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Organic geochemical and mineralogical characterization of the Moroccan Rif bituminous rocks

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Abstract

The Bituminous rocks of the Upper Cretaceous in the Moroccan Rif were subjected to an organic geochemical study which was in the valuation framework of these rocks. In order to determine hydrocarbon potential of the unit, an organic geochemical analysis technique was performed. According to Rock-Eval pyrolysis results (TOC, GP) for four samples (in different sites), the Total Organic Carbon (TOC) contents vary from 0.45 to 4.47 %, and total hydrocarbon generation potential (GP) values are between 0.49 to 13.1 mgHC/g rock. Hydrogen index (HI) values range from 37 to 282 mgHC/gTOC, suggesting Types II, III and IV kerogen. The analysis by X-ray fluorescence spectrometry has proved that the bituminous rocks samples consist mainly of quartz (SiO_2) (70.04 – 84.46 wt.%), and lower proportions of other mineralogical components. The FTIR spectra are compatible with Rock-Eval pyrolysis results and X-ray fluorescence analysis results.

Keywords: Organic geochemical; Bituminous rocks; kerogen; pyrolyse; X-ray fluorescence; Moroccan Rif.

1. Introduction

Morocco has been ranked seventh with respect to the global reserves of bituminous rock (bituminous shale (oil shale), bituminous marls…) [1]. Thus, the most important deposits are located in Timahdit and Tarfaya regions [2, 3], and have been the subject of several geological and mining studies, laboratory studies as well as tests pyrolysis and direct combustion [4, 5]. Other bituminous rocks have been also discovered in Moroccan Rif region during the past century; however the geochemical and mineralogical studies are scarce [6].

The upper cretaceous bituminous rocks inspected in the present work are located in the northwestern part of the Moroccan Rif, occupied by mountain ranges (altitude above 850 m). These outcrops have been encountered by the quarrying of building materials [7].

The samples collected are sedimentary and metamorphic rocks, characterized by light gauge of layers 0.2 to 0.80 m (2.5 m in areas). They usually contain low content of kerogen which is an organic substance insoluble in usual organic solvents accompanied by a small fraction of soluble hydrocarbons soluble [8-9]. This kerogen liberates an oil of similar appearance to that of crude oil by a non-oxidizing heat treatment between 400 and 500°C [10]. Recently, Kinetic studies showed the possibility to removal of bacteria by adsorbents prepared from Moroccan bituminous shale [11, 12].

In this paper, an organic geochemical and mineralogical characterization has been carried out to obtain information about the origin and evolution of these bituminous rocks and consequently, their petroleum potential and the type of their kerogen.

2. Geological setting of Moroccan Rif

The Moroccan Rif is located in the extreme north of Morocco (western Mediterranean) and constitute an arched alpine orogen surrounding the Alboran Sea (Fig.1). It is made up of an internal zone that comprises overprinted metamorphic complexes including Paleozoic rocks, separated by Flysch units from the external zones corresponding to Mesozoic and Cenozoic sedimentary rocks (Fig. 1). The Moroccan Rif includes three major geological domains or nappe complexes. The External Rif consists of a fold-and thrust belt detached along the Upper Triassic evaporitic beds from the thinned continental crust of the North African margin [13-15]

The Flysch nappes generally overlie the External Rif, with the exception of some klippes that are located on the Internal Zone as the result of a complex evolution [16, 17]. These Flysch units are of Cretaceous-Early Miocene age. Their basement does not crop out at present and may be considered as the deposits of a swell located on ocean or transitional crust in between the External and Internal Zones [13, 14, 18].

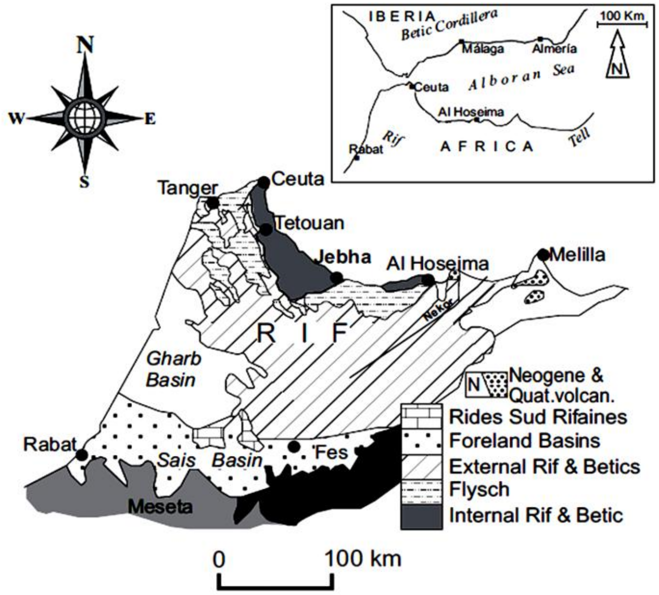

Fig. 1. Geological map of the Moroccan Rif.

2. 1. Study areas

The studied samples of the Upper Cretaceous bituminous rocks in the Moroccan Rif are located in four sites (Table 1) and (Fig.3):

- Tangier Site: located at the east of the city of Tangier, the sample (TA) which was chosen in this site is of type bituminous marls (Fig.3A) that are intercalated with limestone. Tangier Site is situated in the unity of the Melloussa- Chouamat of Flysch Massilienne (Flyschs nappes) (Fig. 2A), of age Upper Cretaceous - Senonien [6, 19].
- Tetouan Site: located at about 3 km to the west of the city of Tetouan. The sample (TE) which was chosen in this site is of type bituminous Phtanites (Fig.3B) that are included in Schistose Marls (Pelites). Tetouan Site is situated in the unity of Internal Tangier (Eastern Facies) of the intrarifaine (External Rif) (Fig.2B), of age Upper Cretaceous - Cenomanian [6, 20].
- Bab Taza Site: located at about 2 km to the east of the city of Bab Taza, the sample (BT) which was chosen in this site is of type bituminous Phtanites (Fig.3C) that are included in Schistose Marls (Pelites). Bab Taza Site

is situated in the unity of Ketama-External Tangier (Formation of Bab Taza) of the intrarifaine (External Rif) (Fig.2C), of age Upper Cretaceous - Cenomanian [6, 21].

- Arba Ayach Site: located at about 63 km SW of the city of Tetouan (about 70 km to the North-east of the city of Larache) on the road Tetouan - Larache, the sample (AA) which was chosen in this site is of type bituminous shale (oil shale) (Fig.3D), of age Upper Cretaceous – Turonian. Arba Ayach Site is situated in the Melloussa- Chouamat of Flysch Massilienne (Flyschs nappes) (Fig.2A), in this site also appear clearly limestones, and marls white [6, 8, 9, 19].

Table 1: The coordinates of each sampling site of the sediments sampled.

Site	Sample	Lithology	Geological age	Longitude (E)	Latitude (N)
Tangier	TA	Marl	Upper Cretaceous - Senonian	5° 46' 33,23''	35° 45' 38,07''
Tetouan	TE	Phtanite	Upper Cretaceous - Cenomanian	5° 27' 32,98''	35° 33' 43,97''
Bab Taza	BT	Phtanite	Upper Cretaceous - Cenomanian	5° 10' 51,02''	35° 3' 45,82''
Arba Ayach	AA	Shale	Upper Cretaceous - Turonian	5° 51' 05,14''	35° 24' 28,54''

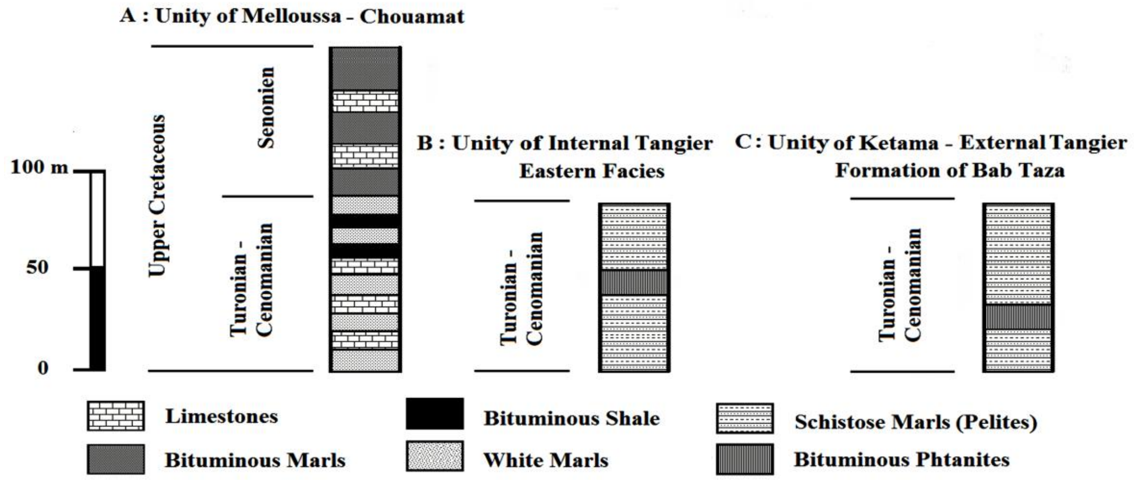

Fig. 2. Stratigraphic columns of Upper Cretaceous age of the unity of Melloussa-Chouamat (Flyschs nappes) and the Intrarif of the unity of Tangier (External Zone), showing the investigated sample position (A: [19]) (B: [20]) (C: [21]).

3. Materials and methods

The four samples (TA, TE, BT, AA) were previously crushed (grain diameter < 180 µm).

3.1. Rock-Eval pyrolysis

The quantity of organic matter in the bituminous rocks samples (between 90 and 120 mg) was evaluated from the Total Organic Carbon (TOC) content and Rock Eval 6 Standard (National Office of Hydrocarbons and Mines, Rabat, Morocco) [22, 23]. This technique was developed at the French Petroleum Institute [24], originally for the purpose of rapid assessment of the organic matter as well as petroleum potential of drillings samples. It is a method to characterize global which is capable to provide a better determination of the type of kerogen. It consists of pyrolyzing a crushed sample in programming of temperature and helium atmosphere. The effluents of pyrolysis generated are quantified according to the temperature.

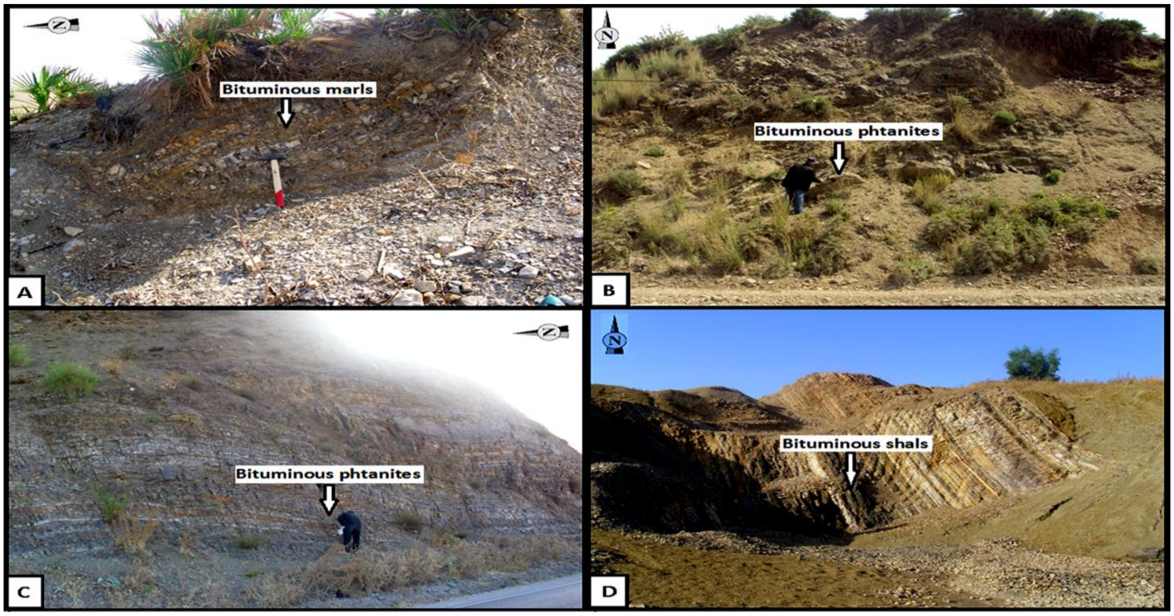

Fig. 3. Photographs for the four sites of the samples from the Upper Cretaceous bituminous rocks.

3.2. X-ray fluorescence spectrometry

Each sample (~4g) was mixed with 4g of boric acid, followed by grinding the mixture in order to homogenize the whole. The X-ray fluorescence (XRF) was carried out using an AXIOS pw4400 spectrometry system. This analytical technique was used to measure the concentration of inorganic composition in these types of rocks [25].

3.3. FTIR analysis

FTIR spectra were recorded on KBr discs. Each sample (~0.5mg) was mixed with 100 mg of dry KBr powder, uniformly mixed and reground. The entire sample was transferred to a die and pressed under vacuum in the standard way. Spectra were recorded between 400 and 4000cm^{-1} using a Vertex 70 Model spectrometer.

4. Results and Discussion

4.1. Rock-Eval pyrolysis

The results of Rock-Eval pyrolysis are summarized in form of mean values in the *table 2* and illustrated by the *figures 4, 5* and *6*.

This method allows evaluating the organic content of a rock (TOC: Total Organic Carbon, in % of the mass of the whole rock). The first peak (S_1) represents the quantity of free hydrocarbons at moderate temperature (250 – 350°C). The second peak (S_2) represents hydrocarbons generated by the pyrolytic degradation of the heavy products and kerogen in the rock (350 – 550°C). The third peak (S_3) represents the quantity of CO and CO_2, produced during this pyrolysis in the range 250°C to 400°C, temperature below that corresponds to beginning of the thermal dissociation of carbonates [26]. The Hydrogen Index (HI) corresponds to the quality and quantity of pyrolyzable organic compounds from S_2 relative to the TOC in the samples (mg HC/g TOC) and it can be successfully used to assess the oil generation potential of the rock and the type of the organic matter. The Oxygen Index (OI) is indirectly related to the quantity of terrestrial organic matter in the sample (mg CO_2/g COT). Both index HI and OI show good correlation with the atomic ratios H/C and O/C obtained by elemental analysis of kerogen and give sufficient information about the origin and degree of maturity of organic matter [24]. The temperature at which the maximum amount of organic hydrocarbons (S_2) is generated is called *T*max [27]. It is a rough measurement of the thermal maturity of organic matter, because of its dependency on the type of organic matter.

The production index (PI = $S_1/S_1 + S_2$) is defined as the ratio of the quantity of oil corresponding to S_1 to the total quantity of hydrocarbon compounds that can be generated by the kerogen and expressed as the sum (GP (total hydrocarbon generation potential) = $S_1 + S_2$) [28]. The two values *T*max and PI are important criteria of the degree of evolution of the rocks [23].

4.1.1. Richness

Total Organic Carbon content (TOC, wt.%) is generally used as an indicator of kerogen and bitumen amounts in the source rock. Organic material content is excellent (> 4%) for the three samples TE, BT, AA, of the Upper Cretaceous bituminous rocks, whereas, the TA sample has a little value (< 0.5%) (Table 2). The value of Total Organic Carbon content is not enough for justifying the potential oil source rocks, while, high organic carbon content is not necessarily potential oil source indicator.

S_1 hydrocarbons are the free hydrocarbons that can be decomposed under heat. The peak values of S_1 hydrocarbons in the four samples TA, TE, BT and AA of the Upper Cretaceous bituminous rocks are successively 0.04, 0.1, 0.49, 0.96 mg HC/g rock (Table 2). According to Peters & Cassa [29], evaluation of S_1 hydrocarbons yields is weak for the TA, TE, BT samples, but contrarily, good for the AA sample of the Upper Cretaceous - Turonian bituminous shale.

S_2 hydrocarbons (mg HC/g rock) depict the recent potential of the source rock sample. S_2 hydrocarbons are derived from the decomposition of kerogens which remain in the rock and high molecule-based hydrocarbons that cannot be revealed by the S_1 peak. Values of S_2 hydrocarbons of the three samples TA, TE, BT from the Upper Cretaceous bituminous rocks are weak, but contrarily, very good (12.14 mg HC /g rock) (Tableau 2) for the AA sample from the Upper Cretaceous - Turonian bituminous shale, which is perfectly consistent with the recent source rock potential [29, 30]. In Fig. 4, which was drawn for total hydrocarbon generation potential (GP = S_1+S_2) and Total Organic Carbon (TOC, %wt), it is shown that the AA sample from the Upper Cretaceous - Turonian bituminous shale has a very good source rock potential, contrary to the other samples of the Upper Cretaceous bituminous rocks.

4.1.2. Quality of organic matter (kerogen type)

HI values of the Upper Cretaceous bituminous rocks have been found as 37, 53 (mg HC/g TOC) in samples TE, BT and 100 (mg HC/g TOC) in TA sample. HI value of the AA sample is 282 (mg HC/g TOC). According to Peters & Cassa [29], HI values indicate that the AA sample is composed of Type II kerogen, from marine origin, this type of kerogen is hydrogen rich and oxygen-poor; this with its good S_2 hydrocarbon yields (12 kg of oil per ton of rock) (Table 2), it is suitable for oil production. TA sample is composed of Type III kerogen, from land origin, likely to generate gas; this type of kerogen is rich in oxygen (Table 2). The other two samples TE and BT are composed of Type IV kerogen, inert to generate hydrocarbons. This type of kerogen is poor in oxygen as hydrogen (Table 2). Kerogen types of Upper Cretaceous bituminous rocks are also determined with HI-Tmax, HI-OI diagrams from the pyrolysis analysis (Table 2). Samples from the different sites were plotted in the HI - Tmax diagram, from which it is seen that the sample plots in the mature zone of Type II, Type III and Type IV kerogen (Fig. 5). S_3 hydrocarbons values of Upper Cretaceous bituminous rocks samples TA, TE, BT and AA are successively 1.13, 2.8, 2.42, and 0.97 mg CO_2/g rock, and oxygen index values (OI) are found 251 (mgCO_2/g TOC) in TA samples, 63 (mg CO_2/g TOC) in TE sample, 54 (mg CO_2/g TOC) in BT sample, and 23 (mg CO_2/g TOC) in AA sample (Table 2). According to HI-OI diagram (Fig. 6), Kerogen types of Upper Cretaceous bituminous rocks samples are Type II for AA sample, Type III for TA sample and Type IV for TE, BT samples which is in agreement with the previous diagram. The S_2/S_3 ratio, which is hydrocarbon type index, was used by Clementz et al. [31] to determine the kerogen type. Similar to HI/OI ratio, this ratio is an indicator of ratio of hydrogen to oxygen. Hydrocarbon type index (S_2/S_3) values of three samples TA, TE, BT are successively 0.39, 0.58, and 0.98 and these values being < 5 may indicate that kerogen type is Type III and Type IV. The S_2/S_3 value of other AA sample is 12.51, the fact that this value is between 10 and 15 (>5) may indicate that kerogen type of the unit is Type II which is suitable for oil production.

Table 2: Rock-Eval Pyrolysis results of the Upper Cretaceous bituminous rocks studied and some the samples of bituminous shale of Timahdit and Tarfaya deposits.

Sample	TOC	S_1	S_2	S_3	HI	OI	T_{max}(°C)	PI	S_2/S_3	GP	MINC(%)
TA	0.45	0.04	0.45	1.13	100	251	439	0.081	0.39	0.49	0.14
TE	4.44	0.1	1.63	2.8	37	63	465	0.057	0.58	1.73	0.42
BT	4.47	0.49	2.38	2.42	53	54	461	0.170	0.98	2.87	0.28
AA	4.3	0.96	12.14	0.97	282	23	440	0.073	12.51	13.1	0.2
Timahdit [32]	10.86	3.51	68.93	1.88	634	17	415	0.04	36.66	72.44	--
Timahdit [33]	17.6	0.92	125.44	3.44	712.7	19.5	426	0.007	36.46	126.36	--
Tarfaya [32]	7.03	4.11	50.06	6.07	712	86	415	0.07	8.33	54.17	--

TOC: Total Organic Carbon, Wt%.
S_1 = Volatile hydrocarbon (HC) content, mg HC/g rock.
S_2 = Remaining HC generative potential, mg HC/g rock.
HI = Hydrogen Index = S_2 x 100/TOC, mg HC/g TOC.
S_3 = Carbon dioxide content, mg CO_2/g rock.
OI = Oxygen Index = S_3 x 100/TOC, mg CO_2/g TOC.
PI = Production Index S_1/S_1+S_2.
GP = total hydrocarbon generation potential = S_1+S_2.
MINC(%) = Mineral Carbon Proportion

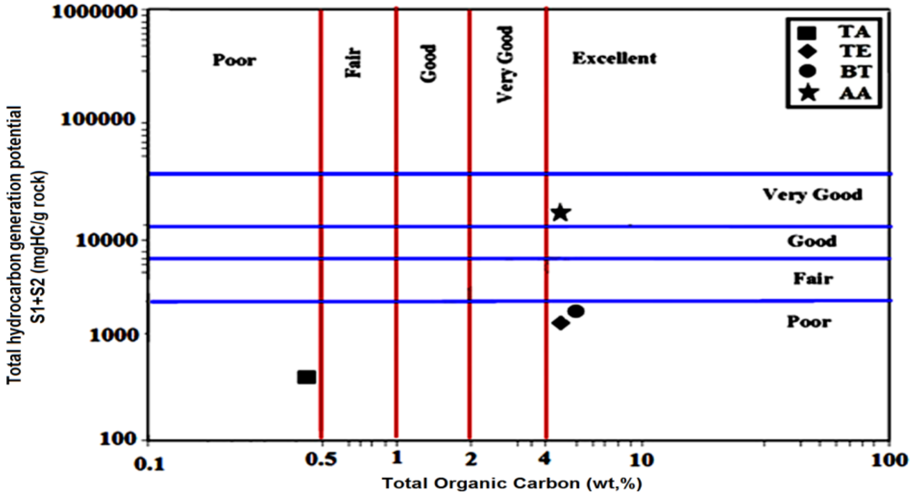

Fig.4. Source rock characterization using plot of total hydrocarbon generation potential versus total organic carbon [34].

4.1.3. Thermal maturity of organic matter

Although source rocks have adequate organic material content and kerogen type is suitable for oil and/or gas production, it takes a long time for them to produce hydrocarbon unless they are buried to a sufficient depth. Thermal maturity of the organic material can be determined by pyrolysis analyses (*T*max, PI).
The *T*max and PI values for AA sample from the Upper Cretaceous-Turonian bituminous shale indicates that it is of early–intermediate mature oil formation stage (Table 2) (Fig. 6), whereas *T*max and PI values of other samples TA, TE and BT are not significant, because of their low S_2 hydrocarbon (< 2.5mg HC/g rock) (Table 2).

4.2. X-ray fluorescence spectrometry

Analysis by X-ray fluorescence of the four studied samples (Table 3) show that they consist of very high content quartz (70.04 - 84.46wt.%), mass concentrations of calcium oxide (CaO) are 0.013 - 0.84wt.% (more important in TA sample), and magnesium oxide (MgO) are 0.47 - 1.32wt.%, indicating the low contents of dolomite and calcite (Carbonate) in the Upper Cretaceous bituminous rocks samples. Mass concentration of aluminum oxide

(Al_2O_3) ranges between 3.90 - 12.34wt.%, ferric oxides (Fe_2O_3) between 0.74 - 3.56wt.%; and sulfur trioxide (SO_3) is 0.08 - 0.74wt.% (more important in AA sample), both the later proportions indicate the low contents of Pyrite (FeS_2). It appears also that the clays are present in different proportions into the studied samples.

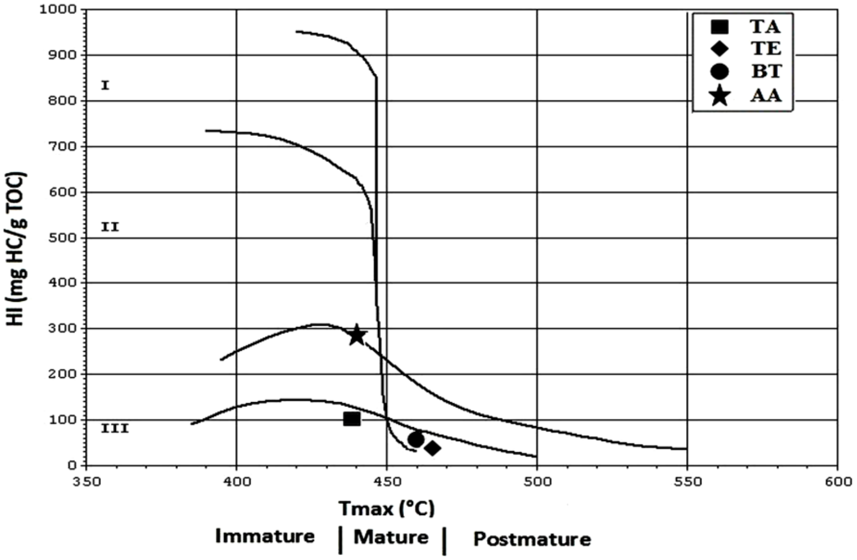

Fig. 5.Plot of Hydrogen Index (HI) versus (Rock-Eval) Tmax values for the samples analyzed showing kerogen quality and thermal maturity stages [35].

Table 3: Results of the mineralogical components of bituminous rocks samples by XRF analysis (wt.%).

	TA	TE	BT	AA
SiO_2	80.22	70.04	73.78	84.46
Al_2O_3	7.929	12.34	11.87	3.908
Fe_2O_3	2.172	3.569	1.808	0.644
CaO	0.84	0.36	0.191	0.013
MgO	1.216	1.31	1.323	0.48
TiO_2	0.2	0.3	0.31	0.09
SO_3	0.1	0.11	0.08	0.74
K_2O	0.64	0.73	0.92	0.23
ZnO	0.14	0.05	0.05	0.05
Na_2O	0.31	1.815	1.246	0.18
MnO_2	0.034	0.09	0.04	0.02
CuO	0.03	0.02	0.04	0.01
P_2O_5	0.05	0.08	0.1	0.02
V_2O_5	0.024	0.1	0.06	0.1
Cr_2O_3	0.02	--	0.04	0.02
BaO	0.02	0.02	0.02	--
NiO	0.01	0.02	0.02	0.01
SrO	0.01	0.031	0.004	0.01
Rb	0.01	0.004	0.01	--
CoO	--	0.04	0.01	0.01
As_2O_3	--	0.031	--	0.004
PbO	--	--	0.01	--
Y_2O_3	--	--	--	0.001
L.O.I	6.01	9.013	8.08	8.983
Total	**99.991**	**99.995**	**100.012**	**99.99**

L.O.I: Loss on Ignition

4.3. FTIR analysis

FTIR spectra of the samples are shown in Fig 7. The bands within the vibration range 400 – 875 cm^{-1} belong to aromatic C-H structures. The 1433 cm^{-1} band of vibration observable in the spectra of TA sample belong to $CaCO_3$; a wide and sharp band of vibration observed in all samples at 1000 cm^{-1} belongs to Si-O-M structure which is compatible with mineral composition. The range 3200–3600 cm^{-1}observed also in all samples belongs to H_2O next to OH and OH of groups: alcoholic, phenolic carboxylic …

In addition, the 3200 and 2800 cm^{-1} band of vibration belongs to C-H structure is normally invisible in the spectrum of the sample with the lowest TOC value, which is compatible with Rock-Eval pyrolysis results (TOC<5%).

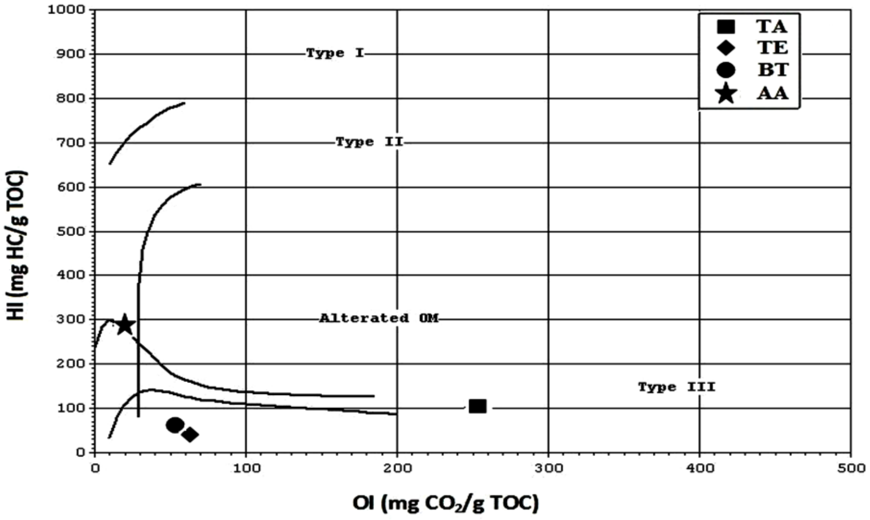

Fig. 6. Plot of Oxygen Index (OI) versus Hydrogen Index (HI) for the Upper Cretaceous bituminous rocks samples [36].

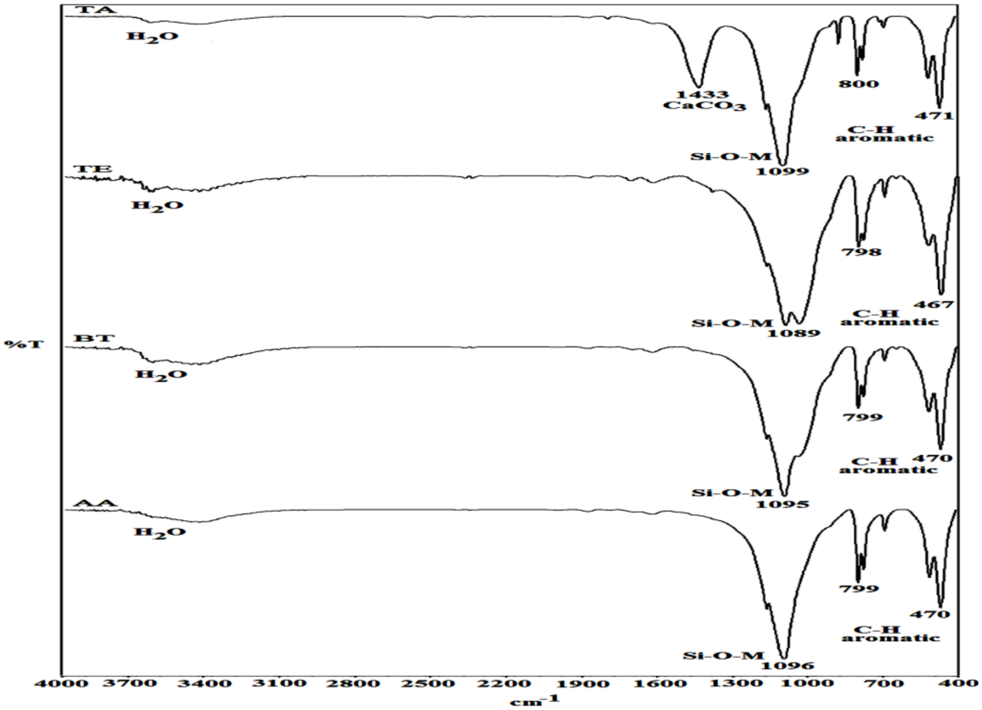

Fig. 7. FTIR spectra of bituminous rocks samples.

Conclusion

In this study, Rock-Eval/TOC analysis indicate that very good generative potential is found in the AA sample (Arba Ayach) of Upper Cretaceous – Turonian bituminous shale in the Moroccan Rif, it has high TOC contents (>4 wt. %), and pyrolysis S_2 yield is 12.14 mg HC/g rock, HI values indicate that it is composed of Type II kerogen from marine origin. If the facies of this rock are found in deeper places in the basin, they could generate significant quantities of hydrocarbons (~ 12kg of oil per ton of rock). Despite this, these source rocks of Arba Ayach are of less value than the source rocks of Timahdit and Tarfaya deposits, which their S_2 hydrocarbons between 50 and 125 kg of oil per ton of rock (Table 2)[32, 33].

The TA sample of Upper Cretaceous-Senonien in the Moroccan Rif is composed of Type III kerogen, from land origin; this type of kerogen is rich in oxygen than hydrogen. The TOC content of TA sample is extremely low in comparison with the other samples because these are located in deeper geological units (therefore more pressure and temperature) than the geological unity wherein the TA sample is located (Fig.2).

Deposit this, The TA sample and other samples (TE and BT) of Upper Cretaceous in the Moroccan Rif are not potential source rocks for hydrocarbons because of their low S_2 hydrocarbon (< 2.5 mg HC /g rock) (Table 2).

The mineralogical components that were found by X-ray fluorescence, show that our samples of Upper Cretaceous bituminous rocks in the Moroccan Rif, characterized by a high content of silica (quartz), and lower contents of dolomite, calcite (Carbonate), and Pyrite.

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