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CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF ARCHAEOLOGICAL BUILDING MATERIALS FROM SEYITÖMER HÖYÜK, KÜTAHYA, TURKEY

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ABSTRACT

This paper focuses on the spectroscopic and thermal analysis of the archaeological samples of mortar and plaster from middle Bronze Age and Achaemenid period in Seyitömer Höyük. The composition of the samples was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric thermal analysis (TG-DTA). The results showed that human used different types of raw materials in the preperation of the mortar and plaster in the Middle Bronze Age and Achaemenid period. The material used in middle Bronze Age contains muscovite whereas the material in Achaemenid period contains albite. Although, the chemical composition of the mortar and plaster used in the period were similar, the calcium content of the plaster is relatively higher than the one of the mortar indicating people's awareness of the binding properties of calcite.

KEYWORDS: Mortar, Plaster, Archaeology, Seyitömer, XRD, XRF

1. INTRODUCTION

The chemical and mineralogical analysis of excavated archaeological materials provides a new approach to our understanding of prehistory, especially in helping to reconstruct past mobility (Ige et al., 2009; Paama et al.,2000; Dello-Russo, 2004; Simpson et al., 2006; Lambert et al., 1982). Although, technology may have been transferred, the raw materials used in construction reflect the local geology and relationship between humankind and materials.

This article focuses on the chemical and mineralogical analysis of mortars and plasters taken from Seyitömer Höyük (mound). The höyük was one of the most important settlements of the Phrygian Empire, where inhabitants manufactured ceramic, metals and glass. It is located in Seyitömer Lignite Company's coal reserve zone in the province of Kütahya, Turkey. The company intends to mine 13 million tons of exploitable coal beneath it. The oval-shaped mound formed over five millennia, which accreted the mound upward to 23.5 meters above the surrounding landscape (Bilgen, 2008). The first excavation was initiated by the Eskişehir Museum Directorate in 1989, was continued by the Afyon Museum Directorate in 1990. During the excavations of 1989-1995 only about 1/10th of the mound was excavated. The latest excavation has started in 2006. The stratigraphy of the mound reorganized in 2008 excavations. Five layers which have different architecture phases were determined. The mound dates from the Early Bronze Age (3000 BC), through Middle Bronze Age (18th millennium), Achaemenid period (500-330 BC), Hellenistic period (330-30 BC), and Roman periods. Over these periods, human used many different materials in construction of living places. Therefore, the chemical composition of the building materials is not only of interest to archaeologists, who wish to explore the relationship of the people to the raw materials, but is also important in the interpretation of data taken from the recovered samples.

The aim of this paper is to investigate mortar and plaster used in the construction of Seyitömer mound, especially, to take a closer look at the difference in the chemical composition of the materials used in middle Bronze Age and Achaemenid period. Through, the use of X-ray fluorescence (XRF), the X-ray diffraction (XRD), the Infrared spectrum (FTIR), scanning electron microscopy (SEM), and thermogravimetric thermal analysis (TG-DTA) techniques. The element variations and crystal structures have been used to shed new light on our understanding of prehistoric preference.

2. EXPERIMENTAL

2.1. Materials

Sixteen samples of mortars and 8 samples of plasters were obtained in different region of mound that are representative of varied environments (Fig. 1, Table 1). Six series of samples have been prepared from the mortars and plasters. The mortar samples are grouped into four according to their location and period and assigned as N1, N2, N3, and N4. The interpretation of chemical composition of construction materials depends on consideration of residues resulted from human activity. In order to eliminate chemical residues, mortar samples were taken between two stones on the wall of mound (Fig. 2). The N1 and N2 groups are from Middle Bronze Age and each of them was prepared from the mixture of 4 mortar samples taken from west (Fig. 2 (a) and east parts of the mound (Fig. 2 (b). The groups N3 and N4 groups from Achaemenid period were mixture of the mortar samples taken from northern (Fig. 2 (c) and southern part of the mound (Fig. 2 (a). The groups N5 (Middle Bronze Age) and N6 (Achaemenid period) were a mixture of plaster samples from different part of the mound (Fig. 3). To minimize impurities on the surface of the wall the uppermost layer of the plaster was removed.

The samples were taken from the remaining plaster on the wall. A portion of each group was ground to a particle size of -63 mm.

Figure 1. Photograph of the excavated Seyitömer mound.

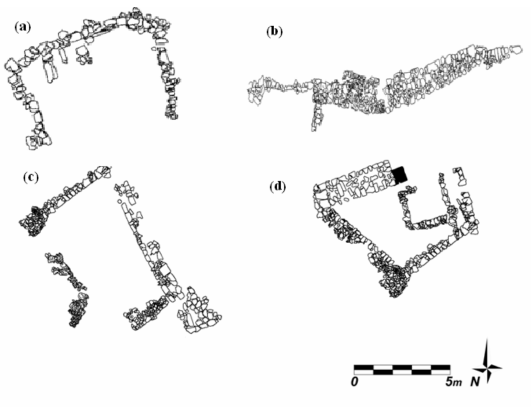


Figure 2. Plan of the excavated Structures a) Middle Bronze age (North wall+south wall), b) Middle Bronze age (East wall+West wall), c)Achaemenid period (North wall+south wall), d) Achaemenid period (East wall+West wall)

Figure 3. Photograph of the wall of the mound

Sample	Period	Location
N1	Midle bronze age	East wall+West wall
N2	Midle bronze age	North wall+south wall
N3	Achaemenid	East wall+West wall
N4	Achaemenid	North wall+south wall
N5	Midle bronze age	South wall
N6	Achaemenid	South wall

2.2. *Techniques*

Chemical compositions of selected samples were determined by using XRF spectrometer (Spectro X-Lab). X-ray diffraction patterns of mortars and plasters were obtained with a Rikagu Miniflex X-ray diffractometer using monochromatic CuK_ radiation operating at 30 kV and 15 mA over the range (2 θ) of scanning 5–70^0. The IR measurements were carried out using a FTIR spectrometer (Bruker Optics, Vertex 70 FT-IR). The FTIR spectra in the region from 400-4000 cm-1 was obtained using KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr. A Diamond TG/DTA thermal analyzer was used to record simultaneous TG, and DTA curves in the static air atmosphere at a heating rate of 10 K min-1 in the temperature range of 35-1000 °C using platinum crucibles. The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM) on specimens' surfaces with gold coating.

3. RESULTS AND DISCUSSION

Chemical composition of mortars and plaster used are given in Table 2. The XRF analyses indicated that the samples consist mainly in Si, Al, Ca and Fe and secondarily in Mg, Na, K, Ti, Cl, S and Mn. A comparison of the materials from Middle Bronze Age (N1 and N2) with the materials from Achaemenid period (N3 and N4) reveals that human have changed the type of the materials used in construction of mound from Middle Bronze Age to Achaemenid period. The concentrations of Al in materials from Midle Bronze Age are higher than that of the material from Achaemenid period. Although the concentration of Mg, Na, K, Ti, Cl, S and Mn nearly remain unchanged in the materials used for two different periods, the Al concentrations in the materials from Achaemenid period decreases while the concentrations of Ca increases in comparison with the early Bronze Age. The materials used as a plaster in Midle Bronze Age and Achaemenid period contain K_2O and Na_2O, respectively.

Table 2. Chemical composition of the excavated materials

	N1	**N2**	**N3**	**N4**	**N5**	**N6**
SiO_2	51.90	57.21	53.17	53.87	50.07	46.30
Al_2O_3	12.26	13.97	8.92	7.99	7.03	6.92
CaO	5.21	2.83	8.2	8.36	12.28	13.44
MgO	4.24	3.33	4.95	4.68	4.97	5.71
Na_2O	-	0.21	2.45	2.49	- 2.51	
K_2O	2.48	2.44	2.38	2.37	1.63	-
P_2O_5	0.38	0.44	1.31	1.58	1.45	2.31
TiO_2	0.51	0.63	0.42	0.40	0.37	0.35
Fe_2O_3	4.93	5.90	4.56	4.65	4.1	3.97
MnO	0.11	0.09	0.14	0.15	0.12	0.15
Cl	0.008	-	0.024	0.004	0.02	0.074
SO_3	0.13	0.20	0.19	0.22	0.32	0.35

The XRD patterns of the excavated building materials are given in Fig. 4. The mineralogy of the materials from all sites is grossly similar and mainly contains quartz, calcite, iron oxide, and dolomite. However, as seen in Fig. 4, there is a marked difference in the mineral types of the materials. The sample from Midle Bronze Age contains muscovite, $KAl_2(AlSi_3O_{10})(F,OH)_2$ and clinochlore, $(Mg, Fe^{2+})_5$ $(Al(OH)_8[AlSi_3O_{10}]$ whereas samples from Achaemenid period contains albite, $NaAlSi_3O_8$. From the chemical composition and crystal morphology of the plaster used in Middles Bronze Age and Achaemenid period it may be clearly understood that human preferred to use materials which contains higher amount of calcite compared to the material used in mortar preparation. Although, the plasters used contains muscovite in the early Bronze Age, materials containing albite in Achaemenid period has been chosen in the plaster preparation.

The DTA curves and the weight loss (TG) of the excavated mortar and plaster samples during heating are presented in Fig. 5, and in Table 3, respectively. The DTA/TG curves of all examined samples exhibited two well-defined weight loss events on heating. The first of these weight loss events corresponds

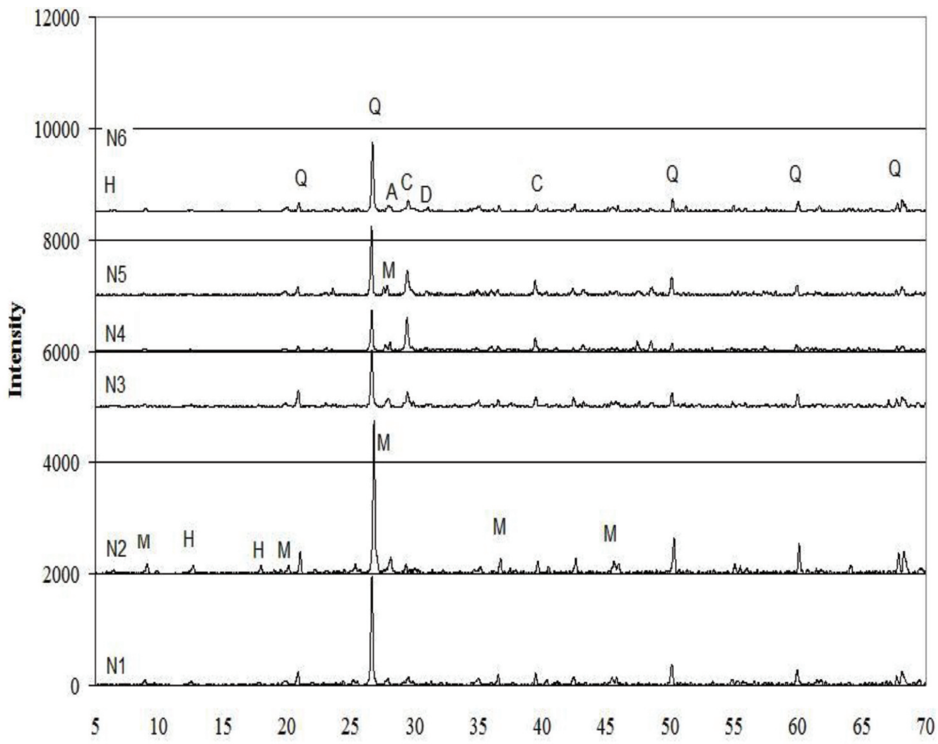


Fig. 4. XRD pattern of the samples used in this study: Q; quartz, M; muscovite, A; albite, C: calcite, H; Clinochlore.

to the loss of dehydration of pore water and molecular water from the samples. The shape and peak temperature of the DTA curve observed for this thermal event varied with the properties of the sample. It is observed that excavated samples lost 2.95–6.89 % of their original mass because of the loss of the water in the temperature range from 35 ^{0}C to 300 ^{0}C (Table 3). The weight loss around 100 ^{0}C is induced by physically absorbed water, whereas those appearing at 200-300 ^{0}C are attributed to bound water (A. Moropoulou et al..1995). The weight losses in the range of 300 –600^{o}C are ascribed to the decomposition of organic compounds and dehydroxylation of clay minerals.

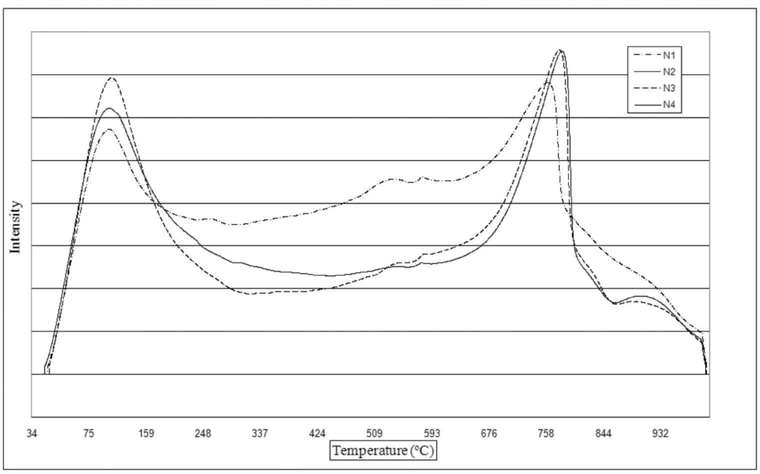


Fig. 5. DTA curves of the samples

Table 3. Weight loss of the excavated materials at different temperatures (% w/w)

	35-100 ^{0}C	100-200 ^{0}C	200-300 ^{0}C	300-400 ^{0}C	400-500 ^{0}C	500-600 ^{0}C	600-1000 ^{0}C
N1	0.78	1.28	0.89	1.03	1.10	1.29	6.04
N2	1.38	0.88	0.53	0.33	0.58	1.08	3.12
N3	2.60	1.70	0.74	0.72	0.85	1.14	7.22
N4	3.19	0.70	0.96	0.61	1.28	1.63	5.35
N5	2.60	1.86	0.80	0.75	0.77	0.97	9.53
N6	3.05	2.33	0.94	1.04	1.06	1.18	9.46

The amount of water loss of the excavated samples depends on the relative humidity of the environment to which they are exposed and chemical content of the sample. As seen in Table 3, the mass loss of the samples from middle Bronze Age is lower than that of the sample from Achaemenind period. The second weight loss above 600^oC in all of samples indicates the decomposition of carbonates. This is shown as an endothermic peak in the DTA curve around 750 ^{0}C. The ranges of weight loss in the decarbonation region of the samples studied were between 3.12 and 9.46 % (Table 3). It seems to be reasonable to assume that human in the middle Bronze Age and

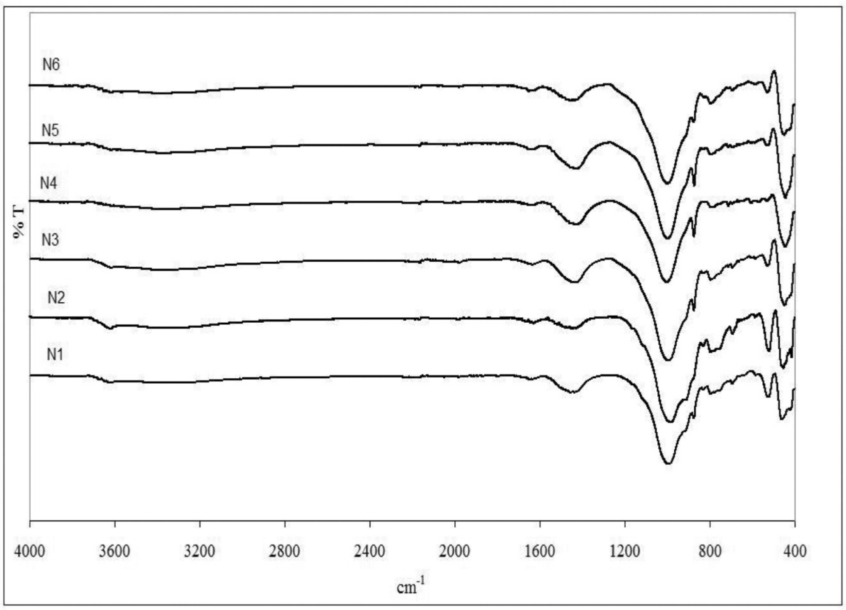


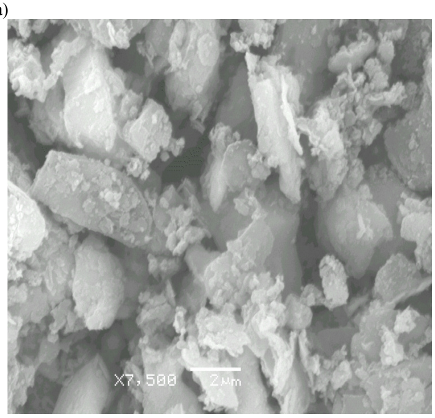
Fig. 6. FTIR spectra of the excavated samples

Achaemenid period used different materials in the preparation of the mortar and plaster. The CaO content of the plaster used in both periods is higher than that of the material used in mortar preparation.

The FTIR spectra of the samples are given in Fig. 6.

The bending vibration band of molecular H_2O appears at around 1636 cm^{-1} in N1. The position of this band in the other samples is gradually shifted from 1636 cm^{-1} to 1651 cm^{1}. The spectrum of the all samples show a broad band of water at around 3360 cm^{-1} due to overlapping asymmetric and symmetric (H-O-H) stretching vibration of Hydrogen bonded water (Madejova, 2003). The band observed at 3616 cm^{-1} (N1 and N2) is referred to the OH stretching vibrations of the structural OH groups. The band observed at around 1420 cm^{-1}, 875 cm^{-1}, and 712 cm^{-1} indicates calcite presence in the samples examined (Bosch Reig et al., 2002). It is noticeable from all the result presented so far that the amounts of calcite content of

a)



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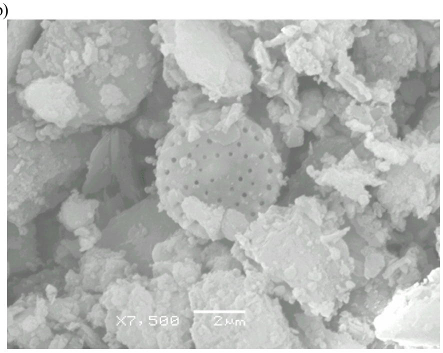

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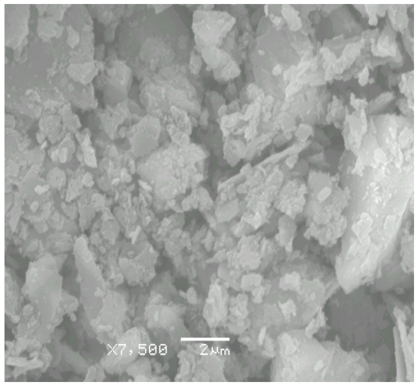

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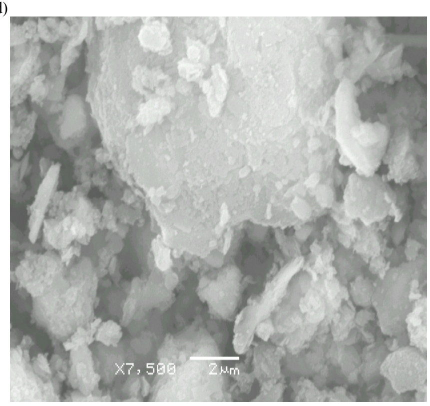
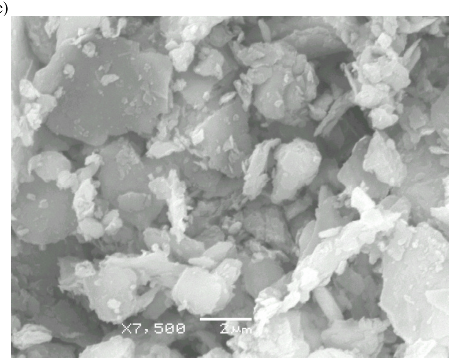


e)



f)

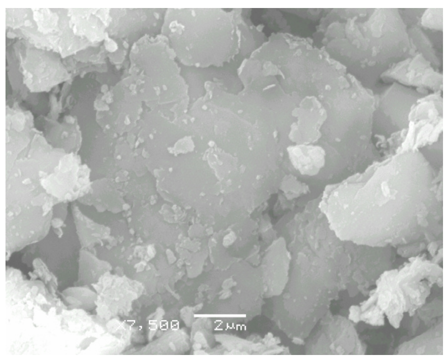


Fig. 7. SEM micrograph of the samples: a)N1, b) N2, c)N3, d) N4, e) N5, f) N6

the mortar used in middle Bronze Age is lower than those in mortar used in Akeamenid period. The band observed at 796 cm^{-1} is assigned to the quartz. The band observed around 1000 cm^{-1} may be attributed to the Si-O stretching vibration and out of plane (~530 cm^{-1}) and in-plane (~443 cm^{-1}) Si-O bending vibrations.

SEM photographs of the excavated samples are shown in Fig. 7.

The microstructure of mortar used in middle Bronze Age was notably different than that developed in the mortar from Achaemenid period. The samples from middle Bronze Age contain more aggregates of larger size and binder contacts between particles were washed out due to degradation process. Although, at first glance, the microstructure of the mortar used in Achaemenid periods appears similar with the mortar used in the middle Bronze Age, Achaemenid period's samples contains more aggregates of smaller size that result in a relatively denser structure. Fig. 7 (e) show the micrographic features of the plaster sample from the Middle Bronze Age and a discernible particulate arrangement due to apparent inter growing of particles. There appears to be no contact between the particles in some cases, whereas in a few cases both edge to edge and edge to face contacts, are seen. The presence of various compounds, such as calcite, results in strong bonding between particles. Although, cement production had not been known in those days, it seems that human discovered the binding properties of the calcite. The micrograph of plaster sample from Achaemenid period (Fig 7(f)) shows the presence of larger particles or aggregates fused together to a form fine matrix. In comparison with the plaster sample from middle Bronze Age, Achaemenid period's sample Fig 7(f)) shows relatively denser structure. This result may be attributed to the calcium oxide and magnesium oxide content of the sample used.

The above result reveal that human have used different raw materials in the construction of Seyitömer mound for the two periods. There are two varieties of mortar prepared from these materials, one rich in muscovite used in the Middle Bronze Age and the other one rich in albite used in the Achaemenid period.

4. CONCLUSIONS

In this study, we present analytical data on mortar and plaster samples obtained from the archeological excavation site of Seyitömer Mound in Turkey. From the results presented in this paper, the conclusions are as follows:

1. The results indicate significant differences in the calcium, aluminum, sodium and potassium content of the samples used in the middle Bronze Age and Achaemenid period. In the middle Bronze Age, the sample contains relatively higher amount of potassium and aluminum.
2. Calcium content of the sample from Achaemenid period is higher than that of the sample used in the middle Bronze Age.
3. In both periods, comparisons of chemical composition of the mortar and plaster samples reveal that human were aware of the binding properties of calcite.
4. SEM photographs of the excavated samples from Achaemenid period shows a denser structure compared to the sample from middle Bronze Age.

Better knowledge of the raw materials used in Achaemenid period indicate that Human examined different raw materials in the preparation of the mortar and plaster during time period and discovered binding properties of the calcite available in this area.

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