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# ARCHEOMETALLURGICAL STUDY OF BRONZE ARTEFACTS (FROM III B.C. TO VI A.D.) EXCAVATED ALONG ALBANIAN COASTLINE

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## ABSTRACT

In this paper we studied different types of copper / copper alloy objects (luxury, tools and exchange objects) excavated in Durrës (ancient city of Epidamnos, Dyrrah) and Ploçë (near Vlora, Ploçë ancient city of Amantia), in Albania. Seven coins and four nails (V-VI A.D.) were found in a macellum monument in the centre of Durrës among ceramics and other metallic objects, while in Amantia a mirror (III B.C.) fragment was one of the findings in a Necropolis tomb along with other luxury objects. The archaeologists of the Centre of Albanological Studies in Tirana and the Archaeological Museum Durrës gave us the possibility to sample these objects, since they were already damaged. The elements composition of the coins, nails and mirror was determined with  $\mu$ -X ray fluorescence ( $\mu$ -XRF); the microstructure inclusions / precipitations were studied with scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and the corrosion products along with the microstructure elements were investigated with optical microscopy (OM), X ray diffraction (XRD) and Vickers microhardness tester. All the objects of this study had a variety of compositions from pure Cu to Cu-Sn, Cu-Pb, Cu-Fe, Cu-Sn-Pb alloys. Most of the coins might have been annealed and then cold worked; unlike the mirror, one coin and all of the nails, the final production step of which might have been casting. The corrosion products detected were quartz, cuprite, cassiterite, cerussite, atacamite/paratacamite, malachite, albite, nantokite, calcite and anorthite, mostly distinguishable also with polarized light. Chemical content such as Pb, S, Sb, As, Si, Fe, Zn, Ag, Bi, Ni might be connected with the sulphite copper mineral preceding the alloys and the fluxes used during production.

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**KEYWORDS:** coins, mirror fragment, nails, antique bronze, Albania, XRF, SEM-EDS, XRD, corrosion

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## 1. INTRODUCTION

Epidamnos or Dyrrah (Durrës) can be compared to the largest cities of the ancient and medieval Mediterranean region. The city of Dyrrah was built by the Illyrian tribe of Taulants, in the XIII-XI centuries B.C. The first inhabitants of Dyrrah before the Illyrians, the Pelasgians, built the first prehistoric settlements in the surroundings of the city. Under the Mediterranean climate conditions, the most suitable place for habitation was Erzen River shore (Ululeus) and the western lowlands around it. On the coast of today Durrës Gulf, the first port named Dyrrah was established. According to ancient authors, this city was founded by two Illyrian origin kings, named Dyrrah and Epidamn. The ancient city had pottery, metal, fabric, leather workshops, ship constructing sites, etc. Proof of the trade development are bronze and silver coins minted in Dyrrah. While the mosaic named "Bukuroshja e Durrësit" (Beauty of Durrës) testifies the urban flourishing. From the I-III century A.D. the city of Dyrrah experienced a period of prosperity, as it became the centre and main port of the Eastern Adriatic coast. The monument of Macellum-Forum in the centre of Durrës was discovered in 1986 and the excavations of the year 2000 brought to light many ceramics and metallic objects. The monument was built around 500 A.D. in honour of Anastasius emperor and the influence of the architecture came from the Roman Empire. (Ceka, 2000; Hoti, 1996; Prendi, 2008)

Amantia, on the other hand, was established at the end of V century B.C. and during the III century B.C. its first coins were minted. It was built on the southeast territories of Vlora, on the hills near Shushica river valley (today Ploçë village). According to ancient authors Amantia was inhabited by Illyrians while the most distinctive architectural elements included the acropolis, stadium, god's temple, necropolis and the city's retaining walls. The first excavations were performed during the XIX century which brought to light ceramics and bronze objects. (Ceka, 2000; Hoti, 1996; Prendi, 2008)

During the Iron Age, production of the first coins began (table 1), such as the Greek silver ones (year 580 B.C.), the gold coins from Lydia west of Turkey (year 550 B.C.) and those of King Philip of Macedonia (year 350 B.C.) which were copied even in England. To increase the hardness and longevity of coins, gold and silver began to create alloys with copper. We can mention coins from Gallia (Belgium) composed of 70%Au and 10%Cu, the English ones containing 47%Au and 40%Cu. Silver coins from Athens (years 196-169 B.C.) contained 0.0076% - 0.33%Au and 0.035% - 5.3%Cu. The main production process of coins was stamping. One coin from Durrës (Dyrrachium) and one coin of the Illyrian King Monounios (III century B.C.) composed of Cu-Ag alloy turned out to be produced by cold stamping after being casted. (Civici *et al*, 2007) Another coin from Durrës (III century B.C.) produced in the same way consisted of a ternary Cu-Sn-Pb alloy. (Dilo *et al*, 2009) Coins from India and China were produced in bronze moulds, in Carthage (Africa) the copper-arsenic combination was preferred because of surface lustre, while copper-nickel coins with up to 22%Ni were produced in northern Afghanistan. Over the centuries, during the Roman Empire coins began to be produced from the copper-zinc alloys (about 20-30%Zn). This happened because it was more economical than gold and had a pleasant yellow colour. The same phenomenon is observed with jewellery in Jordan, where families who aspired socioeconomic statuses used copper and iron in order to mimic gold and silver. Cu-Zn alloys replaced in many cases even Cu-Sn alloys or zinc was added in them forming a ternary Cu-Zn-Sn alloy in order to reduce the cost of objects' production. Brass was produced by adding ZnCO<sub>3</sub> to copper under reduction conditions. (Bachler *et al*, 2006; Betlyon, 1985; Civici *et al*, 2007; Copper, Al-Saad, 2015; Griesser *et al*, 2016; Howgego, 1995; Kemmers *et al*, 2011; Pistofidis *et al*, 2006; Scott, 2012; Scott, 1991; Sedyshev *et al*, 2020; Tylecote, 1992)

*Table 1. Various coins' composition from V century B.C. to years 10-50 A.D. (Civici et al, 2007; Pistofidis et al, 2006; Tylecote, 1992)*

Coins	Dating	Au (%)	Ag (%)	Cu (%)	Pb (%)	Bi (%)	Fe (%)
Terina (Greece)	V century B.C.	0.09	95.32	1.42	2.19	-	-
Philip of Republic of North Macedonia	IV century B.C.	99.7	0.3	-	-	-	-
Corinth (Greece)	IV century B.C.	trace	94.12	4.01	0.57	-	-
Gallia (Belgium)	IV century B.C.	69.02	22.83	8.15	-	-	-
Korkyra (Greece)	III century B.C.	0.307	99	0.28	0.126	0.138	0.119
Dyrrachion	III century B.C.	0.273	95.65	3.61	0.274	0.052	0.111
Illyrian King Monounios	III century B.C.	0.319	96.5	2.78	0.282	0.064	0.025
England	years 40-20 B.C.	57.3	16.4	23.9	-	-	-
Cartagena (Africa)	years 40-20 B.C.	60.8	36.3	2.3	-	-	-
Verica (England)	years 10-50 A.D.	72.2	7.6	17.2	-	-	-

Antique mirrors are unique luxury objects, mainly produced by casting bronze in stone, pottery or wax moulds. They were round flat disks, in some cases equipped with iron or bronze handles, or caryatid stand prototypes, polished on one side for reflection and decorated on the other. Mirrors were fascinating objects, occupying special places in different cultures, even considered sacred and ways to speak with gods. There are numerous beautiful bronze mirrors excavated in Greece, mostly representing gods' figures but also warriors in violent combat, decorated with fine details. This is one of the most popular objects of Greek metalwork and from Late Archaic to Early Hellenistic times the main types were: hand mirror with handles, caryatid stand ones and round box mirrors. The Fogg mirror (middle of IV century B.C.) engraved with winged Eros, is composed by three main sections possibly joined by mechanical peening. In other examples of Greek mirrors Eros appears in different positions such as seated or with outspread wings riding a dolphin and holding a dove. Aphrodite is another goddess which have often decorated antique Greek mirrors with finesse and also Pan, god of the wild. In some cases, they also showed violent combat scenes like the one excavated in Corinth (Hellenistic period). The influence of Greek mirrors' production spread in the Balkans and further in Europe, even in Asia. Etruscan art's elements, that spread all over Italy, derived from Greece. Here is worth mentioning the bronze mirror (IV century B.C.) excavated in Palestrina (east of Rome, Italy) representing three Graces and inspired by a Greek prototype. In China mirrors become popular mostly during the Han dynasty (years 206 B.C. - 220 A.D.) and before that they were most likely imported from the west. Although the decorative figures were locally inspired, the influence was probably Greek.

In order for the mirror's alloy to have a light colour, a better polish quality and most important to increase the reflectivity usually a tin content from 19 to 32% was used. The surface quality was as well increased

by adding lead (approximately 4 - 6%), which also increased the fluidity of the alloy during casting. (Bai, 2011; Buitron, 1971 - 1972; Cerqueira, 2018; Congdon, 1966; Hou, 1981; Richter, 1941; Robinson, 1948; Schulten et al, 1996)

An important element in the object's characterization is the information concerning the raw material used for its production. Copper minerals are divided into three groups: 1) sulphides containing Cu-S bonds, 2) carbonates with Cu-C-O, and 3) silicates with Cu-Si-O bonds. The second and third group are also called oxide minerals, while copper is more easily extracted from sulphides and carbonates. Most of the copper deposits from the Jurassic and Cretaceous periods are included in sulphide minerals of volcanic origin. They are located in Albania, Cyprus and in some areas of Turkey (Kure Asikoy, Murgul Maden, etc.) and they are quite rare in other countries. (Economou-Eliopoulos et al, 2008) Ophiolite Albanian formations (volcanic rock formations) consist in an important connecting element of the Alpine-Dinarid-Hellenid orogenic system (orogenic is the process that leads to a large structural deformation of the Earth's crust). Northern Albanian areas (Rubiku and Mirdita) and the eastern ones (Korçë) have turned out to be rich in copper sulphide minerals, associated with Zn, such as: pyrite, chalcopyrite, sphalerite  $[(Zn,Fe)S]$ , covellite, tennantite  $(Cu_{12}As_4S_{13})$ , tetrahedrite  $[(Cu,Fe)_{12}Sb_4S_{13}]$  and Cu-Zn-Au-Ag compounds. Due to further changes in hydrothermal solutions and oxygen partial pressure, the amount of chalcopyrite began to decrease, creating space for bornite phase. Copper minerals in these territories contain 1-5% Cu and in some cases up to 8-20%, 1-2% Zn associated with Au, as well as: Cd, Sb, Ag, Sn, Se, Te, As, Bi and Y (figure 1). (Çina, 1975; Çina, 1976; Koçi, 1977; Schlagintweit, Gawlick, 1987; Kati, 1988; Osmanlliu, Thanashi, 1997; Economou-Eliopoulos et al, 2008; Hoxha, 2005; Gawlick et al., 2008).

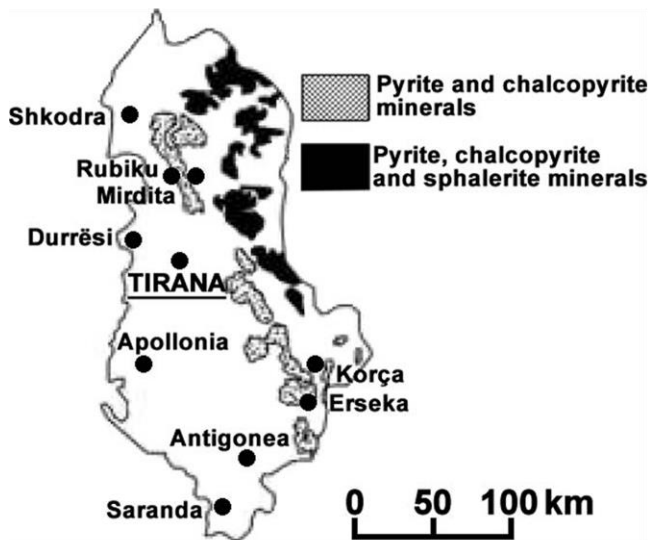


Figure 1. Copper deposits in Albania along with some major cities in these areas (left). (Economou-Eliopoulos et al, 2008) The western and eastern belt of ophiolites in the Balkans (right). (Hoxha, 2014; 2005).

Two of the oldest and most important mines in the Balkans are Rudna Glava (Serbia) and Ai Bunar (Bulgaria). According to several different studies their copper minerals are hydro-carbonates such as: azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) and malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ). (Jovanović, 1978; Gale, Stos-Gale, 1982; Gale, 1991; Jovanović, 2009) Copper deposits have been large and varied in Cyprus since antiquity (Cuprum), even the name of the country is related to this chemical element. They consist of hydro-carbonates and sulfates such as: malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) and chalcopyrite  $\text{CuFeS}_2$  (Constantinou, 1982). While in Greece the areas rich in copper mines are Kamariza, Ilarioni, Kristiana, Agia Varvara, Sounioni and Lavrioni. In these territories, copper was mainly obtained from: native

copper (Cu), cuprite ( $\text{Cu}_2\text{O}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ), olivenite ( $\text{Cu}_2\text{AsO}_4\text{OH}$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) and tetrahedrite [ $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$ ] (figure 2). (Marinos, Petrascheck, 1956) The Alps of Italy are rich in copper minerals, especially sulphides. Etruria (now Tuscany, Umbria, Lazio) in central Italy contains the largest mineral deposits of the entire country, mostly those of Cu-Pb. In southern Italy, copper sulphide minerals and also Pb, Ag, Fe, Sn reserves are concentrated in Calabria, Sardinia and Sicily. Hundreds of melting furnaces, molds, pots, pieces of slag have been excavated in all of Italy territories testifying the local copper extraction processes from its mineral. (Attema et al, 2003; Artioli et al, 2008; Artioli et al, 2008)



Figure 2. Deposits of copper minerals in antiquity shown on the political map of the Balkans and Italy ([www.worldatlas.com/webimage/countrys/europe/balkans.htm](http://www.worldatlas.com/webimage/countrys/europe/balkans.htm)). In italic and underlined letters are marked the copper ore deposits.

The aims of this study are to better understand the alloys composition and the production techniques used in the cases of seven coins with file no 8378, 8425, 8408, 8382, 8414, 8321, 8342 and four nails with file no 8362, 5423, 5475, 8361, all excavated in Durrës (Epidamnos, Dyrrah) and dating from medieval times. Also, to investigate a mirror fragment with file no 127 from the III century B.C. excavated in Ploçë (Amantia). Ancient decorative objects, exchange and parts of objects have been studied in Albania but very few with physical analytical methods. Such investigations have not been performed before on the objects studied. This present project is part of a national campaign in order to better understand the cultural heritage past. (Civici et al, 2007; Çakaj et al, 2016; Çakaj et al, 2016; Çakaj et al, 2015; Çakaj et al, 2014; Çakaj et al, 2012; Dilo et al, 2009; Kouli et al, 2006).

## 2. MATERIALS AND METHODS

Under the restorer supervision it was possible to remove a very small metallic sample (around 8mm<sup>3</sup>) from each object (figure 3). The samples were prepared in the Department of Physics, Faculty of Natural Science, UT and after that the  $\mu$ -XRF, OM, XRD, SEM-EDS, Vickers microhardness test and analysis were performed. The preparation procedure includes mounting the samples in acrylic resin (as shown in Fig. 1), polishing them with SiC abrasive

papers (Buehler P600, P800, P1000, P1200, P2500) and diamond paste (Kemet 6, 3, 1  $\mu$ m). Assembly in acrylic resin frames is usually used in small samples' cases and the polishing process is necessary to eliminate the mechanical damages of the samples' surface that could negatively affect the analytical examinations. The equipment's type along with the main technical characteristics are as follow:

- $\mu$ -XRF → ARTAX Bruker, Mo anode, Rh target, detective capacity from Na to U;
- OM → KOZO XJP304;
- XRD → X'Pert Pro MPD PW 3040/60 Panalytical, Cu K $\alpha$  radiation;
- SEM-EDS → XL30 ESEM-FEI and EDAX Genesis Spectrum with ZAF correction;
- Vickers microhardness tester attached to Metalloplan Leitz optical microscope.

The  $\mu$ -XRF and EDS were used to determine the elemental composition of the alloy and the microstructure inclusions. The corrosion products were studied with XRD while the microhardness values were measured with the Vickers tester. The OM with polarized / reflected light and the SEM were utilized to examine the different alterations of the microstructure due to the production processes and the corrosion products as well. (Bradley et al, 2006; Cullity, 1956; Dudley Creagh et al, 2007; Goldstein et al, 2003; Potts et al, 2008; Wayne, 2009)

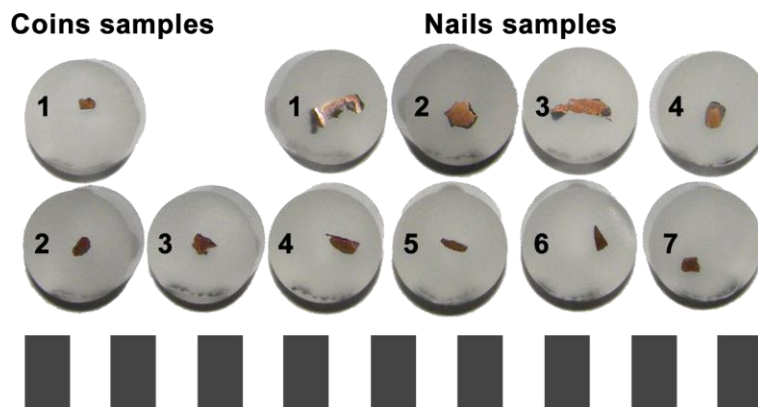
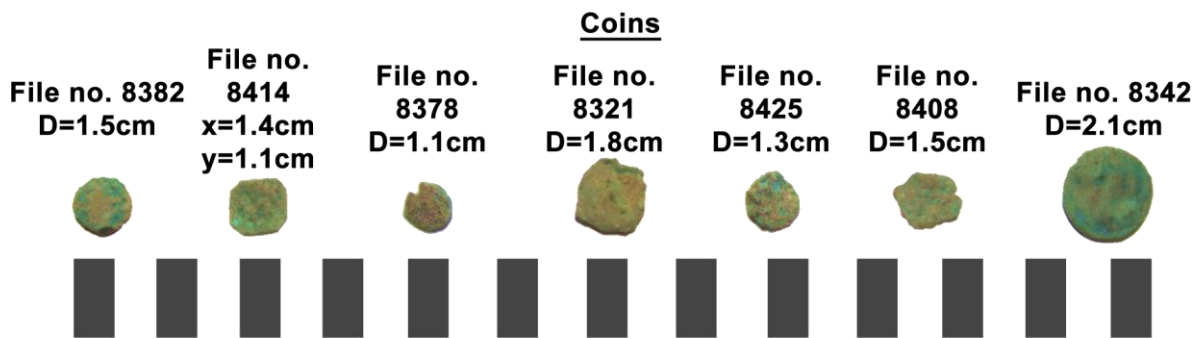
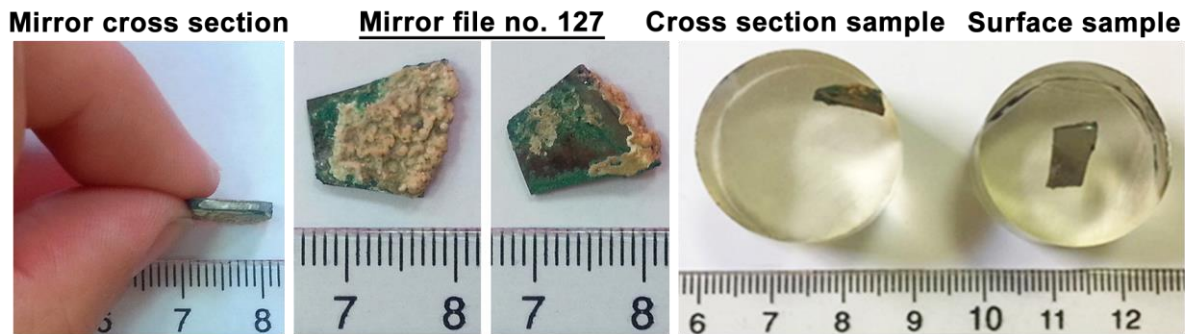
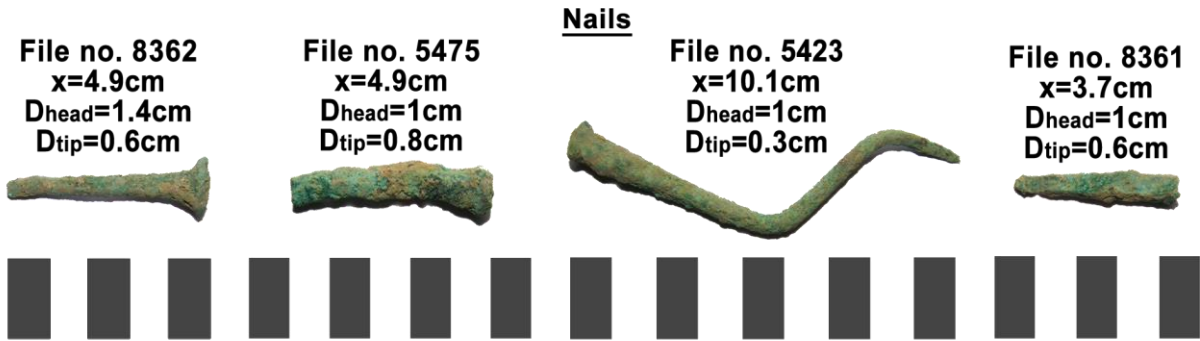


Figure 3. This study's objects and samples, mounted in epoxy resin (7 coins, 4 nails and 1 mirror fragment).

### 3. RESULTS AND DISCUSSIONS

The coins and nails are part of the Archaeological Museum Durrës fund while the mirror fragment

belongs to the Centre of Albanological Studies in Tirana. Archaeological investigation is challenging especially in coins' cases because of the sampling

difficulties but at the same time very important to understand the political and economic developments of a certain region and period. On the other hand, mirrors are considered luxury objects and consequently quite rare. (Betlyon, 1985; Cerqueira, 2018; Howgego, 1995; Kemmers et al, 2011)

Copper forms alloys with tin in order to reduce the melting temperature, increase the hardness and resistance to the corrosion process. The complete solubility of tin in copper occurs for a percentage up to 14% and the alloy has high hardness and low brittleness. When lead is added in bronzes it precipitates along grain boundaries because it is not soluble in copper. Lead is added to lower the melting temperature, to increase the fluidity of metal during casting, to increase the surface quality of the object and in many cases to reduce the cost of production. (Artioli, 2010; ASM Special Handbook, 2001)

Several points are analysed on all of the objects' samples, after being mounted in acrylic resin and polished. This was done because analysing the entire object was not possible and selecting various random points on each sample would give a more accurate result. Based on the  $\mu$  - XRF mean results on table 2 (mean results and standard deviations), coins with file no. 8408, 8414 and 8321 are composed by Cu-Pb alloys with minor elements such as Fe, Cr except 8414 which also contains 1% of Sn. Coins with file no. 8425, 8382, 8342 and nails with file no. 5423, 5475 are pure copper (over 99% Cu) with less than 1% of Pb, Fe, Cr, Ni; and coin's alloy with file no. 8378 is composed by Cu-Sn with 0.6% Pb. Nail with file no. 8362 is a Cu-Fe alloy with 0.3% of Pb and nail with file no. 8361 is a ternary alloy composed by Cu-Sn-Pb with 0.1% Fe.

Table 2. Mean  $\mu$  - XRF results and standard deviations.

Object	File no.	Cu (%)	Pb (%)	Sn (%)	Fe (%)	Cr (%)	As (%)	Ni (%)
Coins	8378	96.4 ± 3.7	0.6 ± 0.05	3 ± 0.3	-	-	-	-
	8425	99.3 ± 4.1	0.6 ± 0.05	-	0.1 ± 0.01	-	-	-
	8408	97.4 ± 4	2.2 ± 0.2	-	0.2 ± 0.01	0.2 ± 0.01	-	-
	8382	99.6 ± 4.5	0.4 ± 0.03	-	-	-	-	-
	8414	96.7 ± 4	2 ± 0.1	1 ± 0.2	0.2 ± 0.01	0.1 ± 0.01	-	-
	8321	97.5 ± 4	2.3 ± 0.2	-	0.2 ± 0.01	-	-	-
	8342	99.1 ± 4.1	0.5 ± 0.05	-	0.1 ± 0.01	0.1 ± 0.01	-	0.2 ± 0.01
Nails	8362	98 ± 4	0.3 ± 0.02	-	1.7 ± 0.01	-	-	-
	5423	99.1 ± 4.1	0.7 ± 0.06	-	0.1 ± 0.01	0.1 ± 0.01	-	-
	5475	99.6 ± 4.2	0.2 ± 0.03	-	0.1 ± 0.01	0.1 ± 0.01	-	-
	8361	90 ± 4	6 ± 0.3	3.9 ± 0.4	0.1 ± 0.01	-	-	-
Mirror surface		41.1 ± 1.7	2 ± 0.1	56 ± 2.3	0.6 ± 0.07	-	0.3 ± 0.02	-
Mirror cross section	127	67.5 ± 2.7	5.6 ± 0.2	24.5 ± 1.1	2 ± 0.1	-	0.4 ± 0.03	-

The corrosion products of metallic objects are formed during chemical reactions between elements that compose the objects and elements from the environment (air, soil, water), such as oxygen, carbon, hydrogen, chlorine, etc. These corrosion products in copper / bronze culture heritage's objects have a sandwich-like structure similar to the Liesegang circles, forming a layered structure with oxide, carbonate, hydroxide, chloride compounds placed on top of each other. The first layer of copper alloy corrosion products contains tenorite CuO, cuprite Cu<sub>2</sub>O, cassiterite SnO<sub>2</sub>, cerussite PbCO<sub>3</sub> and usually is created during the object usage. The second layer, which is placed on top of the first, consists of copper carbonates such as malachite Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>, azurite Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>, brochantite Cu<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub> but also copper chlorides such as atacamite Cu<sub>2</sub>Cl(OH)<sub>3</sub>, paratakamite Cu<sub>3</sub>(OH)<sub>6</sub>Cl<sub>2</sub>, nantocite CuCl, etc. This layer of corrosion products is created during the last period of object's usage and the beginning of its stay in ground or water. In the third layer of copper alloy corrosion, which is usually detached from the object

during excavation, the copper loss process continues (diffusion of Cu from the object to the surroundings) and Cl, Ca, Na, Al, Si salts are formed.

The corrosion products are the first to be examined and they were mechanically removed (with a scalpel) only in seven of the samples of: coins with file no 8378, 8408, 8414, 8321; nails with file no 5423, 5475; mirror with file no 127. It was not possible to remove these products in all of the samples because of the very thin layer of corrosion in them. Quartz is present in the samples of coins with file no 8378, 8408, 8414, 8321, nails with file no 5423, 5475 and mirror with file no 127, while cuprite is detected in all of the coins and nails mentioned above except for the mirror. Quartz and cuprite usually form the first layer of corrosion in copper alloy objects. In Cu-Pb alloys such as coin with file no. 8408, 8321 and in Cu-Sn coin's alloy with file no. 8378, cerussite and cassiterite are detected respectively. These corrosion phases from the first layer, appear red/dark red/blue/yellow/brown/black/grey under the polarized light of the optical microscope. Malachite, atacamite, paratacamite,

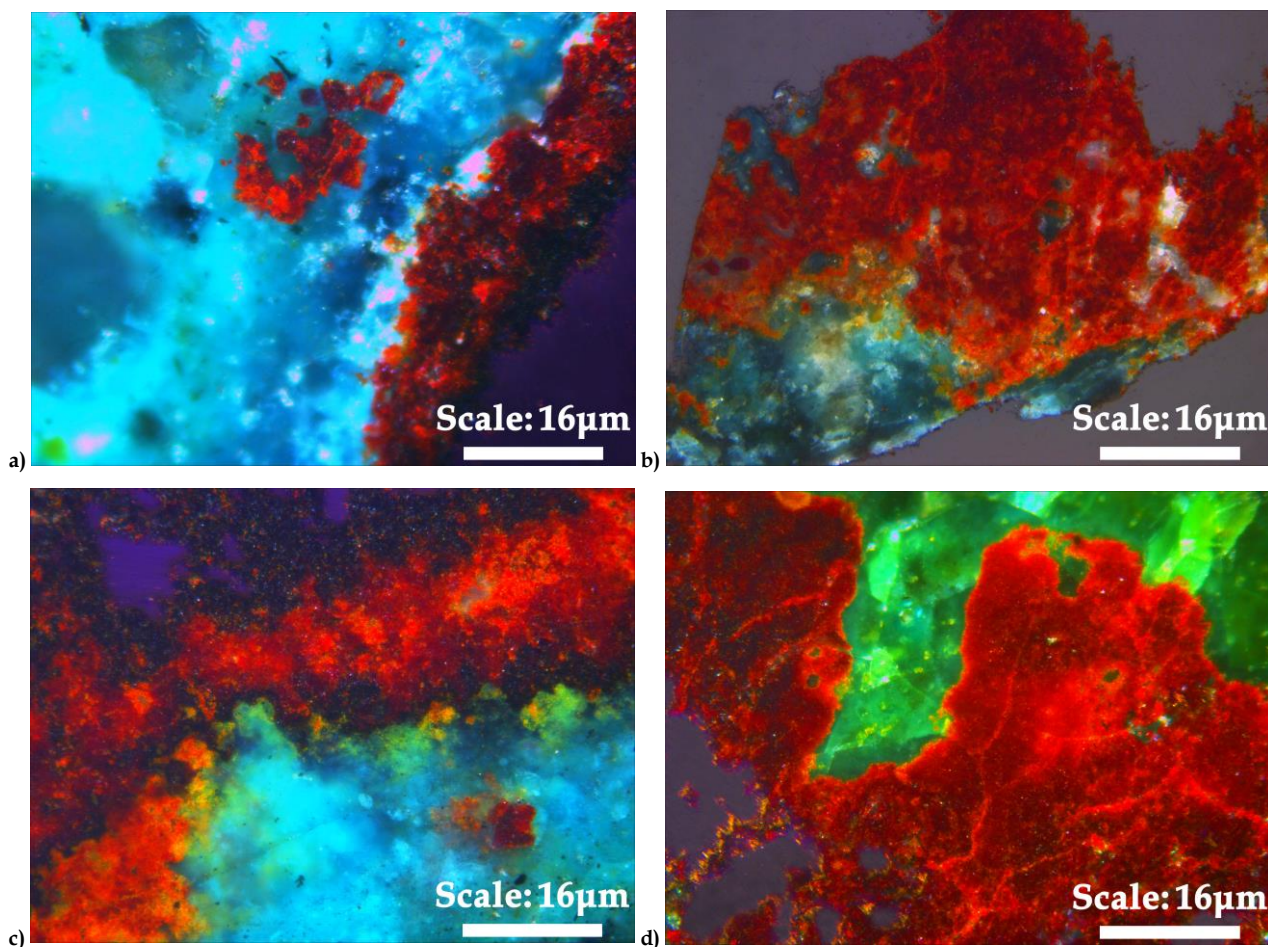
nantokite (components of the second layer of corrosion) are differentiated with the help of XRD while with OM with polarized light they all appear green/dark green/emerald green. Malachite is detected in the samples of nails with file no 5423, 5475 and mirror with file no 127; atacamite is present in the samples of both nails mentioned above and in coins with file no 8414, 8321; paratacamite is detected only in the cases of coin with file no 8414 and nail with file no 5423; while nantokite is part of the corrosion products of coins with file no 8378, 8414 and nail with

file no 5423. The coins' and mirror's corrosion contain also phases from the third layer such as anorthite (coin with file no 8414), calcite (coins with file no 8378, 8408 and mirror with file no 127), albite (coin with file no 8321). (Pracejus, 2008; Scott, 2012; Scott, 1991)

Table 3 shows the qualitative and quantitative results (phases' formula along with their colours observed with polarized light) while in Fig. 4 are presented the corrosion products observed with OM with polarized light.

**Table 3. Qualitative and quantitative XRD results (phases' formula along with their colours observed with polarized light, the calculation error is 2-3% for major phases and 5-10% for minor ones).**

Phases properties / Objects with file no			Coins				Nails		Mirror
Colors in OM with polarized light	Formula	Phases	8378	8408	8414	8321	5423	5475	127
Glassy white	SiO <sub>2</sub>	Quartz (%)	24	9	32	8	2	10	28
Dark red to cochineal red	Cu <sub>2</sub> O	Cuprite (%)	35	31	22	33	44	48	-
White, gray, blue, or green	PbCO <sub>3</sub>	Cerussite (%)	-	37	-	13	-	-	-
Black, brown, red, yellow	SnO <sub>2</sub>	Cassiterite (%)	20	-	-	-	-	-	-
Bright green, dark green, blackish green	Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub>	Malachite (%)	-	-	-	-	18	33	25
Bright green, dark emerald-green to blackish green	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	Atacamite (%)	-	-	5	23	8	9	-
Green	Cu <sub>3</sub> (OH) <sub>6</sub> Cl <sub>2</sub>	Paratacamite (%)	-	-	3	-	24	-	-
White to grey, green	CuCl	Nantokite (%)	8	-	17	-	4	-	-
White, gray, red	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	Anorthite (%)	-	-	22	-	-	-	-
White	CaCO <sub>3</sub>	Calcite (%)	13	23	-	-	-	-	47
White to gray, blue, green, red	NaAlSi <sub>3</sub> O <sub>8</sub>	Albite (%)	-	-	-	22	-	-	-





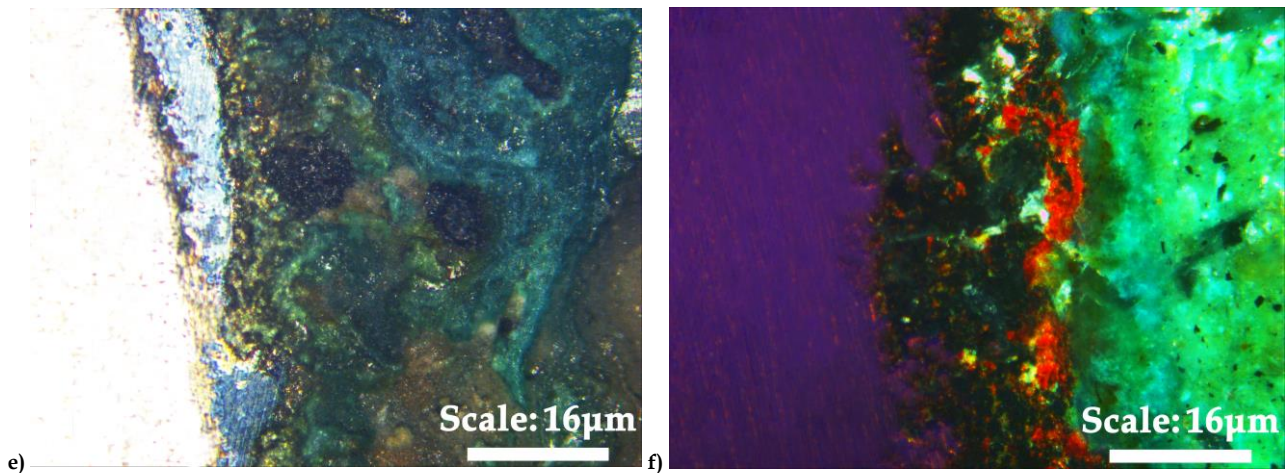


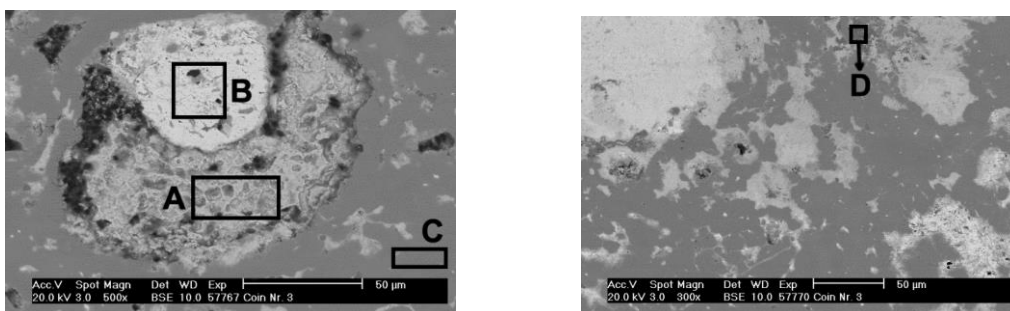
Figure 4. The corrosion products observed with OM with polarized light of: a) coin with file no 8321, b) coin with file no 8378, c) coin with file no 8408, d) coin with file no 8414, e) mirror fragment with file no 127, f) nail with file no 5475.

In ancient times there were precious metals such as native copper and its oxide minerals on the ground layer near the surface. Determination of native copper origin can be done by analysing the presence and percentage of four elements such as As, Ni, Pb and Sb. Most of the surface copper must have been used over time enriching the surrounding area, such as the secondary layer below the surface. This area provided the largest amount of copper but also As and Sb minerals, since they have high solubility in copper. The secondary layer often contains fahlerz-type minerals, such as Cu-As-Sb sulphides  $(CuFe)_{12}(AsSb)_4S_{13}$  or tetrahedrite solid solutions  $(CuFe)_{12}Sb_4S_{13}$  and tennantite  $(CuFe)_{12}As_4S_{13}$ . Deeper areas below the surface contain copper sulphides with low concentrations such as 1-4% Cu. On the other hand, iron oxide, quartz or manganese oxide

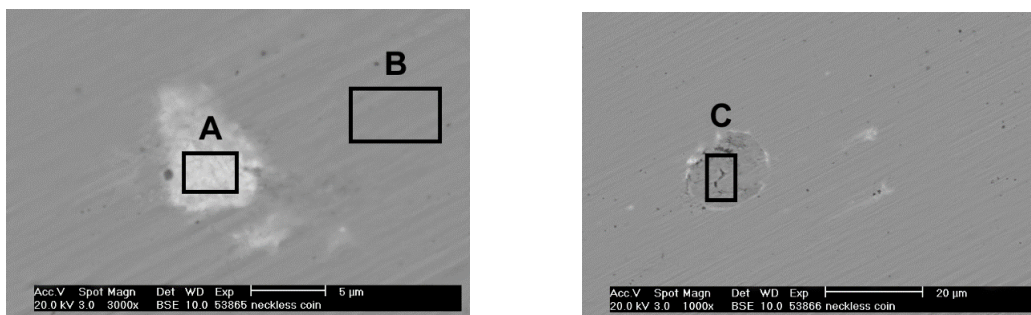
could have been used as a flux during copper oxide minerals' melting while the sulphite minerals could have been roasted using  $SiO_2$  or Fe as a flux. (Bachmann, 1982; Figueiredo, 2011)

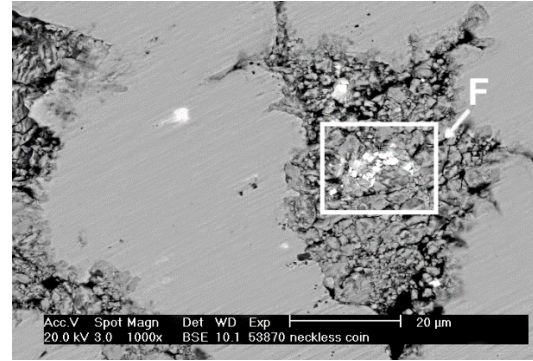
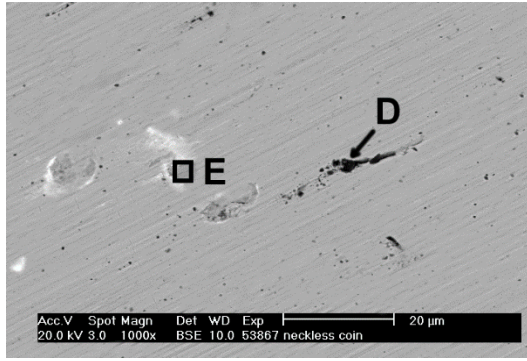
Figures 5, 6, 7 show all of the SEM images while tables 4 and 5 show all the EDS results on distinctive points / areas of all samples of this study (points / areas with different grey shade). On each sample the chemical composition of the areas on the alloy and the points / areas on the inclusions / precipitations were examined with EDS. All of the samples were preliminary carbon coated because of the very small conductive metal area (most of the sample surface is acrylic resin and corrosion). The detection limit for the major elements (with  $Z > Z_{Na}$ ) is of the order of 0.1%, while the accuracy varies from 3% to 12% depending on the elements and their concentration.

File no. 8378

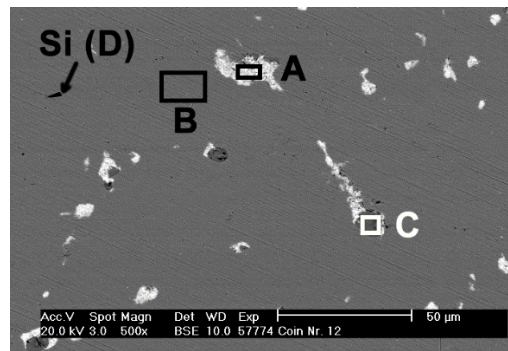


File no. 8425

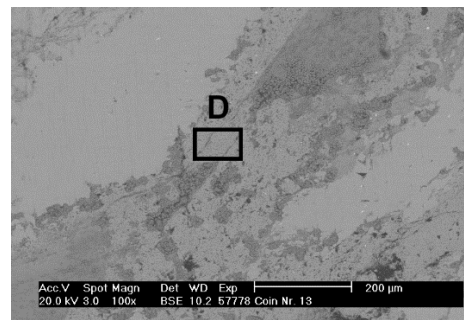
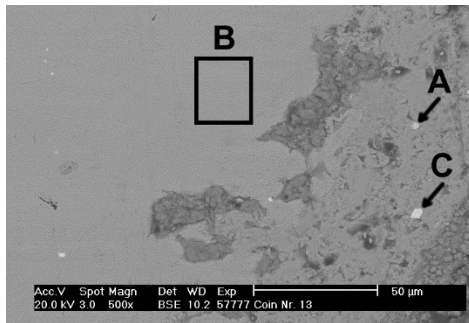




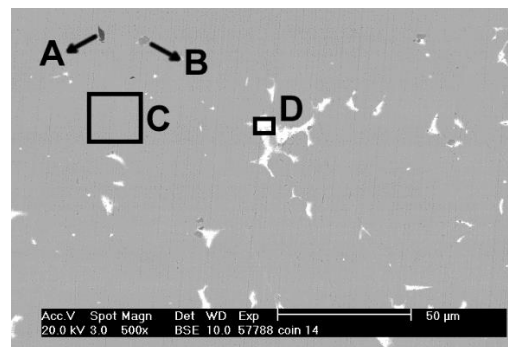
File no. 8408



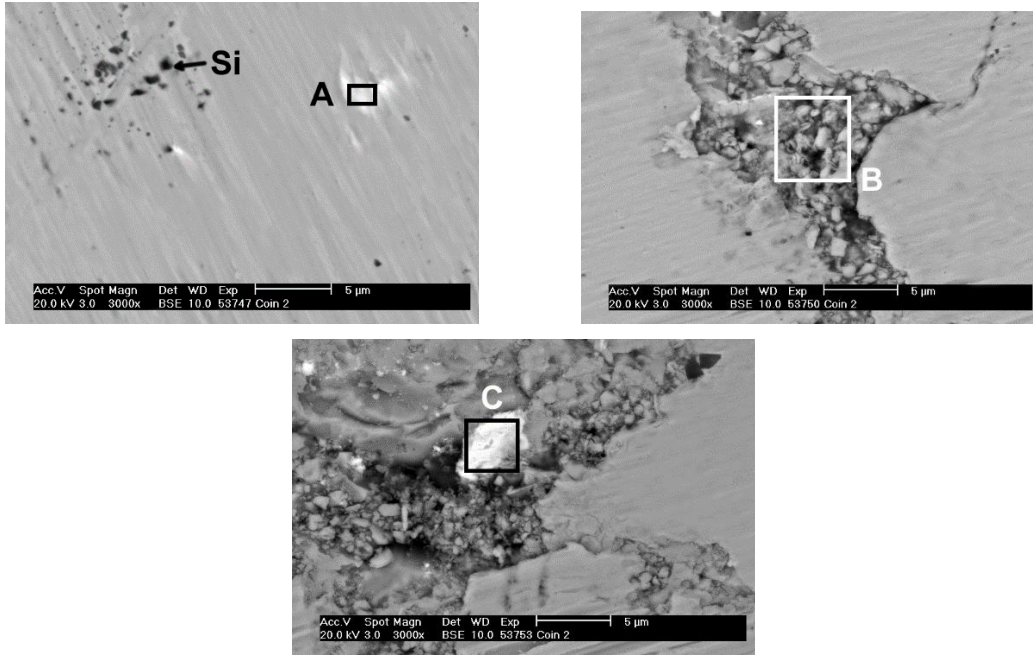
File no. 8382



File no. 8414



File no. 8321



File no. 8342

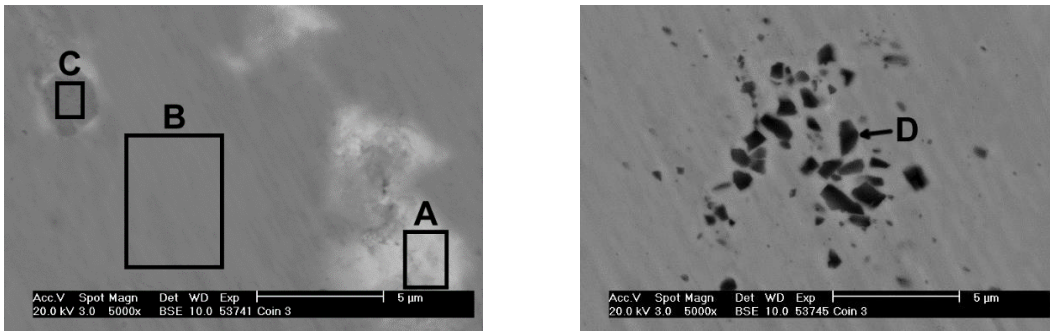
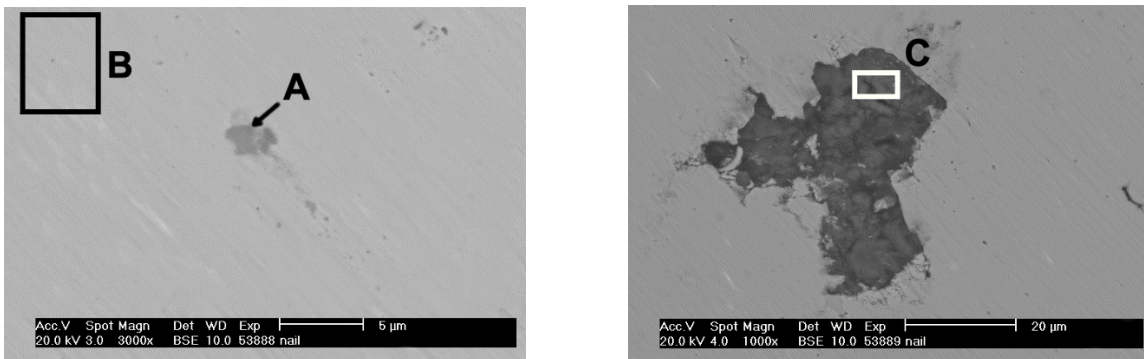
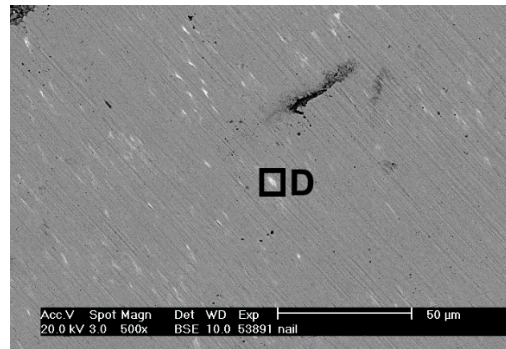


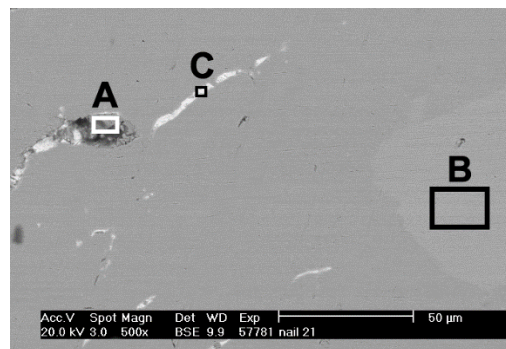
Figure 5. SEM images of all coins' samples (with file no 8378, 8425, 8408, 8382, 8414, 8321, 8342). The points and areas (rectangular) indicated in these images are the ones analysed with EDS and the chemical composition results of which are shown in Table 4.

File no. 8362

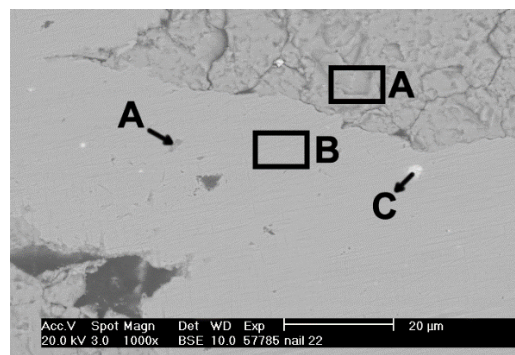




File no. 5423



File no. 5475



File no. 8361

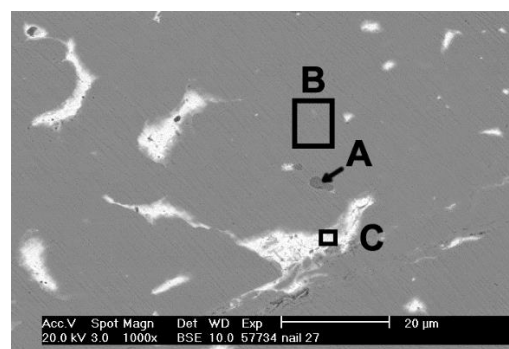


Figure 6. SEM images of all nails' samples (with file no 8362, 5423, 5475, 8361). The points and areas (rectangular) indicated in these images are the ones analysed with EDS and the chemical composition results of which are shown in Table 5.

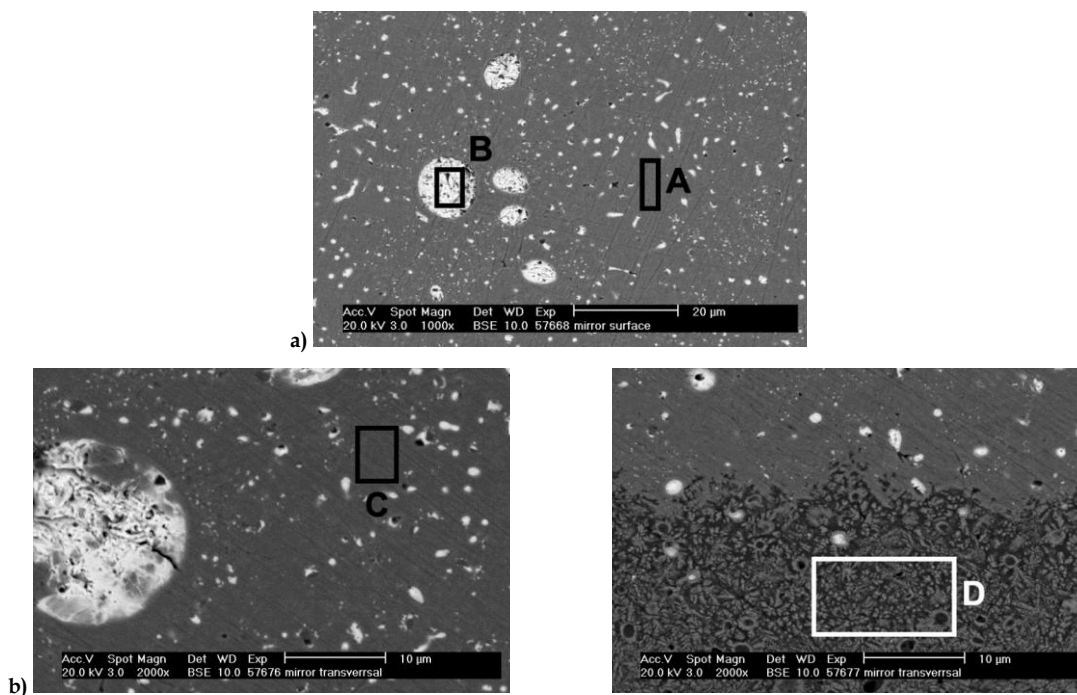


Figure 7. SEM images of the mirror fragment with file no 127, a) sample's surface and b) its cross section. The areas (rectangular) indicated in these images are the ones analysed with EDS and the chemical composition results of which are shown in Table 5.

Table 4. EDS results on distinctive points/ areas of the coins' samples.

Objects with file no / Elements	Cu (%)	Pb (%)	Sn (%)	Fe (%)	Zn (%)	O (%)	Sb (%)	As (%)	Ag (%)	Si (%)	Ni (%)	Cl (%)	Bi (%)	C (%)
Coin 8378	Area A	1.5	73.1	-	-	6.9	-	-	-	-	-	18.5	-	-
	Area B	3.1	91.9	-	-	3.5	-	-	-	1.5	-	-	-	-
	Area C	96.9	-	3.1	-	-	-	-	-	-	-	-	-	-
	Area D	74.7	10.7	-	-	14.6	-	-	-	-	-	-	-	-
	Area A	9.8	68.4	-	-	8.1	12.2	1.5	-	-	-	-	-	-
	Area B	100	-	-	-	-	-	-	-	-	-	-	-	-
Coin 8425	Area C	90.1	-	-	-	1.6	-	-	-	-	-	-	-	8.3
	Point D	30.9	-	-	-	1.7	-	-	-	67.4	-	-	-	-
	Area E	96.8	-	-	-	3.2	-	-	-	-	-	-	-	-
	Area F	9.2	51.8	-	-	12.5	25.7	-	-	-	0.8	-	-	-
	Area A	10	71.6	-	-	10.3	8.1	-	-	-	-	-	-	-
Coin 8408	Area B	100	-	-	-	-	-	-	-	-	-	-	-	-
	Area C	36.3	-	-	-	-	-	-	-	63.7	-	-	-	-
	Point D	83.8	-	-	-	16.2	-	-	-	-	-	-	-	-
	Point A	11.2	-	-	-	-	-	-	88.8	-	-	-	-	-
Coin 8382	Area B	100	-	-	-	-	-	-	-	-	-	-	-	-
	Point C	7.1	54.8	-	2.3	15.4	20.4	-	-	-	-	-	-	-
	Area D	87.5	-	-	-	12.5	-	-	-	-	-	-	-	-
	Point A	47.4	-	-	-	2.1	-	-	-	50.5	-	-	-	-
Coin 8414	Point B	18.7	11.5	-	6	42	21.8	-	-	-	-	-	-	-
	Area C	100	-	-	-	-	-	-	-	-	-	-	-	-
	Area D	11.4	82.9	-	-	5.7	-	-	-	-	-	-	-	-
Coin 8321	Area A	77	23	-	-	-	-	-	-	-	-	-	-	-
	Area B	93.9	-	-	-	5.2	-	-	-	0.9	-	-	-	-
	Area C	11.5	-	-	-	-	-	-	88.5	-	-	-	-	-
	Area A	10.9	53.9	-	-	8	2.8	9.9	-	-	-	-	14.5	-
Coin 8342	Area B	100	-	-	-	-	-	-	-	-	-	-	-	-
	Area C	47.8	6.6	-	-	11.9	16.1	-	-	-	14.9	-	2.7	-
	Point D	75.3	-	-	-	-	-	-	-	24.7	-	-	-	-

**Table 5. EDS results on distinctive points / areas of the nails' and mirror fragment's samples.**

Objects with file no / Elements	Cu (%)	Pb (%)	Sn (%)	Fe (%)	O (%)	Sb (%)	As (%)	S (%)	Ni (%)	Co (%)
Nail	17.3	1.8	-	63	15.9	-	-	2	-	-
8362	97.8	-	-	2.2	-	-	-	-	-	-
	9.1	-	-	45.9	30.8	-	-	-	8.4	5.8
	85.4	12.7	-	1.9	-	-	-	-	-	-
Nail	88.5	-	-	-	11.5	-	-	-	-	-
5423	100	-	-	-	-	-	-	-	-	-
	9.2	64.9	-	-	10.3	-	15.6	-	-	-
Nail	89.6	-	-	-	10.4	-	-	-	-	-
5475	100	-	-	-	-	-	-	-	-	-
	14.4	47	-	2.7	10.7	25.2	-	-	-	-
Nail	81.9	-	-	-	-	-	-	18.1	-	-
8361	93.9	-	6.1	-	-	-	-	-	-	-
	6.8	93.2	-	-	-	-	-	-	-	-
	71.9	-	28.1	-	-	-	-	-	-	-
Mirror	-	96.6	3.4	-	-	-	-	-	-	-
127	70.2	2.7	27.1	-	-	-	-	-	-	-
	42.6	1.9	38.3	-	17.2	-	-	-	-	-

In pure copper objects such as coins with file no. 8425, 8382, 8342 and nails with file no. 5423, 5475 inclusions composed by Pb, Sb, Si, As, Fe, Ag, Ni, Bi are detected with EDS. In bronze alloys (Cu-Sn, Cu-Pb, Cu-Fe, Cu-Sn-Pb) of coins with file no. 8378, 8408, 8414, 8321 and nails with file no. 8362, 8361 besides the above elements, Zn, S, Co are also detected. In the mirror fragment's sample, no inclusions or precipitations are observed or analysed, only the ternary alloy elements Cu-Sn-Pb. The EDS results of the alloys' areas of all samples correspond well to the  $\mu$ -XRF results. Elements, such as Pb, As, Ni, Sb, S, Fe especially in the pure copper objects suggest the possible use of sulphite copper minerals. Since the Albanian northern and eastern territories are rich in such minerals, these objects might have been produced locally from the raw material's excavation up to their final shape. Further analysis in the future might be needed to discuss if the sulphite minerals were excavated in Albania or imported from Greece, Cyprus or even Italy. Mineral provenance analysis for Albanian culture heritage objects have not been performed earlier. Furthermore, we do not have records of copper slag findings in metal work sites which would help us to connect the objects with the mineral, something that is easily done in the case of iron. (Çina, 1975; Çina, 1976; Di Bella et al, 2018; Kati, 1988; Koçi, 1977).

The Vickers microhardness value for pure copper can be increased as a result of different processing from 40-50HV (cast Cu) to 50-60HV (hot worked) and up to 100-120HV (cold worked). Also, alloying with elements such as Sn, Zn, As, Fe, Ni and Pb can increase this microhardness value from 100-120HV for pure cold-worked copper to 120-160HV for 70%Cu-30%Zn, 150-160HV for 97.4%Cu-2.6%As and

220HV for 88%Cu-12%Sn (all cases cold worked). (Scott, 2012; Scott, 1991)

Vickers microhardness test is performed on 6 to 12 random points in each of this study samples (depending on the sample's surface size) and the mean values are calculated. In table 6 are presented the mean HV values along with the relative error in percentage ( $\Delta HV/HV$ ,  $\Delta d=1\mu m$ ). The mirror fragment microhardness values are much higher compared with the other samples because of the high percentage of Sn and Pb in the alloy.

**Table 6. Mean HV values along with the relative error in percentage ( $\Delta HV/HV$ ,  $\Delta d=1\mu m$ ).**

Object	File no.	HV <sub>mean</sub>	$\Delta HV/HV$ (%)
Coins	8378	135.5	4.3
	8425	101.6	4.0
	8408	123.2	4.1
	8382	108.2	4.1
	8414	131.1	4.4
	8321	125.8	4.2
	8342	105.4	4.0
	8362	110.3	4.3
Nails	5423	102.4	3.9
	5475	107.7	4.1
	8361	149.2	4.7
Mirror surface	127	421.7	5.2
Mirror cross section		440.3	5.5

Last, all the samples are etched with ferric chloride solution for 3-15 seconds and the best microstructure images observed with OM and SEM are included in this paper. Half of the objects' microstructures resulted composed by dendrites and half by twins/bended twins (Fig. 8). All of the nails, the mirror fragment and coin with file no. 8378 might have been casted in moulds (dendrite microstructure) as the final step of their production, while all the other coins might have been cold worked after being casted and annealed (microstructure with twins/bended

twins). Cold working increases the object hardness; in the coins' case this process might have been performed for stamping reasons more than to toughen the material. The mirror fragment's sample was expected to be composed of dendrites but this was a little unusual for the nails. We have no further information where they were used but we would have suggested at first that the nails could have been

cold worked resulting in a much higher microhardness value than they actually have. Anyhow their production procedure depends on their usage purpose and the microstructure results for all objects of this study depend on the position where the sample was taken for which we had not have much chooses. (Artioli, 2007; Scott, 2012; Scott, 1991)

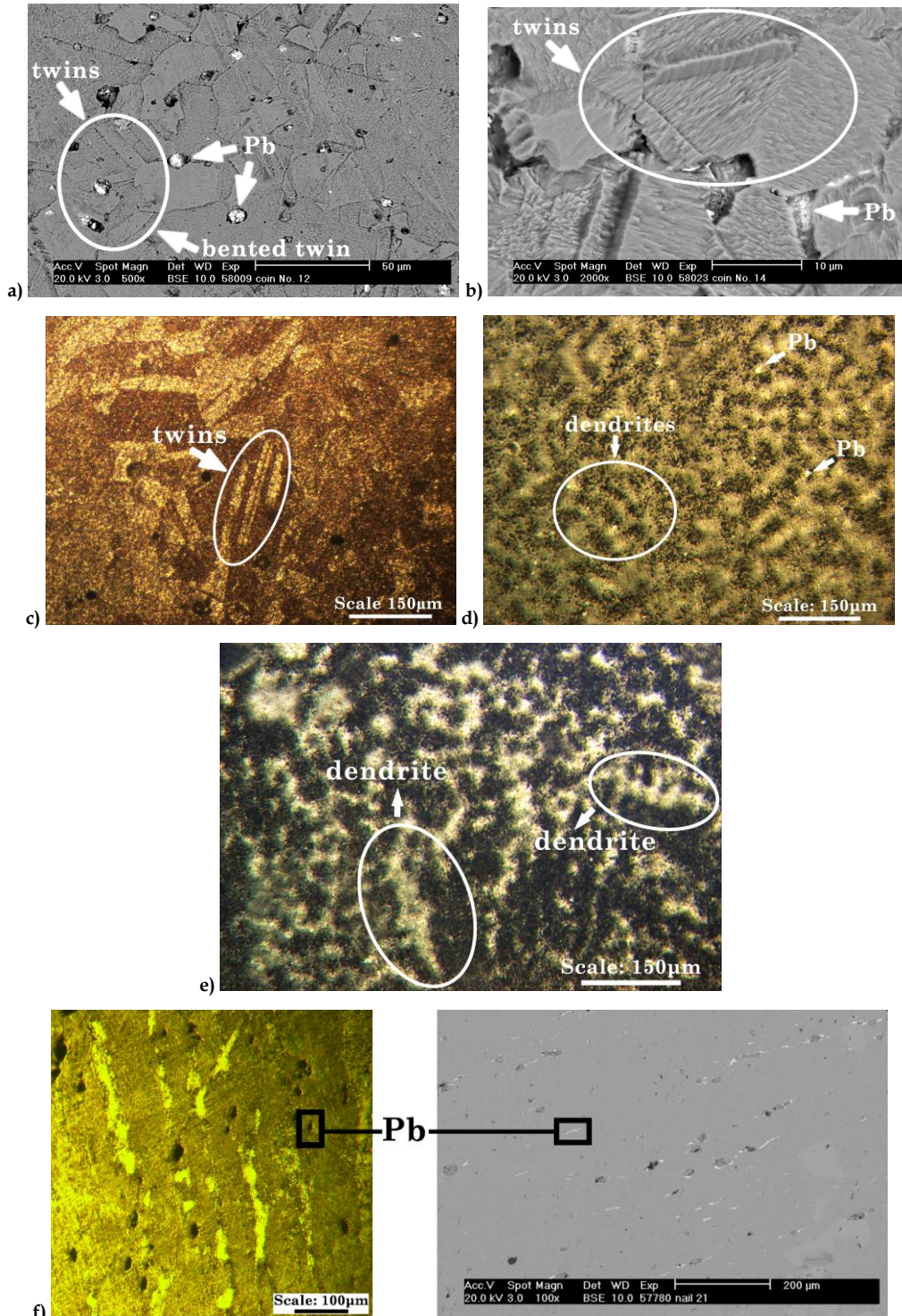


Figure 8. Microstructures observed with SEM and OM with reflected light of: a) coin with file no 8408, b) coin with file no 8414, c) coin with file no 8425, d) mirror fragment's surface (file no 127), e) mirror fragment's cross section (file no 127), f) nail with file no 8361.

#### 4. CONCLUSIONS

The Centre of Albanological Studies in Tirana and the Archaeological Museum Durrës gave us the possibility to study seven coins along with four nails (V-VI A.D.) excavated in a macellum monument in the centre of Durrës (Epidamnos) and a mirror fragment (III B.C.) found in a Necropolis in Ploçë (Amantia). Taking samples was possible due to the objects' damaged state, which were afterwards studied with various analytical techniques.

The objects resulted composed from pure Cu to Cu-Sn, Cu-Pb, Cu-Fe, Cu-Sn-Pb alloys. The mirror fragment, the nails and one coin might have been casted in moulds while additional work might have been performed on all the other coins, such as annealing and then cold working (for example

hammering or coin stamping). The corrosion products detected were quartz, cuprite, cassiterite, cerussite, atacamite/paratacamite, malachite, albite, nantokite, calcite, anorthite from the first, second and third layer of corrosion; mostly distinguishable also with OM polarized light.

Inclusions / precipitations containing elements such as Pb, S, Sb, As, Si, Fe, Zn, Ag, Bi, Ni might be connected with sulphite copper minerals preceding the alloys and with fluxes used during production. These minerals might have been excavated in the northern or eastern Albania, making the objects produced locally from the sulphite copper mineral excavation up to their final shape. Further analysis might be needed in the future to determine if the raw material used to produce these objects was indeed locally excavated or imported (Greece, Cyprus, Italy).

**AUTHOR CONTRIBUTION:** Conceptualization: O. Ç., N. C.; data curation and visualization: O. Ç.; formal analysis and investigation: O. Ç., N. C., G.S., E.Q; resources -writing of the original draft-article, revised corrections: O. Ç.; funding was assured by DAAD (projekt-ID 57068639 & ID 57175715); methodology of sample preparation and analysis procedure were consistent with the literature, provided in the article ; project administration, supervision and validation of the output data: O. Ç. and N. C.; the analytical equipment's software was used by the corresponding authors that performed each formal analysis. There is no programming, coding or software developing in this article.

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#### REFERENCES

- Artioli, G., Baumgarten, B., Marelli, M., Giussani, B., Recchia, S., Nimis, P., Giunti, I., Angelini, I., Omenetto, P. (2008) Chemical and isotopic tracers in Alpine copper deposits: geochemical links between mines and metal. *Geo.Alp.*, vol. 5, 139- 148.
- Artioli, G., Nimis, P., Arca, G., Recchia, S., Marelli, M., Giussani, B. (2008) Geochemical links between copper mines and ancient metallurgy: the Agordo case study. *Rendiconti online Soc. Geol. It.*, vol. 4, 15-18.
- Artioli, G. (2007) Crystallographic texture analysis of archaeological metals: Interpretation of manufacturing techniques. *Appl. Phys. A*, 89, 899-908.
- Artioli, G. (2010) *Scientific methods and cultural heritage*. USA, Oxford University Press.
- Attema, P., Nijboer, A., Zifferero, A., Satijn, O., Alessandri, L., Bierma, M., Bolhuis, E. (2003) Communities and Settlements from the Neolithic to the Early Medieval Period. *Proceedings of the 6th Conference of Italian Archaeology*, University of Groningen, Groningen Institute of Archaeology, The Netherlands, volume I, 4-8.
- ASM Special Handbook (2001) *Copper and Copper Alloys*. USA, ASM International.
- Bachler, M. O., Bišćan, M., Kregarb, Z., Badovinac, I. J., Dobrinić, J. and Milošević, S. (2016) Analysis of antique bronze coins by Laser Induced Breakdown Spectroscopy and multivariate analysis. *Spectrochimica Acta Part B: Atomic Spectroscopy*, Vol. 123, 163-170.
- Bachmann, H. G. (1982) The identification of slags from archaeological sites. *Institute of Archaeology*, No. 6.
- Bai, Y. (2011) On the two traditions of the bronze mirror casting techniques in East Asia. *Chinese Archaeology*, Vol. 11, 176-182.
- Betlyon, J. W. (1985) Guide to Artifacts: Numismatics and Archaeology. *The Biblical Archaeologist*, Vol. 48, No. 3, 162-165.



- Bradley, D. and Creagh, D. (2006) *Physical techniques in the study of art, archaeology and cultural heritage*. The Netherlands, Elsevier.
- Buitron, D. (1971 - 1972) A Greek Bronze Mirror. *Annual Report (Fogg Art Museum)*, No. 1971/1972, 19-24.
- Di Bella, M., Aleo Nero, C., Chiovaro, M., Italiano, F., Quartieri, S., Romano, D., Leonetti, F., Marciandò, G., Sabatino, G. (2018) Archaeometric study of the Hellenistic metallurgy in Sicily: Mineralogical and chemical characterization of iron slags from Punic Panormos (Palermo, Italy). *Mediterranean Archaeology and Archaeometry*, Vol. 18, No 2, 127-139. DOI: 10.5281/zenodo.1297149.
- Ceka, N. (2000) *Përpara se të shkruhej historia*. Albania, SHBLU.
- Cerqueira, F. V. (2018) Erotic mirrors. Eroticism in the mirror. An iconography of love in ancient Greece (Fifth to Fourth century B.C.). *Heródoto, Unifesp, Guarulhos*, Vol. 3, No. 1, 153-187.
- Civici, N., Gjonecaj, Sh., Stamati, F., Dilo, T., Pavlidou, E., Polychroniadis, E. K. and Smit, Z. (2007) Compositional study of IIIrd century BC silver coins from Kreshpan hoard (Albania) using EDXRF spectrometry. *Nuclear Instruments and Methods in Physics Research B*, 258.
- Congdon, L. O. K. (1966) Two Bronze Mirror Caryatids in the National Museum of Warsaw. *American Journal of Archaeology*, Vol. 70, No. 2, 161-165.
- Constantinou, G. (1982) Geological features and ancient exploitation of the cupriferous sulphide orebodies of Cyprus. In J.D. Muhly, R. Maddin & V. Karageorghis (eds), *Early Metallurgy in Cyprus 4000-500 BC*, 13-23, Nicosia
- Copper, H. K., Al-Saad, Z. (2015) Metal jewelry from burials and socioeconomic status in rural Jordan in late antiquity. *Mediterranean Archaeology and Archaeometry*, Vol. 15, No 2, 81-99. DOI: 10.5281/zenodo.16603.
- Cullity, B. D. (1956) *Elements of X-ray diffraction*. USA, Addison-Wesley Publishing.
- Çakaj, O., Dilo, T., Civici, N., Schmidt, G. and Stamati, F. (2016) Study of eight Albanian-Dalmatian axes (XIII-XII B.C.) and six celts (XI-X B.C.) found in northern Albania, by  $\mu$ -XRF, OM, SEM-EDS. *Journal of Archaeological Science: Report*, Elsevier, 9, 219-225.
- Çakaj, O., Dilo, T., Schmidt, G., Civici, N. and Stamati, F. (2016) Fibula and snake bracelet from Albania. A case study by OM, SEM-EDS and XRF. *Scientific Culture Journal*, Vol. 2 (2), 9-18.
- Çakaj, O., Dilo, T., Schmidt, G., Civici, N., Duka, E., Stamati, F. and Tafilica, Z. (2015) Bronze sword from the XIV-XIII century B.C. found in northern Albania, war weapon or monetary exchange tool? *Proceedings of the International Conference Archaeometallurgy in Europe IV*, Madrid, Spain.
- Çakaj, O., Duka, E., Tafilica, Z., Stamati, F., Civici, N. and Dilo, T. (2014) Characterisation of copper alloy antique ornamental accessories found in Northern Albania. *Open Journal of Archaeometry*, Vol. 2 (2).
- Çakaj, O., Duka, E., Tafilica, Z., Stamati, F., Civici, N. and Dilo, T. (2012) Preliminary Investigation of some copper alloy medieval objects from the northern Albania. *Proceedings of the Third Balkan Symposium on Archaeometry "The Unknown Face of the Artwork"*, Bucharest, Romania, 58-64.
- Çina, A. (1975) *Gërshetimet ndërmjet mineraleve dhe shkalla e çlirimit të tyre në xeherorët sulfurorë të bakër-zinkut të disa vendburimeve të vendit tonë*. Albania, Përmbledhje studimesh 2. (in Albanian)
- Çina, A. (1976) *Mbi zonalitetin vertical të pjesës veriore të vendburimit kolçedan të bakrit në Rubik*. Albania, Përmbledhje studimesh 3, 107-116. (in Albanian)
- Dilo, T., Civici, N., Stamati, F. and Çakaj, O. (2009) Archaeometallurgical characterization of some ancient copper and bronze artefacts from Albania. *American Institute of Physics*, 985-990.
- Dudley Creagh, D. and Bradley, D. (editors) (2007) *Physical techniques in the study of art, archaeology and cultural heritage, volume 2*. The Netherlands, Elsevier, 1-274.
- Economou-Eliopoulos, M., Eliopoulos, D. G. and Chryssoulis S. (2008) A comparison of high Au massive sulfide ores hosted in ophiolite complexes of the Balkan Peninsula with modern analogues: Genetic significance. *Ore Geology Reviews*, 33, 81-100.
- Figueiredo, E., Valério, P., Araújo, M. F., Silva, R. J. C. and Soares, A. M. M. (2011) Inclusions and metal composition of ancient copper-based artefacts: a diachronic view by micro-EDXRF and SEM-EDS. *X-Ray Spectrom.*, Vol. 40, 325-332.
- Gale, N. H. (1991) Metals and Metallurgy in the Chalcolithic Period. *Proceedings of the Symposium Chalcolithic Cyprus*, Cyprus. Bulletin of the American Schools of Oriental Research No. 282/283, Symposium: Chalcolithic Cyprus, pp. 37-61.
- Gale, N. H., Stos-Gale, Z. A. (1982) Bronze Age Copper Sources in the Mediterranean: A New Approach. *Science*, vol. 216, no. 4541.

- Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Lyman, C. E., Lifshin, E., Sawyer, L. and Michael, J. R. (2003) *Scanning Electron Microscopy and X-Ray Microanalysis*. USA, Kluwer Academic/Plenum Publishers.
- Gawlick, H. J., Frisch, W., Hoxha, L., Dumitrica, P., Krystyn, L., Lein, R., Missoni, S., Schlagintweit, F. (2008) Mirdita Zone ophiolites and associated sediments in Albania reveal Neotethys Ocean origin, *Int J Earth Sci (Geol Rundsch)* 97:865–881. DOI 10.1007/s00531-007-0193-z
- Griesser, M., Kockelmann, W., Hradil, K. and Traum, R. (2016) New insights into the manufacturing technique and corrosion of high leaded antique bronze coins. *Microchemical Journal*, Vol. 126, 181-193.
- Hoti, A., (1996) Të dhëna arkeologjike për krishtërimin e hershëm në Dyrrah (shek: IV-VII). *Iliria*, Vol. 1-2, 176-177.
- Hou, L. H. (1981) Analysis of an ancient Chinese bronze mirror by fast neutron activation. *Archaeometry* 23, Vol. 2, 217-219.
- Hoxha, L., Scott, P. W., Eyre J. M. (2005) The geological setting of volcanogenic sulphide orebodies in Albanian ophiolites. *Applied Earth Science (Trans. Inst. Min. Metall. B)*, Vol. 114, 33-52. DOI 10.1179/037174505X45487
- Hoxha, L. (2014) Compiling of lithological stratigraphic-tectonic sections, increase substantially resources of Cu-Fe, Cu-Fe, Zn, Au, Ag sulfides hosted by volcanogenic massive sulfide deposits (VMS), in Albanian ophiolites. *Proceedings of the Geological Society of America, USA* (<https://gsa.confex.com/gsa/2014NE/webprogram/Paper234915.html>)
- Howgego, Ch. (1995) *Ancient History from Coins*. New York, Taylor & Francis e-library.
- Jovanović, B. (1978) The oldest copper metallurgy in the Balkans. A study of the diffusion of copper from Asia Minor to Southeastern Europe. *Expedition*, 9-17.
- Jovanović, B. (2009) Beginning of the metal age in the Central Balkans according to the results of the archeometallurgy. *Journal of Mining and Metallurgy*, 45 (2) B, 143- 148.
- Kati, P. (1988) Disa veçori kimiko-mineralogjike të mineraleve kryesore të pasurimit dytësor të bakrit në vendburimet e Mirditës. *Buletini i shkencave gjeologjike*, Vol. 3, 67-74
- Kemmers, F. and Myrberg, N. (2011) Rethinking numismatics. The archaeology of coins. *Archaeological Dialogues*, Vol. 18, Issue 01, 87 – 108.
- Koçi, M. (1977) *Ndryshimet anësore përreth trupave xeherorë të bakrit në bazë të studimeve mineralogjike-petrografike*. Albania, Përmbledhje studimesh 2, 37-47.
- Koui, M., Papandreopoulos, P., Andreopoulou-Mangou, E., Papazoglou-Manioudaki, L., Priftaj-Veveçka, A. and Stamati, F. (2006) Study of Bronze Age copper-based swords of type Naue II and spearheads from Greece and Albania. *Mediterranean Archaeology and Archaeometry* 1, vol. 6, 49-59.
- Marinos, G. P., Petrascheck, W. F. (1956) Lavrion, geological and geophysical research. *IGME Athens* 1, vol. IV, 149-206.
- Osmanliu, A., Thanashi, Dh. (1997) *Antique Culture in Albanian Mines*. Wien, Berichte der Geologischen Bundesanstalt.
- Pistofidis, N., Vourlias, G., Pavlidou, E., Dilo, T., Civici, N., Stamati, F., Gjonegaj, S., Prifti, I., Bilani, O., Stergioudis, G., Polychroniadis, E. K. (2006) On the comparative study of three silver coins of the III-rd century B.C. minted in Korkyra, Dyrrachion and by the Illyrian king Monounios. *Applied Physics A Material Science & Processing*, Vol. 83, 637-642.
- Potts, P. J. and West, M. (2008) *Portable X-ray fluorescence spectrometry capabilities for in situ analysis*. UK, The Royal Society of Chemistry, UK.
- Pracejus, B. (2008) *The ore minerals under the microscope, an optical guide*. Hungary, Elsevier.
- Prendi, F. (2008) *Studime Arkeologjike*. Kosova, ARK-KOS.
- Richter, G. M. A. (1941) A Bronze Mirror of the Hellenistic Period. *The Metropolitan Museum of Art Bulletin*, Vol. 36, No. 8, 168-170.
- Robinson, F. W. (1948) A cast and engraved bronze mirror. *Bulletin of the Detroit Institute of Arts of the City of Detroit*, Vol. 27, No. 3, 67-68.
- Schulten, C., Tensi, H. M. and Högerl, J. (1996) Analyzing the metallurgical and cultural backgrounds of two Han-dynasty bronze-mirror fragments. *JOM*, 57-59.
- Scott, D. A. (2012) *Ancient metals: microstructure and metallurgy volume I*. USA, Conservation Science Press.
- Scott, D. A. (1991) *Metallography and microstructure of ancient and historical metals*. Singapore, The J. Paul Getty Trust.

- Schlagintweit, F., Gawlick, H. J. (1987) *Encrusting Foraminifera from Late Jurassic to Early Cretaceous Reefal Limestones of Albania and the Northern Calcareous Alps*. Wien, Berichte der Geologischen Bundesanstalt.
- Sedyshev, P. V., Simbirtseva, N. V., Yergashov, A. M., Mazhen, S. T., Mareev, Y. D., Shvetsov, V. N., Abramzon, M. G. and Saprykina I. A. (2020) Determining the Elemental Composition of Antique Coins of Phanagorian Treasure by Neutron Spectroscopy at the Pulsed Neutron Source IREN in FLNP JINR. *Physics of Particles and Nuclei Letters*, Vol. 17, No. 3, 389–400.
- Tylecote, R. F. (1992) *A History of Metallurgy*. London, The Institute of Materials.
- Wayne, R. (2009) *Light and Video Microscopy*. USA, Elsevier.
- [www.worldatlas.com/webimage/countrys/europe/balkans.htm](http://www.worldatlas.com/webimage/countrys/europe/balkans.htm)