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Archaeometric Characterization of Ceramic Finds Belonging to the Phrygian, Roman, and Byzantine Periods Ceramics from Yazılıkaya Midas Valley

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Abstract

Yazılıkaya Midas Valley, which forms our area of study, is one of the deep valleys in the south and southeast sections of the region. It is known as The Highlands of Phrygia now split between the modern-day provinces of Eskişehir, Kütahya, and Afyonkarahisar, is located approximately 70 km south of the city of Eskişehir in Turkey.The Akpara Fortress is found at the northern edge of the valley and the Yazılıkaya/Midas Fortress at the southeastern edge. Chemical analysis, XRD, XRD, and SEM/EDX analyzes were performed on the ceramic samples taken from Yazılıkaya Valley. Examining the phases and microstructure properties and evaluating the relevant literature studies determined that the ceramic pieces were fired at approximately 900-950°C in an oxidizing medium and did not contain any glaze layer. To determine whether local clay clays are used in ceramics, samples were taken from 3 different stream beds covered by the area. It can be said that D1 and D2 clays are shaped more easily due to the muscovite phase they contain, and these clays can be used with other additions in these ceramics. However, more samples and detailed studies are needed to support this view.

Yazılıkaya Midas Vadisindeki Frig, Roma ve Bizans Dönemlerine Ait Seramik Buluntuların Arkeometrik Karakterizasyonu

Özet

Çalışma alanımızı oluşturan Yazılıkaya Midas Vadisi, bölgenin güney ve güneydoğu kesimlerinde yer alan derin vadilerden biridir. Günümüzdeki Eskişehir, Kütahya ve Afyonkarahisar illeri arasında bölünmüş olan Frigya Yaylaları olarak bilinir, Türkiye'de Eskişehir şehrinin yaklaşık 70 km güneyinde yer alır. Akpara Kalesi vadinin kuzey ucunda, Yazılıkaya/Midas Kalesi ise güneydoğu ucunda yer almaktadır. Yazılıkaya Vadisi'nden alınan seramik örneklere kimyasal analiz, XRD, XRD ve SEM/EDX analizleri yapılmıştır. Gerek oluşan fazlar, gerekse mikroyapı özellikleri incelenerek ve ilgili literatür çalışmaları değerlendirilerek seramik numunelerin oksitleyici ortamda yaklaşık 900-950°C'de pişirildiği ve herhangi bir sır tabakası uygulanmadığı saptanmıştır. Seramik numunelerin yerel bölgedeki killer ile yapılıp yapılmadığını belirlemek için bölgenin kapsadığı 3 farklı dere yatağından da numuneler alınmıştır. Özellikle D1 ve D2 killerinin içerdiği muskovit fazından dolayı daha kolay şekillendiği ve bu killerin bu seramiklerde başka ilavelerle kullanılabildiği söylenebilir. Ancak bu görüşün desteklenebilmesi için daha fazla numuneye ve detaylı çalışmaya gerek vardır.

1. INTRODUCTION

Among the valleys of the highlands of Phrygia[1], the Yazılıkaya/Midas Valley is home to the most monumental, unparalleled examples of rock-cut monuments and Phrygian settlements. The valley is located within the borders of the Han and Seyitgazi Districts, approximately 70 km south of the city of Eskişehir in Turkey[2]. The valley's suitable topography and bordering rock formations beget the settlement of multiple civilizations in this area. In addition to the valley's cultic monuments dated to the Phrygian Period and the Phrygian, Hellenistic, Roman, and Byzantine Period rock-cut tombs, it is also home to fortress-type settlements to the north and east, veritably forming a border to the valley. The Midas Fortress is located in a rocky region in the south of the Eskişehir Province made up of black-grey volcanic tufa and narrow valleys. This is a significant fortress thanks to its location, unmatched Phrygian-period rock-cut monuments, and rock-cut tombs dating to the Phrygian, Hellenistic, Roman, and Byzantine Periods. The fortress possesses a wide field of vision looking out to the Akpara Fortress in the valley's northern corner, then the fortresses of Gökgöz, Pişmiş, and Kocabaş, all the way to the Kümbet Valley in the west[3]. The fortified settlements and fortress in the Phrygian Highlands were founded on natural hilltops protected by cliffs or very steeps. Located on the edge of plateaus or at high, inaccessible points where they can control entrance and exit to the valleys, these fortresses are noteworthy for their proximity to the surrounding agricultural and forested land. Thanks to their strategic locations, they are all quick and easy to defend. Due to their positions overlooking the roads, nearby routes could be easily controlled from these fortresses.

Most of these fortresses sit atop high, independent hills. Additionally, they are positioned near agricultural areas and sources of water, facing in directions from which they can control their surroundings. The monuments found in Yazılıkaya-Midas Valley and Kümbet Valley to its southeast in particular indicate that these valleys were the Phrygians most important holy areas. For this reason, defensive fortresses were built making use of the valley's topographic make up. Located on the These fortresses were inhabited from the Phrygian Period to Byzantine Period. Thanks to its rock-cut monuments indicative of a variety of settlements, the valley has piqued the interest of many researchers and travelers from the 18th century to today[1,4-8]. Since 2017, we have carried out surveys consisting heavily of documentation in the Yazılıkaya/Midas Valley, and of the Midas Fortress in particular[9-11]. In addition to providing new archeologic finds, this research has, in opposition to common knowledge, determined that the valley's history spans all the way back to the Lower Paleolithic Period[12].

In addition to architecture, ceramics provide tangible proof of culture in the fortress. Both the fortresses and the ceramics found in the lands surrounding them follow a chronology compatible with the architecture in the valley.

Samples taken from the ceramics recovered mainly from the Yazılıkaya/Midas Fortress, Akpara Fortresses, Yapıldak necropolis area found 4.5 km southwest of Yazılıkaya, the Sekiören settlement found near the top of the deep valley located 3 km northeast of Çukurca Village and the Karakuyu area to the southeast of Yazılıkaya, and were analyzed with sand samples pulled from the streambed known as the Sığırcık Kulağı Stream southwest of the Yazılıkaya/Midas Fortress (Fig. 1). The samples were taken from the fortresses and around the tombs.

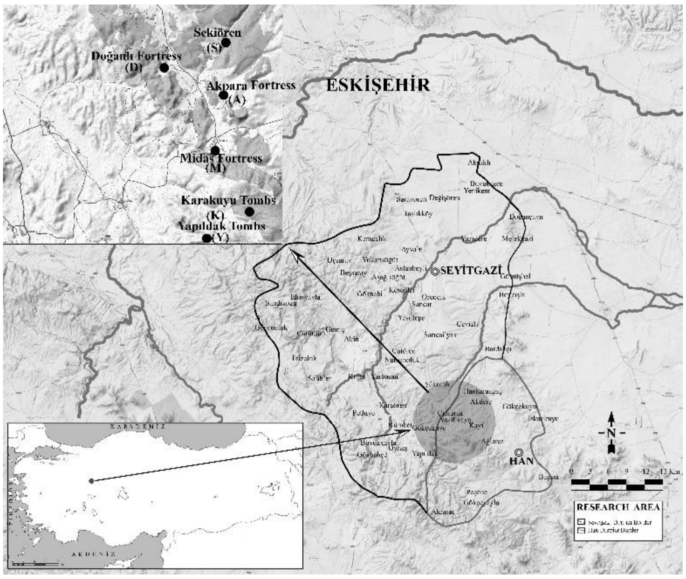

Figure 1. Localization map of the samples

In this work, we will use the ceramic finds recovered from the valley and a characterization of the sand sample taken from the streambed now known as the Sığırcık Kulağı Stream to examine the technology used to produce daily-use ceramics in the valley and whether or not these ceramics display qualities of local production. Ceramics samples for analysis were taken from 5 different ancient settlements which are: Midas and Akpara Fortress, Yapıldak Tombs, Sekiören Settlements, Karakuyu Tombs. The samples taken from the Midas Fortress consist of pithos and fragments of craters among storage containers, pots with cooking jars, and bowls with serving pots. The samples analyzed in this group are ceramics dating to the Phrygian period. Ceramic samples taken from Akpara Fortress are craters from storage containers, bowls from service containers, unguentariums with cosmetic containers, and pieces of jar with cooking vessels. The pottery analyzed in this group is dated to the Phrygian period, while the other pieces are dated to the Roman Period. The ceramics found around the tombs in the Yapıldak Necropolis are pieces of amphora and bowls used as storage containers and they are dated to the Late Roman-Early Byzantine period. The samples of ceramics taken from the Sekiören settlement include pithos, a storage container, bowls, plates and jugs used as serving containers, and jars used as cooking containers. Ceramics evaluated in this group are dated to the Roman and Byzantine Periods. The ceramics found around the rock-cut tombs in Karakuyu Settlement, on the other hand, are ceramics from serving bowls and jars from cooking vessels. These ceramics are also dated to the Late Roman-Early Byzantine Period. All of these ceramics are made on pottery wheel, the clay and slip of these ceramics was shades of gray, buff, light reddish, light reddish brown.

This study is the first study conducted in this region considering these samples. By examining the chemical compositions and phases in it, it aims to be a preliminary reference study for other archaeometric studies in this region in the future.

2. MATERIALS & METHODS

2.1. Selection of the archaeological samples

The ceramic samples investigated were collected at the archaeological site of the Yazılıkaya as given in Fig. 1. According to their differences, and appearance regarding to the color, ornament, function, thickness, 39 broken ceramics samples, and 3 clays (from this region as a powder form) selected for this study (Table 1). Images of the archaeological samples investigated in this study are given in Fig.2 to Fig.6. The colour of the surfaces ranges from beige to reddish-brown. Samples from Midas Fortress, denoted as M1 to M14 (Group M), are given in Fig. 2. Samples' colors of the bodies range from reddish brown to black generally.

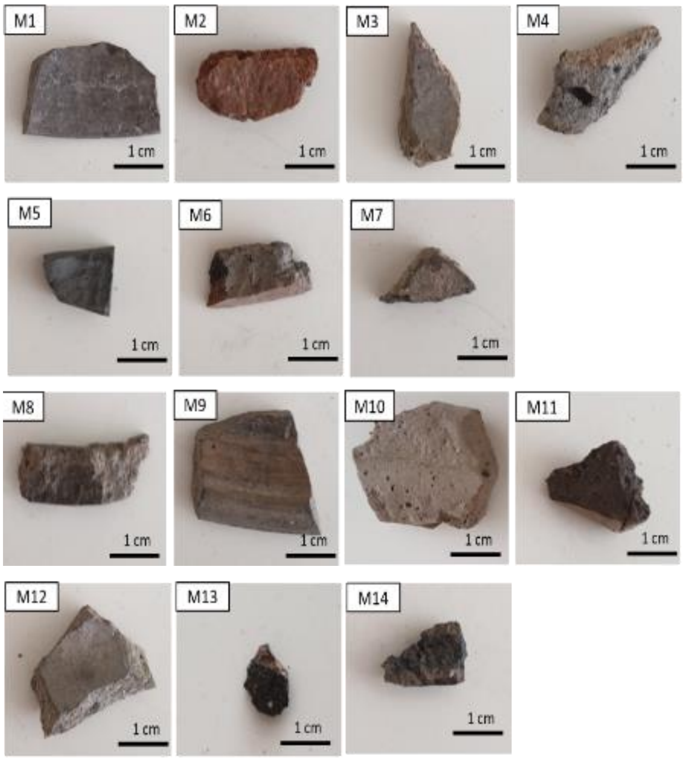

Figure 2. The images of the samples (Group M).

Samples from Akpara Fortress, denoted as A1 to A4 (Group A), are given in Figure 3. A1 has reliefs on the surface. A1, A2 color are generally reddish-brown, A3 color is grey, A4 color is partically black.

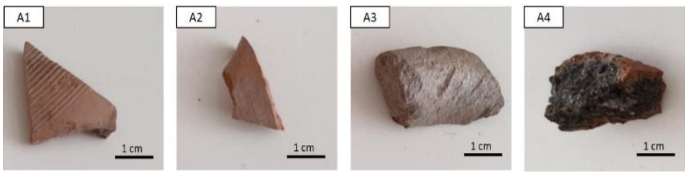

Figure 3. The images of the samples (Group A)

The pictures of the Yapıldak Tomb Samples, denoted as Y1 to Y6 (Group Y), are given in Figure 4.

Pictures of the ceramic samples taken from Karakuyu Tombs, donated as K1 to K3, are shown in Fig. 6. It has a reddish brown color in samples from K1 to K3.

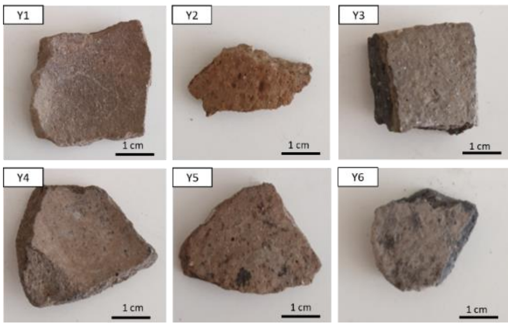

Figure 4. The images of the samples (Group Y)

Figure 5. The images of the samples (Group S)

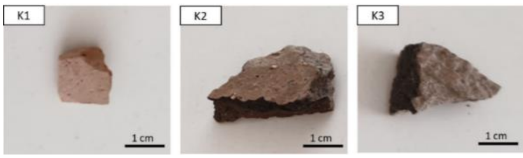

Figure 6. The images of the samples (Group K)

2.2. Preparation of the samples

Samples have been cut by diamond cutting discs and surfaces have been abraded by SiC grinding papers and washed the samples for three days in deionized water to remove all impurities from the deposition. Powders of the samples were prepared in an agate mortar in order to be analysed by XRF and XRD techniques.

2.3. Characterization of the samples

Major oxide content by mass of the ceramic material must be known in order to compare samples. For this purpose, the powdered samples were compressed as pellets in order to perform the analysis with Skyray EDX-6000B, using X-ray fluorescence spectroscopy procedure. EDX 6000B X-ray Fluorescence spectrometer used for XRF analysis. It is a convenient 7 sample auto-carousel for simultaneous XRF analysis of multiple samples. The instrument features low-energy X-rays specifically for excitation of the elements. Pellets were made by grinding several grams (5-10 grams) of precleaned ceramic archeological samples into a fine powder (200-300 mesh). Chemical analysis were carried out as detailed in Table 2.

The crystalline phases of the archeological finds were identified by X-ray diffraction (XRD) method. The analysis were performed on powdered form of samples which were scanned at a scanning speed of 2°/min in the range of 10-70° with CuKα radiation. (λ = 0.154 nm) at 40 kV and 40 mA conditions using RIGAKU 2200 DMAX diffractometer.

The microstructures of the samples were investigated by scanning electron microscopy (SEM) analysis with the use of Philips XL30 SFEG SEM. For SEM observations specimens were prepared by grinding with SiC abrasive papers while being lubricated with water and then polished using diamond pastes. EDX (Oxford Inst. 5108 Link) analysis were performed simultaneously with microstructural observations.

Table 1. Explanation of the samples depend on their region, forms and periods

Sample Name	Find Spot	Form	Period
M1	Midas Fortress	Bowl	Phrygian Period
M2	Midas Fortress	Pithos	Phrygian Period
M3	Midas Fortress	Amphora	Phrygian Period
M4	Midas Fortress	Pithos	Phrygian Period
M5	Midas Fortress	Bowl	Phrygian Period
M6	Midas Fortress	Crater	Phrygian Period
M7	Midas Fortress	Crater	Phrygian Period
M8	Midas Fortress	Jar	Phrygian Period
M9	Midas Fortress	Crater	Phrygian Period
M10	Midas Fortress	Crater	Phrygian Period
M11	Midas Fortress	Jar	Phrygian Period
M12	Midas Fortress	Crater	Phrygian Period
M13	Midas Fortress	Jar	Phrygian Period
M14	Midas Fortress	Jar	Phrygian Period
M15	Sığırcık Kulağı Stream	Powder	Modern Period
D1	Çirkindere Stream	Powder	Modern Period
D2	Eğriova Stream	Powder	Modern Period
A1	Akpara Fortress	Bowl	Roman Period
A2	Akpara Fortress	Unguentarium	Roman Period
A3	Akpara Fortress	Crater	Phrygian Period
A4	Akpara Fortress	Jar	Phrygian Period
Y1	Yapıldak Tombs	Bowl	Late Roman Period-Early Byazantine Period
Y2	Yapıldak Tombs	Bowl	Late Roman Period-Early Byazantine Period
Y3	Yapıldak Tombs	Amphora	Late Roman Period-Early Byazantine Period
Y4	Yapıldak Tombs	Bowl	Late Roman Period-Early Byazantine Period
Y5	Yapıldak Tombs	Bowl	Late Roman Period-Early Byazantine Period
Y6	Yapıldak Tombs	Bowl	Late Roman Period-Early Byazantine Period
S1	Sekiören Settlement	Jar	Roman Period-Byzantine Period
S2	Sekiören Settlement	Jar	Roman Period-Byzantine Period
S3	Sekiören Settlement	Jar	Roman Period-Byzantine Period
S4	Sekiören Settlement	Jar	Roman Period-Byzantine Period
S5	Sekiören Settlement	Bowl	Roman Period-Byzantine Period
S6	Sekiören Settlement	Pithos	Roman Period-Byzantine Period
S7	Sekiören Settlement	Jar	Roman Period-Byzantine Period
S8	Sekiören Settlement	Plate	Roman Period-Byzantine Period
S9	Sekiören Settlement	Bowl	Roman Period-Byzantine Period
S10	Sekiören Settlement	Jar	Roman Period-Byzantine Period
S11	Sekiören Settlement	Jug	Roman Period-Byzantine Period
S12	Sekiören Settlement	Bowl	Roman Period-Byzantine Period
K1	Karakuyu Tombs	Bowl	Late Roman Period-Early Byzantine Period
K2	Karakuyu Tombs	Jar	Late Roman Period-Early Byzantine Period
K3	Karakuyu Tombs	Jar	Late Roman Period-Early Byzantine Period

Table 2. XRF results of ceramic samples from Midas Fortress region

	Samples													
Oxides	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13	M14
Na_2O	0.0876	0.6009	0.0989	0.4860	0.5720	0.0909	0.0767	0.0898	0.0750	0.4537	0.7200	0.0898	0.6200	0.7508
MgO	0.5655	0.5610	0.6633	0.7675	0.6463	0.5643	0.5587	0.4794	0.4863	0.6476	0.3463	0.6794	0.2063	0.3163
Al_2O_3	10.0221	11.5212	9.9864	14.8670	14.3318	9.7834	9.6409	10.0400	9.9652	12.235	14.1118	10.1324	13.1800	14.0800
SiO_2	47.6754	60.3709	45.437	60.2000	61.4658	45.377	45.3580	45.6250	45.798	55.0821	60.5558	46.8155	60.9700	60.2518
P_2O_5	0.1240	0.1236	0.2120	0.1650	0.1777	0.1902	0.1920	0.1902	0.1800	0.1672	0.1177	0.2028	0.01012	0.1017
SO_3	0.1603	0.0234	0.1976	0.00	0.00	0.1775	0.1885	0.1073	0.1462	0.0521	0.00	0.1153	0.00	0.00
K_2O	2.5705	2.3442	2.4150	4.0120	4.1627	2.1115	2.4007	1.9800	2.1012	2.3089	4.1007	1.9331	4.7708	4.6570
CaO	20.5438	2.3054	19.158	3.0989	3.0843	19.575	19.9820	17.2568	19.9800	7.7536	3.0743	18.8258	3.1011	3.2430
TiO_2	0.4306	0.7203	0.3376	1.0200	1.0703	0.1399	0.2398	0.3667	0.1469	0.5603	1.0003	0.3386	1.0500	1.0700
Cr_2O_3	0.0786	0.0546	0.0686	0.0670	0.0729	0.0650	0.0473	0.0567	0.0540	0.0695	0.0529	0.0677	0.0329	0.0399
MnO	0.1120	0.1774	0.102	0.1508	0.1697	0.0920	0.0925	0.1143	0.0811	0.1575	0.1677	0.1273	0.1377	0.1170
Fe_2O_3	3.9590	7.5600	3.8667	7.0989	7.8917	3.5507	3.9458	3.9319	3.9509	5.497	5.8917	3.7309	5.6910	5.3917
L.O.I.	13.6706	15.8983	10.467	8.0669	6.3548	18.2826	18.6726	19.7619	17.0352	15.0155	9.8608	16.9414	10.2308	9.9808

Table 3. Mineralogical content of M group samples

Sample	Minerals/Phases
M1	Quartz, K-fedspar, Scawtite, calcite
M2	Quartz, calcite, K-fedspar, hematite
M3	Quartz, scawtite, calcite
M4	Quartz, calcite, K-fedspar, hematite
M5	Quartz, scawtite, calcite, K-fedspar
M6	Quartz, scawtite, calcite, K-fedspar
M7	Quartz, scawtite, calcite, K-fedspar
M8	Quartz, scawtite, calcite, K-fedspar
M9	Quartz, scawtite, calcite, K-fedspar
M10	Quartz, calcite, hematite, K-fedspar
M11	Quartz, calcite, hematite, K-fedspar
M12	Quartz, calcite, hematite, K-fedspar
M13	Quartz, calcite, hematite, K-fedspar
M14	Quartz, calcite, hematite, K-fedspar

3. RESULTS AND DISCUSSION

3.1. Chemical and mineralogical analysis

Chemical analysis results concluded four major ceramic groups. XRF results of the samples are given in Table 2, Table 4, Table 6, Table 8, Table 10, and Table 12. Table2, shows the chemical analysis of the ceramic samples from Midas Fortress region denoted as M1 to M14.

Quartz (SiO_2), calcite ($CaCO_3$), K-feldspar ($KAlSi_3O_8$), hematite (Fe_2O_3), scawtite ($Ca_7Si_6O_{18}CO_3(OH)_2$) were detected in the samples of Group M (Table 3). The relationship between the presence of minerals, their quantities, sizes and the performance of ceramics may be directly linked to the technological processes by which archaeological ceramics are made.[13] The scawtite was detected in samples M1, M3, M5, M6, M7, M8, and M9. Since ancient earthenware ceramics were almost fired below 1000°C, gehlenite ($Ca_2Al[AlSiO_7]$) should indeed have been formed during oxidizing firing.[13,14] However, this phase is rarely detected in such ceramics with some notable exceptions, for example, when the ceramics were buried under strongly arid conditions. In contrast to this, in contact with soil solutions, gehlenite transforms to zeolitic minerals. Gehlenite reacts with diluted inorganic (HCl) and organic (acetic, oxalic, citric, aspartic, tartaric) acids to hydrogrossularate under moderate humid conditions in the presence of CO_2 to wairakite ($Ca[AlSi_2O_6]2.2H_2O$), garranite ($NaCa_{2.5}[Al_3Si_5O_{16}]_2.14H_2O$), scawtite, and montmorillonite $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}_nH_2O]$, and under very humid conditions in the presence of humic acids and CO_2, to calcium carbonate modifications with different stabilities with respect to calcite that finally remains as the thermodynamically stable phase , together with smectites.[14,15] Quartz, calcite, hematite, and feldspar were dominant for M2, M4, M10, M11, M12, M13, M14 samples. The presence of hematite in the samples should be body colorants of the samples in reddish colors. Depend on the over-firing of the samples color of some samples turned to black such as: M11, M13, and M14.

Chemical analysis of the ceramic samples from Akpara Fortress are given in Table 4. Chemical analysis of samples taken from this region are very similar among themselves.

Table 4. XRF results of ceramic samples from Akpara Fortress

	Samples			
Oxides	A1	A2	A3	A4
Na_2O	0.3289	0.2680	0.2800	0.5629
MgO	0.5827	0.6255	0.7789	0.6072
Al_2O_3	11.6809	11.5907	11.1240	11.4641
SiO_2	52.7705	52.8726	55.7115	52.3251
P_2O_5	0.1233	0.1248	0.2229	0.1348
SO_3	0.0319	0.0308	0.1283	0.0836
K_2O	3.2106	3.109	2.9319	3.1901
CaO	1.7705	1.1980	1.7858	1.8079
TiO_2	0.6090	0.605	0.4000	0.9311
Cr_2O_3	0.0765	0.0892	0.0677	0.0788
MnO	0.1877	0.1980	0.1293	0.22670
Fe_2O_3	6.7809	6.8690	7.8320	9.3106
L.O.I.	21.8466	22.4197	18.607	19.2831

XRD analysis of the Group A samples is given Table 5. The dominant phases for all 4 samples are hematite, quartz, calcite, K-feldspar. Mineralogical, quartz is stable until approximately 1150°C, although a modification from α-to-β- quartz takes place at approximately 573°C. When fired for a long time at high temperatures quartz will recrystallize into the higher temperature silica forms, such as trydimite (867°C) and crystoballite (1250°C). However, quartz is stable even at high temperatures (>1000°C), so it can not be considered for the estimation of the firing temperature.[15-17] Depending on the firing processes such as atmospheric conditions and temperature phase formation phenomena becomes important in the archeological samples.

The oxidation conditions include the removal of carbon and produce a reddish-brown color, resulting from the oxidation of iron and iron-rich minerals such as Fe_2O_3. In oxidizing firing conditions and at an adequate temperature, hematite commonly forms.[17] Well-crystallized hematite is a significant component only at a temperature of 900°C.[18,19] These samples also have calcite phase. Calcite is commonly used as a temper in archeological ceramics, therefore its thermal breakdown can ve often be used as an indicating the firing temperature. For all A group samples have calcite in the XRD analysis. According to the Grapes[20], calcite reacts at 600-700°C, which is unlikely taking into account that it still remains in some pottery sherds.

Chemical analysis of the ceramic samples from Sekiören Settlement are given in Table 6. It is seen that the higher the amount of iron oxide, the darker the color of the samples. In general, the amounts of SiO_2, CaO, K_2O, and Fe_2O_3 in these samples are remarkable. The amount of CaO in S4, S7, S10, S11, S12 samples is higher than the samples in this region, and it has been observed that these samples with high calcite content crumble quite easily.

Table 5. Mineralogical content of A group samples

Sample	Minerals/Phases
A1	Quartz, hematite, K-feldspar, calcite
A2	Quartz, hematite, K-feldspar, calcite
A3	Quartz, hematite, K-feldspar, calcite
A4	Quartz, hematite, K-feldspar, calcite

Table 6. XRF results of ceramic samples from Sekiören Settlement

	Samples											
Oxides	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Na_2O	0.8176	0.9130	0.8270	0.2854	0.6208	0.6129	0.2900	0.8003	0.7900	0.2980	0.3000	0.3400
MgO	0.6129	0.6730	0.6790	0.6560	0.7107	0.6108	0.7579	0.5720	0.4750	0.6129	0.6200	0.6500
Al_2O_3	12.4326	12.5600	13.4700	14.9450	12.0680	11.8612	14.9670	12.3600	11.4800	11.0905	11.5900	11.5283
SiO_2	62.9967	60.2200	60.250	55.0584	60.02	60.5799	60.2850	60.0000	60.0000	50.3020	50.2700	50.2588
P_2O_5	0.1271	0.1100	0.1187	0.1589	0.1575	0.1363	0.1502	0.0900	0.0800	0.1200	0.1306	0.1528
SO_3	0.1015	0.1270	0.1110	0	0	0.0364	0.0450	0.1180	0.1280	0.0269	0.0270	0.0401
K_2O	2.4230	3.3300	3.3550	4.8562	2.5609	2.5462	4.8600	3.3500	3.3700	2.7208	2.7305	2.7671
CaO	1.8992	2.2500	2.4780	6.2380	3.875	2.5374	6.3400	2.2000	2.2200	7.0980	7.5608	8.6956
TiO_2	0.6856	0.7200	0.7545	0.7234	0.7286	0.9133	0.8670	0.6700	0.5747	0.7600	0.6702	0.6975
Cr_2O_3	0.0687	0.0650	0.0690	0.0700	0.675	0.0753	0.0750	0.0550	0.4870	0.0800	0.0755	0.0733
MnO	0.1826	0.1702	0.1832	0.1431	0.1100	0.1874	0.1500	0.1502	0.1500	0.1607	0.1709	0.1849
Fe_2O_3	6.4910	5.2750	6.8774	6.2985	4.3240	7.3695	6.3770	5.0720	5.1780	6.3600	6.4500	7.3827
L.O.I.	11.1605	13.587	10.8272	10.5711	14.95	12.5334	3.8359	14.5625	15.0673	20.3702	19.4045	17.2289

XRD analysis of the Group S is given Table 7. The dominant phases for all 4 samples are generally hematite, quartz, calcite, K-feldspar. All the phases are similar with A group samples.

Table 7. Mineralogical content of S group samples

Sample	Minerals/Phases
S1	Quartz, hematite, K-feldspar, calcite
S2	Quartz, hematite, K-feldspar, calcite
S3	Quartz, hematite, K-feldspar, calcite
S4	Quartz, hematite, K-feldspar, calcite
S5	Quartz, hematite, K-feldspar, calcite
S6	Quartz, hematite, K-feldspar, calcite
S7	Quartz, hematite, K-fedspar, calcite
S8	Quartz, hematite, K-feldspar, calcite
S9	Quartz, hematite, K-feldspar calcite
S10	Quartz, hematite, K-feldspar, calcite
S11	Quartz, hematite, K-feldspar, calcite
S12	Quartz, hematite, K-feldspar, calcite

Chemical analysis of the ceramic samples from Yapıldak Tombs are given in Table 8. The K_2O ratio in Y3, Y4, and Y5 samples is lower than the other samples. The K_2O ratio is 0.5973 wt.%, 0.3909 wt.%, and 0.6736 wt.% in these samples, respectively. Fe_2O_3 content is close to each other in all samples. The XRD results of the samples taken from the Yapıldak Tombs are represented in Table 9. According to these results, quartz, hematite, K-feldspar, and calcite were stand out for Y1, Y2, and Y6 samples. Quartz, hematite and scawtite were obtained for Y3, and Y4. The presence of calcite and scawtite, would lead to infer a maximum firing temperature between 900-950°C.[21] Potassium feldspar phase was not found in Y3, Y4 and Y5 samples, which have very low potassium oxide content in their chemical analysis.

Table 8. XRF results of ceramic samples from Yapıldak Tombs

	Samples					
Oxides	Y1	Y2	Y3	Y4	Y5	Y6
Na_2O	0.6448	0.6000	0.8995	0.7686	0.8295	0.7949
MgO	0.6416	0.5609	0.5973	0.5546	0.5598	0.6213
Al_2O_3	17.2579	13.5022	12.8249	12.9870	13.3230	13.9989
SiO_2	58.3775	60.1701	62.9464	62.4434	60.4780	55.7373
P_2O_5	0.1394	0.1106	0.1282	0.1192	0.1300	0.1536
SO_3	0.1009	0.0204	2.3126	2.2600	2.2348	0.0634
K_2O	3.3229	3.4420	0.5973	0.3909	0.6736	3.7264
CaO	2.3566	2.3205	2.0072	2.0827	1.9902	4.7325
TiO_2	0.9083	0.7130	0.6876	0.7709	0.5893	0.8118
Cr_2O_3	0.0692	0.0536	0.0706	0.0598	0.0503	0.0691
MnO	0.1982	0.1787	0.1854	0.1502	0.1734	0.1754
Fe_2O_3	7.8747	7.3600	6.2915	6.6955	6.2915	6.9117
L.O.I.	8.108	16.6469	10.9649	13.5314	17.6725	12.2037

Table 9. Mineralogical content of Y group samples

Sample	Minerals/Phases
Y1	Quartz, hematite, K-feldspar, calcite
Y2	Quartz, hematite, K-feldspar, calcite
Y3	Quartz, hematite, scawtite, calcite
Y4	Quartz, hematite, scawtite, calcite
Y5	Quartz, hematite, calcite
Y6	Quartz, hematite, K-feldspar, calcite

Another place where archaeological finds were found in the study is the Karakuyu Tombs. These samples are also coded as K1, K2, and K3. Chemical analysis results are given in Table 10. According to the chemical analysis results, the K1 sample results differs from the K2 and K3 samples. In the K1 sample, the CaO ratio is 18.2376 wt. %, Fe_2O_3 ratio is 6.2342 wt.%, SiO_2 ratio is 35.26 wt.%, Fe_2O_3 ratio is 6.2342 wt.%, and Al_2O_3 ratio is 6.12 wt.%. The amount of CaO in this sample is considerably higher than the K2 and K3 samples. In K2 and K3, the amounts of Al_2O_3, K_2O, CaO, Fe_2O_3 components are very close to each other. When evaluated the mineralogical phase analysis, the phases formed in the K1 sample are the dominant of quartz, calcite, scawtite, hematite. In the K2 and K3, the dominant phases are quartz, K-feldspar, hematite, and scawtite. The phases formed in the K2 and K3 are the same (Table 11). The colors of these samples are also similar.

Table 10. XRF results of ceramic samples from Karakuyu Tomb

	Samples		
Oxides	K1	K2	K3
Na_2O	0.0579	0.4234	0.4128
MgO	0.6724	0.6498	0.6492
Al_2O_3	6.1200	17.8716	17.6492
SiO_2	35.2623	50.4000	50.5088
P_2O_5	0.2408	0.1278	0.1579
SO_3	0.2598	0.0514	0.0631
K_2O	0.6477	2.055	2.0721
CaO	18.2376	4.8600	4.7306
TiO_2	0.5961	0.8618	0.9610
Cr_2O_3	0.0975	0.785	0.0790
MnO	0.1789	0.1946	0.1830
Fe_2O_3	6.2342	9.1325	9.2434
L.O.I.	31.3948	12.5871	13.2899

Table 11. Mineralogical content of K group samples

Sample	Minerals/Phases
K1	Quartz (SiO2), scawtite, calcite, hematite
K2	Quartz (SiO2), scawtite, calcite, K-feldspar, hematite
K3	Quartz (SiO2), scawtite, calcite, K-feldspar, hematite

The chemical analysis results of the clay samples (M15, D1, and D2, respectively) taken from the Sığırcık, Çirkindere, and Eğriova Stream are presented in Table 12. Chemical analysis were carried out on 12 main components. XRD analysis of clays were also performed (Table 13). The phases of M15 clay are quartz, potassium feldspar, calcite, and dolomite ($CaMg(CO_3)$). D1 clay has quartz, albite ($NaAlSi_3O_8$), muscovite ($KAl_2(AlSi_3O_{10}(OH)_2)$), calcite and kaolin. D2 clay has quartz, albite, muscovite, calcite, kaolin, and forsterite (Mg_2SiO_4). D1 and D2 clays contain very similar phases. Unlike the D1, the forsterite phase was found in D2 clay. D1 and D2 samples are seen to be more plastic than M15 due to layered clays (such as muscovite) in their structures. The phases formed according to the samples were classified as indicated in Table 14. It can conclude that the examined ceramics were made by making various additions to the local clays in the region (especially D1 and D2 clays with high plasticity). However, the number of clay samples and the analysis techniques will increase to support this. In future studies, it is aimed to increase the number of clay samples and analysis techniques.

Table 12. XRF results of clay samples

	Samples		
Oxides	M15 (clay)	D1 (clay)	D2 (clay)
Na_2O	0.7994	1.9023	1.3670
MgO	1.6116	0.9702	0.4679
Al_2O_3	11.6510	14.2601	13.7896
SiO_2	71.4852	67.6652	67.785
P_2O_5	0.1227	0.2510	0.3324
SO_3	0.0195	0.0960	0.0452
K_2O	3.4242	2.3705	2.9890
CaO	1.2137	1.2013	2.8702
TiO_2	0.1865	0.1922	0.2905
Cr_2O_3	0.0656	0.0051	0.0892
MnO	0.1282	0.1120	0.1549
Fe_2O_3	2.6088	2.7522	2.2648
L.O.I.	7.6936	8.2219	7.5543

Table 13. Mineralogical content of clay samples

Sample	Minerals/Phases
M15 (clay)	Quartz, calcite, dolomite, K-feldspar
D1 (clay)	Quartz, albite, muscovite, calcite, kaolinite
D2 (clay)	Quartz, albite, muscovite, calcite, kaolinite, forsterite

Table 14. Classification of the ceramic samples depending on the phase formations

	Group A	Group B	Group C	Group D	Group E
Phases	Quartz Hematite Calcite	Quartz Hematite Calcite K-feldspar	Quartz Hematite Scawtite Calcite K-Feldspar	Quartz Scawtite Calcite K-feldspar	Quartz Hematite Scawtite Calcite
Labels	Y5	Y1, Y2, Y6 S1-S12 A1-A14 M10-M14	K2, K3	M1,M5,M6 ,M7,M8	K1 Y3, Y4

3.2. Microstructure and microchemical analysis results

Microstructural characteristics were examined with SEM of the samples in order to observe detailed knowledge about samples properties. SEM images of the pottery sherds supplied information about their microstructure, and mineral morphology developed during firing process, which is useful to evaluate the firing temperature and firing technology of the sample.[22-24] In the microstructures grains interconnection and porosity structure (size and distribution) are critical because these factors help to defining the firing temperatures and vitrification level of the samples. Secondary electron images of the samples at the same magnification are given Fig. 7. Samples, which have a high amount of calcium oxide ratio, have a high amount of calcium oxide ratio porous structure is noteworthy in the microstructure especially for M10, and K3 samples. The samples with less calcium oxide (A4, S1, and Y3) have less intertwined pores and porous structure in their microstructure.

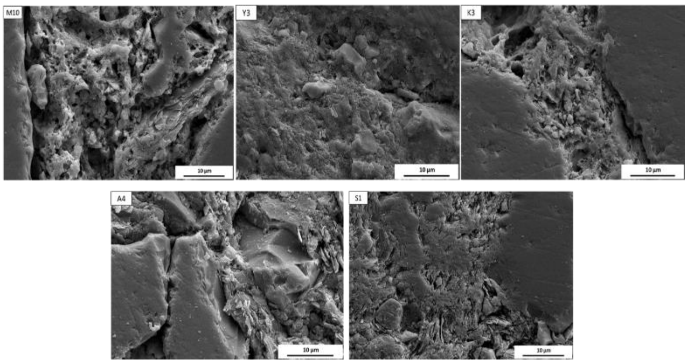

Figure 7. SE (secondary electron) images of the archeological samples

Representative backscattered electron images of the samples at the same magnification are given in Fig. 8. Siliceous and calcium-rich grains in the matrix apparent with the atomic weight contrast in the microstructures. While darker grains belong to the mainly siliceous grains, brighter ones belong to the iron-rich and calcium-rich grains in the microstructures. The grain size generally can reach 100-200 µm. When taking into account that pores (5µm to 50µm) are generally isolated, they show that the total vitrification did not complete during firing.[12] In addition to this, depending on the microstructural analysis, the ceramic bodies were not covered with glaze layers.

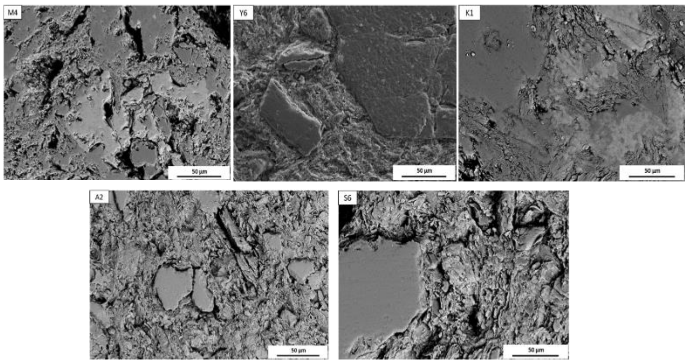

Figure 8. Representative BSE (Back Scattering Electron) images of archeological samples

EDX analysis were carried out to examine the chemical properties of the M4, Y6, K1, A2, and S6. The microstructure view of the M4 sample was taken from the general area (Fig. 9 (a)). EDX analysis from the marked region is given in Fig. 9 (b). Fe, Mg, K, Al, Si, Ca peaks can be seen in this analysis. Au peak is seen in all samples due to the gold-coating for SEM analysis.

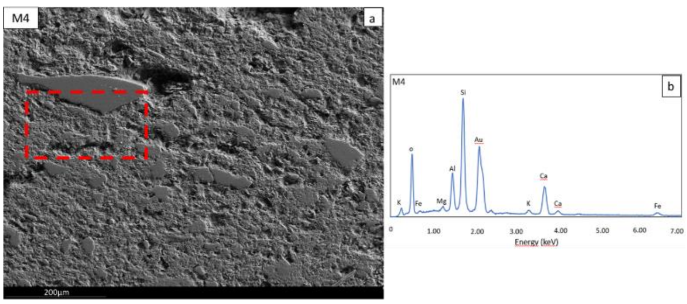

Figure 9. (a) SEM image of the M4 sample, (b) EDX analysis from the red-framed rectangular area

The microstructure view of the Y6 is shown in Fig.10 (a). The result of EDX spectrum analysis taken from the specified red rectangular area is shown in Fig.10 (b). As a result of the EDX analysis, K, Fe, Na, Mg, Al, Si, Au, Ca, and Ti peaks were observed. When compared to the color of the sample, this sample is darker than other samples. Therefore, the titanium peak is more prominent than other samples. This is probably due to impurities in the sample.

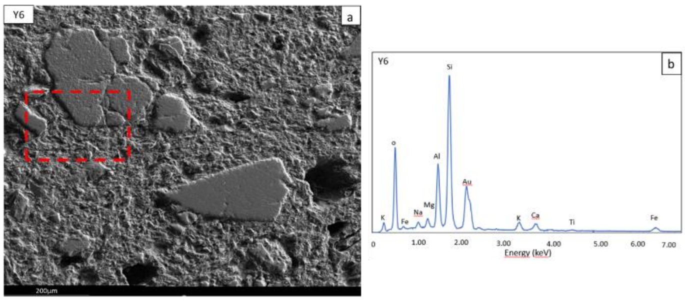

Figure 10. (a) SEM image of the Y6, (b) EDX analysis from the red-framed rectangular area

The microstructure view of the K1 sample is shown in Fig. 11 (a). The result of EDX spectrum analysis taken from the specified red rectangular area is shown in Fig. 11 (b). In EDX analysis, K, Fe, Na, Mg, Al, Si, Au, Ca peaks can be seen in the spectrum.

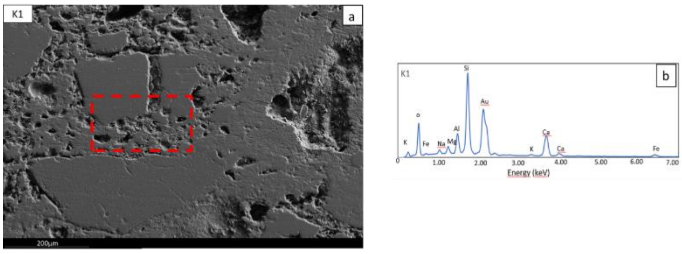

Figure 11. (a) SEM image of the K1 sample, (b) EDX analysis from the red-framed rectangular area

Microstructure view of A2 is given in Fig.12 (a). EDX analysis taken from the specified red rectangular area is shown in Fig.12 (b). K, Fe, Na, Mg, Al, Si, Au, Ca peaks are the main peaks for this sample.

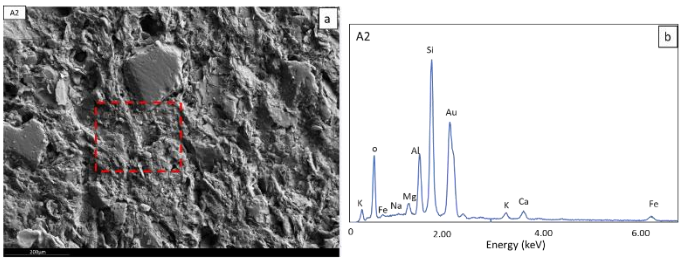

Figure 12. (a) SEM image of the A2, (b) EDX analysis from the red-framed rectangular area

The microstructure image of the S6 is also given in Fig. 13 (a). The result of EDX spectrum analysis taken from the specified red rectangular area is shown in Fig.13 (b). As a result of the EDX analysis, K, Fe, Na, Mg, Al, Si, Au, Ca peaks are seen in this spectrum.

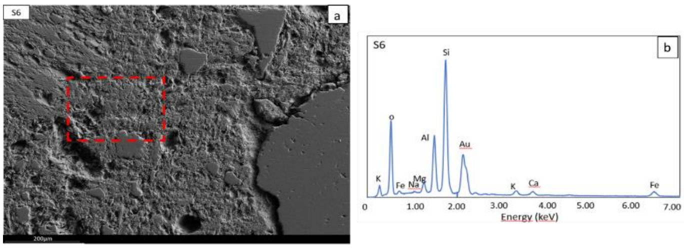

Figure 13. (a) SEM image of the S6 sample, (b) EDX analysis from the red-framed rectangular area

Similar peaks can be seen from the EDX EDX analysis of the samples. However, according to the differences in the chemical analysis, and the XRD analysis of the samples, relative increase and decrease in the peak intensities in EDX analysis can be carried out.

3.3. Estimation of the firing conditions of the samples

The presence or absence of some special mineral or crystals in the archeological samples is generally used to estimate the firing temperature and firing atmosphere.[15,23] Classification of the ceramic samples depends on the phase formations is given in Table 14. By creating groups for dominated phases, it was determined which samples belong to these groups. As can be seen this table, the main phases are: quartz, hematite, K-feldspar, calcite, and smectite. At least three of these phases are common to all-ceramic samples. As can be seen from this table, although there are samples taken from different regions, the phases formed in some samples are the same. This shows that ceramic materials are made using similar heat treatments according to their usage area.

The behaviour of the special crystals or minerals under specific temperature and atmosphere gives information about the clay or raw materials in the ceramic compositions. The minerals present in the samples were quartz, and K-feldspars. They are stable even at high temperatures; therefore, they cannot be evaluated for estimation of the firing temperature of the samples.[15-17] The formation of hematite, calcite and scawtite is very important for estimating the firing temperature and atmosphere of the samples. The presence of calcite and scawtite, would lead to infer a maximum firing temperature between 900-950°C.[19,20] As mentioned before, hematite formation takes place approximately 900°C in the samples. Oxidation conditions include the removal of carbon ($C+O_2 \rightarrow CO_2$) and produce reddish brown color, resulting from the oxidation of iron and iron-rich minerals (Fe_2O_3). In reducing conditions, FeO and Fe_2O_4 are prevalent phases resulting from $Fe_2O_3+CO \rightarrow 2FeO+CO$ or $3Fe_2O_3+CO \rightarrow 2Fe_2O_4+CO$.[13,17] Maghemite, and magnetite forms in reducing atmosphere. These phases generally yield an intensification of dark and black colors. In this study, although some sample's colors were dark gray, and black, only the hematite was observed in the samples. Maghemite and magnetite were not found. Unlike these phases, the presence of the organic substances in the samples plays important role for dark coloration. Under oxidizing circumstances, most of the organic substance is burned out, obtaining in an oxidized reddish-brown color. Even so, due to an oxidizing environment, if firing is carried out fastly and vessels are not allowed a sufficient "soak time", a black core may be formed by the incomplete oxidation of iron or incomplete burning of organic material[13]. Open or pit-fired pottery is rarely fully oxidized as a result of direct contact with fuel (e.g. Wood, ash) and, insufficient firing time for complete oxidation.[24-26] Dark surfaces are in this case not means to reduction, but rather a deposition of carbon and over-firing of the samples.[13,27,28] In the study, phases formed at high temperatures (greater than 1000 degrees) such as mullite, anorthite, cordierite, spinel, wollastonite were not observed in the samples. In light of this information, it can be said that the samples examined in the study were fired under an oxidizing atmosphere in the temperature range of 900-950°C. Coarse grains observed in the samples resulted that grinding of materials used in the production was not enough to obtain fine-grained bodies. Also, they were not covered with a slip or glaze layers. It may also be concluded that firing temperature and soaking time at the peak temperature were not enough to obtain a glassy matrix included new mineral formations.

4. CONCLUSIONS

In this study, archaeometric analysis were made using XRF, XRD, SEM methods for a total of 39 ceramic pieces and 3 clay samples taken from 5 different areas in the Midas Valley located 70 km south of Eskişehir Province and its close vicinity. The chemical, mineralogical and microstructural analysis of the samples were made and interpreted. The ceramics taken from 5 different areas in an area of 64 km2 and analyzed are composed of ceramics dating to different periods including the Phrygian, Roman, and Byzantine Period. Chemical analysis, XRD analyzes, and microstructure analyzes (SEM/EDX) were performed on the ceramic samples obtained in the region. According to the results obtained, it can be said that the ceramic samples were fired in an oxidizing atmosphere between 900-950°C. No glaze application was found in the samples taken from the ceramics. Clay samples were also taken from 3 different stream beds covered by the region, and chemical and XRD analyses of these samples were also carried out. It can be said that these ceramics were made by using these clays with various additions, mainly due to the muscovite phase in the D1 and D2 samples. Clay samples were also taken from 3 different stream beds covered by the region, and chemical and XRD analyses of these samples were also carried out. These ceramics were made by making various additions with the foresight that they could be shaped more quickly due to the muscovite phase in the D1 and D2 samples. However, for this, the number of clay samples taken from the stream beds in the region should be increased, and the characterization methods used should be expanded.

- According to the results obtained, it can be said that the ceramic samples were fired in an oxidizing atmosphere between 900-950°C.
- No glaze application was found in the samples taken from the ceramics.

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Competing Interests

The authors declare no competing interests.

Author Contributions

First author N. Tamsü Selli conceived and supervised the project and evaluated the results. The second author R. Polat and third author Y. Polat contributed to the procurement of archaeological finds and the archaeological interpretation of the results. The fourth author M.S. Öncel contributed to the chemical analysis and interpretation of archaeological finds.

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