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Archaeometric Investigations of Terra-Cotta Sarcophages from the Excavations at Ainos (Enez) Turkey: An EDXRF Study

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In this study 11 clazomenian type sargophagi, found in ancient Ainos, one of the important archaeological site of Turkey, were investigated by EDXRF spectroscopy. The elemental composition of the painted parts and body samples of the sarcophagi were determined and the pigments used in the decorated parts were identified. Chemometric treatment of the XRF data was performed and principle component analysis revealed presence of 3 distinct groups.

Key Words: Ancient terra-cotta sarcophagi, Archaeometry, Inorganic pigments, XRF, EDXRF, Principle component analysis.

INTRODUCTION

Ancient Ainos (Enez) is one of the most important archaeological sites in Turkey[1,2]. The ancient city, with two well preserved harbors, was founded at the northern coast of the Aegean Sea, at the place of where Antic Hebros (Meric) river meets the sea (Fig. 1). The ancient city was established on the calcerous penunsula, belong to mid miocene, which was 25 m high from the sea level. The first residents of Enez have not been known yet but the found remains show that first residents were dated back to 7300 years from now and life has continued till today. The excavations in Enez have been going on for the last 30 years.

Fig. 1. Map of the north-western part of Turkey, where ancient Ainos (Enez) district is noted

In previous studies we have reported the INAA and EDXRF results of ancient coins and vibrational spectra of ancient potteries excavated in ancient Ainos[3,4]. In continuation of our studies on archaeological findings coming from ancient Ainos, in this study, chemical compositions of 11 terro-cotta sarcophagi were investigated by EDXRF spectrometry. The IR spectroscopic results of some of these sargophagi were reported elsewhere[5]. The two of the investigated sarcophagi were found in Cakillik Necropolis of ancient Ainos during the excavations in 2005 and were dated to classical and early classical period and the other 9 of them were found in Su Terazisi Necropolis (Ainos) in 2008, dated to archaic and clasical period. All these sarcophagi are known as Clazomenian type[6] and are discovered unfortunately as fragmented during the excavations.

EXPERIMENTAL

EDXRF analyses were performed using Spectro IQ XIQ01 model spectrometer which was equipped with an air cooled 50 W end-window X-ray tube. The samples were excited for 180 s with a forced-air cooled 25 W Palladium X-ray tube combined with a doubly bent HOPG crystal for monochromatization and polarization of the primary tube spectrum. A silicon drift detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the SDD was better than 175 eV at for MnK_{α} at an input count rate of 10,000 cps. During the measurement, the sample chamber was flushed with helium. All measurement parameters are controlled by the system PC.

The precision and accuracy of the analyses have been checked with international standard, standard reference material 97a flint clay[7] and the results are shown in Table-1. Present results are found to be in agreement to those of SRM[7]. Principle component analysis was performed using The Unscrambler CAMO software.

RESULTS AND DISCUSSION

The two sarcophagi found in Cakillik Necropolis, have decorated parts, but others have not. Thus the body samples of all the 11 sarcophagi and the decorated parts of two sarcophagi were investigated. One of these two decorated sarcophagi (M23) was decorated with 2 cm height egg and dart molding in its inner and outer edges. It has black, white and red decorations. The photograph of sargophagus M23, as discovered, is given in Fig. 2, together with a detailed photograph of the decorated outer edge and a model of this sarcophagus. The sarcophagus has 198 cm × 65 cm × 35 cm dimensions.

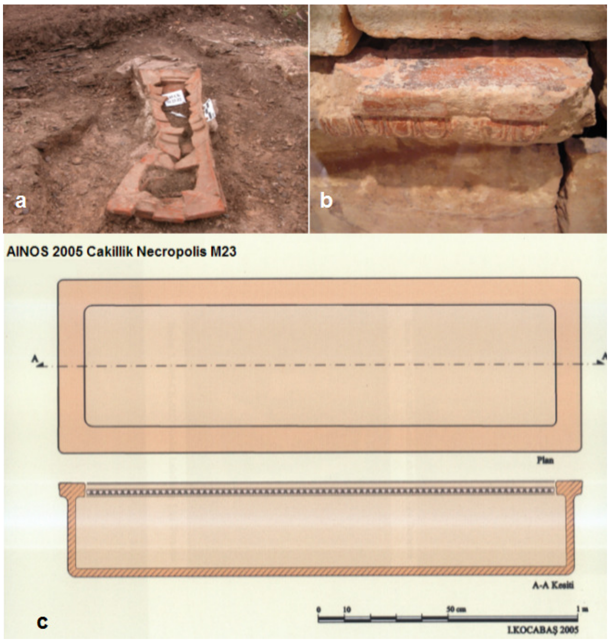

Fig. 2. Photograph of M23, the decorated sarcophagus, dated to classical and early classical period, as it was found in excavation (a) and its a detailed photograph showing the egg and dart molding in its outer edge. The model of M23 sarcophagus, drawn by I. Kocabas

The second decorated sarcophagus, found in Cakillik Necropolis (M26) was decorated with black figure technique. It has men figures in its inner foot-side and head-side. in its decorating panels and sidepiece panels with the tones of red and black colour. Unfortunately, this painting decorations were not conserved completely. The sarcophagus is 2.035 m long and 0.445 m high. The width of its footside is 0.20 m and headside is 0.30 m. Since headside panel is wider than its foodside panel its belongs to "Normal Type" Form 4 Class[6] according to Cook's classification. Fig. 3 shows a photograph of sargophagus M26, as discovered. An expected model of this sarcophagus is also demonstrated in Fig. 3.

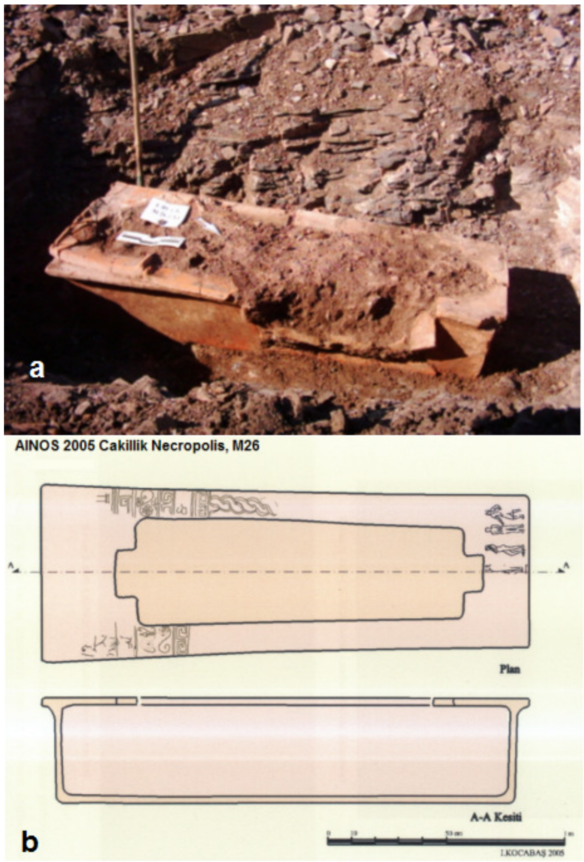

Fig. 3. Photograph of the decorated sarcophagus M26, dated to classical and early classical period, as it was found in excavation (a) and the model of M26 sarcophagus, drawn by I. Kocabas (b)

The other nine terra-cotta sarcophagi (M3, M4, M5, M6, M8, M9, M11, M19, M24), found in 2008 in Su Terazisi Necropolis, were dated to archaic and classical period. All these found as fragmented, during the excavations in Su Terasisi necropolis of ancient Ainos. The photographs of sarcophagi M3, M11 and M19, as discovered are given in Fig. 4.

The EDXRF results of the body samples of all 11 terracotta sarcophagi is given in Fig. 1. The decorated parts of sargophagus M23 and M26 were very small amount therefore EDXRF analysis of these samples were performed qualitatively. In the EDXRF spectra of the white decorated parts of both sargophagi, Ca, Si, Mg and S peaks are dominated. These results indicate that calcite, dolamite and $CaSO_4$ were used as white pigment. Presence of Si, is probably due to quartz. EDXRF spectra of the black coloured parts of the both sarcophagi (M23 and M26) contains Mn, Al and Si peaks,

TABLE-1
SOME ELEMENTAL CONCENTRATIONS (%) OF STANDARD REFERENCE MATERIAL 97a, FLINT CLAY, OBTAINED BY EDXRF ANALYSIS AND ITS CERTIFIED VALUES TAKEN FROM REFERENCE[7]

	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	TiO_2	P_2O_5	MgO
This study	43.75 ± 0.05	39.05 ± 0.05	0.10 ± 0.01	0.43 ± 0.02	0.46 ± 0.04	1.8 ± 0.1	0.39 ± 0.02	0.16 ± 0.02
Ref.[7]	43.67	38.79	0.11	0.45	0.50	1.90	0.36	0.15

Fig. 4. Photographs of M3 (a), M11 (b) and M19 (c) sarcophagi found in Su Terazisi Necropolis

indicating that black colouration is due to manganese oxide pigments. On the other hand from EDXRF spectra of red coloured parts of M23 and M26, it was revealed that for red colouration hematite was used.

The EDXRF analysis results of the body samples of 11 sarcophagi is given in Table-2. The concentrations of SiO_2, MgO, Al_2O_3, CaO, ΣFe_2O_3, MnO, K_2O, Na_2O, TiO_2, P_2O_5, Sr, Rb, Y, S, Cl, V, Cu, Zn, Ba were determined. In order to reveal the data embedded in the chemical composition of sarcophagi, we performed a chemometric method, principle component analysis (PCA). Principle component analysis is a multivare analysis technique that reduces data matrix to their lowest orthogonal space and found to be very informative to obtain hidden data structures[8-11]. Mathematically, principle component analysis is based on an eigenvector decomposition of the covariance matrix of the variables in a data set[12]. Given a data matrix X with m rows of samples and n columns of variables, the covariance matrix of X is defined as:

$$\{\text{cov}](X) = \frac{X^T X}{m-1} \quad (1)$$

here X^T is transpose matrix of data matrix X and m is the number of samples. The result of the principle component analysis procedure is a decomposition of the data matrix X into principal components called score and loading vectors. As matrix notation we can write data matrix X:

$$X = TP^T + E \quad (2)$$

here T is the score matrix, P^T is the transpose of P loading matrix and E is the residual matrix. The matrix related to the sample contributions (T) is called score matrix and the matrix related to the variables contributions (P) is called loadings matrix. The score and loading matrixes contain information on how the samples and variables, respectively, relate to each other. In the present study, X matrix contains chemical compositions of 11 terra-cotta sarcophagi samples, therefore it has 11 rows (corresponding to the number of samples) and 19

TABLE-2
EDXRF ANALYSIS RESULTS OF TERRA-COTTA SARCOPHAGI

Sample (%)	SiO_2	MgO	Al_2O_3	CaO	ΣFe_2O_3	MnO	K_2O	Na_2O	TiO_2	P_2O_5
M 23	55.50 ± 0.05	1.5 ± 0.2	16.40 ± 0.05	0.6 ± 0.1	1.4 ± 0.2	0.10 ± 0.01	1.0 ± 0.1	0.5 ± 0.2	0.5 ± 0.1	0.05 ± 0.01
M 26	58.50 ± 0.05	2.0 ± 0.2	15.25 ± 0.05	1.0 ± 0.1	1.8 ± 0.2	0.20 ± 0.01	1.5 ± 0.1	0.7 ± 0.2	0.6 ± 0.1	0.20 ± 0.02
M 3	61.50 ± 0.05	1.7 ± 0.2	14.80 ± 0.05	1.1 ± 0.1	1.9 ± 0.2	0.03 ± 0.01	1.5 ± 0.1	0.3 ± 0.2	0.8 ± 0.1	0.18 ± 0.02
M 4	60.55 ± 0.05	2.6 ± 0.2	14.50 ± 0.05	1.4 ± 0.1	2.3 ± 0.2	0.04 ± 0.01	1.0 ± 0.1	0.3 ± 0.2	0.8 ± 0.1	0.15 ± 0.02
M 5	62.50 ± 0.05	2.0 ± 0.2	15.90 ± 0.05	1.6 ± 0.1	2.8 ± 0.2	0.03 ± 0.01	1.9 ± 0.1	0.3 ± 0.2	0.7 ± 0.1	0.18 ± 0.02
M 6	61.60 ± 0.05	1.8 ± 0.2	13.70 ± 0.05	1.7 ± 0.1	2.0 ± 0.2	0.03 ± 0.01	1.2 ± 0.1	0.2 ± 0.2	0.7 ± 0.1	0.15 ± 0.02
M 8	60.95 ± 0.05	1.0 ± 0.2	14.20 ± 0.05	1.8 ± 0.1	1.8 ± 0.2	0.03 ± 0.01	1.6 ± 0.1	0.2 ± 0.2	0.6 ± 0.1	0.12 ± 0.01
M 9	61.95 ± 0.05	1.4 ± 0.2	13.70 ± 0.05	1.4 ± 0.1	1.5 ± 0.2	0.02 ± 0.01	1.2 ± 0.1	0.2 ± 0.2	0.7 ± 0.1	0.09 ± 0.01
M 11	59.70 ± 0.05	1.7 ± 0.2	14.80 ± 0.05	1.7 ± 0.1	2.1 ± 0.2	0.05 ± 0.01	1.6 ± 0.1	0.3 ± 0.2	0.8 ± 0.1	0.04 ± 0.01
M19	54.10 ± 0.05	1.2 ± 0.2	11.90 ± 0.05	1.3 ± 0.1	1.6 ± 0.2	0.03 ± 0.01	1.5 ± 0.1	0.3 ± 0.2	0.6 ± 0.1	0.50 ± 0.05
M 24	62.20 ± 0.05	1.6 ± 0.2	15.12 ± 0.05	1.6 ± 0.1	1.6 ± 0.2	0.03 ± 0.01	1.4 ± 0.1	0.2 ± 0.2	0.6 ± 0.1	0.14 ± 0.01
Sample (%)	**Sr**	**Rb**	**Y**	**S**	**Cl**	**V**	**Cu**	**Zn**	**Ba**	**Loss on ignition**
M 23	0.15 ± 0.02	0.05 ± 0.02	0.03 ± 0.01	0.05 ± 0.01	0.15 ± 0.01	0.15 ± 0.02	0.03 ± 0.01	0.02 ± 0.01	0.2 ± 0.02	15.0
M 26	0.03 ± 0.02	0.07 ± 0.01	0.05 ± 0.01	0.21 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.03 ± 0.01	0.3 ± 0.02	17.0
M 3	0.05 ± 0.02	0.03 ± 0.01	0.03 ± 0.01	0.05 ± 0.01	0.07 ± 0.01	0.05 ± 0.01	0.02 ± 0.01	0.06 ± 0.02	0.04 ± 0.01	11.16
M 4	0.03 ± 0.02	0.03 ± 0.01	0.04 ± 0.01	0.12 ± 0.01	0.05 ± 0.01	0.08 ± 0.01	0.02 ± 0.01	0.07 ± 0.02	0.02 ± 0.01	10.72
M 5	0.12 ± 0.02	0.02 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.09 ± 0.01	0.06 ± 0.01	0.02 ± 0.01	0.05 ± 0.01	0.02 ± 0.01	9.85
M 6	0.7 ± 0.02	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.02 0.01 ±	0.08 ± 0.02	0.04 ± 0.01	10.84
M 8	0.05 ± 0.01	0.022 ±	0.03 ± 0.01	0.03 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	0.03 ± 0.1	0.06 ± 0.02	0.09 ± 0.02	12.68
M 9	0.06 ± 0.02	0.03 ± 0.1	0.03 ± 0.01	0.03 ± 0.01	0.07 ± 0.01	0.06 ± 0.01	0.02 ± 0.01	0.06 ± 0.02	0.02 ± 0.01	11.79
M 11	0.15 0.02 ±	0.07 ± 0.02	0.06 ± 0.01	0.04 ± 0.01	0.19 ± 0.02	0.02 ± 0.01	0.04 ± 0.01	0.03 ± 0.1	0.20 ± 0.02	12.89
M19	0.49 0.02 ±	0.02 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.08 ± 0.01	0.06 ± 0.01	0.03 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	12.3
M 24	0.05 0.02 ±	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.06 ± 0.01	0.04 ± 0.01	0.08 ± 0.02	0.07 ± 0.02	0.05 ± 0.01	10.4

columns (corresponding to chemical elemental compositions, Table-2). Score matrix provides information about the samples distribution and grouping, while the loading matrix gives information about the most relevant chemical elements used to obtain this distribution and grouping.

The result of the principle component analysis projection of present data from the original 11-dimensional space into the plane of the first two principal components is shown in Fig. 5, where each sample is presented as a point. The components PC1 and PC2 (Fig. 5) show the greatest contribution to the variance in concentrations (PC1 = 81 %, PC2 = 15 %), whereas the third and fourth components have only minor contributions of 2 and 1 %, respectively. Fig. 6 shows the scores and loadings of principle components PC2 and PC3. Since the first two principal components (PCs) represent 96 % of the total variance, these two components were sufficient to provide effective clustering of the samples origin with clear separation between the groups. The PC1 *versus* PC2 plot is dominated by SiO_2 (high weight to PC1) and Al_2O_3 (high weight to PC2) (Fig. 5b), indicating that the variance in the concentration data can be explained mainly by the concentration variations in Si and Al. As seen in Fig. 5a, scores plot showing the separation of the terra cotta sarcophagi samples into three major clusters; M23 and M24 (negative PC1 and positive PC2 contributions); M19 (negative PC1 and negative PC2 contributions) and other 8 (positive PC1 and positive PC2 contributions). The area (ancient Ainos-Enez) is famous with clay deposits[13,14]. Probably these 3 distinct group terra-sarcophagi were constituted from three different clay beds. It must be reminded that M23 and M24 are archaeologically dated to classical and early classical period whereas the others dated to archaic and clasical period.

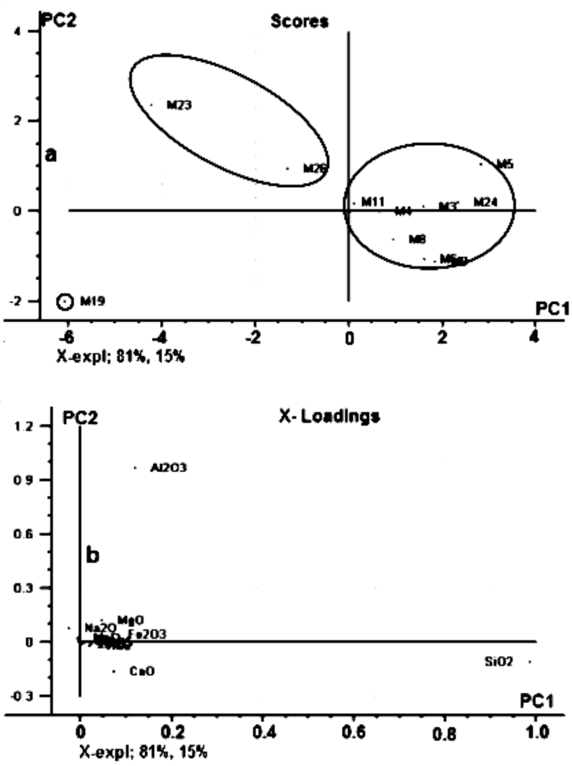

Fig. 5. Scores (a) and loadings (b) plots of PC1 *versus* PC2 obtained from PCA of EDXRF results given in Table-2. Three disting groups are clearly seen (a)

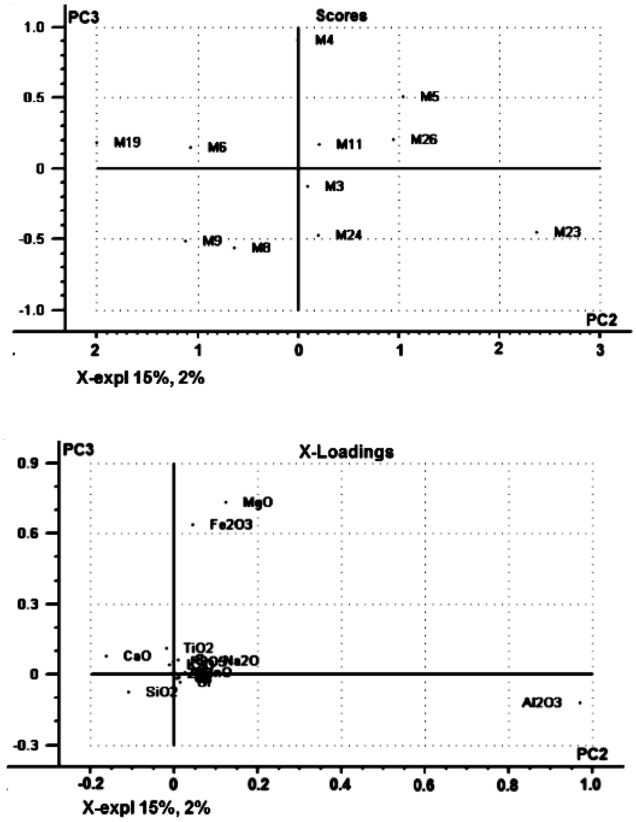

Fig. 6. Scores and loadings plots of PC2 *versus* PC3 obtained from principle component analysis of EDXRF results given in Table-2

Principle component analysis clearly discriminate these sarcophagi obtained different necropolis. On the other hand sarcophagus M19 was also discriminated the other eight sarcophagi found in Su-Terazisi necropolis, probably different clay bed was used for this terra-cotta sarcophagus than the others.

Conclusion

In this study, painting materials and body samples of two decorated terra-cotta sarcophagi and the body samples of 9 terra-cotta sarcophagi, recently excavated in ancient Ainos (Enez) Turkey, were investigated by EDXRF spectrometry. The results indicate that for white, red and black coloured parts of the decorated sarcophagi, calcite, dolomite and $CaSO_4$ (for white colouration), iron oxides (hematite) (for red colouration) and manganese oxides (for black colouration) were used. The two decorated terra-cotta sarcophagi were found in Cakillik Necropolis, whereas the other 9 terra-cotta sarcophagi were found another necropolis (Su Terazisi Necropolis). Principle component analysis clearly discriminate these sarcophagi obtained different necropolis. On the other hand sarcophagus M19 was also discriminated the other eight sarcophagi found in Su-Terazisi necropolis, probably different clay bed was used for this terra-cotta sarcophagus than the others.

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