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RESEARCH ARTICLE

TYPE OF BURIAL AND ADAPTATION OF THE GEOLOGICAL AGES WITH THE SEDIMENTATION OF THE ORGANIC MATTER FOR THE DIFFERENT LAYERS FOR THE TARFAYA'S OIL SHALE DEPOSIT (MOROCCO)

Ahmed Malal, Doha Lahmadi and Abdeljabbar Attaoui
Department of Chemistry Faculty of sciences Ben m'sik Casablanca University Hassan II Morocco.

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Abstract

The Tarfaya's oil shale deposit is of considerable importance and ranks among the marine deposits. The organic matter (kerogen) of this type of shale is quantitatively variable according to the layers ranging from Z0 to Z4 (deep layer) A certain migration of organic matter occurred during burial in the deep layers Z3 and Z4 of the Tarfaya deposit, the light organic matter was concentrated (by rising) in the Z3 layer, conversely the high molecular weight matter descended in the Z4 layer. Dynamic thermogravimetry was used to quantify the overall organic matter and UV spectroscopy was used to monitor the amount of high molecular weight organic matter (heavy organic matter).The sedimentation of organic matter in the Tarfaya deposit, generally formed by algal and zooplankton debris as well as other marine life, depended on the climate of the geological eras. The geological eras in question are the secondary and tertiary eras, and organic matter is logically abundant when the climate is warm.This work allowed us to adapt the geological stages to the variability of the kerogen quantities in the layers. Useful tests in this work are thermogravimetric results in microanalysis by the Red Croft (micro flail thermobalance), UV spectroscopy and dispersive X-ray.

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Introduction:-

Oil shale and petroleum are sedimentary compounds and differ from each other only in the conditions under which they are buried. When these conditions, which are physical constraints such as temperature, pressure and concentration, are aggressive, the organic matter is detached from the rock by natural in situ pyrolysis leading to the formation of oil in the groundwater (catagenesis).

Using three analytical methods, thermogravimetry, dispersive X-ray diffraction and ultraviolet spectroscopy, we have followed in a descriptive way how this organic matter has evolved over time according to the layers in the Tarfaya oil shale deposit. We were able to highlight from which layer of the deposit we observed a migration of organic matter by the effect of these natural physical constraints. This migration of matter is a necessary condition for oil to be produced.

Corresponding Author:- Abdeljabbar Attaoui
Address**:-** Department of Chemistry Faculty of Sciences Ben m'sik Casablanca University Hassan II Morocco.

We also matched the sedimentation of the organic matter of the different layers with the geological stages in which they were formed. The geological eras in question are the secondary and tertiary eras, as organic matter is logically abundant in a warm climate.

This work allowed us to adapt the geological stages to the variability of the quantities of kerogen in the layers of the deposit.

Bibliography

The bibliographical synthesis that we are trying to highlight consists of showing some properties of a certain number of oil shale deposits having as a divergence the difference in geological era of formation; we start with the oil shale of Australia.

Tertiary Oil Shale (Australia)

The tertiary oil shale deposits of eastern Queensland, Australia**((Patterson.J.H, et al 1991)** comprise an important future source of liquid alternative fuels as well as carbonate minerals that are important for screening in processing conditions and thereby limiting sulphur dioxide emissions. This paper characterizes the minerals from the Stuart, Rundle, Condor, Nagoorin, South Nagoorin, Duaringa, Yaamba and Lowmed deposits. The selected samples were analysed using chemical analysis of X-ray diffractometry for the mineral part, thermogravimetry and scanning electron microprobe for analyzing the carbonate minerals which are important in processing including calcite, dolomite, siderite and their complex compounds which occur in different amounts in the different deposits.

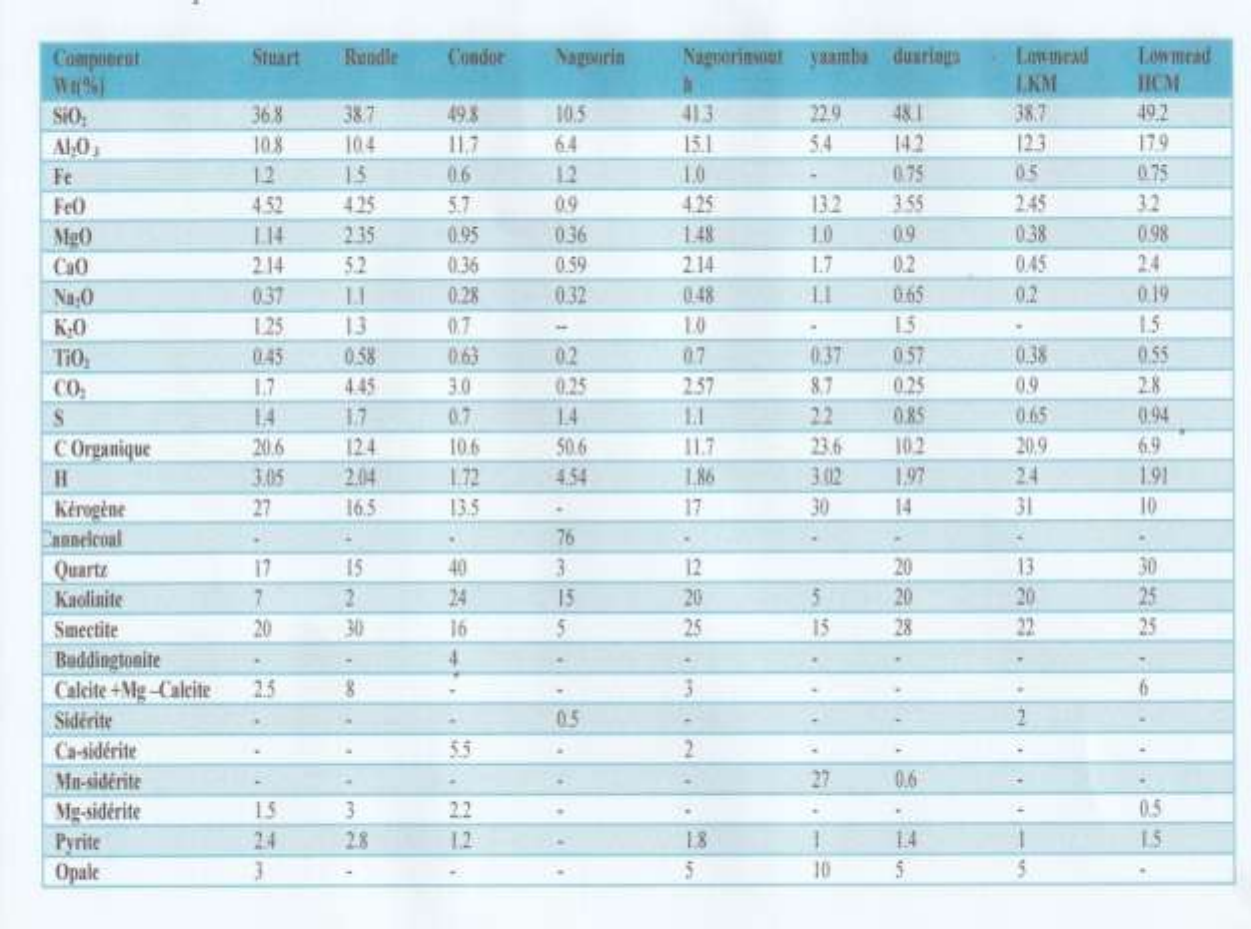
As oil reserves are depleted in the 1990 in Australia, it will be necessary to import much of its crude oil requirements from the tertiary oil market. The oil shales of eastern Queensland represent a diverse and important future source of liquid fuels. As a result, a number of shale studies are ongoing with respect to Australian oil shale production **(Gannon,A.J et al. 1989,Wright,B.C,1989)** The reserves of the above deposits are estimated after conversion to oil to be in excess of 26 billion barrels. The Australian projects by order of magnitude cover the characteristics of oil production from shale. The geochemistry, geology and general mineralogy of Australian tertiary shale oil have been described **(Lindner,A.W, 1983)** and the mineralogy and inorganic geochemistry have been presented in Eastern Shale (surveys conducted in 1987) **(Patterson,J.H, 1987)**.

This paper describes the mineralogy of the complex and variable carbonates observed on top of the oil shale and discusses the implications of the processes. In addition, other forms of work linking the minerals and their reactions in Australian tertiary oil shale have been studied.

Several analytical techniques such as X-ray fluorescence spectroscopy, scanning electron microscopy, TG, thermogravimetric DTG have been used.

Chemical and mineralogical analyses for the oil shale deposits are shown in Table 1 **(Patterson. J.H et al 1991, Patterson, J.H,Ramsden.A.R and Dale.L.S,1988, Coshel.L et al,1986, Coshell,L et al,1987 and Patterson.J.H, H.Hutton.A.C, and Henstridge.D.A,1988)** .

Table 1:- The chemical and mineralogical analyses of Australian Tertiary oil shale compositions:



Component Wt(%)	Stuart	Rundle	Condor	Nagoorin	Nagoorinsouth	yaamba	duaringa	Lowmead LKM	Lowmead HCM
SiO_2	36.8	38.7	49.8	10.5	41.3	22.9	48.1	38.7	49.2
Al_2O_3	10.8	10.4	11.7	6.4	15.1	5.4	14.2	12.3	17.9
Fe	1.2	1.5	0.6	1.2	1.0	-	0.75	0.5	0.75
FeO	4.52	4.25	5.7	0.9	4.25	13.2	3.55	2.45	3.2
MgO	1.14	2.35	0.95	0.36	1.48	1.0	0.9	0.38	0.98
CaO	2.14	5.2	0.36	0.59	2.14	1.7	0.2	0.45	2.4
Na_2O	0.37	1.1	0.28	0.32	0.48	1.1	0.65	0.2	0.19
K_2O	1.25	1.3	0.7	--	1.0	-	1.5	-	1.5
TiO_2	0.45	0.58	0.63	0.2	0.7	0.37	0.57	0.38	0.55
CO_2	1.7	4.45	3.0	0.25	2.57	8.7	0.25	0.9	2.8
S	1.4	1.7	0.7	1.4	1.1	2.2	0.85	0.65	0.94
C Organique	20.6	12.4	10.6	50.6	11.7	23.6	10.2	20.9	6.9
H	3.05	2.04	1.72	4.54	1.86	3.02	1.97	2.4	1.91
Kérogène	27	16.5	13.5	-	17	30	14	31	10
Cannelcoal	-	-	-	76	-	-	-	-	-
Quartz	17	15	40	3	12		20	13	30
Kaolinite	7	2	24	15	20	5	20	20	25
Smectite	20	30	16	5	25	15	28	22	25
Buddingtonite	-	-	4	-	-	-	-	-	-
Calcite +Mg –Calcite	2.5	8	-	-	3	-	-	-	6
Sidérite	-	-	-	0.5	-	-	-	2	-
Ca-sidérite	-	-	5.5	-	2	-	-	-	-
Mn-sidérite	-	-	-	-	-	27	0.6	-	-
Mg-sidérite	1.5	3	2.2	-	-	-	-	-	0.5
Pyrite	2.4	2.8	1.2	-	1.8	1	1.4	1	1.5
Opale	3	-	-	-	5	10	5	5	-

Primary and secondary oil shale (Spain)

We continue our literature review with the oil shale of Spain. Four of the main oil shale units of Spain were examined by organic geochemical and petrographic methods. The samples included three lacustrine shale (Carboniferous of Puertollano; Cretaceous of Liames and Miocene of Rubielos de Mora) and one marine Lower Jurassic shale (Punta delCuerno). The petrographic observations show a dominance of liptodetrinite associated with strained bitumen and mineral matter. The structured geochemical work shows that the soluble organic matter is a mixture of terrestrial and aquatic derivatives, with lacustrine samples recovered as terrestrial plants. The stronger fluorescence maturity parameters and the presence of thermally unstable biomarkers indicate that the samples are all immature, although the Carboniferous sample approaches oils. Micro-fluorimetric maturity assessment is optimised for immature samples if measurements are restricted to liptinitial compounds **(Michael A Kruge and Isabel Suarez-Ruiz, 1991)**.

This study is an organic geochemical and petrographic investigation of four of the main oil shale units in Spain.

The oldest of the series (sample CP) is of Carboniferous age (upper Stephanian B) from the province of Puertollano in Ciudad Real in central Spain, deposited in a lacustrine environment. The second (JP) shale sample is a Lower Jurassic (Pliensbachian) marine from Punta Del Cuerno in the province of Cantabria in northern Spain **(Suarez-Ruiz,I.and Prado, 1986).The third sample (KL)** is a Cretaceous lacustrine deposit at Rubielos de Mora in the province of Teruel, north-east Spain.

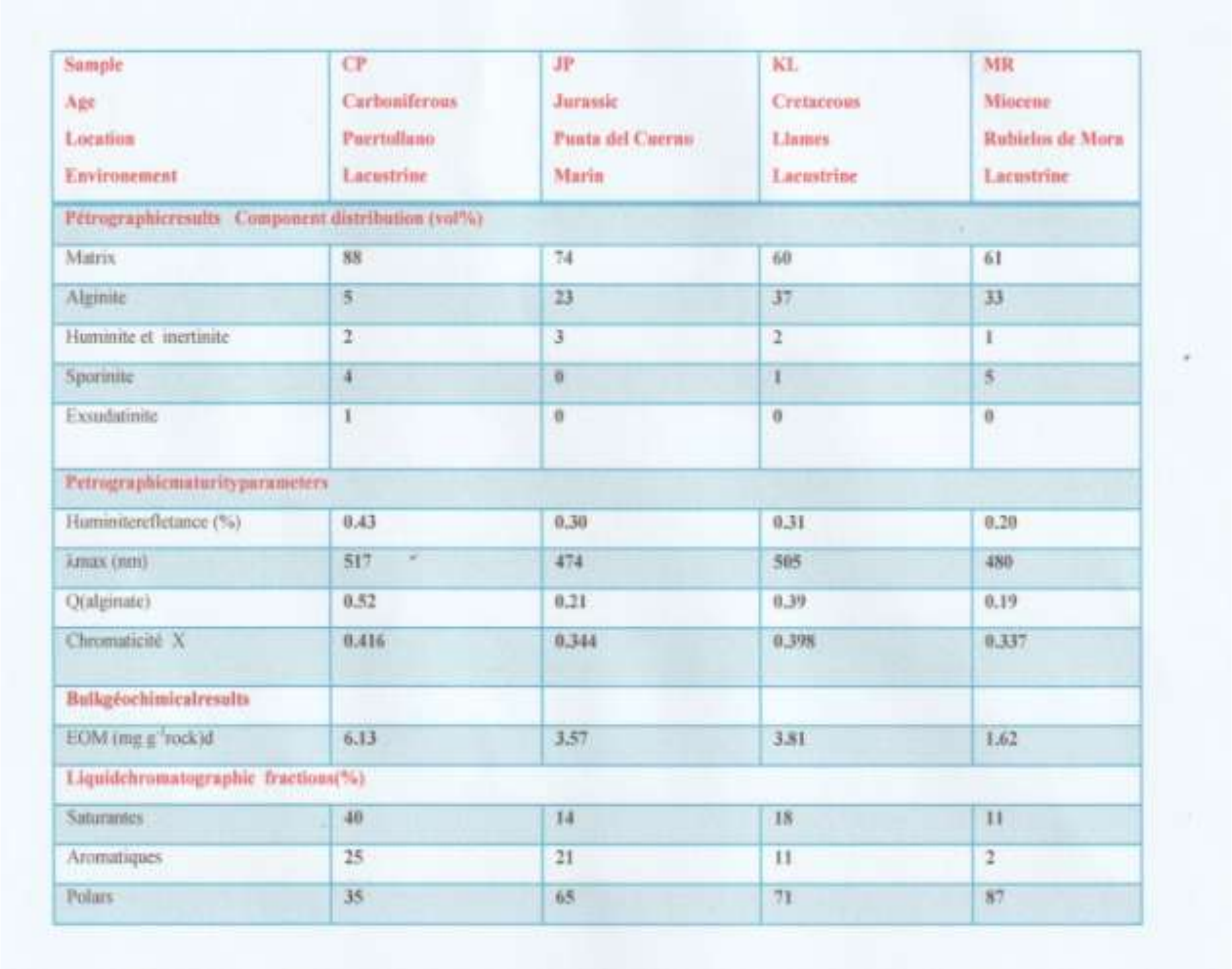
The techniques used for the petrographic determination of organic matter are fluorescence spectroscopy and chromatography **(Anadon,P., Cabrera, L,. and Julia,R, Blackwell Sientific, Oxfor, p.353).**

Concerning the organic petrology study, sample CP is black shale, containing liptodetrinite associated with coloured bitumen, mineral matter associated with a main organic component (Table 1). It also contains minor alginite (including botrycoccus), including pollen, exsudatinite and huminite. JP is a calcareous, black shale resembling liptodetrinite/bitumen staining as the main one. Organic component alginite including Tasmanites and Nostocopsis is abundant and huminite and sporinite are minor. Sample KL is black shale containing liptodetrinite and layered bitumen as predominant, with abundant alginite, including Botryococus, huminite and inertinite are in the minority. The MR sample is a grey laminated shale with liptodetrinite in abundance compared to coloured bitumen and alginite and also contains a low concentration of pollen (Botryococcus and other types). The low reflection values of the Cretaceous sample were previously attributed to reflection suppression by impregnation of the algal huminite bitumen. **(Gomez Borrego, M.A, 1990)** However, the low values of the fluorescence parameters suggest that the corrected low reflection indicates the level of maturation.

Regarding the organic geochemistry study, with the increase in huminite reflection, the yields of extractable organic matter (EOM) increased from 1.6 to 6.1mg g-1 per gram of rock (Table 1). 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 2).

Table 2:- Petrographic, biological and geochemical results (10).



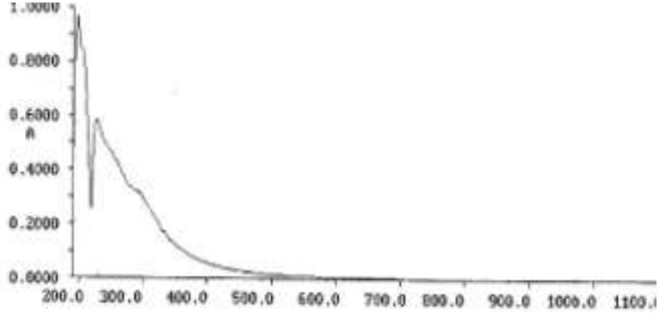
Sample	CP	JP	KL	MR
Age	Carboniferous	Jurassic	Cretaceous	Miocene
Location	Puertollano	Punta del Cuerno	Llames	Rubielos de Mora
Environement	Lacustrine	Marin	Lacustrine	Lacustrine
Pétrographicresults Component distribution (vol%)				
Matrix	88	74	60	61
Alginite	5	23	37	33
Huminite et inertinite	2	3	2	1
Sporinite	4	0	1	5
Exsudatinite	1	0	0	0
Petrographicmaturityparameters				
Huminitereflétance (%)	0.43	0.30	0.31	0.20
λmax (nm)	517	474	505	480
Q(alginate)	0.52	0.21	0.39	0.19
Chromaticité X	0.416	0.344	0.398	0.337
Bulkgéochimicalresults				
EOM (mg g^{-1}rock)d	6.13	3.57	3.81	1.62
Liquidchromatographic fractions(%)				
Saturantes	40	14	18	11
Aromatiques	25	21	11	2
Polars	35	65	71	87

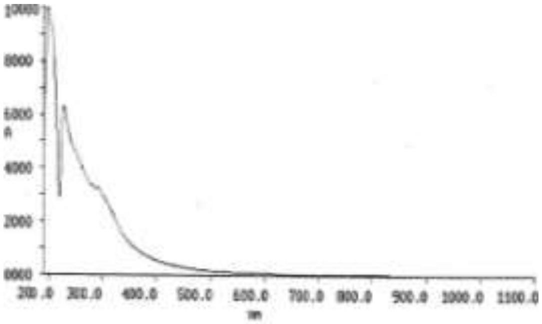
We conclude for this work **(Michael A Kruge and Isabel Suarez-Ruiz, 1991)**, showing that the oil shale of Spain are found in different geographical areas and have different geological ages and their formation environment are different petrographic observations show a dominance liptodetrinite associated with coloured bitumen, mineral matter of origin and alginite as well as a lack of continental structure talaginite and botrycoccus are predominant in the lacustrine samples while tasmanites in the marine samples. Geochemical work shows that soluble organic matter from aqueous soil derivatives and lacustrine samples preclude continental plants

Experimental work:

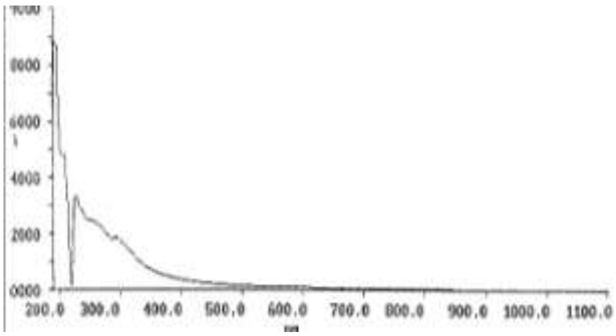
Solubility in chloroform

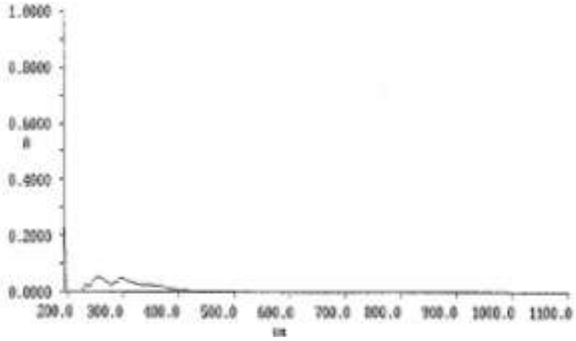
We followed the steps: first we took 6 beakers we put 1 gram of oil shale, this quantity is attacked by 50 cm3 of a $CHCl_3$ (chloroform) solution at a concentration of 0.17 mole/l. The basic character is remarkable pH=10.2. A stirring of 10 min with heating was carried out, after which the material was left to decant for 3 min, and then filtration was carried out using filter paper. The 6 samples previously prepared were subjected to UV light and the A=f (λ) spectra of the different layers are shown in the following figure:



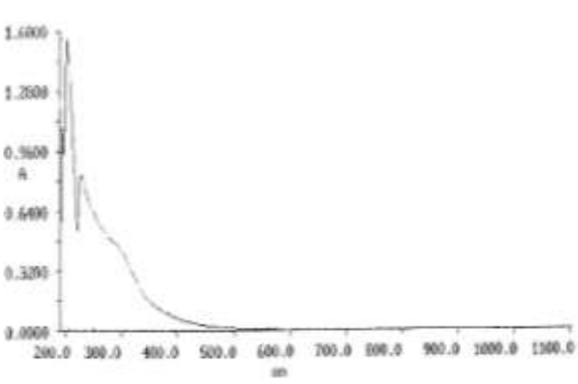


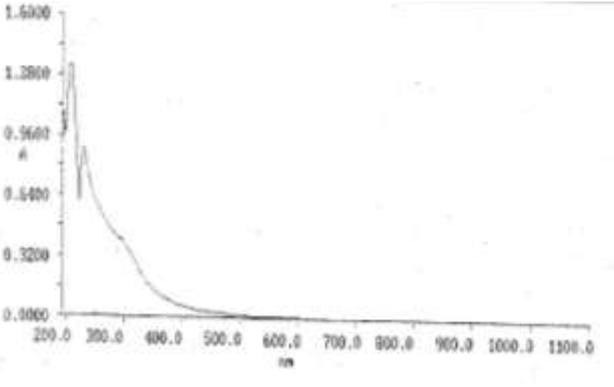
Z0 Layer Z1 Layer





Z2 Layer Z3 Layer





Z4 Layer M Layer

Figure 4:- UV spectrum of the solute after filtration of the different layers of the Tarfaya deposit and the M layer of the Timahdit deposit solubilized with chloroform at a temperature of 97°C.

The absorbance of the different samples with their corresponding wavelengths allowed us to arrive at the concentration of the material solubilized by chloroform at different layers (the calibration of the apparatus was carried out by methylene blue and gave us the cell constant εl=5.04A.l.mol-1)

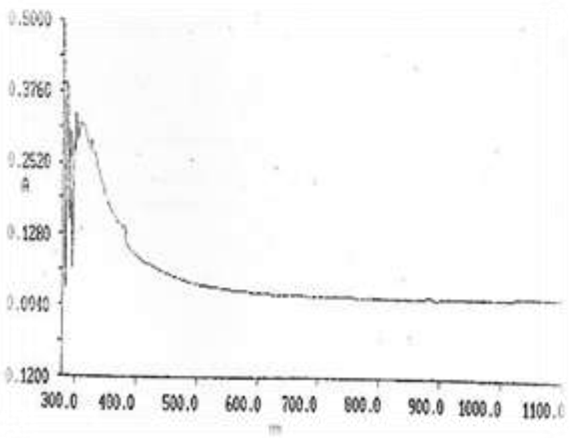
Sample	Absorbance A	L of wave(nm)	Concentration mol/l
Z0	0,966	200	0,192
	0,577	231,818	0,114
Z1	1,00	204,545	0,198
	0,633	231,818	0,126
Z2	0,883	195,454	0,175
	0,333	231,818	0,066
Z3	0,222	192,0	0,044
	0,05	255	0,01
Z4	1,564	206,818	0,310
	0,835	231,818	0,166
Ti	1,342	206,818	0,266
	0,889	231,818	0,176

Table 3:- Absorbance, wavelengths and concentrations of the different layers solubilized by chloroform.

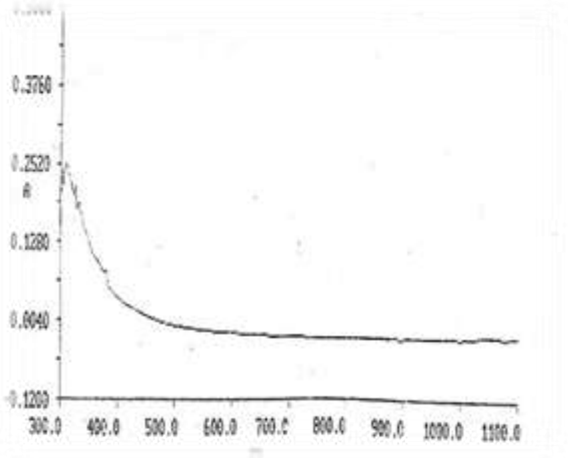
A multiplicity of values is present for all the samples, two values for each oil shale layer. We noted a very remarkable drop for the Z3 layer, yet the ultraviolet allows us to have knowledge of the heavy constituents (high molecular weight) of the oil shale **(S.Hafid, 2008, A.AitLahssen 2008).**

Solubility in distilled water

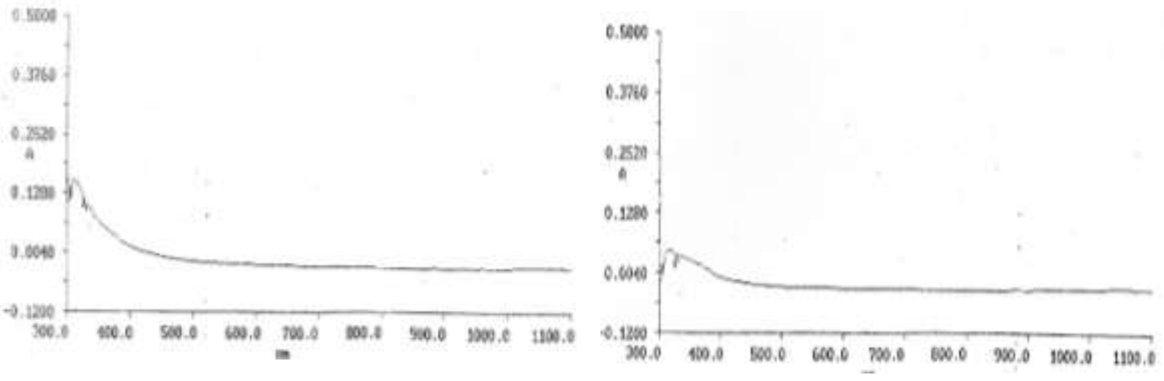
We prepared 6 solutions containing 1 gramme of crushed shale (ticks Z0, Z1, Z2, Z3, Z4 and Ti) in 50 cm^3 of distilled water for 10 minutes, we left the solutions to decant for 3 minutes, and then those solutions was decanted for 3 minutes, and then filtered into test tubes. The following spectral represent the UV for thosesamples:



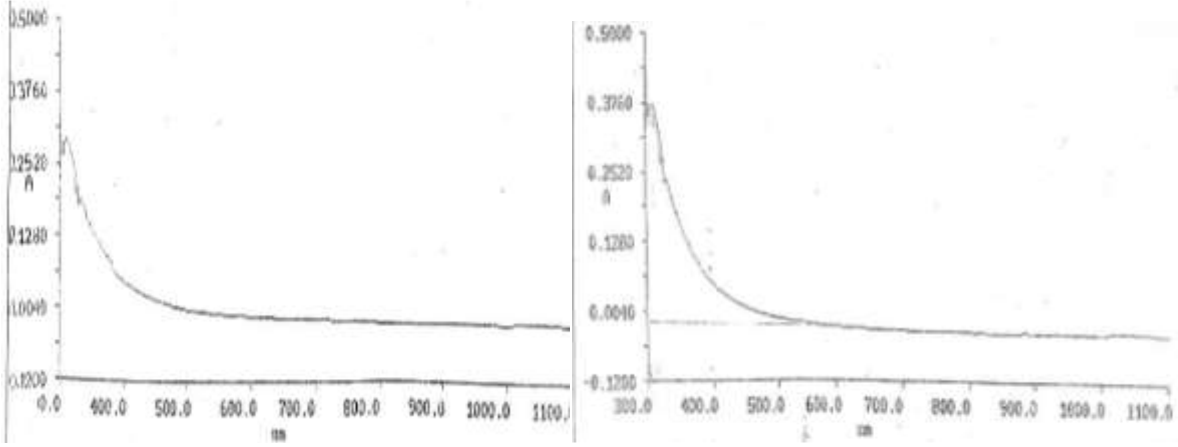
Z0 Layer



Z1 Layer



Z2 Layer Z3 Layer



Z4 Layer M Layer

Figure 5:- UV spectrum of the solute after filtration of the different layers of the Tarfaya deposit and the M layer of the Timahdit deposit solubilized with distilled water at a temperature of 97°C.

After UV analysis of the different oil shale samples and calculation of the concentrations, we have compiled the results in Table 4:

Sample	Absorbance A	L of wave(nm)	Concentration mol/l
Z0	0,3897	291,756	0,0773
	0,3208	314,205	0,0664
Z1	0,2520	312,021	0,0500
Z2	0,1521	314,023	0,0301
Z3	0,0487	308,027	0,0097
Z4	0,2967	314,010	0,0588
Ti	0,3760	304,021	0,0746
	0,3209	316,021	0,0636

Table 4:- Absorbance, wavelengths and concentrations of the different layers solubilized by distilled water.

From the same observation we note a low concentration of high molecular weight hydrocarbons for the Z3 layer, observing the thermogravimetric tests we notethe opposite, i.e. that this layer contains the highest percentage of overall organic matter **(Ouajih, H., Attaoui .A, 2022)** which leads us to say that this layer (Z3) is formed only by light hydrocarbons.

Characteristics	**samples**	
origin	Tarfaya	Timahdit

Zone	Z_0	Z_1	Z_2	Z_3	Z_4	Ti
Percentageloss	6,5	12,3	7,4	16,4	14,4	11,49
DTG peaktemperature	-	427	404	401	398	406

Interpretation of the phenomena using the two techniques

By combining the two techniques, thermogravimetry and UV analysis, we found that for the first three layers Z0, Z1 and Z3 the order of the two techniques is probably identical.

sample	Thermogravimetry Perrcentage of total organic matter	UV, concentration of high molecular weight organic matter(chloroform)
Z0	6,5	0,153
Z1	12,13	0,162
Z2	7,4	0,1205

Since both techniques identify the same order presumably this confirms for each layer that the concentration of total organic matter and high molecular weight organic matter. Hence we have no displacement of material during this burial. However, if we take the last two layers Z3 and Z4 of the deposit, we observe an opposite effect.

sample	Thermogravimetry Perrcentage of total organic matter	UV, concentration of high molecular weight organic matter (chloroform)
Z3	16,4	0,027
Z4	14,4	0,238

The Z3 layer is more concentrated in total organic matter and has a low concentration of high molecular weight organic matter, while Z4 is less concentrated in total organic matter and

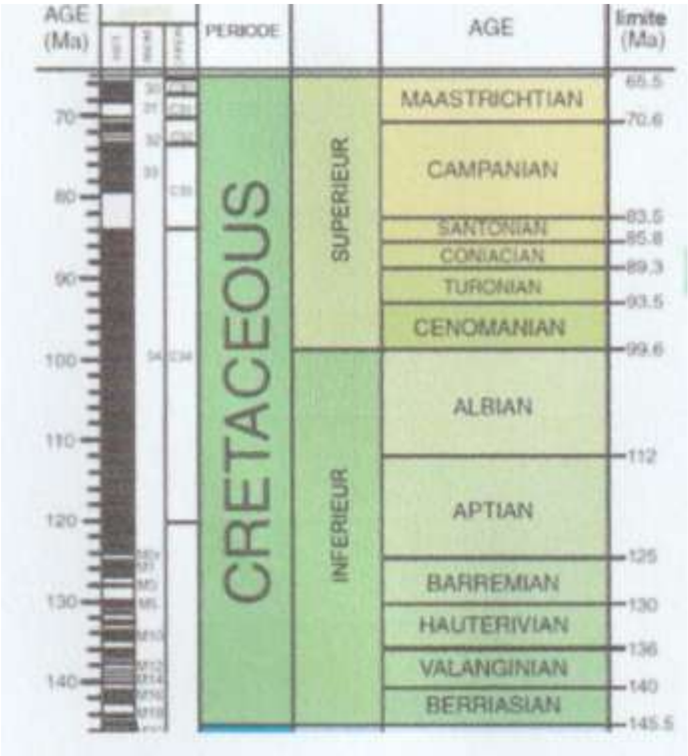
Z4 is less concentrated in total organic matter and highly concentrated in high molecular weight organic matter. By reasoning the stresses during burial caused the high molecular weight organic matter to move downwards (due to density) and the light organic matter to rise. The burial of these two layers was carried out under physical constraints (temperature, pressure and concentration) that were influential enough to cause migration caused a migration along the two evidences, a descent of the high molecular weight hydrocarbons and a rise of the light and a rise in the light ones.

It is also worth noting the high reactivity of the material in the Z4 layer should also be noted, as the DTG peak temperature for this layer is relatively low (389 °C, 21 °C).

The same order for t the last two layers was observed when distilled water was used as a solvent and similarly for Z3 a drop in high molecular weight organic material relative to the Z4 layer and also confirms the migration of material. This can only be explained by the phenomenon of in situ pyrolysis occurring in this geological stage of the secondary era(Upper Cretaceous).

Geological layers of the Upper Cretaceous (secondary era)

The following table represents the geological stages of the secondary era where we observe those of the Upper Cretaceous where the sedimentation of the different layersof the Tarfaya deposit. The Z0 layer on the surface was formed during the glacial era (tertiary)

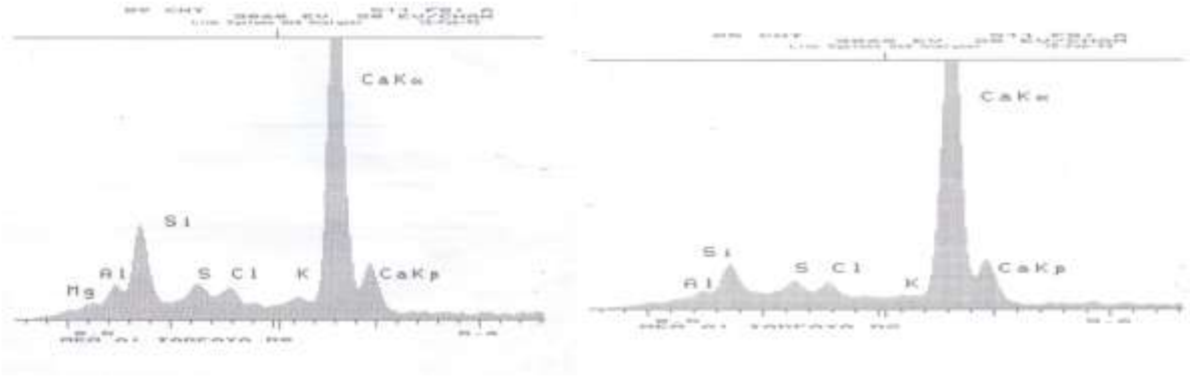


Dispersive X-ray diffraction analysis:

For the dispersive X-ray analysis (figure 5) **(S. Adli, 2016)** we have taken care of the case of calcium, the following table represents the peak size by applied voltage of the calcium element for the different layers of the site:

Element : Ca Sample	H/u in cm $(ev)^{-1}$
Z_0	$5.2 .10^{-3}$
Z_1	$4.5 .10^{-3}$
Z_2	$5.3 .10^{-3}$
Z_3	$4.9 .10^{-3}$
Z_4	$4.2 .10^{-3}$
Timahdit	$4.1 .10^{-3}$

The analysis of the results shows that the amount of calcium is high in the Z0 and Z2 samples, which are the layers with the lowest organic matter content, a result compatible with the thermogravimetric tests.



Z0 Z2

Figure 5:- Analyse RX dispersive.

The stages of the geological eras have different climates; we have hot and cold climates. Organic matter (kerogen) was formed by sedimentation which varies according to the climate, if the climate is warm the sedimentation is abundant and vice versa.

The Turonian and Cenomanian stages had a warm climate and were the consequence of a relatively high concentration of organic matter; this is the case of Z3 and Z4.

Afterwards, in the Senonian (including the Campanian, Santonian and Coniacian), we noted a lowering of temperature producing a low concentration of organic matter in these conditions, which is the case of the following layer Z2.

Then the climate became warm for the second time, this is the case of the secondary era stage: Maestrichtian (Z1).

Finally, we move on to the Tertiary Era known as the Ice Age (cold climate), which was the case for Z0. We have put together these findings in the following table:

The oïl shale layer	Percentage of organicmatter	Geologicalage
Z_0	**6,5%**	Tertiary
Z_1	**12,13%**	Maestrichtian (secondary)
Z_2	**7,4%**	Senonian (secondary)
Z_3	**16,4%**	Turonian (secondary)
Z_4	**14,4%**	Cenomanian (secondary)
Timahdit	**11,49%**	----

Conclusion:-

The first result of combining the analytical techniques used is that for the first three layers Z0, Z1 and Z2 in the deposit the same order has been respected, i.e. the amount of overall organic matter varies in the same ratio as the high molecular weight organic matter. Burial over time for these first three layers was carried out under light physical stresses, but sufficient to shift aliphatic towards aromatics with depth.

Secondly, for Z3 and Z4 unlike the first three layers, we observe a migration of the high molecular weight organic matter down to the Z4 layer (higher concentration) and the light organic matter concentrates in Z3. In fact for this case the physical constraints during burial are quite strong (sign of cat agenesis) This can only be explained by the phenomenon of in situ pyrolysis occurring in this geological stage of the secondary era (Upper Cretaceous). The high reactivity for organic matter in the Z4 layer (DTG) is also noteworthy, as well as the fact that the same order of characterisation was observed using either chloroform or distilled water as a solvent.The stages of the geological eras have different climates, we have hot and cold climates.

The organic matter (Kerogen) was formed by sedimentation, which varies according to the climate, if the climate is hot the sedimentation is abundant and conversely. The quality of this organic matter could be determined by thermogravimetry. Through this work we have been able to adapt the stage of formation according to the era considered in relation to the quantity of this organic matter, so we gather in the following table the stage of formation of each layer of the Tarfaya deposit and we note a rather high compatibility of the phenomenon.

The oïl shale layer	Percentage of organicmatter	Geologicalage
Z_0	**6,5%**	Beginning of the Tertiary Era (cold climate)
Z_1	**12,13%**	Maestrichtian (secondary) (warm climate)
Z_2	**7,4%**	Senonian (secondary) (cold climate)
Z_3	**16,4%**	Turonian (secondary)

		(warm climate)
Z_4	**14,4%**	Cenomanian (secondary) (warm climate)
Timahdit	**11,49%**	----

In summary, we reaffirm the predominant effect of climate on the abundance of this organic matter in a given layer of the Tarfaya deposit.

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