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RESEARCH ARTICLE

Comparative study for hydrodesulphurization (HDS) and hydrogenation of the constituent elements in lacustrine oil shale deposit at Timahdit (Morocco).

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Abstract

Hydrodesulphurization (HDS) and hydrogenation are carried out by thermal treatment using hydrogen (H₂) with the objective of either removing sulphur from the material, or improving the yield of the organic material, or finally forming hydrides by reaction of the elements contained in the mineral matrix with hydrogen. The reaction kinetics are simpler when hydrogen is used compared to pyrolysis, the order of the reaction is equal to unity (**A. Attaoui: 1993**). The Timahdit (Morocco) oil shale lake deposit is composed, apart from organic matter (kerogen), of a considerable number of metallic, metalloid and non-metallic elements constituting the mineral matrix. We carried out the hydrogen treatment in a dynamic regime (21°C/mn) in thermogravimetry by the Red-Croft balance (**A. Attaoui et al: 2022**). The choice of the Z1 layer of the Tarfaya marine deposit was made because of the similarity in the quantity of organic matter between this layer and that of the Timahdit deposit (M2).

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Introduction:-

The choice of the M2 layer of Timahdit and the Z1 layer of Tarfaya was made because they had similar amounts of organic matter (**H. Ouajih and A. Attaoui: 2022**). Despite the similarity in quantity of organic matter between these two layers, several differences in quantity and quality were revealed. Chlorine is non-existent in the Timahdit deposit. Sodium is part of the organic matter (**A. Attaoui et al: 2022**). We also note the significant concentration of silicon and aluminum which are compounds of clays and quartz (SiO₂).

Taking into account the geological stage of formation for Z1 which was the Maestrichtian (Upper Cretaceous of the Secondary Era) and since we noted a similarity of concentration for the Timahdit M2 layer and Z1, thus the two layers were formed at the same geological stage (Maestrichtian). This study will complement others carried out specifically for marine deposits (**M. Hafid, A. Attaoui; 2022, M. Nadif, A. Attaoui: 2022**). The analytical techniques used during this study are thermogravimetry, X-ray diffraction and X-ray diffraction in dispersive coupled with scanning electron microscopy.

1/ Bibliographical study:

For this study, we will mention some works on the action of hydrogen on oil shale. The minerals, treated with hydrogen at 500°C, are active in HDS (Hydrodesulphurization) reactions which convert thiophene into hydrocarbons and hydrogen sulphide. Other reactions such as cracking, polymerization, isomerization and hydrogenolysis have also been observed. As to which specific elements contribute most to the observed reaction

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behavior, it was proposed that iron, present mainly as siderite and in combination with magnesium and calcium as a complex carbonate, is catalytically active. The overall reactions (Y. Sakata and C.E. Jr. Hmrin: 1983). The deuterodesulphurization (DDS) of thiophene was studied on PbMo6S8 at 400°C using a flow-through micro reactor (J.W. Bensoo et al: 1995). There is evidence that 1, 3-butadiene is the first product to be desulphurized; its deuterium content was established by ¹H NMR and mass spectrometry. At different levels of thiophene conversion (0.86-10.2%), the amount of incorporated deuterium remains constant at 3.47 D (deuterium) atoms per molecule. The unconverted thiophene contains 0.42 D atoms at 10.2% thiophene conversion but only 0.05 D atoms at 0.86% conversion. Catalytic hydrodesulphurization (HDS) is a large-scale industrial process for the removal of sulphur from oil feedstocks. Thiophene has been studied extensively as a model for this process. The reaction of thiophene with H₂ over supported HDS catalysts, Co-MO /Al₂O₃ and Ni-W / Al₂O₃ produce H₂S and a mixture of 4-carbon hydrocarbons (V.I. Komarewsky et al: 1951, S. Kolboe et al: 1966) 1,3-butadiene, 1-butene, cis- and trans-2-butene and butane has also been studied. Of the C₄ products, bond cleavage as it is detected (K.F. McCarty and G.L. Schrader: 1987) under reduced hydrogen pressure when its hydrogenation to butenes and butane is less favorable.

One equivalent of H₂ removes S as H₂S to regenerate the active site. Under condition chose, where the amount of D₂ is much greater than that of thiophene, this mechanism predicts the addition of a D atom in each step a and b. During isomerisation, a third D atom is added to the 5-position, while D or H is lost from the 3-position. The 2,3-DHT(dihydrothiophene) formed in step b could be bound through both the olefin and the sulphur shown, or through only the S atom; only sulphide coordination is observed in its transition metal complexes (N.N. Sauer and R.J. Angelici: 1987, G.N. Glavee, L.M. Daniels and R.J. Angelici: 1989, G.N. Glavee, L.M. Daniels and R.J. Angelici: 1989).

In the latter case, H or D could be lost from position 3 since either side of the ring may contact the surface as a result of rapid sulphur inversion and ring reversal. This type of inversion is known to occur in S-coordinated 2, 3-DHT complexes. Because the isotopic effect of deuterium (T.H. Lowry and K.S. Richardson: 1987, F.O. Rice and T.A. Vanderslice: 1958) will cause the C(3)-D bond to be stronger than the C(3)-H bond in 2,3- DHT, the 3-position of 2,5-DHT will probably contain more D than H. An estimated k_H/k_D isotope effect of 2.3 at 400°C is calculated from the difference in the zero-point energies for C-H and C-D bonds which leads to 0.70 D atoms at C(3) of 2.5-DHT. An isotopic effect has been measured for the H , D abstraction of CH₃CD₃ by .CH, at 401°C; this k_H/ k_Dvalue (3.33) predicts 0.77 carbon atoms at C(3).

Estimates of k_H/k_D lead to similar estimates of deuterium content (0.70 or 0.77 D) at C (3) 2.5 DHT. Using the value of 0.77 D, the whole DHT will contain about 2.8 D. In the desulphurization step (d), no deuterium is incorporated and the resulting BDE should contain 2.8 D, and these deuterium atoms should be distributed as follows: 0.77 D to DA, 1.0 D to DB, and 1.0 to Dc. (It is not possible to predict whether the deuterium content at DB, and Dc will be equal or unequal.) A second mechanism involving partial hydrogenation of thiophene has been proposed by Kwart, Schuit and Gates (H. Kwatt, G.C.A. Schuit and B.C. Gates: 1980).

The analysis of the shale are presented in Table 1 of the 20 elements, eight (arsenic, barium, cadmium, chromium, mercury, lead, selenium and silver) were analyzed (M.C. Mensinger et al: 1992)

Table 1:- Ultimate analysis of oil shale hydroretorted.

		Alabama	Indiana	Beneficiated Indiana
Moisture(wt%)		0.94	1.56	1.88
Ultimate analysis finale (wt%)	Organic carbone	15.94	12.95	28.05
	Mineral carbone	0.07	0.08	0.05
	Hydrogen	1.57	1.48	2.81
	Oxygen	2.90	3.16	5.41
	Nitrogn	0.49	0.35	0.74
	Sulphur	9.05	2.93	2.71
Gross calorific value	Ash	73.59	80.25	61.11
	MJ / Kg	7.60	5.81	12.52
Fischer assay(I t ⁻¹)	Btu Ib ⁻¹	3266	2497	5385
	Test de Fischer (I t ⁻¹)	53	54	108

(gallon ton- I)	(gallon ton- I)	12.7	12.9	25.9
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Table 2:- Elemental analysis of oil shale hydroretorted.

Elément (wt%)	Alabama	Indiana	Beneficiated Indiana
Calcium	0.24	6.88	0.34
Iron	7.49	0.34	7.49
Potassium	2.70	3.99	3.00
Magnesium	0.64	3.00	0.70
Sodium	0.34	0.70	0.34
Silicon	22.10	0.41	22.10
Titanium	0.36	24.80	0.41
Aluminum	489	6,88	5,32

Most of the deposits have a different mineralogical composition, notably calcite and dolomite (2.5-8% by mass) are found in the Southern deposit and in the Lowmead Stuart Rundle deposit. These deposits also contain 3.5% by mass of siderite.

One study is an organic geochemical and petrographic investigation of four of the major oil shale units in Spain (Michael A Kruge and Isabel Suarez-Ruiz: 1991).

The oldest of the series (sample CP) is of Carboniferous age (upper Stephanian B) from the Puertollano province of Ciudad Real in central Spain, deposited in a lacustrine environment. The second (JP) shale sample is a lower Jurassic. (The third sample (KL) is a Cretaceous lacustrine deposit at Rubielos de Mora in the province of Teruel, northern Spain. The KL sample is black shale containing liptodetrinite and layered bitumen as predominant, with abundant alginite, including Botryococcus, huminite and inertinite are in minority. The MR sample is grey foliated shale with liptodetrinite in abundance compared to the colored bitumen and alginite and also contains a low concentration of pollen (Botryococcus and other types) and lesser amounts of pollen. The biological and geological results of this Spanish shale are collected in the following table 3:

Table 3:- Petrographic, biological and geochemical results:

Sample	CP	JP	KL	MR
Age	Carboniferous	Jurassic	Cretaceous	Miocene
Location	Puertollano	Punta del Coorno	Llames	Rubielos de Mora
Environment	Lacustrine	Marin	Lacustrine	Lacustrine
Petrographic results Composot 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
Petrographic maturity parameters				
Huminiterreflectance (%)	0.43	0.30	0.31	0.20
Amx (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
Bulk geochemical results				
LOM (mg g ⁻¹ rock id)	6.13	3.57	3.81	1.62
Liquid chromatographic fractions (%)				
Saturantes	40	14	18	11
Aromatiques	25	21	11	2
Polars	35	65	71	87

2/ Experimental

2.1/ Thermogravimetric analysis:

Thermogravimetric analysis (TGA) is a classical method widely used in materials and energy sciences and geology to determine the weight variations of materials. It graphically observes mineral decomposition or reactions through peaks or valleys. The purpose of this analysis is to characterize materials by directly measuring mass loss as a function of temperature and/or time. It measures the change in mass of a sample when it is subjected to a temperature program, under a controlled atmosphere. This change can be a mass loss (vapor emission) or a gain (gas fixation, oxidation). Experiments can be performed in an oxidizing or inert atmosphere.

The thermo-microbalance is the Red-Croft which is a setaram used for thermogravimetric (TG) measurements related to degradation in dynamic regime. It has a resolution of 0.1 μg . In our conditions, it operates between room temperature and 750°C, with different heating rate: 21°C/min, 15°C/min and 09°C/min.

This top-loading thermobalance is easy and safe to use, having no hanging wires or exposed fragile parts. The following picture shows a thermobalance from the Setaram series called Redcroft, which is a flail thermobalance with a compensation system based on a photoelectric source to keep the sample at the same position in the furnace, thus avoiding the temperature gradient due to sample movement in the furnace.

2.2/ X-ray diffraction.

In this study, the phase identification of the shale mineral material was carried out on powder by using a C.G.R (Theta 60) X-ray diffractometer with a copper anticathode of wavelength of 1.54051Å.

The following X-ray spectra correspond to the M layer of Timahdit (Fig.1) and the Z4 layer of Tarfaya (Fig. 2):

1st peak, at $2\theta = 20.91$; corresponds to dolomite ($\text{CaMg}(\text{CO}_3)_2$);

2nd peak, at $2\theta = 23.1$; corresponds to quartz (SiO_2);

3rd peak, at $2\theta = 30.86$; corresponds to calcite (CaCO_3).

The main mineral compounds are therefore dolomite, quartz and calcite, which are found in the two samples in slightly different quantities.

Fig 1:- X-ray spectra for M2 layer (Timahdit).

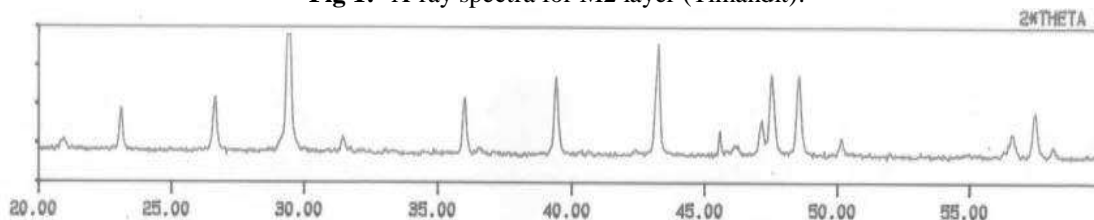
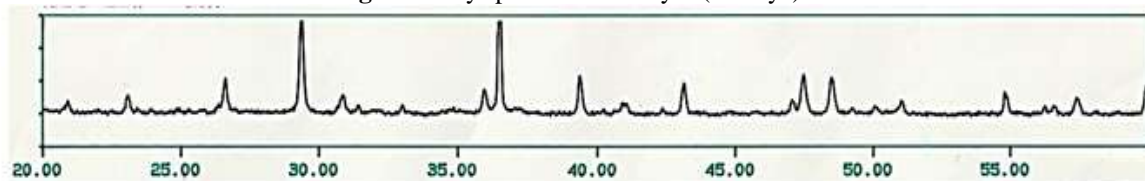


Fig 2:- X-ray spectra for Z1 layer (Tarfaya).



The X-ray diffraction peaks of the Z1 layer are more accentuated in amplitude than those of Timahdit's M2 layer, thus proving the amount of high mineral matter compared to M.

2.3/ X-ray diffraction in dispersive for the crude and hydrotreated samples at 550°C and at 750°C.

Scanning electron microscopy (SEM) is a technique based on the analysis of electron-matter interactions. The surface of the sample is subjected to a bombardment of electrons. Some radiation (backscattered electrons, secondary electrons and X-rays) is emitted as a result of the multiple collisions between the electrons that scan the surface and the atoms of the material under test. This radiation is analyzed by different detectors to build an image of the surface and to observe the presence of elements in the analyzed area. Both samples were examined under the scanning electron

microscope. Figures 3, 5 and 7 show the photos of the M2 layer before and after hydrotreating (550°C and 750°C) and figures 4, 6 and 8 show the photos of the Z1 layer before and after hydrotreating idem.

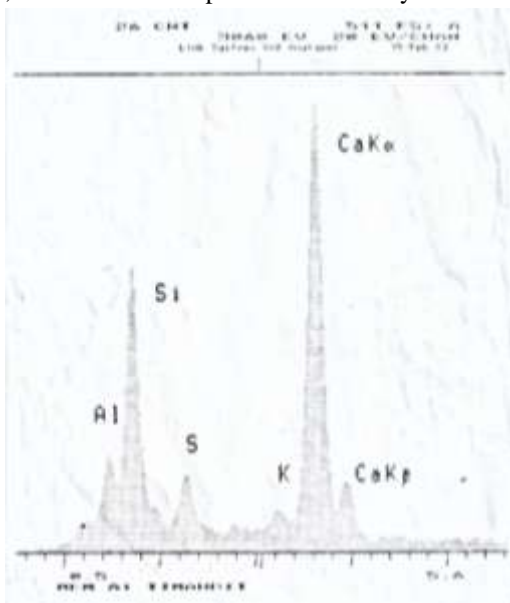


Fig3:RawM2 layer

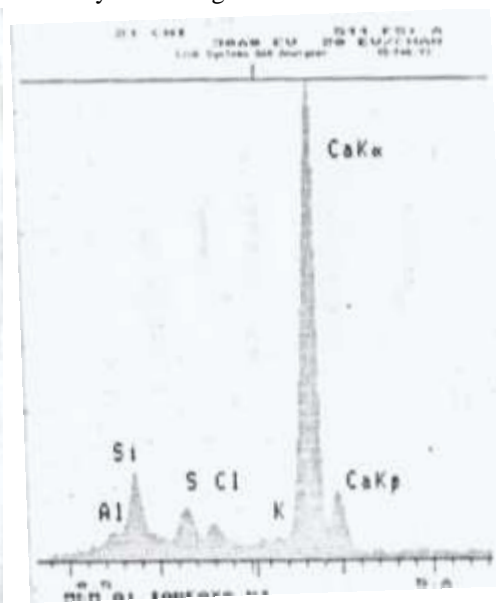


Fig4: RawZ1layer

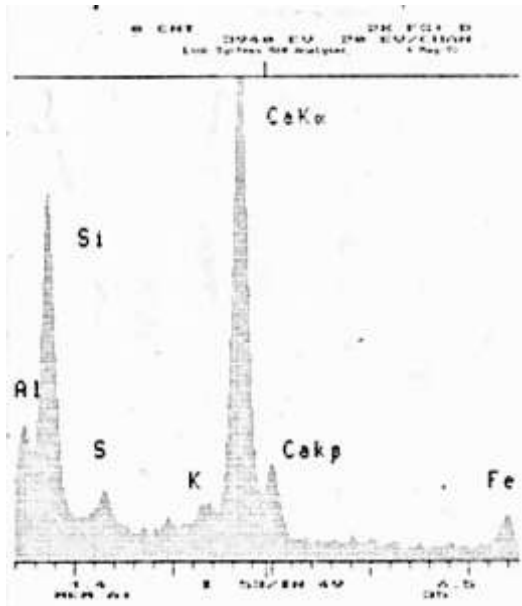


Fig 5:- M2 hydrotreated at 550°C

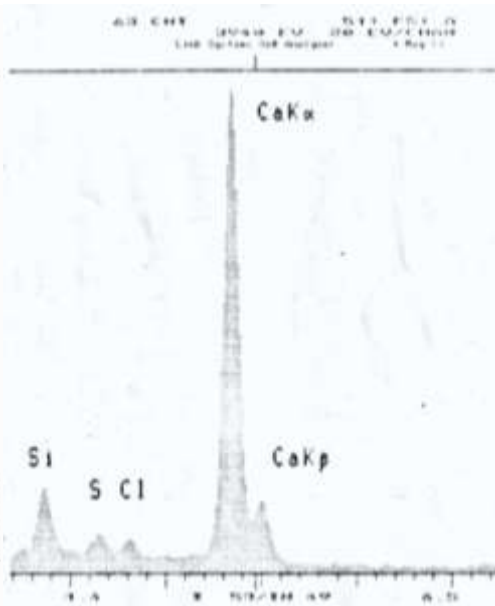


Fig 6 :- Z1 hydrotreated at 550°C

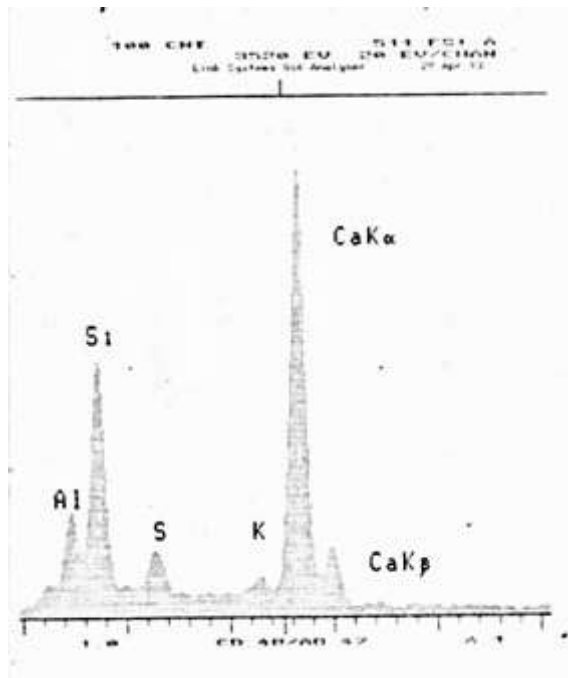


Fig 7:- M2 hydrotreated at 750°C

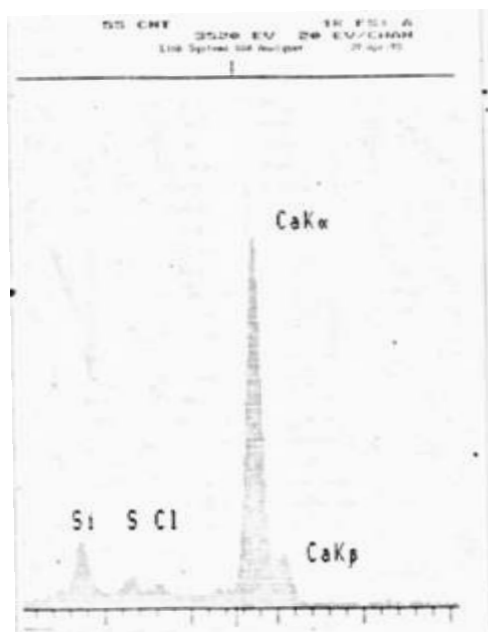


Fig 8:- Z1 hydrotreated at 750°C.

3/ Table of Results:-

The following table 4: shows the different measurements of the peaks of the previous spectra as well as the percentages of the elements constituting the oil shale. These values are attributed to differences temperatures, firstly ambient, then hydrotreating.

These spectra have led to the results shown in the following table 4. It should be remembered that the spectra with which the measurements and calculations were made have A4 shapes, the spectra in the text are reduced shapes.

Table 4:- Percentage of chemical elements in the Timahdit (Ti=M2) and Tarfaya oil shale at different states.

Composition	Type of oil shale	M ₂ (cm)	Z ₁ (cm)	%M ₂	%Z ₁	%M ₂ /%Z ₁
Silicon	Raw	11,5	3,6	27,4	10,97	2,5
	Treated by H ₂ at 550°C	14,6	3,25	28,3	10,78	2,63
	Treated by H ₂ at 750°C	9,5	2,1	25,2	11,5	2,19
Aluminum	Raw	4,0	1,20	9,5	3,69	2,57
	Treated by H ₂ at 550°C	5,5	0,95	10,7	3,15	3,34
	Treated by H ₂ at 750°C	3,8	3,4	10,1	3,29	3,06
Sulphur	Raw	3,1	1	7,4	6,55	1,13
	Treated by H ₂ at 550°C	2,4	0,8	5,4	4,97	1,09
	Treated by H ₂ at 750°C	2,5	0,7	6,6	5,8	1,14
Potassium	Raw	1,8	2,15	2,9	3,2	0,91
	Treated by H ₂ at 550°C	2,4	1,50	4,6	2,9	1,59
	Treated by H ₂ at 750°C	1,5	1,05	4,0	4,3	0,93
Calcium K _α	Raw	18,1	19,6	43,2	59,8	0,72
	Treated by H ₂ at 550°C	20,7	18,6	40,2	61,7	0,65

	TreatedbyH2at750°C	16,6	11,6	44,0	63,6	0,69
Calcium K β	Raw	2,9	2,8	6,9	8,5	0,81
	TreatedbyH2at550°C	3,9	2,8	7,6	9,3	0,82
	TreatedbyH2at750°C	2,7	1,7	7,2	9,3	0,77
Magnesium	Raw	1,1	0,6	2,6	1,8	1,44
	TreatedbyH2at550°C	2,8	0,6	5,4	1,99	2,71
	TreatedbyH2at750°C	1,1	0,45	2,9	2,46	1,18
Chlorine	Raw	0	1,5	0	4,57	0
	TreatedbyH2at550°C	0	1,3	0	4,31	0
	TreatedbyH2at750°C	0	0,75	0	4,11	0

It should be noted that the Ti variety of Timahdit is the M2 layer

4/ Results and Discussion:-

The above table represents the peak size for an A4 shape according to the SEM recorder, to which we have the coupling with XRD. The table also presents the percentages of each element relative to the others for each different layer of oil shale varieties (M2 of the Timahdit lake deposit and Z1 of the Tarfaya marine deposit).

We will represent the different percentages of the different elements constituting the oil shale layers of Timahdit (M2) and Tarfaya (Z1) first in the raw state in figure 9, then the hydrotreated samples in the Red-Croft balance in a dynamic regime (21°C/mn), with a hydrogen flow rate of 20 cm³/mn and at a temperature of 550°C in figure 10 and finally the hydrotreated samples at a temperature of 750°C in figure 11

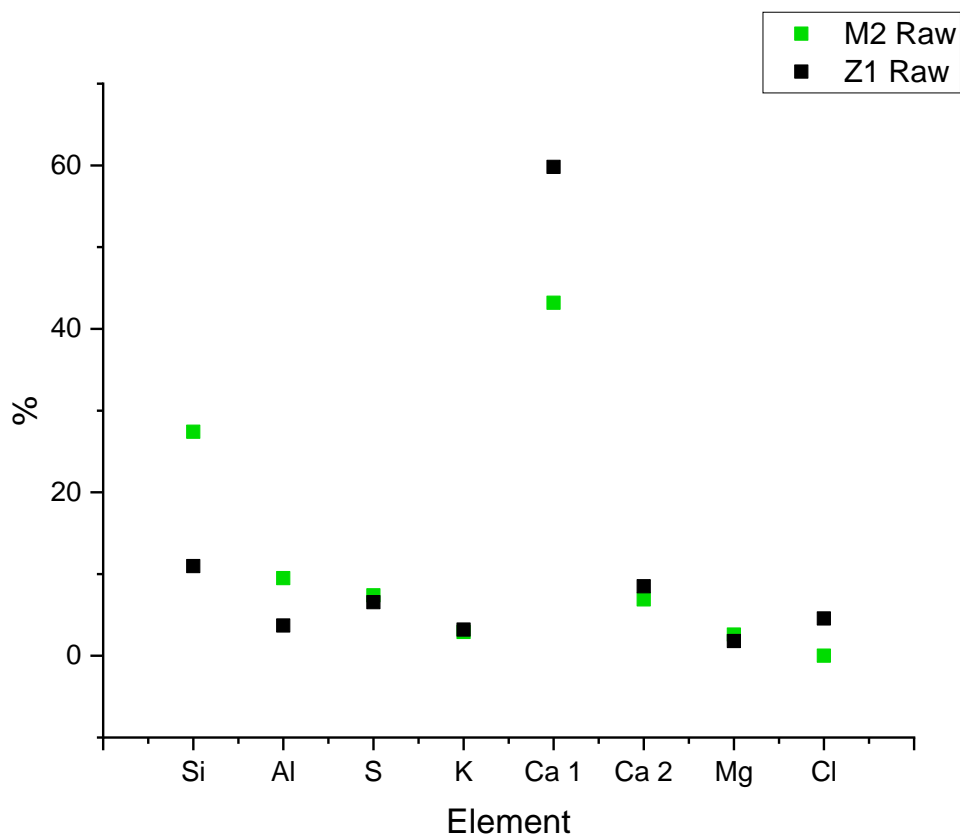


Fig 9:- Percentage of constituent elements in the shale layers of the two varieties Ti (M2) and Z1 in the raw condition.

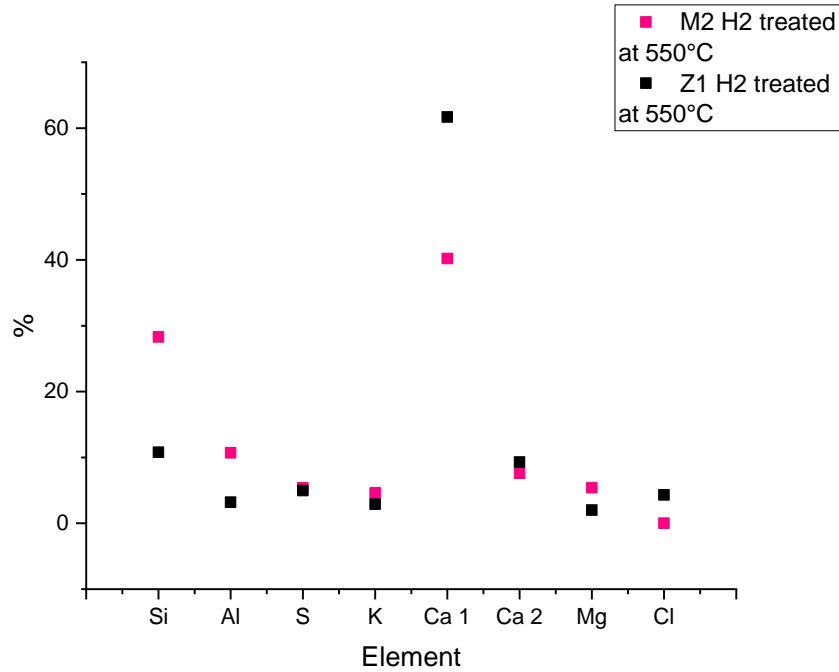


Fig 10:- Percentage of constituent elements in the layers of shale of both Ti(M2) and Z1 varieties hydrotreated at 550°C..

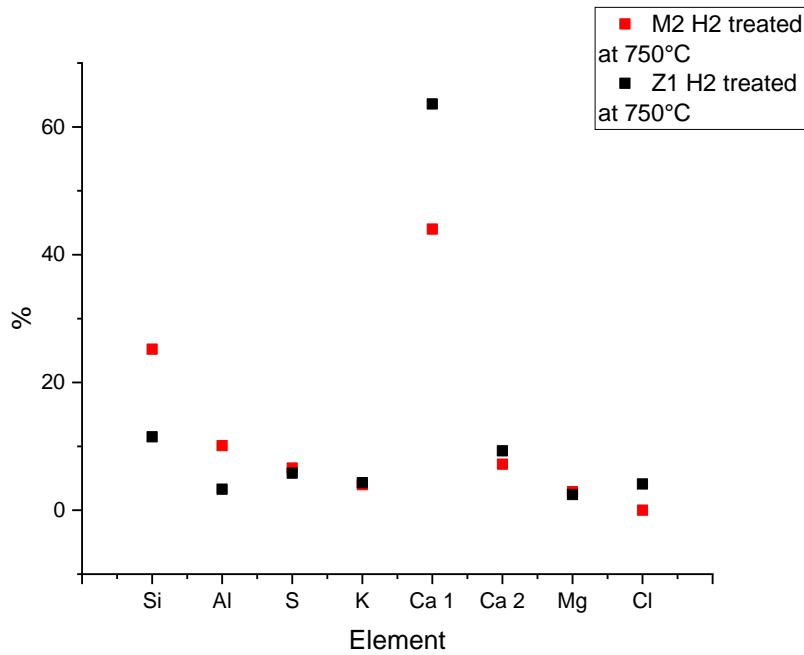


Fig 11:- Percentage of constituent elements in the layers of shale of both Ti(M2) and Z1 varieties hydrotreated at 750°C.

We will similarly represent the percentage results in histograms for each constituent; normally we have eight constituents according to the XRD peaks. These histograms are given for each layer together in the raw state, hydrotreated at 550°C and hydrotreated at 750°C. Also we represent the percentage ratio (Ti% / Z1%) for each corresponding element.

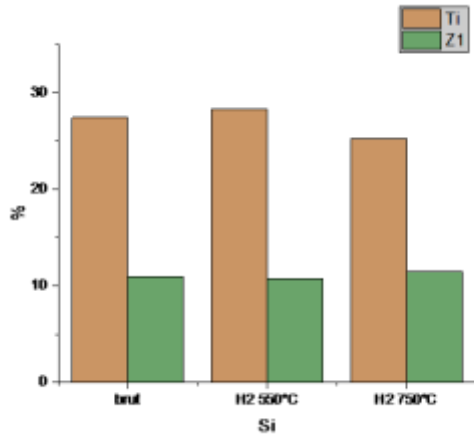


Fig 12:- Percentage of silicon for each layer raw, hydrotreated at 550°C and at 750°C

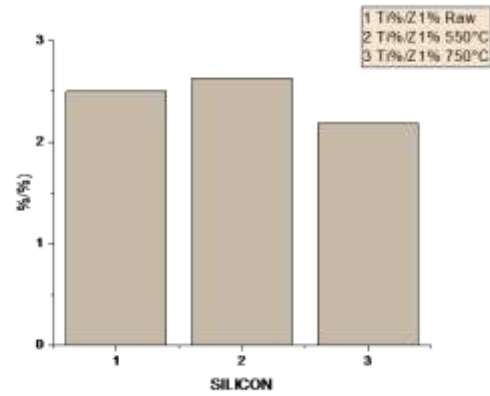


Fig 13:- Percentage ratio (Ti/Z1) for silicon raw, hydrotreated at 550°C and at 750°C

A.

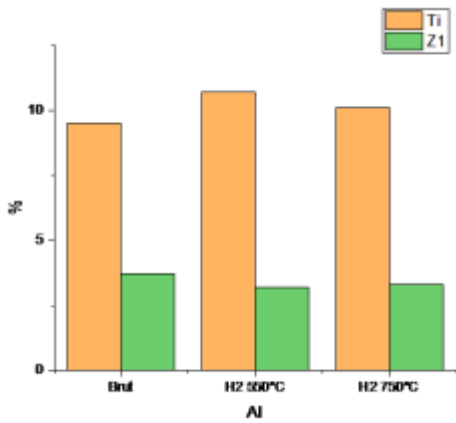


Fig 14:- Percentage of aluminum for each layer raw, hydrotreated at 550°C and at 750°C

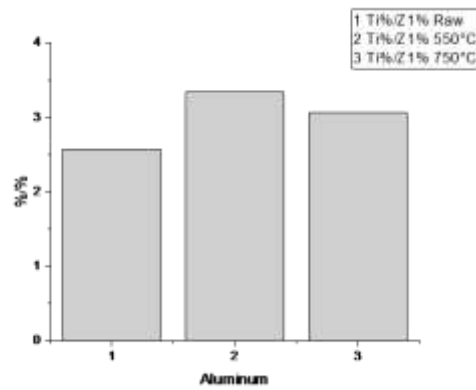


Fig 15:- Percentage ratio (Ti/Z1) for aluminum raw, hydrotreated at 550°C and at 750°C

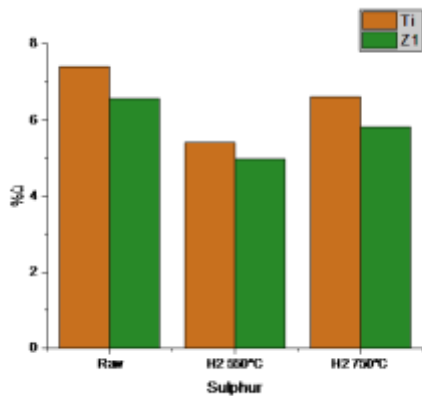


Fig 16:- Percentage of sulphur for each layer raw, hydrotreated at 550°C and at 750°C

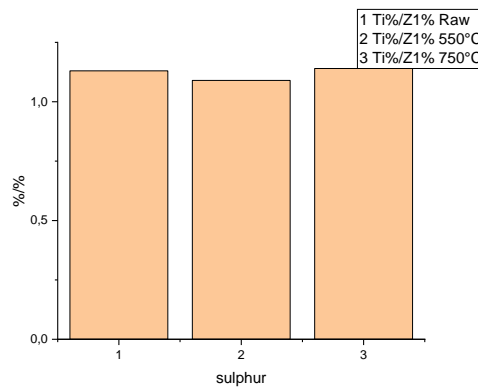


Fig 17:- Percentage ratio (Ti/Z1) for sulphur raw, hydrotreated at 550°C and at 750°C

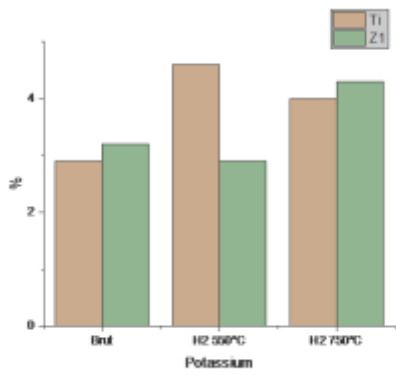


Fig 18:- Percentage of potassium for each layer raw, hydrotreated at 550°C and at 750°C

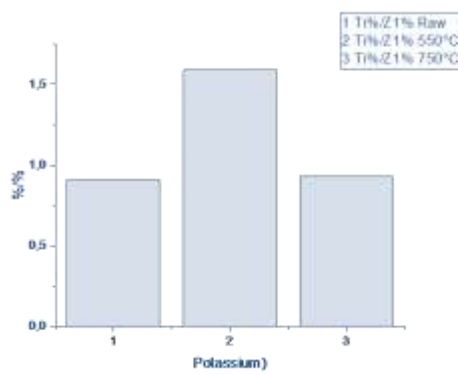


Fig 19:- Percentage ratio (Ti/Z1) for potassium raw, hydrotreated at 550°C and at 750°C

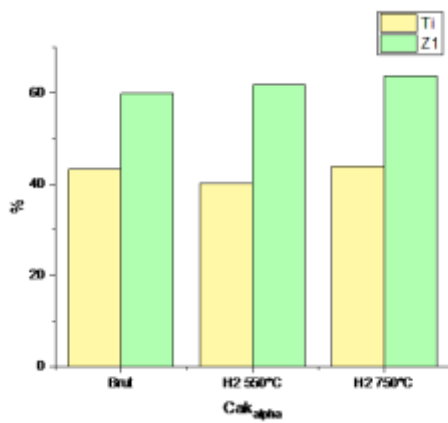


Fig 20:- Percentage of CaKα for each layer raw, hydrotreated at 550°C and at 750°C

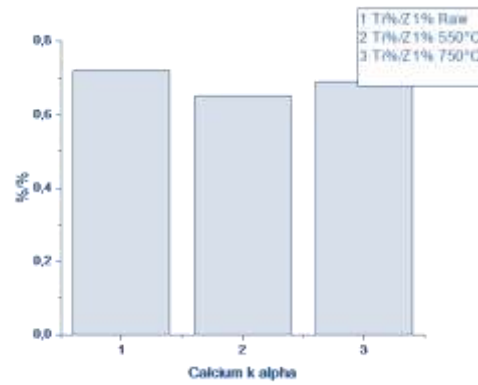


Fig 21:- Percentage ratio (Ti/Z1) for CaKα raw, hydrotreated at 550°C and at 750°C

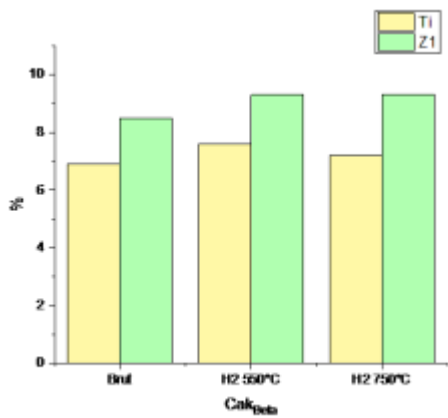


Fig 22:- Percentage of CaKβ for each layer raw, hydrotreated at 550°C and at 750°C

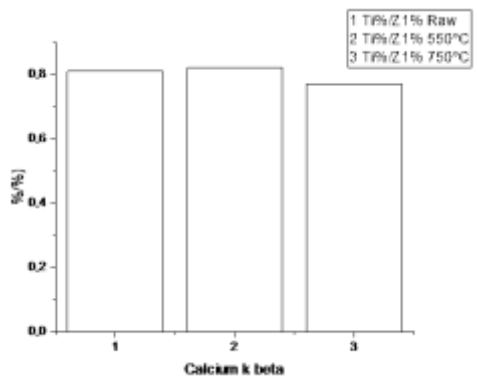


Fig 23:- Percentage ratio (Ti/Z1) for CaKβ raw, hydrotreated at 550°C and at 750°C

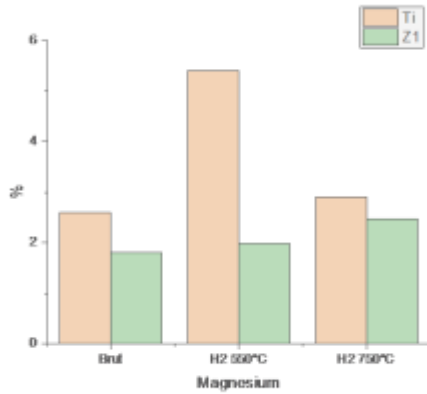


Fig 24:- Percentage of Magnesium for each layer raw, hydrotreated at 550°C and at 750°C

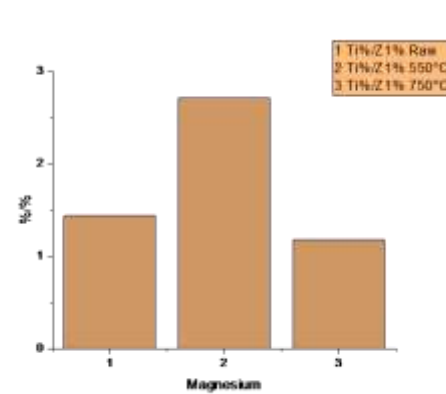


Fig 13:- Percentage ratio (Ti/Z1) for Magnesium raw, hydrotreated at 550°C and at 750°C

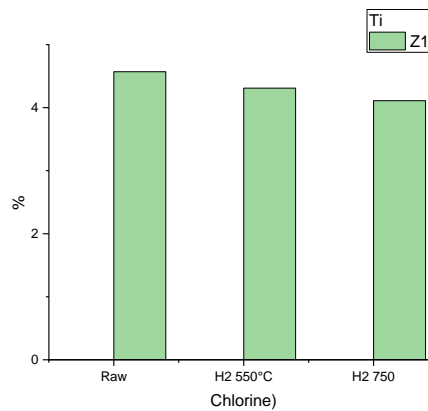


Fig 26:- Percentage of chlorine for each layer raw, hydrotreated at 550°C and at 750°C

Several observations have been made according to the previous curves and the histograms plotted: The high concentration of silicon and aluminium in the M2 layer of the lake deposit, due to the presence of clays in the Timahdit lake deposit. A percentage of 2.5 times higher when we see the histogram presenting the ratio %Ti / %Z1.

The reactivity of the designed reactions is also noteworthy, as the comparative reactivity for the preparation of silanes and alanes in the presence of hydrogen can be seen for these two varieties due to the fact that the ratio %M2 / %Z1 increases from ambient to 550°. This means that the percentage of these two elements decreases for the Z1 layer, which explains the high reactivity of this marine layer towards hydrogen.

For sulphur, there is a high affinity for hydrogen, as well as a slightly higher concentration in the lake deposit (M2).

Potassium is concentrated in the marine layer (Z1), and there is also a high reactivity for this layer in hydrogenation between ambient and 550°C.

CaK α and CaK β are also more concentrated at the marine deposit (Z1), a noticeable reactivity for M2 concerning CaK α .

Contrary to magnesium, we note a sensitive reactivity for the Z1 layer and a higher concentration for the lake deposit.

Finally we note the absence of chlorine in this lake deposit.

Conclusion:-

This study was carried out for the Timahdit lake deposit (Morocco), firstly in a descriptive way and in comparison with the Z1 layer of the Tarfaya marine deposit (Morocco). The chosen layer of the lake deposit is the M2 (Ti) layer. This choice was made because both layers have the same amount of organic matter. The formation of the Z1 layer occurred during the secondary era in the Upper Cretaceous, more precisely in the Maestrichtian (type of) geological stage.

The hydrodesulphurization reaction designed for sulphur and the hydrogenation reaction carried out at the same time were done by a microthermobalance called Red-Croft in a dynamic regime (21°C/min) and a hydrogen pressure of one atmosphere and a flow rate of 20 cm³/min.

The analyses were carried out by dispersive X-ray diffraction, an instrument that is coupled to the scanning electron microscope.

Several results were obtained, firstly the high concentration of silicon and aluminum in the M2 layer of the lake deposit, due to the presence of clays in the Timahdit lake deposit. A percentage of 2.5 times higher when we see the histogram presenting the ratio %Ti / %Z1. We have seen the reactivity of the reactions designed; indeed we can know the comparative reactivity for the preparation of silanes and alanes in the presence of hydrogen for these two varieties due to the fact that the ratio %M2 / %Z1 increases from ambient to 550°. This means that the percentage of these two elements decrease for the Z1 layer, which explains the high reactivity of this marine layer towards hydrogen.

We have noted a high affinity for sulphur to hydrogen, and a slightly higher concentration for the lacustrine deposit (M2).

Potassium is concentrated in the marine layer (Z1), with a high reactivity for this layer in hydrogenation between ambient and 550°C.

For calcium K α and calcium K β we note that they are more concentrated at the marine deposit (Z1), a sensitive reactivity for M2 concerning CaK α .

On the contrary for magnesium, we note a sensitive reactivity for the Z1 layer and a higher concentration for the lacustrine deposit.

Finally, we note the absence of chlorine in the Timahdit lacustrine deposit.

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