

CHARACTERIZATION AND THERMAL BEHAVIOR OF JEBEL RESSAS CLAY

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ABSTRACT

The present study deals with the Jebel Ressay clay thermal behavior related to its mineralogical composition. The mineralogical study of the material consisted on the characterization of the fine fraction by chemical analysis (CA), X-ray diffraction (XRD), infrared spectroscopy (IR) and cation exchange capacity (CEC). The results show that the material is an interstratified illite-smectite mixed with kaolinite. The illite phase in the purified fraction is about 80 %. The CEC and the specific area values of the purified fraction are respectively 39.93 meq/100g of fired clay and 325 m²/g. The thermal behavior of the raw clay is determined by differential thermal analysis (DTA), thermogravimetric analysis (TGA), dilatometry and dry feature. The clay has dehydration, dehydroxylation and carbonate decomposition temperatures respectively at 92°C-281°C, 503°C and 732°C, a low loss of weight (5.39 %) with a low shrinkage after drying (Rs = 2.39 %) and firing (Rc = 1.8 %) treatments. The temperature of vitrification is about 820°C. This clay sample is suitable for the manufacture of ceramic tiles.

Keywords: illite, thermal analysis, thermogravimetric analysis, ceramic, Jebel Ressay clay.

RESUME

Le présent travail concerne l'étude thermique reliée à la composition minéralogique de l'argile de Jebel Ressay. L'étude minéralogique consiste en la caractérisation de la fraction argileuse par analyse chimique, diffraction des rayons X, spectroscopie infrarouge et mesure de la capacité d'échange cationique (CEC). Les résultats montrent que l'argile de Jebel Ressay est un interstratifié illite-smectite mélangé avec de la kaolinite. La fraction purifiée est formée par 80 % d'illite. La CEC et la surface spécifique sont respectivement égales à 39.93 meq/100g d'argile calcinée et 325m²/g. Le comportement thermique de l'argile brute est déterminé en utilisant les analyses thermique différentielle (ATD), thermogravimétrique (ATG), dilatométrique et du comportement au séchage. L'argile de Jebel Ressay présente des températures de déshydratation, de déshydroxylation et de décomposition des carbonates, respectivement à 92°C-281°C, 503°C et 732°C, ainsi qu'une faible perte de masse (5.39 %) et un faible retrait après séchage (Rs = 2.39 %) et après cuisson (Rc = 1.8 %). La température de vitrification est égale à 820°C. Cette argile présente les caractéristiques thermiques requises pour la fabrication des carreaux céramiques.

Mots clefs : illite, analyse thermique, analyse thermogravimétrique, céramique, argile Jebel Ressay.

INTRODUCTION

Clays are widely used in the manufacture of many traditional ceramics. Each ceramic product requires clays having particular and appropriate characteristics. They must not contain a swelling phase, their loss of weight and shrinkage, after drying and firing, have to be low. The thermal behavior related to the mineralogical composition of clays, determines their possible use in the ceramic industry.

The present study aims to define the mineralogical composition and the thermal behavior of a Tunisian clay extracted from a deposit located near Tunis, called Jebel Ressayas.

MATERIAL AND METHODS

Material and samples preparation

Several samples were taken from Jebel Ressayas in different areas at regular intervals (~15m). Each area corresponds to a depth between -1m to -10m. In order to have a representative sample of the deposit, the material taken from the deposit was intensively mixed, then grinded with an agate mortar. The powder sieved through a 100 μ m mesh is representative of the deposit. The less than 100 μ m fraction was purified by repeating cation exchange with NaCl solution (1N) followed by washing, sedimentation and dialysis [1]. The fine clean sediment was dried at 50°C, then sift at 63 μ m. The selected sample was indicated by JRC; "p" was added to indicate the purified fraction.

Experimental methods

Major and trace elements were measured by atomic absorption spectrometry using a PYE UNICAM PU 9000 spectrometer. The results were expressed in oxide percentages.

The X-ray diffraction was conducted on powder and oriented samples. For the latter, slides were prepared with purified and wet clay. Some of these were dried at room temperature, other were glycolated for one hour and other heated for three hours at 550°C. The composition of the impurities was determined from the X-ray pattern of the raw sample.

The diffractograms were obtained with a Philips PW1710 diffractometer with a Cu-anticathode at 40 kV and 20 mA and processed with a Philips PC-APD (version 2.0). The qualitative results were evaluated according to established procedures [2-3-4].

The infrared spectra were recorded with a Perkin Elmer 1000 spectrophotometer. The frequencies range is 350 cm^{-1} to 4000 cm^{-1} . The samples were prepared as pastilles containing

2 mg of clay mixed with 200 mg of KBr.

The cation exchange capacity (CEC) and the specific area of the purified fraction were determined using the methylene blue adsorption isotherms. The amounts of methylene blue adsorbed by the purified sample are plotted against the amounts of methylene blue in the initial solution. If M_f meq of methylene blue are adsorbed per 100g of clay when the surface is covered, and if A_m is the area per molecule in Å^2 , the surface area per g of clay is : $M_f \times A_m \times 6.02 \times 10^{-2} \text{ m}^2/\text{g}$ [5]. The area per adsorbed molecule of methylene blue equals 135 Å^2 [6].

The differential thermal analysis and the thermogravimetric analysis (DTA -TGA), were operated by heating the raw clay within argon atmosphere at a rate of 10°C per min and measuring simultaneously the loss of weight and the difference in temperature between the sample and an inert standard material (Al_2O_3). The used equipment is a Seteram TGDTA 92.

The firing characteristics of the raw clay were determined by heating the sample up to 900°C using an ADAMEL LHOMARGY, DM 15 dilatometer. The sample (65mm x 5mm x 5mm) was semi-dry pressed from the powder (fraction < $100 \mu\text{m}$). The pressed sample was dried overnight at 40°C then heated in a horizontal tubular furnace at a heating rate of $10^\circ\text{C}/\text{min}$. The results of linear changes $(\frac{\Delta l}{l} \%)$ were plotted as a function of heating temperature.

The dry feature of the raw clay was recorded using a "barellatographe" ADAMEL LHOMARGY, BI, which measures, within 24h, the change in length and the loss of weight. Two similar samples were prepared in the shape of a slide by adding water to the raw powder until the obtention of a normal paste which does not stick to fingers. One sample was used for recording the curve; the second sample was used to equilibrate the apparatus weighing system. When the sample finished up shrinking, its drying is continued at 110°C . The weight (m) and length (l) of each slide were measured before recording and after complete drying. The result of weight change $(\frac{\Delta m}{m} \%)$ was plotted as a function of the length change $(\frac{\Delta l}{l} \%)$.

RESULTS AND DISCUSSION

Chemical analysis and structural formula

The chemical composition (major elements) of the raw and purified clay is indicated on Table I. The following preliminary characters may be noticed :

- The total percentage of the oxides is close to 100 % for both raw and purified samples.

- The $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio ranges between 1 and 2 for the purified fraction, which indicates a sample containing a mixture of kaolinite ($\text{SiO}_2 / \text{Al}_2\text{O}_3 \# 1$) [7] and smectite or micas ($\text{SiO}_2 / \text{Al}_2\text{O}_3 \# 2$) [8].

- The rate of Fe_2O_3 after purification rises from 5.72 % to 6 %, indicating that the iron is contained in the clay mineral structure.

- The amount of potassium increases after purification and sodic exchange, showing that the potassium is not exchangeable. Its presence shows an illitic phase.

- The carbonate content ($\text{CaCO}_3 + \text{MgCO}_3$) in the raw clay expressed in percentage of oxides is 6.74 %. Whereas in the purified sample it is 2.56 %.

- The MgO content is weakly increased after purification and sodic exchange, indicating that Mg^{2+} is in the internal structure of the clay.

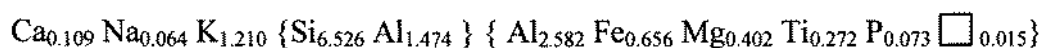
- the CaO content in the purified sample is drastically decreased. This result indicates that the majority of calcium in the raw clay is in the carbonate form.

TABLE I : Chemical analysis of JRC and JRCp

Elements oxide %	Samples	
	JRC % in weight	JRCp % in weight
SiO_2	50.79	44.80
Al_2O_3	16.62	23.60
Fe_2O_3	5.72	6.00
CaO	5.05	0.70
MgO	1.69	1.86
Na_2O	1.18	0.23
K_2O	2.72	4.00
TiO_2	2.92	2.50
P_2O_5	0.084	0.60
Loss of weight	13.80	15.48
Total	100.5	99.77

The structural formula of fired clay is determined using the Charles Mauguin [9] method. This method consists of the transformation of oxides percentages, obtained by chemical analysis, into molecular numbers. Each oxide was then decomposed into oxygen and cation. If the oxygen total number is N, the decomposed oxides were multiplied by $22/N$. The result was expressed in atoms number for 22 oxygen atoms (table II).

The results indicated in table II lead to the following formula :



According to this formula, the following points may be noticed :

- The number of octahedric cations (Al, Fe and Mg) is near 4. JRC is a dioctahedral clay.
- The load per mesh value is 1.503.
- The rate of tetrahedral substitution is 98%.
- The illite phase in the purified clay fraction is estimated at 80 %.
- The CEC value is 37 meq / 100 g of fired clay. It agrees with the literature which indicates that illite clay has a CEC between 10 and 40 meq/100g of fired clay [10].

TABLE II : Structural formula of sodic and fired clay

Element	Oxide per 100g of fired JRCp	Number of O ₂ per 100g of fired JRCp	Number of O ₂ per mesh	Number of ions
Si	53	1.7666	13.052	6.526
Al	28	0.8235	6.084	4.056
Fe	7.10	0.1332	0.984	0.656
Ca	0.83	0.0148	0.109	0.109
Mg	2.20	0.0545	0.402	0.402
Na	0.27	4.35x10 ⁻³	0.032	0.064
K	4.73	0.0820	0.605	1.210
Ti	2.95	0.0738	0.545	0.272
P	0.71	25x10 ⁻³	0.184	0.073
Total	-	2.9777	-	-

X-ray diffraction

According to the diffractogram of the raw clay (fig.1), the kaolinite (reflection at 7.15 Å) and the illite (reflection at 9.95 Å) are detected. The quartz (reflections at 4.26 Å and 3.34 Å) and the calcite (reflections at 3.03 Å) are the essential impurities present in this clay.

The X-ray patterns of the purified clay (fig. 2a-b-c) show reflections at 7.17 Å and 3.55 Å which disappear after heating at 550°C; these reflections confirm the presence of the kaolinite phase. The peaks at 9.93 Å, 4.99 Å and 3.33 Å are detected in all the samples; they are due to the presence of illite.

The peak observed at 14.65 Å in a glycolated sample can indicate the presence of vermiculite or smectite [11].

The low amount of magnesium in JRC determined by chemical analysis (table I) and the dioctahedral character of this clay reveals the presence of a smectite phase. However, according to Reynolds and Hower [12], the position of the 002 reflection is very sensible to the presence of illite in an illite-smectite interstratified. It varies from 8.46 Å for a pure smectite to 10.1 Å for a

pure illite and it is equal to 9.45 Å when the percentage of smectite fraction is 35 %. For the glycolated sample (fig.2-b), the 002 reflection appears at 9.96 Å. The smectite fraction is thus estimated between 20 % and 25 % which agrees with the result obtained by chemical analysis (80 % of illite).

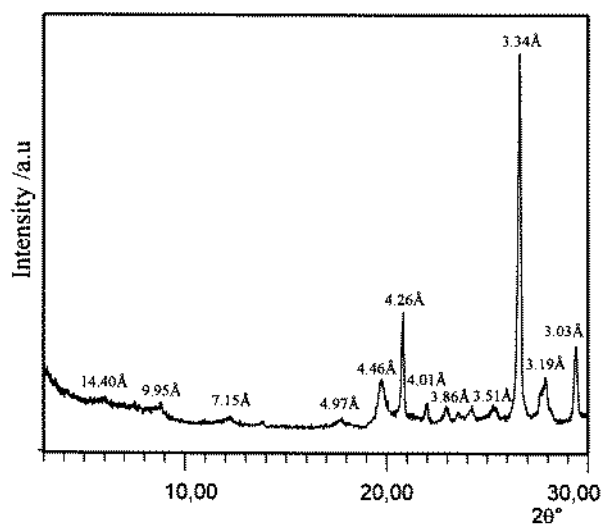


Figure 1 : X-ray diffractogram of raw clay

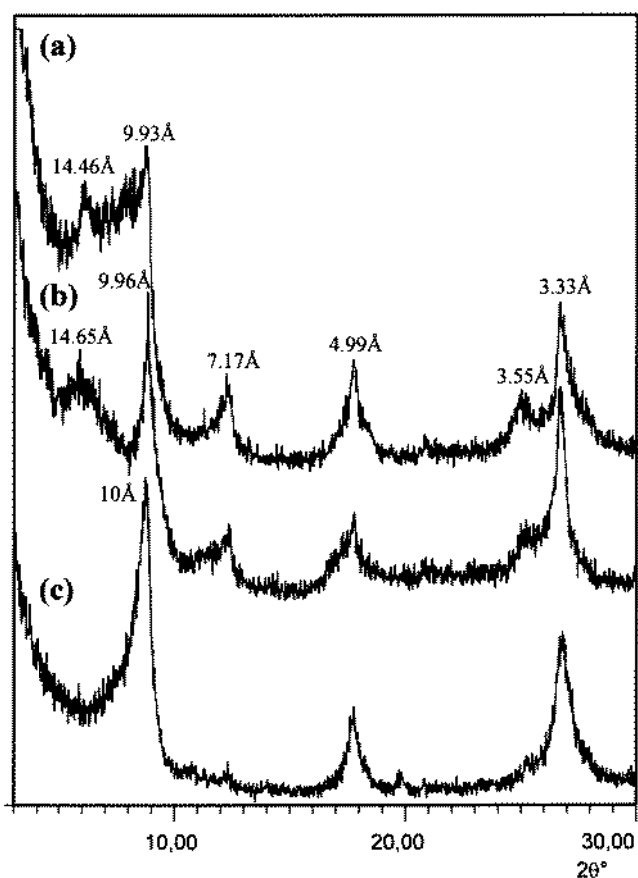


Figure 2 : X-ray diffractograms of oriented samples :
a- dried at room temperature, b- glycolated for one hour, c- heated for three hours at 550°C.

Infrared spectroscopy

The identification of the clay mineral by infrared spectroscopy has been based on previous studies [13-14].

The infrared spectrum of JRCp (fig. 3) shows :

- bands at 695 cm^{-1} and 915 cm^{-1} , appearing with low intensity, indicating the presence of kaolinite in minor quantity [11].

- bands at 3440 cm^{-1} and at 1630 cm^{-1} corresponding, respectively, to the valency and deformation vibration of water used in hydration of clay.

- a band at 1200 cm^{-1} with high intensity characterizes the valency vibration of SiO_2 of the

clay. Deformation bands appear around 525 cm^{-1} for Si-O-Al vibration, 471 cm^{-1} for Si-O-Si and around 427 cm^{-1} for Si-O-Fe vibration.

The JRC infrared spectrum (fig.3) contains additional bands at 780 cm^{-1} and 800 cm^{-1} revealing the presence of the quartz and band at 1430 cm^{-1} corresponding to the carbonate (calcite or dolomite).

Methylene blue adsorption isotherm of the purified fraction

From the methylene blue adsorption curve of the purified clay fraction (fig.4), M_f is equal to 10.8 g of methylene blue per 100g of clay which corresponds to 33.75 meq / 100g of clay. Thus the CEC value is equal to 39.93 meq / 100g of fired clay. This CEC value agrees with that calculated by chemical analysis (37 meq / 100g of fired clay). The specific surface area is estimated at $325\text{ m}^2/\text{g}$.

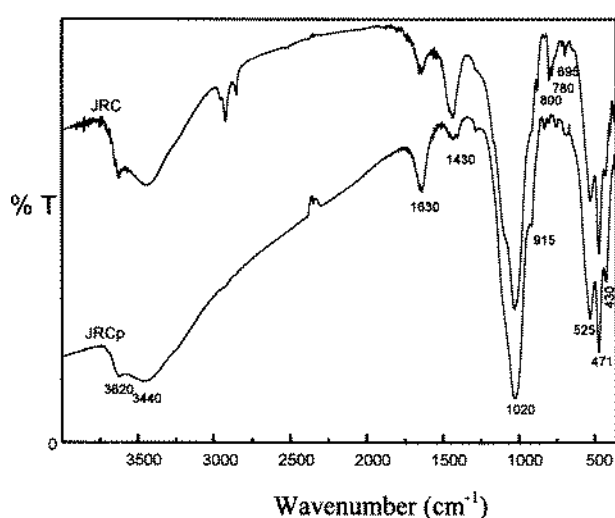


Figure 3 : infrared spectra of JRC and JRCp

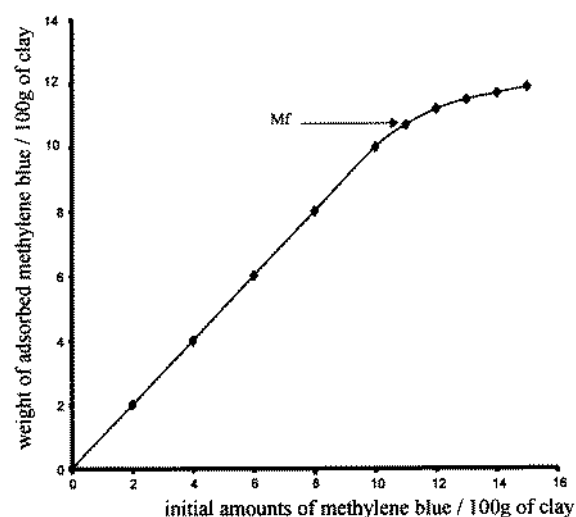


Figure 4 : adsorption isotherm of methylene blue on a purified clay

Differential thermal analysis and thermogravimetric analysis (DTA-TGA)

The interpretation [15-16-17] of the DTA-TGA curves (fig.5) leads to the following results:

- a significant endothermic peak at 92°C followed by a low endothermic peaks at 161°C and 281°C are observed. At the same time the TGA curve shows a weight loss of about 0.98 %.

These transformations are due to the removal, respectively, of adsorbed and interlayer water from the clay mineral. The high intensity of the first peak confirms the presence of a swelling phase (smectite) interstratified with non swelling clay (illite) [18].

- an endothermic peak at 503°C appears in DTA curve, which corresponds to a weight loss of 1.80 % in the TGA curve. This reaction corresponds to the loss of hydroxyl groups from the clay mineral structure. The peak is broad (diffuse) because of the low content of kaolinite in the sample.

- an endothermic peak at 732°C with a weight loss of 2.61% can be attributed to the carbonate decomposition.

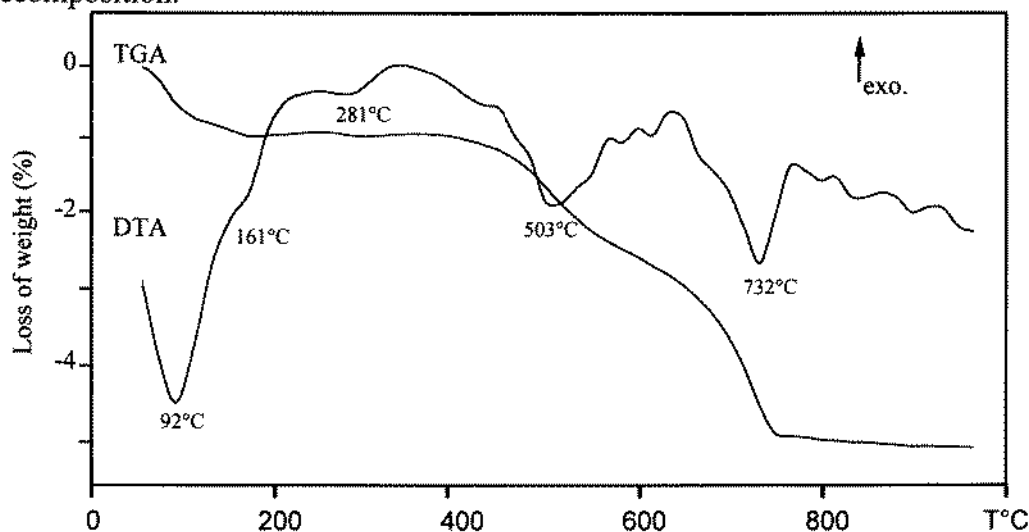


Figure 5 : DTA-TGA curves of raw clay

Dilatometry

The dimensional change observed after firing of the raw clay (fig.6) can be described as follows :

- a slight expansion, followed by a shrink between room temperature and 180°C, can be attributed to the loss of the adsorbed water,

- a progressive and slow expansion starting at 180°C can be related to the loss of interlayer water,

- a rapid expansion between 550°C and 750°C can correspond to several phenomena : dehydroxylation of the clay, allotropic transformation of quartz α to quartz β and carbonate decomposition.

- a slight shrinkage starting at 750°C is attributed to the formation of a vitreous phase.

- a rapid continuous shrinkage noticed above 820°C can correspond to the vitrification of clay. The presence of high content of Fe_2O_3 and K_2O in the sample accelerates the vitrification process, due to the fluxing effects induced by these oxides [19].

The vitrification temperature determined at the onset of the liquid phase formation is 820°C. This low value of the vitrification temperature can be explained by the presence of fluxing agents

mainly iron, relative low alumina content (16.62 %) and high amount of illite.

The final shrinkage after firing at 965°C is 1.8 %.

Dry feature

Figure 7 illustrates the feature of crude sample after drying. We notice that the proportion of moisture water is about 5.73 %, and that of interlayer water is about 12.52 %. The total shrinkage after drying is 2.39 %. The studied clay contains so a high amount of sand [20].

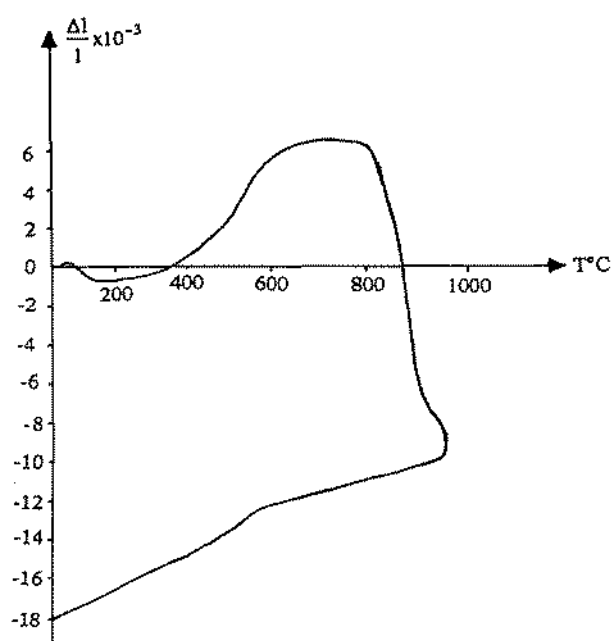


Figure 6 : Thermodilatometry analysis of JRC

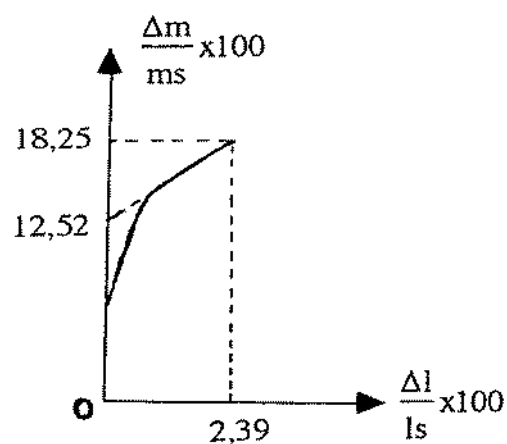


Figure 7 : Dry curve of raw clay

CONCLUSION

The composition of the Jebel Ressas clay was determined according to the chemical analysis, X-ray diffraction, infrared spectroscopy, adsorption isotherm of methylene blue and thermal methods. The dominant minerals in the raw sample are quartz, carbonate and illite whereas in the purified sample they are illite, smectite and kaolinite. The measured JRCp CEC is 39.93 meq/100g of fired clay, it confirms that the sample is not a swelling clay.

The thermal study (DTA-TGA) of the Jebel Ressas clay leads to a confirmation that this clay is not a swelling one as it shows a dehydration at 92°C-281°C and a dehydroxylation at 503°C corresponding to a weak loss of weight respectively equal to 0.98 % and 1.80%.

The dilatometry curve shows a vitrification temperature at 820°C and a shrinkage after firing equal to 1.8 %. The dry curve shows a shrinkage after drying equal to 2.39 %.

Thus JRC clay possesses a suitable mineralogical composition and thermal behavior for the manufacture of ceramic tiles.

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