Evaluation of Oligocene-Miocene clay from northern part of Palmyra region (Syria) for industrial ceramic applications

Abdulsalam Turkmani* **Muhammed Khaled Yazbek*** *

Abstract

Clay of the northern Palmyra region is one of the most important raw material used in Syrian ceramics industry. This study is focused on the evaluation of various laboratory analyses such as: chemical analysis (XRF), mineral X-ray diffraction analysis (XRD), differential thermal analysis (DTA), and semi-industrial tests carried out on samples collected on two representative locations of the upper Oligocene in AlMkamen valley (**MK**) and lower Miocene in AlZukara valley (**ZR**) of northern part of Palmyra, Syria. Chemical results classify the (MK) and (ZR) clays as semi-plastic red clay slightly carbonate and (eliminate probable) illite-chlorite clays with a very fine particle size distribution. Content of SiO_2 between 46.28-57.66%, Al_2O_3 13.81-25.2%, Fe_2O_3 3.47-11.58%, CaO 1.15-7.19%, Na_2O+K_2O varied between 3.34-3.71%. Based on clay chemical composition and iron and carbonate content, these deposits can be considered as red firing clays. Their mineralogical composition is mainly represented by illite, kaolinite and quartz, and accessories minerals such as calcite, feldspar, phillipsite and goethite. The results of the DTA test confirm the presence of gypsum and quartz phases in (MK) clay. Ceramic testing shows good green and dry bending strength values which varied between 9-14 kg/cm², at 1160°C to 1180°C. Water absorption moves from 14.6 % at 1120°C to 2.2% at 1180°C to 1.6% at 1200°C. Breaking load after firing changes from 400 to 590 kg/cm². At 1200°C (MK) clay reaches a perfect vitrification. After firing, color of clay changes from orange-hazel to red brown at 1180°C. Technological results confirm the suitability of the studied clays to produce floor and wall ceramic tiles. Using one of the two types of clay into ceramic body, or both types together, gave satisfactory industrial results.

Key Words: Ceramic – Clay – Industry – Palmyra

Corresponding authors
*Geo Mining L.L.C, Geological Studies and Consulting, Damascus, Syria.
E-mail address: abdulsalam.turkmani@gmail.com
** Geological Dept. Faculty of Science –Al Baath University- Syria.
E-mail address: mkhyzbek68@gmail.com

تقييم غضاريات الأوليغوسين- الميوسين من الجزء الشمالي من منطقة تدمر (سوريا) لتطبيقات صناعة السيراميك

عبد السلام تركماني * محمد خالد يزبك**

الخلاصة

تعتبر غضاريات منطقة شمال تدمر من أهم المواد الخام المستخدمة في صناعة السيراميك السوري. تركز هذه الدراسة على تقييم تلك الغضاريات بناء" على مجموعة كبيرة من الدراسات الحقلية والمخبرية والتي تشمل تحليل حيود الأشعة السينية (XRD) والتحاليل الكيميائية (XRF) والتحليل الحراري التفاضلي (DTA,TG) وكذلك الاختبارات نصف الصناعية. لقد أجريت التحاليل على العينات التي تم جمعها من موقعين اثنين ممثلين لعمري الأوليغوسين والميوسين في الجزء الشمالي من تدمر. حيث يمثل وادي الذكارة غضاريات أسفل الميوسين ، وتمثل غضاريات وادي المكمين الأوليغوسين الأعلى. دلت التحاليل المختلفة على أن الغضاريات المدروسة تصنف على أنها غضاريات حمراء شبه لدنة، الى لدنة، ذات محتوى قليل من كربونات الكالسيوم، كلوريتيه- ايلليتة التركيب، تتصف بتوزع دقيق جدًا لحجم الحبات. بناءً على التركيب الكيميائي للغضاريات ومحتوى الحديد والكربونات، يمكن اعتبار هذه الرواسب بمثابة غضاريات حمراء، محتوى أوكسيد السيليسيوم يتراوح ما بين 46.28-57.66٪، أوكسيد الألمنيوم13.81 - 25.2٪، أكاسيد الحديد 3.47-11.5٪، أوكسيد الكالسيوم 1.15-7.19٪، مجموع القلويات تتراوح بين 3.34-3.71٪. أما التركيب الفلزي فهو مؤلف بشكل أساسي من الكاولينيت والإيليت والكوارتز وملحقاتها من فلزات الكالسيت والفلسبار والفيليبسيت والغوتيت. تؤكد نتائج اختبار التحليل الحراري التفاضلي وجود أطوار الجبس والكوارتز في غضاريات وادي المكمين. بينت الاختبارات نصف الصناعية أن بلاطات السيراميك الممثلة لتلك الغضاريات ذات قيم جيدة لمقاومة الكسرالأخضر والجاف والتي تراوحت بين 9-14 كغ / سم^2 ، عند 1160 درجة مئوية إلى 1180 درجة مئوية. ينتقل امتصاص الماء من 14.6٪ عند 1120 درجة مئوية إلى 2.2٪ عند 1180 درجة مئوية إلى 1.6٪ عند 1200 درجة مئوية. تتغير مقاومة الكسر بعد الحرق من 400 إلى 590 كجم / سم^2 ، يصل الغضار إلى درجة التزجج المثالية عند 1200 درجة مئوية. بعد الحرق ، يتغير لون الغضار من اللون البرتقالي البندقي إلى الأحمر البني عند 1180 درجة مئوية. تؤكد النتائج التكنولوجية ملاءمة الغضاريات المدروسة لإنتاج بلاط السيراميك للأرضيات والجدران. وذلك باستخدام أحد نوعي الغضار في جسم بلاطة السيراميك، أو كلا النوعين معًا، ليعطي نتائج صناعية عالية الكفاءة.

الكلمات المفتاحية: سيراميك - غضار - صناعة - تدمر

* Geo Mining L.L.C, Geological Studies and Consulting, Damascus, Syria
E-mail address: abdulsalam.turkmani@gmail.com
** قسم الجيولوجيا - كلية العلوم - جامعة البعث
E-mail address: mkhyzbek68@gmail.com

1. Introduction

Syria is one of the most ancient civilizations in the world; its history has been known from **clay** tablets used in writing treaties and agreements signed by the Syrian kingdoms, especially the library of the Ebla Kingdom. Ceramics is defined (Wilson 1935; Ries1927; Committee on Definition of the Term "Ceramics," 1920; Norton, 1952) as *"the arts and sciences of making products and articles mainly or totally from "earthy" nonmetallic raw materials excepting fuels and ores of metals with high temperature treatment"*. Clay technology in ceramic field, therefore, includes evaluation of their technological characteristics at room-temperature and their behavior at high temperatures.

Syrian clays are considered as raw materials suitable for various industrial purposes, as in the ceramic and brick industry (Qatma, 1999), in the manufactures of drilling fluids, and some of them in the cement industry (Ponikarov et al., 1964).

Clay deposits in Syria are present in different geological ages, from the upper Triassic period to Quaternary age.

This article is focused on AlMkamen valley (**MK**) clay of Upper Oligocene and clay deposits of AlZukara valley (**ZR**) in the Lower Miocene of Palmyra area. These two sites represent great importance sources for the Syrian ceramic industry.

2. Geological Setting

Most important clay deposits are found in the northern part of the Al-Daw basin (Palmyra chain) (Fig. 1), they belong to the upper Oligocene and lower Miocene. The Oligocene rocks are extremely different and very variable in composition, in some localities they are terrigenous and clay-carbonate (sandstone, clay, marl, limestone) in the others – calcareous reefoidal rocks with algal and coral structures. This complex formation consisting mainly of shallow-water sediments, algal-coral reef limestone, marl, carbonate and noncarbonated clay, sand and sandstone. Vertically and laterally the rocks are rapidly replaced by one type to another (Ponikarov et al.,1967)

Sediments of Neogene are represented by continental deposits, in contrast to the marine deposits of the Paleogene and Cretaceous. The tectonic movements that occurred during Neogene period led to the activation of erosion, weathering, and transportation and sedimentation of the products to valleys that were filled with mixed deposits. They consist of alternations of red clay, sandy clay, green silty marl, limestone, flint and conglomerate.

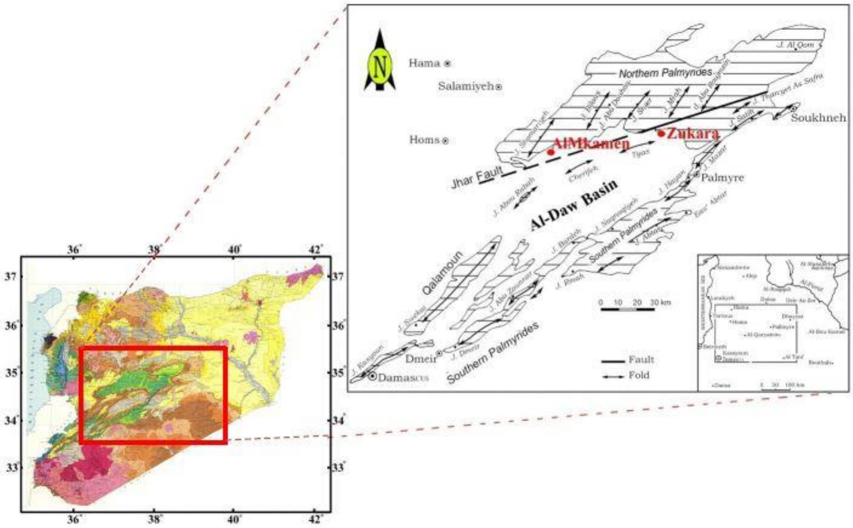

Figure 1: Syrian Map 1:1000000 show the studied area in Palmyra chain, includes the upper Oligocene clay of AlMkamen valley; and the lower Miocene clay in AlZukara valley; Ponikarov et al., 1964.

2.1 Upper Oligocene Clay AlMkamen valley (MK)

Clays of the Upper Oligocene known in the Palmyrides have greenish and bluish color, slightly carbonate, with a small silt portion. The clay in northern Palmyrides Mountain (Fig.1) is 29 m thick composed of 2 or 3 m beds alternating with marls, quartz sandstones and ferruginous siltstones. The upper formation contains grey, generally noncarbonated clays with thickness about 50 m.

Upper Oligocene clay deposits occur in this site on the edge of the geological basin with north-east and south-west 220° direction, and they are divided in two sections:

Lower section: It's composed of gray-greenish clay bearing gypsum, with clayey limestone and limestone. The thickness of the lower section is about 30 m.

Upper section: it's composed of interbedded white -yellowish limestone, gray-greenish clay bearing gypsum, yellow marl, gray-greenish clay bearing gypsum, yellow clay with sand, yellow sand and sandstone with sandy clay, grey clay with green, bluish and brownish shades. Thin intercalations of feldspar-quartz siltstone and yellow sandstone are also present in this section. Total thickness of the upper part is 60 m and the thicknesses of the clay layer suitable for ceramic production is about 11 meters, as shown in (Fig. 2).

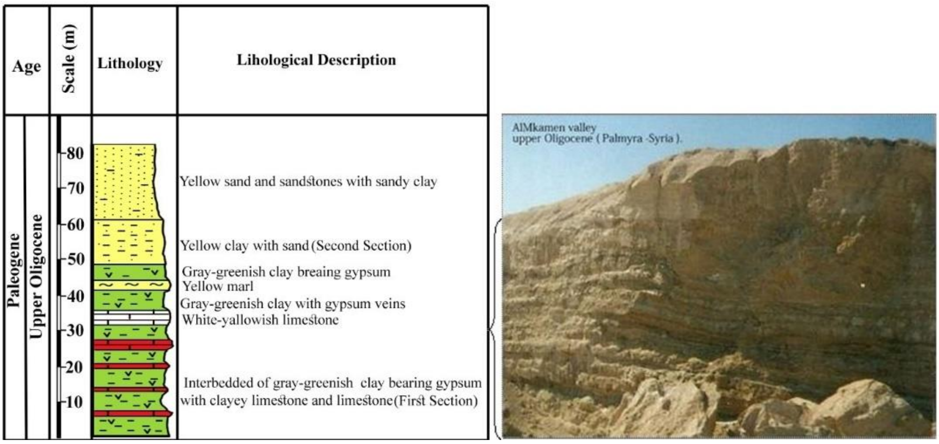

*Figure 2: Stratigraphical description of the upper Oligocene clay (**MK**)*

1.1 Miocene clay Al Zukara valley (ZR)

Lower Miocene continental rocks are known along the sides of the Al-Daw basin (Fig. 1). They have a different lithological composition with sharp changes of facies (Ponikarov *et al*., 1967). Brownish sandy clay or white sandstone (occasionally conglomerates) lies at the base of the sequence with evident traces of erosion. Upwards comes an alternation of sandstone and limestone beds. The thickness of red clays becomes maximum at the foots of the slopes 20 or 30 m, towards high hills where clay material is replaced by gravels. Clay had probably been formed as a result of basalt and carbonate rock laterization. Al Zukara valley is located 20 km on the western side of Palmyra city. The lower Miocene clay deposits in Al Zukara valley extend 15 km from north to south, and it is characterized by a lateral change from clay to sandy clay. The total layer thickness reaches 44 m, and the thickness of clay layers is about 15 m (Fig. 3).

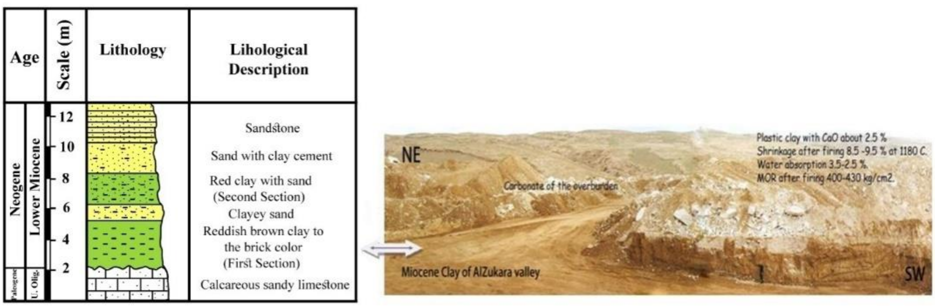

*Figure 3: Stratigraphical description of the lower Miocene clay (**ZR**)*

3. Analyses methods

50 representative samples from two locations (**MK**) and (**ZR**) studied and analyzed using XRD, XRF, and DTA in the laboratories of General Establishment of Geology and Minerals Resources, followed by semi-industrial analyzes were carried out at the Masa Ceramic Manufacture Laboratory in Syria.

Sample preparation All the samples were dried for a 24 h in laboratory drier at temperature of 110 °C. *Removing Carbonates before clay Separation by Hydrochloric Acid Treatment followed by clay separation method.*

3.1 Chemical Analysis using *Sequential ART 8410 X-Ray Fluorescence Spectrometer instrument,* Chemical analysis were made mixing 10 g of micronized powder with Spectromelt A-B which consist of di-lithium tertaborate $Li_2 B_4 O_7$, lithum borate Li BO_2, lanthanum oxide in the following proportions: (15: 29: 56). The mixtures were dosed in a mould of an oleodynamic press adding a specific pressure of 2000 kg/cm² to produce round samples. This analysis allows the determination of the following main oxides present in raw materials: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, MnO, Na_2O, K_2O. 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) .

3.2 Mineralogical analysis X-ray diffraction (XRD) analysis was performed using an automated (*Philips type: PW1840*) diffractometer equipment with Cu Ka 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°.

3.3 DTA&TG analysis the DTA/TG analysis was made with (DTG-60H SHIMADZU) simultaneous thermal analyzer.

3.4 Physical-ceramic properties They have been determined on small tiles (50x100 mm) produced with a laboratory press. Method for preparing the tile powder was the following:

- wet grinding of the material in a laboratory jar until reaching a maximum residue of 2-4 % over 0.063 mm span sieve (230 meshes)
- sieving of the slip on a 0.180 mm span sieve (80 meshes)
- drying of the suspension in an oven at 110 °C temperature
- Fragmentation and pulverization of the dry material in a laboratory hammer mill.
- wetting of the powder up to 5-6 % water and screening in a 0.6 mm mesh span sieve (30 meshes)
- Pressing of the powder in a laboratory hydraulic press.

4. Discussion and results

4.1 Chemical composition of the deposits clay in (MK) and (ZR)

Table.1 shows the chemical composition of (**MK**) clays. The major oxides of the first level are characterized by silica content variable between 46.91-51.11%, Al_2O_3 18.70-19.44% and CaO 4.63-6.99%. Clay of (**MK**) upper level of show an increase of sand content with silica between 54.02-66.12% and $Al_2O_3$13.81-21.47%. Al_2O_3 content between 13.8 to 21.47% indicates the presence of clay minerals of kaolinite group which increases refractory grade of these clays. Contents of the other oxides are: CaO 1.15-6.99%, MgO1.17-1.76%, Fe_2O_3 3.47-9.17 %, Na_2O+ K_2O about 0.7%. High L.O.I. values can be probably explained for the decarbonation and dehydration reaction of gypsum as evident in DTA analysis.

Table 1 Chemical analysis of upper Oligocene clays (**MK**)

Sample-ID	SiO_2 %	TiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	MnO %	Na_2O %	K_2O %	L.O.I. %
Mk1	49.78	0.89	18.31	4.74	6.99	1.17	0	0.35	3.12	12.26
Mk2	46.91	1.03	18.7	4.83	6.38	1.7	0.1	0.48	3.14	16.15
Mk3	49.91	0.98	19.5	4.64	4.23	1.6	1	0.38	3.3	14.5
Mk4	51.11	0.96	19.44	4.85	4.63	1.76	0.06	0.5	2.2	14.49
Mk5	55.71	1.16	21.47	3.47	1.15	1.54	0.1	1.07	3.5	10.42
Mk6	54.02	0.87	19.22	5.33	2.19	1.29	0	0.4	3.64	13.5
Mk7	60.66	0.49	13.81	9.17	2.04	1.28	0	0.89	2.69	9.69
Mk8	66.12	0.87	14.17	5.33	2.19	1.29	0	0.4	3.64	5.99
MK	54.27	0.90	18.07	5.29	3.72	1.45	0.15	0.55	3.15	12.12

Mk1 - Mk3: Lower section of (MK) clay, Mk4 - Mk8: Upper section of (MK) clay, MK: Average content of (MK) clay.

Chemical analysis of AlZukara clay (**ZR**) in Table.2 show that SiO_2 content varied between 47.18% in the lower section to 56.23 % in the upper section, Al_2O_3 content ranging from 25.20% to17.57% in the second section. High iron content is observed 5.26 % to 11.58 %. L.O.I. varied between 10.5 % to 15.82%. More refractory clay samples show higher percentage of L.O.I. Based on the chemical composition of the studied clays, they can be classified as Illite-chlorite clays nature (as indicated in Fabbri & Fiori, 1985). Iron oxide content, is the main chromophore agent in the clays and it's responsible of their reddish color after firing (Abajo

Manual sobre Fabricacio´n de Baldosas MF, 2000) and (Bertolotti, 2014). According to (Dondi et al., 2014) data, red clays include every iron-rich clay material with Fe_2O_3 over 3%, carbonates below 10%, so these clays can be classified as red clays (Fig. 4).

Table 2 Chemical analysis of lower Miocene clay (**ZR**)

Sample-ID	SiO_2 %	TiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	MnO %	Na_2O %	K_2O %	L.O.I. %
Zr 1	47.96	0.57	22.6	11.58	1.12	0.71	0.1	1.84	2.22	12.14
Zr 2	46.28	0.92	21.11	9.5	1.73	1.65	0.1	0.2	2.88	15.82
Zr 3	47.18	0.89	22.41	9.14	3.53	2.1	0.1	0.85	3.03	11
Zr 4	47.47	0.91	20.42	7.29	7.19	1.47	0	0.18	3	12.5
Zr 5	48.39	0.71	24.57	9.18	2.81	2.01	0	0.39	2.45	10.34
Zr 6	48.28	0.62	25.2	9.5	2.2	2.27	0.01	0.51	2.28	10.05
Zr 7	52.45	0.26	22.51	5.26	3.05	2.02	0	0.81	2.8	10.62
Zr 8	56.23	0.94	17.57	7.39	2.9	0.58	0	0.27	3.65	10.5
Zr9	57.58	0.75	17.65	4.79	3.13	2.02	0.1	0.44	2.64	10.89

Zr1-Zr6: Lower section of (ZR) clay, Zr7-Zr9: Upper section of Al (ZR) clay, ZR: Average content of (ZR) clay.

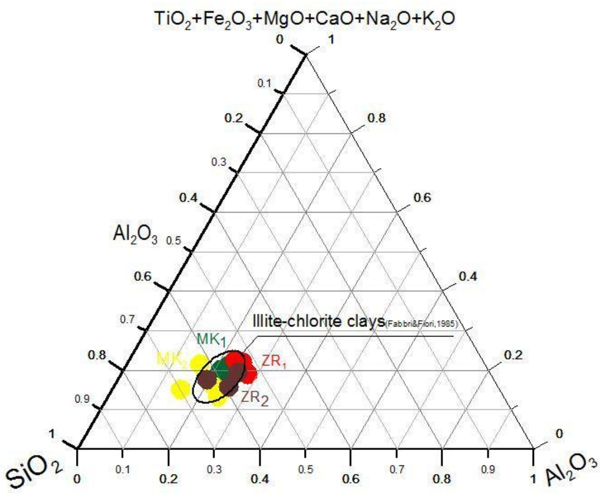

Figure: 4A
SiO_2 / Al_2O_3 / TiO_2+ Fe_2O_3+MgO+CaO+Na_2O+K_2O
tertiary diagram showing composition fields of red gres clays (Fabbri&Fiori, 1985)

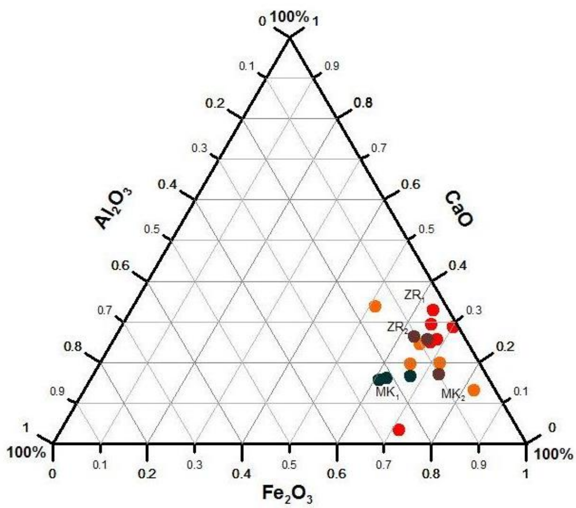

Figure: 4B
Fe_2O_3 /Al_2O_3 /TiO_2
Diagram it shows high iron content and low carbonates contents in the lower section of Zukara clay (Zr1, 2, 3, 4). $CaCO_3$ content increases in the upper part of Mkamen clay (Mk1, Mk2) due to contaminated by limestone.

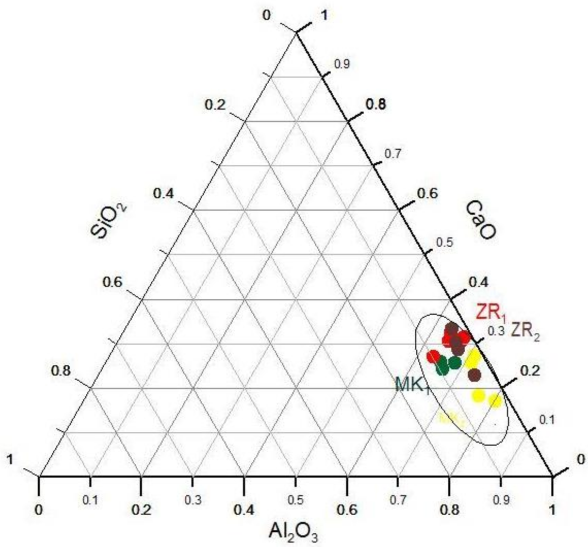

Figure: 4C
Al_2O_3/ Fe_2O_3 / CaO
Diagram shows the similar chemical composition of (ZR) and (MK) clays, with an increasing Al_2O_3 and decreasing SiO_2 content in (ZR) clay. SiO_2 content is higher in the upper section of (MK5) clay due to the predominant presence of the sandy clay.

*Figure: 4D Color of the Palmyra clay after firing at different temperatures. Lower Miocene (**ZR**) and Upper Oligocene (**MK**).*

4.2 XRD analysis

By measuring the intensity of the diffraction lines and comparing them with the standards, it turns out that the mineral composition of Miocene clay in Al Zukara valley indicated in Table (3) has the following composition: kaolinite is predominated in first section with quartz, while calcite and other minerals such as illite, goethite and phillipsite are present in lower percentage. On the contrary calcite, quartz and secondary minerals are present in higher proportion in the second level clays with appearance of illite, K-feldspar and montmorillonite. Upper Oligocene clay of (MK) mainly including illite, kaolinite, calcite and feldspar (Fig.5).

Table 3: Mineralogical composition of Oligocene-Miocene Palmyra clay

Location	Kaolinite	Illite	Quartz	Calcite	Feldspar	Montmorillonite	Goethite	Phillipsite	Sum
Lower section (ZR)	46	20	25	5	0	1	2	1	100
Upper section (ZR)	38	15	25	18	2	1	0	1	100
Lower section (MK)	13	48	29	7	3	0	0	0	100
Upper section (MK)	11	45	33	8	3	0	0	0	100

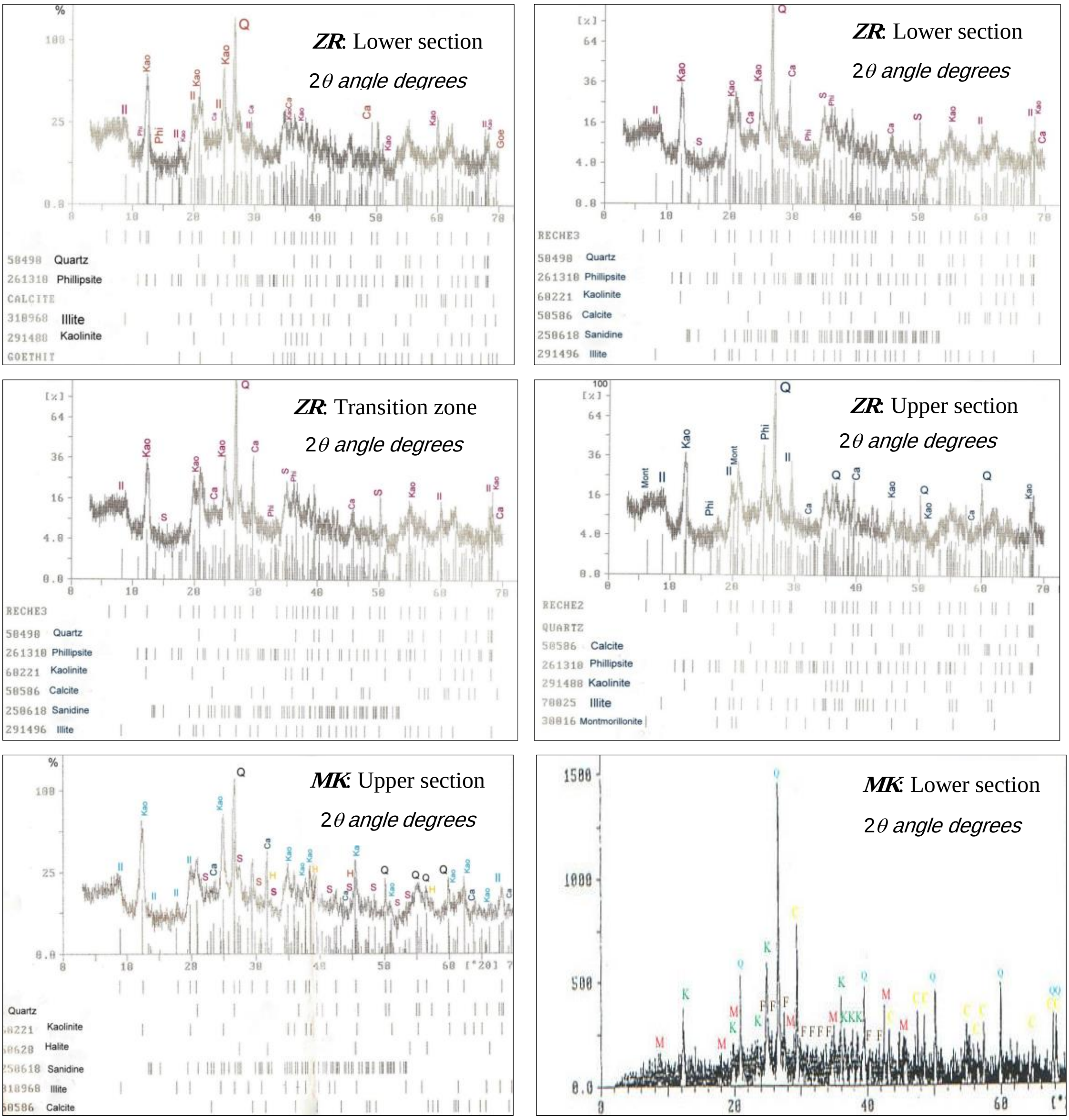

*Figure 5: X-Ray Diffraction of the upper Oligocene (**MK**) and lower Miocene (**ZR**) clay.*

4.3 DTA& TG analysis

Differential thermal analysis (DTA) made on upper Oligocene (**MK**) and lower Miocene clay (**ZR**) show similar patterns except some minor variations. In all the diagrams are present two kaolinite peaks due to a strong endothermic curve at 550°C to 600°C and a strong exothermic peak between 900°C to 1000°C. The first one corresponding to kaolinite and illite dehydration reaction and formation of meta-kaolinite, follow by exothermic peak due to mullite and/ or Al_2O_3 crystallization. (Fig. 6A). According to Carthew (1955), the amplitude of the endothermic peak at 600°C is practically proportional to kaolinite weight and increases with particle size and decreases with kaolinite crystallinity degree. Speil (1944) has discovered that the area of the endothermic peak at about 600°C in kaolinite DTA decreases with decreasing particle size of the kaolinite.

Two endothermic peaks present between in AlMkamen clay 120°C to 150°C indicate to dehydration reaction of gypsum. According to Rowland (1955), clays with monovalent cations exhibit one endothermic loop at about 150°C; most clay with divalent cations have a second loop or a shoulder on a loop similar to the monovalent loop at a higher temperature (220°C). (Fig. 6A). Miocene clay samples from AlZukara valley show strong endothermic peak at approximately 94°C that represent clay dehydration, and endothermic peak at approximately 311°C not reported in typical kaolinite and illite DTA curves (e.g. Carthew, 1955; Grim and Rowland, 1944). It can be attributed to the occurrence of hydrous iron oxide phase such as goethite dehydroxilation (e.g. Kulp and Trites, 1951). Endothermic curve at 655°C corresponding escape of H_2O of aluminite. The decarbonation reaction of calcite about 781°C was detected in the structure as well as the formation of quasi-amorphous materials (Fig. 6B)

TG analysis: Clays (MK) and (**ZR**) showed a main important loss of weight corresponding of the temperature of clay minerals crystal destruction (500-600°C).

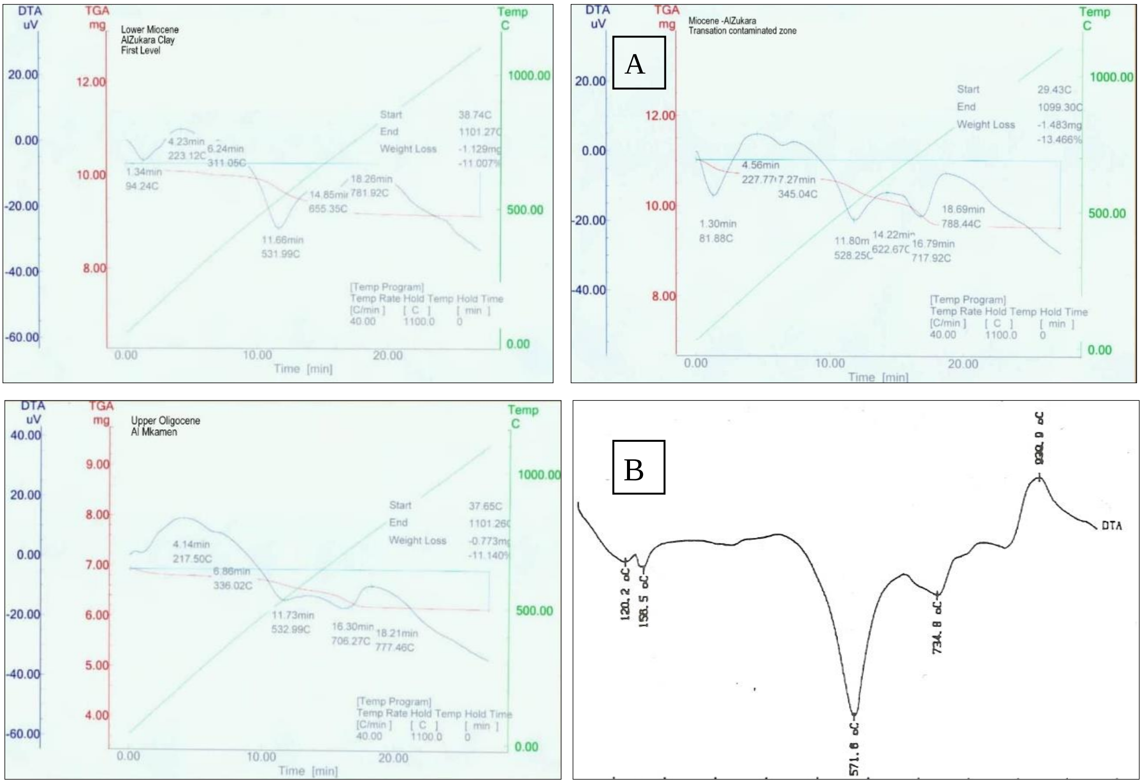

Figure 6. Differential thermal analysis curves (DTA) for two clay samples from the upper Oligocene clay in Makamen valley (A), and lower Miocene clay Zukara valley (B).

(A). Diagrams show two endothermic peaks at 120°Cand 150°C due the dehydration reaction of gypsum and two strong peaks, the first one at 571°C linked to the transformation of the kaolin into metakaolinite with the loss of the interstitial water, and the second exothermal peak at 930°C linked to mullite phase formation.

(B). Diagrams show endothermic peak at approximately 94°C linked to clay dehydration, and endothermic peak at approximately 300°C linked to the dehydroxilation of goethite α-FeOOH α $-Fe_2O_3 \rightarrow H_2O$. *Decarbonation reaction of calcite was detected about 781°C as well as the formation of quasi-amorphous materials.*

4.4 Physical-Chemical properties of upper Oligocene (MK) and lower Miocene (ZR)

Tests have been made "tiles" formed with moulding pressure of 300 kg/sq.cm. On the obtained specimen were determined technological-ceramic characteristics as breaking load before and after firing, shrinkage and water absorption. Semi-industrial tests made in laboratory (Turkmani, 2005, 2009) gave the results indicated in the tables (4 and 5). Obtained results were compared with (La Tecnologia Ceramica,2004*).*

Table 4: Physical properties of upper Oligocene clay (**MK**).

Specification	Temperature °C	Value
"Green" breaking load before drying (kg/cm²)	110	9-14
Breaking load after drying (kg/cm²)	130	22-30
Breaking load after firing (kg/cm²)	1040	165-175
Breaking load after firing (kg/cm²)	1120	225-250
Breaking load after firing (kg/cm²)	1140	270-285
Breaking load after firing (kg/cm²)	1160	410
Breaking load after firing (kg/cm²)	1180	450
Shrinkage (%)	1120	-1.90
Shrinkage (%)	1160	-5.80
Shrinkage (%)	1180	-8.3
Water absorption (%)	1180	2.6
Color after firing	1040 -1180	From yellow- light grey - brown

Table 5: Physical properties of Miocene clay (**ZR**)

Specification	Temperature °C	Value
"Green" breaking load before drying (kg/cm²)	110	10.5-13.50
Breaking load after drying (kg/cm²)	130	24.5-30
Breaking load after firing (kg/cm²)	1040	250-330
Breaking load after firing (kg/cm²)	1120	330-340
Breaking load after firing (kg/cm²)	1140	380-400
Breaking load after firing (kg/cm²)	1160	480
Breaking load after firing (kg/cm²)	1180	500
Shrinkage (%)	1180	-10.8
Water absorption (%)	1180	2.2
Breaking load after firing (kg/cm²)	1200	590
Shrinkage (%)	1200	-11.60
Color after firing	1040 -1200	From red to dark brown

The results of laboratory and semi-industrial experiments on clay were done using a laboratory electric oven, at a temperature of not less than 1040°C, and a maximum temperature of 1200°C, during a 80-minute cycle.

4.5 Summary of the analytical results

1) Chemical results classify AlMkamen valley (**MK**) clay as semi plastic/plastic slightly carbonates red clay showing a very fine particle grain size distribution. Average chemical content of (**MK**) clay is: SiO_2 54.17%, Al_2O_3 17.87%, Fe_2O_3 5.38%, Na_2O+K_2O 3.71%. Mineralogical composition consists mainly of illite, quartz, kaolinite, some carbonates and gypsum. DTA results confirm the presence of gypsum and quartz phases.
2) Green and dried bending strength of AlMkamen clay (9-14 kg/cm²) shows normal to very good values. After firing, the clay shows a refractory behavior, from 1120 to 1160°C, as synthesized in the following diagram. At higher temperatures melting oxides like Fe_2O_3 start working and values water absorption values decrease (from 12.30 to 2.6 %) and shrinkage change quickly (from 1.9 to 9.3 %) (Fig. 7).

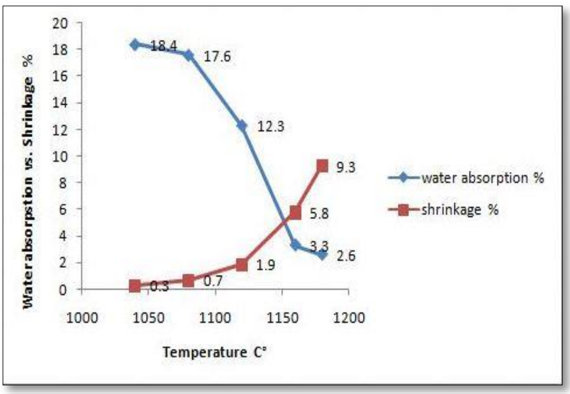

Figure 7: Fired shrinkage and water absorption at different temperatures of upper Oligocine clay –Al Mkamen valley.

3) This change is also determined by higher value of bending strength at 1160°C of 410 kg/cm² to 450kg/cm² at 1180°C. While after firing at 1200 C° the clay (**MK**) over fires. The first section of (**MK**) clay could be considered well for floor tiles, although the presence of gypsum in the clay could cause subsequent problems during the firing process.
4) The clay of the upper section of (**MK**) characterized by medium to low plasticity and medium breaking load 165-250 kg/cm² and it could be suitable for good for wall tiles.

5) AlZukara clay (**ZR**) its fine grain size semi-plastic to plastic clay, with very low residue over 63 µm. It's mainly composed of kaolinite as major plastic phase in association with quartz, calcite and K-feldspar phase.
6) AlZukara clay (**ZR**) (essentially the lower section ZR_1-ZR_6) presents very good bending strength values before drying about 13.50 kg/cm² and medium-high value between 24.20 to 30 kg/cm² after drying. This clay start melting as shown in the (Fig. 8) at 1160°C to 1180°C when the value of water absorption changes from 14.6 % at 1120°C to 2.2% at 1180°C and to 1.6% at 1200°C Breaking load values after firing move from 400 to 480 and to 590 kg/cm² at 1200°C the clay looks perfectly vitrified (Fig. 8).

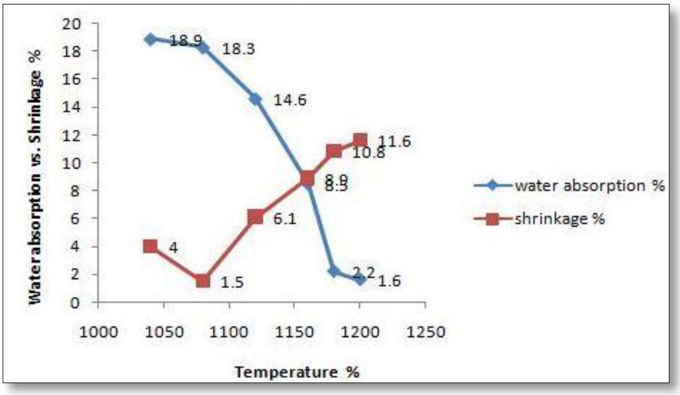

Figure 8: Fired shrinkage and water absorption at different temperatures of lower Miocene clay –Al Zukara valley

7) The results of the thermal and mineralogical analysis show that the first section of Zukara clay (ZR_1-ZR_6) can be considered as a very good clay for floor ceramic tiles and the second section (ZR_7-ZR_8), rich in carbonate and sand it is good to produce wall tiles, which the physical analysis results showing high water absorption reaching 21.5 % and low shrinkage 0.2% and low bending strength 170 kg/cm².

5. Conclusions

The results of the semi-industrial tests indicate that the northern clay of Palmyra region from the upper Oligocene (MK) and the lower Miocene (ZR) are suitable for the production of floor and wall ceramic tiles. However, their industrial importance varies according to their mineral composition and thus their different industrial properties. For example, in our opinion, to increase the mechanical resistance of a tile body composition we can use 3-5% of the lower section of Al Mkamen clay (MK1 to MK3) plus 20 % of the upper part section (MK5-MK6). Zukara clay (ZR) it's very good clay especially the lower section (ZR1 to ZR6) suitable for producing high quality ceramic floor tiles.

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