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RESEARCH ARTICLE

THE FIVE REASONS PROVING THAT THE TIMAHDIT OIL SHALE DEPOSIT IS LACUSTRINE

Awatif Farah, Nasreddine Azouaz, Abdeljabbar Attaoui, Imane Sadek and Fouzia Taous

Department of Chemistry, Faculty of Sciences, Casablanca, University Hassan IIMorocco.

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Abstract

Three types of sedimentation occur during the formation of oil shales, either in marine locations, in lacustrine locations and on the continent. The Timahdit oil shale deposit is located in the Atlas Mountains, In this work we counted four reasons to confirm that this deposit called Timahdit is a lacustrine deposit. The techniques used during this study are dispersive X-ray diffraction, infrared spectroscopy, thermogravimetry (DTG) and atomic absorption. X-ray diffraction in dispersive allowed us to identify qualitatively and in an elementary way the elements, for example the element chlorine. Infrared spectroscopy allowed us to follow the two compounds of the oil shales, aliphatic hydrocarbons and aromatic hydrocarbons and to relate the two compounds in mass. Thermogravimetry (DTG) allowed us to compare the reactivity of the Timahdit deposit with that of the Tarfaya marine deposit. Atomic adsorption allowed us to quantitatively follow the sodium element and to make a comparison with the Tarfaya marine deposit which is located in the Atlantic Ocean.

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Introduction:-

The first research into the estimation of oil shale in Morocco was carried out in Tangier with the creation of the Tangier Oil Shale Company. This company had built a pilot plant with a daily capacity of 80 tons of oil shale between 1939 and 1945. The Timahdit and Tarfaya deposits were only discovered later (Tarfaya in 1966 and Timahdit in 1974).

Research for the development of oil shales experienced considerable development worldwide between 1973 and 1979, following the oil crises. Thus for our country, the two deposits of Timahdit and Tarfaya were the subject of several geological and mining studies, laboratory studies as well as pyrolysis, hydrolysis and direct combustion tests.

Morocco affected its own experience and developed the T3 process (initial of the three deposits of Tangier, Tarfaya and Timahdit), thanks to the geological, mining and laboratory works, carried out from 1975 to 1985, which allowed, in addition to the highlighting of the reserves in place, to show that the Moroccan shale could be valorized by pyrolysis for the production of hydrocarbons. (Moussa.Saadi: 1981)

This work, carried out in four experimental sections, allowed us to seek the identification of the Timahdit deposit (either as a lacustrine or marine deposit)

Corresponding Author:- Abdeljabbar Attaoui

Address:- Department of Chemistry, Faculty of Sciences, Casablanca, University Hassan IIMorocco.

1/Bibliographic study

Four types of oil shale from Spain (**M. A. Kruge et al: 1991**) were studied by the geochemical and petrographic method; three of the samples were of a lacustrine nature and one of a maritime nature. The petrographic method shows a dominance of liphodetrinite associated with the bitumen contained in the mineral matter, as well as a similarity of the tertiary structure concerning the organic matter. As for the geochemical method, it shows the presence of organic matter which is a mixture of tertiary and aquatic derivatives. We mention beforehand the works carried out on Kerogenes isolated from their mineral matrix

(**J. Espitalie et al: 1973, B. Tissole et al: 1973, B. Durand et al: 1972, B. Durand et al: 1973**) which showed that it is possible to classify the different types of kerogen and to follow their physico-chemical transformations during burial. Van Krevelen was able to show that certain shale lineages can be classified using a diagram showing the atomic composition of the three main elements (C, H and O) of the kerogens as H/C and O/C (**V. Krevelen: 1951**). He assigned that samples corresponding to the same type of organic deposit group together on a curve called "evolutionary path". One can distinguish several of these evolutionary paths that correspond to different natures of organic matter, kerogenes, composed almost exclusively of algae, are located on a path with a high H/C ratio and a low O/C ratio. On the contrary, the kerogenes, consisting mainly of higher plant debris and continental material, have a high O/C ratio and a low H/C ratio.

Regarding the organic geochemistry study, the yields of extractable organic matter (EOM) increased from 1.6 to 6.1mg g⁻¹ per gram of rock (Table 1)(**Michael A Kruge and Isabel Suarez-Ruiz: 1991, A. Attaoui et al: 2022**),. In addition, the percentage of saturated hydrocarbons in the extracts increased from 11 to 40%, aromatic hydrocarbons increased from 2 to 25% and polar compounds decreased from 87 to 35%. Although the marine Jurassic and Cretaceous lake samples have approximately the same reflection and EOM values, the ratio of saturated to aromatic hydrocarbons for the lake sample (1.6) is higher than those in the marine environment (0.7). A predominance of saturated over aromatic compounds is observed in the lake samples.

Table 1:- Petrographic, biological and geochemical results.

Sample Age Location Environement	CP Carboniferous Puertollano Lacustrine	JP Jurassic Punta del Cuerno Marin	KL Cretaceous Llames Lacustrine	MR Miocene Rubielos de Mora Lacustrine
Liquidchromatographic fractions(%)				
Saturantes	40	14	18	11
Aromatiques	25	21	11	2
Polars	35	65	71	87

2/Origin of samples

The oil shales studied were kindly provided by the Ministry of Energy and Mines and by ONAREP. These rocks come from two important Moroccan deposits; one is located in the Saharan region (Tarfaya) and the other in the Middle Atlas (Timahdit, layer M).

The Tarfaya deposit is located to the east of the town of Tarfaya, and extends from SebkatTah in the south-west to OuedAmmaFatna in the north-east, i.e. over approximately 125 km. It is limited to 50 km to the North-West-South. The total reserves of the Tarfaya bituminous marls (Cenomanian, Turonian, Coniacian,Companian...) are estimated at more than 200 billion tonnes with an average of 50 to 60 litres per tonne. Some layers can contain up to 100 litres/ton.

The Timahdit deposit is located in the heart of the Middle Atlas, 35 km south of Azrou. It is made up of two synclines, EL Koubbat and BouAngueur, separated by the Jebel Hayane anticline and affected by an important tectonic accident. Both synclines are composed of Upper Cretaceous deposits and are overlain by Paleogene formations. The average oil content for this deposit is 74l/tonne. Some layers reach a grade of 130l/ton and the total reserves amount to 18 billion tons (**Moussa. Saadi: 1981**)

3/ Characterization of two average samples.

The interest of the knowledge of the chemical or physical characteristics is that it allows valorizing this shale. In table 2, we will gather some of the characteristics of two average samples from the two deposits.

Deposit Characteristics	Moyen sample of Timahdit's deposit(25)	Moyen sample of Tarfaya's deposit
density	2,21	2,24
HCV Kcal/kg	1340	1228
% Ash	64	59,46
CO ₂	20,4	26,07
Organic matter	15,8	14,47
% C _{tot}	18,34	17,74
% C _{min}	5,57	7,72
% C _{org}	12,77	10,62
% S _{tot}	2,26	1,92
% S _{org}	1,54	1,6
% S _{pyr}	0,60	0,31
% S _{sul}	0,12	-

Table 2:- Characteristics of two average samples from *Tarfaya and Timahdit.

* Communication from the Ministry of Energy and Mines and ONAREP

Mineral matter

The identification of the phases of the mineral matter of the shale in this study was carried out on powder using a C.G.R Theta 60 X-ray diffractometer with a copper anti-cathode of wavelength 1.54051. X-ray diffraction is a qualitative analysis technique; to obtain the quantity of the rock's constituents, it is necessary to use other techniques, such as thermogravimetry and dispersive X-ray diffraction, which make it possible to identify the constituent elements. We will gather in table 3 the mineralogical composition made by some authors (**M. Taibi et al: 1985, O. Bikri et al: 1981, C.Y.Cha:1981**) respectively for the deposits of Tarfaya, Timahdit and Colorado.

Deposit constituents	Tarfaya	Timahdit	Colorado
Dolomite(CaMg(CO ₃) ₂)%	4,1	15,9	32
Calcite CaCO ₃ %	59,2	41,5	16
Quartz (SiO ₂)%	-	19,5	15
Clay(Illite,Kaolinite)%	28,4	13,4	0
Pyrite (FeS ₂) %	2,4	1,8	1
FeCO ₃ + Fe ₂ O ₃ %	-	1,8	-
TiO ₂ +phosphate %	1,2	2,4	-
Other elements %	4,7	3,7	-

Table 3:- Composition of mineral matter of three varieties of shale: Timahdit; Tarfaya and Colorado.

The organic matrix

It represents 12 to 24% of the total mass of the shale and originates from matter initially present in plants such as algae and trees or microorganisms (bacteria and fungi). It varies significantly from one deposit to another.

Oil shale contain organic matter called kerogen: an abundant form of fossil organic matter that results from the accumulation in a reducing environment in lake or marine mud of the debris of algae or zooplankton living in surface waters, possibly reworked by bacteria active in the mud. Its structure is not sufficiently well known, it is generally considered to be a three-dimensional macromolecule made up of polycyclic rings linked together by aliphatic chains or heteroatomic bonds.

The general composition of kerogen varies and depends on the nature of the organic matter from which it is derived and the environment in which it is deposited.

As in living organisms, the kerogen in sediments generally consists of carbon, hydrogen and oxygen, with small amounts of nitrogen and significant amounts of sulphur. The composition of the kerogen varies significantly with the nature of the initial biomass and the sedimentation conditions.

Depending on the origin of the organic matter, kerogen is classified into three types:

- Type I kerogen, which is derived from planktonic lake biomass.
- Type II kerogen, which is derived from marine planktonic biomass.
- Type III kerogen, derived from higher plant biomass.

4/Experimental part.

4.1:Comparative study of the two deposits of Tarfaya and Timahdit (thermogravimetry)

The reactivity of a marine deposit is superior to that of a lacustrine deposit, in this objective we are going to compare the reactivity of the two deposits considered. The Tarfaya deposit is marine; it runs along the Atlantic Ocean, a large part of it is still immersed in this ocean.

The pyrolysis of the oil shale was carried out for both varieties in a dynamic regime up to 750°C in a nitrogen atmosphere (PN₂= 1atm flow rate = 9 cm³/min) on samples with a particle size of 0.05 mm and a mass of between 1.4 and 2.5 mg. This mass range was determined by studying the mass effect and corresponds to the zone where this effect is no longer felt. The results obtained on the two varieties of Tarfaya and Timahdit shale are shown in the figure (A. Attaoui et al., 1992). On these curves, three distinct regions of mass loss are observed

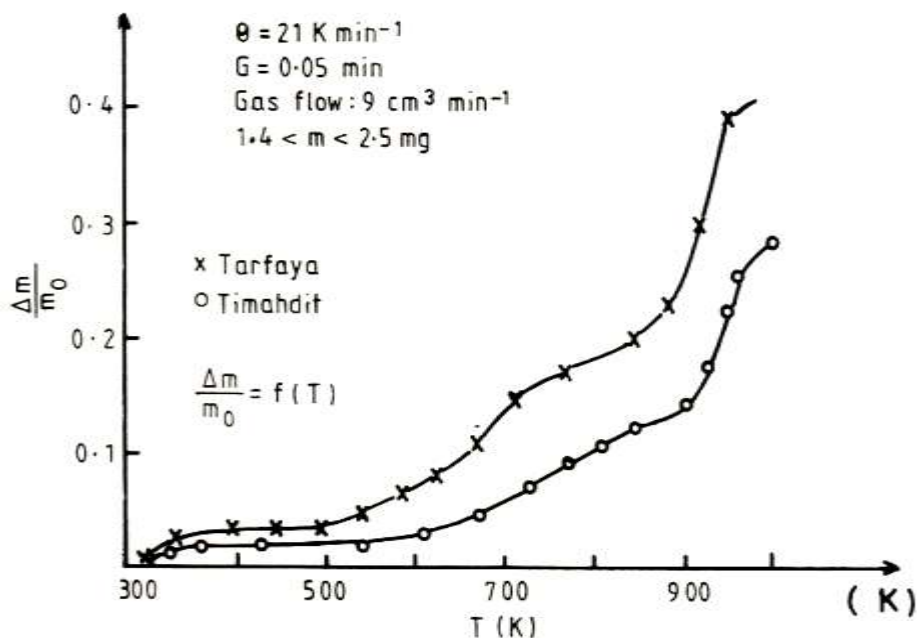


Fig1:- Thermograms in $\Delta m/m_0$ of the pyrolysis of two oil shale varieties.

The decomposition in this temperature range, which is 250 to 520°C, occurs with a percentage loss of 13.7% for the Tarfaya shale and 11.4% for the Timahdit shale. The temperature range corresponds to the oil production stage, which is usually called the primary pyrolysis stage. Figure 2 shows this stage in terms of the degree of advancement, and we show the instantaneous rates of this decomposition in Figure 3.

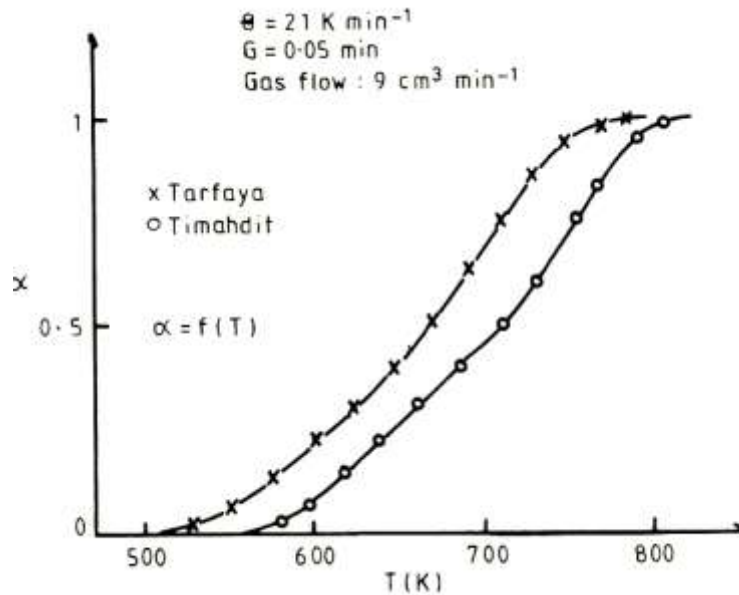


Fig 2:- Thermograms $\alpha = f(T)$ of pyrolysis.

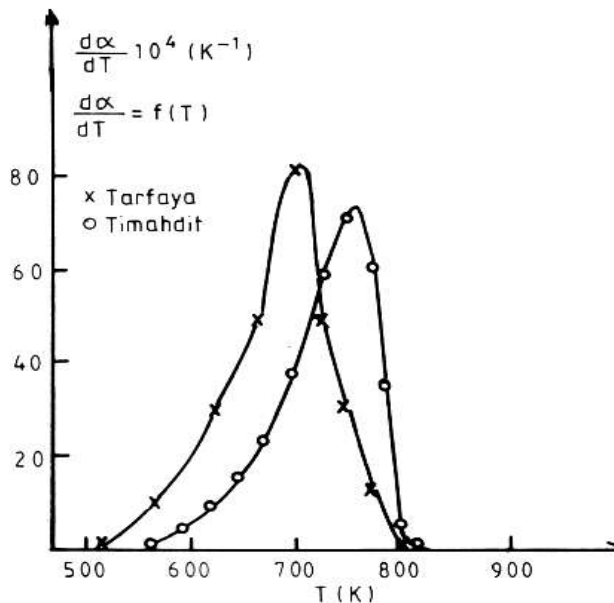


Fig 3:- Transformation rate of pyrolysis for both varieties for both varieties.

The comparison of the instantaneous rates of the two varieties of shale as a function of temperature shows that the Tarfaya shale is more reactive than the Timahdit shale. Indeed, a temperature difference of at least 60°C separates the maximum loss rate for Tarfaya from Timahdit.

We adopted the non-linear model for the calculation of the activation energies using the mathematical modelling of Coats-Redfern by taking the reaction order of 1.6 valued by the Friedman model (Coats-Redfern: 1964, Friedman: 1965)

The Coats-Redfern equation for an order different from 1 is :

$$1-(1-\alpha)^{1-n} / 1-n = k_0 RT^2 (1-2RT/E) \exp (-E/RT)/\theta E \text{ pour } n \neq 1$$

The Coats-Redfern equation for an order different from 1 is :

$$1-(1-\alpha)^{1-n} / 1-n = k_0 RT^2 (1-2RT/E) \exp (-E/RT)/E \text{ for } n \neq 1$$

It is therefore possible to determine the value of the apparent activation energy from the slope of the line by plotting: $\ln [(1-\alpha)^{1-n}/T^2 (1-n)] = f(1/T)$ for $n \neq 1$.

The activation energies calculated for the two varieties

Tarfaya $E_a = 71, 8 \text{ KJ/mol}$

Timahdit $E_a = 78 \text{ KJ/mol}$

The Tarfaya shale is more reactive, kinetically, than the Timahdit shale. This reactivity results in a rather low pyrolysis temperature.

4.2: Calculation of the ratio of the mass aliphatic unsaturated hydrocarbons to the mass aromatic hydrocarbons (infra-red spectroscopy)

In this paragraph we will calculate the ratio of the mass of aliphatic unsaturated hydrocarbons to the mass of aromatic hydrocarbons using infrared spectroscopy.

Generally, to analyze the organic matter of oil shale, it must be extracted from the rock, for which appropriate techniques and solvents are used, for example the use of a sox let. We also mention the extraction of oils from shale using water with CO and Na_2CO_3 by heating at a rate of 8.5°K/min ; it has been observed that the effect of extraction (or its quantity) decreases with water, CO and Na_2CO_3 than in the presence of water and CO. It becomes even smaller in the presence of water and argon. The maximum yield is obtained at a CO pressure of 1 MPa (**T. Funazukuri et al: 1988**). Similarly the Chinese Maoming shale was subjected to supercritical extraction using organic fluids, water and toluene separately. Under these conditions it was found that polar compounds are more easily decomposed with water than with toluene (**T. Funazukuri et al: 1988***). The yield of non-polar compounds is not affected by the solvent. After extraction of this organic material, its analysis is done by spectroscopic methods such as Infrared, Ultra-Violet, and so on.

In our study, samples of shale belonging to the different layers were placed in test tubes to which tetrachloroethane (1, 1, 1) was added as a solvent for one week at room temperature. After that the analysis of the extracted organic matter is done by Infrared spectroscopy.

The spectra in figures 4, 5, 6, 7, 8 and 9 correspond respectively to the Z0, Z1, Z2, Z3, and Z4 zones of Tarfaya and the M layer of the Timahdit deposit.

The principle spectroscopic bands around 1580 and 3300 cm^{-1} correspond respectively to monocyclic unsaturated hydrocarbons (monosubstituted, disubstituted, trisubstituted, tetrasubstituted and pentasubstituted) and to aliphatic unsaturated hydrocarbons such as alkynes. Concerning metals in organic matter from fossil products (oil, shale, coal), they are bound to porphyrin macrocycles in the form of metallorhynes, which are extracted using a soled (**A. Saoiabi: 1988**). The quantity of organic matter obtained is of the order of 1% and 1.18% by gross mass for the Timahdit and Tarfaya deposits. The solvent used is chloroform or methylene chloride ($\text{CH}_2 = \text{Cl}_2$). For our work, cold tetrachloroethane is used (fig. I.R). The organic matter extracted is unsaturated aliphatic and aromatic hydrocarbons for both deposits and for all samples.

In conclusion, the organic matter of the different oil shale samples from the two deposits corresponds to unsaturated, aliphatic and aromatic hydrocarbon compounds, and the quality of this material does not change from one sample to another.

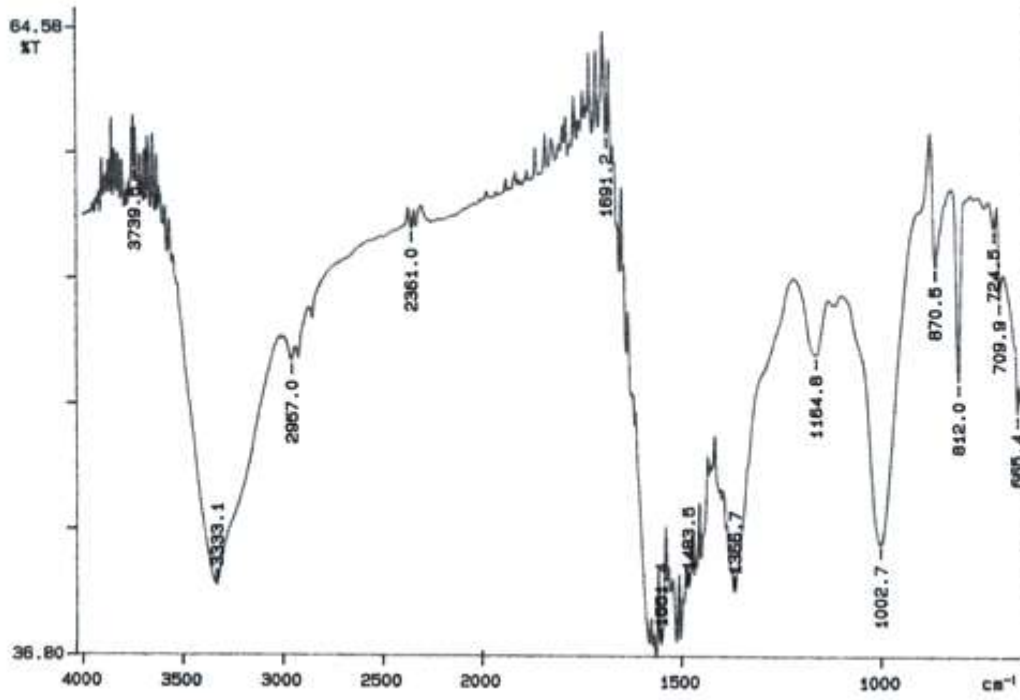


Fig. 4:- Infrared spectrum of ZO (Tarfaya) oil shale solubilized by tetrachloroethane.

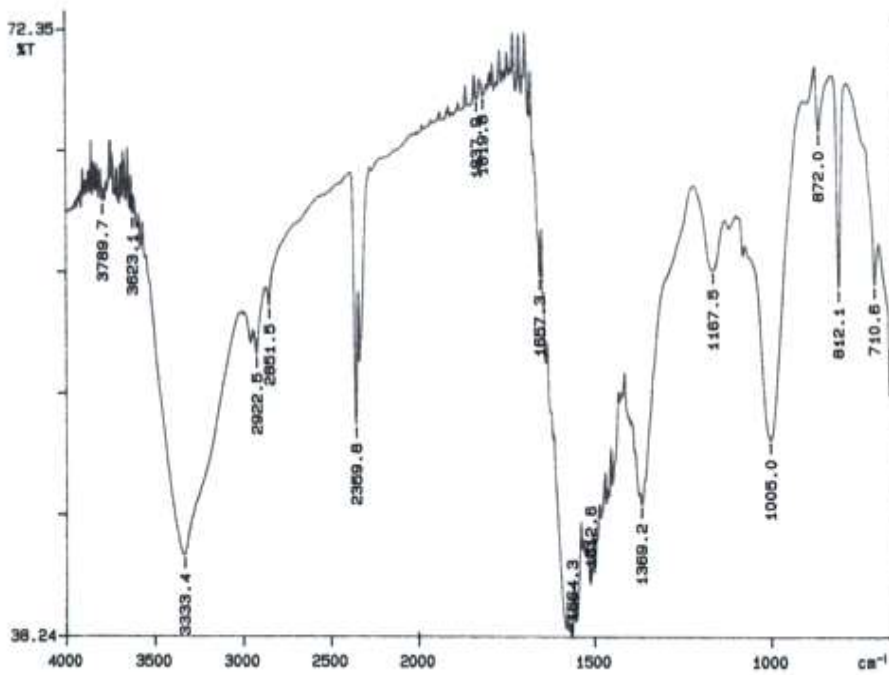


Fig. 5:- Infrared spectrum of Z1 (Tarfaya) oil shale solubilised by tetrachloroethane.

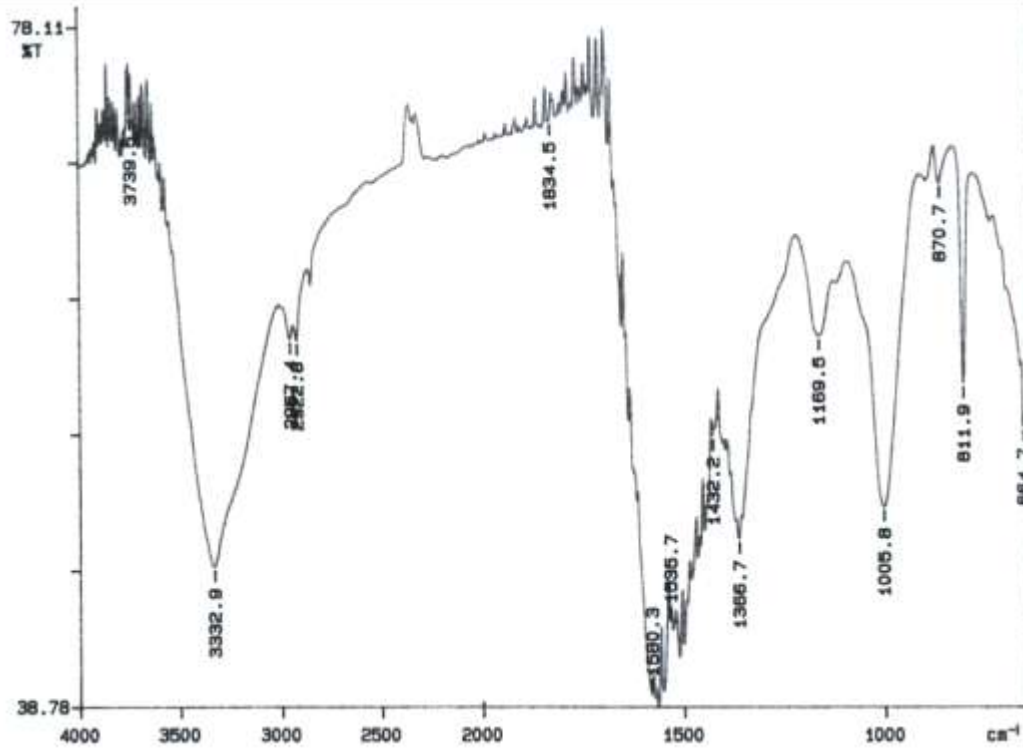


Fig. 6:- Infrared spectrum of Z2(Tarfaya) oil shale solubilised by tetrachloroethane.

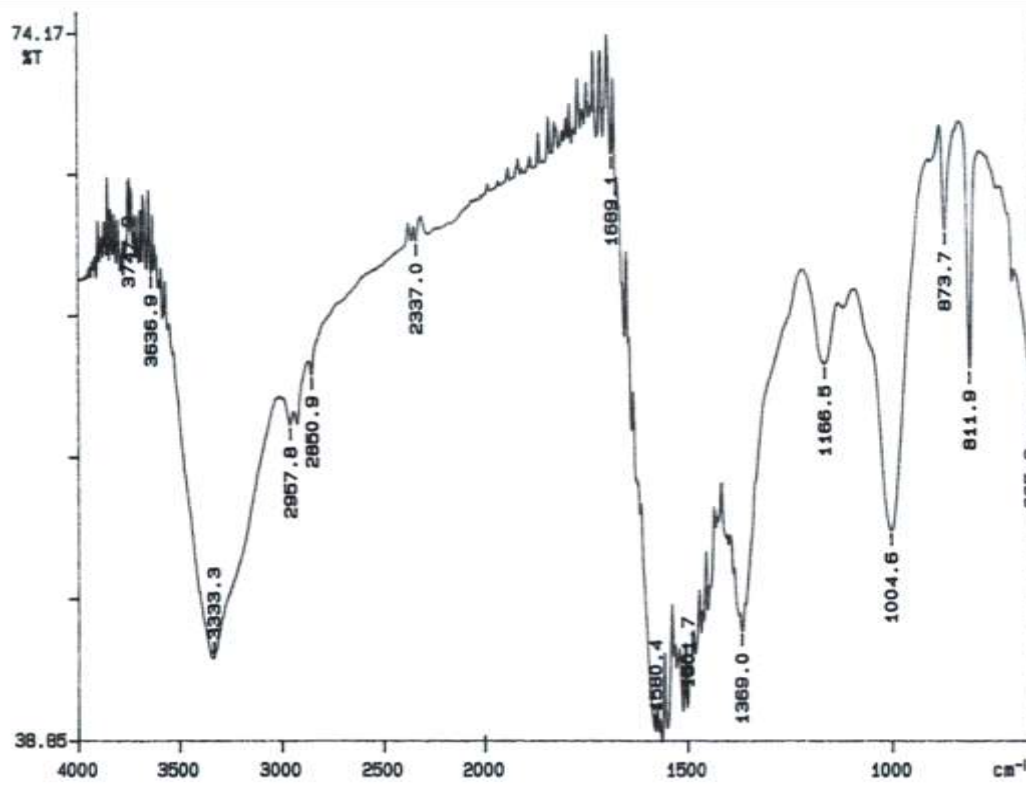


Fig. 7:- Infrared spectrum of Z3(Tarfaya) oil shale solubilised by tetrachloroethane.

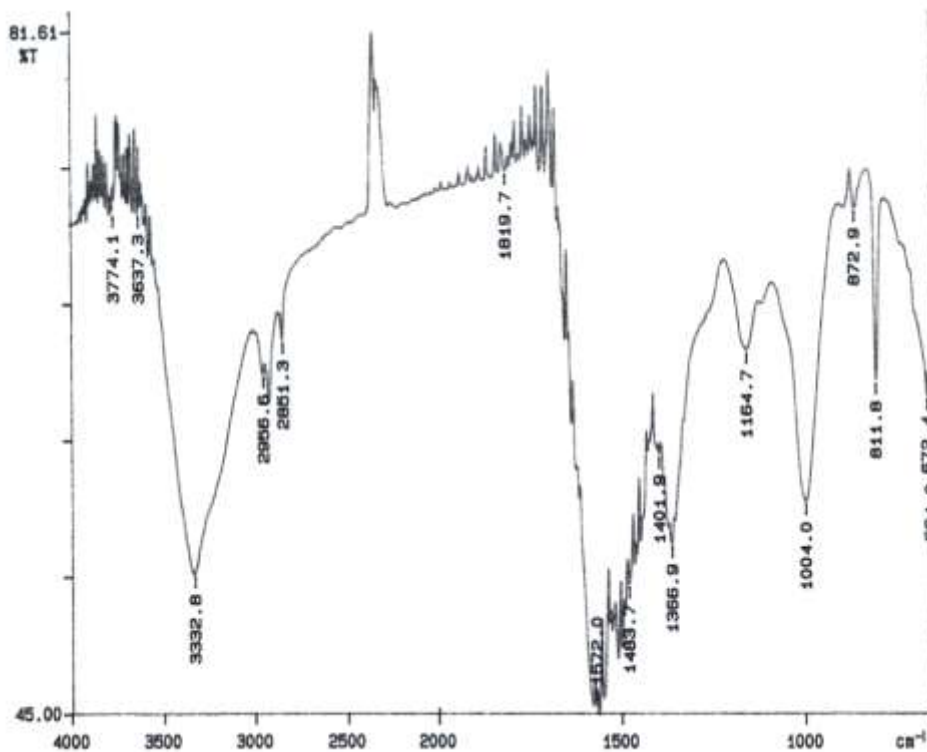


Fig. 8:- Infrared spectrum of Z4(Tarfaya) oil shale solubilised by tetrachloroethane.

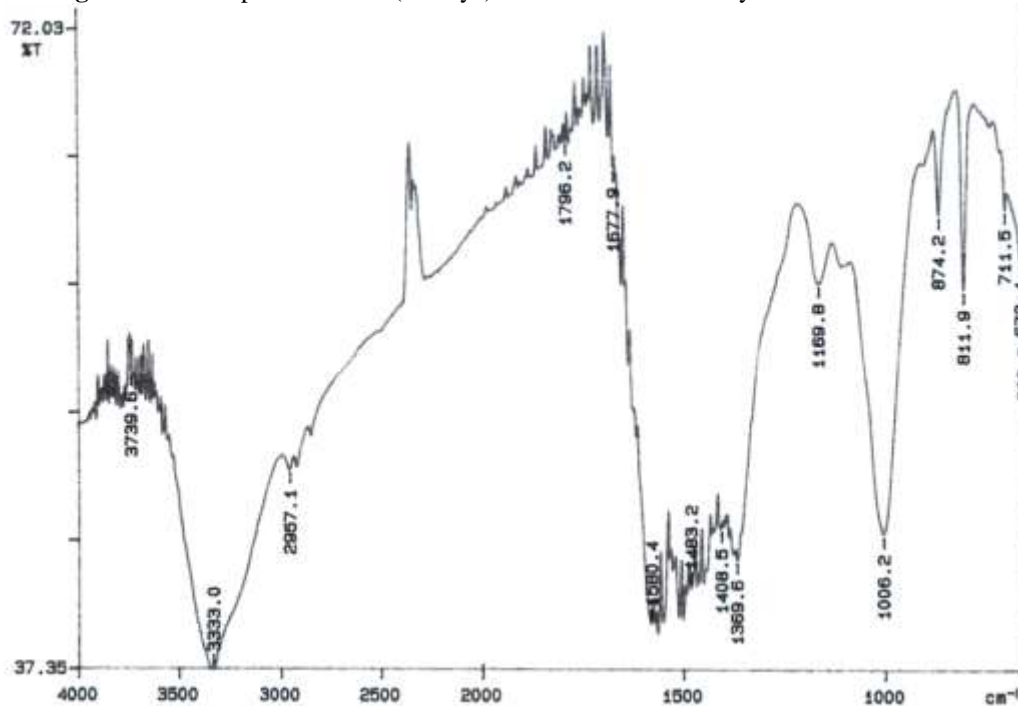


Fig.9:- Infrared spectrum of M(Timahdit) oil shale solubilised by tetrachloroethane.

The areas of the peaks at the frequencies of 1580 cm (aliphatic unsaturates) and 3300 cm (aromatics) are proportional to the corresponding mass quantities. Therefore we calculated the ratio of these areas which is proportional to the mass ratio of the two compounds mentioned. The following table represents this ratio.

Sample	Z0	Z1	Z2	Z3	Z4	Ti
Report m_{ins}/m_{aro}	0,73	0,82	0,66	0,72	0,69	1,29

We represent this report in the following figure:

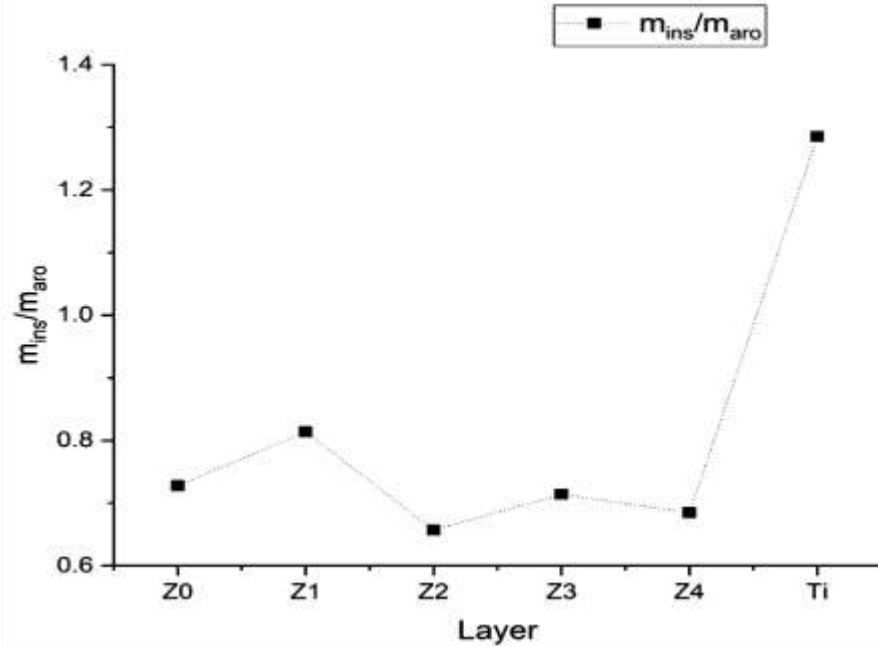


Fig 10:- Report m_{ins}/m_{aro} for different layers.

We observe this different ratio between the Timahdit deposit and the Tarfaya deposit. This difference in ratio confirms the lacustrine quality of the Timahdit deposit

4.3: Presence of chlorine in Tarfaya and its absence in Timahdit, as well as the presence of silicon and aluminium (elements of clays) is remarkable in Timahdit (dispersive X-ray).

The following spectra represent the dispersive XR(Dispersif) of two samples, one Z4 from Tarfaya and the other the M layer from Timahdit

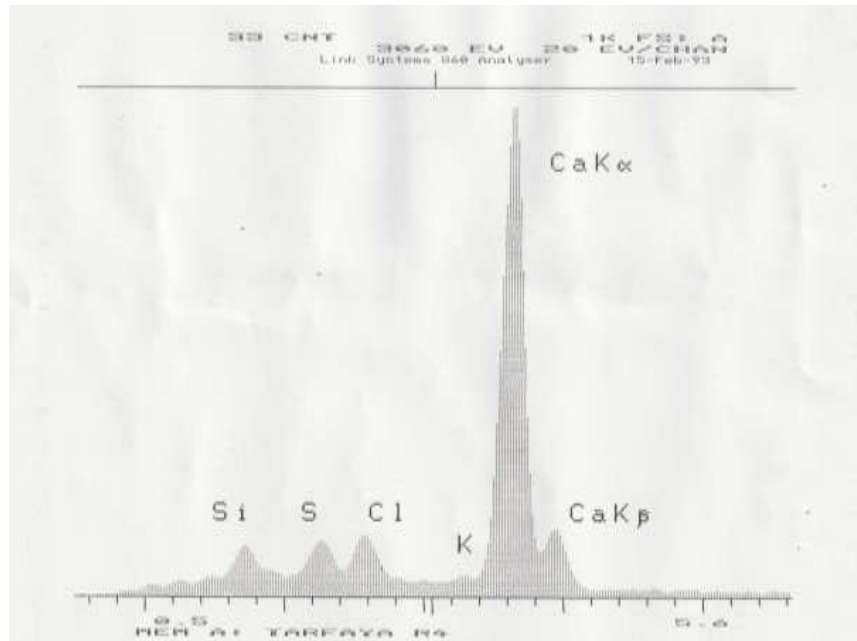


Fig. 11:- RX dispersifs pour Tarfaya (Z4).

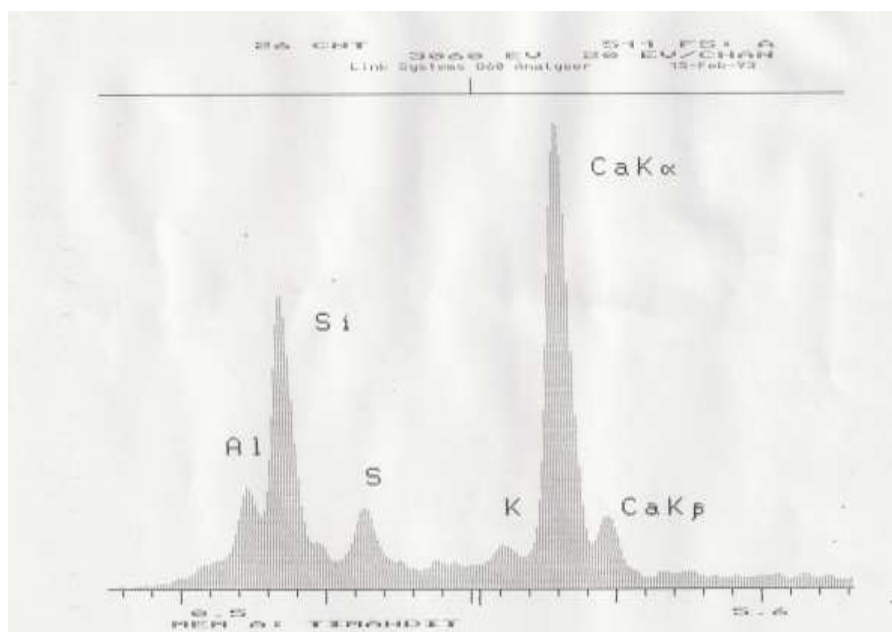


Fig.12:- RX dispersifs pour Timahdit(M).

We will compare the presence of the different constituents of the two samples:

*Calcium is in almost identical proportion for both deposits.

*Potassium is slightly concentrated in Timahdit.

*Chlorine is non-existent in Timahdit whereas it is found in the marine deposit of Tarfaya.

*Sulphur is slightly concentrated in Timahdit.

*Silicon and aluminium, which are compounds of clays called aluminium silicates, are concentrated in Timahdit, whereas aluminium is non-existent in Tarfaya.

4.4: Determination of sodium (Atomic absorption).

Atomic absorption spectrometry (AAS) is a privileged tool for analysis in environmental sciences. Coupled with a graphite furnace, AAS allows the determination of major and trace elements in various types of substrates: plants, soils, sediments, rocks, food, solid waste, liquid effluents, groundwater, surface water, waste water, etc.

We have a Thermo Electron FS 95 spectrometer operating in graphite furnace mode with electro thermal atomization, and a Varian 50AA spectrometer with flame atomization.

In principle, the spectrometry AAS consists of vaporizing the liquid sample and heating it with a flame or oven. In flame mode, the equipment can be used for both absorption and emission spectrometry. The flame is directed towards a light emitted by an appropriate lamp emitting the characteristic wavelengths of the element of interest. As they pass through the flame, the light waves - whose wavelengths correspond to the element being measured - are absorbed by the excited ions present in the flame. The absorption is measured using a dispersive prism and a photocell and is directly proportional to the concentration of the element. When the atoms of an element have been excited, their return to the ground state is accompanied by the emission of light of a well-defined frequency F specific to that element. The same element dispersed in a flame has the property of absorbing any radiation of the same frequency F . These results in an absorption of the incident radiation related to the concentration of the element in question. In flame mode, the detection limit is in the ppm range. The sensitivity of flame mode determinations is limited by secondary reactions (evaporation) and the very short time spent in the flame. To increase the sensitivity of the assay, it is necessary to reduce or eliminate these two factors by atomization. This is done in a graphite furnace of reduced volume under an inert atmosphere. The detection limit is then in the ppm range. The applications developed in our laboratory allow the following elements to be measured in flame mode and in the graphite furnace: Na, K, Ca, Mg, Mn, Fe, Cd, Cr, Cu, Ni, Pb, Co, Zn, As,... These determinations have supported several studies on the functioning of soils, the characterization of liquid samples (soil solution, river and marine waters) and the behavior of trace metals in soils and estuaries.

The raw oil shales(layer Z1 for Tarfaya and layer M for Timahdit, these two layers have a similar percentage of organic matter) were treated in an oven set once at 500C0 and once at 800C0 in combustion for one hour in an isothermal process, the aim of which was to eliminate the organic matrix at 500C0 and then eliminate the carbonates at 800C0 .

After this combustion treatment, 0.5g of the raw shale and 0.5g of the shale treated at 500C0 and 800C0 were taken and a volume of 20ml of sulphuric acid H₂SO₄ (0.1N) was added.

4.4.1: Calibration

Calibration was carried out with NaCl, which ppm was prepared in the presence of H₂SO₄ under the same solubility conditions. The results of the analysis of NaCl in solution taken as reference are as follows:

Absorbance	Ppm
0.210	20 ppm
0.252	40 ppm
0.255	60 ppm
0.259	80 ppm
0.264	100 ppm

The following figure 13 shows the absorbance =f (ppm)

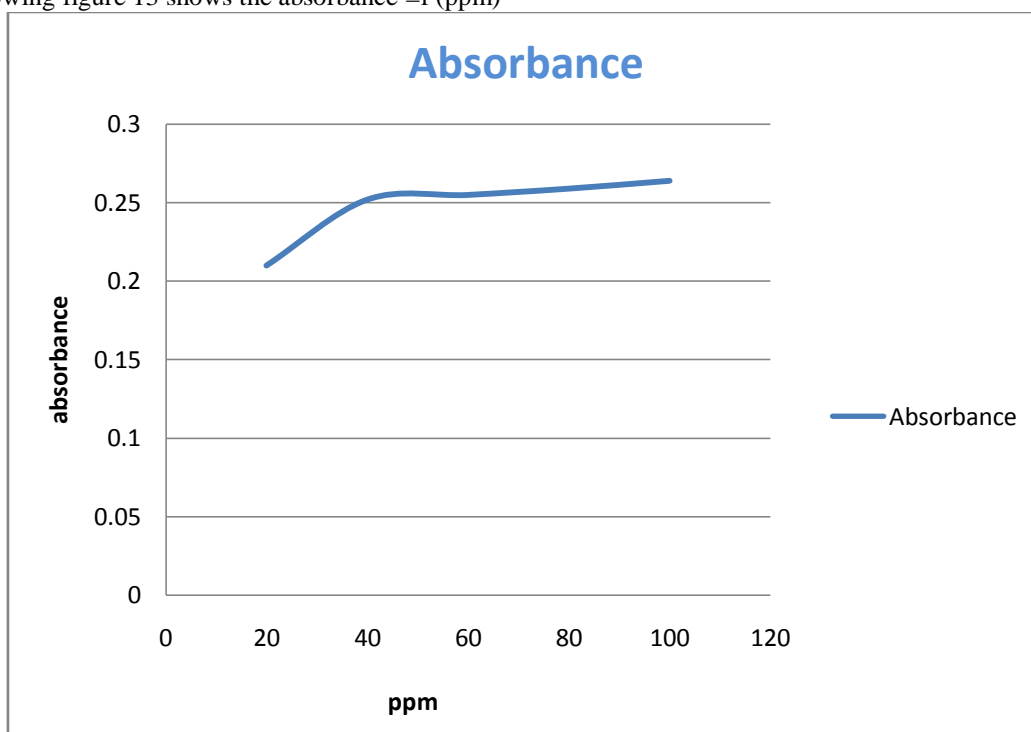


Fig.13:-Na Cl calibration to highlight sodium.

4.4.2: Processing the results

We calculated the slopes between 40 ppm and 60 ppm, then between 60 ppm and 80 ppm, then between 80 ppm and 100 ppm

$$P1=1,5 \cdot 10^{-4}$$

$$P2=2 \cdot 10^{-4}$$

$$P3=2,5 \cdot 10^{-4}$$

Average of the slopes :

$$P=(P1+P2+P3)/3 =2 \cdot 10^{-4}$$

To obtain the ppm value for each sample, simply divide the absorbance by the average slope:

$$\text{ppm} = \text{absorbance} / \text{average P}$$

The following table shows the results of the absorbance tests at different temperatures for the two deposits.

Temperature	Ambiant	500°C	800°C
A (Timahdit)	1,607	1,557	1,603
A(Tarfaya (marin))	2,290	2,342	2,304

Similarly, using the slope of the calibration we arrive at the ppm of the two deposits as a function of temperature:

Temperature	Ambiant	500°C	800°C
ppm (Timahdit)	8035	7785	8015
ppm(Tarfaya (marin))	11450	11710	11520

Several findings were noted, firstly the high sodium concentration for the Tarfaya marine deposit relative to Timahdit . The percentage presence of sodium in the Timahdit deposit relative to Tarfaya for the three temperatures is as follows

- Ambiant 70.2%
- 500°C 60,5%
- 800°C 69,6%

By increasing the temperature from ambient to 500°C (temperature of decomposition of the organic matter) we note that the sodium for the Timahdit sample decreases, which means that this sodium is inserted into the organic part as a substitute element, whereas for the Tarfaya sample this sodium remains in its marine environment.

Conclusion:-

Three possibilities of burial of sedimentary material have occurred in either marine, lacustrine or continental environments. The variation of the H/C ratio as a function of O/C according to the Van Krevelen diagram is to be considered. This leads us to three types of kerogen, type I, type II and type III.

To identify that a deposit is lacustrine, for example the Timahdit deposit, several hypotheses must be verified:

1/ First of all, the reactivity in our case of the Timahdit deposit is lower than that of the Tarfaya marine deposit, we have revealed this by thermogravimetry in dynamic regime and by DTG, 60°C separates the two DTG peaks, and by adopting the mathematical model of Coast-Redfern in dynamic regime for a fractional order, $n=1,6$, we end up with the activation energies E_a (Timahdit) =78 KJ/mol, E_a (Tarfaya) = 71, 8 KJ/mol

2/ The calculation of the m_{ins}/m_{aro} ratio using the Infrared spectroscopic method is found to be high for a lacustrine deposit compared to a marine deposit, a hypothesis that has been verified for Timahdit compared to Tarfaya respectively:

Sample	Z0	Z1	Z2	Z3	Z4	Ti
Report m_{ins}/m_{aro}	0,73	0,82	0,66	0,72	0,69	1,29

3/ Absence of chlorine for Timahdit and presence for Tarfaya (dispersive X-ray). Also by this dispersive X-ray diffraction we noted the significant presence of silicon and aluminum which are the elements of the aluminum silicates (clays) in the Timahdit deposit. Aluminum is non-existent in the Tarfaya deposit.

4/The sodium quantified by the method of analysis: atomic absorption revealed to us that this sodium is concentrated in the marine deposit of Tarfaya compared to the deposit of Timahdit, we estimate the double in presence. Similarly, the sodium in the Timahdit deposit is linked to the organic skeleton because at 500°C in combustion we note its partial departure with the organic matter, unlike Tarfaya, which remains in the medium at this temperature. Whereas at 800°C we observe its partial departure (departure of sodium) with the mineral matter for the Tarfaya marine deposit.

Finally, these hypotheses, of which there are five, have led us to confirm the lacustrine nature of the Timahdit deposit.

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