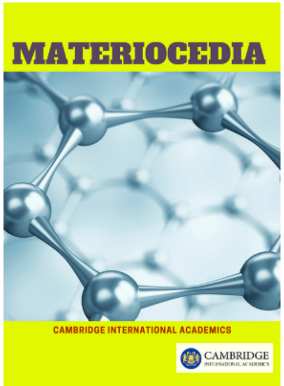

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Analytical study of ancient ceramics from the archaeological site of Aghmat, southern Morocco

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Abstract: This paper explores Aghmat archaeological materials (VII centuries) using two types of ceramics, come from a recent archaeological excavation in (Morocco) in order to enhance documentation, conservation and restoration issues, then putting into value the architectural heritage. Fortuitously discovered in 2005, Aghmat village has allowed the reformulation of several hypotheses about Aghmat population skills in construction and handicrafts. Even though the areal extent of this archaeological site exceeds 20 Km^2, no traces of furnaces have been found yet, only ruins of buildings and streets. Bricks and pottery samples were the most abundant types of ceramics founded. Mineralogical and chemical analyses of this materials provided information about the origin of raw materials and manufacturing process. The chemical compositions indicated that SiO_2, Al_2O_3 and Fe_2O_3 are major elements while K_2O and MgO are less abundant. The ceramics were produced using at least two raw materials, non-calcareous clay of permo-triassic age for bricks, and carbonate quaternary clays for pottery samples, as the calcium oxide content is generally more than 10%.

Keywords: Archaeology, Aghmat ceramics, Pottery, manufacturing process, Morocco

1. Introduction:

Archaeological studies concern the ancient pottery are very rare at a regional level, with the exception of some recent studies that concern mainly Saadian tombs of Marrakech (Casas et al., 2008, Ben Daoud et al., 2013) and the Saadian sugar factory of Chichaoua (Gamrani et al., 2012, Gamrani, 2014). Particularly on the medieval city of Aghmat no previous study was made, known in the ancient texts to have predated the arrival of Islam in Morocco at the beginning of VII centuries. Consequently, the main aim of this study is to define the manufacturing technology of the first pottery productions in the site of Aghmat, by microscopic observations and the identification of mineralogical phases presents in materials extracted from various places of this archaeological site. The manufacturing technology includes the origin and the characteristics of raw clay materials, the maximal temperature and the cooking conditions. This study's results are going to be an essential database for any restoration attempt and conservation vestiges of this abandoned city. For anthropologists and archaeologists interested in material culture, and who use material culture to understand past cultures, our results verifies the ability to reconstruct the history of manufacturing ceramic objects from materials recently explored.

1.1. Geographical location of Aghmat

The Aghmat's medieval site is located in the village of Ghmat (province of El Haouz) in 32 Km southeast of Marrakech city (Fig. 1). The site was established in the Haouz south border and opened into the north on the big reliefs of the High Atlas. The access to the Ghmat rural district is made by the road of green Ourika valley which marks passage between the mountain and the lowland. Archaeological estimates made during the company of exploration in Ghmat show that the medieval city stretches over an area about 20.800 m^2, bigger than the surface of the actual village.

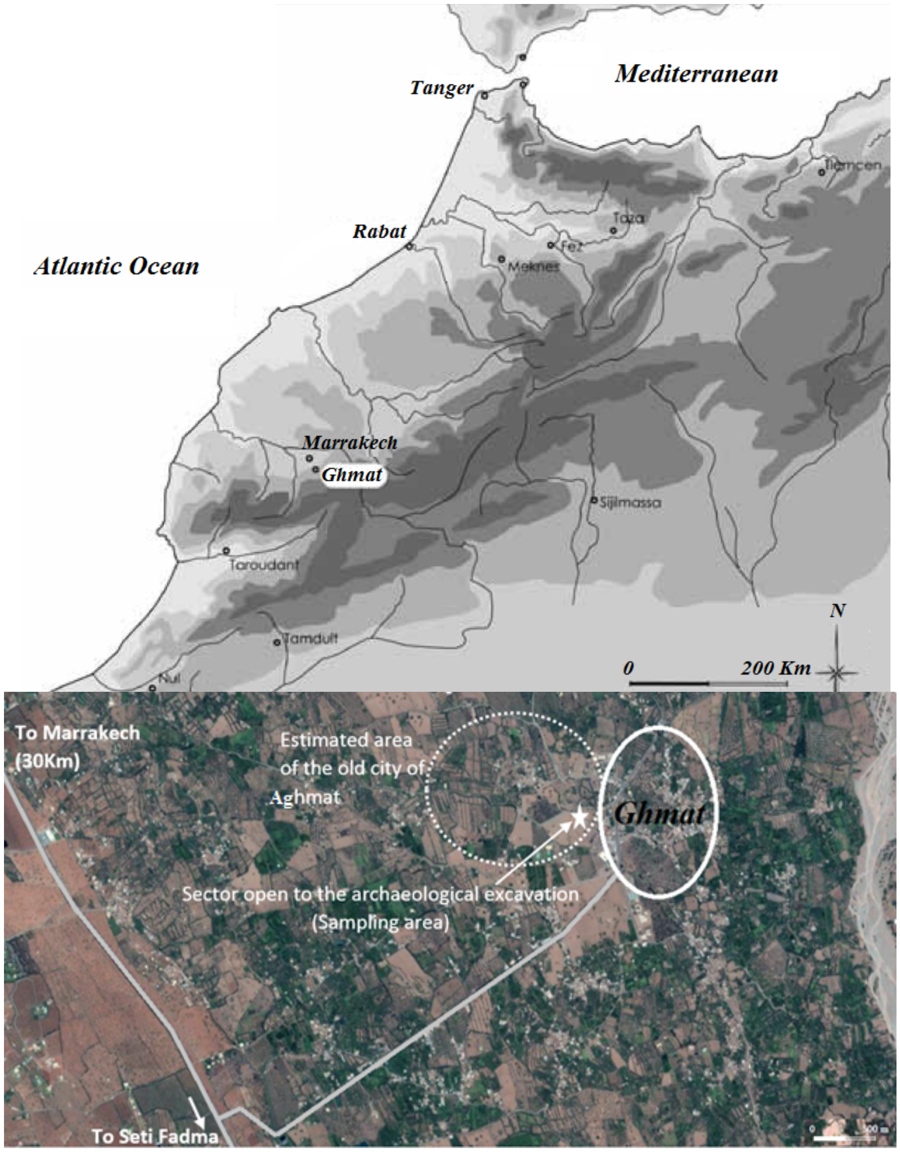

Fig. 1: Geographic location of the city of Aghmat

1.2. The Aghmat medieval city History

It is about relics of an ancient city related by historiographic texts date for VII centuries, this city was developed through its position in the middle of the Atlas as being a commercial seat that links up Al Andalous in the north with the south Saharan caravans and Ifriqiya in the East. At the arrival of Idrissides (VIII century in IX centuries), considered to be the founders of the first Moroccan state, the city begins having more economic brightness, and it heaves at the rank of the capital at the end of the X century, afterwards it became a political and religious pole in the reign of Almoravides (XI and XII centuries). Aghmat remains the capital of this dynasty for about 13 years, before the construction of Marrakech city in 1071 by Youssef Ibn Tachfin, which became the new capital.

1.3. The discovery of the site Aghmat

This archaeological site was discovered in a haphazard way. Workers, by digging close to a road to get a cable fell on relics. A company of archaeological body searches led by an international team of professionals in 2005 has allowed the discovery of other unearthing in the region of Aghmat.

The first withdrawn patch was a splendid black stone basin of an ancient mosque ablution room. Disappeared during 7 centuries, the first capital of dynasty Almoravide comes out again from earth.

2. *Materials and methods*

2.1. Materials

In this study, six samples were taken from the Aghmat site, three samples of bricks interspersed on the wall of the Hammamet (ancient baths) GHB11, GHB12 and GHB13, and three samples of pottery GHP11, GHP12 and GHP13, which constitute residues of decoration pottery and dishes of Aghmat population in VII century (Fig. 2 and 3).

(A) (B)

Fig. 2: Remains of the Palace (A) and the Hammam (B) from the ancient city of Aghmat

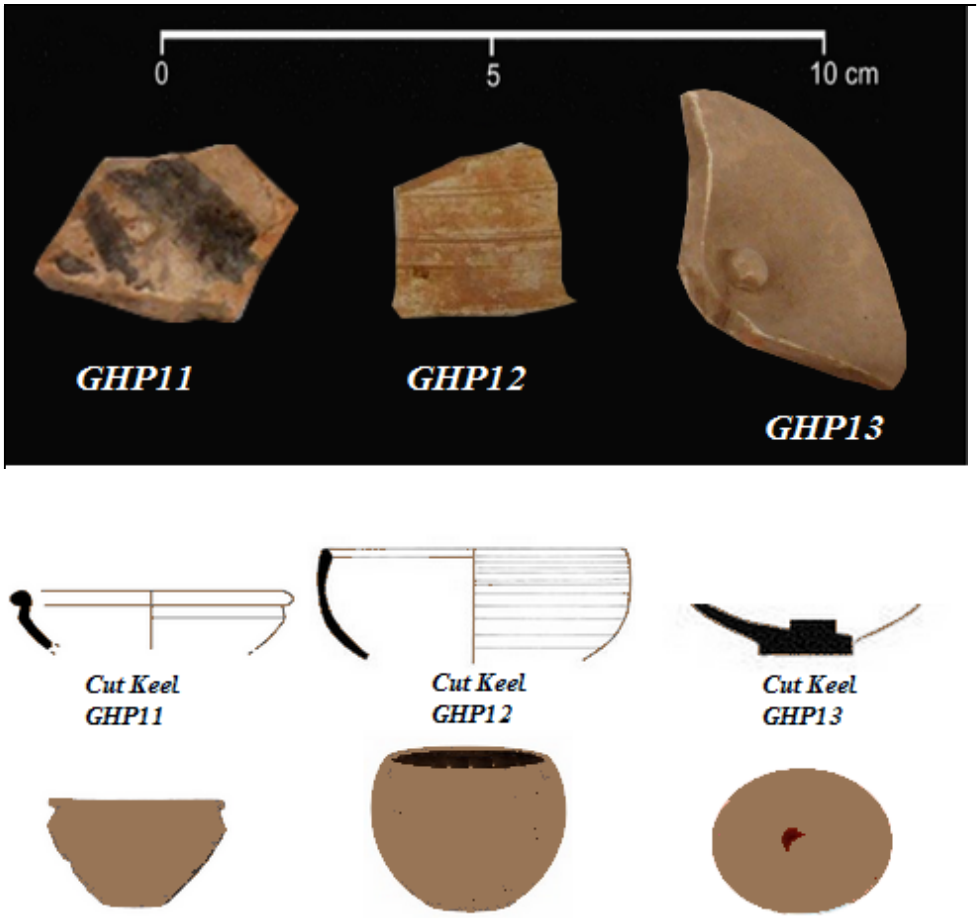

Fig. 3: Shape of the pottery fragment with their cross sections

2.2. Methods

The mineralogical phases present in the terracotta were identified by X-ray diffraction (XRD) using a powder diffractometer (X'Pert Pro-MPDPhilips / PANalytical x-ray diffractometer with copper anticathode). Explored angular range is between 5° and 60° 2Θ. The obtained diffractograms are assigned by comparison with the data of the reference sheets A.S.T.M. (American Society for Testing and Materials).

Chemical analysis of the major elements was performed by X-ray fluorescence spectroscopy (XRF) using a Panalytical Axios spectrometer equipped with Rh tube, the gas used was argon / methane and the data program of treatment was IQ+. For complete chemical analysis, LOI was also determined by heating samples at 1000 ° C for 2 h.

The maximum cooking temperature was determined by experimental annealing tests, a part of each type of ceramic was removed and grinded in agate mortar, then annealed for 4 hours in an electric oven from 500 °C to 1000 °C. The mineralogical evolution during firing was followed by X-ray diffraction (XRD), to identify in wish temperature a change in the basic mineralogical composition will be observed. When we exceed the cooking temperature where the pottery has been cooked previously, some mineralogical phases disappear then replaced by others more stable, thus helping to determine the cooking temperature for each sample.

3. *Results and discussion*

3.1. Bricks

3.1.1. Mineralogical composition

The mineralogical analyses show that the samples of bricks have an identical mineralogical composition except for the sample GHB13 which is comparatively rich in calcite (4%), diopside (5%), gehlenite (3%) and muscovite (16%). Minerals abounding are quartz (33% - 46%), plagioclases (20% - 25%) and K-feldspaths (10% - 13%) (Table 1). Content of hematite is about 4 %, responsible for the red colour of samples after baking (Abajo, 2000; Daoudi et al., 2014).

Table 1: Mineralogical composition (in %) of Aghmat bricks

	Qz	*Plg*	*Fk*	*Ca*	*Di*	*Geh*	*Hem*	*Mus*	*Spl*
GHB11	46	25	10	1	1	1	4	11	1
GHB12	46	23	11	1	1	1	4	12	1
GHB13	33	20	13	4	5	3	5	16	1

3.1.2. Chemical composition

In Aghmat bricks, the silica contents, expressed as SiO_2, vary between 59.1 and 71.8%. The alkaline content does not exceed 5.1% (in % by mass of Na_2O and K_2). Iron is present at an average content (5.4 ± 0.1%) of Fe_2O_3 for GHB11 and GHB12, and 7.1% for GHB13, this sample is relatively rich in Al_2O_3, CaO and MgO (Table 2), so it comes probably from another raw material than that used for the first two bricks. The P_2O_5 contents are less than 0.5%, it is considered the amount usually present in the clays.

Table 2: Chemical composition (major elements) analysed by X-ray fluorescence spectroscopy of brick samples

	SiO_2	*TiO_2*	*Al_2O_3*	*Fe_2O_3*	*MnO*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*P_2O_5*	*LOI*
GHB11	71.8	0.9	13.9	5.3	0.1	1.5	1.29	2	3.1	0.1	0.6
GHB12	69	0.9	13.8	5.5	0.1	1.6	1.7	1.4	3	0.2	2.5
GHB13	59.1	0.9	16	7.1	0.1	3.8	4.4	1.2	3.7	0.3	3.5

3.1.3. Bricks firing temperature

The results of the DRX analysis reported in Table 1 show that the clay fraction was completely disappeared in the brick samples, suggesting a baking temperature ≥ 900 °C, chlorite and kaolinite decompose at About 550 °C, followed by smectite at 700 °C and illite at 900 °C (Cultrone et al., 2004; Fiori et al., 2011). The low calcite content also suggests a baking temperature ≥ 700 °C, at this level the calcite decomposes by promoting the formation of Ca-Silicates phases (Diopside and Gehlenite), they appear more stable under these conditions (Maniatis et al., 1983, Trindade et al., 2009, El Ouahabi et al., 2015), these neoformed phases expand between 700 ° and 900 °C. Muscovite begins melting at 800 °C and disappears completely at 1000 °C (Cultrone, 2001). This shows that the GHB13 sample, relatively rich in muscovite, diopside and gehlenite was cooked at a temperature less than that adopted for the other samples. Hematite gives a red color to bricks when this mineral is subjected to a baking temperature between 700 °C and 900 °C in an oxidizing medium (Centeno et al., 2011). The three samples still contain considerable levels of plagioclases, they start to decompose around 1100 °C. The formation of spinel ($MgAl_2O_4$) depends on the chemical composition of raw materials used in the manufacture of these bricks, it appears at a temperature ≥ 900 °C (Sanz et al., 2007). These results show that samples GHB11 and GHB12 were cooked in an oxidizing atmosphere at a temperature between 900°C and 950 °C while GHB13 was baked between 850 °C and 900 °C.

These temperatures were examined by experimental annealing tests by exposing a portion of each sample to different temperatures from 500 °C to 1000 °C. Below 900 °C there was no change in the mineralogical composition of the recalcined bricks. Around 900 °C, the mineral phases of bricks begin to react, the muscovite peaks disappear at 1000 °C. and the spinel begins to develop (Fig 4).

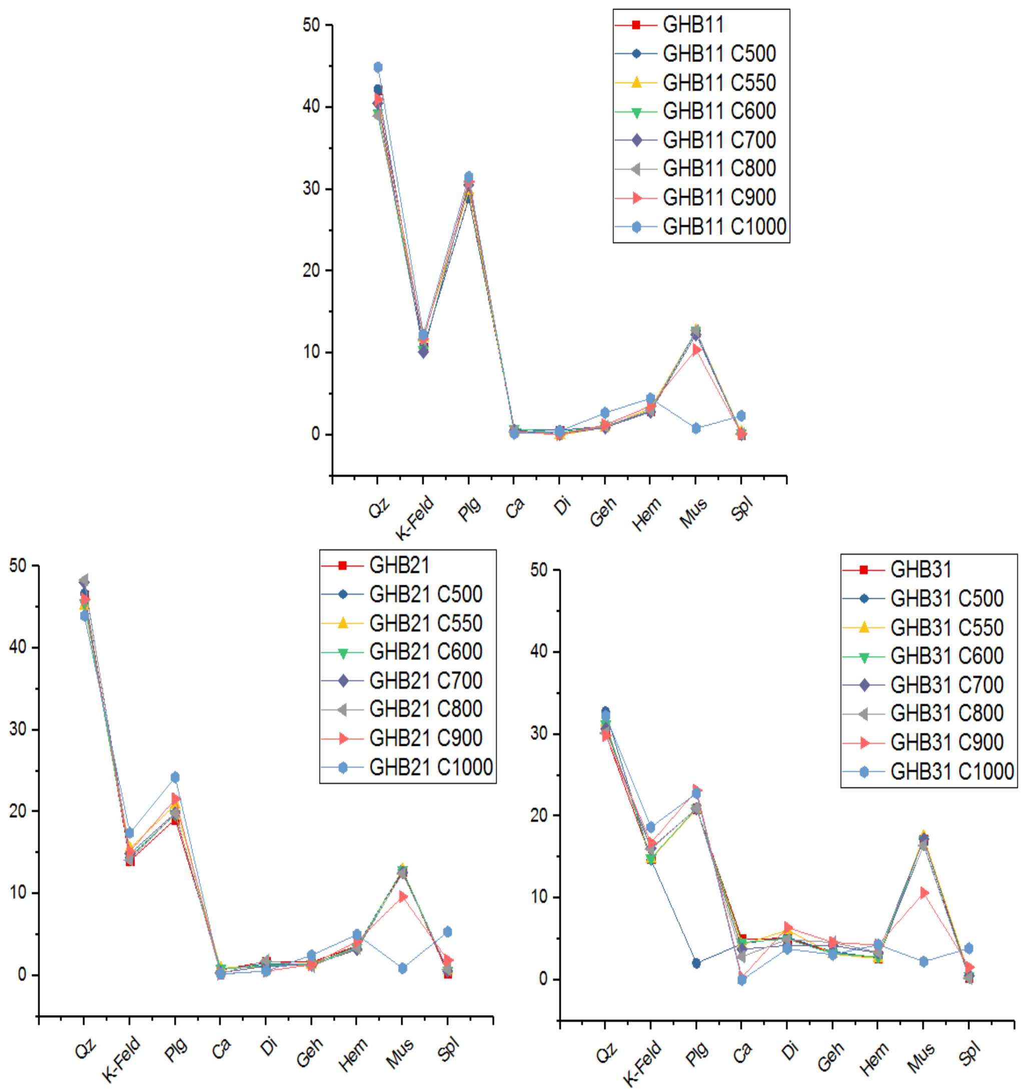

Fig. 4: Experimental baking tests of Aghmat brick samples, the results of DRX analysis show a change in the mineralogical composition from 900 °C.

3.2. Pottery

3.2.1. Mineralogical composition

Contrary to bricks, samples of Aghmat pottery GHP11, GHP12 and GHP13, are more heterogeneous from mineralogical point of view, this is due to the process of manufacture devoted for every type of pottery. Diopside mineral phase, formed by the reaction between Ca, Mg and Si, is well developed in the three samples (24 % - 30 %). Enstatite ($Mg_2Si_2O_6$) was identified (2 % - 6 %) in DRX diffractograms. Quartz, plagioclases and K-feldspaths are the most abounding minerals, while calcite and gehlenite are present at low quantities (Table 3).

Table 3: Mineralogical composition (in %) of Aghmat pottery

	Qz	*Plg*	*Fk*	*Ca*	*Di*	*Geh*	*Hem*	*Mus*	*Spl*
GHP11	25	11	12	4	24	2	5	11	6
GHP12	24	8	21	2	30	4	4	4	3
GHP13	24	17	13	3	28	3	4	6	2

3.2.2. Chemical composition

The most abundant oxides in the pottery samples are SiO_2, Al_2O_3, CaO and Fe_2O_3, when K_2O, MgO and Na_2O are present with few amounts, and TiO_2, P_2O_5 as traces. The samples show the same chemical composition (Table 4), so the heterogeneity observed in the mineralogical composition is not due to the raw material, seems to be the same used for the three samples, but to the cooking temperature adopted for each pottery.

Table 4: Chemical composition (major elements) of pottery samples

	SiO_2	*TiO_2*	*Al_2O_3*	*Fe_2O_3*	*MnO*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*P_2O_5*	*LOI*
GHP11	54.4	0.8	15.9	6.3	0.1	2.7	10.8	0.9	3.9	0.4	3.5
GHP12	53.3	0.8	16	6.6	0.1	2.9	12	0.9	3.6	0.4	3.5
GHP13	56	0.8	14.3	6	0.1	3.1	11.7	1.1	2.9	0.3	3.2

3.2.3. Pottery firing temperature

The low calcite content in the pottery samples is related to advanced carbonate decomposition beyond 700 °C, this promotes the development of Ca-Silicate phases. The presence of Mg favors the diopside's evolution instead of gehlenite in these samples (Peters and Iberg 1987, Dondi et al., 1998, El Ouahabi et al., 2015). The high diopside content also indicates that cooking temperature was optimal for the evolution of this phase, it is estimated between 800 °C and 900 °C. At this temperature, the evolution of enstatite in the diffractogram peaks at 3.17, 2.54 and 1.48 Å, is attributed to the presence of MgO in the clay raw material (Hernandez et al., 2005). Any vitrification phases were observed in these samples because they appear in carbonate-rich materials after 950 °C (Hajjaji and Kacim, 2004).

The annealing tests of the Aghmat pottery indicate that GHP11 has been cooked at a temperature about 800 °C, followed by GHP13 then GHP12 at 900 °C. Beyond this temperature, the mineralogical composition of the samples changes, muscovite peaks are halved before disappearing around 1000 °C. The total calcite decomposition took place at 900 °C. At this stage, the phases of the diopside and the gehlenite reach their maximums. Hematite and gehlenite are the most stable phases until 1000 °C (Fig. 5).

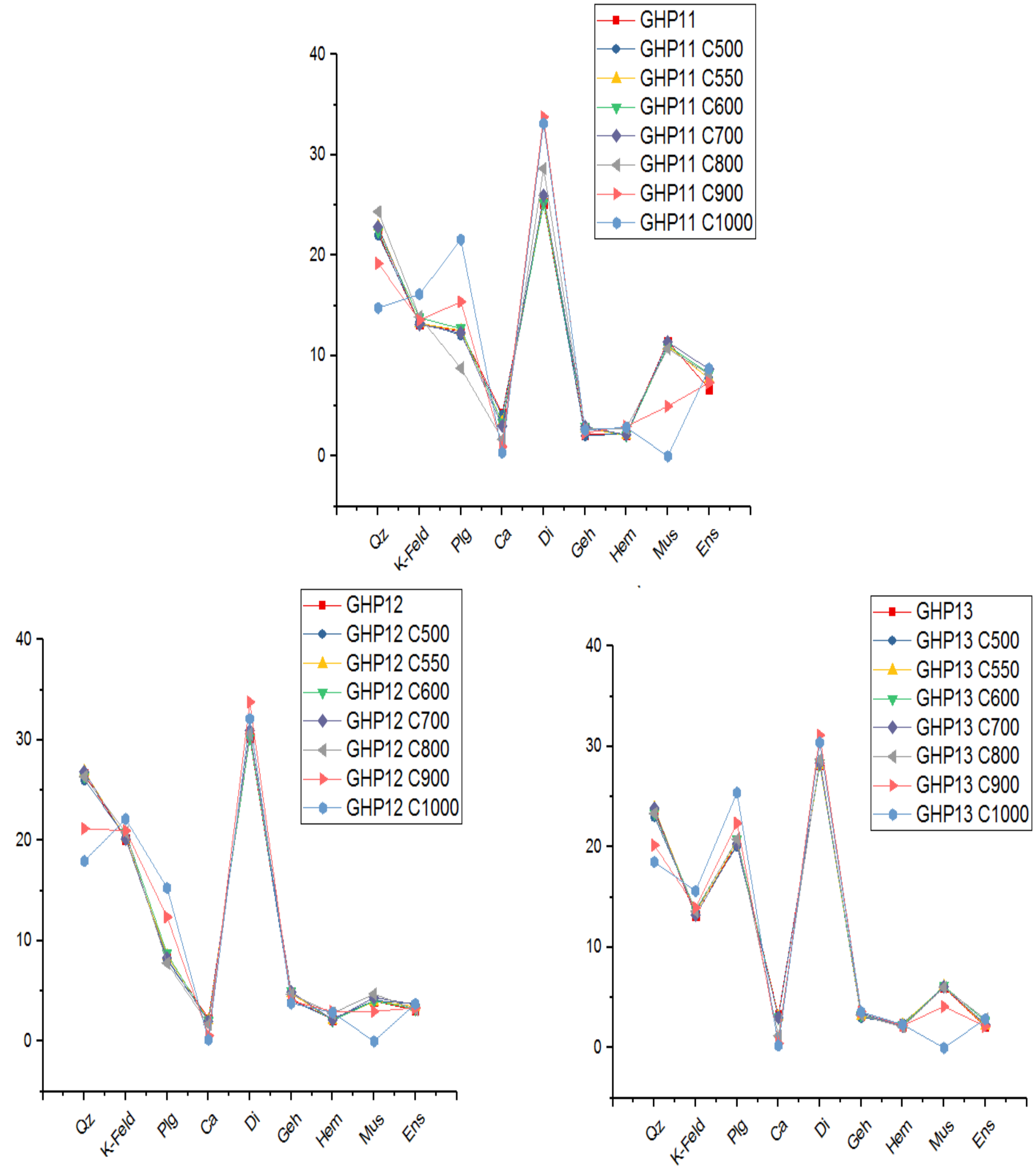

Fig. 5: Results of annealing tests of Aghmat pottery. The content of muscovite, quartz and calcite decreases at around 900 ° C, while plagioclases continue to develop.

3.3. The origin of raw materials used in the manufacture of Aghmat archaeological ceramics:

In order to produce resistant ceramics with high durability, Aghmat potters have sought raw materials that possess appropriate technical properties (plasticity, grain size, etc.) around the city. Each type of ceramic requests different raw clay materials, traditional pottery requires shaping the piece by hand according to the desired form, this needs a plastic material rich in clay minerals and carbonates. The population of Aghmat has used clays of Oued N'Fis and Tamslouht located about 25 km in the west of their city, these materials are rich in illite, smectite and Calcite (Fig. 6).

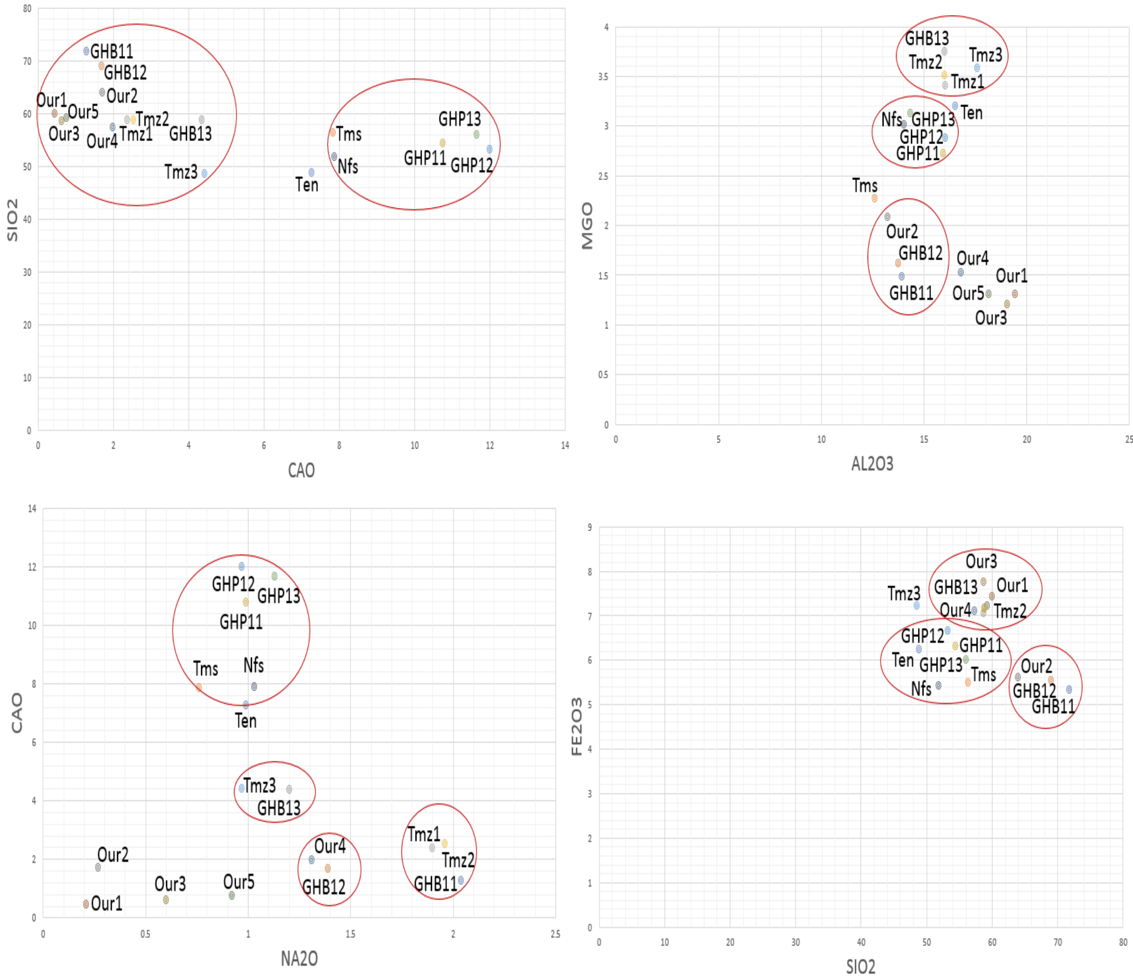

Fig. 6: Binary diagrams based on results of Aghmat samples chemical analysis in correlation with clays of the Ghmat area.

Whereas for the building bricks, these ancient potters used local materials like clays of Ourika and Tamazouzt (2 Km in the east of Aghmat), these materials contain low quantities of CaO and MgO but rich in iron oxide (Fig. 7). The low amount of carbonates in the raw material used in structural ceramics allows to avoid the development of microcracks in bricks during cooking in high-temperature (Riccardi et al., 1999; Cultrone et al., 2004); Spinel is formed in these materials by the reaction between MgO and Al_2O_3 which maintains the structure of the brick after firing.
For GHB13 sample, which is mineralogically different from the other brick samples, leads us to think about two hypotheses, either the raw material used in the manufacture of this brick was extracted in another site where the CaO supply were active, or this variation is due to the manufacturing technology by mixing Tamazouzt clays with carbonate clays to improve the quality of these bricks. These two hypotheses allow us to think that this sample belongs to another generation of brick and that perhaps the construction work of this Hammam knew two different phases where the building materials were changed.

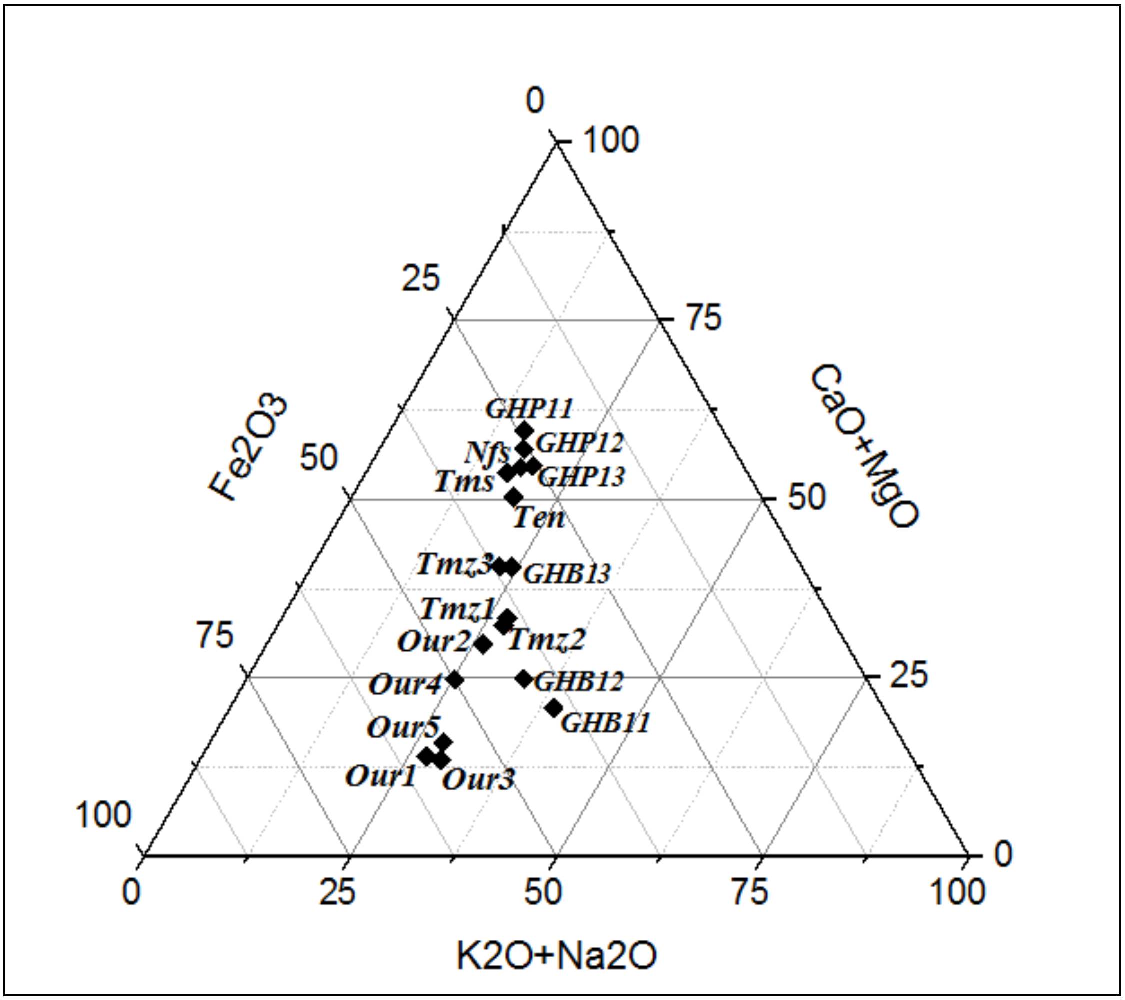

Fig. 7: Triangular diagram (Fe_2O_3 / $K_2O + Na_2O$ / $CaO + MgO$) of the Ghmat ceramics chemical composition compared to the clays of the Ghmat region (Our: Ourika, Tmz: Tamazouzt, Tms: Tamslouht, Nfs: N'Fis).

4. *Conclusion :*

The archaeometry study of the ancient ceramics of Aghmat city led to significant results in terms of the archaeological item. The building bricks were produced locally using an illite clay low in calcium and rich in iron, these clays belong to the red stratum permo-triassic exposed in the Aghmat region, the bricks have undergone oxidative cooking in conventional furnaces at a temperature about 900 °C .Furthermore, Aghmat pottery was made from carbonate quaternary clays brought at 25 km in the west of the imperial city. The plasticity of these clays facilitates the shaping of the pieces and maintains their forms after cooking at a temperature between 800 and 900 °C. These samples have a homogeneous mineralogical composition, while the crystalline phase composition is different, due to the variable cooking level and the position of the parts in the furnace.

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