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PHYSICOCHEMICAL CHARACTERIZATION AND THERMAL BEHAVIOUR OF TWO TUNISIANS KAOLINS

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1. Introduction

Ceramic product depends on the nature and the properties of utilised raw material. The increase in temperature for singly fired ceramic clays exceed the energy threshold of the reactivity of mineral material and produces a series of reaction and transformations that lead to the formation of new phases and the disappearance of others [1]. For the some firing conditions the halloysite clay produced a higher bulk density than the kaolinite clay as well as finer mullite crystals. Mullite is formed in kaolinite clay at a lower temperature than in halloysite clay [2]. The kaolinite forms metakaolinite by heating from 550°C to 950°C, and mullite mainly forms above 1200°C [3].

The objective of this paper is to study the thermal transformation of two Tunisians kaolins chooses.

2. Materials and methods

Two samples are selected for this study: Kasserine clay (K) and Tabarka clay (T). We add a suffix “b” or “p” to indicate respectively if the clay is crude or purified.

Purification:

The clay fraction was purified by classical methods [4], repeated cation exchange with 1N NaCl solution, washing and sedimentation and dialysis. The fine clean sediment was freeze dried.

Chemical analysis:

The samples are attacked by a mixture of three acids (HCl, H_2SO_4 and HNO_3); all elements pass in solution only the silica that it measured out by gravimetric [5].

The chemical elements, as Al, Fe, Mg, Ca, Na and K are measured by atomic absorption.

X-ray diffraction:

Mineralogical analysis was performed by XRD, using a Philips diffractometer PW 1050/81, with the $K\alpha_{1,2}$ radiation of the copper. In this method, oriented specimens are prepared on glass microscope slides. The slides have a density of 20 mg of samples and were successively given treatment of:

i) Drying at 20°C
ii) Heating for two hours an 500°C

Infrared spectroscopy:

FT-IR spectra were recorded in the region 4000-350 cm^{-1} in an EQUINOX model 55 infrared Fourier transform spectrometer, using the KBr pellet technique (about 2 mg of sample and 200 mg of KBr were used in the preparation of the pellets).

Cation exchange capacity:

Clay is saturated first with other solutions. The excess of the reagent added is measured by volumetric method.

N_2 adsorption experiments:

The specific surface areas of the samples were determined by the corresponding nitrogen adsorption isotherms at 77 K, obtained from Micrometric Autosorb 2050 Analyser, after out degassing the samples at 120°C, with the residual pressure of 10-5 mmHg. The BET method was used for the corresponding calculations. Total pore volume (Vt) was determined at P/P0=0.98.

3. Results and discussion

3.1 Characterization of the two clays:

The centesimal compositions of raw and purified samples are given in Table 1. The following preliminary points may be noticed:

a) The loss on ignition of the Kasserine clay is very important (33.20 %); it can be due to the presence of a supplementary water layer.

b) The (SiO_2/Al_2O_3) ratio is close to 1 for all samples. Therefore we can deduct that the two minerals are of types 1/1.

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c) The (SiO_2/Al_2O_3) ratio of the Tabarka clay (1.15) is very close to the theoretical kaolinite 1.18 [6].

d) The amounts of SiO_2 (38.77 %) and Al_2O_3 (37.20 %) of purified Tabarka clay are nearly equal to those given by the literature for a kaolinite.

Table 1. Chemical analysis of the samples

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	ZnO	PF
K_b	35,12	28,90	0,19	0,63	0,28	1,29	0,15	0,24	33,20
K_p	45,95	28,52	0,17	0,08	0,12	0,08	0,14	0,25	24,69
T_b	44,36	38,77	0,50	0,33	0,08	0,11	0,02	0,17	15,66
T_P	46,03	37,20	0,46	0,36	0,08	0,05	0,04	0,19	15,59

The XRD pattern of the Tabarka clay (fig.1) shows sharp peaks at *d* = 7.15, 4.45, 4.35, 4.17, 3.84 and 3.57 Å due to well crystallized kaolinite [7].

The XRD pattern of the Kasserine clay (fig.2) shows sharp peaks at *d* = 10, 4.48, 3.34 and 2.58 Å due to halloysite $4H_2O$ [8].

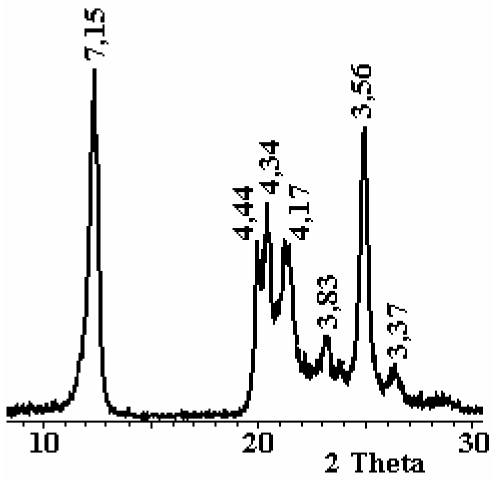

Fig. 1. XRD pattern of crude Tabarka clay

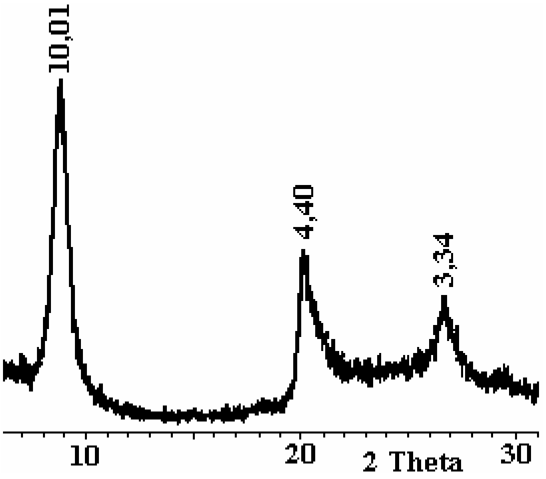

Fig. 2. XRD pattern of crude Kasserine clay

The diffractograms (fig.3) show that these two samples are respectively of kaolinite and halloysite that will be destroyed at 500°C. The confirmation of our results with those gotten by other authors [9] is returned in the following Table.

Table 2. Identification of samples

Minerals	Normal Glass	Glass heated at 500°C
Kaolinite	7,29 Å	Détruite
Halloysite	10 Å	Détruite

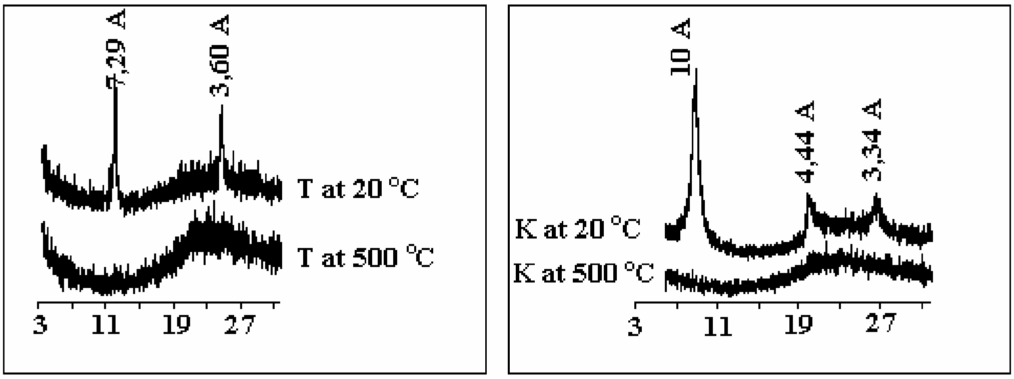

Fig. 3. XRD of oriented films of purified samples and heated at 500°C

The exam of IR spectra shows that (fig. 4, 5):

a) IR spectra of raw and purified samples are identical; so no foulness associated to the two clays.

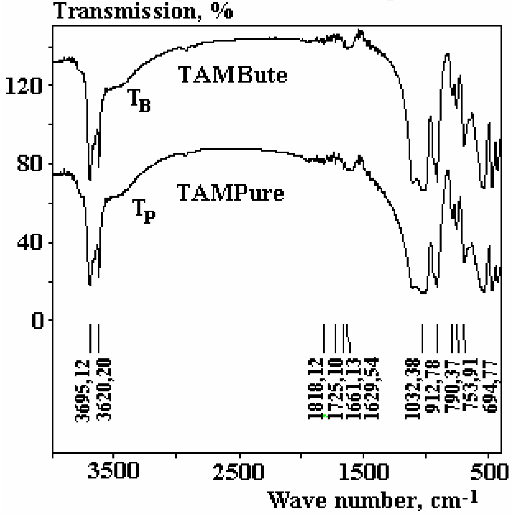

Fig. 4. IR spectra of raw and purified Tabarka clay

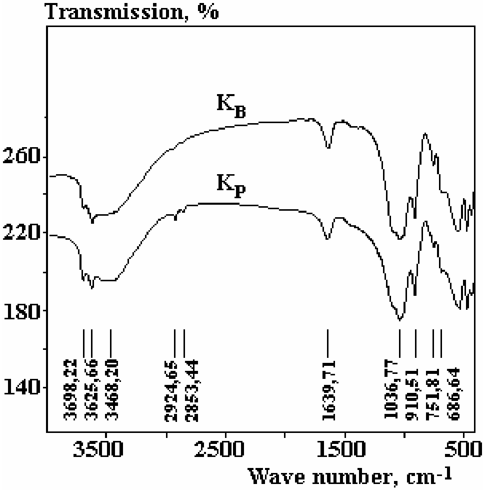

Fig. 5. IR spectra of raw and purified Kasserine clay

b) In the region between 3500 and 4000 cm^{-1}, the IR spectrum of the Tabarka clay (fig.4) shows thins and intense bands whereas the bands of the kasserine clay (fig.5) are larges and less intense. It proves that Tabarka clay is better crystallized than Kasserine clay.

c) Referring on results of IR spectroscopic analysis for a kaolinite, given by Vander Marel and Bentels Pacher in 1976, we deduce that Tabarka clay is a kaolinite well-crystallized (Table 3).

Table 3. IR bands (cm^{-1}) of Tabarka clay

3695, 3660 and 3620	Al-OH of valence
940 and 913	Al-OH of deformation
1032	Si-O-Si of valence
1005	Si-O-Al of valence
695 and 539	Si-O-Al of deformation

d) Fig.5 shows bands at 3698, 3625 1036 and 912 cm^{-1} characterizes the clayey mineral of kaolin family [10]. The adsorption massif at 3468 cm^{-1} and the band of deformation at 1640 cm^{-1} (vibrations OH of the hydration water clay), show that the kasserine clay is a halloysite.

Fig. 6 presents the DTA curves of the studied samples. The main changes pointed out by TG and DTA, during the heating of the samples are the following:

a) Lower to 200°C: a first endothermic pick that can be correlated with a pre-dehydration process, which takes place as a results of the reorganization in the octahedral layer, first occurring at the OH of the surface [11]. This explains the importance of the first loss of the Kasserine sample (Table 4) in relation to the one of the Tabarka sample.

b) 500–600°C: a second endothermic pick due to dehydroxylation of the clay. During this temperature kaolinite forms metakaolinite by dehydroxylation [12].

c) 976–1000°C: an exothermic pick that doesn't correspond to a weight loss but it indicates the transition of phase to high temperature of the amorphous product, due to the decomposition of the kaolinite. In well-crystallized samples the decomposition of kaolinite starts at higher temperature [13]. So the observation of these two picks of our samples permits us to conclude that Tabarka sample is better crystallized than Kasserine sample.

d) The calculation of losses in mass (Table 4) of kasserine clay and Tabarka clay shows that it is respectively a halloysite and a kaolinite [14].

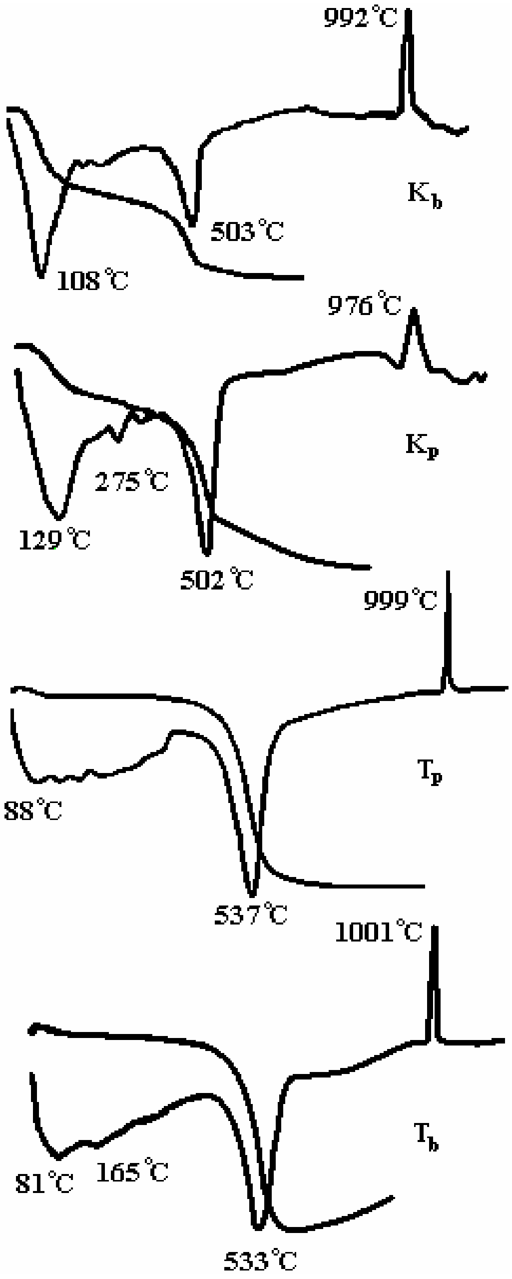

Fig. 6. DTA curves of crude and purified samples

Table 4. Losses in mass of samples

Samples	**1^{ist} loss (%) T < 200°C**	**2^{sd} loss (%) 400 < T< 600°C**
K_b	3,89	5,04
K_p	1,44	6,62
T_b	0,50	12,77
T_p	1,32	13,78
Weight Losses *(Ross and Kerr, 1931)*		
Kaolinite	1 – 2 %	13 %
Halloysite	2 – 4 %	6 – 14 %

Fig.7. presents the isotherms of adsorption-desorption of Kasserine clay and Tabarka clay.

The raw sample of kasserine has an important power of adsorption compared to the purified sample.

The adsorption - desorption isotherms of Tabarka clay are confounded. This clay is not porous characteristic of kaolinite. Whereas the isotherms of desorption of the Kasserine clay present hysteretic buckles what indicates that this clay is porous.

The Kasserine clay presents the best power of adsorption of the two clays.

Specific surface values, determined from the isotherms of adsorption, of the two samples are represented in the following Table:

Table 5. Specific surface of samples

Samples	**Specific surface (m^2/g)**
K_b	233,96
k_p	128,27
T_b	24,57
T_p	24,60

The specific surface is not sufficient for the characterization of clayey mineral. The specific surface of kaolinite is lower to 25 m^2/g [15]. In our case the specific surface value of Tabarka clay (Table 5) its 24.5 m^2/g corresponds to kaolinite.

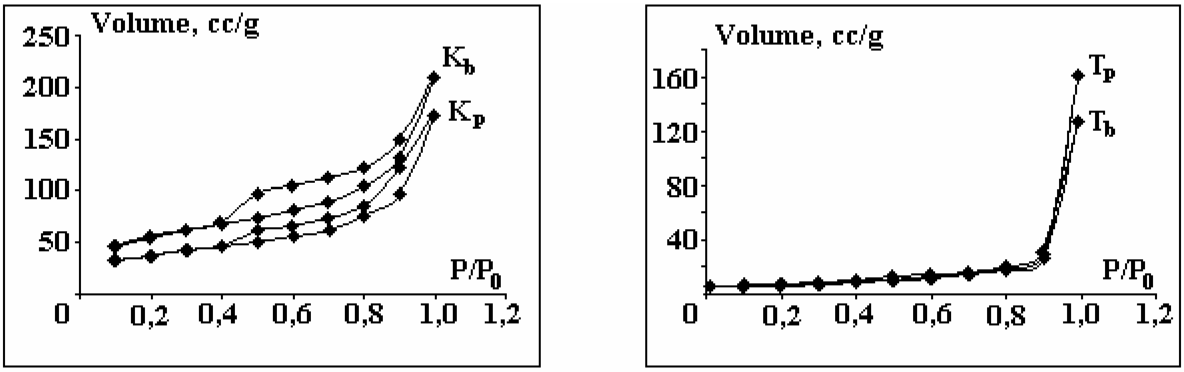

Fig. 7. Isotherms of adsorption-desorption of Kasserine clay and Tabarka clay

The values of C.E.C of the raw and purified clays are nearly identical (Table 6), what confirm that these two samples don't contain any foulness.

According to the literature values [16] of the C.E.C we noted that:

a) The C.E.C of the Kasserine sample (40.11 méq/100g of clay charred), corresponds to Halloysite 4H2O.

b) The value of the C.E.C of the Tabarka sample (3,15 méq/100gs of heated clay), corresponds to kaolinite.

Table 6. C.E.C of samples

samples	**C.E.C (méq/100g of heated clay)**
K_b	40,11
K_p	39,84
T_b	3,15
T_p	3,15
C.E.C of some clayey minerals (Kelley, 1948)	
Kaolinite	3 - 15
Halloysite $2H_2O$	5 - 10
Halloysite $4H_2O$	40 - 50

3.2 Study of the thermal behaviour of the kaolinite of Tabarka and the halloysite of Kasserine:

The thermal analysis is realized by heating samples to different temperatures (100, 300, 500, 700, 1000 and 1200°C), during one hour. The heated samples are analyzed by different techniques (XRD, IR and specific surface analysis).

3.2.1 Study of the thermal Behavior by XRD:

Fig. 8, 9 present respectively the XRD patterns to different temperatures of the Tabarka and Kasserine samples.

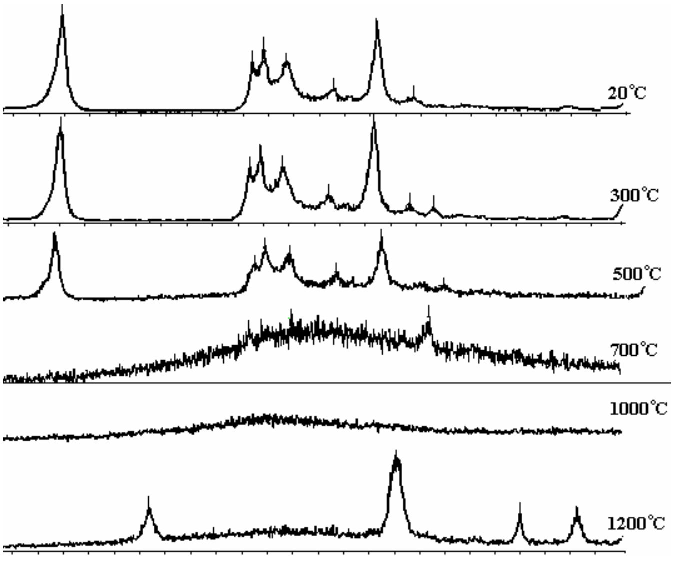

Fig. 8. XRD patterns of Tabarka samples to different temperatures

The XRD patterns at 100°C (fig. 9), shows a sharp peaks at *d*= 7.41, 4.41 and 3.59 Å characteristic of kaolinite, what explains the departure of water molecules of the halloysite. The kaolinite is destroyed to 550°C due to the formation of an amorphous dehydration product identified as metakaolinite after an endothermic reaction. At 1000°C, the structure of the two samples is completely changed what interpreted by the formation of crystalline product from the next amorphous intermediate phase results in a prominent exothermic reaction at 980°C [17]. The two difractograms obtained at 1200°C, show a sharp peaks at *d*=5.41, 3.41, 2.89 and 2,70 Å relatives to a new phase that is the mullite.

The diffractogram of Tunisian mullite (fig. 10) gotten by thermal treatment of the Tabarka clay is simulated to XRD pattern of a pure mullite (fig. 11) but picks are less resolute that can be due to a bad crystallization.

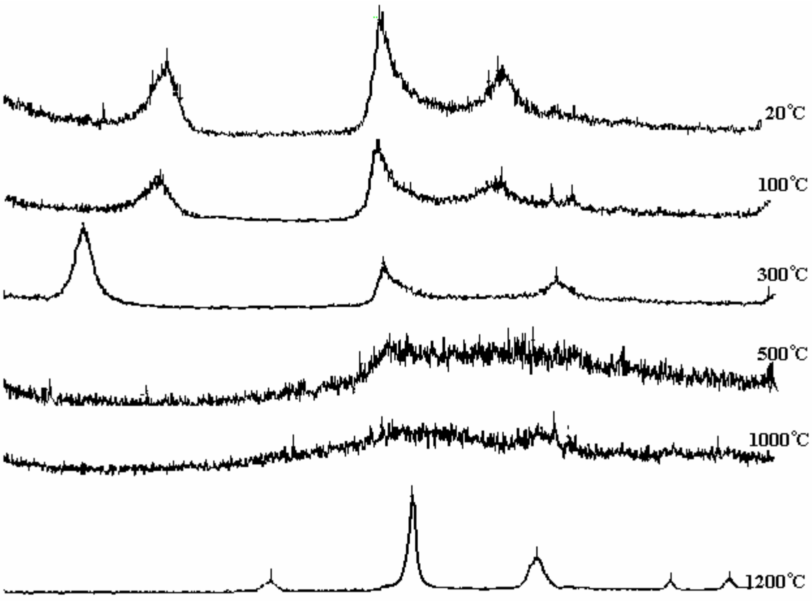

Fig. 9. XRD patterns of Kasserine samples to different temperatures

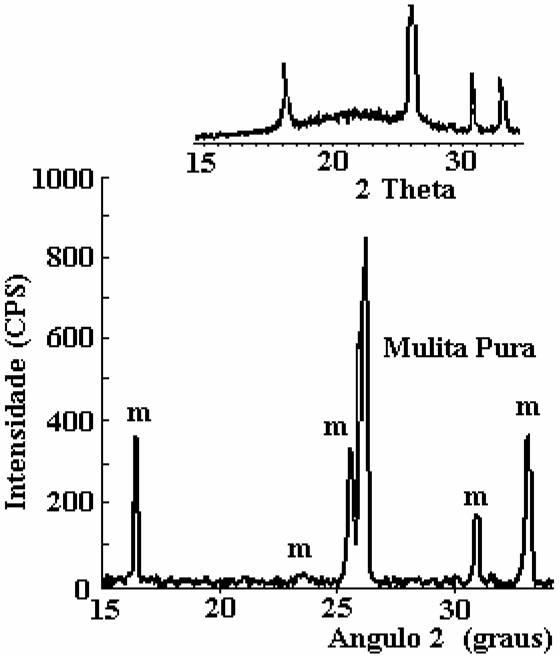

Fig. 10. XRD pattern of Tabarka clay heated at 1200°C and the diffractogram of pure mullite (M. F. de Souza and J. Yamamoto, 1999)[18]

3.2.2 Study of the thermal Behavior by IR:

Fig.11 and 12 present respectively the IR spectera of Kassserine and Tabarka samples, obtained after thermal treatment. After the thermal treatment of samples, the transformation of kaolinite to metakaolinite is confirmed by the absence of detectable Al-O-H bands at 913 cm^{-1}. The reduction of 539 and 913 cm^{-1} and the appearance of a new band at 786 cm^{-1} can be connected with the change from octahedral coordination of Al^{3+} in kaolinite to tetrahedral coordination in metakaolinite [19]. The characteristic bands of kaolinite have been disappeared after the thermal treatment over 500°C. a new band at 2850-3500 cm^{-1} is observed in the sample treated at 700°C and is reduced as the treatment temperature is increased.

The specters of the two clay samples, heated to 1200 °C, show the apparition of a new phase are similar to the mullite spectera (fig. 13) observed using FTIR. This mullite is prepared from sol-gel process by the synthesis of the pure aluminosiloxane [20].

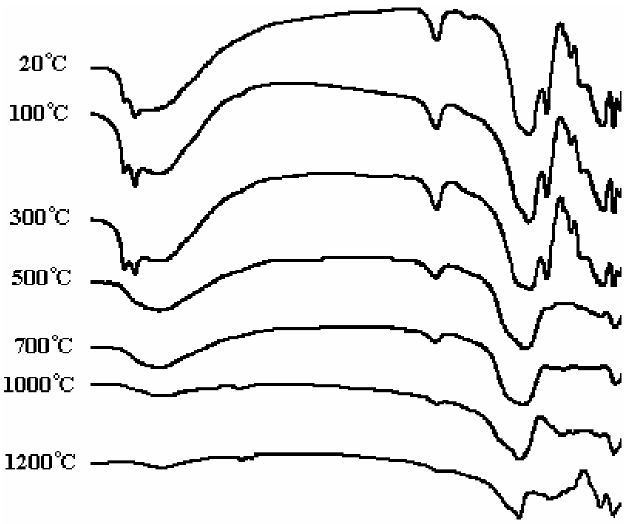

Fig. 11. IR of kasserine samples after thermal treatment

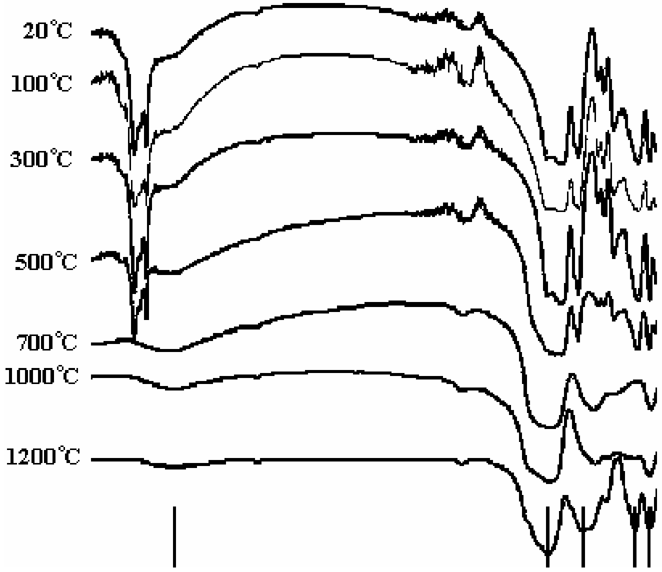

Fig. 12. IR of Tabarka samples after thermal treatment

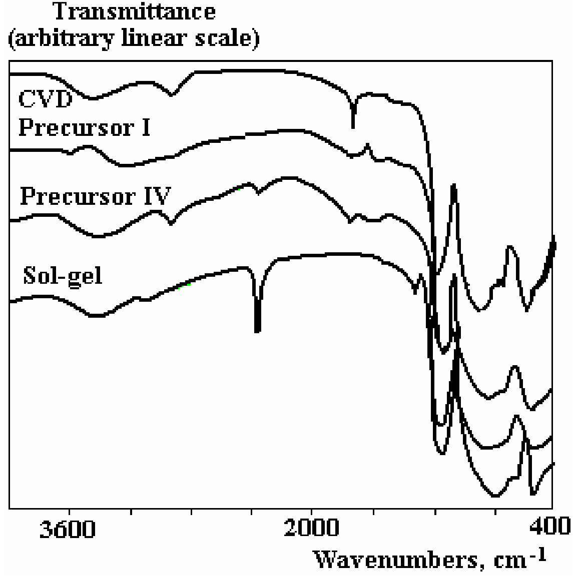

Fig. 13. Chemical homogeneity in mullite prepared from polymeric precursors can be observed using FTIR (Treadwell et al., 1996)

3.2.3 Study of the thermal Behavior by specific surface:

Fig. 14 presents the adsorption – desorption isotherms of kasserine samples after thermal treatment, show a progressive diminution of the porosity until completely disappears at 1200°C.

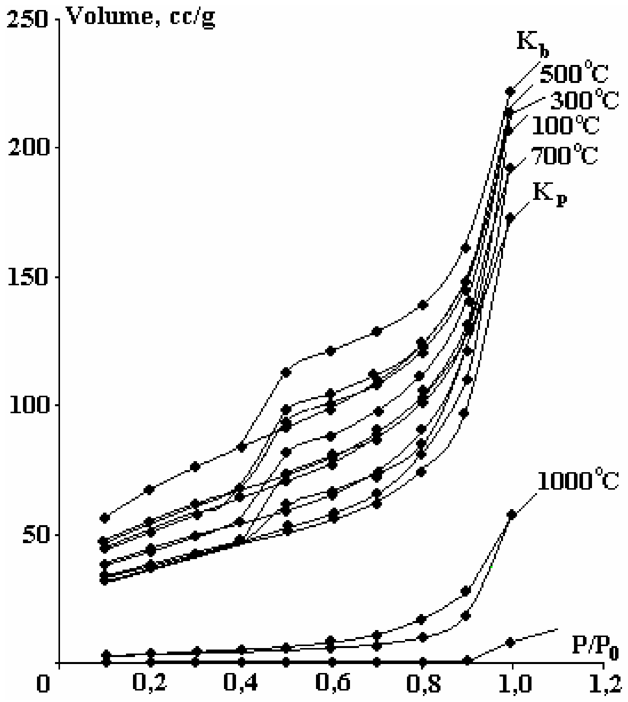

Fig. 14. Adsorption-desorption isotherms of Kasserine samples after thermal treatment

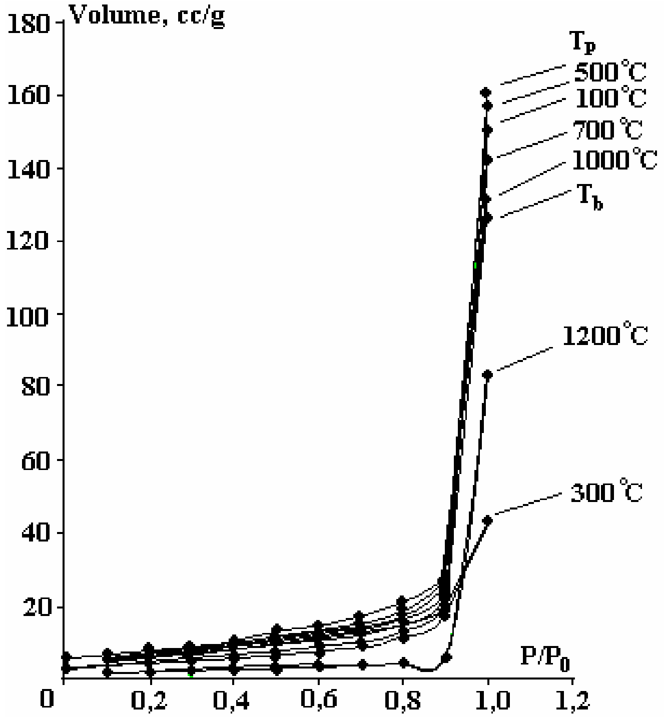

Fig. 15. Adsorption-desorption isotherms of Tabarka samples after thermal treatment

The specific surfaces of two clays obtained after thermal treatment are represented in the following table:

Table 7. Specific surface of samples after thermal treatment

Temperature (°C)		20	100	300	500	700	1000	1200
Specific surface (m^2/g)	K	233,96	178,80	178,12	149,83	130,01	12,29	0,61
	T	24,57	22,77	23,92	22,15	21,74	15,19	5,92

The specific surface of Kasserine clay (233.96 m^2/g to 20°C) remains very important until the temperature of 700°C, what reveals some catalytic applications to high temperature.

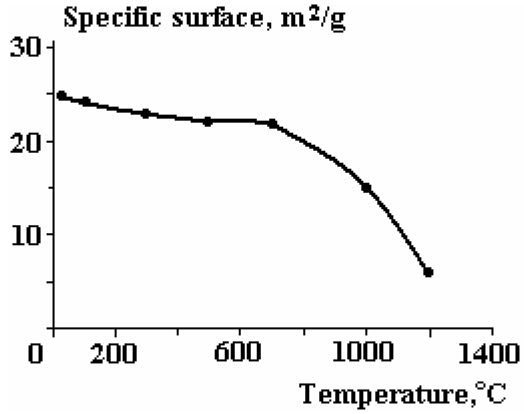

Fig. 16. Evolution of the specific surface of Tabarka clay according to the temperature

The specific surface of Tabarka clay according to the temperature (fig.16) remains constant until 700°C. One will note the extreme stability of the total surface developed by this clay during the phase of the dehydroxylation. Therefore the dehydroxylation doesn't entail any modifications important of the texture of the kaolinite.

The representation of the evolution of the specific surface of Kasserine clay, according to the temperature (fig.17) show that:

a) A slightly decreases of the surface in the begin of the dehydroxylation.

b) The surface remains constant in the second stage of the déshydroxylation (100°C to 700°C). One will note the extreme stability of the total surface developed by kasserine sample during this phase.

c) An abrupt diminution at 700°C that is interpreted by a process of sintering.

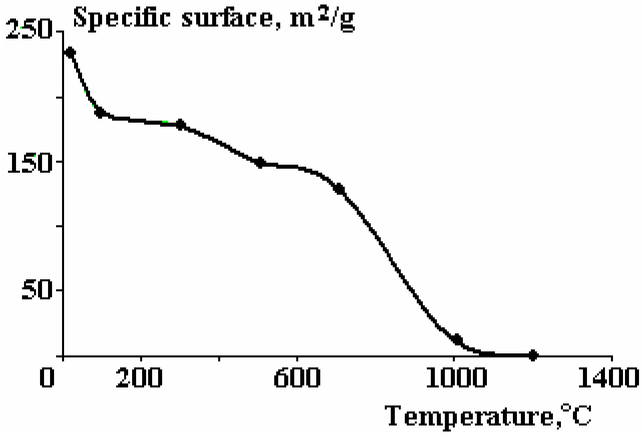

Fig. 17. Evolution of the specific surface of Kasserine clay according to the temperature

4. Conclusion

The selected clays differ by their mineralogical properties. The Tabarka is a well-crystallized kaolinite. Whereas the Kasserine clay is a hydrated halloysite characterized by a important specific surface (233.96 m^2/g). The evolution of specific surface according to the temperature of the Kasserine samples after thermal treatment shows an abrupt diminution at 700°C that are interpreted by a process of sintering. The thermal treatment of the two clays at 1200°C, shows the apparition of a new phase that is the mullite. This mullite is identical to mullite gotten by the process sol-gel from the synthesis of the pure aluminosiloxane.

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Summary

The object of this work is to study the physicochemical proprieties and the thermal behaviour of two Tunisians kaolins. The two samples selected from Tabarka and Kasserine are tested by chemical analysis (CA), X-ray diffraction (XRD), differential thermal analysis (DTA), infrared spectroscopy (IR), cation exchange capacities (CEC) and specific areas (BET) in order to determine their chemical and mineralogical composition and structural differences. This study showed that the clay of Tabarka is a well crystallized kaolinite and the clay of Kasserine is a halloysite $4H_2$Ò, containing amorphous alumina. The evolution of specific surface according to the temperature of the Kasserine samples after thermal treatment shows an abrupt diminution at 700°C that are interpreted by a process of sintering. The thermal treatment of the two clays at 1200°C, shows the apparition of a new phase that is the mullite. This mullite is identical to mullite gotten by the process sol-gel from the synthesis of the pure aluminosiloxane.