Scientific Report on the Experimental Part of Identification and Reproduction of Nabataean Pottery
"CERAMED Project"

INCO (2003-2005)- Contract Number ICA3-CT-2002-10018

Talal S. Akasheh*, Daniela Ferro, Bilal Khrisat, Maram Naes,
Queen Rania Institute of Tourism and Heritage, The Hashemite University, Zarqa, Jordan

Abstract

Different scientific methods were used for studying reproduction techniques of Nabataean pottery. Firing experiments of Petra-local clay from three sites (Ayn at-Tinah, at-Tayyiba, ar-Rajif Road) were operated at different temperatures using different firing programs for comparison purposes with Nabataean pottery, best matched results were found with Ayn at-Tinah clay sample at 850^{0}C according to Fourier Transform Infra Red Spectroscopy (FTIR) analysis, Optical Microscope (OM) analysis, Energy Dispersive-X-Ray Fluorescence (ED-XRF) wet chemical analysis and color comparison. Painting studies are also in progress with promising preliminary results with the support of Energy Dispersive Scanning Electron Microscope (ED/SEM) analysis. Novel clay pretreatments and painting mixtures were studied as well.

INTRODUCTION

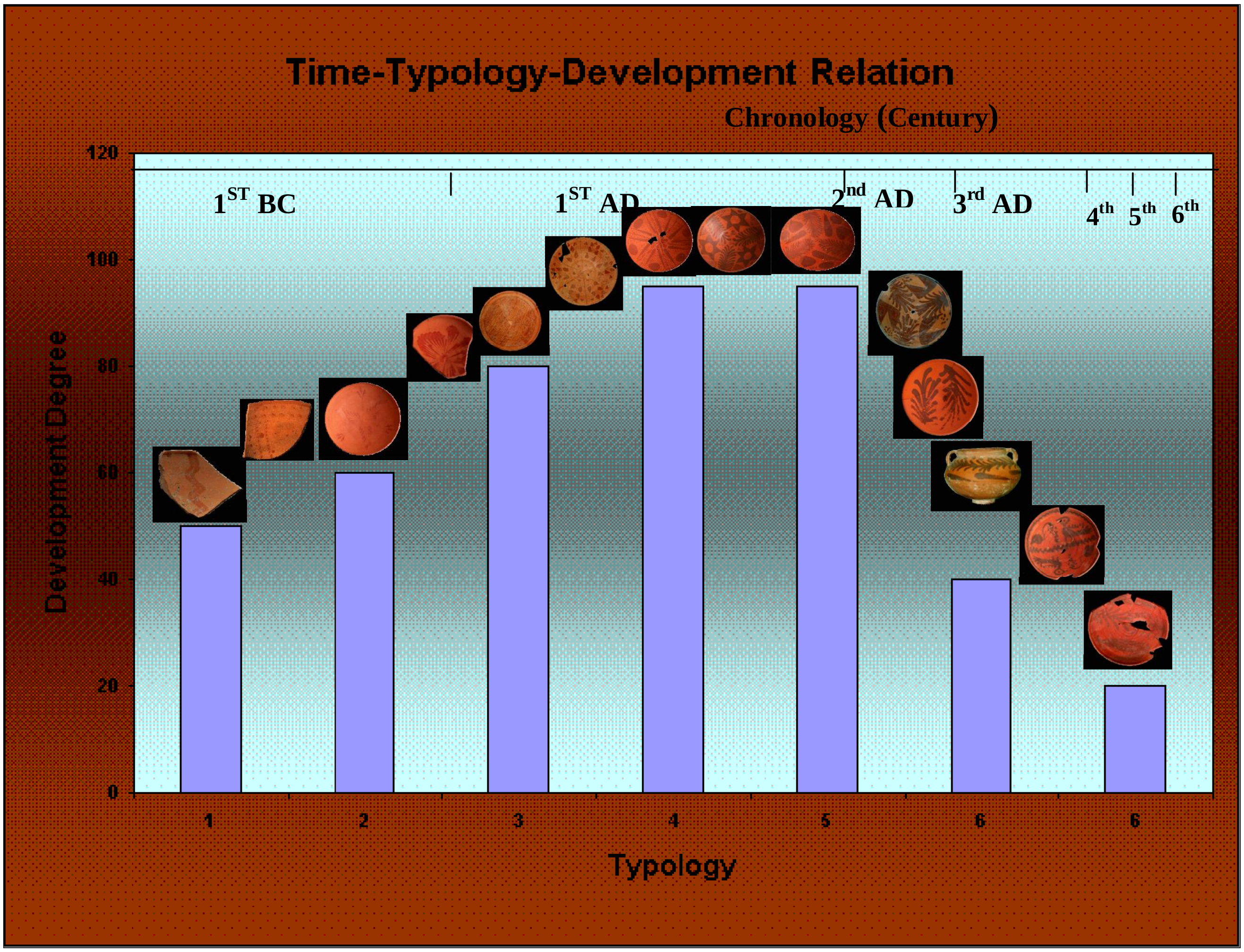
NABATAEAN POTTERY

The Nabataeans fine "eggshell" wares are the most idiosyncratic products for the Nabataean culture. These fine wares were either plain, slipped or decorated with painting, impressing or rouletting, or combinations of these decorative techniques. These wares have been noted in scholarly literature as early as 1908 (by G. Dalman who noted large quantities of broken fine vessels in Petra), although it was not until 1930 that Agnes Conway and George Horsfield clearly identified them as Nabataean products. Most painted forms are open bowls with rounded bases, although other forms such as juglets and cups are also common. The fabrics and painting styles are represented by six main, chronologically significant, types. It should be noted that overlaps between these types have been observed, indicating an evolution of styles rather than abrupt breaks.

Petra was a major centre of pottery production, as attested by the discovery of a large kiln site at az-Zurraba (between Petra and Wadi Musa). Distinctive Nabataean pottery was found in large quantities throughout the Nabataean kingdom, but it rarely appears beyond its boundaries.

In addition to az-Zurraba, other three sites were proposed as possible clay mines. Thus clay samples extracted from them were all tested for provenance study [1]. These sites are: Ayn at-Tinah, at-Tayyiba and ar-Rajif Road clay mines. Further support for provenance results was sought by conducting firing experiments. These experiments provide answers to some basic questions relating the production technique such as: using which clay? Which pretreatment method? To what temperature? Following which firing program was the production technique conducted? Comparison the results of firing experiments with the Nabataean pottery analysis will lead us to conclude the actual production technique used by the Nabataeans to produce their characteristic fine ware.

A novel relationship that correlates Chronology-Typology-Degree of Development was settled down and supported by samples showing decoration, shape and painting samples variations with each of the three correlated bases. It is noted that the pattern of paint and decoration starts by plates being divided into two equal semicircles. The division becomes more elaborated in time reaching many diagonal parts as well as six equal segments in the first century AD and ends with semicircular division during the fourth to sixth century AD.



EXPERIMENTAL PART

Previous Work

Studying possible production centers through analysis of selected clay samples from different sites where original pottery artifacts were found, pottery sherds were analyzed and chemically identified using wet chemical analysis in addition to Fourier Transform Infra Red Spectroscopy (FTIR) analysis. Comparing the FTIR spectra of both sherd body and paint for the same sherd sample indicates invaluable difference which does not reflect any chemical composition change. To get useful information, Far Infra Red analysis is conducted in the meantime.
Computerized Axial Tomography (CT-Scan) was performed successfully to our artifacts resulting in assurance for homogeneous clay composition in addition to some invisible rim rolling that could not be detected without applying this technique.

Recent Work

Scanning Electron Microscope (SEM) was used in our analysis in collaboration with Yarmouk University (YU), Irbid-Jordan. Results were encouraging and will be completed. Primary results indicated the high content of Iron as (Iron Oxide) in the paint fraction of the analyzed sherd, which support wet chemical analysis and forthcoming optical microscope results.

For representative samples, thin sections were made and analyzed by Optical Microscope (OM). Absolutely all samples indicate strongly the richness of clay matrix by iron oxides, which appeared as hematite and magnetite. Hematite predominates with its deep red and reddish-brown color very well noticed in all analyzed samples. Magnetite appeared as well in very dark red and black spots spread all over the clay matrix. Thermal conversion of magnetite into hematite at very high temperature (>600^oC) could be the reason beyond hematite distribution in the material without exact distinguished structure. Quartz and Plagioclase were found in minor amounts compared to iron oxide minerals. Traces of Biotite were found hidden and not very obvious due to high content of iron oxides that is screening the matrix of the thin sections. Very minor traces of Limonite and Chlorite were found in some samples, but were very common for the yellowish-green clay sample from Ayn at-Tinnah site near Petra.

One of the samples was stereoscopically different from other analyzed sherds, as it was black and looked like badly fired or fired under extreme reduction conditions. This sample when analyzed under the microscope indicated high content of organic matter that appeared as black material in a grayish matrix (NRP-T2-40). ED-XRF is now being applied to our samples and we have achieved primary results for a set of samples indicating the high content of iron, manganese was also detected in samples in lower amounts than others. Titanium and manganese were also detected. Obviously, the firing conditions were the most important factor that affects the degree of material oxidation and/or reduction within the firing process. And so the next stage of our research was to study the best firing conditions to be applied for manufacturing best type of pottery.

Clay samples were collected from three sites: Ayn Attinah (two samples), Attaybeh (one sample) and Arrajef Road (two samples). Samples from the same site or origin were different in their stereoscopic, physical and chemical properties. Table (1) below represents these differences. Prior to any step testing the clay samples, they were wet cleaned using tap water for the removal of any floating impurities. Wet sieving of the washed clay was the next step for the removal of large insoluble solid impurities (1mm diameter particle size). The washed clay was then kept fully immersed in water using wide deep containers, and from time to time the clay was circularly shaken by hand, allowed to settle down, and the dirty water decanted. This step was repeated at least seven times. After that another wet sieving was operated to obtain the finest particle size, impurity-free and salt-free clay that forms the colloidal system in the washed clay, the last step being accomplished using distilled water.

Since any strange contamination will disturb the purity of the clay and so the homogeneity of the produced pieces, washing was repeated seven times –after many trials seven washings were convenient- till we reached the desired purity of the clay. The washed clay was put in white clean plisse open to air for few days to evaporate excess water. Then muddy clay, ready for modeling was obtained.

Table (1): Origin, stereoscopic, physical and chemical properties of the tested clay samples

Clay Mine	Sample Number	Stereoscopic Properties	Physical Properties			Mineralogical Determination	
			Grain Size	Specific Gravity	Moisture Content	%$CaCO_3$	%Fe_2O_3
Attaybeh	1	Reddish-Brown clay	28.96	2.639	0.519	7.7	2.94
Ayn Attinah	2	Yellowish clay	24.7	3.849	0.447	8.3	1.90
	5	Greenish clay	25.0	3.145	0.507	5.3	1.45
Arrajef Road	3	Yellowish-Green clay	27.4	2.731	0.555	2.2	0.88
	4	Reddish-Brown clay	23.1	3.361	0.508	2.4	2.47

Firing Experiments

Slips of the muddy clays were hand-made, trying to obtain the thinnest size closest to the thickness of the Nabataean ceramics. Slips were then set to different firing programs called as experimental packages, each has multi variables that are: the maximum firing (peak) temperature (T_P), firing rate (r) from 300^0C to the peak temperature, time of firing at the peak temperature (t).
Following is the structure identifying each firing program or experimental package- where LCEP refers to Low Calcareous Experimental Package- written as:

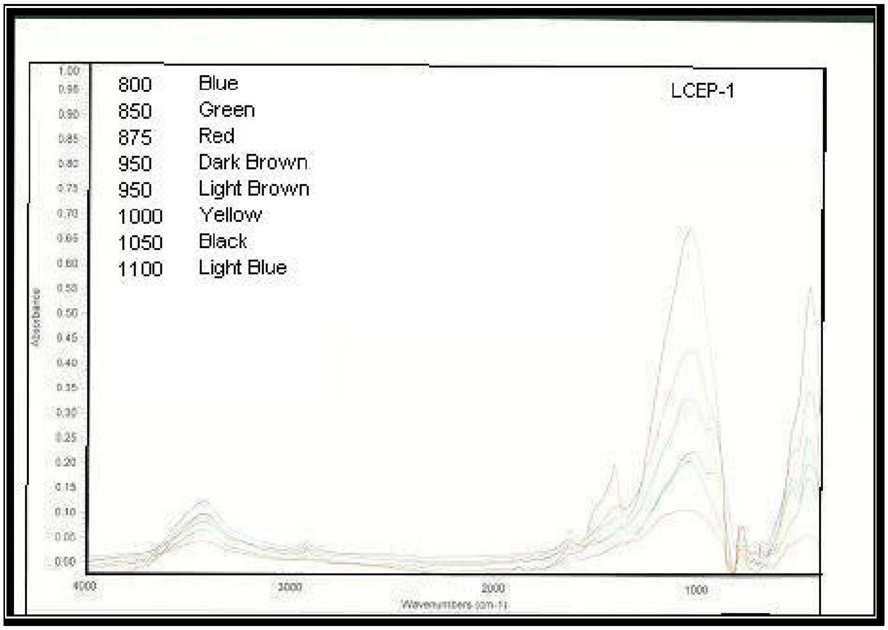
$$\textbf{LCEP \# - r - t - } \mathbf{T_P}$$

Where, # refers to clay sample number (1-5)
r: represents the rate of firing from 300^oC to T_P
T_P: is the peak temperature, which is maintained for a particular time that is represented as (t).

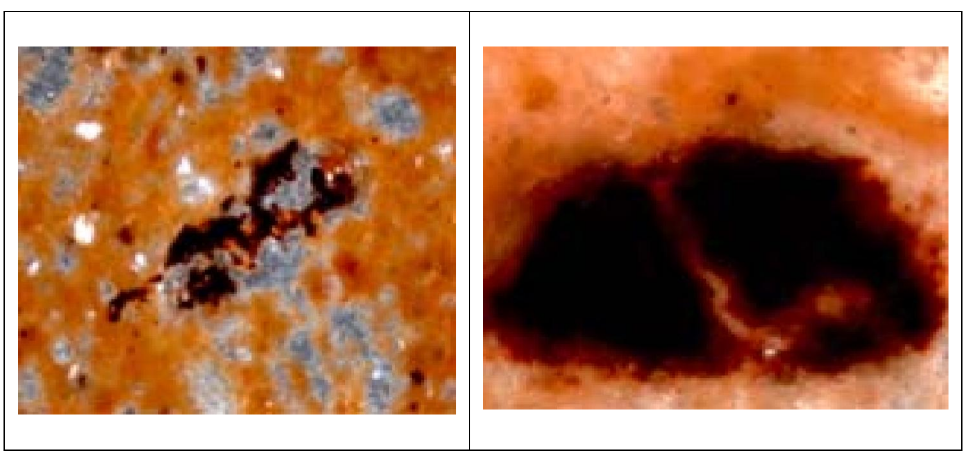
The fired slips where then cooled down to room temperature then analyzed by both available techniques: FTIR and OM. Representative result is shown in chart (1) for

FTIR analysis and in images (1 and 2) for OM analysis. The samples reach steady state spectra at around 850°C.

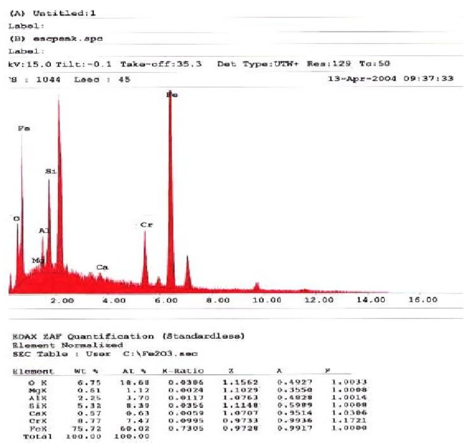
Chart (1): FTIR spectra of clay sample number (1) fired according to different experimental packages



Images (1 and 2): Optical Microscope Images of selected clay and slip samples



Figures (1 and 2): Scanning Electron Microscope Analysis of some sherds, which indicates the high content (light color) of iron in the painted part of the surface of the sherd.



Element	Wt %	At %	K-Ratio	Z	A	F
O K	6.75	18.68	0.0386	1.1562	0.4927	1.0033
MgK	0.61	1.12	0.0024	1.1029	0.3550	1.0008
AlK	2.25	3.70	0.0117	1.0763	0.4828	1.0014
SiK	5.32	8.39	0.0356	1.1148	0.5989	1.0008
CaK	0.57	0.63	0.0059	1.0707	0.9514	1.0306
CrK	8.77	7.47	0.0995	0.9733	0.9936	1.1721
FeK	75.72	60.02	0.7305	0.9728	0.9917	1.0000
Total	100.00	100.00				

PAINTING EXPERIMENTS

Different experiments were conducted in order to investigate the best paint mix that best matches the Nabataean paints for its color and composition. These experiments included preparing and testing about fifty mixtures consisting of natural minerals basically from Petra region, in addition to two samples from the Dead sea and the southern part of Jordan. These minerals were particularly hematite and magnetite as well as limonite. Other materials included in the mixes were the crust extract of black olive, and natural vegetal charcoal. The original area clays were also included, the finest particle size was sieved and tested with previously mentioned minerals to form the paint.

After the stage of paint mixes preparation, firing them to the best temperature was conducted. So, another experimental package for firing temperatures was performed following the same procedure mentioned earlier. Sometimes, for the same maximum firing temperature different programs were tested by changing the firing rate at multi-temperature ranges, as well as changing the time that the peak temperature is kept constant at it.

Results obtained were analyzed by FTIR and relying on the color degree match with that for Nabataean paint.

RESULTS AND CONCLUSIONS

The quality of the workmanship and the ceramic material improved reaching a maximum during the first and the second century AD, but declined in time thereafter. From the analysis we have conducted low quality ceramics having higher calcite and dolomite content. The color as well changed with time and from type to another. It started almost red paint in the first and second century (type 1 and 2) with limited decorations like needle shape circular collections. Then it turns into darker red to reddish-brown that differs very slightly between small number of the studied samples.

Clays and iron oxides are the main components found using Optical Microscope. Hematite appeared red-light brown color, while magnetite as dark-brown to black spots. Quartz crystals often appeared with white-gray interference colors. Feldspar (plagioclase) was not well defined. One of the tested samples contained organic matter, which is evident as grayish-brown colored matrix. Sometimes Biotite is present but masked by the red color of the iron oxides.

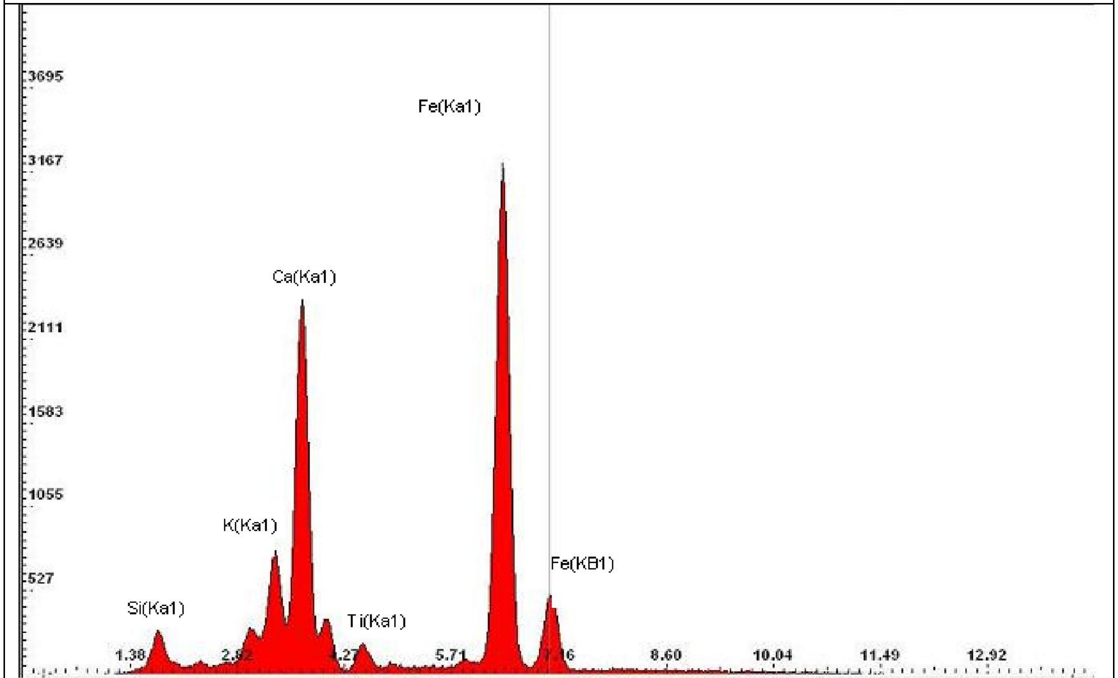
SEM analysis supports the previously obtained result that is the high content of iron oxides, the presence of quartz as well was very clear. Clay minerals were also found. The porous texture in some samples was clear under the SEM with a magnification till 5 and 10 micrometer. Some phosphorous mineral was found in the body of the sherd. Quartz content varied from sample to another depending on the typology of that sherd, its thickness and quality. That is, for type one and two the content of quartz was 16% by weight regarding the other components and this ratio is larger than that for sherds of types three, four and early five that was about 8%. Whereas, for sherds from the latest type five and type six, quartz content exceeds that for the first and second and reached about 20-25% out if the total weight ratio for other measured components.

The paint was analysed as well by SEM showing the main components of it to be iron and manganese oxides. The ratio between these two oxides varied from sherd to another depending on the typology of that sherd. That is, for the first type the main component of the paint was iron oxide. Whereas, in the second type manganese oxide started to appear very slowly with very low amounts compared to the paint of the third, fourth and fifth types, where manganese oxide appeared with relatively higher ratios that was almost constant in these types. Type six and late type five, showed the highest ratio of manganese oxide but even so iron oxide content has the higher content.

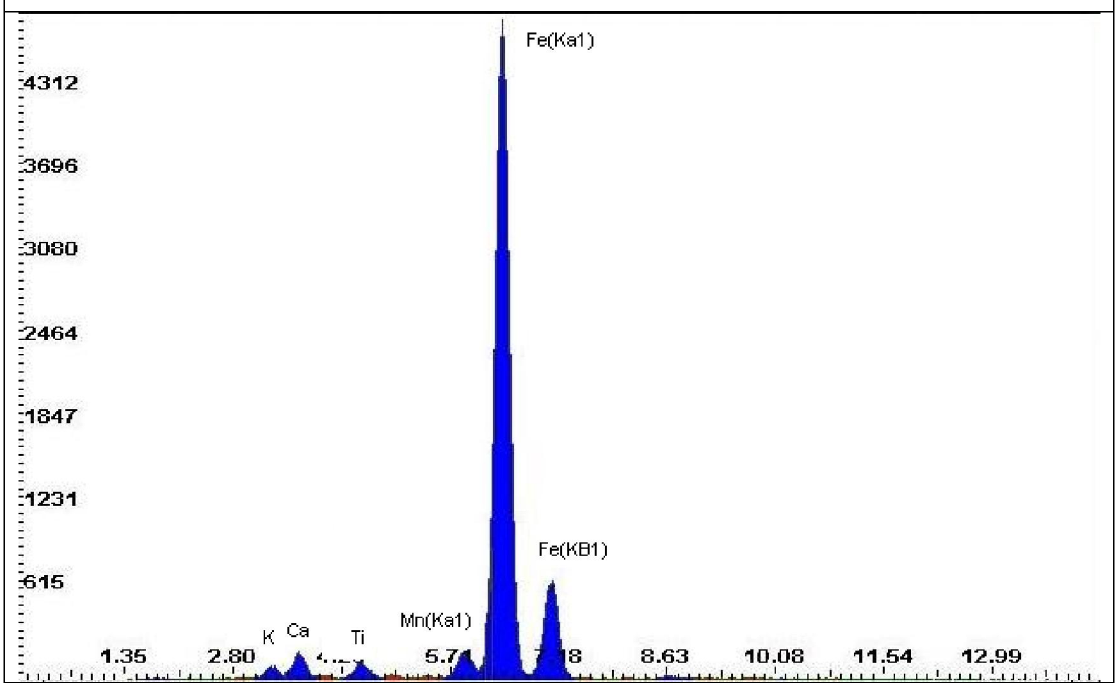
Complete agreement with SEM results was the results of XRF, which were conducted in the Hashemite University using the new portable instrument. Selected results and spectra are shown below.

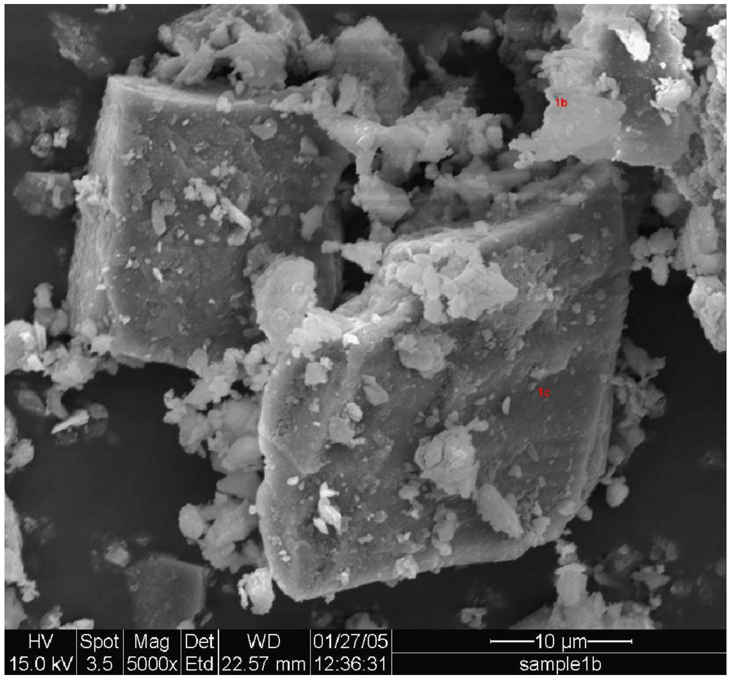
According to the paint experiments and the experimental packages, the best firing temperature was that at 850^{o}C, whereas the painting experiments still in progress and no final conclusion should be given in this stage, but very promising results and colors with 100% natural paint mixes are obtained. All what can be said in this stage is that the best match paint mixture was that which includes the hematite and magnetite, as well as the addition of fine red clay that is originally from ar-Rajif road.

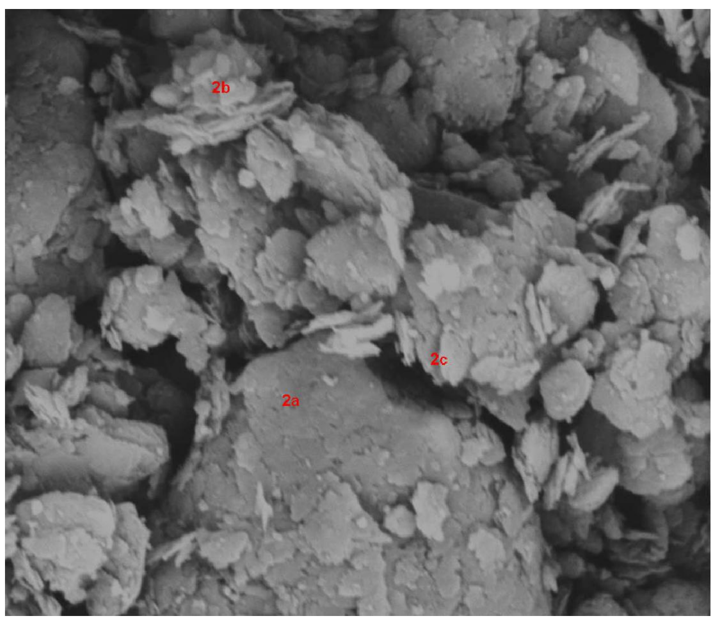
XRF SPECTRUM OF PAINTED SHERD SAMPLE NUMBER WMS 011



XRF SPECTRUM OF SHERD SAMPLE NUMBER WMS 028




1b
1c
HV
15.0 kV
Spot
3.5
Mag
5000x
Det
Etd
WD
22.57 mm
01/27/05
12:36:31
10 µm
sample1b


2b
2c
2a