Oil Shale, 2013, Vol. 30, No. 4, pp. 536–549
doi: 10.3176/oil.2013.4.06
ISSN 0208-189X

THERMAL AND MINERALOGICAL STUDIES OF MOROCCAN RIF BITUMINOUS ROCKS

KHALIHENA GROUNE*, MOHAMMED HALIM, SAÏD ARSALANE

Mohammed V University, Agdal, Faculty of Sciences of Rabat, Department of Chemistry, 4 Avenue Ibn Battuta, BP 1014, 10000 Rabat, Morocco

Abstract. *A study was conducted on four bituminous rock samples from Tangier, Tetouan, Bab Taza and Arba Ayach deposits (samples TA, TE, BT, AA, respectively) in the Rif region of northern Morocco. The study was carried out using thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluorescence (XFR), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and scanning electron microscopy with energy dispersive spectrum analysis (SEM-EDX).*

The results obtained by these methods showed that the organic part of TA, TE, BT and AA samples was 5.59 wt%, 6.73 wt%, 4.77 wt% and 7.53 wt%, respectively. Therefore these bituminous rocks can be considered a perspective energy resource. The dominant mineral phase in all samples is quartz (70.04–84.46 wt%). Clay minerals (illite, chlorite) and other mineral components are present in different low-weight proportions.

Keywords: *mineralogy, bituminous rocks, thermogravimetry, X-ray diffraction, X-ray fluorescence, Moroccan Rif.*

1. Introduction

With reference to energy resources such as crude oil or natural gas, Morocco depends almost fully on the outside. However, geological studies have demonstrated that Morocco ranks seventh in bituminous rock reserves in the world with an estimated 50 billion barrels of oil of bituminous rock deposits found in the northern, central and southern regions of the country [1]. This nonconventional resource might be envisaged at least for internal requirements in the long term.

Bituminous rocks (bituminous shale, bituminous marls) are fine-grained sedimentary rocks that yield a significant proportion of oil of similar appearance to that of crude oil by pyrolysis [2–5]. It can be burnt directly as

* Corresponding author: e-mail *khalihena.groune@yahoo.fr*

low-grade fuel for the production of electricity and heating purposes, but it is also a valuable chemical feedstock [6, 7].

During the past few decades, there has been an increasing interest in the utilization of these bituminous rock deposits as an alternative energy source [8]. Knowledge about the mineralogy and trace element distribution in raw bituminous rocks after retorting is highly important for various exploitation programs.

This study is focused on the Tangier deposit (Moroccan Rif in the northern part of Morocco), which was discovered in the past century by quarrying building materials there and is considered the country's first deposit of bituminous rocks (Fig. 1) [9–11]. This region has not been studied in detail, according to literature. The mineralogy and inorganic elemental composition of Moroccan Rif bituminous rocks were investigated by thermogravimetric (TGA) and X-ray diffraction (XRD) analysis, X-ray fluorescence spectrometry (XRF), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and scanning electron microscopy (SEM).

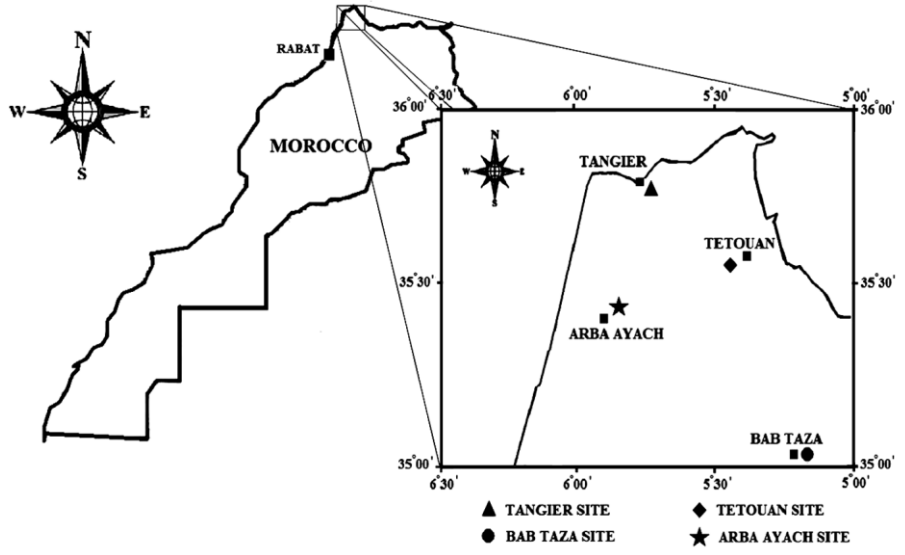

Fig. 1. Map of the Moroccan Rif and locations of the four sampling sites of the study.

2. Experimental

2.1. Sampling and stratigraphy

This work was carried out on four samples, which were stratigraphically selected from northern Morocco (Table 1, Figs. 1 and 2). Only one sample was collected from the outcrops at each site. The samples averaged about 20 kg in weight and were collected at a depth of 20 to 80 cm.

Table 1. Latitude and longitude coordinates of each sampling site of the rocks sampled

Site	Symbol of sample	Lithology	Geological age	Longitude (E)	Latitude (N)
Tangier	TA	Marl	Upper Cretaceous-Senonian	5° 46' 33.23"	35° 45' 38.07"
Tetouan	TE	Shale	Upper Cretaceous-Cenomanian	5° 27' 32.98"	35° 33' 43.97"
Bab Taza	BT	Shale	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"

The Tangier and Arba Ayach deposits of bituminous rocks are located within the western basin of the Moroccan Rif, the Tangier site is located in the east of Tangier city and the Arba Ayach site is located in the east of Arba Ayach village (Fig. 1). The bituminous marls of the Tangier site are Upper Cretaceous-Senonian in age and alternate with limestone (Fig. 2A) [11, 12]. The oil shales of the Arba Ayach site are of Upper Cretaceous-Turonian age and alternate with limestone and white marl (Fig. 2A) [11–14].

The Tetouan and Bab Taza deposits of bituminous shales are located within the eastern side of the Moroccan Rif, the Tetouan site is located in the west of Tetouan city and the Bab Taza site in the east of Bab Taza village (Fig. 1). The bituminous shales of Tetouan and Bab Taz sites are Upper Cretaceous-Cenomanian in age and are included in schistose marls (Figs. 2B, 2C) [15, 16].

The four samples collected were subsequently crushed, homogenized and sieved (to < 180 μm).

2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of raw shale [17] is commonly used to measure the mass change of a sample as a function of temperature and time, in a controlled atmosphere. In this study, the analysis of the selected raw samples of bituminous rocks (5 to 10 mg of the crushed product) was performed using a Labsys Evo 1F thermal analyzer (Setaram, France). The temperature range of the TGA analysis was from 30 °C to 950 °C, and the rate at which the temperature increased was 10 °C/min. Helium was used as an inert gas to prevent the sample from oxidizing and as a carrier gas to remove the gaseous products during the analytical process.

2.3. X-ray diffractometry (XRD)

X-ray diffraction was used to identify the main minerals (mass content higher than 5%) in the sample. The analyses were performed with powdered rock samples by using a Brucker D8 Advance diffractometer equipped with

a copper anticathode ($\lambda_{CuK\alpha}$ = 1.541838 Å). The analytical conditions were 40 kV, 40 mA, Ni filter, angular range from 2.5 to 65°2θ (powder), 2.5 to 35°2θ (oriented preparations of clay) and counting time 45 s/2°2θ.
In order to determine the nature of clay minerals, the crude sample was crushed and pulverized using a chromed steel ring crusher. The clay fraction

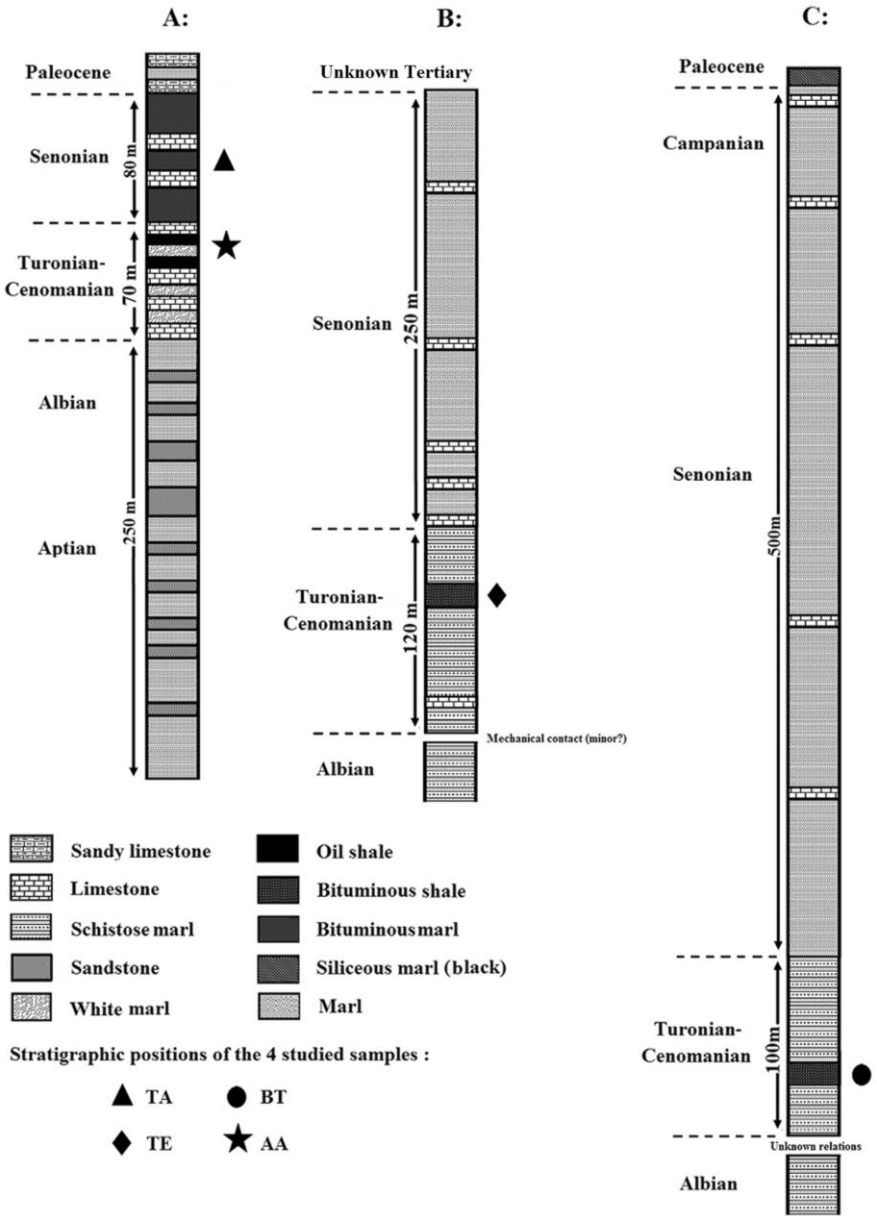

Fig. 2. Generalized stratigraphy of the Cretaceous and Paleocene rocks of A: Flyschs nappes [12], B: internal Tangier [15], C: external Tangier [16] of the Moroccan Rif.

was separated from the whole sample by ultracentrifugation of the < 2 μm fraction and mounted as an oriented aggregate mount [18]. This could be a very useful technique for the identification of clay minerals. The clay samples in oriented mounts have been successively analyzed after three separate treatments: air drying, glycolation and heat treatment at 550 °C [19–21].

2.4. X-ray fluorescence spectrometry (XRF)

X-ray fluorescence spectrometry is an analytical technique used to identify and measure the concentration of inorganic elements in these types of rocks. The selected raw samples of bituminous rocks of the Moroccan Rif were analyzed using an FX AXIOS PW4400 X-ray fluorescence (XRF) spectrometer system.

2.5. ICP-AES analyses

The determination of mass concentrations of inorganic elements in these types of sedimentary rocks is possibly done by inductively coupled plasma-atomic emission spectrometry (ICP-AES) [22, 23]. In this study, the selected raw samples were analyzed using a Jobin Yvon Ultima 2 m spectrometer after digestion in HF acid.

2.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a qualitative or semi-quantitative technique useful for determining particle composition and morphology. Besides the surface elemental analysis, SEM is also employed to obtain topographic images of mineral grains and determine their distribution.

Each sample of the whole rock was analyzed by a Cambridge Stereoscan 120 instrument coupled with an elemental analysis (EDX) unit. The apparatus was adjusted at 7–10 mm WD, 30 kV HV and 10000X magnification.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

Figure 3 shows the thermal behavior of raw samples of bituminous rocks of the Moroccan Rif heated up to the final temperature of 950 °C. The TG-DTG curves indicate that the decomposition process occurs in three main stages. At a temperature below 200 °C, the weight loss observed in all samples is attributed to the loss of moisture and interlayer water from the clay minerals which are present in the raw samples. The weight loss from about 200 to 600 °C corresponds to the degradation of organic matter (OM) [24, 25] (Table 2). According to our previous studies, the various organic geochemical parameters (Rock-Eval parameters) indicated that the organic matters (kerogen) of the studied samples are of types II, III and IV [26]. These results are comparable with those obtained for bituminous rocks of Timahdit and Tarfaya deposits, but in lower proportions [27–29].

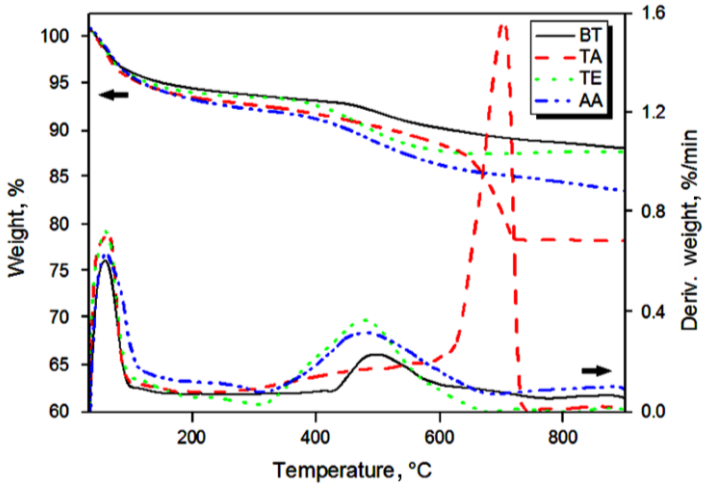

Fig. 3. TG and DTG curves of bituminous rock samples.

Table 2. TGA results for the studied samples of the Moroccon Rif and a sample of the Timahdit deposit

Sample	Water, %	OM, %	Carbonate, %
TA	4.7	5.59	10.65
TE	4.13	6.73	0.31
BT	3.48	4.77	2.51
AA	4.60	7.53	3.31
Sample of Timahdit	1.0	16.6	~35

Heating above 600 °C leads to the decomposition of mineral matter at temperatures between 600 and 800 °C due to the presence of carbonate species [30] (Table 2). In this range, the TA sample showed a high rate of weight loss contrary to the other samples examined.

Table 2 shows the comparison of the TGA results obtained (mainly organic matter) for the Moroccan Rif samples and an oil shale sample of the Timahdit deposit in the middle of Morocco [29]. These results indicate that the bituminous rocks of the Moroccan Rif contain a significant proportion of OM, which could be considered as a potential energy resource, such as the bituminous rocks of the Timahdit deposit.

3.2. X-ray diffractometry (XRD)

3.2.1. Overall mineralogy

X-ray powder diffractograms show that the major constituents of these samples are quartz, calcite and plagioclase (Fig. 4). Quartz is abundant in all samples. Calcite with some traces of hematite is found only in the sample TA. Plagioclase is present in all samples except the sample AA.

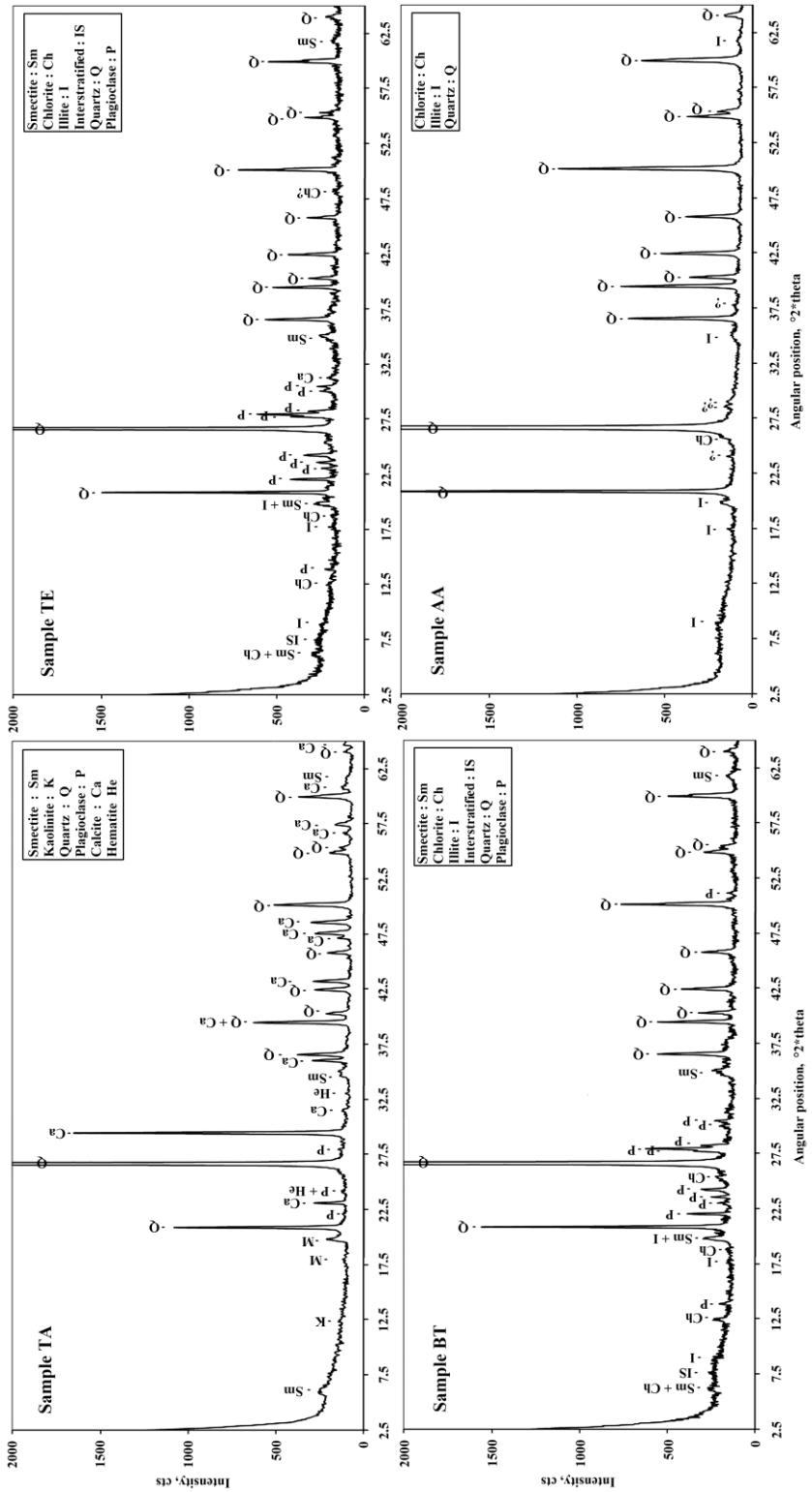

Fig. 4. X-ray diffraction analyses of the four studied samples.

Clay minerals are scarce or at least less visible on the untreated materials (no decomposition of cement). Table 3 provides a semi-quantification of major minerals using their major reflections and the reflection at 4.48 Å for all clays.

Table 3. The semi-quantitative X-ray diffraction analysis of major minerals of bituminous rock samples

Sample	Quartz	Calcite	Plagioclase	Hematite	Clay minerals
TA	++++	+++	tr	tr	++
TE	++++		++		+
BT	++++		++		++
AA	+++++				+

3.2.2. Clay mineralogy

The mineral composition (Fig. 5) of the fraction smaller than 2 μm of the samples studied is qualitatively shown in Table 4. After decomposing cements (carbonate and organic matter), it appears that the most abundant clay minerals are not chlorite or illite, but phases of a swelling type smectite or interstratified illite/smectite. Smectite dominates in the sample TA while for the samples BT and TE it is interstratified, swelling from 11.6 to 11.9 Å (with a superlattice to 29 Å) after glycolation. Furthermore, it is noticed that the AA material is virtually devoid of clay fraction, except some traces of chlorite and illite on the threshold of detection limit.

3.3. X-ray fluorescence spectrometry (XRF)

X-ray fluorescence analysis of the four studied samples (Table 5) shows that their content of quartz is very high (70.04–84.46 wt%), the mass concentration of calcium oxide (CaO) is 0.013–0.84 wt% and magnesium oxide (MgO) 0.47–1.32 wt%, indicating the low contents of dolomite and calcite (carbonate) in the bituminous rock samples. The mass concentration of aluminum oxide (Al_2O_3) ranges between 3.90 and 12.34 wt%, ferric oxide (Fe_2O_3) between 0.74 and 3.56 wt% and sulfur trioxide (SO_3) from 0.08 to 0.74 wt%; the two last proportion ranges indicate the low content of pyrite (FeS_2). It also appears that clay is present in the studied samples in different proportions.

These results corroborate those obtained by XRD analysis. It is clear that quartz is the dominant product in all samples while mass concentrations of calcium oxide (CaO) and magnesium oxide (MgO) are high only in the TA sample unlike the other samples. In addition, the presence of an appreciable amount of carbonates in the sample TA was also confirmed by thermogravimetric analysis.

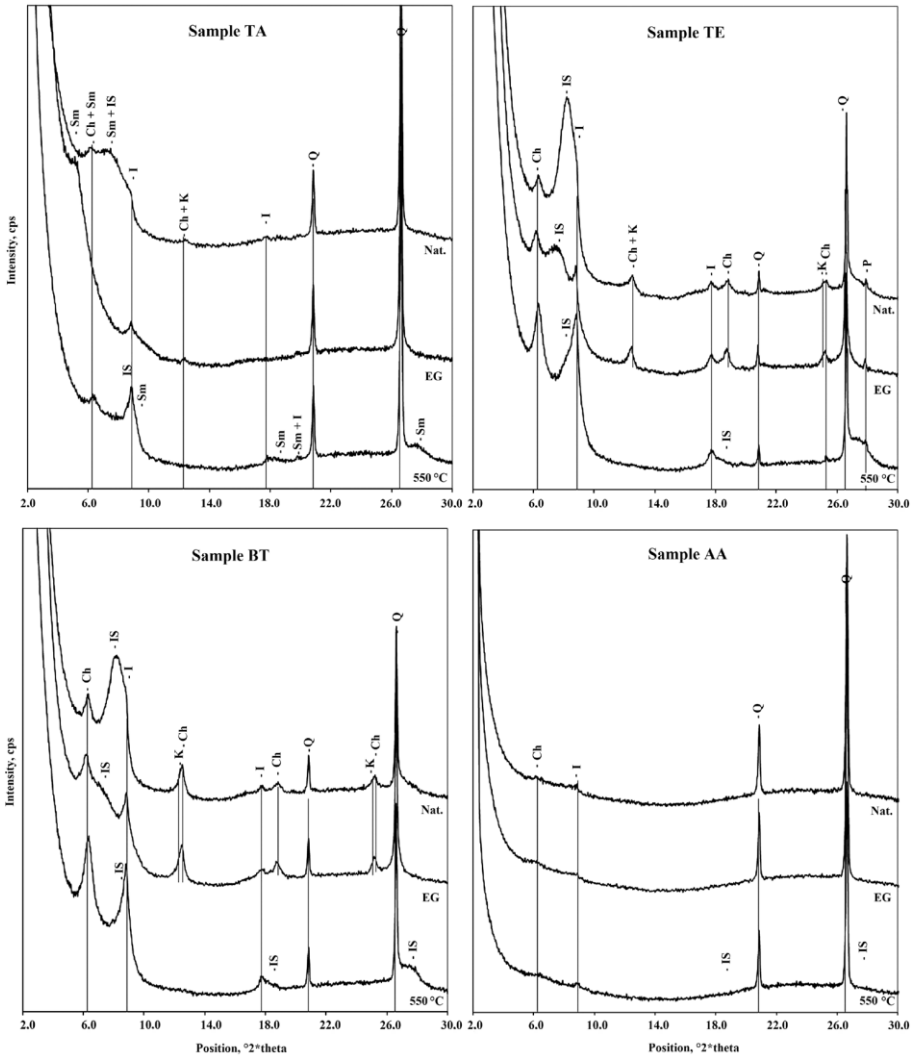

Fig. 5. X-ray diffraction analyses of the < 2 μ fraction of the four studied samples: Nat – untreated sample; EG – glycolated sample; H – sample heated to 550 °C; Ch – chlorite; IS – interstratified illite and smectite; I – illite; K – kaolinite; Q – quartz; P – plagioclase.

Table 4. The mineral composition of the < 2 μm fraction of the samples

Sample	Chlorite	Smectite	Interstratified	Illite	Kaolinite
TA	+	+++	+	+	
TE	++		+++	+	+
BT	++		+++	+	+
AA	tr			tr	

Table 5. Major, minor and trace element XRF analyses of 4 samples, 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

3.4. ICP-AES analyses

The mass concentrations of inorganic elements in the raw samples of different bituminous rocks are given in Table 6. As indicated in this table, the mass concentrations of ten inorganic elements have been chosen for each sample. It appears that silica dominates (32.2–39.3 wt%), followed by aluminum (2.44–5.88 wt%), except in the TA sample the mass concentration of calcium is much higher (5.6 wt%) than in the other samples. The mass concentrations of the rest of the inorganic elements are equal to or less than 1 wt%.

Table 6. Mass concentrations of inorganic elements in the bituminous rock samples of the Moroccan Rif by ICP-AES analysis

Sample, wt%	Al	Ca	Fe	K	Mg	Na	P	S	Si	Ti
AA	2.44	0.032	0.228	0.563	0.229	0.170	0.012	0.304	39.300	0.031
BT	5.88	0.159	0.596	0.996	0.350	1.080	0.013	0.0209	34.100	0.148
TE	5.34	0.251	1.208	0.888	0.350	0.860	0.035	0.0209	32.900	0.076
TA	3.31	5.607	1.045	0.640	0.498	0.203	0.053	0.04	32.200	0.074

3.5. Scanning electron micrography (SEM)

Figure 6 shows the SEM-EDX analysis of natural untreated samples of rocks. The SEM observations reveal some differences in particle morphlogy

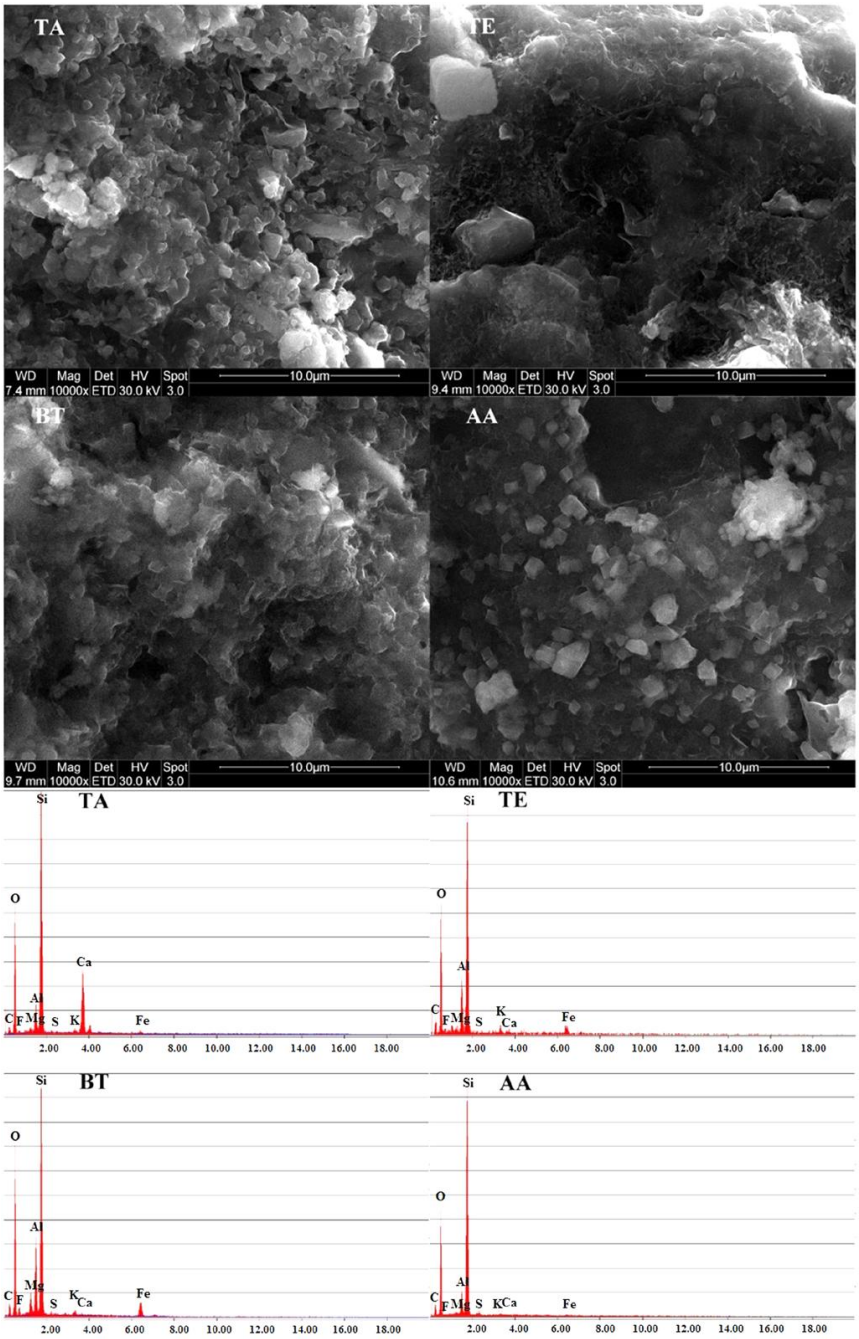

Fig. 6. SEMs for the bituminous rock samples studied.

between the samples. From the micrograph of the TA sample it is seen that the sample surface is mainly composed of small particles on the order of 1 μm. However, the surface of the sample TE appears to be compact and dominated by particles aggregates. The microstructure of the sample BT is composed of large holes and heterogeneous particles of different sizes. The surface of the sample AA consists of homogeneously dispersed particles. The EDX analysis demonstrates that the chemical composition of the samples surface is dominated by quartz species and aluminum oxide, especially for the samples TE and BT. The carbon peaks observed in the EDX spectrum (Fig. 6) indicate the content of total carbon, which includes the organic carbon (as organic matter) and mineral carbon (as carbonate). These results are in good agreement with the findings obtained by the above analytical techniques.

4. Conclusions

In the present work, different analytical techniques were used to determine the mineral composition of the studied bituminous rocks in the Moroccan Rif.

The dominant phase in the raw bituminous rock samples studied was quartz, calcite was present only in the sample TA (bituminous marls). Minor amounts of clay and other minerals were also detected.

Based on TGA results it was concluded that the organic part of bituminous rock samples studied could be considered as a potential energy resource and the samples can be ranked according to organic content as follows: AA > TE > TA > BT.

Acknowledgment

The authors are grateful for the financial support for this project from the University of Mohammed V - Agdal, Rabat, Morocco (Grant SCH04/09), and from the Hassan II Academy of Science and Technology, Rabat, Morocco.

REFERENCES

1. Bouchta, R., Zemmouri, O. *Geological Study and reserves of oil shale deposit of Timahdit*, Ministry of Energy and Mines. Mines Review, Geology and Energy, Rabat, 1981 (in French).
2. Tissot, B. P., Welte, D. H. *Petroleum Formation and Occurrence*. Springer, Berlin, 1984.
3. Hutton, A. C. Petrographic classification of oil shales. *Int. J. Coal Geol.*, 1987, **8**(3), 203–231.

4. Burger, J. The exploitation of oil shale; general information and future prospective. *Rev. IFP*, 1973, 28, 315 (in French).
5. Peters, K. E., Cassa, M. R. Applied source rock geochemistry. In: *The Petroleum System: From Source to Trap* (Magoon, L. B., Dow, W. G., eds.), AAPG, 1994, **60**, 93–120.
6. Brendow, K. Global oil shale issues and perspectives. Synthesis of the Symposium on Oil Shale held in Tallinn (Estonia) on 18 and 19 November 2002. *Oil Shale*, 2003, **20**(1), 81–92.
7. Sööt, P. M., Voll, H., Kõiv, T.-A. Utilization of oil shale retort gas. *Oil Shale*, 2012, **29**(3), 248–267.
8. Altun, N. E., Hiçyilmaz, C., Hwang, J.-Y., Suat Bağci, A., Kök, M. V. Oil shales in the world and Turkey; reserves, current situation and future prospects: a review. *Oil Shale*, 2006, **23**(3), 211–227.
9. Berthelot, Ch. *Carbonization of oil shales in France*. Factory St. Hilaire (Allier), October, 1938 (in French).
10. Berthelot, Ch. *The deposits of oil shales and limestones of Tangier and Mogador*, December, 1938 (in French).
11. Nejma, M. *Contribution in the development from rock to kerogen of Timahdit*. PhD thesis Es-Sciences, Mohammed V University, Rabat, 1989 (in French).
12. Durand-Delga, M., Olivier, P. Geological map of Melloussa Rif 1/50.000. *Notes and Mem. Geol. serv. Morocco*, 1988, N°296 (in French).
13. Saadi, M., Bouhaouli, A., Hilali, E. A., Ider, E. H., Ralhali, T. Moroccan bituminous rocks. Specially Devoted to oil shale in Morocco. *Geology and Energy, Ministry of Energy and Mines* N°50, 1981 (in French).
14. Clarion, D. L. *Notes on Western Atlas oil shale*. Report. S. C. P. / Mid / N°131, May, 1934 (in French).
15. Durand-Delga, M., Kornprost, J. Geological map of Tetouan–Ras Mazari Rif 1/50.000. *Notes and Mem. Geol. serv. Morocco*, 1985, N°292 (in French).
16. Kornprost, J., Wildi, W., Nold, M., Gutnie, M., Lespinasse, P. Geological map of Bab Taza Rif 1/50.000. *Notes and Mem. Geol. serv. Morocco*, 1980, N°288 (in French).
17. Belkbir, L., Barkia, H., Gérard, N. Investigation of diffusional phenomenon in the oil shale of Timahdit (Morocco), Role of sedimented plans. *Thermochim. Acta*, 1986, **103**(1), 147–150.
18. Gibbs, R. J. Preparation of X-ray diffraction mounts. In: *Procedures in Sedimentary Petrology* (Carver, R. E., ed.). John Wiley and Sons Inc., New York, 1971, 531–540.
19. Griffin, G. M. Interpretation of X-ray diffraction data. In: *Procedures in Sedimentary Petrology* (Carver, R. E., ed.). John Wiley and Sons Inc., New York, 1971, 541–569.
20. Hardy, R. G., Tucker, M. E. X-ray powder diffraction of sediments. In: *Techniques in Sedimentology* (Tucker, M. E., ed.). Blackwell, Oxford, UK, 1988, 191–228.
21. Moore, D. M., Reynolds, Jr., R. C. *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd ed. Oxford University Press, Oxford, 1997.
22. Wilkerson, C. L. Trace metal composition of Green River retorted shale oil. *Fuel*, 1982, **61**(1), 63–70.
23. Orupõld, K., Habicht, J., Tenno, T. Leaching behaviour of oil shale semicoke: compliance with the waste acceptance criteria for landfills. *Oil Shale*, 2008, **25**(2), 267–275.

24. Jaber, J. O., Probert, S. D. Pyrolysis and gasification kinetics of Jordanian oil shales. *Appl. Energ*., 1999, **63**(4), 269–286.
25. Han, X. X., Jiang, X. M., Cui, Z. G. Studies of the effect of retorting factors on the yield of shale oil for a new comprehensive utilization technology of oil shale. *Appl. Energ*., 2009, **86**(11), 2381–2385.
26. Groune, K., Halim, M., Benmakhlouf, M., Arsalane, S., Lemee, L., Ambles, A. Organic geochemical and mineralogical characterization of the Moroccan Rif bituminous rocks. *J. Mater. Environ. Sci*., 2013, **4**(4), 472–481.
27. Amblès, A., Halim, M., Jacquesy, J.-C., Vitorovic, D., Ziyad, M. Characterization of kerogen from Timahdit shale (Y-layer) based on multistage alkaline permanganate degradation. *Fuel*, 1994, **73**(1), 17–24.
28. Halim, M. *Study of sedimentary organic matter, Timahdit and Tarfaya deposits*. PhD thesis Es-Sciences, Mohammed V University, Rabat, 1993 (in French).
29. Saoiabi, A., Doukkali, A., Hamad, M., Zrineh, A., Ferhat, M., Debyser, Y. Thermal behavior of Timahdit oil shale (Morocco). *C. R. Acad. Sci., Paris, Chimie/Chemistry*, 2001, 4, 361–366 (in French).
30. Aboulkas, A., El Harfi, K. Study of the kinetics and mechanisms of thermal decomposition of Moroccan Tarfaya oil shale and its kerogen. *Oil Shale*, 2008, **25**(4), 426-443.

Presented by A. Siirde
Received November 21, 2012