of indigenous marine

(phytoplanktonic) organic matter, resulting from primary productivity, and part of another so-called allochthonous category coming from terrestrial inputs. This proves a continental influence within sedimentation area.

The kerogen has been buried at depths having subjected it to an average Tmax of 423.15 ° C, suggesting its immaturity. Thus, this high amount of Organic matter type II, immature, with average S2 values of 9.72 mg HC / g rock, indicates a medium to excellent petroleum potential. At maturity, these formations will be able to expel for one gram of rock, average 9.72 mg of hydrocarbon, making them very good potential source rocks.

2.2. Black shales palynofacies

The organic matter in Turonian is mostly amorphous (70 to 100%) in regards of the low contents of vitrinite and inertinite (0-30%, **Figure 3**). The figured fraction of this organic matter is made up of rare dinocysts and miospores which initiate their diversification towards the top of Turonian.

Although the facies is dominated by the Amorphe Organic matter, the presence of organic matter type II / III within the samples of top of Turonian and that of miospores show a marine depositional environment under a weak continental influence.

Turonian organic matter is moderately fluorescent in order of 3, indicating a good proportion of hydrogen corroborated by high average value of HI (**Table II, Figure 3**) of 336.22 mg HC / g TOC.

This organic material is moderately well-preserved suggesting an anoxic deposition paleoenvironment under an anaerobic water common. The values of the moderately high fluorescence preservation index (PFI) associated with the presence of dinocysts and the predominance of amorphous organic matter reflect existence of a sapropelic marine facies in anoxic environment under a very weak continental influence.

Concerning the burial temperature and consequently the maturity of the organic matter, the visual analysis shows values of color index of miospores oscillating between 3.5 and 4.5 (FIG. 6) with rare peaks giving up to 5, thus indicating an equally immature organic material.

III. DISCUSSION

Wathever its source, most organic matter (90%) in the marine domain is subjected to both aerobic recycling in the oxic water column and microbial degradation (in the case of sulfate-reducing bacteria) before possibly incorporated into sediment Huc [15].

The existence during Middle Cretaceous of particular environmental conditions causing an exceptional accumulation of sediments rich in organic matter has been subject of much works which will serve to discuss those of the present work [1,3,14,16-27].

III.1. Type of Organic Matter

The organic matter encountered is types I and II, rarely type II / III, with low oxygen (OI) and high hydrogen index(HI) greater than 300mg HC / g TOC. This organic matter is therefore of essentially marine origin. These results, provided by the Rock Eval method are confirmed by the analysis of palynofacies which reveals an organic matter almost exclusively amorphous and therefore of marine origin. According to Crumiere *et al.*[19] this type of facies described in the THOMEL formations in France (Vocontian basin) corresponds to a sudden modification of organic content of the rocks shown by simultaneous increases in total organic carbon and of hydrogen index (1 H greater than 200 mg HC / g TOC). Black shales essentially contain "amorphous" sapropelic organic matter of marine origin and a little organic terrigenous material (mainly woody tissue).

III.2. Quantity of Organic Matter and Potential Oil

According to Mbassani[14], black shales account for about 29% of the world's source-rocks as observed in this work with excellent oil potential exceeding sometimes 4% weight. These rates are higher than the total organic carbon contents observed by Jenkys *et al.*[16] in Western Australia (average 2.7% weight) and Caron[24] in Tunisia (2% weight). In Europe, Bonareli formations, in central Italy (Marches Ombrie), on the other hand, in black argillites interbedded with dark siliceous layers rich in radiolaria, the organic carbon content reaches 23% weight[3,17]. In France, in the "Thomel formations of vocontian basin, these rates are around 2.5% Soua.[3]

In North Africa, the Bahloul Formation in Tunisia is represented by an alternation of laminated black and limestones, and dark laminated marl and very rich in organic matter, in which total organic carbon can reach 8% weight[3].

In Morocco, black shales of the High Atlas region are marly lithologic entities which alternate with limestones rich in siliceous nodules containing immature organic matter, which rates exceed 11% weight[14]. Drilling at the Rio Grande Ridge revealed through the work of Herbin *et al*.[18] reported by Kouassi[5] that the total organic carbon contents in the Senegalo-Mauritanian basin are an average of 10%, sometimes reaching 40%. This value corresponds to the highest organic carbon content ever found on the West African margin.

In the South of the Anti-Atlas, the Tarfaya region's oil shales, encountered in outcrops on the Cenomanian and Turonian layer sand described by Kolonic *et al*.[25], contain total organic carbon contents above 18 %weight.

In Indian Ocean, Australia, DSDP sites 258 Leg 26 show organic matter values of up to 2.7% weight[1].The difference in the organic matter rates between the abovementioned could be explained by a difference in primary productivity at the water surface, or a difference in the anoxic intensity, ie the deposition environment, or the difference in climate. Indeed cold preserves the organic matter better.

The black shales cited are considered as the main source rocks of the said basins. In the Ivorian basin, the best total organic carbon contents are also found in black shales. These formations would then be as in Senegal, Morocco, Italy, France and elsewhere the main source-rocks of the basins.

III. 3. Maturity of Organic Matter

The Tmax provided by the Rock Eval 6 method is less than 435 °C indicating an immature organic material, therefore, its has not reached the oil window. These results are confirmed by the visual microscopic analysis which showed that the organic matter of the black shales is immature from the spore coloration indices (ICS) around 4.5. This thermal immaturity observed in black shales of Côte d'Ivoire sedimentary basin is also found in Morocco [14].

CONCLUSION

The organic matter encountered in this study is essentially marine and rarely mixed (marine and continental). These are potential source rocks with good to excellent petroleum potential. These rocks are immature but, at maturity, they would be able to produce large quantities of liquid hydrocarbons. Visual analysis of macerae revealed essentially amorphous organic matter and fluorescent confirming its marine origin.

The results of the Rock Eval 6 analysis as well as those of the visual observation show that the organic matter is immature. The black shales facies observed is characterized by amorphous organic matter, deposited in marine environment where marine organic matter types I, II and rarely II / III are developed. The organic matter is well preserved as evidenced by the good fluorescence of order 4.

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