A PRELIMINARY ARCHAEOMETALLURGICAL EXAMINATION OF SOME BRONZE COINS FROM KOMANA

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

AYŞEN ELŞEN AYDIN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ARCHAEOMETRY

SEPTEMBER 2019

Approval of the thesis:

A PRELIMINARY ARCHAEOMETALLURGICAL EXAMINATION OF SOME BRONZE COINS FROM KOMANA

submitted by **AYŞEN ELŞEN AYDIN** in partial fulfillment of the requirements for the degree of **Master of Science in Archaeometry Department, Middle East Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, Graduate School of **Natural and Applied Sciences** _____

Prof. Dr. Musa Doğan
Head of Department, **Archaeometry** _____

Prof. Dr. Deniz Burcu Erciyas
Supervisor, **Archaeometry, METU** _____

Assoc. Prof. Dr. Zeynep Işıl Kalaylıoğlu
Co-Supervisor, **Statistics, METU** _____

Examining Committee Members:

Prof. Dr. Ali Kalkanlı
Metallurgical and Material Engineering, METU _____

Prof. Dr. Deniz Burcu Erciyas
Archaeometry, METU _____

Assoc. Prof. Dr. Ali Akın Akyol
Con. and Rest. of Cultural Properties, AHBVU _____

Date: 04.09.2019

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Surname: Ayşen Elşen Aydın

Signature:

ABSTRACT

A PRELIMINARY ARCHAEOMETALLURGICAL EXAMINATION OF SOME BRONZE COINS FROM KOMANA

Aydın, Ayşen Elşen
Master of Science, Archaeometry
Supervisor: Prof. Dr. Deniz Burcu Erciyas
Co-Supervisor: Assoc. Prof. Dr. Zeynep Işıl Kalaylıoğlu

September 2019, 74 pages

This thesis comprises archaeometallurgical investigations on some coins found in archaeological excavations at the ancient settlement of Komana-Tokat. Micro-XRF and Scanning Electron Microscope analysis methods were used in this study. By means of these methods, it was aimed to obtain information about the alloy compositions of the coins found at this site dating to different periods. This is also the first archaeometallurgical study on the coins found in Komana. According to the results of the analysis, the elemental compositions of the mines were determined. The results obtained gave information about the alloys of Byzantine/post-Byzantine coins found in Komana.

Keywords: Komana, Archaeometallurgy, Micro-XRF, Scanning Electron Microscope, Bronze.

ÖZ

KOMANA'YA AİT BAZI BRONZE SİKKELERİN ARKEOMETALURJİK İNCELEMESİ

Aydın, Ayşen Elşen
Yüksek Lisans, Arkeometri
Tez Danışmanı: Prof. Dr. Deniz Burcu Erciyas
Ortak Tez Danışmanı: Doç. Dr. Zeynep Işıl Kalaylıoğlu

Eylül 2019, 74 sayfa

Bu tez, antik bir yerleşim yeri olan Komana-Tokat'ta yapılan arkeolojik kazılarda bulunan bazı sikkeler üzerinde arkeometalurjik incelemeleri kapsamaktadır. Bu incelemeler kapsamında Micro-XRF ve Taramalı Elektron Mikroskobu analiz yöntemleri kullanılmıştır. Bu yöntemler sayesinde Komana'da bulunan sikkelerin elemental kompozisyonlarına bakılarak, bölgenin farklı dönemlerdeki alaşım kompozisyonları hakkında bilgiler elde edilmesi amaçlanmıştır. Aynı zamanda bu çalışma Komana'da bulunan sikkeler üzerinde gerçekleştirilen ilk arkeometalurjik çalışmadır. Analiz sonuçlarına göre kullanılan madenlerin element kompozisyonları belirlenmiştir. Elde edilen sonuçlar, Komana'da bulunan Bizans sikkelerinin alaşımları ile ilgili bilgi vermiştir.

Anahtar Kelimeler: Komana, Arkeometalurji, Micro-XRF,Taramalı Elektron Mikroskobu, Bronze.

To my family

ACKNOWLEDGEMENTS

I would like to thank my great supporter and also my Supervisor Prof. Dr. Burcu Eciyas, my Co-Supervisor Assoc. Dr. Zeynep Işıl Kalaylıoğlu and another supporter Assoc. Dr. Ali Akın Akyol for not only making this thesis possible but also for their great support and encouragement throughout this work. Whenever I needed support, you were always there for me. Without your presence, such work would never have arisen. I would also like to thank Assoc. Dr. Mahmut Aydın who is head of Archaeometry Department at Batman University, for his valuable comments.

I would like to thank MAKLAB employees of Hacı Bayram Veli University Cultural Heritage Protection and Restoration Department to make possible the analysis.

I would like to express my sincere gratitude to my dear friend İsmail Calayır for helping to taking photograph to the materials.

I would like to thank all my friends for their psychological support during this time.

I would like to thank my dear teacher Alime Begümşen Ergenekon, who prepared me psychologically for this process. I would like to thank all the staff of the Student Affairs at Middle East Technical University, especially Sema Karaca, Akile Koç, Ceylan Yatağan, Suzan Er and Toprak Akkanat, for being with me in this process. I am grateful to my spiritual mother, H. Fatoş Gür, for all her support during my entire university life.

My warmest and most sincere thanks to my family. Your love and support made everything possible for me. Mommy, you are the color of my life.

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF GRAPHS

GRAPHS

CHAPTER 1

INTRODUCTION

1.1. INTRODUCTION

Archaeometry, an academic field, gives us the opportunity to make numerical interpretation of archeology. Archaeometry, an outcome of the merging of hard science with archaeology, provides the opportunity to evaluate archaeological data through scientific methods.

Archaeometry, which is an interdisciplinary field, was accepted as a science with the establishment of the journal Archaeometry in 1958 (Rehren & Pernicka, 2008). Archaeometallurgy, on its own, was formed as a sub-branch of archaeometry and numerous publications and conferences were held exclusively for metals.

The work on archaeological metals already began in the early 19th century (Caley, 1949). Caley's (1949) article describes the first quantitative study of a chemist named M. H. Klaproth on a Roman coin. Comparative and systematic investigations of ancient metal objects were conducted by von Fellenberg (1866). In the late 1920s, an analysis of the nickel content of the metals found in the Royal Cemetery in Mesopotamia was carried out (Woolley, 1931) and a report on the origin of Sumerian copper was published (Desch, 1928-1939).

With the development of optical emission spectrometer, a new analytical method after the 1930s, it was possible to determine the trace level of many elements. Thus, extensive analytical programs on ancient metals and ores were initiated. The history of metals originated mainly from the second half of the 19th century and in the late 1960s and early 1970s, C.S. Smith, R. Tylecote and H.G. Bachmann have contributed in this area (Rehren & Pernicka, 2008). In this sense, the literature is quite extensive and studies have been published in archaeological journals as well

as engineering and natural sciences journals. The best references in this area are Tylecote (1987), Rostoker and Branson (1990) and Craddock (1995).

Metal played an important role in most of the ancient societies, especially with the Chalcolithic period, followed by the Bronze Age and Iron Age. Starting already in the Chalcolithic period, metal production technology showed a gradual development and reached to the present day. Archaeometallurgy generally deals with questions regarding the production, distribution and use of metals in human history (Gilmour B. & Northover, n.d.). In this sense, the use of metal objects can be divided into three basic categories: metals produced for decorative purposes (jewelry, inlays and other accessories), metals produced for military purposes (weapons and armor), and metals produced for utilitarian purposes (coinage, tools and general implements) (Rehren & Pernicka, 2008). In the production of these metals, different metal properties which could have been perceived in ancient times such as hardness, density and color were utilized. The reason for the archaeometric studies on these metals has been to understand the characteristics of different periods and whether production techniques have changed in regard to these properties.

The metallurgical activities in Anatolia accelerated in the second half of the 3rd millennium B.C. and metal processing workshops were found in each settlement examined (Yalçın & Özbal, n.d.). The arsenic copper was discovered by the miners of this period and then high quality copper was obtained. It was observed that both color and quality of copper increased with arsenic and also that the casting properties of copper improved depending on the amount of arsenic. Then, in 2800 B.C., great advances were made in arsenic copper production technology. Arsenic copper was used until the beginning of the Late Bronze Age. Arsenic was used due to shortage of tin to make bronze (Yalçın & Özbal, n.d.). The first samples of other metals that were relatively pure were found in the Late Chalcolithic period (Yalçın Ü. , 2013). Towards the end of this period, the use of bronze, a copper tin mixture, is the most important achievement in Anatolian metallurgy.

The use of bronze has brought about new changes and mass production of metals began. In the Middle Bronze Age, the art of casting continued uninterruptedly based on previous experience (Yalçın & Özbal, n.d.). As a result, the quality of bronze production increased with the use of tin instead of arsenic and the use of tin spread to all parts of Anatolia. According to Yalçın (2013), the resulting metal continues industry was very advanced in terms of quality and quantity, and these techniques have to be used in the Hellenistic and Roman periods. In particular, coins were produced from bronze "*A small piece of round in the form of a disc, bearing the mark and emblem of the competent authority or state, which sets itself has on weight and commits itself to be recirculated and undertakes to take it back on demand.*" (Tekin, 1993). Coins were made of bronze as well as gold, silver and copper.

Bronze coins and metals from the Medieval layers of the Hellenistic sanctuary of Komana constitutes the data of this study. These bronze objects, excavated from two different excavation areas at Komana, had corroded heavily and for the most part had lost their original form. However, it is still possible to identity them as coins.

The dataset also includes some bronzes objects other than coins. Through a comparison of coins and other bronzes. It is aimed to understand possible differences in alloys used for coins. In this way, some information regarding the economy of the periods could be derived.

Komana is located at the northwest of Tokat province and at this site there are ongoing surface surveys and intensive archaeological studies that started in 2004. The site has a lot of potential understanding the Hellenistic sanctuary which was located in the Iris valley. The excavations revealed a lot of information on the Byzantine at Komana as well. An interdisciplinary team from Middle East Technical University, Graduate Program in Settlement Archaeology works with Prof. Dr. Burcu Erciyas at this site. The results of this indicate that both surface

survey and archaeological excavations hold a great potential for understanding the post-Byzantine period. Archaeometric studies with these pieces make it possible to gain insight into the economic dynamics of that period and to obtain more information about it. Using archaeometry, in this sense, will allow the archaeologist who collects the archaeological data obtained in traditional ways to examine the collected data in multidimensional way. In addition to this, during this study, the archaeological data collected were evaluated theoretically and it was aimed to provide a new perspective with the spectrographic method applied on the archeological elements.

Firstly, they come from well dated contexts and secondly they are hoped to bring light to some of the economic and political questions the excavation team has regarding these periods. Additionally, there is no archaeometric study on the coins. This analysis on these bronzes will help enrich the archaeometric database both in this region in Anatolia in general.

The thesis is organized in 4 sections including Introduction and Conclusion. In this Chapter, Chapter 1, limitations of these study and some brief information about Komana and its background. Additionally, previous archaeometric studies will be introduced in this chapter.

In Chapter 2, the coins that were collected from Komana and the methods will be explained for archaeometallurgical analysis. Coins, used techniques and technical devices will be introduced in detail. This chapter will be based on spectrographic techniques and the datum that collected from analysis, will be later used to understand elemental analysis of bronze coins of the period roughly between 11^{th} – 14^{th} centuries.

In Chapter 3, results of the analysis and discussion of elemental composition of Komana's based on the bronze coins from 11^{th} – 14^{th} centuries will be explained.

In Chapter 4 conclusion of this study will be presented. In this Chapter, the summary of research results and future aspects of the study will be summarized.

1.2. LIMITATIONS

In this thesis, elemental compositions of bronze coins from Komana were examined and non-coin bronze objects from the same region were used for comparison. The sample set could not be selected in accordance with a certain standard due to the unexpectedly short field work and regulations restricting. The spectrometric methods used in the thesis were conducted by laboratory technicians and experts due to budget and time constraints. However, the analyses could not be multiplied. The main reason for this is the lack of academic budget for archaeometric studies. The elimination of these problems for other archaeometric studies that will be carried out in the future will contribute to the collection of healthier data and contribute fully the academic literature.

1.3. GENERAL INFORMATION ABOUT KOMANA

Tokat province is located in the Central Black Sea region of the Black Sea region in Turkey. The population of Tokat is 616,646 and the area is 9958 km^2. The average altitude is 623 meter (Tokat İl Kültür Turizm Müdürlüğü, 2019).

Komana, situated today in and around Gümenek, is located on Tokat-Niksar road and is located in the northwest of Tokat. Komana is an ancient Hellenistic sanctuary site. It is one of the two temple states which were active in Pontus. The greatest of these temple state was Komana and it was dedicated to the Mother Goddess Ma. Komana is also the first settlement of Tokat and it was a commercial center that had received a lot of visitors and merchants from the environment. The region expended considerably during the role of the Pontus Kings and the Roman Empire period and spread over an area of about 8 km in diameter. The excavated parts of Komana that can be seen today are located on hill called Hamamtepe (Erciyas, 2015).

Figure 1. Map of Anatolia showing the position of Tokat

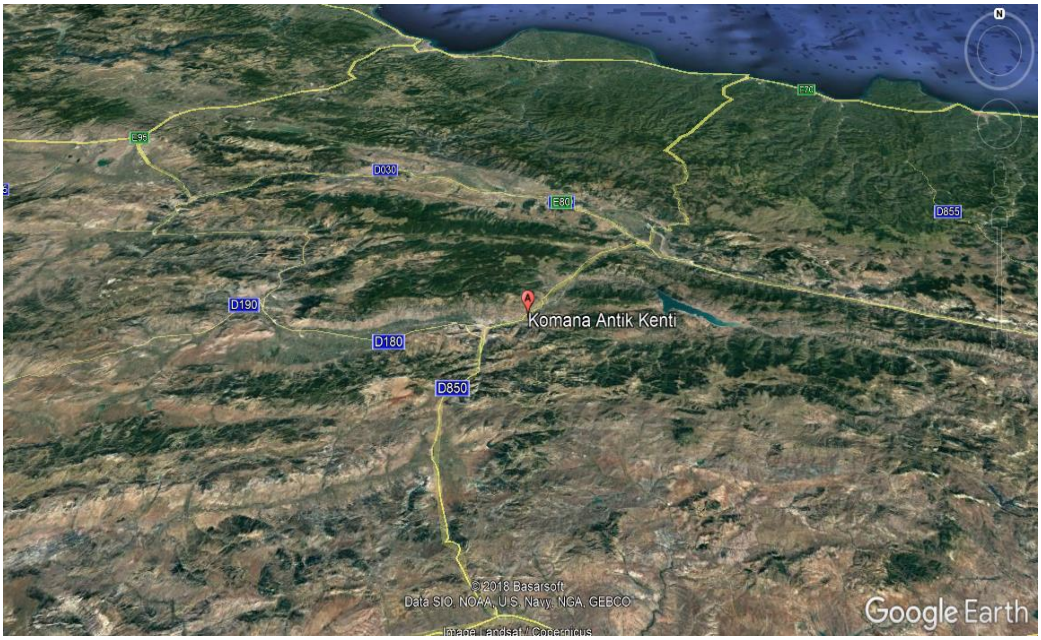


Figure 2. Geographical position of Komana from Google Earth

Figure 3. A Closer view of Komana from Google Earth

At the beginning of the 1840s, Hamilton was among the first visitor of Komana (Hamilton, 1842). After him, in the 1890s Hogarth and Munro visited Komana (Hogarth & Munro , 1893). In the 1900s, Anderson went to Komana. He as the first guy to mentioned name Gümenek. He also described the archaeological remains in detail including architectural structures (Anderson, 1902).

However, the first archaeological surface survey was carried out in 2004 by a team from Middle East Technical University. Archaeological surveys started with Hamamtepe and its continued expanding through the Merkez İlçe until 2009. Surveys indicated that in addition to the Hellenistic period sanctuary settlement continued intensively in this fertile area through the Ottoman period (Erciyas, 2012).

Figure 4. Hamamtepe Archaeological Site (Tatbul, 2017)

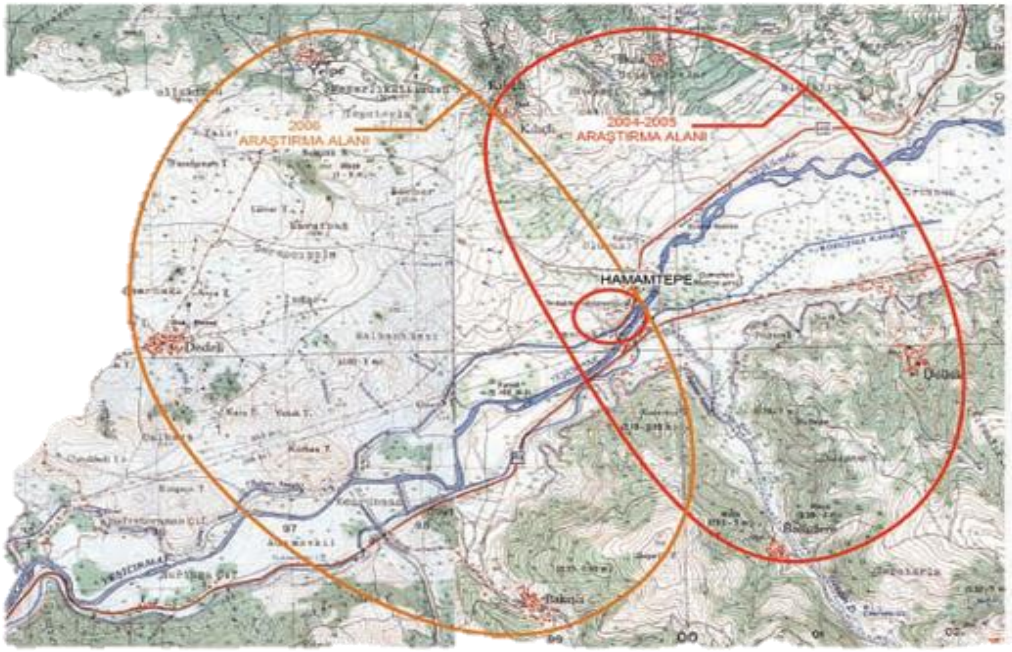


Figure 5. Hamamtepe Archaeological Site Map for Showing Surface Examination (Komana Archaeological Research Project, 2014)

1.4. THE HISTORICAL & ECONOMIC DYNAMICS OF KOMANA

Komana is a sanctuary dedicated to the Goddess Ma, who had a warrior like character (Erciyas, 2012). The excavations from which the data for this thesis was collected took places at a hill called Hamamtepe. Hamamtepe was inhabited starting as early as the Hellenistic period and continued until recently. The Byzantine period (7th - 8th century) was observed with ceramics and numismatic dating. The 11^{th}-12^{th} centuries (the Middle Byzantine Period) is represented by a cemetery and 2 chapels. The dating of this period was determined by architectural decorations, bronze reliquary and ceremonial and frescoes. Danishmends and Seljuks (12th - 14th century) established dominance in the region in the following centuries, and then the region came under the control of the Ottoman Period (17th - 18th century) (Erciyas, 2019).

Plans of this site representing different periods are below.

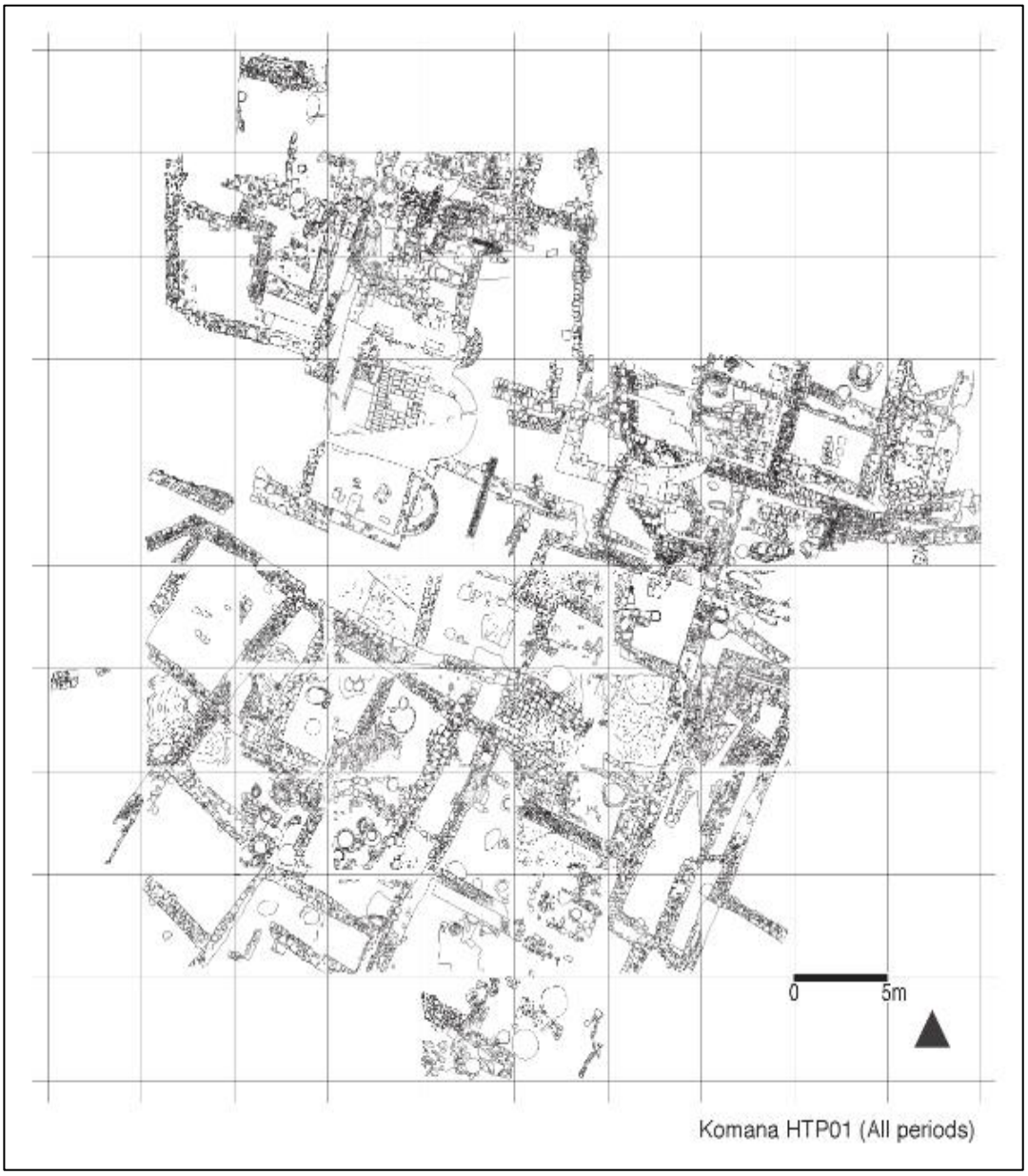


Figure 6. Plans of every period of Hamamtepe

1.5. THE PREVIOUS ARCHAEOMETRIC STUDIES OF KOMANA REGION

There are various archaeological and archaeometric studies are continuing at Komana. Mehmet Bilgi Er, a graduate student of Archaeometry program at the Middle East Technical University, is conducting an archaeometric study on the

Middle Byzantine period pottery from Komana with Assoc. Dr. Gülay Ertaş for his Ph.D.. Additionally, Canbek Altundal is conducting research for his M.Sc. thesis, an archaeometric study on the glaze of the same ceramics. However, there is no archaeometallurgical studies on the metals coming from the site. This thesis is the first archaeometallurgical study on Komana bronze objects.

CHAPTER 2

MATERIALS AND METHOD

2.1. BRONZES

Mankind started using metals with natural metals. As the first natural metals, copper, gold and silver ornaments were used only for pots, bowls, glasses, cups and tools. People who have discovered that low-melting galena (PbS) can melt on fire have applied it to other metals, especially copper (Yılmaz & Kurnaz, 2001).

Copper is a very important metal both in archaeological and metallurgical terms. It is the first metal used by human beings and copper has been a raw material for many objects from ornaments to weapons throughout history. In this respect, it has a special place in our cultural history. The melting point of the copper is 1084 ° C. It is soft, red colored and easy to process than other metals. Natural copper can be found in nature in the form of small pellets or beads, or in spongy or laminated forms. There are trace amounts of Ag, As, Fe, Co, Cd, Pb, Ni, Sb and Sn in copper ore (Özenbaş, 1996). Copper ore deposits are mainly found in veins in gabbro and peridotitic rocks. The copper minerals on the surface are different secondary copper mineralization, such as malachite, brochantite, chrysocolla, caprice, melaconite and azurite containing up to 30% copper. Oxides on the surface are the most easily accessible copper ores in most regions (Moorey, 1994).

One of the most common uses of copper is its alloys with other metals. Among the alloys, tin and zinc are the most important ones. In ancient times, tin alloys were called bronze. Compared to bronze pure copper, it has gained importance with its hardness, durability and easy casting properties (Yılmaz & Kurnaz, 2001). The

bronze color, which looks more pleasing to the eye, is preferred over red copper in some cases. Therefore, bronze is one of the more common archaeological metal find.

2.1.1. Corrosion of Bronze

Bronze corrodes faster when it comes into contact with the atmosphere than other metals (Erhan, Girginer, & Tekin, 2008). It can be composed of bronze copper-tin, copper-antimony, copper-arsenic, copper-lead or copper-zinc mixtures. The reason for the incorporation of these elements in copper is that the melting of the copper facilitates casting (Copper Development Association Inc., 2017). The status of bronze finds depends on the type of alloy and the climate and environment at conditions (Başaran, 1980).

All of the archaeological finds have a layer of corrosion in surface. This situation does not depend on whether the archaeological finds emerge from underground or above ground. Especially bronze objects are affected by salt, oxygen and moisture and this corrosion is called bronze disease (Kocabaş, 1998). Chloride ions play a major role in the basic chemical change that causes this disease. If no action is taken for this deterioration, the reaction continues until the metal is exhausted. Degradation of bronzes depends on two different environments; aerobic and anaerobic. In an aerobic environment, the circulation of oxygen is high and is generally referred to as above ground. The anaerobic environment is used to describe environments where oxygen is absent or too low (Erhan, Girginer, & Tekin, 2008).

Under normal conditions, a metallic copper is oxidized and ionized. This oxidation equation is given below:

$$Cu^0 \rightarrow Cu^+ + e^- \qquad \text{or} \qquad Cu^0 \rightarrow Cu^{+2} + 2e^-$$

If there are free chlorine ions in the environment, they form *nantokite*. This is copper (I) chloride and it is white in color. This layer forms as the first layer on the metal in

the presence of chlorine ions. The following chemical equations represent this phenomena:

$$2Cu^{+} + 2Cl^{-} \rightarrow Cu_2Cl_2 \qquad \text{or} \qquad Cu^{+} + Cl^{-} \rightarrow CuCl$$

Decomposition reactions after *nantokit*e formation are entirely dependent on the environment in which the bronze is present. If bronze is in an aerobic environment, copper (II) chloride is formed. The light green and powdery patina on the surface that occurs as a result of this reaction is called paratachamide. If there is a green and bulky patina, it is called *atacamide*.

The following reaction is an equilibrium reaction and the resulting hydrochloric acid (HCl) penetrates very quickly into the metal to regenerate the nantokite (Özen, 1999).

$$2Cu_2Cl_2 + 4H_2O + O \leftrightarrow CuCl_2.3Cu(OH)_2 + 2HCl$$

All of the above reactions are repeated one after the other and, if no action is taken, they continue until the metal is destroyed.

If the environment is an anaerobic (usually subsoil) environment, in the absence of oxygen, chlorite ions form nantokite that interact with water to form cuprite. This reaction moves very slowly and it can affect copper in metallic form, depending on the oxygen in the environment. Following reaction explains that phenomena:

$$Cu_2Cl_2 + H_2O \leftrightarrow Cu_2O + 2HCl$$

As shown in the following reaction, if there is no oxygen in the environment, it remains in balance as long as the ambient conditions do not deteriorate (Özen, 1999).

$$2Cu^{0} + 2HCl + \frac{1}{2}O_2 \leftrightarrow Cu_2Cl_2 + H_2O$$

However, there is a small amount of oxygen in subsoil conditions. This oxygen may be present in the soil, in the cavities on the archaeological find itself, in the air trapped in the metal during casting, or dissolved in water (Erhan, Girginer, & Tekin, 2008).

Corrosion processes of archaeological bronze specimens are as follows:

Copper Corrosion Process in Archaeological Bronze Works

Starter Product	Reaction	Result Product	
Cu^{+2}	+ ½ O_2	**Cu_2O**	Küprit
$2Cu^{+2}$	+ O_2	**CuO**	Tenorit
Cu^{+2}	+ $2H_2O$	**$Cu(OH)_2$**	Bakır(II)Hidroksit
Cu_2O	+ ½ O_2		
$Cu(OH)_2$	+ Cu^{+2}	**Cu_2O + H_2O**	Küprit
Cu_2O	+ H_2O + CO_3^{-2}	**$Cu_2(OH_2)CO_3$**	Malahit
$Cu_2(OH_2)CO_3$	+ CO_3^{-2} + CO_2	**$Cu_2(CO_3)_2(OH)_2$** + H_2O	Azurit
	+ yanma (>400°C) Ve yüksek pH	**3CuO** + $2CO_2$ + H_2O	Tenorit
CuO	+ H_2O	**$Cu(OH)_2$**	Bakır(II)Hidroksit
$4Cu(OH)_2$	+ SO_4^{-2} + 2 H^+	**$CuSO_4$. 3$Cu(OH)_2$**	Brokantit
$CuSO_4$. $3Cu(OH)_2$	+ $2Cl^-$	**$CuCl_2$.3$Cu(OH)_2$** +SO_4^{-2}	Paratakamit/ Atakamit
	+ $2CO_2^-$	**$Cu_2(OH_2)CO_3$**	Malahit
2Cu	+ $2HCl^-$	**2CuCl** + H^+	Nantokit
2CuCl	+ H_2O	**Cu_2O** + $2H^+$ + $2Cl^-$	Küprit
4CuCl	+ O	**$2Cu(OH)_3Cl$** + $4H_2O$	Paratakamit/ Atakamit
Cu	½ O_2 + H^+ + HS^-	**CuS** + H_2O	Kovellit
CuS	3Cu+7/2+O_2+3H_2O	**$CuSO_4$. 3$Cu(OH)_2$**	Brokantit
2Cu	½ O_2 + H^+ + HS^-	**Cu_2S** + H_2	Kalkosit
Cu_2S	2Cu+7/2+O_2+3H_2O	**$CuSO_4$.3$Cu(OH)_2$**	Brokantit

Figure 7. Physical and Chemical Change of Bronze in Times

There are many types of corrosion shaped according to the character of bronzes. For archaeological bronze objects, it is possible to examine these types of corrosion in three groups: homogeneous corrosion, regional corrosion and corrosion caused by interaction of different metals (Karatak, 2018).

Uniform corrosion: It is a kind of corrosion that occurs at the same speed on the entire metal surface (Landolt, 2007). On a macroscopic scale, it is not possible to distinguish between cathodic and anodic regions. That is, the entire surface of the metal acts as both the cathode and the anode at the same time, and the entire metal surface is eroded / thinner at the same depth (Yalçın & Koç, 1997). Following figure, figure 8, shows uniform corrosion.

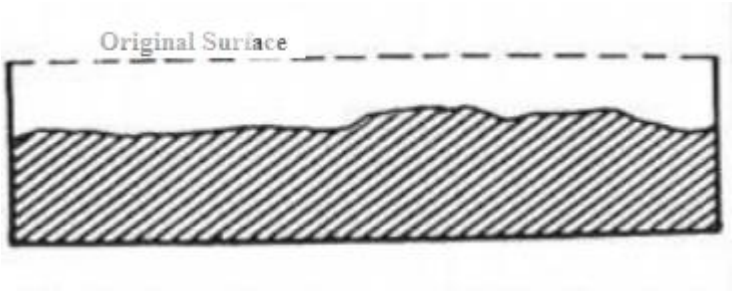


Figure 8. Layout of Uniform Corrosion (Yalçın & Koç, 1997)

Regional Corrosion: These corrosion do not spread to the entire metal surface. Corrosion condenses in a small area (Yalçın & Koç, 1997). The best example of this type of corrosion is pitting corrosion. The pits caused by pitting corrosion are sometimes too small to be visible or the pit is not noticeable because it is filled with corrosion products (Landolt, 2007). Following figures, figure 9 and figure 10, show layout of regional corrosion and types of pitting corrosion.

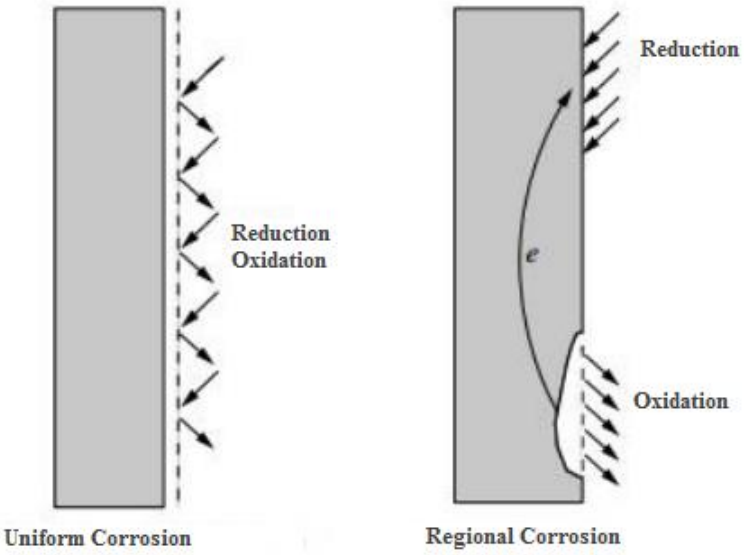


Figure 9. Layout Uniform Corrosion and Regional Corrosion on Metal Surface (Landolt, 2007)

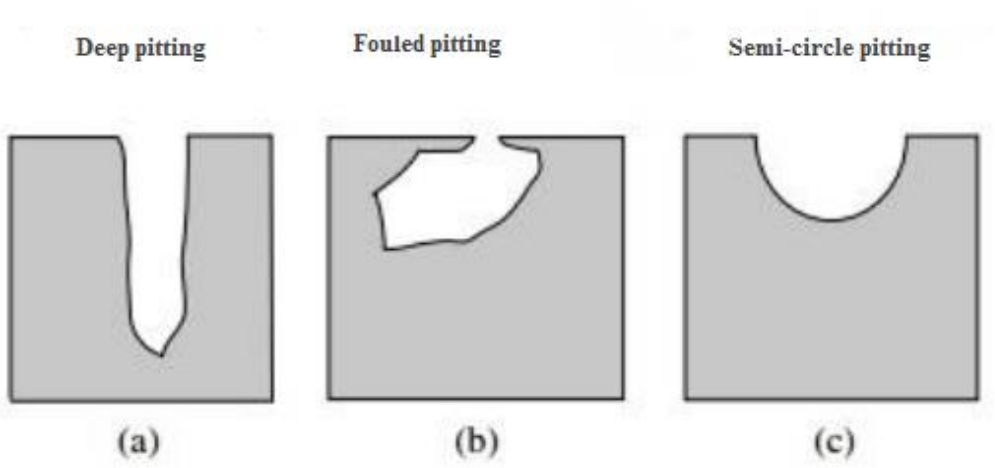


Figure 10. Types of Pitting Corrosion (Landolt, 2007)

Corrosion as a result of the interaction of different metals: Metals exhibit different anode-cathode behavior depending on the type of elements in their content. When two different metals are bonded together by an electrical bond (contact) in a corrosive environment, the metal is corroded as the anode, the electrode potential of which is more electronegative. This corrosion is also known as bimetallic corrosion

(Yalçın & Koç, 1997). In short, as a result of the electrical interaction between both metals, whichever metal is more stable (noble) protects itself, it consumes less noble metal (Landolt, 2007). Following figure, figure 11, describe corrosion as a result of the interaction of different metals.

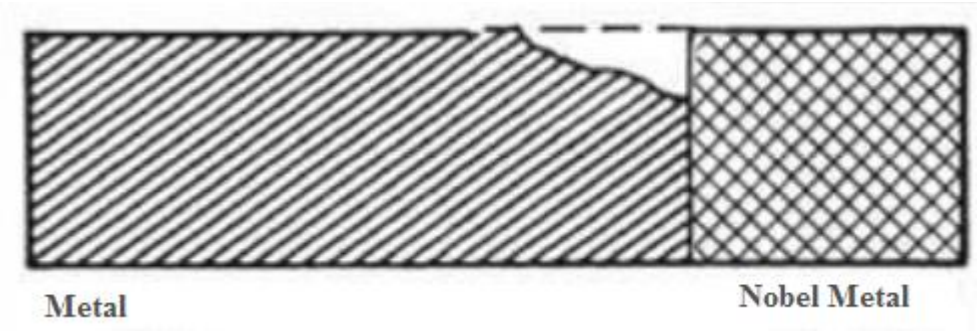


Figure 11. Layout of Corrosion As A Result of the Interaction of Different Metals (Landolt, 2007)

2.2. MANUFACTURING OF BRONZE COINS

Most of the archaeological metal objects are made of bronze alloy (Erhan, Girginer, & Tekin, 2008). Coins are also mostly made of bronze alloys and coins are produced by striking techniques.

Coins used for trade are metals that are easy to transport for trade, as well as longevity. Since metals are easy to cast and melt, they bear signs of the period they belong. These marks were stamped on one side of the coin with a device of a certain design (Erhan, Girginer, & Tekin, 2008).

Before the emergence of the Industrial Age, coins were struck by hand (Made How, n.d.). A round metal cavity was placed on an anvil equipped with a printing plate. Another mold was attached to a mallet, which is then placed on top of the cavity. The hammer was then tapped onto the coins, resulting in a pressure of 7 tons. Following figure is representing striking of coins with hammer.

Figure 12. Illustration of Coin Production

Sometimes two or three strokes were required to obtain the appropriate pattern on the coins (The Royal Mint Museum, n.d.). When the molds were heated before the hammer blow, the required number of strokes decrease in the coins put into the molds, but the Roman coins received a cold blow.

2.3. MATERIALS

In this thesis, bronze coins from Komana belonging to different periods are examined. For comparison with these coins from Komana, unidentified bronze objects were also included in the material set. In this thesis, the term amorphous is used for these unidentified objects. These amorphous objects were also found at Komana from layers representing different periods. The sample set consists of a total of 9 pieces. 8 of them are coins and 1 of is an amorphous bronze object.

These pieces were excavated between 2011 and 2017. There is no other archaeometallurgical study conducted for these coins. Therefore, this study will be a pioneering study for extracting information on metal production and use at the site.

Coins and bronze objects from Komana are listed as follows:

Table 1. List of Bronze Metals Analyzed

INVENTORY NUMBER	LAYER	SECTOR NUMBER	PERIOD
KARP13-HTP01-449 COIN	T11	282/583	Danishmend/Seljuk
KARP11-HTP01-092 COIN	T06	277/603	Middle Byzantine
KARP16-HTP01-216 COIN	T05	292/603	Early Byzantine
KARP11-HTP01-428 COIN	T04	257/613	Middle Byzantine

Table 2. Cont'd.

KARP17-HTP04-013 COIN	T05	317/668	Danishmend/Seljuk
KARP11-HTP01-080 COIN	T06	277/603	Middle Byzantine
KARP15-HTP01-139 COIN	SURFACE	297/603	No Date
KARP17-HTP01-284 COIN	T15	297/608	Middle Byzantine
KARP13-HTP01-454 AMORPHOUS	T04	282/608	Middle Byzantine

On this table, Inventory Number is a number given by the excavation. In this number the year indicates the year of excavation. (KARP) stands for Komana Archaeological Research Project, HTP stands for Hamamtepe and the number is the excavation area on Hamamtepe. Following part of the Inventory Number is the find number. (T) represents the soil strata (layer) in which the object was discovered. The sector number represents the coordinates of the excavated sector. Finally, period is the rough dating for the object.

As can be seen, 8 out of the 9 bronze sample sets are coins. Among the materials in the sample set, there is one amorphous non-coin bronze object. 2 coins (KARP17-HTP04-013 COIN and KARP13-HTP01-449 COIN) belong to the Danishmend/Seljuk period. Additionally 1 coin which is named as KARP15-HTP01-139 COIN has no periodic information. In addition, the material coded KARP15-HTP01-139 COIN is a coin which went through conservation. None of the others were conserved and all objects (except KARP15-HTP01-139 COIN) are heavily corroded.

Detailed information as well as photographs of the objects are given in Appendix A, including the complete illustrated and descriptive list of them.

In the remainder of the thesis, the KARP and HTP codes were removed for convenience in especially the analyses. The materials are defined just with their identity and number, like COIN449 or AMORPHOUS454.

2.4. ANALYSIS METHOD OF THE STUDY

As mentioned in Chapter 1, the aim of this study is to obtain clues about the economic dynamics of the 11^{th} and 14^{th} centuries by looking at the elemental compositions of bronze coins. In order to make this interpretation, the coins were compared elementally with one unidentified bronze object. For this study two spectrometric analyses were used; Micro X-Ray Fluorescence (Micro-XRF) and Scanning Electron Microscope (SEM-EDX).

In addition to these spectrometric methods, coins and amorphous objects collected for comparison were photographed with X-Ray radiography and stereomicroscope.

2.4.1. X-RAY Fluorescence and Production of Result with XRF

In archaeological studies, supporting the theoretical knowledge of archaeologists and providing quantitative data is very important in terms of establishing a database for future archaeological studies. This will facilitate the interpretation of archaeological artifacts for new excavation sites or previously obtained quantitative data. One of the most important issues is to avoid damaging the objects found while conducting archaeometrical studies. It is important to analyze the archaeological finds without damage. Therefore, the use of non-destructive methods has increased in recent years.

Especially XRF is the most common spectrometric method used in archaeometric studies (Rehren & Pernicka, 2008). Since it is a non-destructive analytical method, it has become a very broad and well-established application and a very thorough analysis technique (Beckhoff, Kanngeieber, Langhoff, Wedell , & Wolff, 2006). With the discovery of X-ray by Wilhelm K. Roentgen, a German physicist, this technology has evolved since the 1950s. With the formation of the first principles of XRF in the 1960s, the first commercial instruments were developed in the 1970s. In

1970, the lithium drifted silicon detector was developed, and this technology is still in use today. XRF has become an instrument used for detailed techniques in laboratories as it is affordable and the operational power continues to increase. Therefore, the use of XRF gained momentum and opened the door to new developments. Especially with the development of portable and hand-held devices, XRF has become more flexible especially in archaeometric studies (Beckhoff et al., 2006).

XRF is based on X-rays. X-rays are wavelengths caused by slowing down high-energy electrons or electron transitions in the inner orbits of atoms. These wavelengths are between 0.1-100 Å (10-11 - 10-8 m). They are electromagnetic waves whose energy varies between 0,125-125 keV (Figure 6). (Arslan, 2016). There is an inverse relationship between the wavelength and energy of the X-rays:

$E = h \, x \, c \, / \, \lambda$ (2.1)

Where E is the energy of the photon; h, Planck constant (6,626 x10-34 Joules. seconds); c is the velocity of light (3x108 m / s) and λ is the wavelength (nm) of the beam.

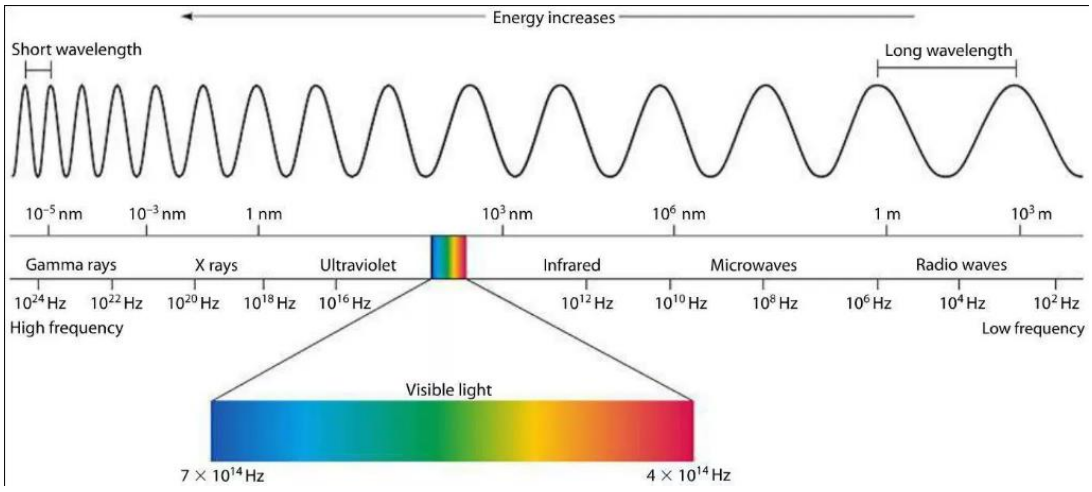


Figure 13. Electromagnetic Spectrum

X-rays have both wave and particle properties and they are invisible to the eye. Afterall, they have no weight and are not affected by electrical or magnetic fields. They spread in lines with the speed of light. The X-rays also give a continuous spectrum, which is absorbed and partially irradiated during passage through the material. This scattered part continues to interact with the name of the secondary radiation. X - rays, with some of the substances that fall on it creates shimmering during the irradiation. This glare is called fluoresence (Yaylı, 2013).

It is possible to perform a non-destructive chemical analysis by X-ray spectrometer. When the electron moves towards the anode at high speed, it loses its energy and deviates from its path when it is under the influence of the nucleus. This will cause the electron to gain acceleration and make electromagnetic radiation, allowing it to emit photons. This results in a continuous X-ray spectrum. This phenomenon is also called Bremsstrahlung (braking) radiation (Yaylı, 2013). Another form of X-ray formation occurs when the high-speed electron strikes the anode metal and detaches an electron from the anode's orbit. Thus, the atoms lose their stability. To regain their stability, the electrons in the outer orbital try to fill the electron spaces in the inner orbital. As much as the difference in energy between these two trajectories, a radiation occurs and this occurs as an X-ray. These X-rays are characteristic and are defined as secondary X-rays or fluorescent radiation (Yaylı, 2013). Secondary X-ray formation (or fluorescent) can be seen in Figure 9.

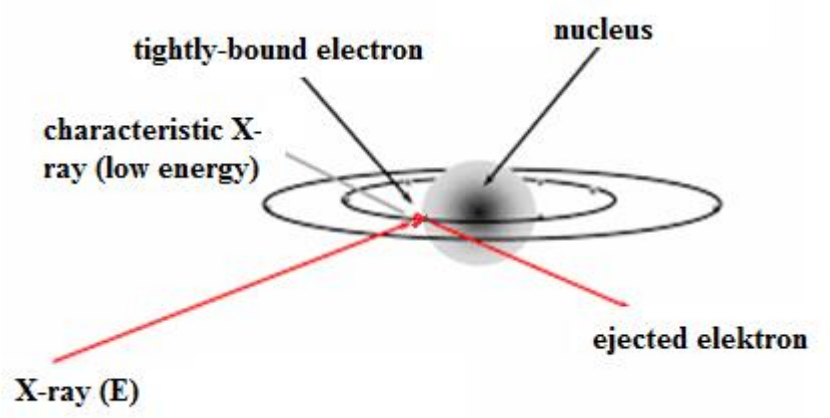


Figure 14. Secondary (fluorescent) X-ray formation (Yaylı, 2013)

Fluorescent radiation can be analyzed by sequencing the energies of photons (energy distribution analysis) or by separating the wavelengths of radiation (wavelength distribution analysis) (Skog, Holler, & Crouch, 2007). The intensity of each characteristic radiation is directly related to the amount of each element in the material. The wavelength of these elements is different for each element and has a distinctive feature. In other words, these radiations are fingerprints of that element. By determining the wavelength of the radiation, the genus of the element is determined and the concentration of the element is determined by measuring the intensity of this detected beam (Skog et al., 2007).

Qualitative, semi-quantitative and quantitative analysis can be performed elementally using X-ray fluorescence method. This method is rapid and a large number of elements can be analyzed in a few minutes (Tykot, 2015).The sample preparation requirement is low and the sample is not damaged in any way during the analysis. It is therefore a reproducible type of analysis. Its sensitivity is better than other methods (Ferreti, 2000).

2.4.2. Micro X-Ray Fluorescence

Micro-X-ray fluorescence (Micro-XRF) is a basic analysis technique that allows the examination of very small samples. Micro-XRF uses the working principle of the

traditional XRF method. That is, it uses direct X-ray excitation for elemental analysis. However, unlike conventional XRF, it uses X-ray optics to limit the size of the excitation beam or to focus the excitation beam to a small point on the sample surface. In this way, the properties on the sample can be analyzed. X-ray optics offer an alternative way to create small focal points with high X-ray flux on the sample surface for Micro-XRF applications (XOS, 2019).

The Micro-XRF is suitable for archaeological objects which are not in-situ, because it gives more accurate measurement results.

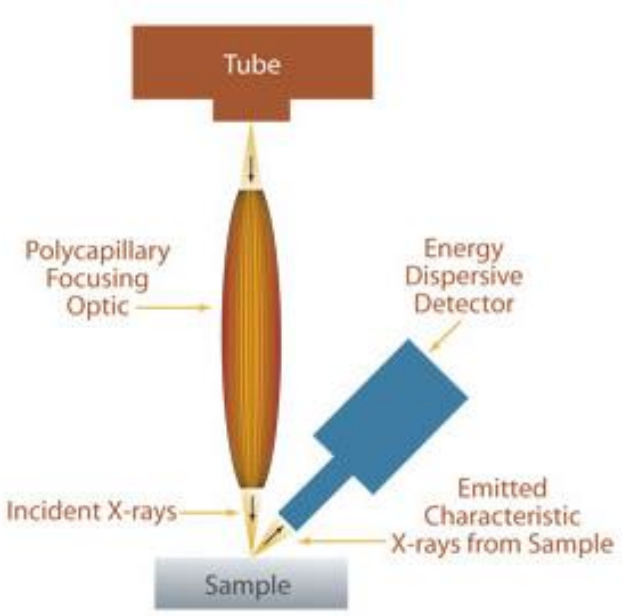


Figure 15. Standard Micro XRF configuration (XOS, 2019)

)

This study was conducted in Maklab (material conservation labratory) on September 6, 2019 at Ankara Hacı Bayram Veli University. All coins and amorphous bronze object analyses were done with Micro XRF.

The model and features of the Micro XRF instrument used are as follows:

- Model: Spectro Midex-M
- Detector: SDD
- Excitation: X-ray tube, molybdeum (Mo) anode, 48 kV max.
- Dimensions: Height 740 mm (29.1 in), Width 580 mm (22.8 in), Depth 670 mm (26.4 in), Weight 55 - 70 kg (121 - 154 lbs) depending on configuration
- Sample Chamber: Video system to display sample image, Manually adjustable sample table
- Power Supply: Operating voltage 95-120V/200-240V, 50/60 Hz, Power consumption spectrometer: 200 W
- Evaluation system: External computer system; Windows operating system, keyboard, mouse, monitor, printer
- Software: Menu-based software for control of spectrometer functions and evaluation of data
- Analyses: Fundamental Parameters program FP+ for element analysis of alloys, Calibration for RoHS compliance screening of plastics and composite material
- Options: Motor driven XYZ precision table with a maximum travel path of 240x178x160 mm/ 9.4x7.0x5.3“ (WxDxH) maximum sample weight of 3 kg/6.6 lbs

2.4.3. X-Ray Radiography (Roentgen)

X-ray radiography (Roentgen) is an imaging technique related to the internal structure of matter with X-rays. In this technique, the sample is placed on a radiation-sensitive film or screen opposite the radiation source (Tuğrul, 2012) . The sample is then irradiated in this position for a period of time and intensity. This time is called the exposure time. At the end of the exposure time, for example, a contrast image is displayed in light and dark tones. The light areas observed in this image represent areas where material thickness or density is high; dark areas represent areas where material thickness or density is low. This tone difference is explained by

changes in the radiation absorption capacity of materials with varying density and thickness. In low-density or thin materials, since the material does not absorb the radiation too much, a large amount of radiation passes through the film, resulting in dark areas. In the case of high density or thick materials, the opposite is true, the areas seen are light colored.

The corrosion on the bronzes examined in this study can be seen clearly with naked eyes. For this reason X-ray radiography were used to determine whether the corrosion has completely consumed the original metal or not. The images proved that below the corrosion layers there was healthy metal objects. X-ray radiography were applied for all coins and the amorphous object.

2.4.4. Stereo Microscope

Stereo microscope is a type of optical microscope designed to magnify and observe a sample using light reflected from the surface of an object. The stereo microscope provides an opportunity to study surface topography in the analysis of samples that require a three-dimensional view (Nothnagle, Chambers, & Davidson, 2019).

A stereo microscope is often used to examine the surfaces of solid specimens or to perform close studies such as dissection, microsurgery, clock making, circuit board production or inspection, and fracture surfaces such as fractography and forensic engineering. They are therefore widely used in the manufacturing industry for production, inspection and quality control. Stereo microscopes are important tools in archaeology and it provides an opportunity to define the surface appearance of archaeological specimens (Nothnagle, Chambers, & Davidson, 2019). The stereo microscope can be equipped with a dual-eyepiece, as well as with the developing technology to photograph the samples with a digital display.

In this study, stereo microscope was used to identify the corrosion zone on the surface of the coins and non-coin amorphous bronze objects.

2.4.5. Scanning Electron Microscope

Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of the sample with electron beam focusing on the surface (Ponting, 2004). The electrons interact with the atoms in the sample to produce various signals containing information about surface topography and composition of the sample. In the scanning electron microscope, electrons are accelerated by 1 kV - 30 kV. The electron beam is controlled by electromagnetic and electrostatic lenses and focuses on a small point. The sample surface is scanned with a focused electron beam (Toolbox, 2015). Electrons interact with the sample and then produce various electrons and radiation detected. Secondary and backscattered electrons are mainly used for x-rays for imaging purposes for analysis of the composition. The secondary electrons of each scanned point of the scanned area are collected by detectors that convert the signal intensity into an image. That is, scanning electron microscopy provides an image of the surface area of the sample (Zhou, Apkarian, Wang, & Joy, n.d.). The entire path of the beam is kept under vacuum to prevent electrons from interacting with air molecules. Samples must be conductive and well grounded to prevent load buildup. Figure 15 shows the layout of the scanning electron microscope.

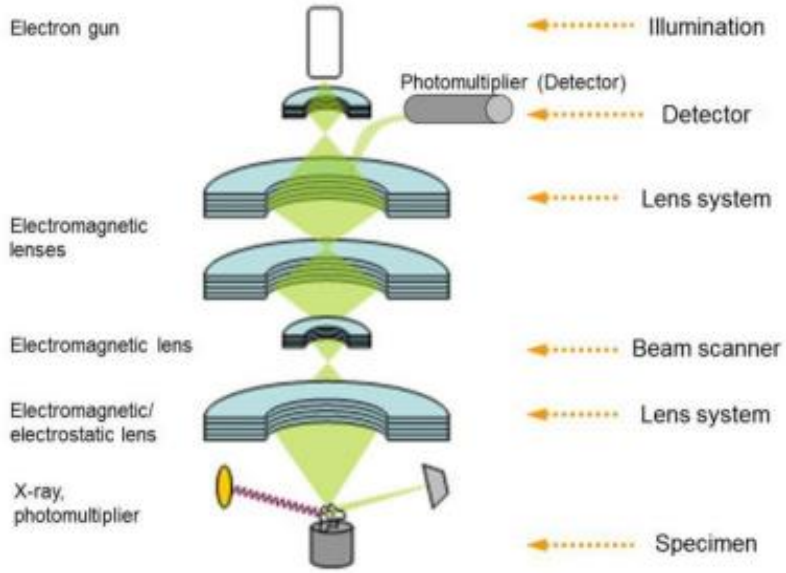


Figure 16. Layout of scanning electron microscope (Toolbox, 2015)

Images from scanning electron microscopy can be very valuable in archeology. This spectrometric method makes it possible to perform microanalysis from a small area of an object. This technique also provides composition information about different areas of the same image and is very useful in the study of archaeological materials (Ponting, 2004).

In this study, SEM analysis was conducted for COIN013 coded coin.

2.5. METHOD OF THE STUDY

2.5.1. Sample Preparation

In this study, elemental analysis of all samples were done with the Micro-XRF, X-ray Radiography, Stereo-microscope and SEM-EDX. Instruments operation conditions were explained in Chapter 2.4.

Bronze objects from Komana contain a very high amount of corrosion. Excessive corrosion in bronzes is caused by a series of chemical reactions of copper so it is the reason of bronze disease (Asolati, Grazzi, Canovaro, & Calliari, 2013). If these chemical degradations are not intervened, bronze which is under the corrosion can be completely lost. X-ray showed that all of the objects contained metal. So, each object could be analyzed. A stereo microscope was used to focus on the corrosion zones of the objects. True scale, stereo microscope and x-ray photographs of the materials are represented at Appendix A.

- For Micro XRF analysis, limestone layer on the surface of coins and bronze amorphous objectwere cleaned. Analysis was done for all samples (both coins and the amorphous bronze object).

- For stereo microscope and X-ray radiography analyses, no intervention was made to the samples. Analysis was done for all samples (both coin and amorphous bronze objects).

- For SEM analysis, small pieces of specimens were removed from the samples to see the inside of the samples. The samples were then placed on the adhesive stand and analyzed for cross-sectional surfaces. Example selected for SEM analysis is COIN013.

According to the results of the analysis, the elementary compositions of the bronze objects have been obtained. This information has been used to provide clues about the economy of Komana.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. RESULTS

3.1.1. Visual Examination

X-ray radiographs of all samples were taken to see if metallic cores were found under the corrosion layers of the samples. As a result of the analysis, it was found that there was still metallic layer under the corrosion layers of all samples. X-ray radiography of the samples is given below, figure17.

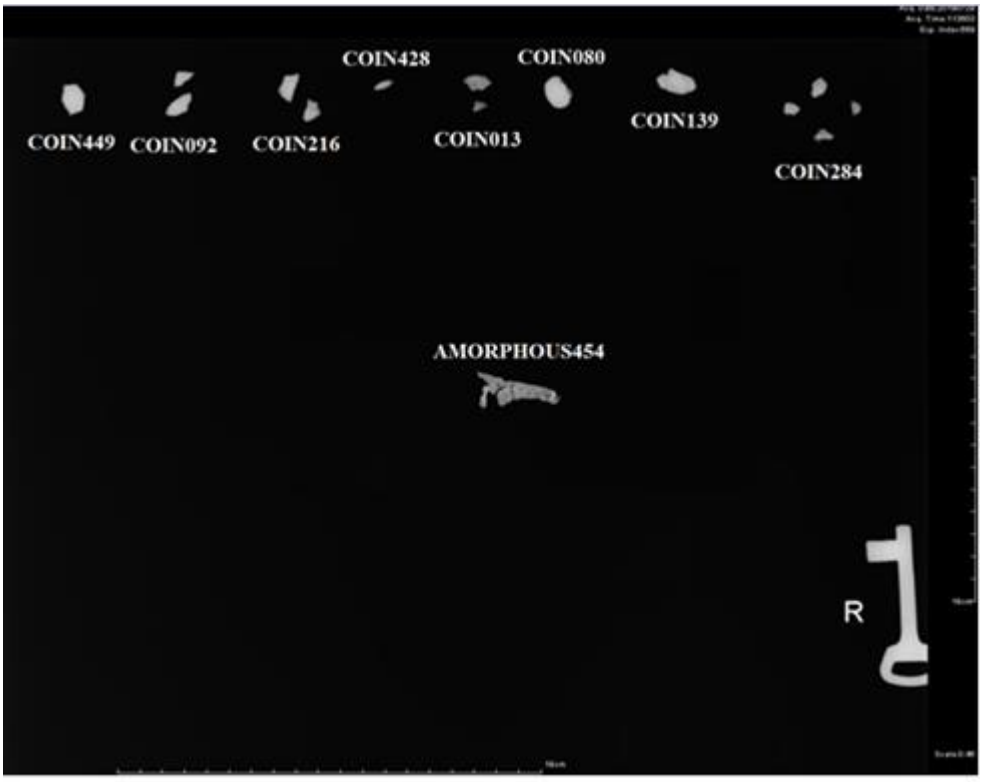


Figure 17. X-ray Radiography View

In addition to X-ray radiography, the views of all samples were photographed with a stereo-microscope to see the degradation zones. Figure 18 illustrates stereo-microscope images of the samples COIN449 and AMORPHOUS454.

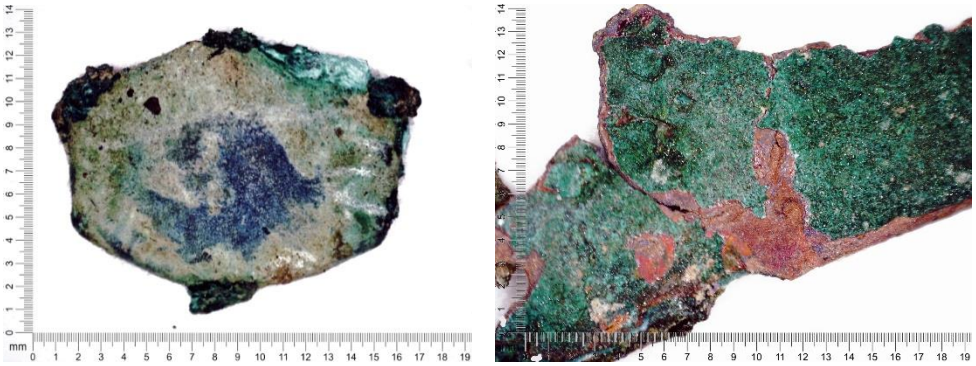


Figure 18. Stereo Microscope View of COIN449 and AMORPHOUS454

X-ray radiography, stereo microscope and visible real-size images of all samples are given in Appendix A.

3.1.2. Micro-XRF Examination

All 9 bronze samples were analyzed with Micro XRF. The basic elements that make up the bronze alloys were taken as selective elements. These elements are Cu, Sn, Zn, Ag, Pb, Sb and Fe.

Micro XRF analysis results are given in Table 2 and Table 3.

Table 3. Selective Elements Concentrations for Coins (taken from Micro XRF)

Sample	Period	Unit	Cu	Sn	Zn	Ag	Pb	Sb	Fe
COIN449	**Danismends/Seljuk**	%	94,16	0,009	0,005	0,026	2,30	0,011	0,394
COIN092	**Middle Byzantine**	%	81,55	17,53	0,005	0,021	0,004	0,019	0,057
COIN216	**Early Byzantine**	%	87,73	8,92	0,006	0,082	1,20	0,097	0,861
COIN428	**Middle Byzantine**	%	87,49	10,97	0,006	0,009	0,547	0,191	0,006
COIN013	**Danishmends/Seljuk**	%	83,77	0,007	0,004	0,010	4,38	0,010	0,004
COIN080	**Middle Byzantine**	%	93,95	2,68	0,005	0,471	0,034	0,013	0,005
COIN139	**No Date**	%	42,56	7,09	5,75	8,00	33,44	0,640	0,257
COIN284	**Middle Byzantine**	%	89,24	9,16	0,006	0,132	0,134	0,259	0,005
AVERAGE		%	82,06	7,97	0,643	0,974	4,26	0,183	0,659

Table 4. Selective Elements Concentrations for Amorphous (taken from Micro XRF)

Sample	Period	Unit	Cu	Sn	Zn	Ag	Pb	Sb	Fe
AMORPHOUS454	**Middle Byzantine /Church**	**%**	90,99	0,050	3,36	0,023	2,23	0,040	0,290

According to the results of the Micro XRF, COIN139 coded coin is notable because of its low copper content. All results of the Micro XRF analysis and the graphs are given in Appendix B.

3.1.3. SEM-EDX Examination

SEM-EDX analysis was performed on COIN013 as previously mentioned. Three different points were measured for this sample. Measurements were taken especially from the areas where the crack was visible on the section surfaces. SEM analysis result of the selected sample is given below.

Table 5. COIN013 SEM Result

Sample Name	Reading	Cu	Pb	Fe
COIN013	Number	Conc. (%)	Conc. (%)	Conc. (%)
Seljuk	1	77,950	0,000	2,830
	2	87,980	6,310	0,340
	3	88,300	5,090	0,660
	Average	**84,743**	**3,800**	**1,277**

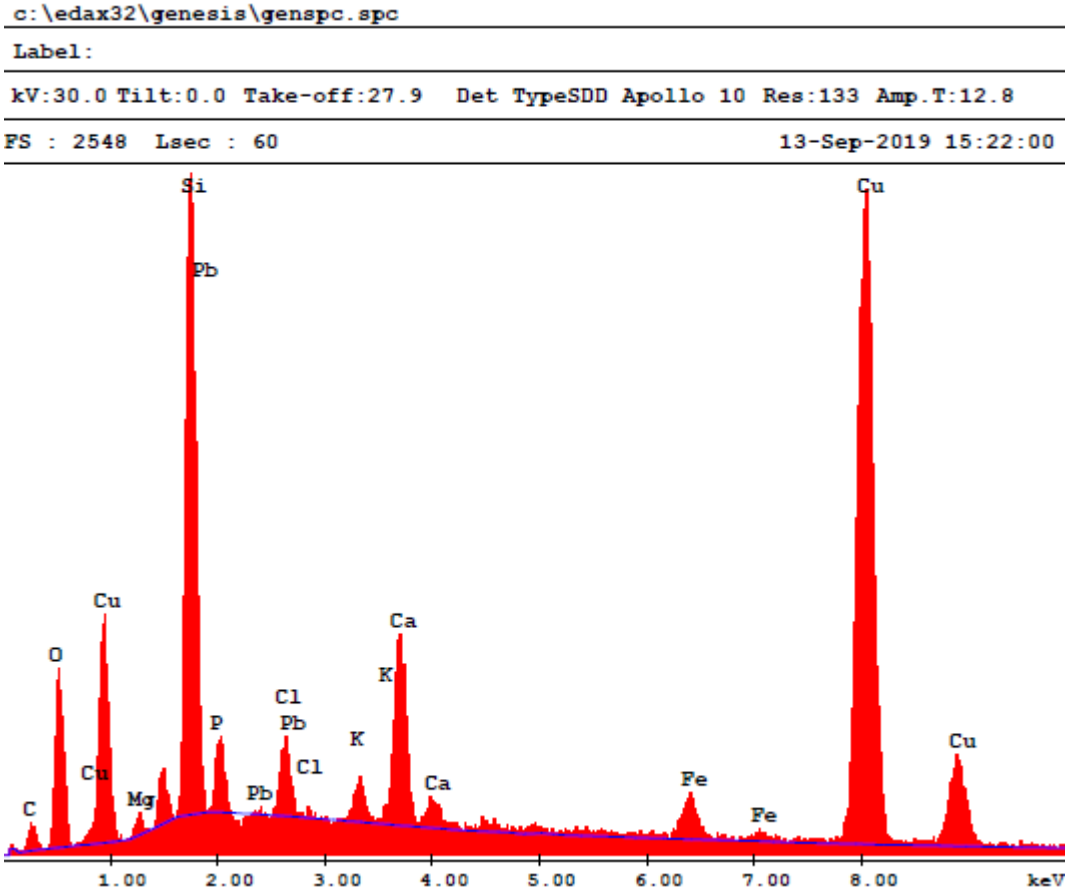


Figure 19. SEM Analysis Image Reading 1

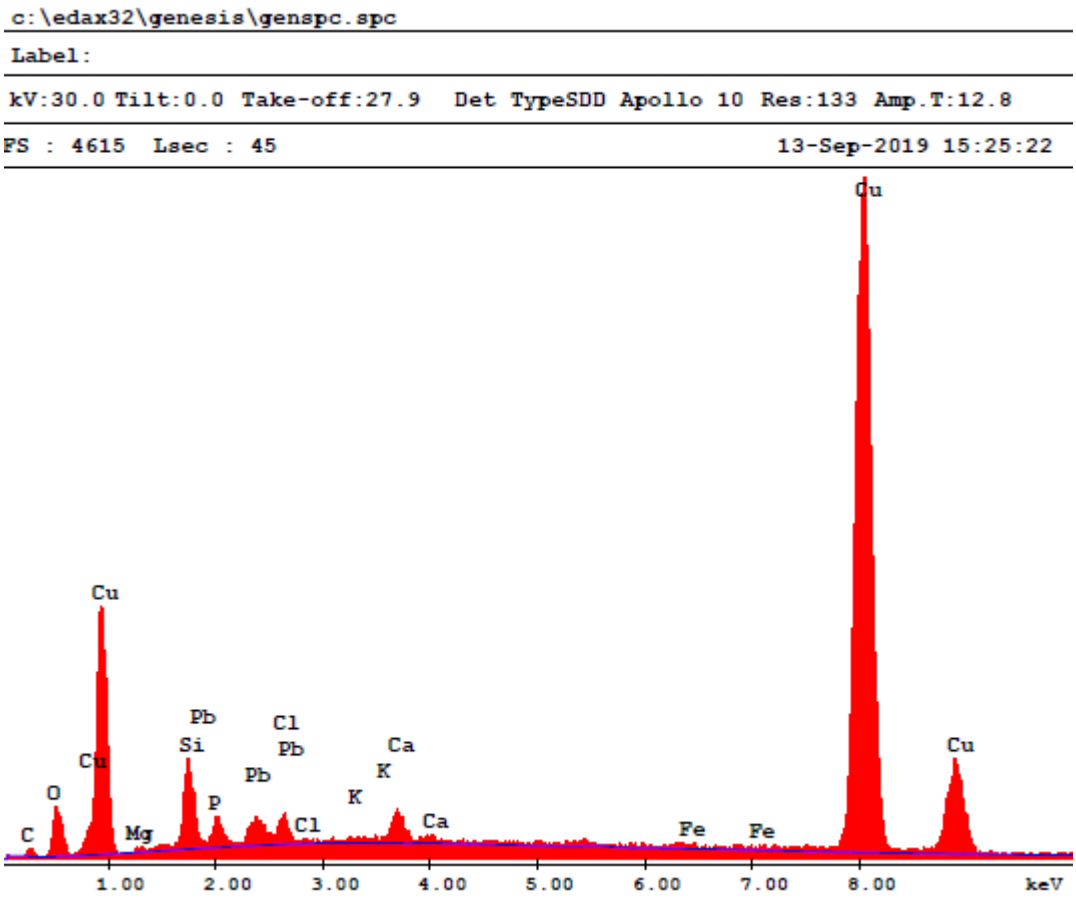


Figure 20. SEM Analysis Image Reading 2

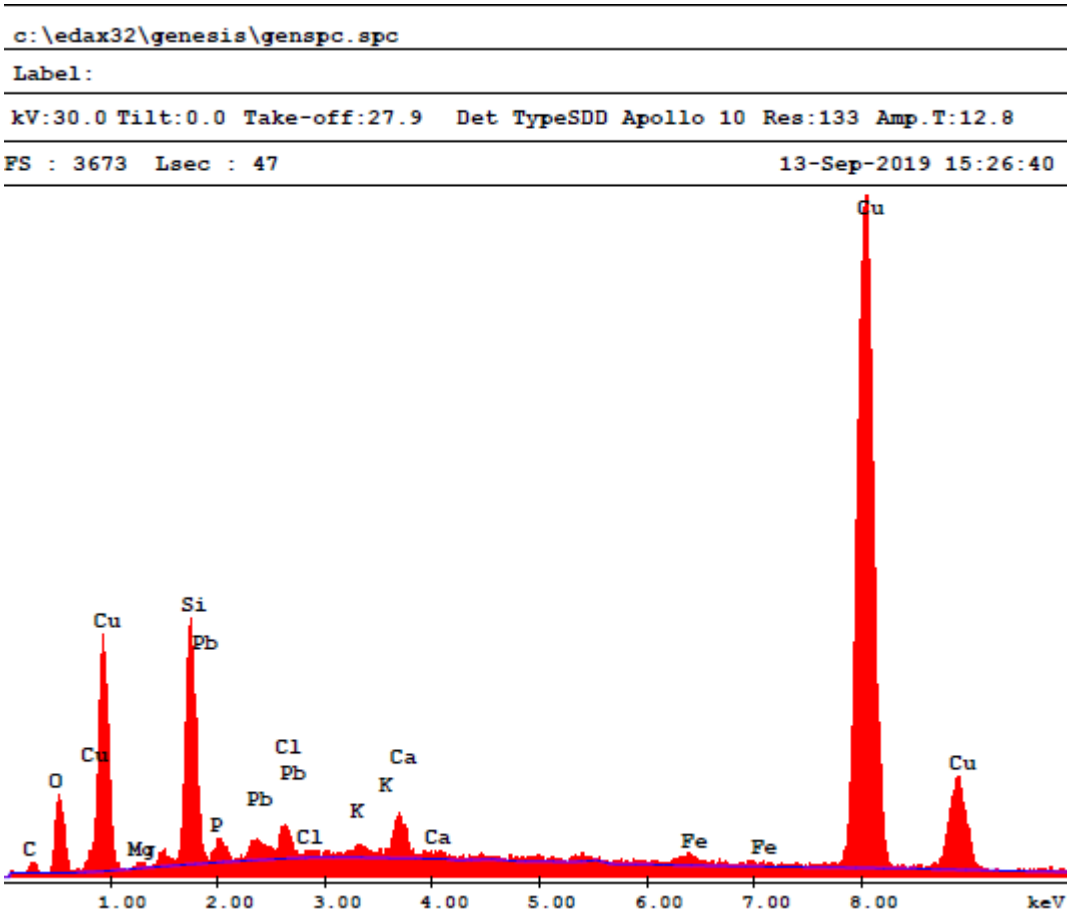


Figure 21. SEM Analysis Image Reading 3

3.2. DISCUSSION

In order to correctly interpret the results in Chapter 3.1, it is necessary to first define the main elements of bronze and their functions.

- **Copper (Cu)**

Copper is a metal with red and brown appearance. It has high electrical and thermal conductivity properties. Copper is extremely resistant to atmospheric conditions. Its strength is low, casting and welding ability is not good (Oğuz, 1989). However, according to Oğuz (1989), due to its cubic surface centered crystal structure, it can be shaped cold. It is a metal that can be hammered. Additionally, the main substance of bronze is copper (Moorey, 1994).

- **Tin (Sn)**

Another important element of bronze materials is tin because tin makes bronzes more resistant to corrosion. The term bronze can generally be used for any alloy covering copper and tin in varying proportions (Moorey, 1994). For the alloy defined as bronze, it is sufficient that the percentage of tin in the copper is between 6% - 10%. Alloys containing 10% tin are called quality bronze (Esin, 1969). The discovery of the high quality bronze ratio is known to occur as a result of many trials (Özbal, 2013) and this alloy, which is described as high quality bronze, is very rigid. In bronze, which is ideal for daily use, it is sufficient that the tin content in the Cu-Sn alloy is in the range of 3-5%, and the bronze with these qualities is called quality bronze (Zimmerman & Yıldırım, 2008). Increasing the tin ratio facilitates the casting procedure and provides a close color to bronzes (Zimmerman & Yıldırım, 2008). Hot forming of copper takes place between 700 °C and 900 °C. In tin alloys, this temperature rises to 1020 ° C-1045 °C. Cast tin bronze with 20% tin is suitable for bells production only because of excessive brittleness (Akdoğan Eker, 2008).

- **Lead (Pb)**

Another important alloy in the materials used in this study is lead. The task of lead in the alloy is to provide good workability and pressure resistance (Akdoğan Eker, 2008). Reduces cost because it is cheap. The main disadvantage is its easy oxidation (Akdoğan Eker, 2008).

- **Antimony (Sb)**

Varied opinions have been expressed as to the effect of antimony upon copper, brass, and bronze. Antimony causes brittleness of copper alloys (Corby, 2012). Antimony present in amounts over 0.5 per cent decreases both the tensile strength and the elongation of bronzes (Dews, 1930). Although antimony is rarely added to bronzes intentionally, it is usually present to a small extent. Additionally, Zinc and copper may also contain small amounts of antimony. The antimony content of bronze obviously may be increased considerably if unserviceable and "worn out"

bronze bearings carrying either lead-base or tin-base babbitt metal are used as a portion of the furnace charge (Effect of Antimony on The Mechanical Properties of A Bearing Bronze, 1932).

- **Zinc (Zn)**

Another important alloying material for bronze is zinc. Just like tin, zinc added to copper strengthens and hardens the alloy. Tin is more effective in strengthening copper than zinc, but is also more expensive (St. John, 1931).

- **Iron (Fe)**

Iron is a magnetic and gray colored metal that can be flattened by forging. Pure iron element has a melting point of 1535 ºC and a boiling point of 2750 ºC. It exists both in the form of a metallic free state (native) and as an ore. Iron content in bronzes increases tensile strength. It also provide hardness to alloy (Budd & Ottoway, 1995).

- **Silver (Ag)**

Silver is a late rusting element, but it breaks quickly because it is very soft. Therefore it is used as alloying material with heavy metals. Another reason for its use as alloy material is that pure silver is expensive. When used with antimony, zinc and tin, it gives to the alloy hardness and brightness.

Samples from Komana are dated to the Early Byzantine, Middle Byzantine and Danishmend/Seljuk periods in chronological order. COIN216 is dated to the Early Byzantine period. Coins COIN092, COIN428, COIN080, COIN284 and AMORPHOUS454 belong to the Middle Byzantine period. COIN139 could not be dated to a period and was conserved. .

The elemental composition of COIN216 belonging to the Early Byzantine period was 87.73% Cu and 8.92% Sn. It is known that copper ratio of an ideal bronze is 90% and tin ratio is 10% (Esin, 1969). For this reason, it can be suggested that this coin represents almost an ideal bronze coin for the Byzantine period. The iron (Fe)

ratio in this coin is about 2%. The role of iron in alloys is to provide hardness. Therefore, although it is the oldest coin in the sample set, it still contains a bronze core under corrosion, as seen in X-ray radiography.

The Cu ratios of COIN092, COIN428, COIN080, COIN284 coins belonging to the Middle Byzantine period are 81,55%, 87,49%, 93,95%, and 89,24%, respectively. The Sn ratios of these coins are 17,53%, 10,97%, 2,68%, and 9,16%, respectively. Among these coins, the highest copper ratio / lowest tin ratio belongs to COIN080. None of these coins contain Zn, Ag, Pb, Sb and Fe elements over 1%. The AMORPHOUS454 coded non-coin bronze object dated to the same period has Cu ratio of 90.99% and Sn ratio of 0.050%. Other notable alloying elements in this example are Zn and Pb, with element percentages of 3.36% and 2.23%, respectively. Except COIN092 from the Middle Byzantine Period, other coins can be considered to represent ideal bronze. The AMORPHOUS454 from this same period which was included in the sample set for comparison is far from ideal bronze due to the amount of Sn contained in it. Zinc and lead were also used as alloy materials. Because copper is a soft raw material, it can be said that the elements that will add hardness to the alloy have been avoided for ease of shaping and Zn and Pb have been added for increasing its durability.

There are two coins dated to the Seljuk Period, COIN449 and COIN013, respectively. Of these coins, the Cu content of the COIN449 coded coin was 94.16% and the Sn ratio was 0.009%. In the coin coded COIN013, Cu ratio is 93.77% and Sn ratio is 0.007%. In these two coins, Pb is the most striking element and the percentage of Pb is 4.38% and 2.30%, respectively. These two coins are far from what is identified as ideal bronze. COIN013 is also the coin selected for SEM-EDX analysis and the Cu ratio according to SEM analysis is 84.74%. Since Sn ratio is below 1%, it is not seen in SEM. According to SEM results, the percentage of Pb in COIN013 is 3.8%. Therefore, these coins dated to Seljuk Period are not bronze. If there is no dominant element other than lead, it certainly will be easier to corrode. The main reason for using lead may be its low cost (Akdoğan Eker, 2008).

Coin coded COIN139 is a coin that has undergone conservation. The Cu ratio in this coin is 42.56% and the Sn ratio is 7.09%. This coin has a high rate of Zn, Ag and Pb, and its percentages are 5.75%, 8.00% and 33.44%, respectively. Because silver is both expensive and soft under normal conditions, it is not used in alloys up to 8% (Genç, 2017). According to Genç (2007), this high silver content may be due to conservation. The height in the lead ratio must also be due to conservation.

Tin, zinc and lead are the most commonly used alloy materials for bronze and these elements with low melting temperature facilitate the casting of bronze (Aran, 2007). According to Aran (2007), these alloy materials increase the hardness of copper, a soft material, and these alloy materials are cheaper than tin. The disadvantage of lead among these alloy materials is that it is oxidizes quickly (Aran, 2007). However, zinc has de-oxidation properties. So it can be concluded that, lead and zinc are used to reduce the percentage of tin which is the most expensive alloy material. As a result, less corrosion was observed in materials with high zinc content. Therefore, it not possible to suggest that the presence of lead in the bronzes was result of inadequate purification technology. There are different amounts of lead in the objects dated to the 11^{th}-14^{th} centuries. From this point of view, it would not be wrong to say that lead, tin and iron alloy bronzes were deliberately made.

Amorphous 454 has more zinc than all other materials and this object has less corrosion than other materials at first glance. Zinc gives almost perfect mold filling properties to alloys, but also provides high hardness, good machinability, better casting in thin sections and a successful coating technique (Yalçın & Şuşoğlu, 2012). Zinc also has a low melting cost.

Except for the coin coded COIN139, silver concentrations are very low in other materials. Thus, the silver element, which can be called as trace element in objects, may show that metal workmanship and purification techniques are advanced.

In the light of all this information, it can be suggested that Komana made coins with excellent bronze alloys during the Early and Middle Byzantine periods. During the

Seljuk period, tin, an expensive alloying element, was avoided and lead was used instead of tin to facilitate the pouring of copper and to ensure the longevity of the coin.

CHAPTER 4

CONCLUSION

In this study, the elemental compositions of bronze objects excavated at Komana, were determined with the aim of providing the archaeologists the necessary background for future studies on the economy at the site.

This thesis is the first archaeometallurgical study on bronze coins of Komana. Bronze, copper-based alloys make up most of the archaeological metals. Spectrometric analysis methods were used on the bronzes from Komana. Micro X-ray Fluorescence and Scanning Electron Microscopy were used as analysis methods and elemental compositions of bronze metals were investigated. X-ray radiography and Stereo Microscope were used for visual examination. A total of 9 bronze alloys were investigated in the context of this study. Eight of them are coins and 1 is a non-coin bronze object (amorphous) which was used as comparison for coins. These bronze samples dating to the 11^{th}-14^{th} centuries were heavily corroded, thus for Micro XRF, the limestone layer on the samples was removed. In addition a small piece was removed from the selected sample for SEM-EDX analysis. X-Ray radiography of metals was taken in order to visually inspect whether there was a metal core. They were photographed by Stereo Microscope to focus and identify the corrosion zones.

According to the analysis results, tin, which is an important element for alloys and retards corrosion, was used more extensively in the Byzantine period coins than bronze object. In the Seljuk period coins, Zn and Pb ratios were determined to be higher. The task of zinc and lead in the alloy is to create a harder and more durable bronze. Moreover, these two elements, one of the basic elements of alloys, are less expensive than tin. Therefore, it reduces the quality of bronze.

Coins and amorphous objects from Komana are heavily corroded, with no sign of the emperors of the time so the dating is based on the excavated layers. Recently radiocarbon dates have confirmed the relative dates suggested by the excavators for various layers and levels. In addition, the sample set is very small which makes it very difficult to comment on a general elemental composition. In the same way, it would be premature to propose interpretations on the economy of these different periods at Komana. However, the good quality of the Early and Middle Byzantine coins in comparison to the later Seljuk period coins may indicate an economic strand during this very critical period in Anatolia. The Danishmend/Seljuk period at Komana represents the time of the arrival of the Turkish Beyliqs in Anatolia and continuous political unrest due to constant battles between the Byzantines and the Turks followed by clashes between different Turkic groups. It is very likely that tin as an expensive and imported alloy material could scarcely be found and instead lead was used. Future studies on better dated coins using a portable XRF machine could help support the preliminary suggestions made here.

The excavation team was also concerned with the differences in the level of corrosion between the coins and other objects. Although only one comparative material could be analyzed due to different limitations, it could be observed that indeed this object had very different alloy composition with zinc in higher proportions. Zinc is not only less prone to corrosion but also a better alloy for objects which will likely be work more extensively for shaping and molding.

Overall, a general understanding concerning the elemental compositions of Komana bronzes could be discerned which can only serve as the beginning of a large corpus which could be built in the future.

REFERENCES

Akdoğan Eker, A. (2008, 11 28). Bakır ve Bakır Alaşımları. İstanbul. 7 17, 2019 tarihinde alındı

Alper, G. (2003). *Alüminyum Sürekli Döküm Yöntemi İle Üretilmiş 5052 – 5182 Alüminyum Alaşımlarının Şekillendirilebilirlik Kabiliyetlerinin Belirlenmesi.* İstanbul: İstanbul Teknik Üniversitesi.

Altun, M. (2016). *Veri Mdenciliği ve Uygulama Alanları.* Antalya: Akdeniz University. doi:10.13140/RG.2.2.28802.48329

Anderson, J. (1902). *Studia Pontica I: A Journey of Exploration in Pontus.* Bruxelles.

Aran, A. (2007). *Döküm Teknolojisi İmal Usülleri Ders Notları.* İstanbul: İstanbul Teknik Üniversitesi.

Arslan, M. (2016). *Çimento Üretim Proseslerinde Eritiş Metoduyla Hazırlanmış Numunelerin WDXEF Analizleri ve Hata Etkilerinin İncelenmesi, Yüksek Lisans Tezi.* Bursa : Bursa Teknik Üniversitesi.

Asolati, M., Grazzi, F., Canovaro, C., & Calliari, I. (2013). Characterization of bronze Roman coins of the fifth century called nummi through different analytical techniques. *Applied Physics A Materials Science & Processing*. doi:DOI 10.1007/s00339-013-7730-3

Aydın, M., & Gür, B. (2019). Ege Tipi Bir Ustura ve Üzerindeki Tekstil Kalıntılarının Arkeolojik ve Arkeometrik Analizleri Yoluyla Miken Saray Organizasyonundaki Tunç ve Tekstil Endüstrileri Üzerine Bir Değerlendirme. *Olba* , 115-132.

Başaran, S. (1980). Arkeoloji'de Tunç Eserlerin Restorasyon ve Konservasyon Sorunları. *Arkeoloji ve Sanat*, 29-34.

Beckhoff, B., Kanngeieber, B., Langhoff, N., Wedell , R., & Wolff, H. (2006). *Handbook of Practical X-Ray Fluorescence Analysis.* Berlin: Verlag Berlin Heidelberg.

Budd, P., & Ottoway, B. (1995). *Eneolithic Arsenical copper – chance or choice?* Archaeological institute. Bor: Belgrade and the Museum of mining and metallurgy.

Caley, E. (1949). Klaproth As A Pioneer In The Chemical Investigation of Antiquities. *J. Chem. Edu.*, *26*, 242-247, 268.

Charles, J. (1967, January). Early Arsenical Bronzes – A Metallurgical view. *American Journal of Archaeology, 71,* 21-26.

Copper Development Association Inc. (2017, 01 11). *Copper Alloys*. 7 22, 2019 tarihinde copper. org: https://www.copper.org/applications/architecture/arch_dhb/technical-discussion/copper_alloys/ adresinden alındı

Corby, G. (2012). The Metallurgy of Antimony. *Journal of of Chemie der Erde Geochemistry, 72*, 3-8.

Craddock, P. (1995). *Early Metal Mining and Production.* Edinburgh University Press.

Desch, C. (1928-1939). *Sumerian Copper. Interim Report.* Man. .

Dews, H. (1930). *Metallurgy of Bronzes.* New York: Sir Isaac Pitman & Sons.

Effect of Antimony on The Mechanical Properties of A Bearing Bronze. (1932). *Bureau of Standards Journal of Research, 8*, 625-634.

Erciyas, D. (2012). Komana ve Çevresinde Çağlar Boyu Yerleşim. A. Akyol, & K. Özdemir (Dü) içinde, *Türkiyede Arkeometrinin Ulu Çınarları. Prof. Dr. Ay Melek Özer ve Prof. Dr. Şahinde Demirci'ye Armağan* (s. 163-171). İstanbul: Homer Kitapevi.

Erciyas, D. (2015). Komana Ortaçağ Yerleşimi, The Medieval Settlement at Komana, Monografi 1. D. Erciyas, & M. Tatbul (Dü). içinde Ankara: Ege Yayınları.

Erciyas, D. (2019). Archaeology At Komana. D. Erciyas, & M. Acara Eser (Dü) içinde, *Komana Small Finds* (s. 1-26). İstanbul: Ege Yayınları.

Erciyas, D., Sökmen, E., & Kalaycı, T. (2006). Komana Arkeolojik Araştırma Projesi. Komana, Türkiye. Komana Arkeolojik Araştırma Projesi: http://www.komana.org/sv23.html adresinden alındı

Erhan, F., Girginer, S., & Tekin, O. (2008). Mersin Arkeoloji Müzesi'nden Bir Grup Antik Dönem Etüdlük Sikkesinin Temizlik ve Koruma Çalışmaları ile Tarihlendirilmesi. *Ç.Ü. Sosyal Bilimler Enstitüsü Dergisi, 17*, 133-162.

Esin, U. (1969). Kuantitatif Spektral Analiz Yardımıyla Anadolu'da Başlangıcından Asur Ticaret Kolonileri Çağına Kadar Tunç Madenciliği. *İstanbul Üniversitesi Edebiyat Fakültesi*(1407), 107.

Ferreti, M. (2000). X-ray Fluorescence Applications for the Study and Conservation of Cultural Heritage. D. Creagh, & D. Bradley içinde, *Radiation in Art and Archaeometry* (s. 285-295). Elsevier Science B.V.

Genç, U. (2017). Arkeolojik Metallerin Konservasyonuna Genel Bakış. D. BORAK içinde, *KONSERVATÖR-RESTORATÖR UĞUR GENÇ VE MESLEK HAYATI* (s. 473-494). İstanbul : MİMAR SİNAN GÜZEL SANATLAR ÜNİVERSİTESİ GÜZEL SANATLAR FAKÜLTESİ SANAT ESERLERİ KONSERVASYONU VE RESTORASYONU BÖLÜMÜ.

Gilmour B., & Northover, P. (n.d.). The Metallurgy of Artillery. In: Archaeometallurgy in Europe. *Proceedings, 2*, 253-261.

Hamilton, W. (1842). *Research in Asia Minor, Pontus, and Armenia* (Cilt I). London.

Hogarth, D., & Munro , J. (1893). *Moderna and Ancient Roads in Eastern Asia Minor*. London.

Holmes, C. (2008). Political-Historical Survey. E. Jeffreys, J. Haldon, & R. Cormack (Dü) içinde, *The Oxford Handbook of Byzantine Studies* (s. 271-280). Oxford: Oxford University Press.

Karatak, A. (2018). *DASKYLEİON ARKEOLOJİK ALANI DOĞU VE GÜNEY NEKROPOLLERİNDEN ELE GEÇEN BİR GRUP METAL BULUNTU ÜZERİNE ARKEOMETRİK İNCELEMELER.* Ankara: Gazi Üniversitesi .

Kayaalp, G., Şahinler, S., & Yazgan, E. (2000). Aşamalı Kümeleme Analizi (Hierarchical Cluster Analysis) Yöntemlerinin Karşılaştırılmalı Olarak İncelenmesi. (s. 154-163). Adana: Çukurova Üniversitesi.

Kocabaş, U. (1998). *Arkeolojik Sualtı Kalıntılarının Konservasyonu.* İstanbul.

Komana Archaeological Research Project. (2014). KARP: http://komana.org/pd3.html adresinden alındı

Laiou, A. (2002). *The Economic History of Byzantium: From the Seventh through the Fifteenth Century*. Washington D. C.: Dumbarton Oaks.

Laiou, A., & Morrison , C. (2007). *The Byzantine Economy.* Cambridge: Cambridge Medieval Textbooks.

Landolt, D. (2007). *Corrosion And Surface Chemistry of Metals.* Florida: CRC Press.

Made How. (n.d.). *Coin*. 8 1, 2019 tarihinde How Products are Made: http://www.madehow.com/Volume-2/Coin.html adresinden alındı

Manly, B. (2005). *Multivariate Statistical Methods: A Primer* (Third Edition b.). Chapman and Hall.

Moorey, P. (1994). *Ancient Mesopotamian Materials and Industries.* Oxford- New York: Clarendon Press.

Nothnagle, P., Chambers, W., & Davidson, M. (2019). *Microscopyu-The Source of Microscopy Education*. 09 05, 2019 tarihinde Introduction To Stereomicroscopy: https://www.microscopyu.com/techniques/stereomicroscopy/introduction-to-stereomicroscopy adresinden alındı

Oğuz, B. (1989). Malzeme Bilgisine Giriş. *Oerlikon*, 1-8.

Özbal, H. (2013). Başlangıcından Demir Çağı Sonuna Kadar Anadolu Madencilerinin ve Ustalarının Teknolojik Başarılarının Kısa Bir Değerlendirmesi. *III. ODTÜ Arkeometri Çalıştayı Bildiriler Kitabı* (s. 29-36). Ankara: ODTÜ.

Özen, L. (1999). Bronz Hastalığı (Kanseri). *Anadolu Medeniyetler Müzesi Yıllığı*, 291-294.

Özenbaş, M. (1996). Metal Malzemenin Tarihteki Gelişimi. *Bilim ve Teknik*, 48-49.

Ponting, M. (2004). The scanning electron microscope and the archaeologist. *Physics Education*, 166-172. doi:10.1088/0031-9120/39/2/004

Rehren, T., & Pernicka, E. (2008). Coins, Artefacts and Isotopes-Archaeometallurgy and Archaeometry. *Archaeometry Journal, 50*, 232-248.

Rostoker, W., & Bronson, B. (1990). *Pre-Industrial Iron- Its Tecnology and Ethnology. Archeomaterials Monograph* (Cilt 1). Philadelphia.

Ryck, D., Adriaens, A., & Adams, F. (2005). An Overview of Mesopotamian Bronze Metallurgy During the 3rd Millennium BC. *Journal of Cultural Heritage, 6*(3), 261-268.

Sandu, I., Ursulescu, N., Sandu, I., Bounegru, O., Sandu, I., & Alexandru, A. (2013, November 27). Pedological Stratification Effect of Corrosion and

Contamination Products on Byzantine Bronze Artefacts. *The International Journal of Corrosion Processes and Corrosion Control*, 256-266. doi:https://doi.org/10.1179/174327807X234688

Shackley, S. (2010). Is the Reliability and Validity In Portable X-Ray Fluorence Spectrometry (PXRF)? *SAA Archaeological Record, 10*, 17-20.

Sharma, S. (1996). *Applied Multivariate Techniques.* New York: John Wiley and Sons, Inc.

Skog, D., Holler, F., & Crouch, S. (2007). *Principles of İnstrumental Analysis* (Sixth b.). Thomson Brooks/Cole.

St. John, H. (1931). The Influence of Impurities in Foundry Brasses & Bronzes, Metals & Alloys. *Bureau of Standards Journal of Research, 2*, 243.

Tatbul, M. (2017). *Indentifying Medieval Komana In The 12th - 13th Centruies THrough Spatial Analysıs of Archaeological Data With A Multidisciplinary Approach.* Ankara: DPhil Thesis METU.

Tekin, O. (1993). *Bibliography of Ancient Numismatics for Anatolia: Antik Anadolu Nümismatiği Bibliyograyası.* İstanbul.

The Royal Mint Museum. (n.d.). *royalmintmuseum.org*. 8 1, 2019 tarihinde How Coins Are Made: http://www.royalmintmuseum.org.uk/education-and-learning/schools-and-colleges/activities-and-lesson-packs/key-stage-2-activities/how-coins-are-made/design-die-making.html adresinden alındı

Thornton, C., Lamberg-Karlovsky, C., Liezers, M., & Young, S. (2002, December). On pins and needles: tracing the evolution of copper-based alloying at Tepe Yahya, Iran, via ICP-MS analysis of Common-place items. *Journal of Archaeological Science, 29*(12), 1451-1460.

Tokat İl Kültür Turizm Müdürlüğü. (2019). *T.C. Kültür ve Turizm Bakanlığı*. 06 16, 2019 tarihinde tokat.ktb: https://tokat.ktb.gov.tr/TR-60574/genel-bilgiler.html adresinden alındı

Tuğrul, B. (2012). Metal Buluntular Üzerinde Yapılan Radyografik Çalışmalara Genel Bakış. A. Akyol, & K. Özdemir içinde, *Arkeometrinin Ulu Çınarları: Prof. Dr. Ay Melek Özer ve Prof. Dr. Şahinde Demirciye Armağan* (s. 49-56). Ankara: Homer Kitapevi.

Tykot, R. H. (2015). Using Nondestructive Portable X-ray Fluorescence Spectrometers on Stone, Ceramics, Metals, and Other Materials in Museums: Advantages and Limitations. *Applied Spectroscopy*, 43-55.

Tylecote, R. (1987). *The Early History of Metallurgy in Europe.* Longman.

v. Fellenberg, L. (1866). *Analysen Von Antiken Byronzen.* Mitt. naturf. Ges. Bern 1866.

Von Fellenberg, L. (1866). *Analysen Von Antiken Byronzen.* Mitt. naturf. Ges. Bern 1866.

Wang, A., & Mou, C. (n.d.). A Novel Efficient Au-Ag Alloy Catalyst System: Preparation, Activity, and Characterization. *Materials Chemistry*, 55-57.

Woolley, C. (1931). Excavation at Ur. *The Antiquaries Journal, 11*, 344.

XOS. (2019). *xos.com*. September 5, 2019 tarihinde Micro X-ray Fluorescence (μXRF): https://www.xos.com/Micro-XRF adresinden alındı

Yalçın, U., & Şuşoğlu, İ. (2012). *Çinko – Alüminyum Alaşımlarında Katı Çökelme Sertleşmesi.* Trabzon: Karadeniz Teknik Üniversitesi .

Yalçın, Ü. (2013). Türkiye Arkeolojisinde Metal: Arkeolojik ve Arkeometrik Çalışmalar. I. A. Çalıştayı içinde, *Anadolu Madenciliği.* Ankara: Orta Doğu Teknik Üniversitesi Yayınları.

Yalçın, Ü., & Koç, T. (1997). *Mühendisler İçin Korozyon.* Ankara: TMMOB Kimya Mühendisleri Odası Yayınları.

Yalçın, Ü., & Özbal, H. (n.d.). *History of Mining And Metallurgy In Anatolia.* 04 27, 2019 tarihinde https://www.scribd.com/document/218993191/History-of-Mining-and-Metallurgy-in-Anatolia adresinden alındı

Yaylı, M. (2013). *Farklı Marka Ofis Kağıtlarında XRF Yöntemiyle Element Analizi Yüksek Lisans Tezi.* Trabzon: Karadeniz Teknik Üniversitesi.

Yılmaz, Ş., & Kurnaz, C. (2001, March). Metalurjik Süreçler ve Arkeometalurji. *SAÜ Fen Bilimleri Enstitü Dergisi, 5*(1), 45-49.

Yüksel, H. (2014). Heykel Döküm Tekniklerinden Mum Yok Etme Tekniği ile Bronz Döküm. *Akdeniz Sanat Dergisi, 7*(14), 73-84.

Zimmerman , T., & Yıldırım, T. (2008). Three Best to Have in Plenty – Rethinking Central Anatolian Early Bronze Age Alloying Traditions. Ü. Yalçın, H. Özbal, & A. Paşamehmetoğlu (Dü.), International Conference AMITEM, Ancient Mining in Turkey and the Eastern Mediterranean içinde, (s. 87-91). Ankara.

APPENDICES

A. Full Visual of Bronze Objects

In this part, the coins and the object from Komana are presented. There are three views for each material which are: normal scale view, X-Ray radiography view and stereomicroscope view, respectively.

- **Coin:** KARP13-HTP01-449, Seljuk Period:

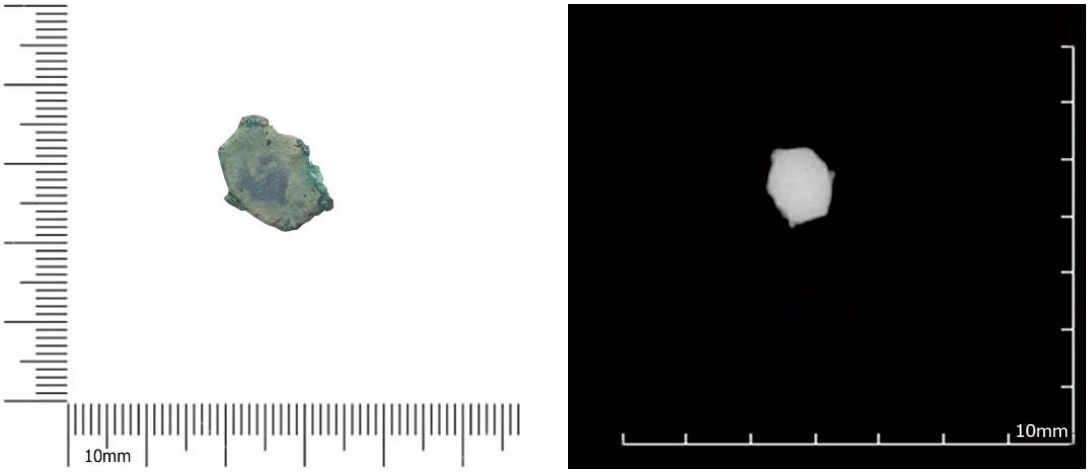


Figure 22. KARP13-HTP01-449 Coin. Normal Scale and Rontgen view

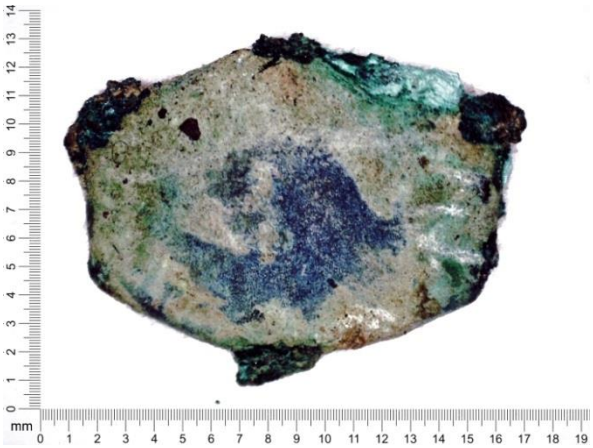


Figure 23. KARP13-HTP01-449 Coin. Under the Stereo Microscope view

Explanation: Coin with heavy corrosion: unshaped and broken. Corrosions were not removed.

Weight: 1.1 gr

- **Coin:** KARP11-HTP01-092, Middle Byzantine Period:

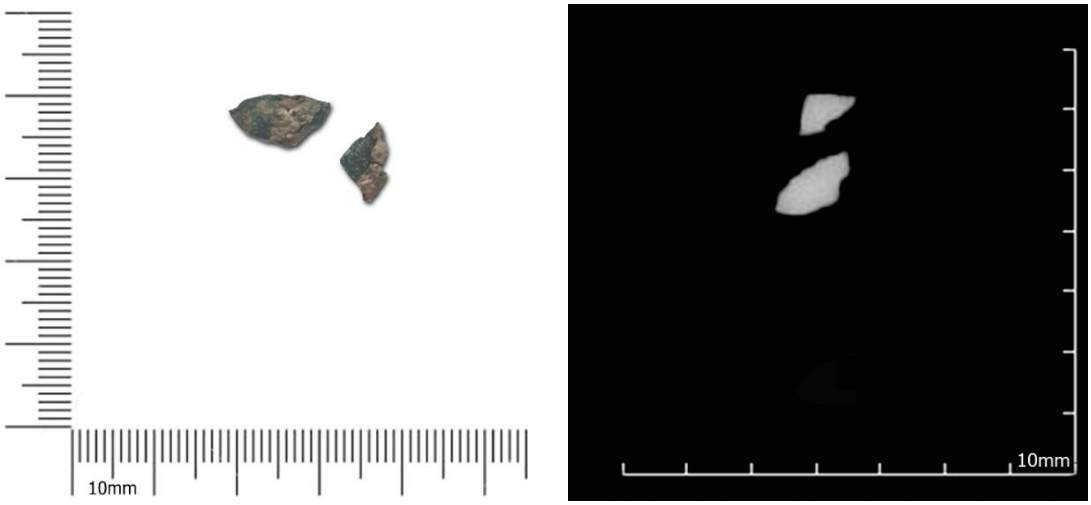


Figure 24. KARP11 HTP01- 092 Coin. Normal Scale and Rontgen view.

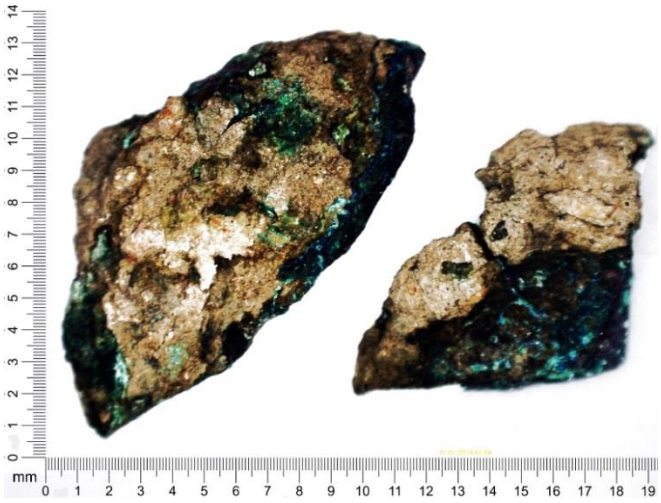


Figure 25. KARP11 HTP01- 092 Coin. Under the Stereo Microscope view.

Coin with heavy corrosion: unshaped and broken. Corrosions were not removed.

Weight: 1.4 gr

- **Coin:** KARP16-HTP01-216, Early Byzantine Period:

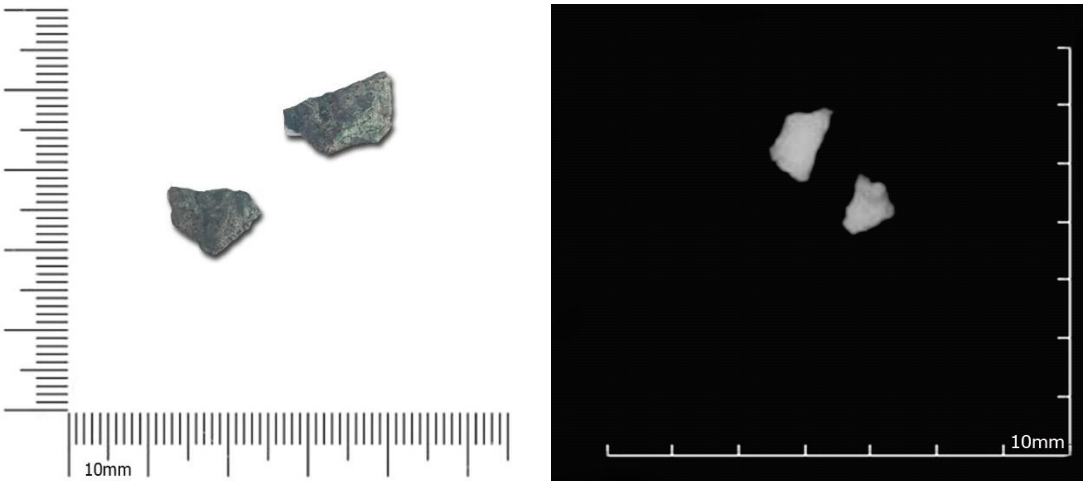


Figure 26. KARP16-HTP01-216 Coin. Normal Scale and Rontgen view.

Figure 27. KARP16-HTP01-216 Coin. Under the Stereo Microscope view.

Coin with heavy corrosion: unshaped and broken. Corrosions were not removed.

Weight: 0.9 gr

- **Coin:** KARP11-HTP01-428, Middle Byzantine Period:

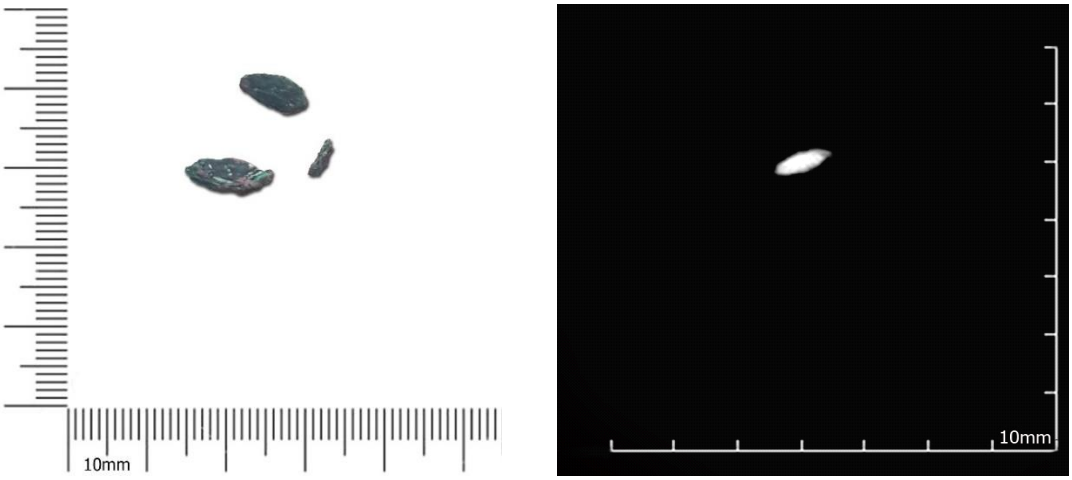


Figure 28. KARP11-HTP01-428 Coin. Normal Scale and Rontgen view.

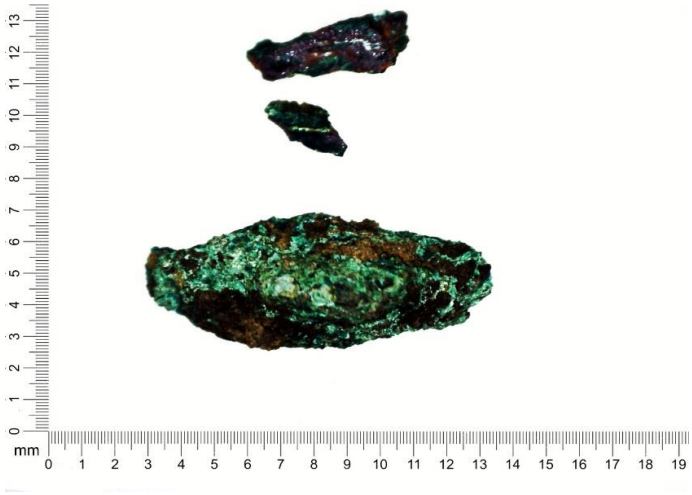


Figure 29. KARP11-HTP01-428 Coin. Under the Stereo Microscope view.

Coin with heavy corrosion: unshaped and broken. Corrosions were not removed. The Rontgen view includes just the small part of broken coin.

Weight: 0.4 gr

- **Coin:** KARP17-HTP04-013, Seljuk Period:

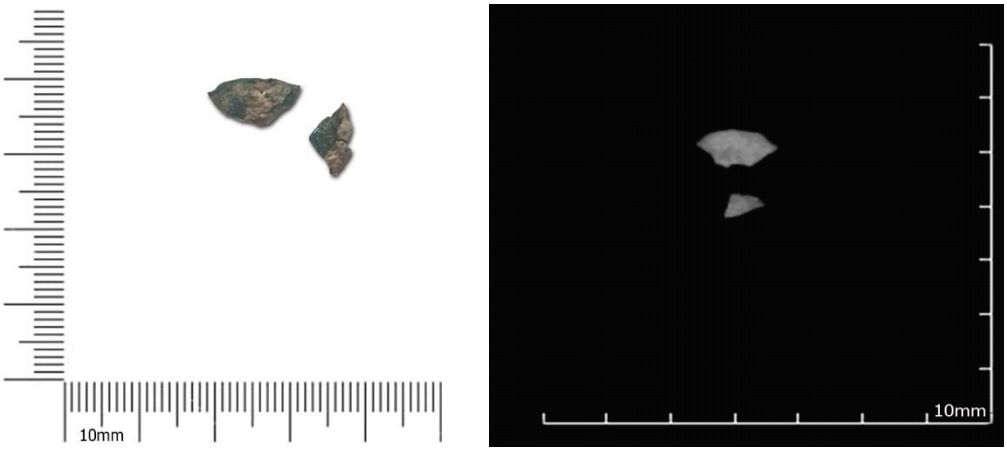


Figure 30. KARP17-HTP04-013Coin. Normal Scale and Rontgen view.

Figure 31. KARP17-HTP04-013Coin. Under the Stereo Microscope view.

Coin with corrosion: quarter round shaped and broken nearly middle part. Existing corrosions were not removed.

Weight: 0.3 gr.

- **Coin:** KARP11-HTP01-080, Middle Byzantine Period:

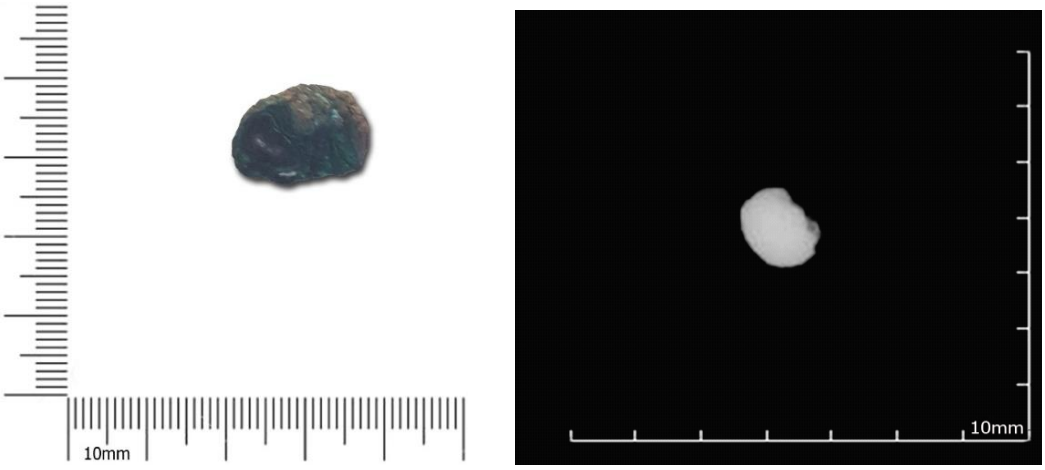


Figure 32. KARP11-HTP01-080. Normal Scale and Rontgen view.

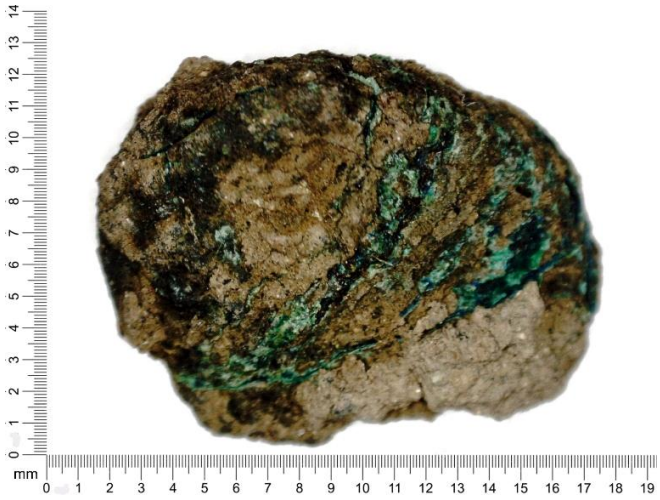


Figure 33. KARP11-HTP01-080. Under the Stereo Microscope view.

Coin with heavy corrosion: nearly round and missing. Corrosions were not removed.

Weight: 1.7 gr

- **Coin:** KARP15-HTP01-139, Undated:

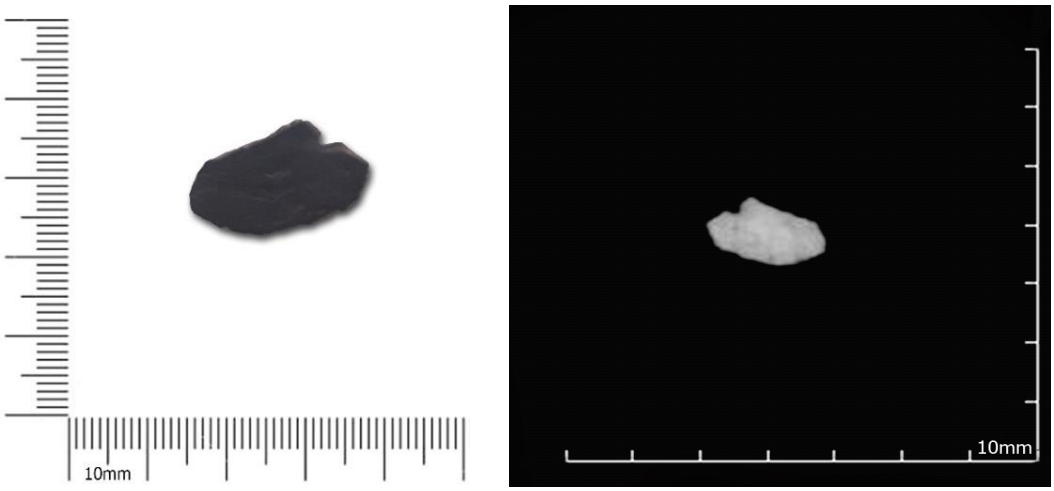


Figure 34. KARP15-HTP01-139 Coin. Normal Scale and Rontgen view.

Figure 35. KARP15-HTP01-139 Coin. Under the Stereo Microscope view.

Coin with nearly clear about corrosion: Nearly semi-round shaped and broken. Conversation was done previously.

Weight: 0.8 gr

- **Coin:** KARP17-HTP01-284, Middle Byzantine Period:

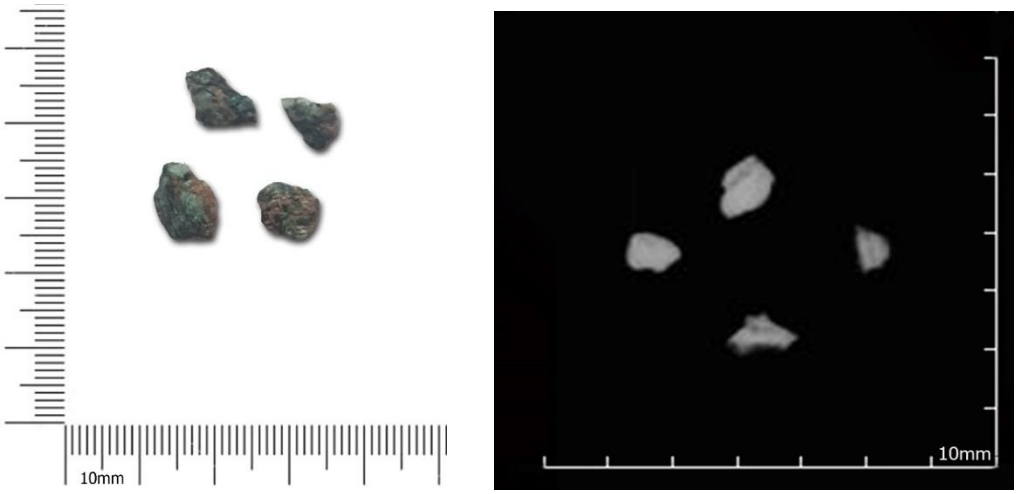


Figure 36. KARP17-HTP01-284 Coin. Normal Scale and Rontgen view.

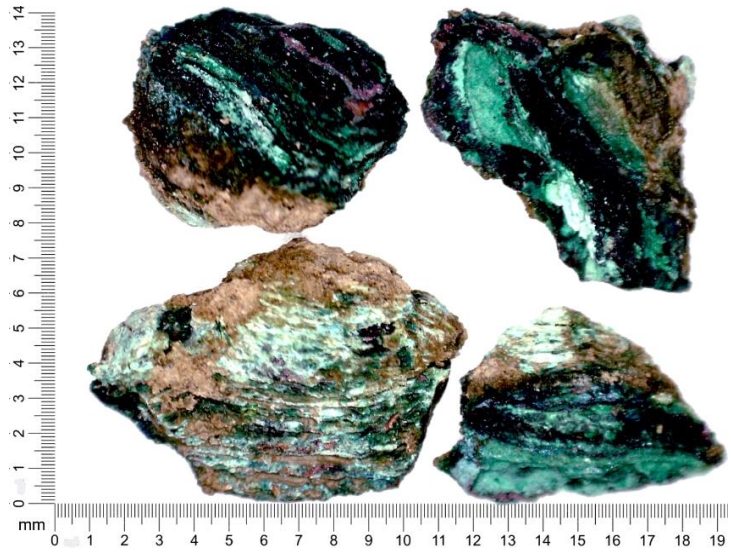


Figure 37. KARP17-HTP01-284 Coin. Under the Stereo Microscope view.

Coin with heavy corrosion: unshaped and broken. Corrosions were not removed.

Weight: 1.0 gr

- **Amorphous:** KARP13-HTP01-454, Middle Byzantine Period:

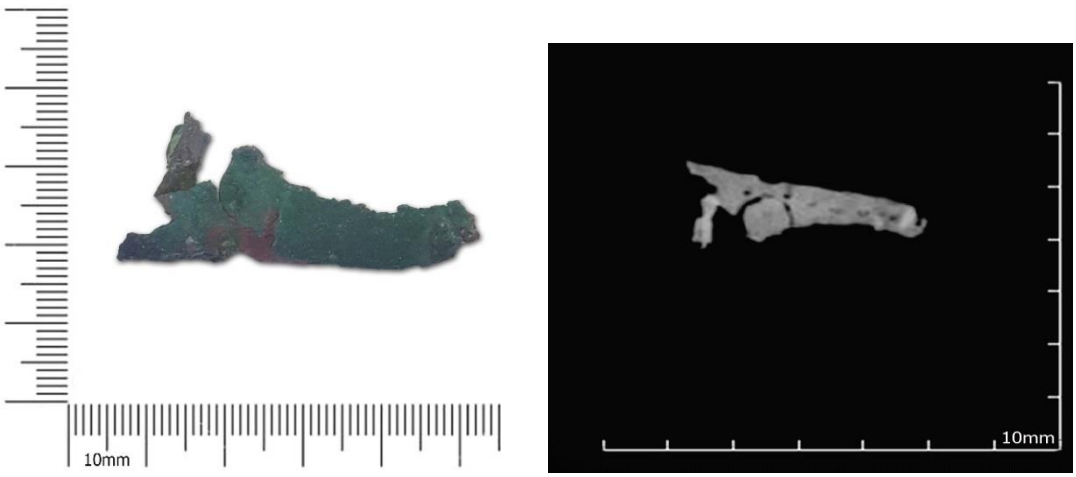


Figure 38. KARP13-HTP01-454 Amorphous. Normal Scale and Rontgen view.

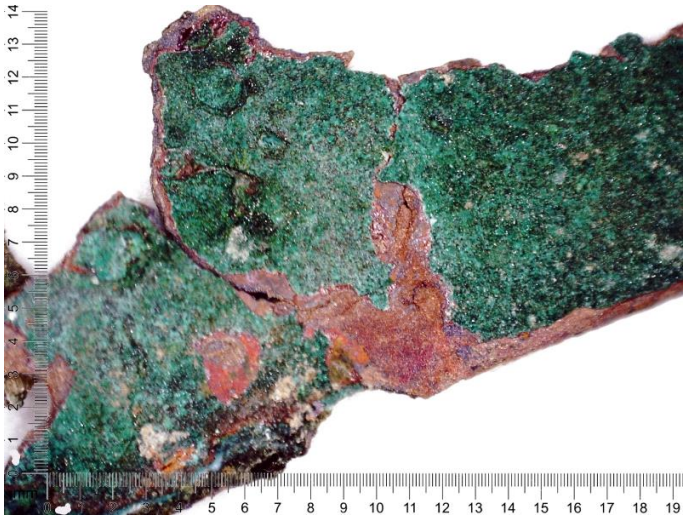


Figure 39. KARP13-HTP01-454 Amorphous. Nearly middle part of under the Stereo Microscope view.

Amorphous with corrosion: unshaped and broken. Corrosions were not removed.

Weight: 1.1 gr

B. Full Excel Table for Coins and Amorphous Object

Figure 40. Full Excel Table for Coins and Amorphous Object

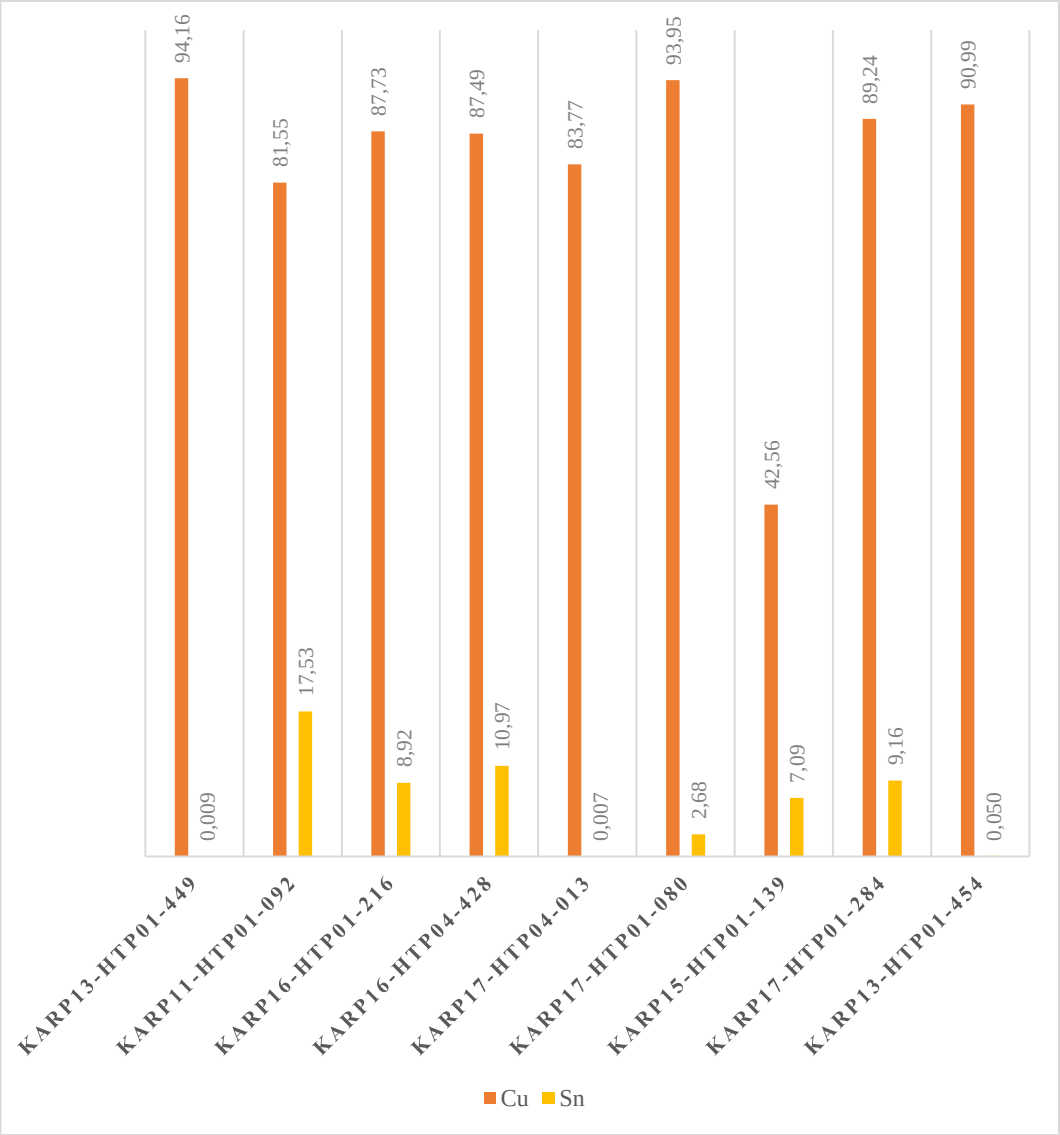
Analyzer																											
SPECTRO MIDEX-M Micro XRF			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP13-HTP01-449	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Seljuk/İşlik		0,018	0,014	0,007	0,009	0,394	0,005	0,049	94,16	0,005	0,004	0,050	0,026	1,00	0,002	0,011	0,026	0,006	0,008	0,009	0,011	0,010	0,001	0,020	0,020	2,30
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP11-HTP01-092	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Middle Byzantine/Church		0,022	0,014	0,009	0,007	0,057	0,004	0,049	81,55	0,005	0,007	0,050	0,020	0,565	0,002	0,009	0,021	0,011	0,015	17,53	0,019	0,025	0,001	0,020	0,020	0,004
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP16-HTP01-216	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Early Byzantine		0,021	0,020	0,034	0,019	0,861	0,004	0,006	87,73	0,006	0,014	0,050	0,020	0,793	0,002	0,011	0,082	0,011	0,013	8,92	0,097	0,025	0,001	0,020	0,020	1,20
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP16-HTP04-428	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Middle Byzantine/Church		0,021	0,013	0,009	0,007	0,006	0,004	0,006	87,49	0,006	0,014	0,050	0,020	0,573	0,002	0,007	0,009	0,010	0,012	10,97	0,191	0,025	0,001	0,020	0,020	0,547
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.07.2019	KARP17-HTP04-013	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Seljuk/İşlik		0,016	0,010	0,007	0,005	0,004	0,003	0,005	83,77	0,004	0,008	0,050	0,042	0,748	0,002	0,005	0,010	0,050	0,014	0,007	0,010	0,025	0,001	0,020	0,020	0,383
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP17-HTP01-080	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Middle Byzantine/Church		0,018	0,012	0,007	0,006	0,005	0,003	0,006	93,95	0,005	0,011	0,050	0,020	0,843	0,002	0,006	0,471	0,008	0,010	2,68	0,013	0,011	0,001	0,020	0,020	0,034
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP15-HTP01-139	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	No Date		0,035	0,024	0,014	0,011	0,257	0,007	0,088	42,56	5,75	0,009	0,076	0,007	1,85	0,002	0,024	8,00	0,020	0,023	7,09	0,640	0,025	0,001	0,020	0,020	33,44
			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP17-HTP01-284	Coin	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Middle Byzantine/Church		0,018	0,012	0,008	0,006	0,005	0,004	0,006	89,24	0,006	0,010	0,050	0,020	0,839	0,002	0,007	0,132	0,014	0,013	9,16	0,259	0,011	0,001	0,020	0,020	0,134

			Elements																								
Date	Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
16.09.2019	KARP13-HTP01-454	Amorphous	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)	Conc. (%)
	Middle Byzantine/Church		0,016	0,011	0,006	0,005	0,290	0,003	0,070	90,99	3,36	0,003	0,050	0,025	0,901	0,002	0,018	0,023	0,050	0,006	0,050	0,040	0,025	0,001	0,020	0,020	2,23

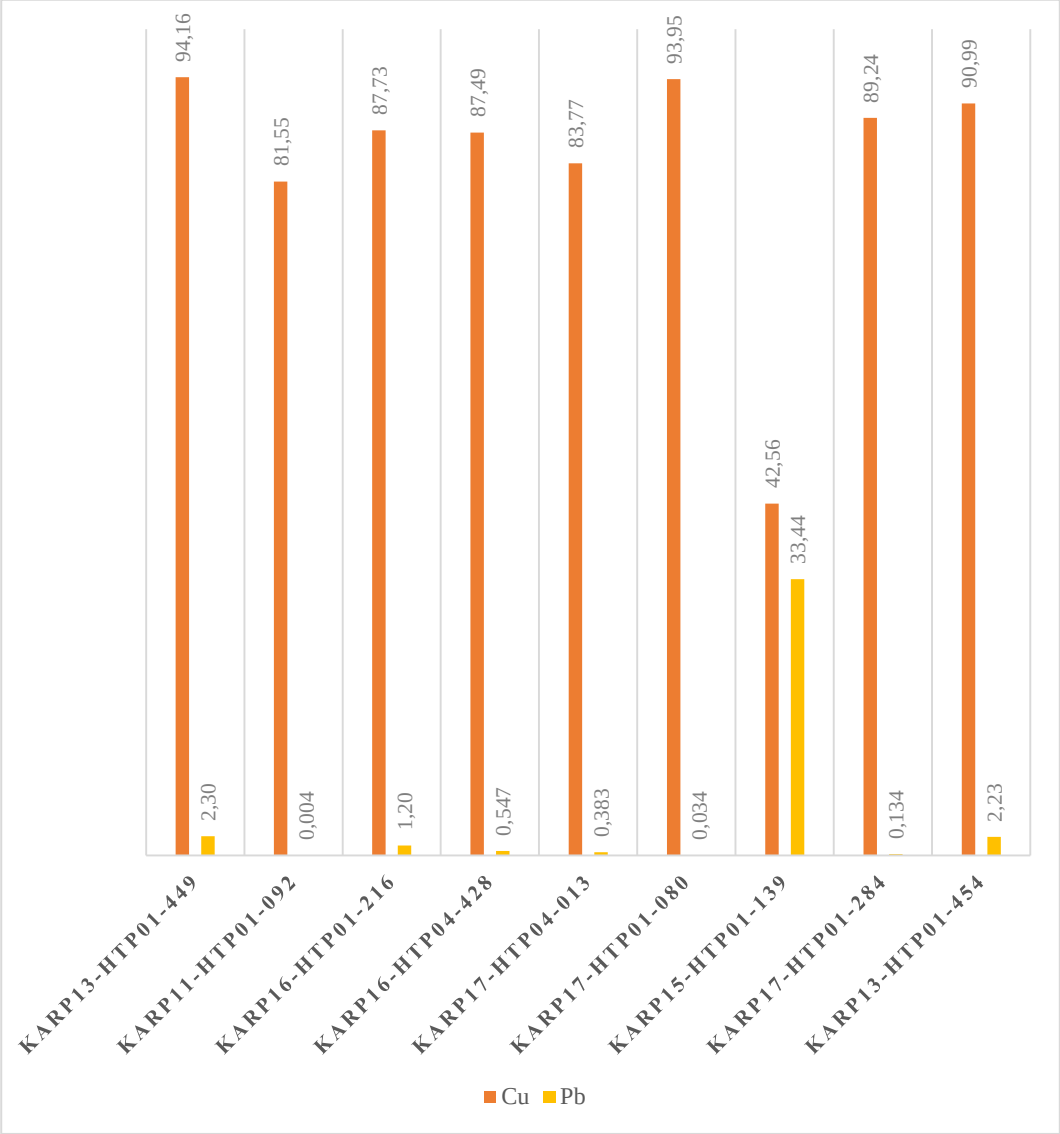
			Elements																								
Sample Name	Description	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Zr	Nb	Mo	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Ir	Pt	Au	Pb
KARP13-HTP01-449	COIN	0,018	0,014	0,007	0,009	0,394	0,005	0,049	94,16	0,005	0,004	0,050	0,026	1,00	0,002	0,011	0,026	0,006	0,008	0,009	0,011	0,010	0,001	0,020	0,020	2,30
KARP11-HTP01-092	COIN	0,022	0,014	0,009	0,007	0,057	0,004	0,049	81,55	0,005	0,007	0,050	0,020	0,565	0,002	0,009	0,021	0,011	0,015	17,53	0,019	0,025	0,001	0,020	0,020	0,004
KARP16-HTP01-216	COIN	0,021	0,020	0,034	0,019	0,861	0,004	0,006	87,73	0,006	0,014	0,050	0,020	0,793	0,002	0,011	0,082	0,011	0,013	8,92	0,097	0,025	0,001	0,020	0,020	1,20
KARP16-HTP04-428	COIN	0,021	0,013	0,009	0,007	0,006	0,004	0,006	87,49	0,006	0,014	0,050	0,020	0,573	0,002	0,007	0,009	0,010	0,012	10,97	0,191	0,025	0,001	0,020	0,020	0,547
KARP17-HTP04-013	COIN	0,016	0,010	0,007	0,005	0,004	0,003	0,005	83,77	0,004	0,008	0,050	0,042	0,748	0,002	0,005	0,010	0,050	0,014	0,007	0,010	0,025	0,001	0,020	0,020	0,383
KARP17-HTP01-080	COIN	0,018	0,012	0,007	0,006	0,005	0,003	0,006	93,95	0,005	0,011	0,050	0,020	0,843	0,002	0,006	0,471	0,008	0,010	2,68	0,013	0,011	0,001	0,020	0,020	0,034
KARP15-HTP01-139	COIN	0,035	0,024	0,014	0,011	0,257	0,007	0,088	42,56	5,75	0,009	0,076	0,007	1,85	0,002	0,024	8,00	0,020	0,023	7,09	0,640	0,025	0,001	0,020	0,020	33,44
KARP17-HTP01-284	COIN	0,018	0,012	0,008	0,006	0,005	0,004	0,006	89,24	0,006	0,010	0,050	0,020	0,839	0,002	0,007	0,132	0,014	0,013	9,16	0,259	0,011	0,001	0,020	0,020	0,134
Standart Deviation		0,006	0,005	0,009	0,005	0,305	0,001	0,032	16,744	2,029	0,003	0,009	0,010	0,410	0,000	0,006	2,795	0,014	0,005	5,993	0,217	0,007	0,000	0,000	0,000	11,616

C. Concentration Graphs for Coins and Amorphous Object

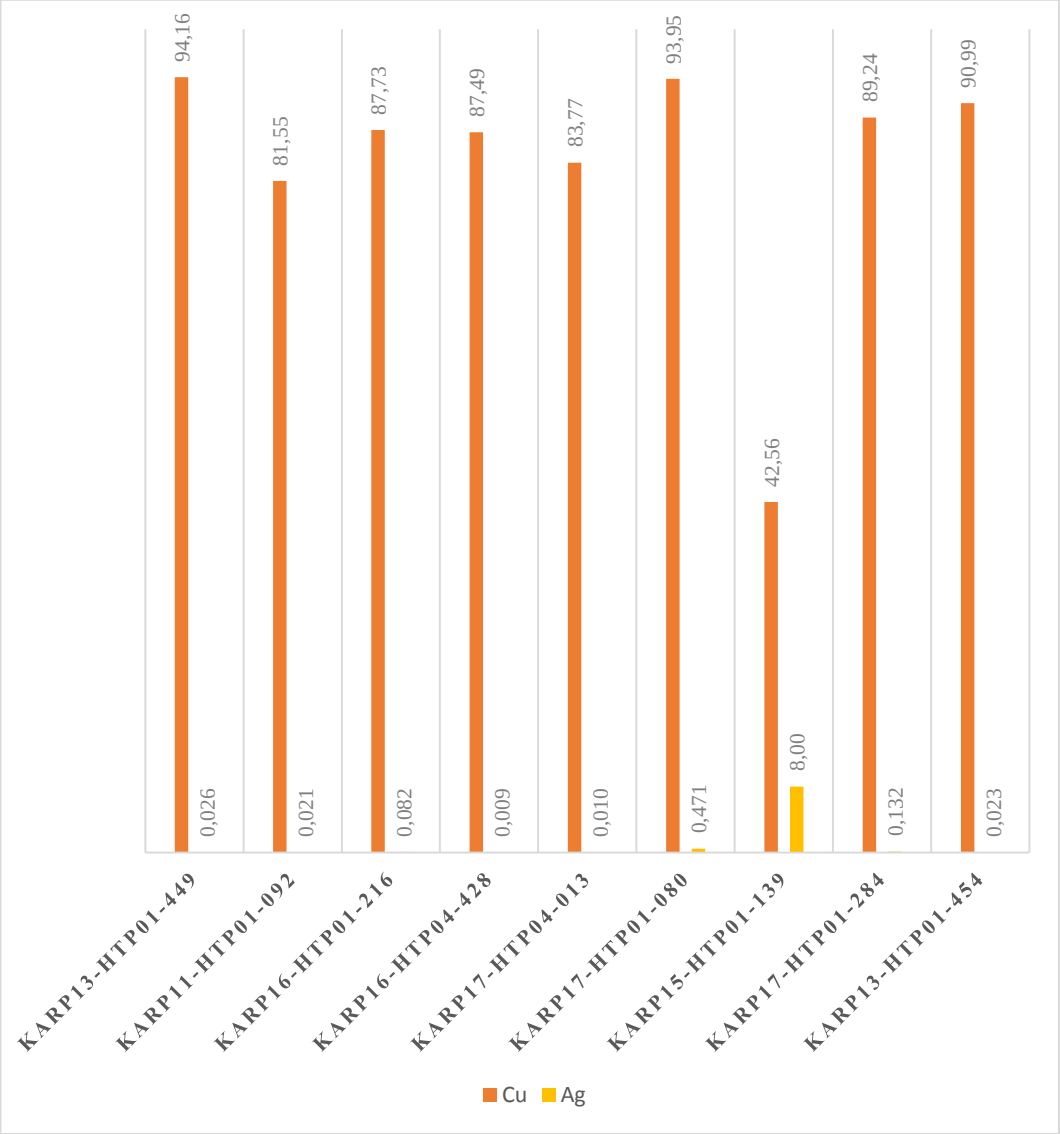
Concentration graphs are given below for all bronze samples.



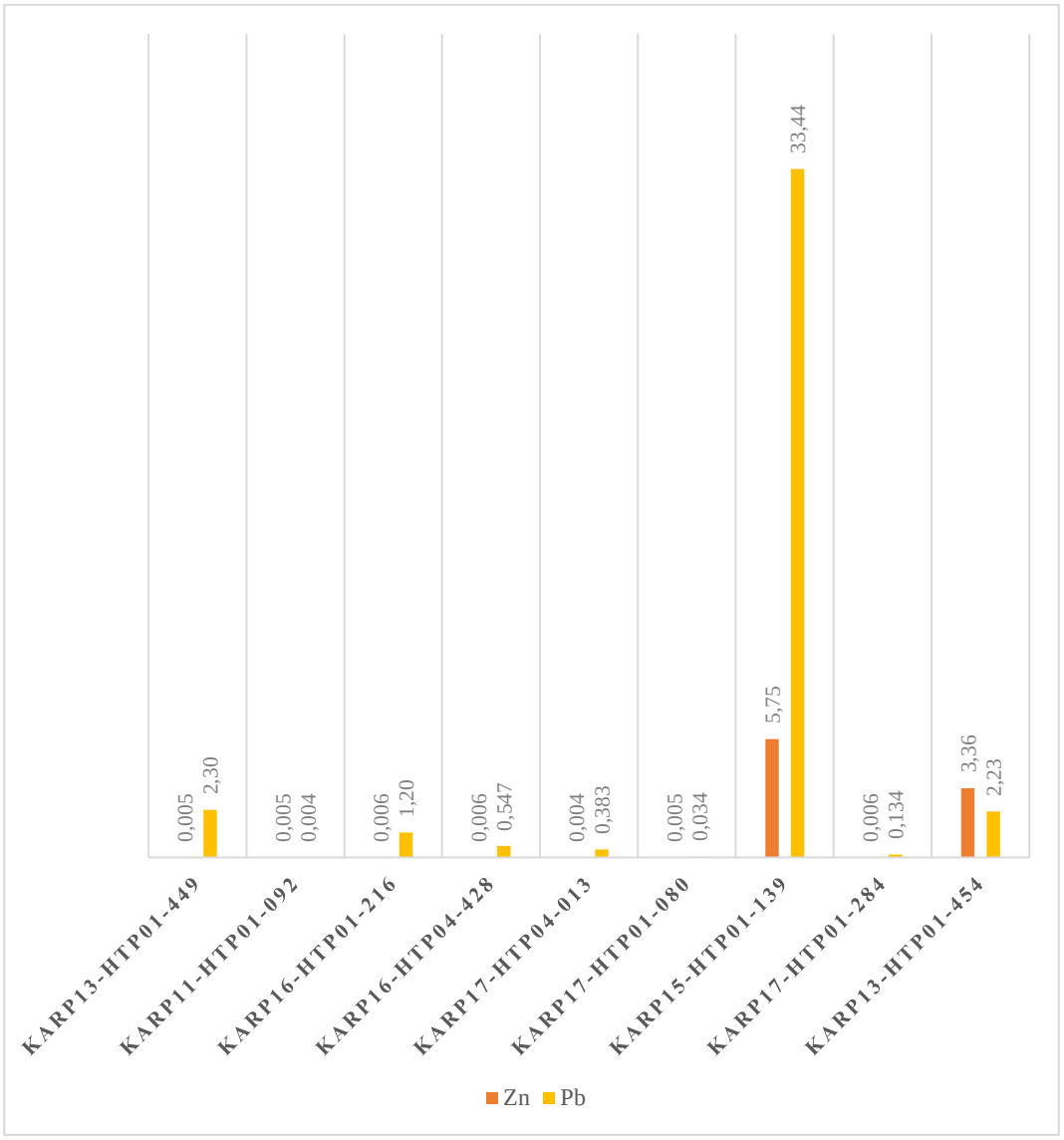
Graph 1. Cu-Sn Concentration Ratio (%)



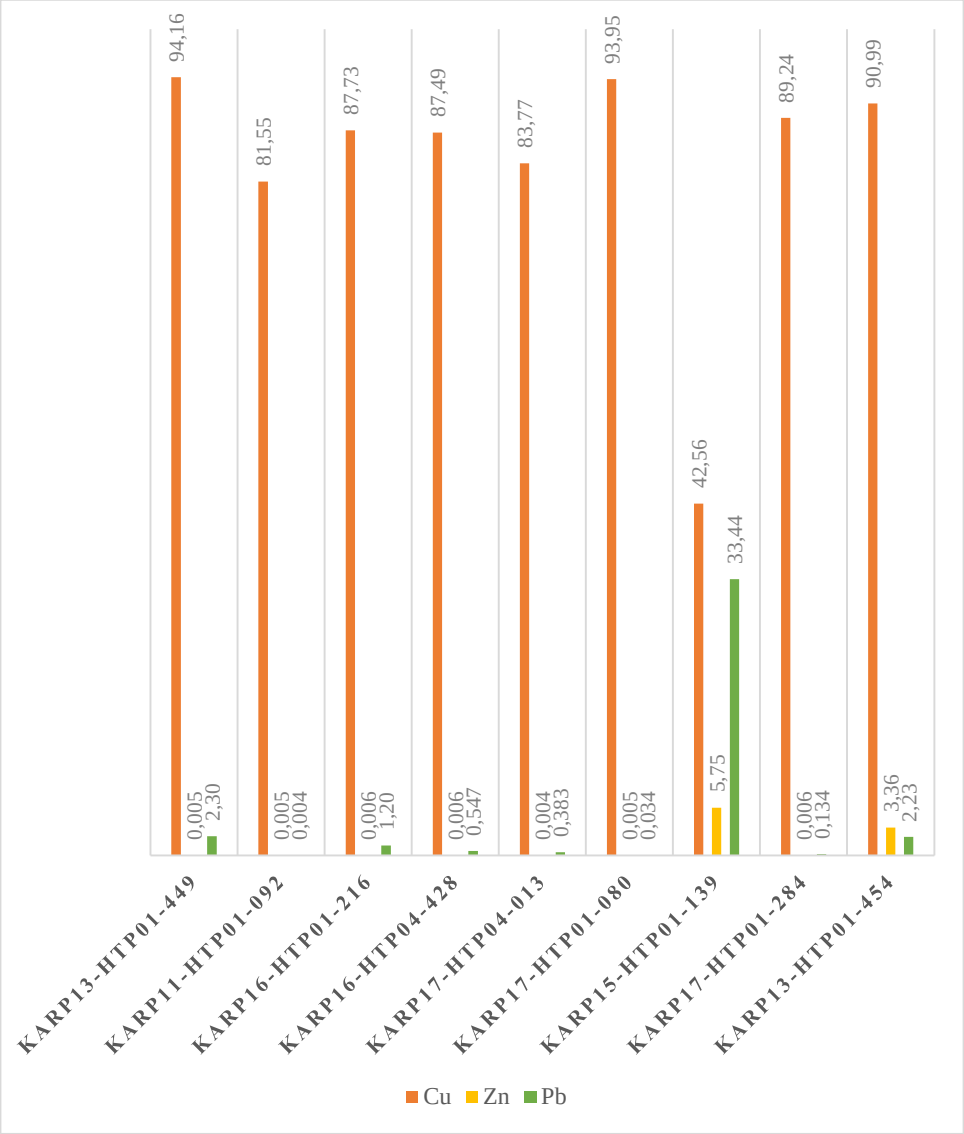
Graph 2. Cu-Pb Concentration Ratio (%)



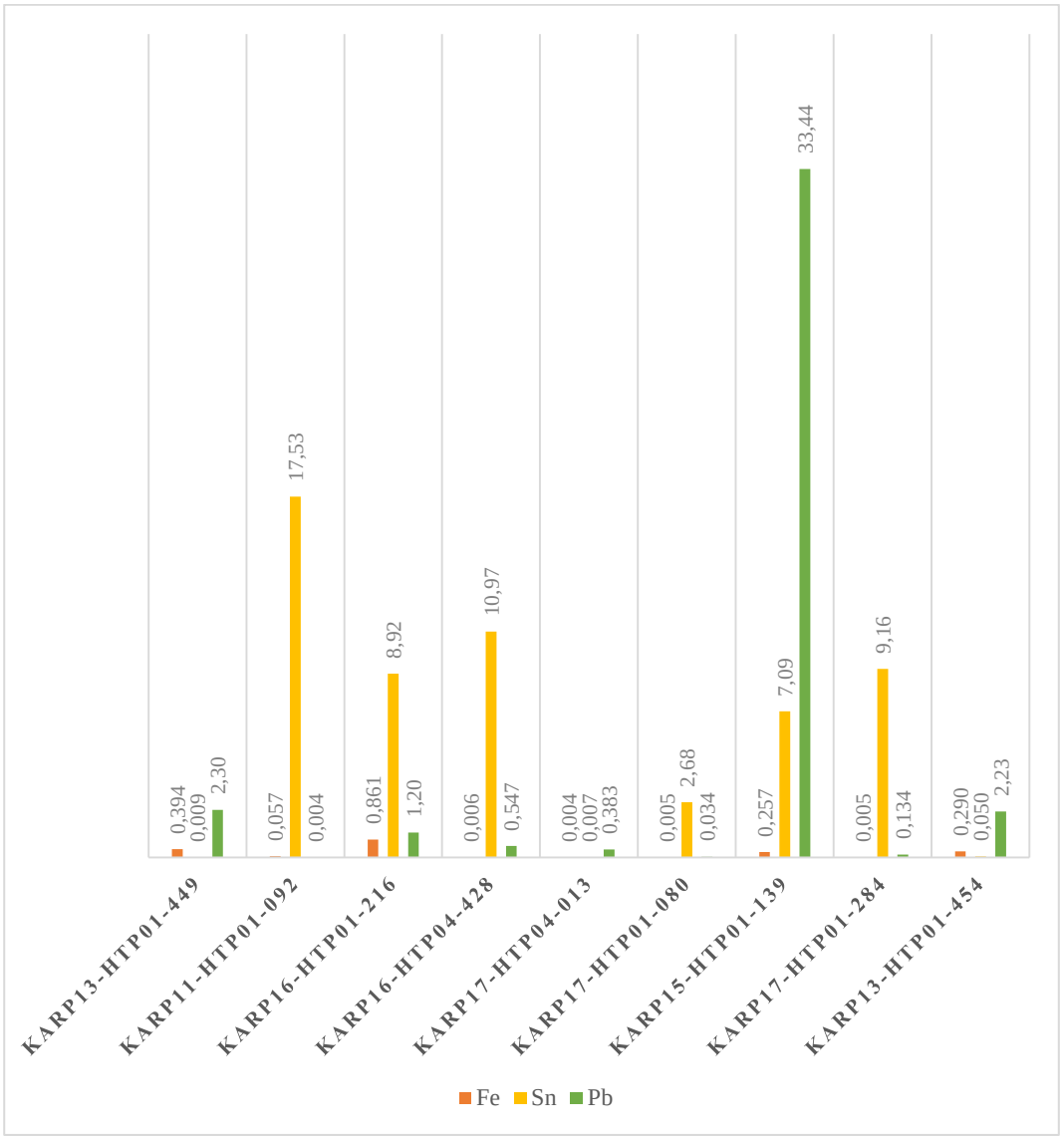
Graph 3. Cu-Ag Concentration Ratio (%)



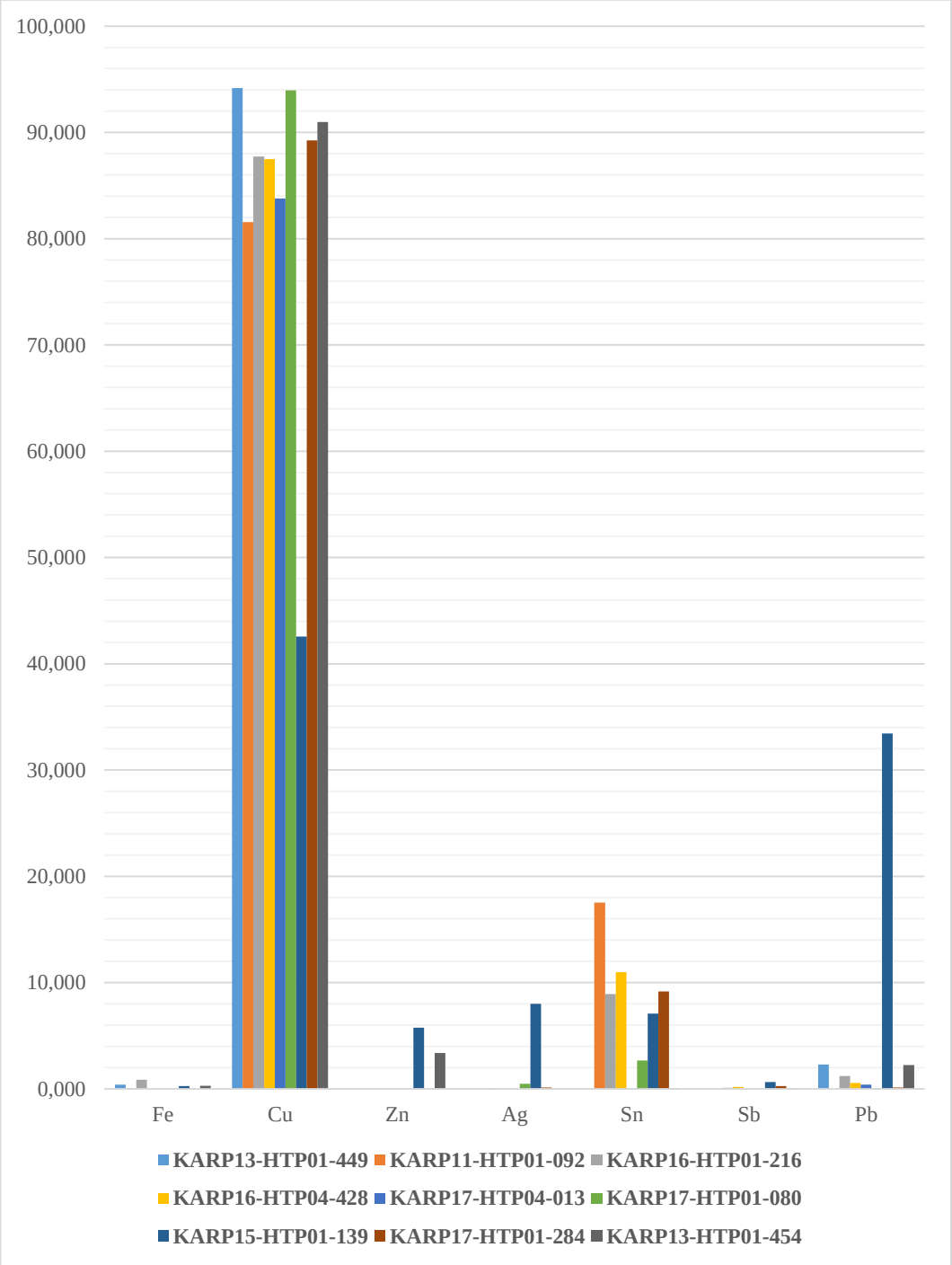
Graph 4. Zn-Pb Concentration Ratios (%)



Graph 5. Cu-Zn-Sn Concentration Ratios (%)



Graph 6. Fe-Sn-Pb Concentration Ratios (%)



Graph 7. Cluster of Bronze Material in terms of Selective Alloy Elements Concentration Ratios (%)