MULTIFACETED ANALYSIS OF GLAZED CERAMICS FROM JORDAN: RAW MATERIALS AND TECHNOLOGICAL ASPECTS

Firas Alawneh* , Fadi Balaawi
Department of Conservation Science, Queen Rania Faculty of Tourism & Heritage
Hashemite University, Zarqa, Jordan.

Raed Alghazawi
Department of Sustainable Tourism, Queen Rania Faculty of Tourism & Heritage
Hashemite University, Zarqa, Jordan.

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1. Introduction

Generally, glaze production can be dated back to the end of the 5th century BC and seems to have been present in Mesopotamia, Egypt, and Syria. Glazed pottery likely originated in the 16th century BC in the same areas [1, 2]. Glazes were used for decorative and technical purposes, to hide some defective features and to improve material properties [3]. Islamic ceramic productions are considered among the highest quality in terms of raw material preparation, formation, decoration, use of bright colors and controlling firing temperatures [4]. Glazed pottery in the Ayyubid and Mamluk periods is distinguished by its high purity paste, firing temperature and decoration [5]. Different types of glazes have been produced, including alkaline, lead, and mixtures of both [1,2,3,4]. The availability of large quantities of Ayyubi/Mamluk glazed ceramics also indicates Jordan's important role in the trade route between Egypt and Syria [5,6]. One of the main characteristics of high-lead-content glazes is their relatively low melting temperatures [6–8].

The samples for this research were collected from the Tel Al-Husun archaeological site. The study area is located in the new northern part of Al Husun village and dominates the plains of Hawran on the northern and eastern sides, approximately 25 km south of Irbid city (Figure 1). The archaeological site was very important during the Ayyubid and Mamluk periods, therefore the many excavations conducted resulted in the discovery of different archaeological features as well as many finds and artifacts. The aim of this research is to determine the lead glaze ceramic technology employed and possibly identify the sources of the clay used. This will allow us to recognize the level of technical progress, quality and skill attained to achieve the above results. 43 glazed pottery fragments dated to the Ayyubid and Mamluk periods were chosen for this study (Figure 2).

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* Corresponding author: Firas-alawneh@hu.edu.jo

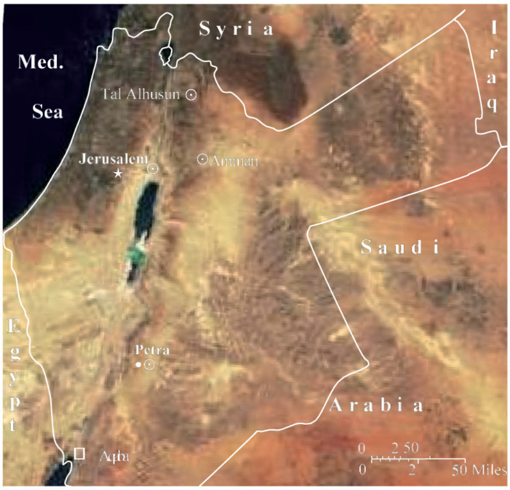


Figure 1. Map of the Southern Levant with the archaeological sites selected for the study indicated by the sign ⊙.

Chemical methods and statistical analyses provide archaeologists with a powerful set of data for the characterization and interpretation of cultural resources. The goal of statistical analyses is to recognize compositionally homogeneous groups within the analytical database. Similar objects are classified into groups according to color and typology, as well as the relationship between artifacts and their environments.

In order to determine their possible provenance and production technology, samples were studied by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), optical microscope and X-ray powder diffraction (XRD) and their chemical, mineralogical and textural features analyzed. Compositional data was statistically processed with multivariate analysis using SYSTAT 11 software 2011. To obtain further information about possible source areas of raw materials used in ceramic production, clays were also sampled in the studied areas. To better understand the firing technology of the pottery, firing experiments were conducted for clays with compositions comparable with those of the ceramic sherds.

The study also describes the multidirectional, socio-cultural exchange and economic trade patterns within the region, and between adjacent regions. Importation from adjacent provinces, moreover, cannot be excluded for certain samples.

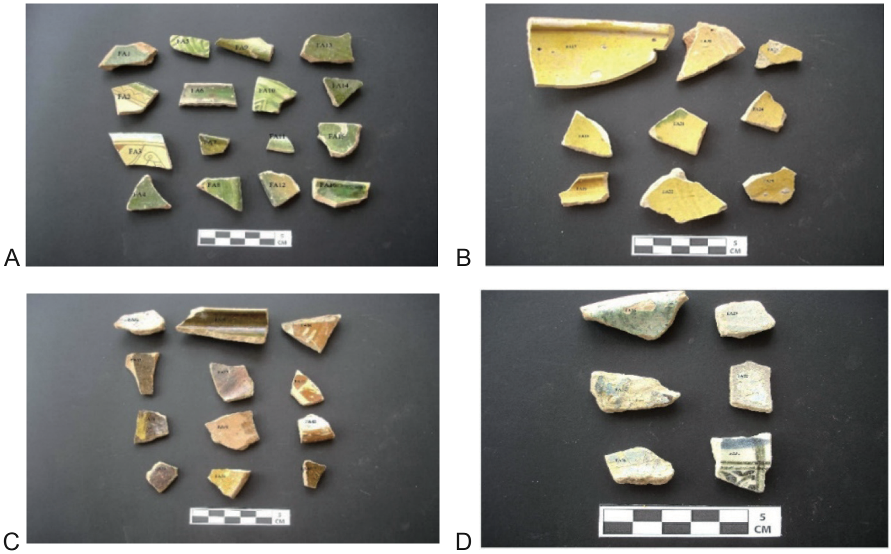


Figure 2. Photographs of studied glazed ceramic samples: groups A, B, C and D

2. Materials and methods

Archaeometric studies of ancient ceramics from Jordan are very scarce. They consist mostly of disconnected case studies that principally focus on individual sites, such as the Chalcolithic pottery from Teleilat Ghassul [10], the Nabatean pottery from Petra [3, 13] or the Middle Bronze pottery from Hayyat. Instead, what is required is a systematic study aimed at creating a comprehensive database that includes most clay deposits and ceramic production sites from the different geographical areas and historical periods. It is worth noting here the role-model and remarkable experience of the Institute of Mineralogy & Petrography at Fribourg University, Switzerland, where over 100 reference groups have been established since 1974. Therefore, the modest project we are proposing here is intended to be the initial phase of a multiphase project aimed at creating the type of database that would serve a large number of archaeologists working in the area. In the short run, and due to lack of such a database, special focus will be given in this study to chemical and petrographic, inter- and intra-regional, and compositional variations of the clay deposits. Obviously, adopting such a new approach to the particular case of ceramics from Jordan is based, above all, on these practical considerations.

Studying the provenance of ancient ceramics has long been based primarily on the mathematical treatment of geochemical data. Less attention has been paid to phase and textural analysis. For instance, mineralogical and petrographic approaches are introduced to the field only much later [11]. However, in some cases (e.g. fine ceramics), chemical analysis might be the major tool employed to characterize the products and to determine their origin satisfactorily. In some other cases (e.g. coarse ceramics), petrographic analysis can be at least as powerful as the former [12]. It is worth remembering that a chemical approach may have some limitations due to: (i) inter and intra-site variance (little or too much) of the different chemical constituents of the original clay material; (ii) representativeness of the specimen analyzed; (iii) number of samples analyzed; (iv) chemical instability in some of its different constituents, which can suffer dramatic alteration during manufacturing, use, or burial conditions of the artifact. Meanwhile, coupling the chemical and mineralogical/petrographic analyses minimizes the risk of misinterpreting chemical data because of these limitations. Mineralogical and petrographic analyses provide additional and complementary tools for the characterization and determination of the origin of ceramic artifacts. Combining chemical and mineralogical-petrographic approaches has been widely and successfully applied to provenance studies of ceramic artifacts, as has been demonstrated by the increasing number of archaeometric papers. There is good reason to think that this integrated approach is similarly applicable to the provenance study of ceramic products from Jordan.

A series of judiciously chosen and complementary methods were used in the analysis of ceramic artifacts, glazes and clay materials. These methods characterized the compositional, phase-identification and textural/morphological aspects of the samples. The chemical composition of the ceramic bodies and glaze layers were determined by a Perkin Elmer Optima ICP–AES mineralogical (phase) analysis using X-Ray Diffraction (XRD), and petrographic (textural) analysis using Polarized Light Microscopy (PLM). Scanning Electron Microscopy (SEM) was occasionally used to complement PLM for some representative samples to verify ceramic sherd microstructure (morphology and size of pores, vitrification, etc.). Fortunately, the analysis of ceramic artifacts can be conducted using nondestructive techniques and/or with minute amounts of the sample, thus preserving these often-valuable artifacts.

As part of the proposed ceramic study, we included a program of analysis for clay materials, to be collected in proximity of the selected archaeological site. Priority was given to historic mining areas that have been identified by archaeologists [13]. Whenever pottery kilns were identified and excavated [14], residual clay and ceramic waste material were sampled for analysis. In addition to being unchallenged evidence for local fabrication, the latter can reveal some invaluable information on ceramic fabrication techniques and may provide an excellent opportunity to establish any ceramic reference group(s), characteristic of both the geographic area and historical period. We selected and analyzed 43 ceramic artifact samples that represented the different colors (Figure 2). Clay materials were collected in proximity of archaeological sites at a rate of 3 samples/deposit.

3. Results and discussion

Provenance determination of pottery found in archaeological excavations is a significant task to undertake in understanding ancient civilization. In other words, the search for an answer to the question of where the pottery was produced is based on the results of analysis. Research has been conducted for many years [14-22]. There are mainly two approaches in use: chemical analysis of the elemental concentrations, and mineralogical investigations using petrography. In this research, an approach combining both methods was employed. Petrographic analysis is most commonly employed in archaeology to identify the mineral components present in clays used to manufacture ceramic vessels and other pottery objects [23-25]. This data can then be used to link the artifacts to geological source areas, using the clay together with the mineral and rock fragments (usually called “inclusions”) often added by potters to modify the properties of the clay.

The ICP–AES is an analytical technique based on the principles of atomic spectroscopy and has become the leading technology for the routine analysis of archaeological samples. From the ICP–AES measurement, the concentrations of eight major elements (MgO, Al_2O_3, SiO_2, N_2O, K_2O, CaO, TiO_2 and FeO) were obtained. In Tables 1, 2, 3, 4, 5, 6, 7 and 8 are shown the results of the ICP–AES of the four sets of potsherds and the glazed layers. The ceramics are primarily composed of silica and alumina, with substantial amounts of iron, magnesium, and calcium oxides and lesser amounts of sodium and titanium oxides.

Table 1. Normalized body composition for ceramic sherds – group A

	SiO_2%	TiO_2%	Al_2O_3%	FeO%	MgO%	CaO%	K_2O%	Na_2O%
FA1	68.12	0.68	12.74	8.03	3.21	4.29	2.76	0.17
FA2	61.92	0.73	8.25	2.16	2.83	19.52	0.87	3.72
FA3	58.23	0.61	9.23	4.16	3.51	18.36	0.96	4.94
FA4	61.20	1.01	22.45	4.49	2.63	6.36	1.75	0.11
FA5	66.50	0.90	16.02	6.70	2.11	5.60	2.06	0.11
FA6	69.56	0.91	16.69	5.97	2.32	2.13	0.69	1.73
FA7	73.35	1.16	18.89	2.47	1.01	1.45	1.35	0.32
FA8	66.32	1.16	19.87	3.30	1.32	5.9	1.70	0.43
FA9	67.28	1.17	16.14	7.20	4.57	2.24	0.68	0.72
FA10	69.18	0.70	13.5	7.75	3.21	3.32	2.06	0.28
FA11	73.27	0.67	13.23	4.28	1.37	2.64	0.89	3.65
FA12	70.16	1.04	19.82	2.96	1.44	2.51	1.79	0.28
FA13	65.01	0.80	16.7	5.10	1.98	5.16	1.14	4.11
FA14	68.12	1.10	20.51	3.26	1.26	3.68	1.65	0.42
FA15	65.51	1.27	21.07	3.05	1.7	4.82	2.25	0.33
FA16	68.07	0.63	17.4	4.60	2.84	2.50	3.07	0.89
Average	66.98	0.90	16.40	4.71	2.33	5.65	1.60	1.38

Table 2. Normalized body composition for ceramic sherds – group B

	SiO2%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	K2O%	Na2O%
FA17	70.14	0.66	11.4	6.49	2.43	6.66	1.9	0.32
FA18	72.7	0.73	12.12	3.2	2.33	7.34	0.95	0.63
FA19	70.28	0.91	12.2	4.1	1.87	8.29	1.87	0.48
FA20	61.7	1.01	22.45	4.58	2.34	6.36	1.33	0.23
FA21	68.12	0.94	16.02	5.98	1.47	4.94	1.99	0.54

FA22	65.37	0.91	16.39	3.97	2.86	7.71	2.01	0.78
FA23	70.56	1.29	16.25	1.87	1.87	6.7	1.22	0.24
FA24	71.56	1.7	19.36	2.88	1.2	2.41	0.78	0.11
FA25	68.53	1.17	16.1	3.7	1.88	7.55	0.82	0.25
Average	68.77	1.03	15.81	4.08	2.02	6.44	1.43	0.39

Table 3. Normalized body composition for ceramic sherds – group C

	SiO2%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	K2O%	Na2O%
FA26	73.61	0.35	17.5	1.06	2.87	2.32	2.12	0.17
FA27	76.51	0.66	12.22	1.65	1.87	2.55	0.82	3.72
FA28	70.1	0.46	13.7	3.1	2.3	4.44	0.96	4.94
FA29	67.71	0.77	18.2	2.7	1.98	6.93	1.6	0.11
FA30	72.67	0.67	16.55	1.9	2.6	3.44	2.06	0.11
FA31	71.7	0.89	15.17	1.99	2.88	4.88	0.69	1.8
Average	72.05	0.63	15.55	2.06	2.41	4.09	1.37	1.80

Table 4. Normalized body composition for ceramic sherds – group D

	SiO2%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	K2O%	Na2O%
FA32	68.34	0.42	16.5	3.2	3.21	6.4	1.82	0.11
FA33	68.65	0.63	17.3	2.88	2.83	5.22	0.95	1.54
FA34	69.74	0.77	15	2.44	3.51	7.11	1.11	0.32
FA35	69.99	0.83	16.6	3.01	2.62	4.88	1.23	0.84
FA36	59.9	0.91	19.7	4.51	2.14	11.2	0.99	0.65
FA37	70.56	0.67	13.56	2.79	2.68	7.85	1.13	0.76
FA38	69.77	0.84	18.34	3.66	1.25	4.33	0.85	0.96
FA39	68.3	0.65	20.1	2.78	2.12	5.22	0.67	0.16
FA40	71.5	0.48	18.5	3.45	2.65	2.1	0.77	0.55
FA41	70.92	0.99	15.91	2.54	3.01	4.89	0.99	0.76
FA42	71.14	0.78	13.12	3.95	2.22	6.76	1.42	0.61
FA43	67.87	0.66	17.55	5.13	1.78	4.43	1.36	1.22
Average	68.89	0.71	16.84	3.361	2.50	5.86	1.10	0.70

Table 5. Normalized glaze composition for ceramic sherds – group A

	SiO2%	PbO%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	Na2O%	CuO%
FA1	46.65	48.10	0.22	3.60	0.24	0.03	0.18	0.20	0.32
FA2	40.85	52.20	0.19	4.70	0.97	0.21	0.16	0.14	0.29
FA3	43.86	48.50	0.36	5.30	0.57	0.02	0.82	0.05	0.36
FA4	41.56	50.42	0.42	5.60	0.35	0.43	0.61	0.14	0.35
FA5	40.30	51.88	0.36	5.40	0.36	0.18	0.54	0.17	0.28
FA6	48.33	42.40	0.41	6.40	0.91	0.22	0.62	0.15	0.37
FA7	41.28	51.70	0.32	4.30	0.54	0.22	0.78	0.20	0.41
FA8	40.20	53.46	0.18	3.50	0.68	0.45	0.92	0.09	0.36
FA9	42.10	50.92	0.10	4.40	0.64	0.33	0.64	0.12	0.32
FA10	40.20	50.90	0.44	5.90	0.78	0.15	0.72	0.13	0.38
FA11	40.30	49.37	0.36	7.60	0.49	0.16	0.85	0.22	0.31
FA12	46.36	45.54	0.47	5.10	0.62	0.11	0.91	0.33	0.31
FA13	40.20	50.33	0.52	7.00	0.18	0.27	0.94	0.10	0.29
FA14	40.40	49.30	0.23	8.47	0.26	0.11	0.57	0.12	0.34
FA15	40.72	50.20	0.33	6.91	0.33	0.17	0.55	0.17	0.35
FA16	45.70	45.24	0.57	6.55	0.18	0.22	0.88	0.21	0.33
Average	42.5	49.40	0.34	5.67	0.50	0.20	0.66	0.15	0.36

Table 6. Normalized glaze composition for ceramic sherds – group B

	SiO2%	PbO%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	Na2O%	CuO%
FA17	41.30	47.42	0.42	8.87	0.44	0.16	0.76	0.03	0.01
FA18	43.20	45.47	0.65	8.37	0.31	0.42	0.85	0.04	0.00
FA19	43.90	46.09	0.81	7.14	0.20	0.31	0.75	0.16	0.00
FA20	43.77	44.58	0.64	8.46	0.61	0.29	0.67	0.09	0.00
FA21	42.10	45.45	0.55	8.66	0.81	0.25	0.79	0.60	0.00
FA22	47.50	42.07	0.30	8.41	0.26	0.25	0.68	0.17	0.06
FA23	44.81	45.10	0.28	7.06	0.54	0.60	0.91	0.15	0.00
FA24	40.10	52.29	0.19	4.68	0.28	0.71	0.75	0.37	0.00
FA25	44.90	47.69	0.24	4.59	0.37	0.71	0.64	0.22	0.00
Average	43.50	46.24	0.45	7.36	0.42	0.41	0.75	0.20	0.007

Table 7. Normalized glaze composition for ceramic sherds – group C

	SiO2%	PbO%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	Na2O%	CuO%
FA26	42.10	48.83	0.49	5.85	0.74	0.73	0.63	0.13	0.01
FA27	42.80	48.65	0.67	4.94	0.95	0.67	0.51	0.40	0.02
FA28	43.90	47.60	0.17	6.15	0.34	0.57	0.89	0.28	0.00
FA29	45.22	47.10	0.29	5.23	0.19	0.66	0.97	0.12	0.04
FA30	44.05	46.10	0.37	7.24	0.38	0.86	0.59	0.16	0.01
FA31	41.30	47.10	0.81	7.32	0.45	0.97	0.83	0.39	0.00
Average	43.22	47.56	0.46	6.12	0.50	0.74	0.73	0.24	0.01

Table 8. Normalized glaze composition for ceramic sherds group D

	SiO2%	PbO%	TiO2%	Al2O3%	FeO%	MgO%	CaO%	Na2O%	CuO%
FA32	45.30	45.77	0.42	5.66	0.44	0.63	0.78	0.47	0.00
FA33	40.70	48.64	0.57	7.22	0.54	0.95	0.46	0.25	0.00
FA34	41.70	49.46	0.26	5.87	0.66	0.87	0.66	0.40	0.00
FA35	40.10	51.10	0.19	4.04	0.67	0.64	0.92	0.63	0.00
FA36	42.90	46.41	0.45	6.94	0.57	1.14	0.85	0.52	0.00
FA37	43.20	45.16	0.77	8.02	0.16	1.19	0.88	0.40	0.00
FA38	40.60	50.19	0.52	6.02	0.22	0.92	0.69	0.29	0.00
FA39	43.20	48.57	0.18	5.30	0.85	0.83	0.71	0.11	0.03
FA40	42.10	47.58	0.28	6.69	1.20	1.07	0.80	0.16	0.00
FA41	45.30	46.17	0.39	6.00	0.64	0.37	0.67	0.18	0.00
FA42	45.16	45.98	0.28	5.58	1.02	0.40	0.37	0.72	0.37
FA43	42.10	51.78	0.28	4.42	0.48	0.17	0.20	0.14	0.25
Average	42.69	48.06	0.38	5.98	0.62	0.76	0.66	0.35	0.05

Multivariate statistical analyses were applied in order to obtain more conclusive information from the datasets. Principal component analysis was used as a tool to graphically examine the grouping pattern of the samples in terms of chemical composition, i.e. to see if there were partitions in terms of pottery type. At the outset, the PCA was conducted on the entire data set consisting of all 43 ceramic sherds. The first two principal components subsume 69.752% of the total variance in the data set (Table 9), revealing a well segregated pattern between ceramic sherds. This means the data are highly correlated and can be indicated by the two principal components. The first two components, which describe most of the total variance in the elemental composition, usually best separate the different groups of samples based on the variance of its chemical composition. Statistical methods have been employed in archaeology since the 1950s and have often been used to study the provenance of artifacts (Figure 3) and show the bivariate plots of the two first principal components. This separation into groups can be attributed to the use of different componential raw materials in making the ceramics.

Table 9. Result of PCA performed on the dataset for all samples.

Component	Total	% of Variance	Cumulative %
1	3.022	43.166	43.166
2	1.861	26.585	69.752
3	1.235	16.542	86.294

(Total Variance Explained)

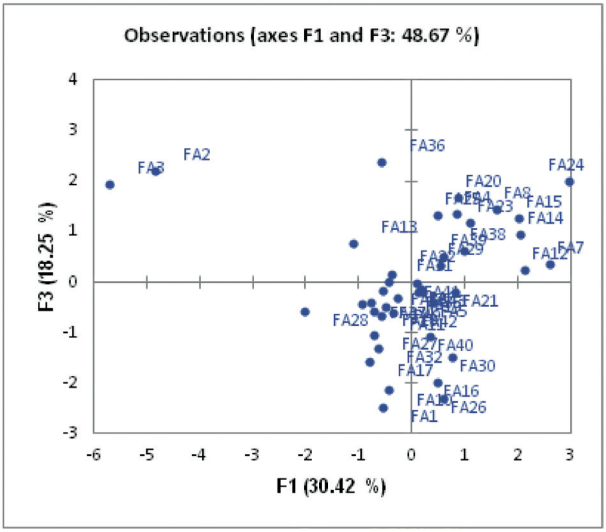


Figure 3. A bivariate plot of the first and third principal components showing the grouping of ceramic samples.

The bivariate plot shows that samples based on the similarity of chemical compositions were separated into four groups: Group 1 is located in the lower right region of Figure 3; samples of Group 2 are located in the upper right part of Figure 3. The sample for Group 3 is in the lower left section of Figure 3 while the rest of the samples are in the upper left part of the plot.

A primary division of the chemical data into two relatively distinct compositional groups is observable when all of the pottery samples (n = 43) are examined using RQ-mode PCA (Figure 4). Compressing the variability of seven element concentrations for each Tal Al Husun sample, the two dimensions represented in the biplot (principal components 1 and 2) account for about 69.75 percent of the original chemical variability in the entire data set. As illustrated in Figure 4, Group 1, Group 2, Group 3 and Group 4 separate from each other along the largest dimension of variation (principal component 1), which accounts for 43.166 percent of the original variability in the data set. Group 1 samples are characterized by high concentrations of calcium, magnesium and potassium. In contrast, Group 2 samples are low in the former elements and enriched in aluminum, titanium and silicon. This indicates that sixteen samples fall into Group 1, while nine samples are identified as Group 2, six samples belonging to Group 3 and the rest are represented by Group 4.

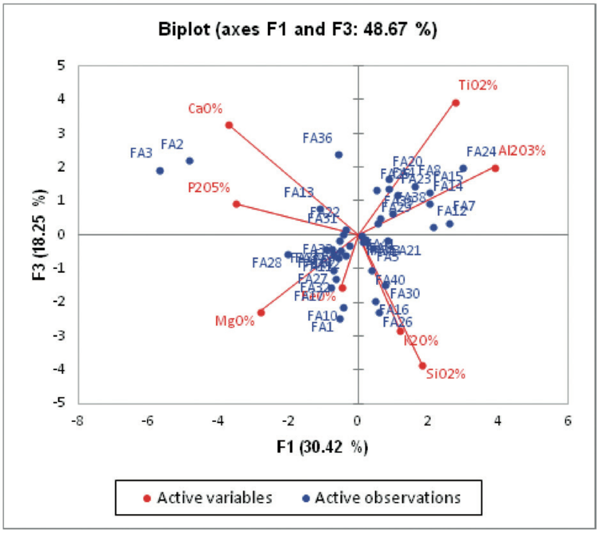


Figure 4. PCA biplot for Tal Al Husun samples

In order to confirm the previous samples' grouping by principle component analysis, a hierarchical clustering strategy was employed. It used the Ward method as a grouping rule according to the Euclidean distance computed on standardized co-ordinates. It generated the dendrograms in Figure 5 for the Tal Al Husun samples and show some remarkable features. The dendrogram in Figure 5 shows four groups. Group 2 contains sample FA23, FA24, FA28 and FA33, and is characterized by large concentrations of potassium and calcium and low concentrations of silica, except for sample FA2. However, Group 1, which includes samples FA3, FA4, FA5, FA6, FA7, FA8, FA9, FA10, FA11, and FA12, is also characterized by large concentrations of SiO_2, Al_2O_3 and low concentrations of K2O and CaO. Separation of samples on the basis of their composition can be due to natural differences in the clay composition.

Chemical analysis of the ceramic paste indicates that the content of the raw materials was very similar. As can be seen in Figure 6, the ternary plot shows the homogeneity of clay materials were made of non-calcareous, non-ferrous clay in general, except those in Group 4, which were made of calcareous and non-ferrous paste, while the third group was made from non-ferrous paste. This indicates the potter's high experience and knowledge in terms of clay selection, proportions, firing temperature, as well as glazing method and types. In the third group, the potter chose a ferrous paste to produce brown colored pottery, because he knew that it would be coated with a brownish layer as well. To produce a yellow and bright glazed ceramic, the potter chose a calcareous clay paste.

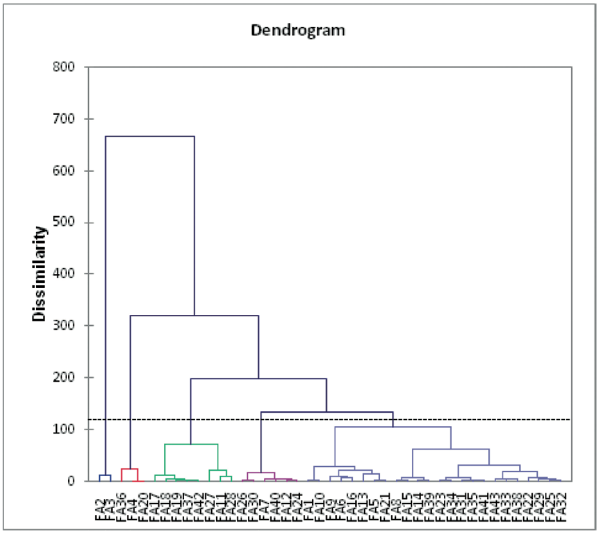


Figure 5. A dendrogram obtained by cluster analysis (Ward's method) of studied pottery sherds.

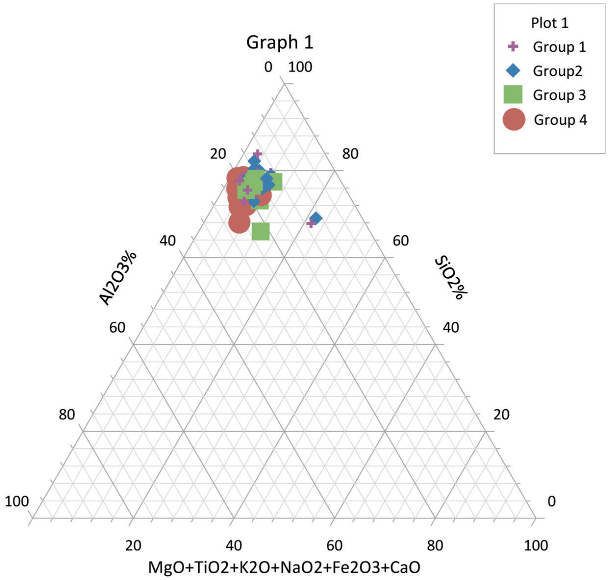


Figure 6. Ternary plot for SiO_2-Al_2O_3-alkalis+alkali earths shows the homogeneity of the studied ceramic samples.

The results in Tables 5, 6, 7 and 8 show that lead oxide was the main modifier which was added to produce the glaze layer. The glaze layer can be classified into high lead glaze where the percentage of lead oxide is between (52.29%) and (42.07%) (Figure 9). The chemical analysis in Tables 5, 6, 7 and 8 show that pottery fragments were made and produced using high-lead glaze, where lead oxide was added as the main modifier with an average of 49.40%. Silica was the main component with an average of 43.22%. The glaze also contains a small amount of alkalis (low alkalis) with an average of 0.21% and a very low amount of earth alkalis which reached an average of 0.75%. A relatively high content of alumina with an average of 6.25 % was also observed.

It seems that the potter used lead oxide and silica or chert to produce high lead glazes. The presence of low levels of alkali and alkaline earths may be indicative that it came unintentionally with the raw materials. Moreover, the relatively high percentage of alumina is an indication of clay origin. This confirms that the potter used sandstone as a basic material rather than using flint. In terms of colorants, it seems that the green color in Group A samples was a result of using copper oxide. In the dark-green glaze pottery, the average amount of copper oxide was (0.38%), while this amount decreased in the light green pottery to 0.29 %. Iron oxide was also used to give the brown color of the glaze layer, Group B had an average of about 0.42% while Group D had 0.62%.

3.1. Lead glaze technology

There are two ways to obtain lead glaze – either by brushing the surface with PbO, PbS or by immersing it in a mixture of lead mixed with silica [24,25]. The studied samples are characterized by the presence of a glaze layer on the inner surfaces, while the outer surfaces show low glaze ripple marks.

Based on the above, the technology for lead glaze was produced neither by immersing the body in the glaze solution nor by using a lead powder. In this method, lead is often applied to pottery vessels before drying and then fired one time, resulting in a severe interaction between the glaze and the body of the pottery. This was not the case for our samples. If so, the presence of reactive alkali, calcium, and aluminum, would be found scattered on the surface of the body. Tables 5, 6, 7 and 8 show that alkaline and earth alkaline ratios are very low in the glaze layer. This indicates that there is no interaction with the body of the pottery. The relatively high content of alumina could be explained by its presence within the glaze layer, or it has been added by the potter to obtain the desired glaze (Figure 7) [26-28].

It seems that in the case of our samples, the glazed layer was applied to the fired pottery using a brush. In order to confirm this assumption, interaction between the glaze layer and the body was studied under a scanning electron microscope. Figure 8 shows a clear boundary between the glazed layers and the pottery body in all studied samples, as well as the absence of interaction between them. This indicates the use of a double-combustion method in its production. Applying glaze on a pre-fired body produced the best product in terms of properties, where the hardened body acquires stiffness and durability. This procedure makes the glazing smooth and easy to handle [3,29].

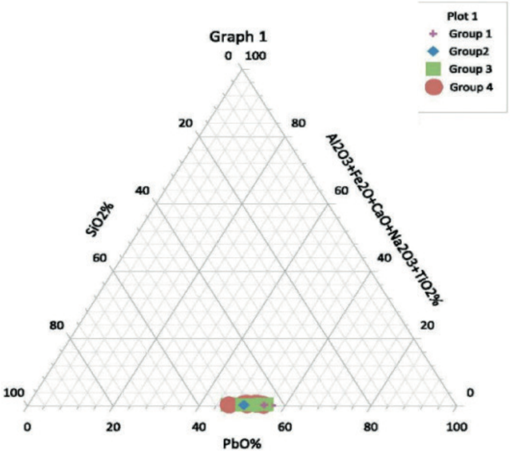


Figure 7. Ternary plot for glaze layer samples

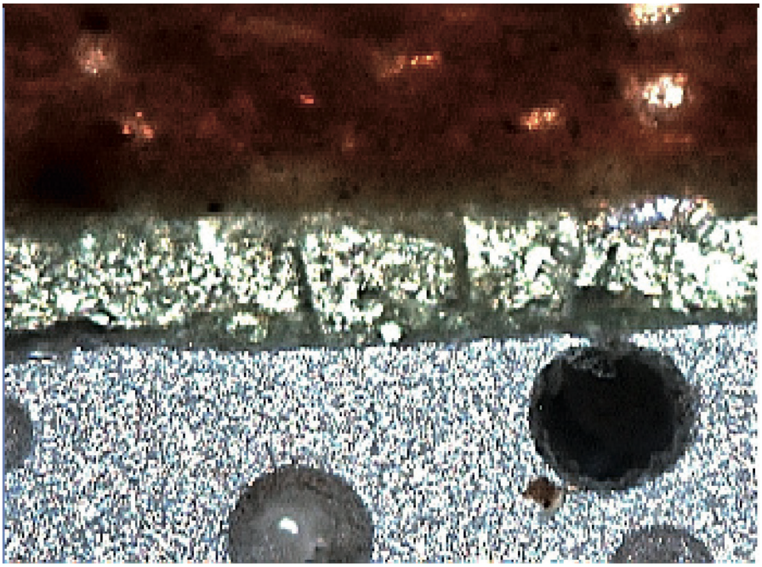
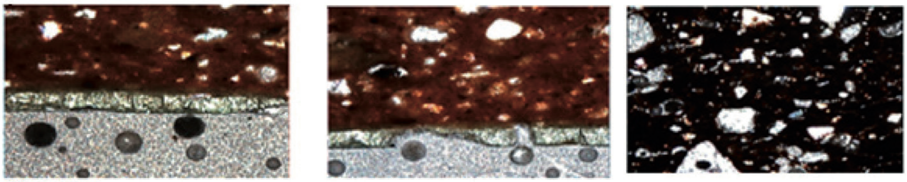
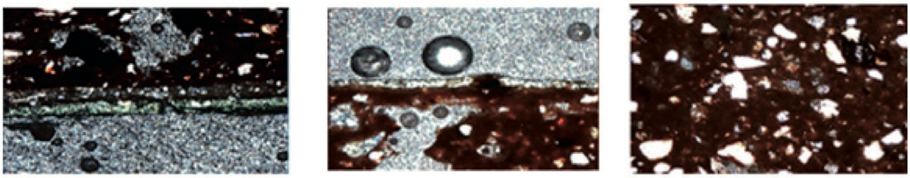


Figure 8. Micrograph showing the boundary between glaze layer and pottery body

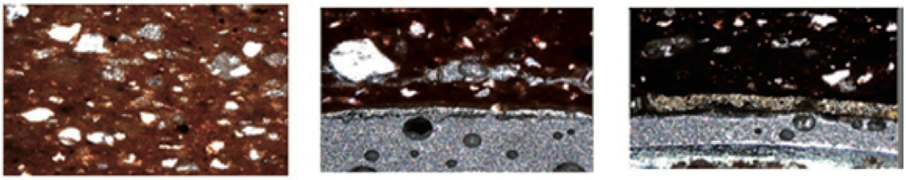
Mineralogical analysis results show similarity among the minerals which are part of the inclusions. For instance, quartz predominates. In Group A, petrographic inspection for FA1, FA8 and FA13 show remarkable similarities among the inclusions and the matrices (Figure 9). As can be seen from Figure 9a, b, c and d, the matrix in both sections is reddish brown and almost has the same morphology. The inclusions mainly consist of quartz, and it seems to be present naturally in the clay. Figure 9 shows photomicrographs for samples belonging to the subgroup a, b, c and d. Samples FA14 and FA22, FA29 and FA40 seem to be similar and all of them have quartz and calcite as inclusions; they also have a fine dark matrix. This in turn points to the idea that these samples probably have the same provenance.-They also share common coarse grain quartz as an inclusion. This in turn suggests the possibility of having the same clay material and hence the same origin. The identified inclusions in the previous samples consist mainly of quartz, plagioclase and calcite.



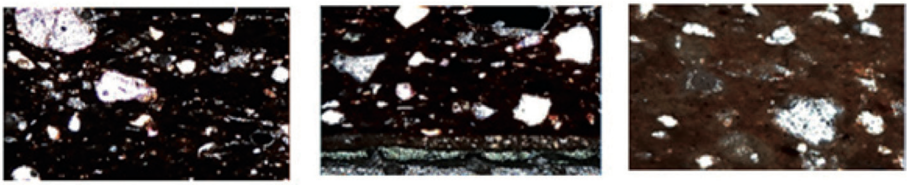
Group a



Group b



Group c



Group d

Figure 9. Representative micrographs for glazed ceramic samples for groups a, b, c and d.

Nevertheless, clay deposits can vary in chemical and mineralogical composition depending on their deposition level and geographical location. This explains the similar chemical composition of clays and rocks in that region. The fact that the potter used clay with the same composition means a local ceramic industry.

In order to assess the validity of pottery classification, and obtain a better understanding of their fabrication technology, the ceramic sherds of the three sites were characterized by XRD. Observation of the diffraction patterns for samples from these sites revealed important similarities. In fact, the different mineral assemblages which account for all samples can be proposed according to the observed mineralogical phases (Table 10, 11, 12 and 13). Representative XRD diagrams of these assemblages are shown in Figures 10 and 11. The first assemblage is represented by the XRD pattern of sample FA19. It exhibits quartz (Qz) and plagioclase (Pl) as the most intense peaks. In addition, important peaks are observed that correspond to hematite (He) and calcite (Ca) which are also found, but with peaks of lower intensity. Samples FA13, FA25, and FA31 are also ascribed to this assemblage. The second assemblage is represented by the XRD pattern of sample FA21 (Figure 11). Here, illite and calcite have totally decomposed, and pyroxene, gehlenite and plagioclase are more developed, while quartz (Qz) peaks are clearly observed. Samples FA11 and FA28 are also ascribed to this assemblage. Alkali feldspar can be observed in some cases and not in others. Hematite is also well observed in most samples of this assemblage.

Table 10. The mineral assemblages identified in ceramic sherds group a.

Sample	Phases				
FA1	Quartz	Plagioclase	Hematite	Gehlenite	
FA2	Quartz	Plagioclase	Hematite		
FA3	Quartz	Plagioclase	Gehlenite	Calcite	
FA4	Quartz	Calcite	Gehlenite	Plagioclase	Hematite Illite
FA5	Quartz	Calcite	Plagioclase	Illite	
FA6	Quartz	Calcite	Gehlenite	Plagioclase	Hematite
FA7	Quartz	Plagioclase	Calcite	Magnetite	
FA8	Quartz	Plagioclase	K-feldspar	Gehlenite	Hematite
FA9	Quartz	Hematite	Illite		
FA10	Quartz	Plagioclase	K-feldspar	Calcite	
FA11	Quartz	Hematite	Plagioclase		
FA12	Quartz	Plagioclase	K-feldspar	Gehlenite	Hematite
FA13	Quartz	Illite	Hematite		
FA14	Quartz	Plagioclase	Calcite	Hematite	Illite
FA15	Quartz	Plagioclase	K-feldspar	Calcite	Gehlenite Hematite

Table 11. The mineral assemblages identified in ceramic sherds group b.

Sample	Phases					
FA17	Quartz	Calcite	Plagioclase	Hematite		
FA18	Quartz	Plagioclase	K-feldspar	Gehlenite	Hematite	Calcite
FA19	Pyroxene	Diopside	Quartz	Gehlenite	Plagioclase	
FA20	Quartz	Calcite	Plagioclase	Hematite	Gehlenite	
FA21	Quartz	Calcite	Hematite	Mullite	Gehlenite	
FA22	Quartz	Plagioclase	Hematite	Gehlenite		
FA23	Quartz	Plagioclase	K-feldspar	Calcite	Gehlenite	Hematite
FA24	Quartz	Plagioclase	Gehlenite			
FA25	Quartz	Calcite	Plagioclase	Hematite	Gehlenite	Quartz

Table 12. The mineral assemblages identified in ceramic sherds group c.

Sample	Phases					
FA26	Quartz	Plagioclase	K-feldspar	Hematite	Calcite	Gehlenite
FA27	Quartz	Plagioclase	Gehlenite	Hematite	Calcite	
FA28	Quartz	Calcite	Gehlenite	Plagioclase	Hematite	
FA29	Quartz	Plagioclase	Gehlenite	Calcite		
FA30	Quartz	Plagioclase	K-feldspar	Calcite		
FA31	Calcite	Quartz	Gehlenite	Hematite		

Table 13. The mineral assemblages identified in ceramic sherds – group D.

Sample	Phases					
FA32	Quartz	Plagioclase	K-feldspar	Hematite	Calcite	
FA33	Quartz	Gehlenite	Diopside	Plagioclase	Hematite	Pyroxene
FA34	Quartz	Gehlenite	Calcite	Plagioclase	K-feldspar	
FA35	Quartz	Calcite	Gehlenite	Plagioclase	Hematite	
FA36	Quartz	Plagioclase	K-feldspar	Gehlenite	Pyroxene	Hematite
FA37	Quartz	Plagioclase	K-feldspar	Hematite	Illite	
FA38	Quartz	Calcite	Illite			
FA39	Quartz	Plagioclase	K-feldspar	Calcite	Hematite	
FA40	Pyroxene	Plagioclase	K-feldspar	Quartz	Hematite	
FA41	Quartz	Calcite	Hematite	Plagioclase		
FA42	Quartz	Plagioclase	Gehlenite	Calcite	Hematite	
FA43	Quartz	Calcite	Plagioclase	K-feldspar	Illite	Hematite

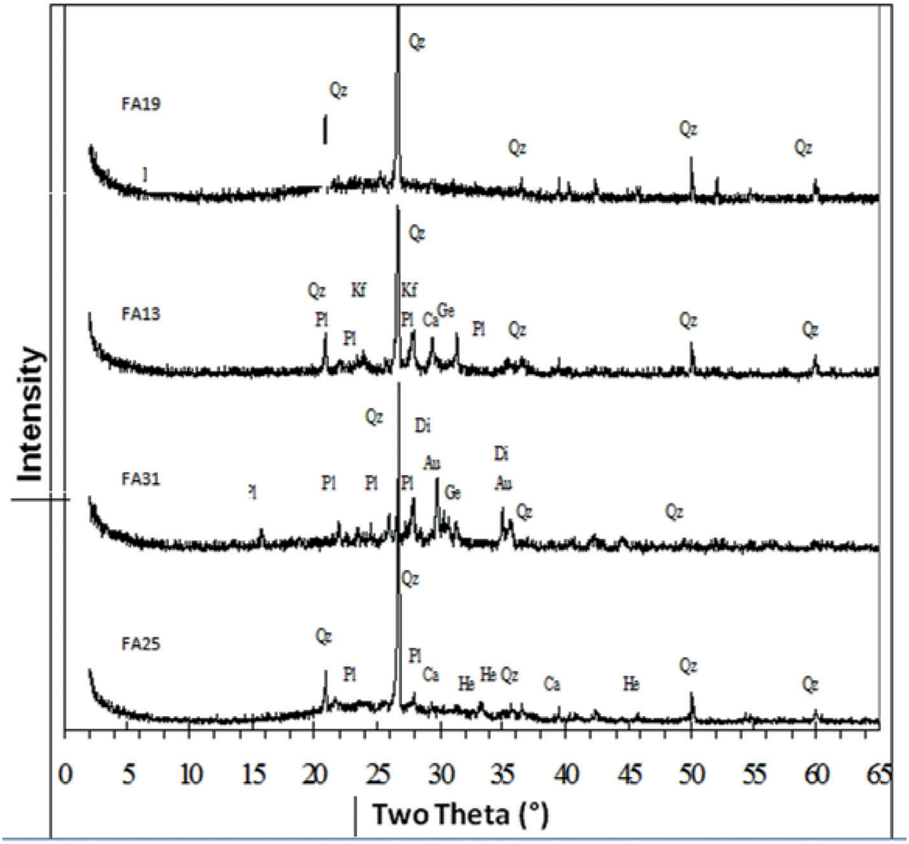


Figure 10. Representative XRD patterns of the samples from the Tal Al Husun site. The indicated mineral phases are: quartz (Qz), plagioclase (Pl), K-feldspar (KF), calcite (Ca), gehlenite (Ge), hematite (He), augite (Au) and diopside (Di).

By reviewing the mineral assemblages in Tables 10, 11, 12 and 13 and using petrographic results, one can notice the similarity among them. Thus, for the different groups that have been segregated according to their similarities, the following results can be concluded: Group A shows that the potter either tended to add the same inclusion ratio ≈ 50 % in FA102-JA and FA19 samples (Figure 9), or he might have used the same clay source with this natural distribution of inclusion. Inclusion in this group has the same size distribution and morphology 0.1 – 0.40mm in size, with a rounded to sub rounded shape, and occasionally has some sharp edge grains (Figure 9 a). The phase analysis results for Group A, showed the same phases. For Group B samples, the proportion of the inclusion is less than 23 % (Figure 9). The mineral assemblages are quartz, plagioclase, calcite, hematite, gehlenite, K-feldspar and pyroxene. Inclusions tend to have small size grains. Group 2 showed samples with the same dark matrix, and less inclusion ratios (~ 3 %) (Figure 9), with a rounded to sub-rounded shape. The same technology was used on samples belonging to the same chemical group.

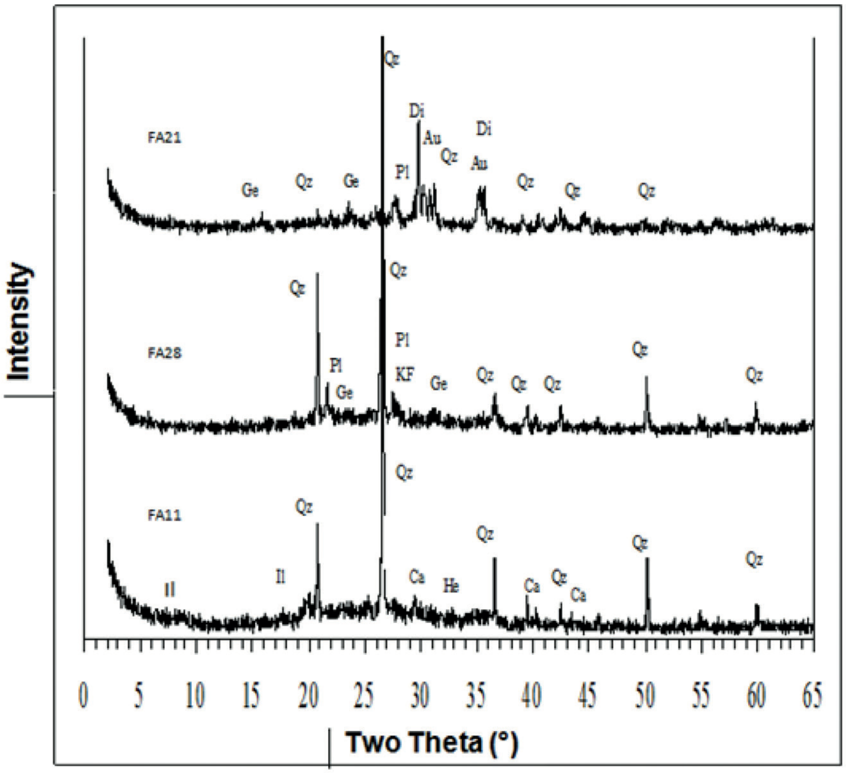


Figure 11. Representative XRD patterns of the samples from the Tal Al Husun site. The indicated mineral phases are: illite (Il), quartz (Qz), plagioclase (Pl), K-feldspar (KF), calcite (Ca), gehlenite (Ge), hematite (He), augite (Au) and diopside (Di).

The presence or absence of specific mineral phases in a ceramic product gives information on production technology.

Estimation of firing temperature may therefore be done on the basis of mineral assemblage, as the occurrence or absence of specific mineral phases at a given bulk composition provides constraints on the maximum firing temperature. It should be noted that the time and conditions of the firing process do not necessarily achieve a mineral assemblage which is at a thermodynamic equilibrium. This must be remembered in any attempt to predict the firing properties [25, 30]. However, a preliminary rough estimation of the firing temperature for each of the above mineral assemblages and interpretation of the mineralogical composition is still useful as a starting point. In order to explore this possibility, experiments were carried out on clay samples collected at the studied site.

The clay samples were fired under oxidizing conditions over a large temperature range (Figure 12). The original clay contains the following phases: illite-montmorillonite, calcite, dolomite, plagioclase, and quartz. As the temperature rises and reaches 500°C, the illite–montmorillonite mix layer is completely decomposed. At 600°C and before the temperature reaches 600°C, dolomite and calcite peaks are still seen. At 700°C and over, the peaks decomposed. When the temperature reaches 800°C, illite peaks start to decompose and low fire phases are absent. The intensity of clay peaks decreases over 800°C and disappear around 900°C. At over 900°C, new firing phases of pyroxene and hematite begin to crystallize.

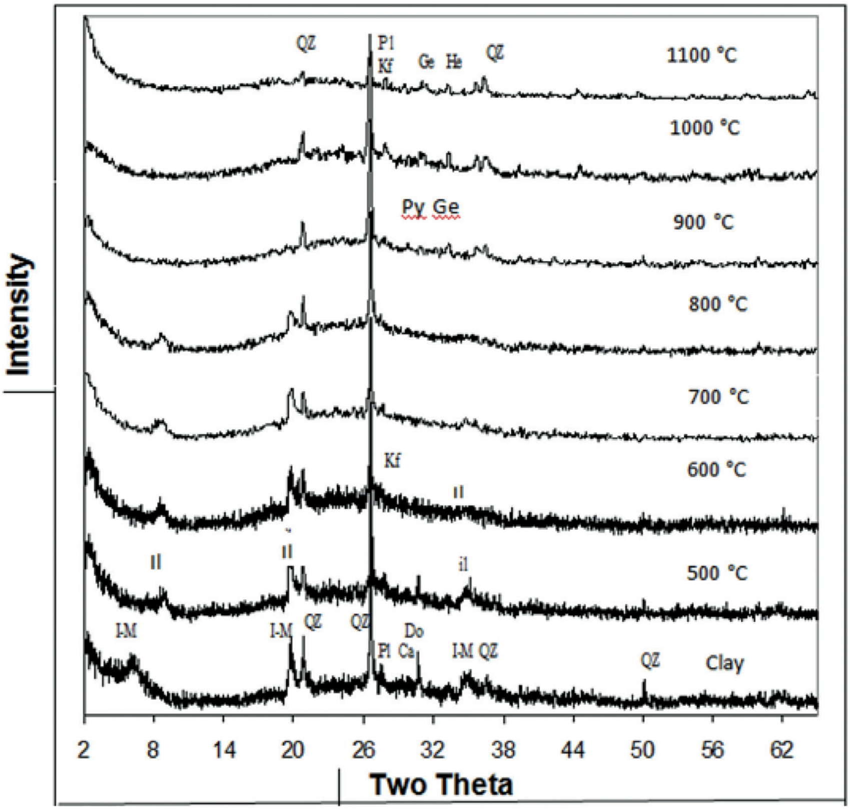


Figure 12. XRD patterns for clay sample, fired at different temperatures range under oxidizing conditions. The indicated mineral phases are: illite –montmorillonite (I-M), illite (Il), quartz (Qz), plagioclase (Pl), K-feldspar (Kf), calcite (Ca), gehlenite (Ge), pyroxene (Py), and hematite (He).

In addition, some primary phases also exhibit clear changes. Illite starts to undergo a decomposition process that is completed between 850°C and 900°C. In contrast, the illite (110) reflection is not essentially affected below 900–950°C and it is stable up to 1000–1050° C [31]. On the other hand, plagioclase shows an increasing intensity of the peaks that must be related to the crystallization of plagioclase minerals anorthite and albite. The growth of plagioclase peaks could overlap the weak peaks attributed to K-feldspar, which could otherwise also have decomposed at temperatures between 900°C and 950°C. Over 900°C, a new increase in intensity in pyroxene and gehlenite peaks is observed after the total decomposition of illite. Again, at over 1000°C, pyroxene and plagioclase peaks exhibit a further increase in intensity. At this temperature, quartz starts a reaction that continues up to 1100°C. Hematite – FeO is observed at a high temperature even at 1100°C. As the temperature goes up, calcite peaks start to decline until they vanish at 900 °C. Periclase, lime, and larnite peaks start to appear at 800°C and its intensity increases until 1100°C. At 900°C and over, gehlenite and pyroxene start to develop and increase, until reaching 1100°C. Plagioclase and K-feldspar peaks were seen once, but sometimes it is hard to distinguish them due to overlapping. Quartz peaks decline due to the reaction involved in forming larnite and pyroxene. By comparing the results of the mineral phases for both fired clay and the analyzed samples it seems that the potter fired his pottery at a temperature that exceeded 1000°C (Figure 13).

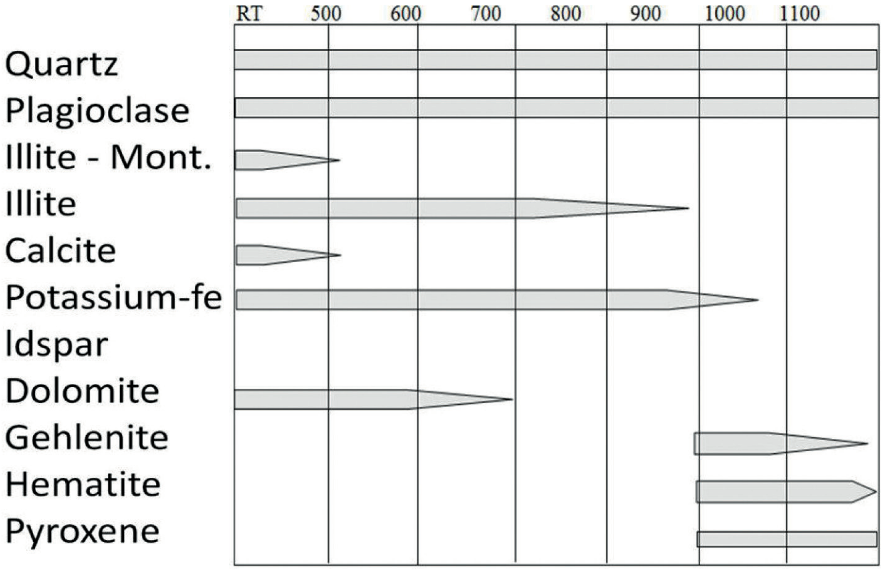


Figure 13. A bar diagram of firing experiments carried out on clay sample, in oxidizing conditions with heating rate of 2°C/ min, the indicated phases are: quartz; plagioclase; illite –montmorillonite; illite, calcite, gehlenite; pyroxene; hematite; dolomite; and potassium feldspar, R: room temperature.

4. Conclusions

It seems that in the region studied, the clays used to manufacture the ceramics are probably of local origin. The geological diversity attested in the area seems to support this conclusion of local clay sources [32]. The definition of some outliers among the samples from the region suggests another local clay source may have been used, or these samples could have been imported from another area. These imports are clearly identifiable by their distinct mineralogical and chemical characteristics.

Based on the mineral assemblages observed with XRD and the color of the sherds, the Ayyubid/Mamluk potter fired his pottery in a double-combustion method at a temperature exceeding 1000°C.

They used copper to obtain a green color and iron oxides for a reddish brown and yellow color. Lead glaze was used, and the glazed layer was applied using a brush to the fired pottery. The glaze is more compatible with clay containing a high proportion of quartz. The presence of lead enables the potter to control the color and viscosity of the glaze.

We can say that the Ayyubid/Mamluk potter was highly skilled, accurate and aware of material properties and knew the exact amount and ratios which had to be added to obtain a high-quality product.

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Biographical notes

Firas Alawneh is an Associate Professor of conservation science at the Hashemite University; in 2006 he obtained a PhD in material science and engineering at Arizona State University. Vice Dean at Queen Rania Faculty of Tourism and Heritage, as well as the head of the Department of Conservation Science since 2016. He has participated in several archaeological excavations, international projects, workshops and training courses. He teaches conservation science, including conservation and restoration theory and practice, materials characterization, history of architecture, documentation, and other courses. His research interests include conservation, restoration, material analysis and the history of architecture. He is the author of more than 30 publications in these areas.

Raed Alghazawi was born in 1972 in Irbid, Jordan. In 2000 he enrolled in the MA program in applied science in archaeology at Yarmouk University in Irbid, Jordan. The focus of the MA program was in museology and he graduated with a Master's degree in 2003. After completion of his MA, he started working at the Hashemite University, in the Queen Rania Faculty of Tourism and Heritage as a lecturer, with the primary task of teaching courses in museum studies. In 2006 he was awarded a grant to study his PhD in the Netherlands. In 2011 he finished his PhD studies. He is currently working as an associated professor at the Hashemite University in Zarqa, Jordan.

Fadi Balaawi graduated in July 2000 obtaining a M.Sc. in Earth and Environmental Sciences (Geochemistry, Sedimentology and Petroleum Geology), at the Earth and Environmental Department, Faculty of Science Yarmouk University. In September 2002 he obtained his second MA in Principles of Conservation, at the Institute of Archaeology, University College London, London: UK. In June 2006 he obtained a PhD in Conservation and Management of Archaeological sites, at the Institute of Archaeology, University College London, London, UK. From September 2016 to the present, he has been Dean of the Queen Rania Faculty of Tourism and Heritage, The Hashemite University, Zarqa, Jordan.

Summary

The aim of this work was to study the chemical and micro-structural composition of Ayyubid/Mamluk glazed ceramics excavated from Tal Al Husun, Jordan. The investigations were conducted to obtain information on raw materials and their technical processing (provenance and technology). To identify the clay materials and the glaze, ceramic bodies as well as glazed layers were analyzed using ICP–AES, optical microscope and X-ray diffraction (XRD). The samples were classified into four groups according to their clay paste and ceramic color. Results revealed that the ceramic object was made of a homogeneous paste (composed of non-calcareous, non-ferrous clay) containing a high proportion of quartz; the study also indicated that the ceramic samples had a high lead (Pb) content. This type of glaze was prepared by brushing the body of the pottery vessels with a mixture of lead and silicate solution. The analysis by scanning electron microscope, X-ray diffraction and optical microscope showed that the Ayyubid/Mamluk potter fired his pottery using a double-combustion method at a temperature exceeding 1000° C. As for the raw material used in the manufacture of the clay paste, evidence shows that the pottery body was made of local source material, while the glaze material was not locally available, and this is evidence that it was imported.

Riassunto

Scopo di questo lavoro è stato lo studio della composizione chimica e microstrutturale delle ceramiche invetriate di Ayybid/Mamluk scavate dal sito di Tal Al Husun in Giordania. Le ricerche sono state condotte per ottenere informazioni sulle materie prime e sui procedimenti tecnici. Per identificare i materiali e la superficie vetrosa, campioni ceramici e superfici vetrose sono state sottoposte ad analisi ICP-AES, microscopia ottica e diffrazione a RX (XRD). I campioni sono stati classificati in quattro gruppi secondo l'impasto argilloso e il colore ceramico. I risultati hanno evidenziato che l'oggetto ceramico è stato fatto di una pasta omogenea (composta da argilla non calcarea, ma ferrosa) contenente un'alta quantità di quarzo e che i campioni ceramici avevano un alto contenuto di piombo (Pb).

Questo tipo di superficie vitrea è stato preparato pennellando il recipiente di ceramica con una soluzione di piombo e silicato. L'analisi con microscopio elettronico a scansione, diffrazione a RX e microscopio ottico ha mostrato che il vasaio di Ayybid/Mamluk aveva cotto la sua ceramica usando un metodo di doppia combustione ad una temperatura al di sopra di 1000° C.

Come per la materia prima usata nella lavorazione della pasta di argilla, l'evidenza mostra che il corpo della ceramica è stato fatto con materiale locale, mentre il materiale vetroso non era disponibile localmente e, perciò, è stato importato.