ISSN: 2639-7455

Research Article

Earth & Environmental Science Research & Reviews

Lower Cretaceous Clay in Anti-Lebanon Mountains, Syria And Their Importance in Ceramic Manufacturing

Abdulsalam Turkmani*

Geo Mining L.L.C, Geological Studies and Consulting, Damascus, Syria.

***Corresponding author**

Abdulsalam Turkmani, Geo Mining L.L.C, Geological Studies and Consulting, Damascus, Syria.
E-mail address: abdulsalam.turkmani@gmail.com

Submitted: 13 Jan 2022; **Accepted**: 21 Jan 2022; **Published**: 25 Jan 2022

Citation: *Abdulsalam Turkmani (2022) Lower Cretaceous Clay in Anti-Lebanon Mountains, Syria And Their Importance in Ceramic Manufacturing. Eart & Envi Scie Res & Rev, 5 (1): 01-07.*

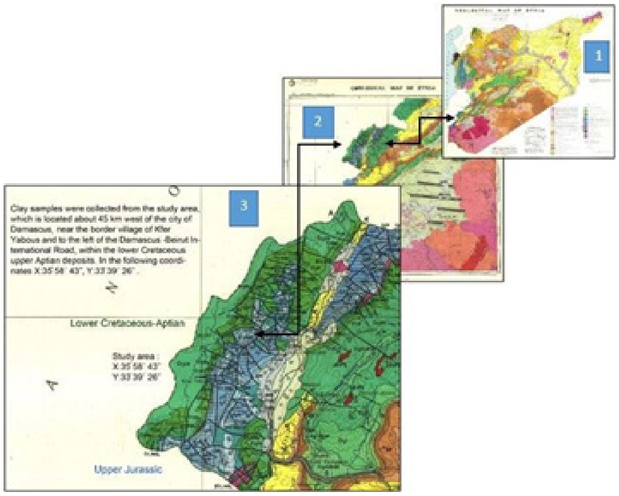
Abstract

Lower Cretaceous rocks are exposed only in the mountain regions of Syria, such as the Anti Lebanon mountain on the western side of Damascus. The lower cretaceous sequences are made up of different rocks. The upper and middle parts of the section are composed mainly of carbonate sediments and less frequently gypsum and anhydrite. The lower beds are mainly composed of sandstone, conglomerate and clay. Clay samples were collected from the study area, which is located about 45 km west of the city of Damascus, near the border village of Kfer Yabous and to the left of the Damascus -Beirut International Road, within the lower Cretaceous upper Aptian deposits. The properties of clay were carried out by X-ray diffraction (XRD) and, X-ray fluorescence (XRF) and Thermal Analysis (DTA-TG-DSC) techniques. The studied clay samples are mainly composed of kaolinite, quartz, mica-illite and same feldspar. Chemical analysis shows a content of SiO_2 that varies from 46.06 to 73 % and Al_2O_3 between 14.55 and 26.56 %. Total content of staining oxides (Fe_2O_3 + TiO_2) is between 4.3 and 12.5 %. The physical properties were determined by studying their behavior before and after firing. They showed low bending strength values (22.5 kg/cm²) after drying, and after firing at 1180°C (about 247 kg/cm²). Water absorption value at 1180 °C was about 10 %. The coefficient thermal expansion coefficient (CTE) at 1140°C was 2,137 x 10^{-5} All obtained results confirm the suitability of this clay for the ceramic industry.

Keywords: Anti- Lebanon mountain, Damascus, Ceramic, Clay, Thermal Analysis, Thermal expansion coefficient

Introduction

Cretaceous rocks are widely known in mountainous areas of Syria, and the lower cretaceous rocks are occurring in five locations, one of them is the Anti-Lebanon Mountains. The lower Cretaceous complex is made up of different rocks. The upper and middle parts of the section is composed of limestone, dolomite, marl and less frequently gypsum and anhydrite. Lower Cretaceous levels are mainly composed of sandstone known as "Gres de base", clay, gravel and conglomerate [1]. The thickness of the lower Cretaceous varies from a few dozens to several hundred meters (Fig.1).



Clay samples were collected from the study area, which is located about 45 km west of the city of Damascus, near the border village of Kfer Yabous and to the left of the Damascus -Beirut International Road, within the lower Cretaceous upper Aptian deposits. In the following coordinates X:35 58' 43", Y:33 39' 26" .

Figure 1: (1) Syrian Map 1:1000000, Ponikarov et al,1966, (2) Syrian Map 1:200000, Ponikarov et al,1963, (3) Study area, Kfer Yabousvillage, Lower Cretaceous-Upper Aptian.

Geological Setting and Materials

In the Anti-Lebanon Mountains, the lower Aptian beds transgressivley lie on the Tithonian. They are mainly composed of variegated quartz sandstones: grey, with carbonate-clay cement and brown, red-brown and bright-yellow with ferruginous cement. The sandstones contain lenses of grey clay, gritstone and conglomerate. The deposits described are characterized by iron ore accumulations present in the ore as oolites, nodules, concretions and incrustations which are particularly frequent in the upper and lower beds of section [2]. Sandstone and clays outcrops show presence of carbonaceous matter, petrified fragments of animal bones, pyrite and amber grains. The sandstones are frequently cross-bedded due to an alternation of more and less coarse-grained varieties. Basalt, anamesite, dolerite and tuff beds are found within the terrigenous rocks at different levels [2, 3]. The middle and upper carbonate beds of the Aptian sequence in the Anti- Lebanon are composed of white and grey, massive, limestone. The limestone outcrops show marl, clay and sandy limestone interbeds. This part of the Aptian sequence is widely known in the in Lebanon and Anti-Lebanon and it's a good marker bed known as "Falaise de Blanch" (Fig.1). Clay samples were collected from the study area, which is located about 45 km west of the city of Damascus, near the border village of Kfer Yabous and to the left side of Damascus-Beirut International Road, within the lower Cretaceous upper Aptian deposits. Their geographical coordinates are Long.35° 58′43″, Lat.33° 39′26″ (Fig.2).

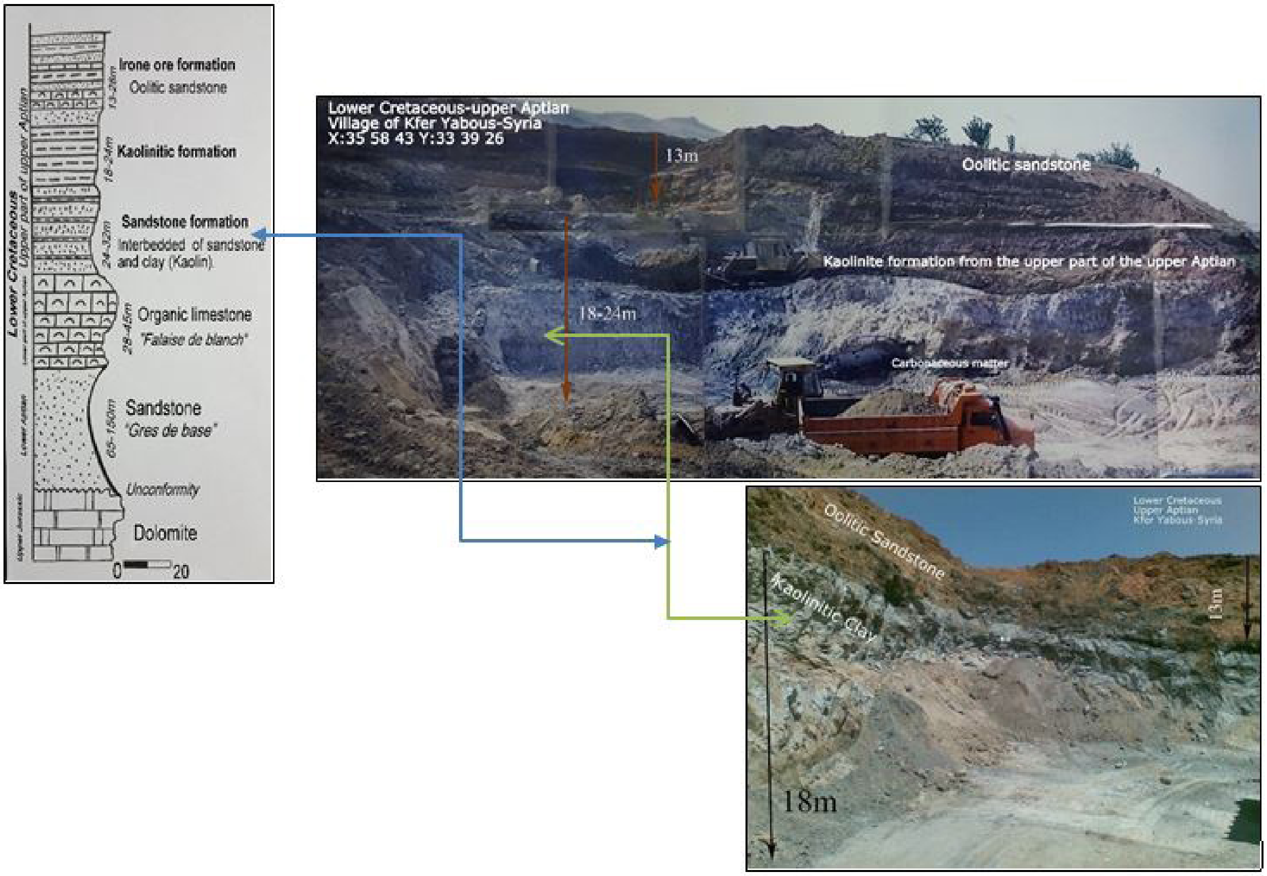


Figure 2: Stratigraphic column of the study area. Typical exposure of lower Cretaceous clay in the Yabous, showing the upper part of the upper Aptian

Methods

- ***Chemical analysis*** was determined by 31T Sequential ART 841031T X-Ray Fluorescence Spectrometer. This analysis allows the determination of the main oxides present in raw materials. The analysis is completed by the measurement of loss of ignition L.O.I (10 g of the same powders used to prepare pellet samples were fired in porcelain crucibles on a laboratory muffle kiln and weighed before and after firing, the firing cycle was: 3 h at 1050 °C with 1 hour at the maximum temperature).
- ***Mineralogical composition*** of the collected clay samples was determined by X-ray diffraction analysis using a Philips PW1840 diffractometer equipped with Cu-Kα radiation source and at a step size angle of 0.02°, scan rate of 2° in 2θ unit, and a scan range from 10° to 70°.
- ***Thermal analysis*** including TG, DSC, DTG and DTA techniques, were performed with a coupled (DTG-60H SHIMADZU) equipment, and Orton Standard, model DIL 2012 STD to measure the cubic thermal expansion (CTE).

Results and discussion

• *Chemical composition*

XRF Chemical composition analyses made on the Kfer Yabous clays (Table.1) show that they are relatively rich in silica (49.06-73.14 %) and they have low content of calcium (0.3-1.05 %) with some exceptions (until 3.92 %) as a result of contamination with (the) calcareous levels. Iron oxide content is variable but always high in all the samples (2.2-12. 5 %). The presence of potassium oxide is variable probably due to the relatively large amount of illite content (1.24-3.76 %). The content of Al2O3 (13.54-26.56 %) indicates the presence of clay minerals of kaolinite group which gives increasing refractory behavior of these clays.

Table 1: Chemical composition of Upper Aptian clay of Kfer Yabous.

Oxide %	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	L.O.I.
K-1	63.51	3.16	18.92	5.58	0.76	0.56	0.16	2.6	0.1	0.01	4.26
K-2	62.42	3.14	18.56	5.55	0.32	1.05	0.14	2.85	0.15	0.01	5.23
K-3	69.74	1.7	15.49	3.5	0.64	0.19	0.11	1.15	0.12	0.01	7.3
K-4	68.67	2.4	17.33	2.99	0.43	0.1	0.2	1.7	0.08	0.01	6.1
K-5	73.4	2.1	14.6	2.2	0.3	0.3	0.2	1.6	0	0.16	5.3
K-6	73.14	1.87	14.38	2.53	0.33	0.6	0.07	1.32	0	0.09	5.36
K-7	72.27	1.97	13.54	3.96	0.25	0.28	0.09	1.24	0	0.07	4.51
K-8	56.33	1.56	26.56	2.64	0.65	0.25	0.17	0.83	0.11	0.01	10.58
K-9	50.61	0.35	23.69	6	3.13	1.47	1.92	3.76	0.35	0.25	8.5
K-10	50.89	1.56	25.89	5.74	2	1.16	1.92	3.31	0.48	0.07	5.4
K-11	56.88	1.79	21.66	2.25	0.66	3.92	0.27	2.25	0	0.24	9.05
K-12	49.06	0	23.07	12.5	2.29	2.06	0.11	1.47	0.12	0.02	9.7
K-13	48.91	0.38	24.25	11.21	0.21	0.3	0.05	1.36	0	0	12.5
K-14	54.55	2.13	26.59	5.72	0.98	0.55	0.1	1.75	0.11	0	7.45

Samples: K_a *(1,2,3,4,5,6,7) clay lenses mixed with sandstone.* K_b *(8,9,10,11,12,13,14) represent kaolinite formation.*

Chemical analysis of clay samples K_b (8,9,10,11,12,13,14) from the kaolinite formation show that the ratio of SiO_2/Al_2O_3 ranges from 1 to 2 %, while that percentage rises to 5 % in samples Ka (1,2,3,4,5,6,7) which represent clay layers mixed with the sandstone, this is due to the presence of large amount of quartz in those samples. The study of different Kfer Yabous clays indicates that the clay lenses mixed with sandstone (Ka) are richer in silica with a lower content of Al_2O_3. Flux elements such as (Fe_2O_3, MgO, K_2O and Na_2O) have a considerable effect on the thermal behavior and properties of the final ceramic products (Fig.3). In general, KferYabous clays are characterized by high iron content and low carbonate content, as well as high silica oxide content. According to [4] data, it is possible to classify KferYabous clays as red firing low plasticity raw materials without carbonates. L.O.I probably, partially is due to the quantities of organic matter, carbon dioxide and sulphur which are clearly present in the studied site (Fig.2) and this is confirmed also in DTA analysis. Loss on ignition (L.O.I) was measured by calcination of micronized and dried powders at 1000 °C.

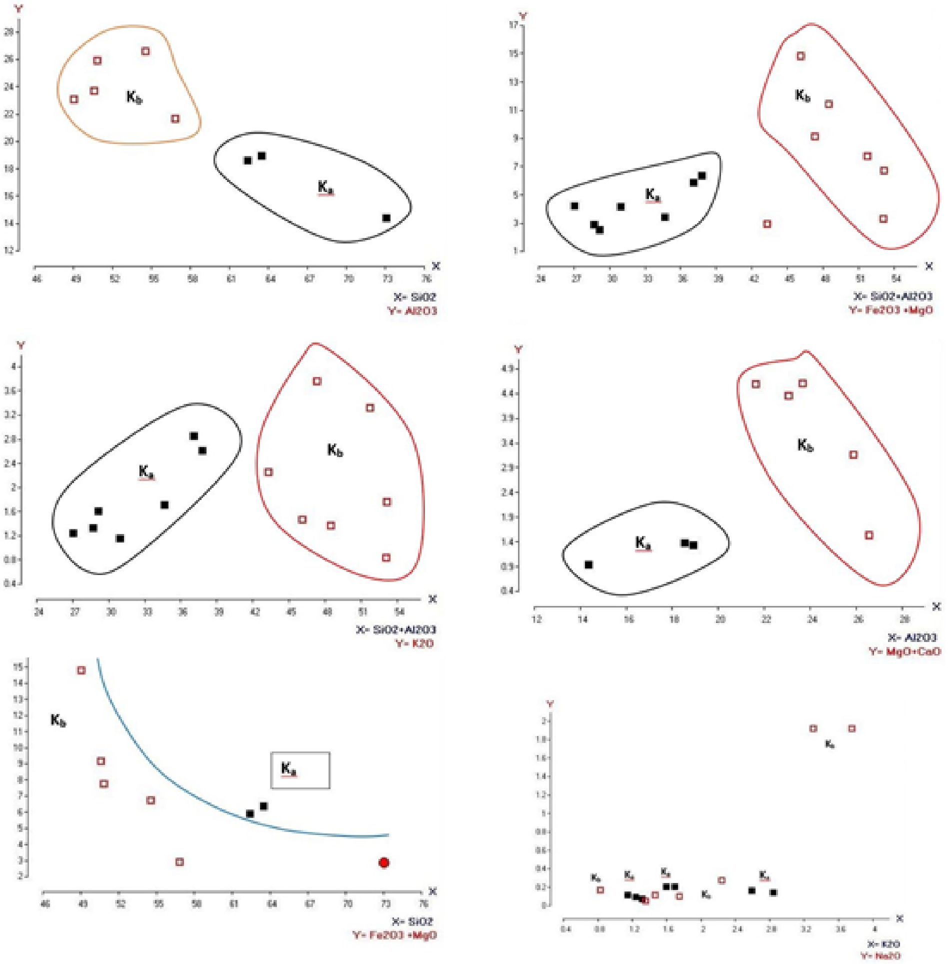


Figure 3: Variation in the chemical composition of the major oxides (wt.%).

Kfer Yabous clay: (K_a) Samples of clay lenses mixed with sandstone. (K_b) Samples of kaolinite formation.

X-ray diffraction (XRD) analysis XRD analyses showed that the Kfer Yabous clays are composed by kaolinite, mica/illite, and quartz. However,

- considering the diffractogram and the intensity peaks, free quartz is present in all the samples and it varies between 70 % in K_a and 20 % in K_b (Fig. 4).

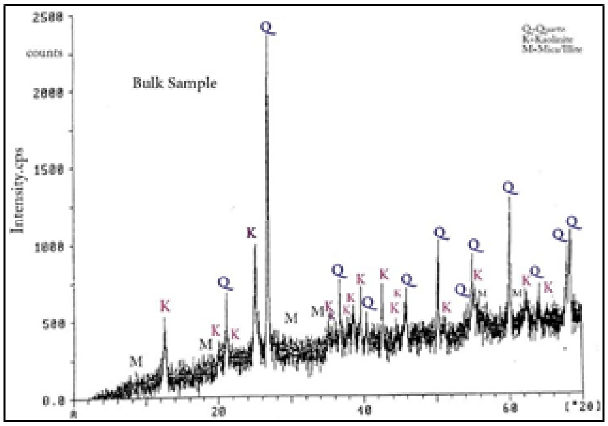


Figure 4: X-Ray Diffraction of the Bulk Sample from lower Cretaceous clay in the western part of Damascus-Syria, Kfer Yabous.

• *Thermal methods (TG, DSC, and DTA)*

These techniques have identified the presence of Kaolinite and Muscovite/ Illite clayey phases. Also, the non-plastics phase, Quartz, is present. A linear heating rate of 12°C per minute and 100 percent sensitivity were used to test quartz with curves for the minerals obtained at 50 percent of maximum sensitivity. The gradual slope from 200 to 450°C is indicative of organic materials with sharper section of the curve at 437°C (Fig.5a) representing pyrite FeS_2 [5].

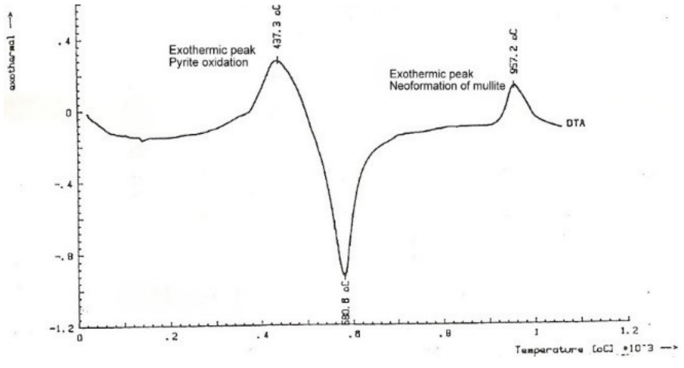


Figure 5(a) : DTA curve of Kfer Yabous Clay

The presence of quartz is shown in DSC (Fig.4b &c) curves by the small endothermic reaction at 573°C which corresponds to the structural transition of trigonal (α)quartz to hexagonal(β) quartz. Many investigators have recorded the endothermic reaction of kaolinite at 450-700°C and strong exothermic peak at 980 to1000°C, as visible in DTA test of Kfer Yabous Clay.

The endothermic peak accompanies the dehydration of the mineral according to [6], and the exothermic reaction is associated with the formation of Y-AI_2O_3. Dehydration curves published by [7] indicate that the initiation of the dehydration reaction of kaolinite occurs at an even lower temperature (at about 380°C) (as we can see in Fig.5b, c).

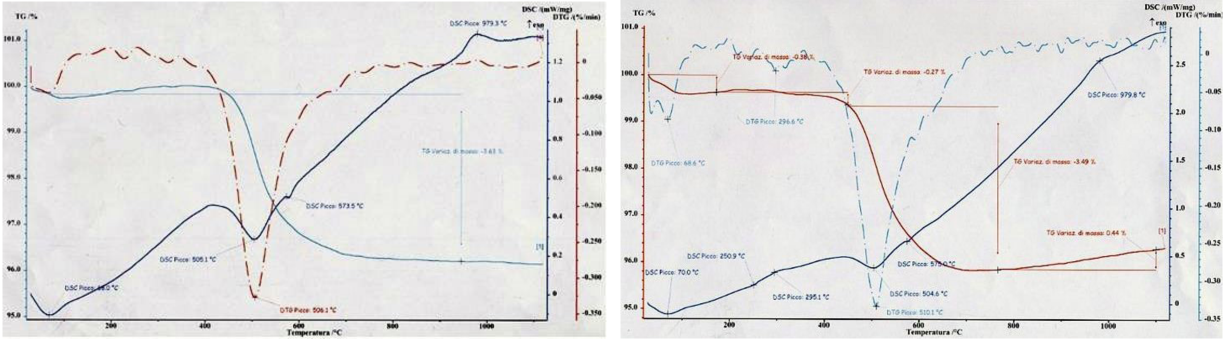


Figure 5 (b,c): TG.DSC,DTG curves of Kfer Yabous Clay

Thermogravimetric analysis, TG curve (Fig.5b&c) shows slight 0.27 % weight decrease until 450°C probably due to water evaporation. From 450°C to around 600°C, TG curve show also weight loss as result of dehydration of structured water. Usually the size of DSC peak is small, [8] explained this state by the presence of organic matter which replaces some of the adsorbed water in clay minerals. The presence of organic molecules on the clay surface makes it hydrophobic, so, the peak of the maximum appears at lower temperature [9].

Ceramic testing

With dried and ground powder of clay material tiles with size of 50x100 mm were prepared and pressed at 300 kg/cm². The resulting samples were fired in laboratory muffle kiln with cycle of 5 hours at the temperature of 1180°C. For correct rheological parameters with viscosity at 2,5°E it was necessary to add 0,3% of sodium trypoliphosphate and reaching a density of 1500 g/l.

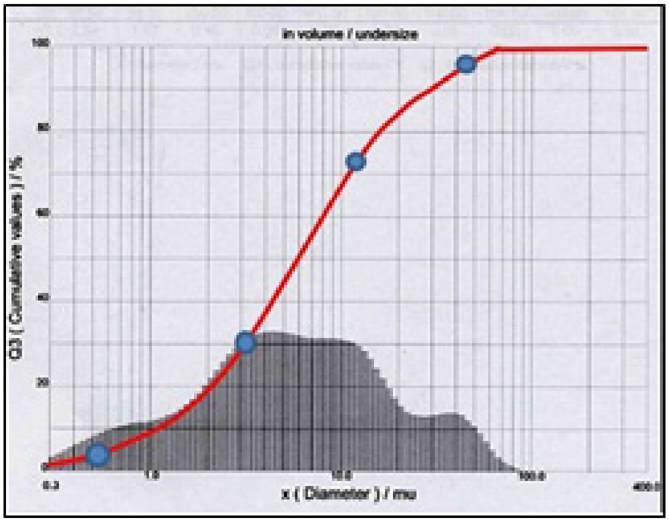


Figure 6: Grain Size Distribution of Representative Clay Samples of Kfer Yabous.

Particle size distribution of studied clay samples was a key factor in determining its potential applications as clay products, particularly clay fraction [10, 11].

Granulometric analysis indicated in Fig. 6, show for 80% of cumulative value under diameter of 20 µm. Particle size distribution can classify Kfer Yabous samples as silty clay and usable for ceramic products.

Kfer Yabous clay presents medium low bending strength values (about 22,5 Kg/cm2) after drying. Firing behavior at 1120°C clay shows water absorption percentage closer to 13 %, after that the value decreases only to 10 % at 1180°C (Fig.7a). (The) Firing results indicate that this clay presents during firing a refractory behavior, shrinkage values do not change very much from 1120 to 1180°C (Fig.7b) and in the same way between 1120 and 1180°C water absorption values decreases by 2 % (Fig.7c) as can be seen in Table 2. The bending strength of this clay after firing is always low, because the highest value is closer to 250 kg/cm² at 1180°C.

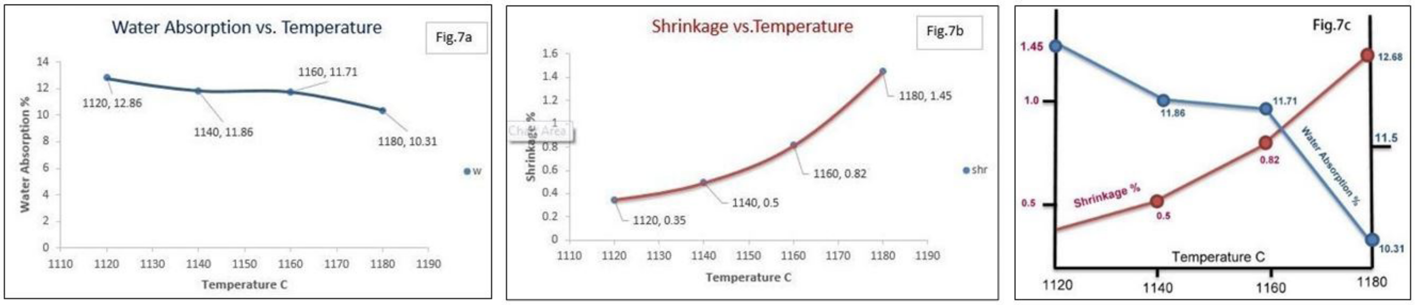


Figure 7: Fired Shrinkage and Water Absorption at Different Temperatures of Kfer Yabous clay.

The **coefficient of thermal expansion** (CTE) is an important parameter in choosing the proper glaze for a ceramic material. If the CTE of the glaze is higher than the one of the ceramic body, it will cause tension in the ceramic tile during cooling and it can cause a network of cracks and a weaker finished product. The coefficient thermal expansion of Kfer Yabous clay at 1140°C is 2,137 x 10 -5, it was measured using Orton Dilatometer which records reversible and irreversible changes in length (expansion and shrinkage) during heating and cooling.

Color Iron oxide presence is responsible for the orange-hazel color after firing [12]. The yellow to brown color indicating the presence of organic material [13]. Based on the chemical composition Kfer Yabous clays can be classified as Illite-chlorite clays [14]. (Fig.8).

Table 2: Characteristics of unfired and fired tiles of Kfer Yabous clay

Characteristics of the unfired semi-finished material		
Specific pressure of Moulding	Kg/cm^2	300
Powder Moisture	%	5.80
Die Dimensions	mm	100X50
Pressed Thickness	mm	6.86
Dimension of pressed tile	mm	100.28
Expansion after pressing	%	0.28
Green bending strength	Kg/cm^2	13.3
Dimension of dry tile	mm	100.00
Dried bending strength	Kg/cm^2	22.5
Drying shrinkage	%	0.27

Characteristics of the fired material Laboratory Electric kiln					
Temperature/Cycle	°C/min	1120/80	1140/80	1160/80	1180/80
Shrinkage after firing	Kg/cm^2	0.35	0.50	0.82	1.45
Water absorption	%	12.68	11.86	11.72	10.31
Fired bending strength	Kg/cm^2	142.2	184.5	195.6	247.8
Black core	no				
Color after firing from light brown - brown					
Thermal expansion coefficient 213.77 x 10-7 /°C. at 1140 °C					

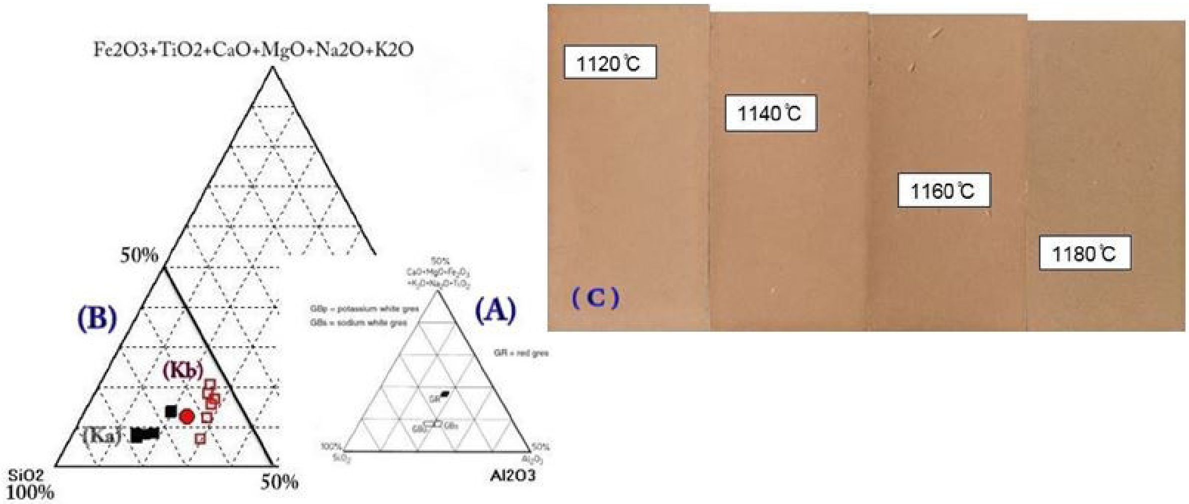


Figure 8: SiO_2 / Al_2O_3 / TiO_2+ Fe_2O_3+MgO+CaO+Na_2O+K_2O Tertiary Diagram Showing Composition Fields of Red Gres Clays:

(A) (Data from Fabbri and Fiori, 1985) [14].
(B): Kfer Yabous clay:(Ka) clay lenses mixed with sandstone. (Kb) Samples kaolinite formation.
(C): Kfer Yabous Ceramic bodies fired at different temperatures.

Conclusion

The results of Mineralogical and chemical studies made on of Kfer Yabous clay samples allow to classify them as red low plastic clays, composed of Kaolinite, Mica-Illite, Quartz. Technological tests carried out on pressed tiles indicate that at firing temperature of 1120 -1180°C was they can reach a shrinkage between 0.35 to 1.45 % and water absorption of 12.68-10.31 %. Furthermore, the studied clays showed rapid drying with satisfactory firing shrinkage in line with typical standards. In conclusion, the deposits of the Kfer Yabous clays, from the western part of Syria, showed the required specifications and satisfactory technological behaviour that would allow their use as raw materials for the preparation of good quality ceramic tiles [15].

References

1. Dubertret L (1949) Carte géologique au 50.000, feuille de Zebdani et noti xplicative. République syrienne, Ministère de travaux publiques.
2. Ponikarov V P, et al., (1966) The Geological map of Syria, scale 1/1000 000 and explanatory notes.111.
3. Ponikarov V P, et al., (1967) The Geological map of Syria, scale 1/500000 and explanatory notes.229 p.
4. Dondi M, Bertolotti G P, (2021) Basic Guidelines for Prospecting and Technological Assessment of Clays for the Ceramic Industry, Part 1, Research and Development, Raw Materials, Interceram 4, 70: 36-46.
5. Földvári M (2011) Handbook of thermogravimetric system of minerals and its use in geological practice, Occasional Papers of the Geological Institute of Hungary, volume: 213: 180.
6. Ewell R H, Insley H (1935) Hydrothermal synthesis of kaolinite, dickite, beidellite, and nontronite: Jour. Research, U. S.Bur. Statistics, 15: 173-186.
7. Nutting P G (1943) Some standard thermal dehydration curves of minerals. U.S. Geol. Survey. Prof Paper 197E: 197-217.
8. Yariv S (1991) Differential thermal analysis (DTA) of organo-clay complexes. In: Smykatz- Kloss W, Warne SSJ, editors. Lecture notes in earth sciences 38. Thermal analysis in the geosciences. Berlin: Springer; 328-351.
9. Labus M (2017) Thermal methods implementation in analysis of fine-grained rocks • containing organic matter. J Therm Anal Calorim, 129: 965-973.
10. Mahmoudi S, Srasra E, Zargouni F (2008a) Characterization of Valangenian–Hauterivian clays of northwestern Tunisia for ceramic. Arab J Sci Eng 33: 229-243.
11. Venkatramanan S, Ramkumar T, Anithamary I (2011) Distribution of grain size, clay mineralogy and organic matter of surface sediments from Tirumalairajanar Estuary, Tamilnadu, east coast of India. Arab J Geosci 5: 1371-1380.
12. Bertolotti G P (2014) How to evaluate a raw material for a tile body composition? The Persian magazine Articles News Innovations in Ceramic & Tile industry.
13. Ceramic Engineering& Science Proceedings, January-February (1994) A Collection of Papers Presented at the 95th Annual Meeting and the1993 Fall Meeting of the Materials & Equipment and White Wares Divisions, Russell Wood, Proceedings Committee April 19-21, 1993, Cincinnati, OH and September 12-1 5,1993, Huron, OH,468.
14. Fabbri B, Fiori C (1985) Clays and complementary raw materials for stoneware tiles. Mineral. Petrogr. Acta 535-545.
15. Mahmoudi S, Srasra E, Zargouni F (2008b) The use of Tunisian Barremian clay in the traditional ceramic industry: optimization of ceramic properties. Appl Clay Sci 42: 125-129.

Copyright: *©2022 Abdulsalam Turkmani. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.*