

Article

Microstructural Investigation of Some Bronze Artifacts Discovered in a Dacian Site Using Non-Destructive Methods

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Abstract: Dacian civilization flourished on the actual territory of Romania during the Late Iron Age and had its peak from the first century BC to the first century AD. They had intensive relations with Hellenistic and Roman civilizations. Therefore, it is difficult to evaluate the origin of some widely spread artifacts discovered in the Dacian archeological sites. The present research is focused on two bronze artifacts (a bronze coin and a mirror fragment) found in the Alun-Piatra Rosie site and a silver coin found in the Ardeu site. Artifacts were investigated with nondestructive methods such as SEM-EDX for microstructural and elemental characterization, and the crystalline phases were investigated using XRD. Bronze coin proves to be an Istrian issue having an elemental composition of 75.0% Cu, 20.8% Sn, and 4.1% Pb, which corresponds to a structure of Cu grains mixed with Cu₅Sn grains. The bronze mirror fragment has an elemental composition of 52.3% Cu and 47.7% Sn, which corresponds to a structure containing grains of Cu₆Sn₅ mixed with grains of Cu₄₁Sn₁₁. It has a smooth surface that was investigated with AFM microscopy, which evidences a Ra roughness of 51 nm for the patina surface and 33.7 nm for the clean metal surface, proving the high quality of the original mirror luster of the artifact. The silver coin was identified as a Radulești–Hunedoara type meaning that it was produced in local Dacian metallurgic workshops. It has an elemental composition of 63.1% Ag, 25.3% Sn, 7.8% Cu, and small traces of P and Fe, which corresponds to a structure of Ag grains and Ag₃Sn grains. Silver coins show that Dacians uses Sn as alloying element in their metallurgic workshops. Istrian bronze coin proves to be typical for Hellenistic or Roman bronze type with Sn content no more than 25% Sn. The bronze mirror fragment has an unusual composition that might be a result of local metal charge elaboration with several Hellenistic and Roman bronze pieces as raw material and an extra Sn addition during the melting process. This material facilitates the polishing properties of the active surface that has a very low roughness even after 2000 years of ground resting and adherent oxides patina.

Keywords: Dacian artifacts; bronze; nondestructive archeometry



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1. Introduction

Actual bronze alloys are based on the Cu–Sn binary system and are very well standardized and designed for precise technological and industrial purposes [1–4]. The ancient bronze elaboration is not as precise as actual bronzes because of a lack of chemical composition control during smelting but still respects the basics of the Cu–Sn binary system, a

fact sustained by the archeometric information in the literature related to the Bronze Age artifacts [5–8].

Dacian civilization has maximal development from the middle of the first century BC to the beginning of the second century AD. The capital of the Dacian Kingdom was Sarmizegetusa Regia placed in Transylvania (a geographical region in actual Romania), in the Sureanu Mountains area, Figure 1, having a fortress, a sacred area, and civilian settlements with artificial terraces arranged for houses and workshops for different activities such as metallurgical ones. The Dacian capital was naturally protected by the heights of the Sureanu Mountains and was surrounded by fortresses placed in near proximity such as Piatra Rosie Fortress or in advanced positions such as Ardeu Fortress, Figure 1.

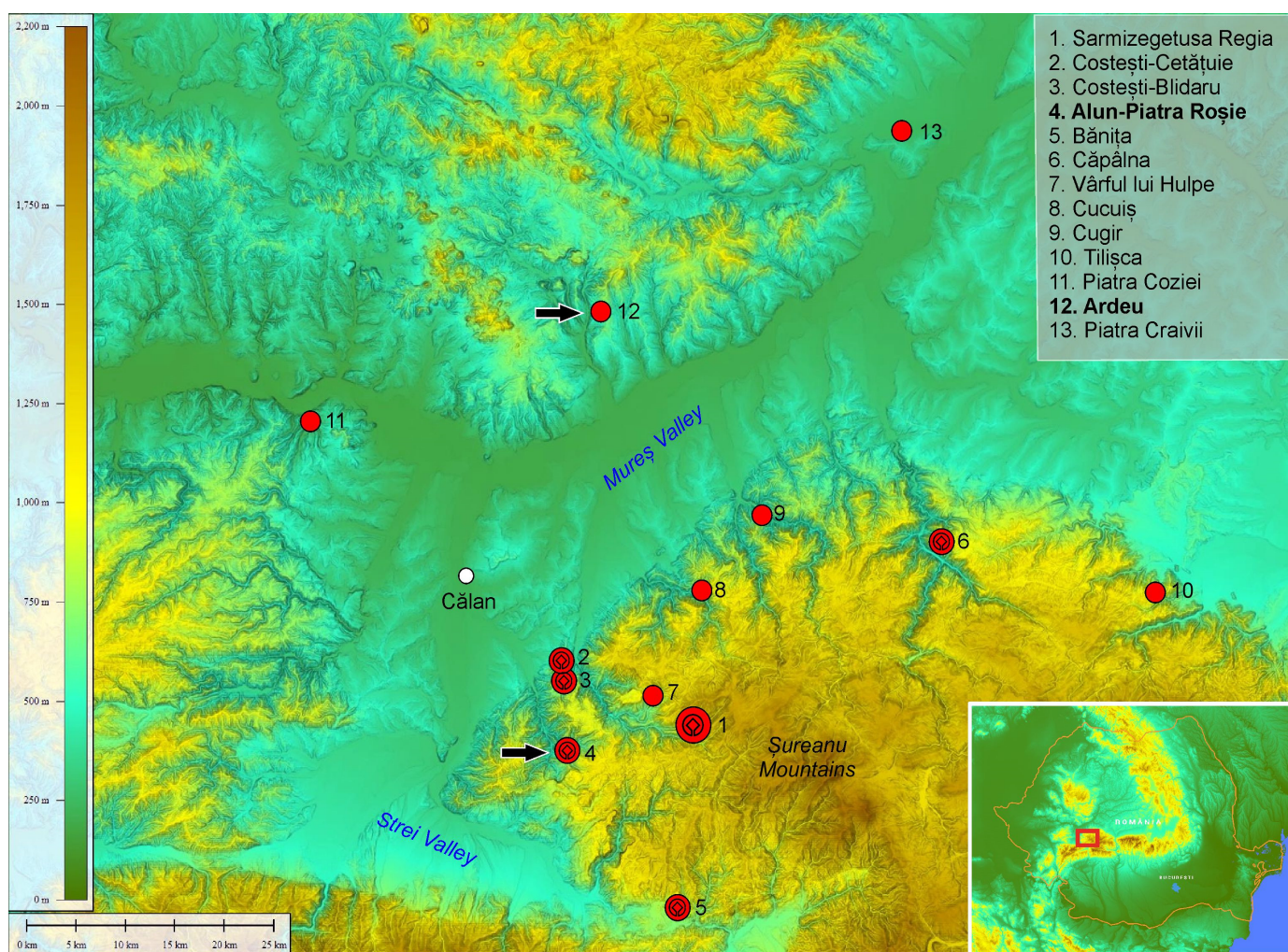


Figure 1. Geographical placement of Dacian Kingdom capital–Sarmizegetusa Regia and the main fortresses around it (GPS coordinates: 45.62269; 23.31042).

These fortresses were the residence of powerful noble men (under command of the Dacian King) who ruled over wide settlements disposed around the forts. The related archeological excavations unearthed a lot of metal artifacts of local origin and also imports from Hellenistic and Roman areas.

Bronze was one of the most important alloys used by Dacians for various domestic objects and ordinary jewels but also for military equipment or harness and chariot parts [9]. Dacian bronze metallurgy was influenced by the Hellenistic and Roman technological aspects that have been adapted to local conditions [9,10]. The bronze quality depends in a great manner on the raw materials used for the smelting charge. Ample evidence exists on the copper ore reduction in the pit furnaces, but less information is available regarding tin

sources [9,10]. Copper ore was available due to the reach surface deposits in the Metaliferi Mountains situated on the opposite side of the Sureanu Mountains regarding to the Mures River, Figure 1, close to the Dacian power center Sarmizegetusa Regia.

There are three main theories regarding Dacian bronze charge composition: the first one supposes that copper base was produced by rich ore reduction in the pit furnaces and tin was obtained by commercial exchanges from Celts [11,12], the second one presumes that the local obtained copper was transformed in bronze by addition of Hellenistic or Roman tin objects, which often contained significant lead amounts, and the third theory states that bronze charge was composed mainly of Hellenistic or Roman bronze object melted together, perhaps with the addition of a small amount of local copper. These bronzes have a maximum tin composition ranging from 20 to 22% and a dendritic microstructure generated by the casting in sand or ceramic molds [13–15]. Data in the literature reveals the same composition and microstructure regarding the Hellenistic bronzes [16,17]. A special casted bronze Hellenistic artifact is the “Bulgarian Head” discovered at Goljamata Kosmatka, which presents a similar elemental composition to our Istrian coins regarding Cu, Sn, Pb amount and some Ag traces [18].

The archeological excavations in the Dacian sites provided much evidence regarding local metallurgical workshops that were equipped with smelting furnaces. Crucibles, melted alloy particles, and slag deposits were found nearby the furnaces, which indicates in situ alloy elaboration [9,10]. Unfortunately, there are fewer archeometric studies conducted on these archeological findings for validating one of the mentioned theories.

The aim of the present study is to bring into light some interesting bronze artifacts discovered in the Dacian site of Alun (Piatra Rosie Dacian Fortress situated nearby Sarmizegetusa Regia) on an artificial terrace close to the fortress [19–22]. Piatra Rosie Dacian fortress is situated in Alun Village (part of Bosorod Commune) Hunedoara County, Romania. The first archeological investigation of this fortress was carried out in 1949 by reputed archeologist Constantin Daicoviciu who unearthed a small part of the site [19]. It remains almost unknown and forgotten until 2014 when an adjacent artificial terrace was investigated in close proximity to the fortress on the property of Dacica Foundation [45°35′59.69″ N, 23° 8′59.00″ E]. The archeological diagnosis of the field was effectuated by nonintrusive methods such as magnetometric and resistive earth profiles as well as photogrammetric analysis. The results indicate potential archeological findings. The excavations revealed the ruins of a rectangular building probably with a wooden superstructure; the side reveals a well-defined ancient walking path of beaten clay. The vicinity revealed parts of a stone pavement with a destination still unclear. A lot of findings were collected from these sections such as pottery, bronze, and iron artifacts including a bronze fibula, an Istrian bronze coin, and a mirror fragment (the last two being investigated in the present article). These findings situate the settlement during the second half of the first century AD.

A second aim of the present research is to use Scanning Electron Microscopy (SEM) elemental maps for the bronze constituents’ grains to avoid polishing implied by the metallographic analysis, which is a destructive analysis.

2. Materials and Methods

2.1. Archeological Artifact Description

The artifacts investigated in the present research were discovered in several archeological excavations of the Dacian sites. The bronze coin, shown in Figure 2a, was found in Alun-Piatra Rosie archeological site (belonging to the Piatra Rosie Dacian Fortress) during the investigation of an artificial terrace situated in the proximity of the fortress.

It is an interesting finding because the coin was an Istrian issue from century 1 BC (Greek colony of Istros placed at the shore of Black Sea) and was discovered in a Dacian intact site by the archeologists. The bronze mirror fragment, shown in Figure 2b, was found on the same archeological site in a section in proximity to the remains of some buildings situated on the artificial terrace. These two bronze artifacts represent the most important samples for the present research because they were found in a Dacian context.



Figure 2. The investigated Dacian artifacts (avers and obverse): (a) bronze coin, (b) bronze mirror fragment discovered at Alun-Piatra Rosie archeological excavation, and (c) silver coin discovered at Ardeu archeological excavation.

The third sample of the present research is a silver coin, shown in Figure 2c, discovered in Ardeu archeological site on section SII positioned at the GPS coordinates [46°0′52.09″ N, 23°8′51.94″ E]. This is a convex coin of Radulesti–Hunedoara type. It is very important for the present research due to the clues that it might contain a significant amount of Sn.

The samples were firstly investigated with the patina layer as observed in Figure 2 and were later cleaned on a small part of the artifact surface that was subjected to immersion in phosphoric acid for 24 h followed by gentle washing with a cotton cloth to avoid abrasion, and the operations were repeated as necessary to reveal the metal core. The cleaning quality was inspected through optical microscopy. Therefore, it was revealed that some small macroscopic areas necessary to observe proper information about metallic structures using nondestructive methods such as Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD).

2.2. Investigation Methods

Scanning Electron Microscopy (SEM) employed a Hitachi SU8230 Scanning Electron Microscope, Tokyo, Japan, and the elemental analysis EDX used an Energy-Dispersive Spectroscopy (EDS) detector X-Max 1160 EDX (Oxford Instruments, Oxford, UK). Samples were mounted on the specimen holder using double adhesive carbon discs to assure proper electrical conduction and were examined on the high-vacuum mode at an acceleration voltage of 30 kV.

X-ray diffraction (XRD) investigation was effectuated with a Bragg–Brentano diffractometer Bruker D8 Advance, Bruker Co., Karlsruhe, Germany. All investigations were performed using Cu K α 1 monochrome radiation $\lambda = 1.54056 \text{ \AA}$ in a 2-theta angle range of about 20–80 degrees depending on the characteristics of the samples. Crystallized compounds identification was effectuated by proper peak matching with the standard database using Match software provided by Crystal Impact Company, Bonn, Germany.

Mineralogical Optical Microscopy (MOM) was used to investigate the samples' patina components. It was performed on a Laboval 2 mineralogical microscope produced by Carl Zeiss Company, Oberkochen, Germany. The images were digitally acquired using a Samsung photographic device at the resolution of 10 MPx, Samsung, Seoul, Republic of Korea.

The Fourier-transform infrared spectroscopy (FTIR) analyses were performed on a FTIR 610 spectrometer (Jasco Corporation, Tokyo, Japan), in the 4000–400 cm^{-1} wavenumber range, using the KBr pellet technique. The resolution of the spectra was 4 cm^{-1} , and scans were repeated 100 times. All FTIR spectra were registered at room temperature.

Atomic Force Microscopy (AFM) was effectuated in tapping mode using a JEOL JSPM 4210 Scanning Probe Microscope produced by Jeol Company, Tokyo, Japan. The mirror

fragment surface was probed with an NSC 15 Hard cantilever produced by MikroMasch Company, Sofia, Bulgaria, having a resonant frequency of 325 kHz and force constant of 40 N/m. The scanning rate was about 1 to 1.5 Hz depending on the surface topography. The sample surface was investigated at a scanned area of $5\ \mu\text{m} \times 5\ \mu\text{m}$ on at least three different macroscopic sites. The obtained images were processed and analyzed with WinSPM 2.0 processing soft Jeol Company, Tokyo, Japan. The surface roughness parameter Ra was measured for each topographic image, and the average value was considered representative and further discussed.

3. Results

Samples within the current research have two important components: the metal core representing the artifacts as they were in antiquity during their active service and the patina representing the oxidation layers caused by the prolonged contact with the resting ground. Both aspects are very important from the archeometric point of view, but in this particular case, the alloy composition and microstructure are more important; therefore, the metallic core investigation is presented before the patina.

3.1. Metallic Core

Istrian bronze coin microstructure is revealed by the SEM image in Figure 3a. There appear large grains of rich copper phase (orange nuance) interlocked with rich Sn dendritic grains (green nuance) as observed in the elemental distribution map. Rich copper grains feature a polyhedral shape and large dimensions in the range of 120–300 μm , a fact that indicates an annealing treatment of the casted blank disk that occurs during the strike of the coin. Sn-rich dendrites are also affected by the blank disc annealing evidencing filaments of approximately 250 μm length and 30 μm thick on the middle vertical position in the elemental map in Figure 3a. The right side of the figure indicates the diffusion between dendrites to form compact areas, which is explained by the intensive heating of the blank before coin striking and perhaps some incidental repeated heating in the archeological context. Inter-dendritic diffusion might be facilitated by the Sn-rich content. The weight percent elemental composition evidenced 75.0% Cu, 20.8% Sn, and 4.1% Pb. Microstructural aspects related to the elemental composition indicate a classic bronze alloy typical for the Roman [13–15] and Hellenistic [16,17,23] artifacts.

Figure 3b presents the bronze mirror microstructure examined with SEM microscopy. It reveals a dense microstructure with two constituents: the first represents a compact matrix with large polyhedral grains ranging from approximately 80 μm to 200 μm that embedded fine spread grains belonging to the second constituent. The second constituent grains have a rectangular shape of approximately 10–50 μm length and 5–8 μm thick formed due to the fragmentation of rich Sn lamellas resulted from casting due to the rapid crystallization under thin wall piece solidification, as indicated by the mirror thickness. The element distribution map reveals that the compact matrix is copper-rich (orange nuance), while dispersed grains are tin-rich (blue nuance). Elemental composition is overwhelming at 52.3% Cu and 47.7% Sn. According to the Cu–Sn equilibrium phase diagram, such composition belongs to a mixture of Cu_6Sn_5 and Cu_3Sn hard intermetallic compounds. It requires further XRD investigation for the proper identification of the copper- and tin-rich phases found in the mirror fragment. This elemental composition is very different compared to the Istrian coin found in the same Dacian site and both Roman and Hellenistic bronzes. It is noteworthy that common Roman bronze mirrors have tin contents of maximum 26%, an important amount of Pb, and traces of other elements [15–17].

Silver coin found in Ardeu archeological site is a very special Dacian issue of Radulești–Hunedoara type, which is reported in the literature to be alloyed with Sn [24]. Its microstructure is presented in Figure 3c revealing a dendritic structure resulted as a consequence of blank disk production by casting. The elemental map reveals some polyhedral-rich silver grains (yellow–green nuance) of approximately 70–100 μm interconnected by thick dendrites with a length of approximately 150 μm and a thickness of 70 μm . Rich silver den-

drites are separated from each other by Sn-rich grains (blue nuance) also having a dendritic shape with a length of approximately 150 μm and thinner of approximately 30–50 μm . The dendrite shape looks like they were fused, a fact explained by the intensive heating before the coin hot strike. This thermal treatment was absolutely necessary to assure enough plasticity for the concave shape of the coin. Several red spots are noticed inside the thin rich grains, which indicates local precipitation of copper most likely facilitated by the heating during the coin strike process. It is in good agreement with the Cu–Pb segregation mentioned for this monetary type in literature [24]. This is sustained by the elemental composition, which is 63.1% Ag, 25.3 Sn, 7.8% Cu, and traces of P and Fe. Low amount of copper sustains small bronze segregations within tin-rich grains signaled in the elemental map with the observed red spots.

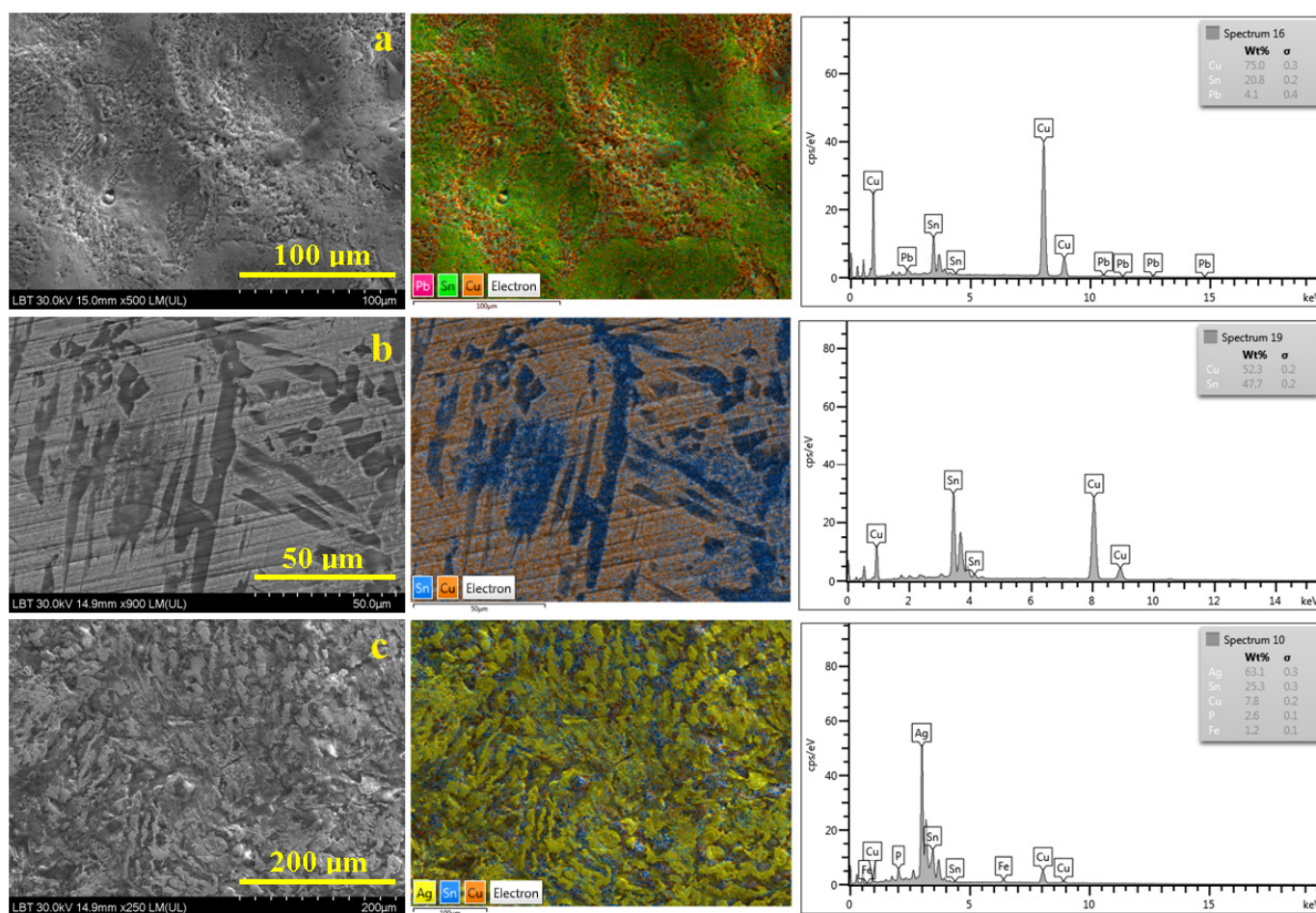


Figure 3. SEM investigation of the metallic surface of the Dacian artifacts: (a) bronze coin, (b) bronze mirror fragment, and (c) silver coin. There are presented SEI images, corresponding elemental maps and EDS spectra.

SEM imaging coupled with EDS map is a powerful tool that brings a strong correlation between microstructural characteristics of the sample and its elemental composition. The elements distribution on the map allows us to observe the microstructural constituents without metallographic analysis (which is relative destructive including abrasion, polishing, and chemical etching). Unfortunately, the elemental composition and distribution do not bring precise information related to the phases that occur in the investigated alloys. Therefore, an XRD investigation is required.

The XRD pattern result for the Istrian bronze coin, as shown in Figure 4a, presents a very intense and broad peak at 42.39 deg, followed by several smaller and broad peaks situated at 49.41 and 72.74 deg.

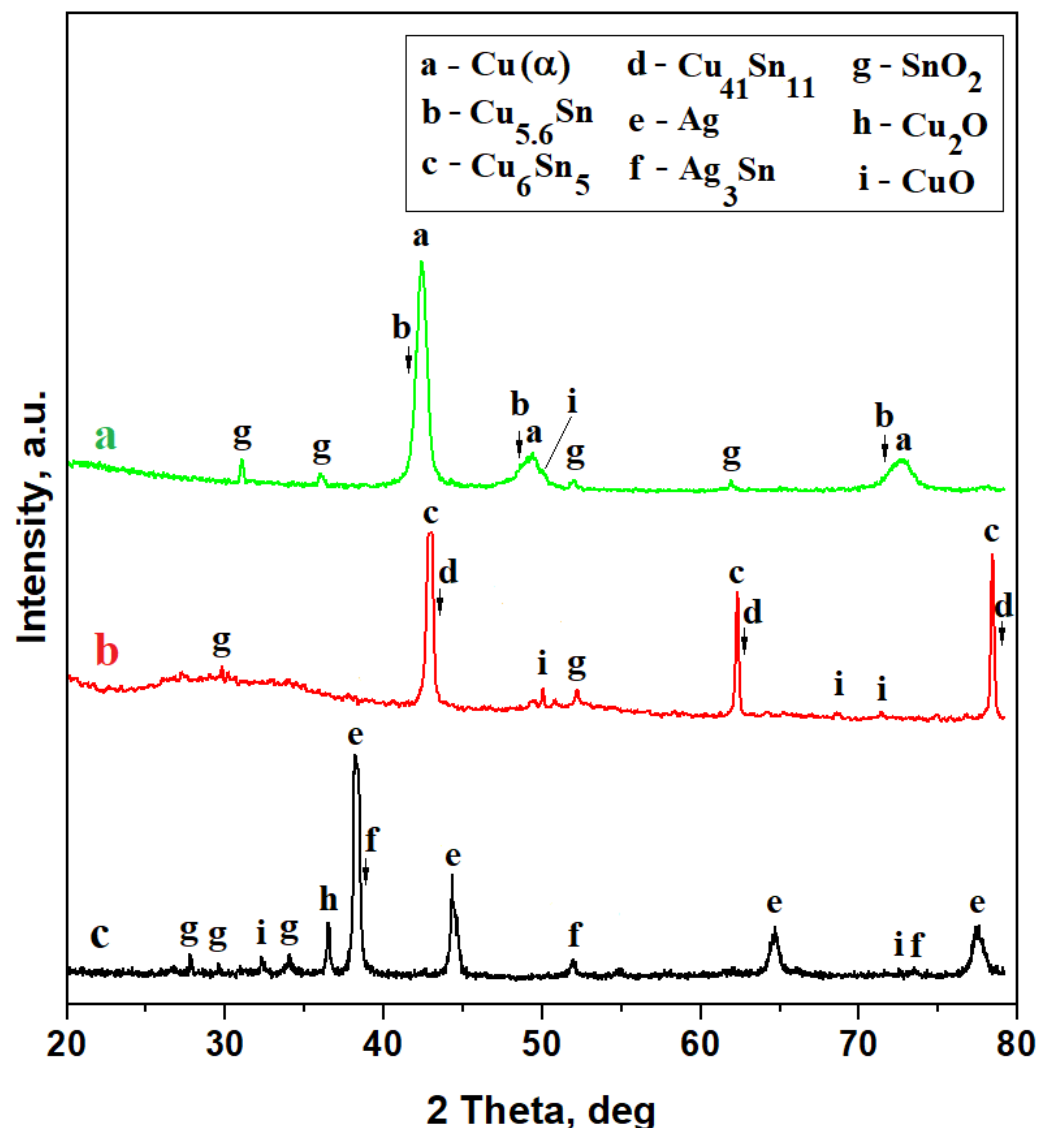


Figure 4. XRD patterns for: (a) bronze coin, (b) bronze mirror fragment, and (c) silver coin.

The database searching results show that broadened peaks belong to two compounds, which are situated closely one to another, merging onto single diffraction peak. The results show that the most representative phase is Cu (according to the Cu–Sn equilibrium phase diagram, it is about α terminal solid solution of approximately 3% Sn in pure Cu) and intermetallic compound $\text{Cu}_{5.6}\text{Sn}$. That occurs due to the rapid cooling after hot strike that prevents formation of the equilibrium intermetallic compound Cu_3Sn . These phases are characteristic for the moderate tin amount bronzes and correspond to the identified elemental composition. This is also in good agreement with the data in literature regarding Roman bronze mirrors [17]. The intermetallic compound that should occur according to the Cu–Sn phase diagram is Cu_3Sn , but considering the small amount of 4.1% Pb in the coin composition, it may affect the equilibrium phases correlated with intensive heating prior striking process followed by a relative quick cooling (usually in water) conducts to precipitation of the $\text{Cu}_{5.6}\text{Sn}$ intermetallic compound. There also occur some small and relatively narrow peaks that merely correspond to traces of oxide phases such as SnO_2 , which are still present on the metal surface as small spots.

The bronze mirror fragment presents an XRD pattern, as shown in Figure 4b, exhibiting several very intense peaks (the most intense one was truncated to assure better visibility of the less intense peaks). These intense peaks are also broadened due to the merging of

the signal of two characteristic compounds that have close positions to each other. The identification with the database search shows that it is Cu_6Sn_5 (tin-rich grains evidenced in Figure 3b) and $\text{Cu}_{41}\text{Sn}_{11}$ (copper-rich grains evidenced in Figure 3b), which corresponds to the elemental composition. The presence of $\text{Cu}_{41}\text{Sn}_{11}$ instead of Cu_3Sn as usual in equilibrium conditions is caused by the rapid cooling of the thin-walled casted plate, which is subjected to a rapid cooling of the melted alloy at the contact with mold surface. Normally, Cu_3Sn would have been developed into the equilibrium condition. However, considering the rapid cooling, the $\text{Cu}_{41}\text{Sn}_{11}$ intermetallic compound is preserved, which is the result of the eutectoid decomposing of γ phase, which occurs at approximately 500 °C. This fact is sustained by the broken lamella of the Cu_6Sn_5 grains that are fragmented during rapid solidification. There also occur some small peaks that belong to the small amount of residual oxides on the metallic surface.

Silver coin elemental composition would indicate a mixture of Ag_3Sn and $\text{Ag}\zeta$ (a silver solid solution in tin hexagonal compact structure according to the Ag–Sn binary system equilibrium phase diagram). XRD pattern in Figure 4c does not sustain the presence of $\text{Ag}\zeta$ but Ag FCC is clearly evidenced. This fact is explained by copper amount of 7.8%, which facilitates Ag FCC domain expansion according to the Ag–Sn–Cu ternary phase diagram. The most intense peak observed at 38.22 deg. in Figure 4c is a convolution result of two peaks of Ag and Ag_3Sn with close position. Several significant silver peaks were observed at 44.33, 64.72, and 77.57 deg, as well as some individual peaks belonging to Ag_3Sn at 54.76 and 73.21 deg. Several oxide peaks were observed at low angles such as Cu_2O and SnO_2 . Oxide presence is caused by patina residual spots.

3.2. Patina

Artifacts patina investigation is very important due to the information regarding the resting process and artifact interaction with the resting ground. The artifacts received with exterior patina layer, as shown in Figure 2, were investigated with SEM–EDX to determine its morphology and elemental composition. The obtained results are summarized in Figure 5.

Istrian bronze coin presents a very complex patina formed by intensive oxidation of the coin metal core at the contact with soil humidity and its minerals. The outermost layer microstructure, as shown in Figure 5a, reveals two major components: the white areas corresponding to the high mineral composition (due to mineral electrical insulator behavior) and black areas corresponding to metal oxide layer (which presents moderate conductivity. For example, SnO_2 is semiconductor [25], and Cu_2O conductivity depends on the crystallite habitus, e.g., octahedrons are highly conductive, cubes are moderate conductively, and rhombic dodecahedron are insulator [26]).

Corresponding elemental map shows that Ca, Si, K, Mg, and Fe are predominantly distributed on the white areas and are related to the resting ground minerals such as calcite, quartz, kaolinite, and muscovite, a fact that should be evidenced in the XRD pattern. Elements such as Cu, Sn, and Pb are predominantly found on the darker areas and correspond to the metal oxides. Complete elemental composition of the Istrian bronze coin patina is presented in Table 1 line a.

The bronze mirror presents a brown, black patina caused by metal core oxidation in a uniform and compact layer. Resting ground spots covers the compact oxide layer, but they are less mixed with the oxides layer. SEM image in Figure 5b reveals the uniformity of the oxides layer evidencing a microstructured network of fine fissures within this layer and several granular cluster of resting ground particles embedded into the oxide. This proves that it was a particular interaction between mirror fragment and soil particles during almost 2000 years of resting. In addition, small parallel repeated horizontal lines are observed, which obviously represents abrasion marks present below the oxide layer, indicating the ancient polish of the mirror surface. This aspect was further investigated with AFM microscopy and discussed after patina investigation subchapter. Yellow greenish uniform nuance of the elemental map in Figure 5b is caused by the uniform distribution

of Cu, Sn, and O, which corresponds to the compact oxide layer. Ca, Al, Si, and Fe are predominantly disposed on the resting ground particle clusters, indicating the presence of silicates such as quartz and phyllosilicates along with traces of calcite. This fact is sustained by the elemental composition presented in Table 1.

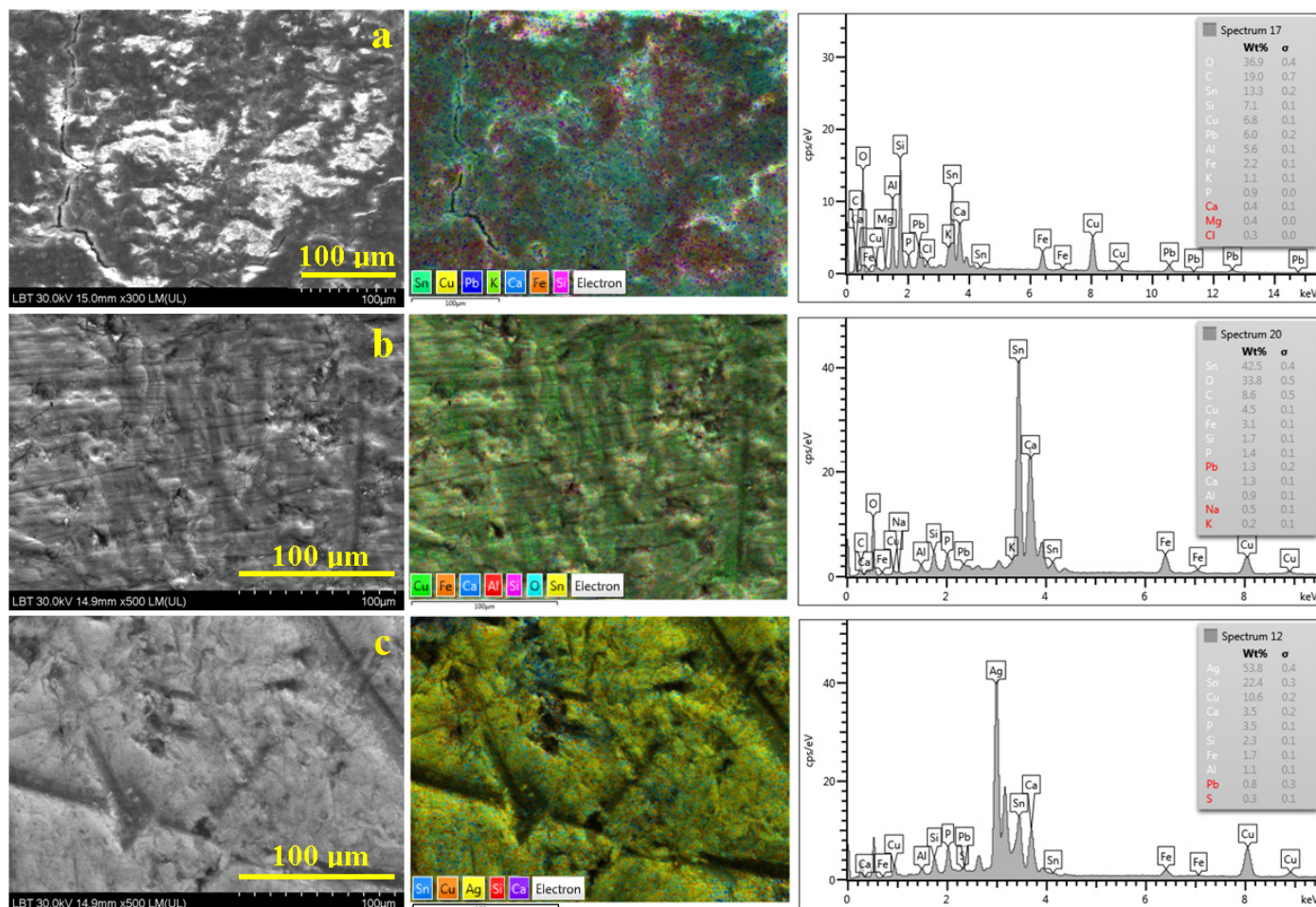


Figure 5. SEM investigation of the patina surface of the Dacian artifacts (SEM image, elemental map, and EDS spectrum): (a) bronze coin, (b) bronze mirror fragment, and (c) silver coin.

Table 1. Patina elemental composition.

	Elements Amount, wt. %															
	O	C	Sn	Si	Cu	Pb	Ag	Al	Fe	Na	K	Ca	Mg	Cl	P	S
a	36.9	19.0	13.3	7.1	6.8	6.0	-	5.6	2.2	-	1.1	0.4	0.4	0.3	-	-
b	33.8	8.6	42.5	1.7	4.5	1.3	-	0.9	-	0.5	0.2	1.3	-	-	1.4	-
c	-	-	22.4	2.3	10.6	0.8	53.8	1.1	1.7	-	-	3.5	-	-	3.5	0.3

Note: (a) Istrian bronze coin; (b) Bronze mirror fragment; and (c) Silver coin.

Patina of silver coin is present only in isolated areas as observed in Figure 2c; therefore, it was relatively difficult to obtain a suitable detail for the elemental map. In consequence, Figure 5c visualizes a large area of the silver coin that was used for obtaining the elemental composition. The most relevant identified elements, shown in Table 1, belong to the metal core being in good agreement with the information related to Figure 2c. There also appear 2.3% Si, 1.1% Al, and 1.7% Fe, along with 3.5% Ca and some amount of P and S. These elements are related to silicates and calcite from the resting ground.

XRD patterns obtained for the metallic core reveal small but significant peaks of cuprite Cu_2O and cassiterite SnO_2 , as shown in Figure 4. On the opposite, the XRD patterns obtained for patina layer are overwhelmed by the relative high intensities of the peaks belonging to Cu and Sn oxides such as cuprite, cassiterite, and tenorite (CuO). The peaks belonging to the mineral particle embedded into the oxide mass are less visible. Therefore, low angle ranges of the XRD were analyzed independently in the range of 10–37 degree 2 Theta, as shown in Figure 6. Furthermore, cassiterite and cuprite peaks dominate the XRD patterns but allow to identify certain peaks that belong to the mineral materials.

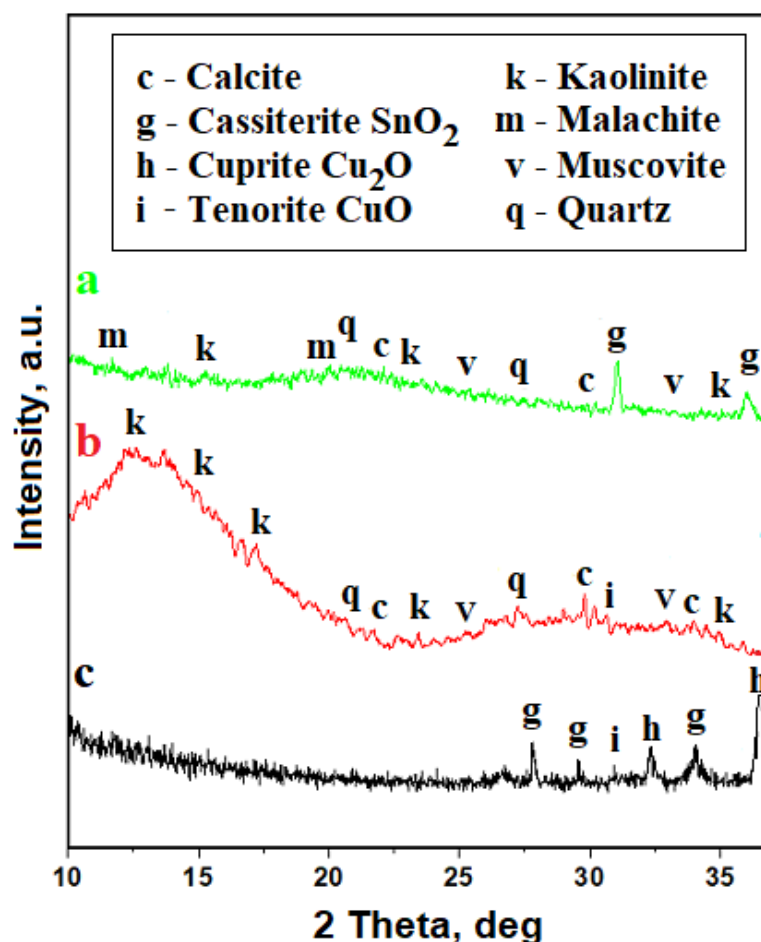


Figure 6. XRD patterns details between 10–30 degree 2 theta to reveal the patina components: (a) bronze coin, (b) bronze mirror fragment, and (c) silver coin.

Therefore, small peaks of kaolinite, muscovite, quartz, and calcite were observed in the XRD pattern of Istrian bronze coin, shown in Figure 6a. There also appear some malachite (copper carbonate hydrate $\text{Cu}_2\text{CO}_3(\text{OH})_2$) peaks, related to the copper oxides alteration in the presence of ground humidity combined with carbonaceous mineral presence such as calcite. This fact is sustained by a significant amount of carbon of approximately 19% wt. observed in the elemental composition of the patina, shown in Table 1.

Malachite is completely absent in the XRD pattern obtained for mirror fragment patina, as shown in Figure 6b, but several peaks belonging to the kaolinite, muscovite, quartz, and calcite are identified. It is in good agreement with the elemental composition of this sample. The absence of malachite indicates a more preserved quality of this artifact. Hence, it was found in the same condition of the soil and weathering, this characteristic must be related to the internal composition of the mirror fragment compared to the Istrian coin.

The XRD pattern of the Radulesti–Hunedoara silver coin, shown in Figure 6c, presents representative peaks for cassiterite and cuprite without soil mineral components. This is

in good agreement with previous observation regarding the advanced clean state of this artifact. Unfortunately, poor XRD results regarding the mineral particles in the patina layer do not allow certification of their presence and only confirm the assumptions made upon the elemental composition and elemental maps obtained with SEM. Additional investigation is required for evidencing the soil mineral particles embedded into the oxide layer. Mineralogical optical microscopy (MOM) is powerful in association with XRD to reveal minerals particles distributed into a certain microstructure such are those shown in Figure 7.

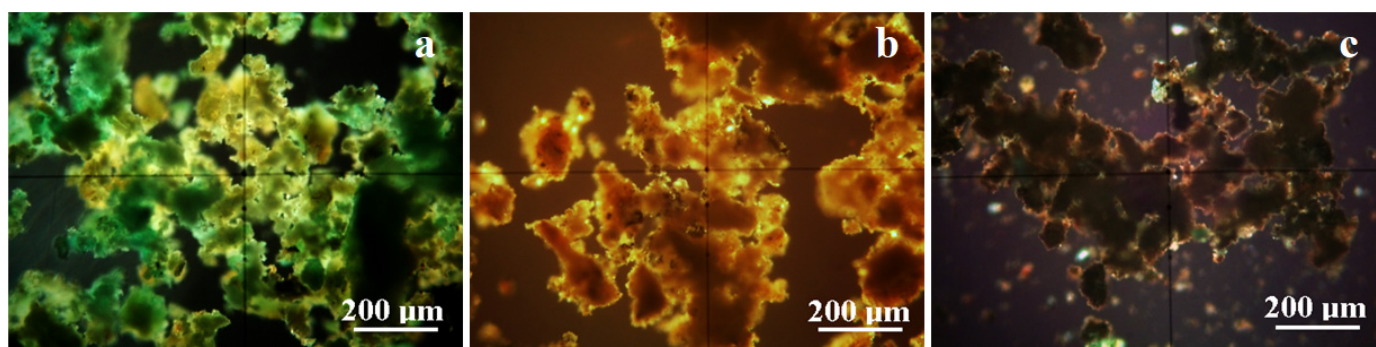


Figure 7. Mineralogical optical microscopy images observed in cross polarized light for the patina collected from the Dacian artifacts: (a) bronze coin, (b) bronze mirror fragment, and (c) silver coin.

MOM was effectuated on the patina powder resulted from the primary steps of cleaning procedures for local metallic core spot exposure. These were inspected under cross polarized light, shown in Figure 7, and each mineral presents a distinct characteristic color. The color nuance strongly depends on the particles position to the microscope optical axe having the maximum glow intensity, which decreases if the sample is rotated around microscope axe until the minimum is reached (situation called extinction).

Istrian bronze coin patina powder is dominated by cassiterite, cuprite, and tenorite mixture that forms compact particles with dark green aspect (cassiterite has forest green nuance, cuprite is dark brown nuance, and tenorite is predominantly black) and sizes ranging from approximately 10–80 µm, shown in Figure 7a. These particles are surrounded by light green ones that relate to the malachite presence. Its occurrence is caused by the weathering degradation of cassiterite, cuprite, and tenorite mixture in presence of calcite. Calcite presence is also observed by large, rounded clusters of approximately 80–120 µm with brown yellow aspect. Several small bright spots of approximately 1–10 µm in size correspond to the quartz. The microstructural aspect of patina particles suggests that cassiterite, cuprite, and tenorite mixture is formed directly on the metallic core gained during the coin circulation that progressively grows during incipient resting. Long time resting under soil conducts to the weathering degradation of the initial patina generates the resting patina that contains malachite and mineral soil particles. This fact is in good agreement with the data in literature [27,28].

Bronze mirror fragment patina powder, shown in Figure 7c, reveals a mixture of resting ground mineral particles such as calcite having yellow–brown nuance and size range between 30–100 µm; quartz particles of approximately 25–40 µm and bright nuance and small particles of kaolinite. They were embedded into the outermost oxide patina layers predominantly formed by cuprite and tenorite, a fact sustained by the small darkens spots having dark brown to black nuance. Cassiterite does not appear in the mirror fragment patina powder, which is in good agreement with XRD observation, as shown in Figure 6b.

Patina powder collected from the most affected areas on the silver coin surfaces reveals an interesting microstructure, shown in Figure 7c. Most of the particles present dark to black nuance that corresponds to the silver oxide Ag_2O and some dark brown that corresponds to cuprite. Ag_2O and Cu_2O are isostructural compounds [29], which facilitate the development of mixed oxide spots on the Radulesti-Hunedoara silver coin

due to its low copper content. Significant Sn amount within this coin forms cassiterite particles of approximately 10–30 μm and green color under cross polars, shown in Figure 7c, independently developed compared to Ag_2O and Cu_2O mixture. This is in good agreement with XRD observation in Figure 6c and with white spots of “tin rust” observed at the macroscopic examination of the coin, shown in Figure 2c.

Water content of patina layer is another major concern related to the long time resting of metallic artifacts onto the ground. Therefore, FTIR spectroscopy can determine water influence on the patina components, as shown in Figure 8.

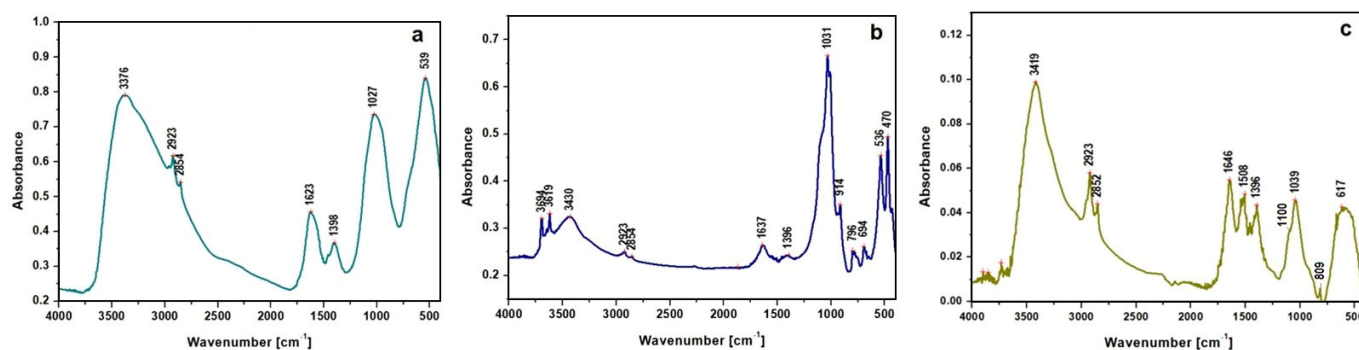


Figure 8. FTIR spectra obtained on patina powder collected from: (a) bronze coin, (b) bronze mirror fragment, and (c) silver coin.

Water molecules might be physically adsorbed onto mineral particles of chemically bonded to the oxide layer. Each type of water presence conducts to distinct FTIR absorption bands. Spectra presented in Figure 8 were analyzed, the values were compared to the data in literature, and the identified absorption bands and their vibration assignment are presented in Table 2.

OH stretching of adsorbed water into the clay lamellar structure presents a broad absorption band in the range of 3376–3419 cm^{-1} , which is very intense for the Istrian bronze coin and less intense for the mirror fragment, shown in Figure 8a,b. There also appear shoulder bands at 3421–3423 cm^{-1} related to the hydroxyl bonds stretching. OH stretching is the dominant absorption band of the silver coin, but it has an absorbance of only 0.10 units proving that there are some small amount of adsorbed water but insignificant compared to the other samples. Similar variation is observed for OH deformation broad band situated from 1646 to 1623 cm^{-1} , which is also related to the adsorbed water.

Carbonate minerals such as calcite and malachite are represented by the asymmetric deformation of $-\text{CO}_3$ group at 617 cm^{-1} . It also appears relevant bands at 914 cm^{-1} C–O–H that belongs to C–O–H out-of-plane bending and $\text{COO}-$ symmetric carboxylate stretching. Carbonates absorption bands for bronze coin are merged with the broad band observed at 539 and 1027 cm^{-1} belonging to the other significant compounds, shown in Figure 8a. C–O–H and $\text{COO}-$ absorption bands within bronze mirror patina confirm the presence of carbonate minerals, shown in Figure 8b. A small band related to the asymmetric deformation carbonate group (0.502 absorbance units, Figure 8c) was observed for the silver coin.

Silicates including quartz are very well represented for the bronze artifacts by Si–O–Si asymmetric stretch in the range of 1027–1039 cm^{-1} , Si–O–Si deformation at 470 cm^{-1} , and Si–O stretching of quartz at 796 cm^{-1} and 809 cm^{-1} , shown in Table 2. It indicates that quartz is more significant on the mirror fragment patina than for the bronze coin. Small amounts of silicates might be found on the silver coin surface as residues from the resting soil but less than the XRD detection limit.

Table 2. FTIR absorption bands assignment.

Compound/ Functional Group	Peak Wavenumber [cm^{-1}]			Vibration Assignment	References
	Histria Coin	Mirror	Silver Coin		
Clay minerals (Silicates)	-	3694	-	OH stretching Absorbed water (free)	[30,31]
	-	3619	-		
	-	3430	3419		
	3376	-	-		
	1623	1637	1646	OH deformation of water Adsorbed water in silicates	[32,33]
Carbonate minerals	617	-	617	asymmetric deformation carbonate group	[34,35]
	914	914		C–O–H out-of-plane bending COO— symmetric carboxylate stretching	[36]
Lipids	2923	2923	2923	Aliphatic CH_2 asymmetric stretching	[31,32]
	2854	2854	2852	Aliphatic CH_2 symmetric stretching	
	1398	1396	1396	Copper and calcium oxalates	
		694		Long alkyl chain of fatty acids and salts	
Silicates	1027	1031	1039	Si–O–Si asymmetric stretch	[32,33]
		470		Si–O–Si deformation	
		796	809	Si–O stretching of quartz	[32]
Sulfide/sulfate ions			~1100	Ag_2S and/or Ag_2SO_4	[37]
Copper oxides		470		O–Cu–O symmetric stretching	[38,39]
	539	536		Cuprite Cu_2O /tenorite CuO	

Additionally, the presence of sulfide/sulfate ions compounds was revealed in the spectral ranges of $\sim 1100 \text{ cm}^{-1}$. The shoulder band of 1100 cm^{-1} can be attributed to the ν_3 triply degenerated vibrational motion of dissolved SO_4^{2-} . It could be stated that these salts may be related to the exposure of the coins to soluble salts in groundwater [39].

Copper oxide absorption bands were found for bronze artifact as O–Cu–O symmetric stretching at 470 cm^{-1} and cuprite/tenorite mixture at $536\text{--}539 \text{ cm}^{-1}$. These absorption bands are very intense and broad due to the significant amount of oxides in the artifact patina.

Unusual finding are the small absorption bands characteristic for lipids traces such as aliphatic CH_2 asymmetric stretching at 2923 cm^{-1} and symmetric stretching at $2852\text{--}2854 \text{ cm}^{-1}$ and copper and calcium oxalates at $1396\text{--}1398 \text{ cm}^{-1}$. Copper oxalates precipitation in patina structure may suggest the long-time interaction with some lipid residues that interfere between oxidized metal and resting ground mineral particles. It happened most likely due to the interaction with some humus compounds from the resting ground. However, their presence is far below the limit detection of the other used investigation techniques.

3.3. Bronze Mirror Fragment Surface Investigation

The bronze mirror fragment is a very unusual artifact because of active surface quality preservation after 2000 years of ground resting. The black areas of the obverse in Figure 2 are still smooth and shiny compared with the obverse that evidences a thicker patina layer. Therefore, atomic force microscopy (AFM) was used for its surface investigation of the smooth oxidized layer, shown in Figure 9a, of the clean metallic surface shown in Figure 9b.

Figure 9a shows a compact layer of oxide material with submicron particles embedded from the resting ground that covers the mirror metallic core. There are embedded boulder aggregates having rounded shape with diameter situated between 300 and $600 \mu\text{m}$ that resemble to the quartz and calcite fine particles observed with the other microscopic

techniques; and lamellar particles with a length of approximately 50–100 nm and 5–20 μm thick that correspond to the clay minerals such as muscovite and kaolinite (this fact agrees with the MOM observation in Figure 7b that clay particles are very fine and difficult to be individualized in the conglomerate mass).

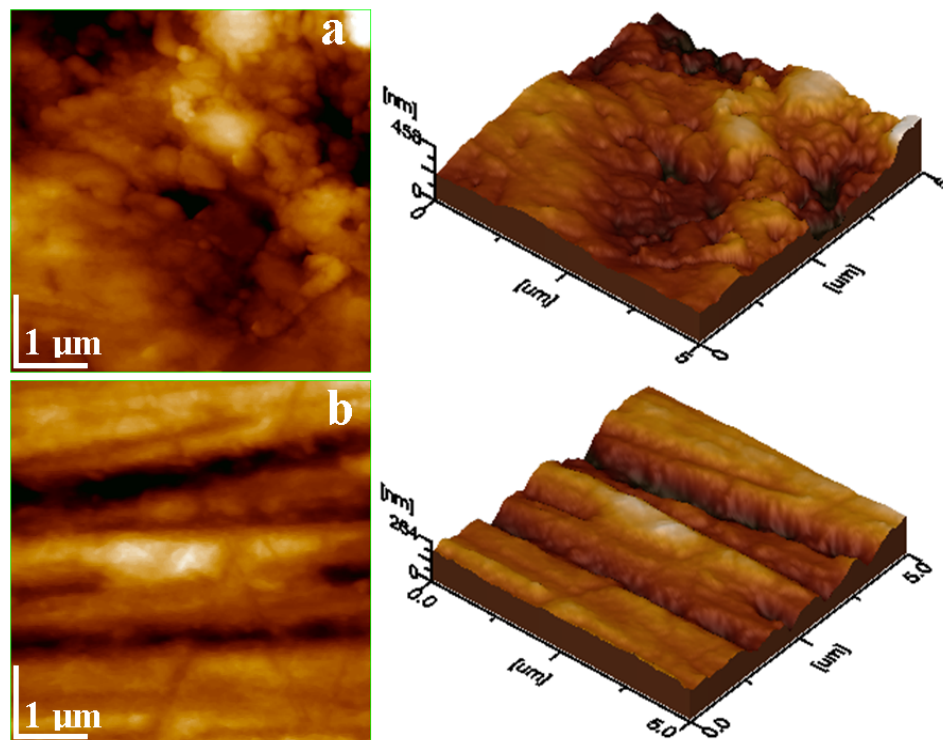


Figure 9. AFM topographic image and correspondent tridimensional profile resulted for the mirror bronze fragment: (a) patina surface and (b) metallic surface.

Tridimensional profile in Figure 9a reveals that embedded submicron particles into the oxide layer affects the surface uniformity at nano structural level causing a roughness of approximately 50 nm, shown in Table 3. The left side of the topographic image reveals a smoothest area with less embedded minerals, allowing the view of some parallel abrasion tracks that originated in the original surface polish. Their relative width is situated in the range of 60–90 nm.

Table 3. Bronze mirror fragment surface parameters measured by AFM.

Surface Parameter	Obverse Smooth Surface	
	Oxidized Side	Metallic Side
Height, nm	458 ± 22.9	51.0 ± 2.55
Ra, nm	264 ± 13.2	33.7 ± 1.68
Abrasion track width, nm	60–90	400–600

Chemical cleaning of the mirror fragment metallic core has the advantage that does not induce abrasion tracks and reveals the surface quality from ancient times. This was also investigated by AFM revealing a smoother surface than the patina layer, shown in Figure 9b, with the roughness of approximately 30 nm, shown in Table 3. The high compactness of the bronze alloy is observed without any micro and nano structural fault proving the high quality of metallurgical processing. AFM topography reveals that the mirror luster was obtained by abrasion with a heterogeneous submicron abrasive powder that generates parallel abrasion tracks of approximately 400–600 nm width.

4. Discussion

The Istros bronze coin was found in a secondary position, brought along with soil from somewhere nearby, for the arrangement of the terrace, together with other artifacts as pottery and metal fragments. Its patina examination evidences a thick layer of oxide and carbonates layer embedding minerals from the resting soil. This fact confirms its discovery in the intact site. It is a small bronze denomination of Istrian issues of Apollo type featuring an eagle on the dolphin back struck on the avers and two countermarks on the obverse featuring the heads of Hermes and Helios. This monetary issue was in circulation during centuries 2–1 BC in Istros and its proximity on the Black Sea shore (e.g., actual region of Dobrudja in Romania). The countermarks on the obverse assured the circulation until the middle of the first century BC. Thus, it is reasonable to assume that these Istrian bronze coins were in circulation when the Piatra Rosie fortress flourished. The experimental results confirms that the coin was manufactured in the Hellenistic and Roman style using a casted bronze disk that was heated until it became “red” and struck by dies hammering followed by relatively rapid cooling (most likely in water) [9,10]. This fact is sustained by the morphologic aspect of the dendritic grains evidenced by SEM-EDX elemental map in Figure 3a. Such microstructure related to the optimal tin content of approximately 20% proves that the bronze within Istros coin was of very good quality for the ancient times.

However, the archeological evidence shows that Dacians have never used bronze coins for trade preferring silver, bronze being used for common jewelry and domestic objects, rarely for military equipment and harness [9,10]. Therefore, why an Istros bronze coin was used by the people of Piatra Rosie settlement? The easy answer would be that it is only a strange coincidence, but there are also 47 similar coins found in several Dacian sites that have been published: a small deposit of 11 coins was found at Calan [40], one piece was found in Costesti–Blidaru area [41], 19 coins were found in older excavations in Costesti–Cetatuie fortress [42], 13 coins were found in recent archeological excavations in the same fortress [43], and 3 other coins were found at Piatra Rosie—one of them was found by Daicoviciu in the first excavations and published [13] and 2 coins were found by amateurs that gave them to the museum [15]. Archeologists’ general opinion is that the Istrian bronze coins were used on ritual purposes due to eagle and laurel branch featured on coin avers, which were symbols of great importance for Dacians [43], and for funeral practice [44]. The general opinion is that Istrian bronze coins were brought into the area of the capital of Dacian Kingdom as battle booty after a military incursion of King Byrebistas at the Black Sea shore Greek colonies, including Istros [40,43]. This explains coin presence into Dacian sites but did not explain why these small and worthless coins were captured and transported to these fortresses. Have they been intended for ritual purposes? It is difficult to answer, but those recent 13 coins found in a grave in Costesti–Cetatuie fortress plead for funeral rituals. However, what if the ritual aspects are the collateral side of the problem and these small bronze coins were part of a bigger bronze capture together with domestic objects and weapons? These objects might be re-used as they were or as raw material for the local metallurgical workshops.

Elemental composition and microstructural aspects of our Istrian bronze coin show that is a high-quality bronze according to the Hellenistic and Roman coinage standards [28,45,46]. Similar elemental composition was reported in literature for Roman bronze mirrors [17,19]. Therefore, the coins–domestic objects interchangeability is proved for Hellenistic and Roman areal. Dacians have adopted many of cultural habits from the Hellenistic and Roman areal, and most likely they used high-quality bronze coins as raw material for jewelry and ornaments productions, which is sustained by the elemental composition of some Dacian bronze bracelets and fibulae [9,10]. The raw material was most likely subjected to melting into a larger bronze charge or used as small ingots for plastic deformation to obtain small products as wires for bracelets and fibulae. For example, an Istrian bronze coin would be sufficient to obtain the bronze sheet necessary for small ornaments production. The initial archeological prospection of Piatra Rosie fortress reports

the presence of an important metallurgical workshop [13,45]; in consequence, the local presence of the Istrian bronze coin might be due to the metallurgical workshop activities.

Bronze elaboration strongly depends on the tin as the principal alloying element. It is relatively difficult to establish the tin origin starting from the discovered bronze artifacts. The opinion regarding the tin provenance in the Dacian bronzes is that either it was imported from the Bohemian region or was obtained from local ores [10]. We found important proves that Dacian used tin as alloying element during charge elaboration. These proves are related to the silver depreciation in Dacian silver tetradrachms (imitations of Hellenistic coins) from the issues starting at the end of the second century BC to the middle of first century AD. These coins belong to the second phase of Dacian coinage [46]. The one discovered at Ardeu has a ternary composition based on Ag–Sn–Cu system as observed by the elemental analysis. The dendrite microstructure shows that the coin was manufactured starting with a casted disk followed by the hot striking. The Dacian tetradrachms had initially (during first issue phase) rich silver title [45] that considerably decreased into the second phase of issue by replacing of silver with tin because of local silver scarce at that time [47,48]. Two Radulesti–Hunedoara coins were reported at Sarmizegetusa Regia: one during 1803–1804 excavations [14] and the other during excavations in the '80s of the last century [49], which is of great importance for the dating of the site's structures. A hoard of twelve pieces found near the capital was analyzed and found to have an unusually high grade of silver (some pieces have more than 90% Ag), explained by the votive destination of the pieces [50]. However, all other pieces of this type that have been analyzed have a very low silver title. The elemental composition of our silver coin corresponds to the Ag–Sn–Cu ternary system respectively rich A–Sn and low Cu content [51], and agrees the nonferrous alloy antique recycling procedures [52].

Bronze mirror fragment was a miscellaneous finding that is expected to be very similar to the Hellenistic and Roman bronzes such as the one identified in the Istros coin. Its archeological importance rose by revealing of its elemental and microstructural composition. The composition is very unusual due to the high purity bronze (elemental composition contains only Cu and Sn) and to the higher amount of tin as evidenced by the EDS elemental analysis. Therefore, microstructure is formed by grains that belong to Cu_6Sn_5 and $\text{Cu}_{41}\text{Sn}_{11}$, and the fragmentation of Sn-rich grains but still with rounded borders indicates a rapid solidification of the casted alloy most likely due to the thin-walled shape of the mirror. Plastic deformation is excluded because of the brittle intermetallic compounds presence. Data in literature report the presence of ceramic molds related to the bronze artifacts casting such as pendants and buttons [53]; unfortunately, no casting mold was found in the proximity of our mirror fragment, but some ceramic molds for bronze chain links casting were found during previous archeological campaigns at Alun-Piatra Rosie [9]. It should be an interesting item to be searched in further archeological investigation at Alun-Piatra Rosie site.

Another exceptional aspect regarding mirror fragment is the quality preservation with a thinner patina layer than the one observed at Istros coin and the low roughness of the polished surface even after it was oxidized under weathering conditions in the resting ground for about 2000 years. It is very interesting that bronze coin evidences a lot of malachite and cassiterite into the patina and the mirror fragment completely lacks these patina components proving a better preservation of this artifact. The reason is questionable: it might occur due to a long time resting in a relative protected space against intensive weathering or is about of a better corrosion resistance, and the elucidation of this aspect requires further investigations. AFM microscopy reveals the high grade of surface polishing with a roughness comparable to actual metallic mirrors. The presence of Cu_6Sn_5 and $\text{Cu}_{41}\text{Sn}_{11}$ intermetallic compounds that are more brittle than low tin amount bronzes facilitates surface polishing preventing formation of deeper scratches. This fact is sustained by AFM results on the metallic surface that detected traces of ancient polishing marks related to a low surface roughness.

Among the populations of the European Iron Age and in the Greek Hellenistic area, mirrors were manufactured from a binary Cu–Sn bronze. The British Iron Age mirrors show a remarkable consistency in the type of alloy, with a tin content of around 10–13% [54]. The analysed mirrors from the Hellenistic period contain up to 12.4% tin [20]. Etruscan mirrors show a constant composition with an average percent of 15% tin [21]. The indigenous metallurgists from Manching (southern Germany) adopted the Mediterranean alloy model, but they replaced the high tin alloys with antimony-rich fahlore copper to produce silver-coloured mirrors during the Middle and Late La Tène period [50]. The tin content of the Gallo–Roman mirrors is between 11 and 23% [55].

In sharp contrast, the Roman mirrors proved to be manufactured from a different type of alloy and by different technology. They were made of a ternary Cu–Sn–Pb alloy and are grouped into two categories: tinned low-tin bronze mirrors (8–10% Sn) and casted high-tin bronze mirrors (approximately 19–25% Sn), with the majority in the first category [56]. The tinned low-tin bronze became an almost standardized recipe for Roman mirrors and is known as *speculum*.

The dating of the mirror fragment from Alun-Piatra Rosie in the second half of the 1st century AD (or rather towards the end of the century) by means of the fibula with which it was associated in the archaeological context, suggests two major possibilities regarding its provenance: Roman import made of unusual alloy composition or a local product with particular alloy smelting characteristics.

Historical data show many bronze mirror findings in Dacian sites, but most of them are related to the Hellenistic and Roman imports and therefore correspond to the typical elemental composition [17–19]. The unusual composition of our bronze mirror fragment may suggest that it is the product of a local metallurgical workshop. Crisan reports discovery of a mirror fragment in a Dacian jewelry workshop in Pecica Village, Romania, along with other bronze artifacts manufactured there [57]. Unfortunately, the elemental composition of this representative artifact was not analyzed yet. Most of the authors consider these mirror fragments as imports [9,10], but our results show that there is a possibility that some of the bronze mirrors to be produced in local workshops. Of course, there are the need for further intensive investigations into a large number of samples for validation of this possibility. The geological aspects are also necessary to be considered in the future research to verify that the local resources were used in the metallurgical activities.

The results obtained show that SEM–EDX is a powerful tool for the artifacts non-destructive method. The elemental map is able to reveal the distinct phases and constituents within the artifact's alloys without polishing and chemical etching. The major lack of this method is the limitation of the metallic surface investigation and brings none information about the inside of the metallic core.

5. Conclusions

The nondestructive investigation of the Dacian artifacts revealed that Istria bronze coin has an elemental composition of 75.0% Cu, 20.8% Sn, and 4.1% Pb, which corresponds to a structure of Cu grains mixed with Cu_{5.6}Sn grains. It was produced by hot strike on a casted bronze disk using metallic dies. The composition and microstructure of Istrian bronze coin is typical for Hellenistic and Roman bronze artifacts such as coins and mirror fragments.

The bronze mirror fragment has an elemental composition of 52.3% Cu and 47.7 Sn, which corresponds to a structure containing grains of Cu₆Sn₅ mixed with grains of Cu₄₁Sn₁₁. The results indicate that it was produced by casting due to the brittle intermetallic compounds identified as microstructural constituents. The ancient polishing procedures generates a smooth surface that was investigated with AFM microscopy that evidences a Ra roughness of 51 nm for the patina surface and 33.7 nm for the clean metal surface, proving the high quality of the original mirror luster of the artifact.

The mismatch between mirror fragments and Roman bronze composition indicate a particularly alloy elaboration and casting that belongs to a metallurgical workshop with its own technological methods. The establishing of this workshop location it is very difficult,

and it could be situated everywhere in Roman Empire, or it might be situated locally in the proximity of the artifact discovery place. Further investigations are required to validate this hypothesis. Tin availability as alloying element for the local Dacian metallurgical workshops was proved by the results obtained on the Radulesti–Hunedoara silver coin.

The silver coin was identified as a Radulesti–Hunedoara type, meaning that it was produced in local Dacian metallurgic workshops. It has an elemental composition of 63.1% Ag, 25.3% Sn, 7.8% Cu, and small traces of P and Fe, which corresponds to a structure of Ag grains and Ag₃Sn grains. It proves that Dacians uses tin as alloying element and was able to elaborate a special bronze charge like the one required for the mirror production.

Bronze artifact patina is a result of the wearing oxide layer formed onto the coin and mirror surface during the active period, which is enhanced by the corrosive condition within resting ground that conducts to the in depth oxidation and the exterior layers are sensitive to the soil humidity and mineral particles that are embedded into the corrosion product.

The nondestructive methods such as SEM microscopy coupled with EDS elemental investigation and X-ray diffraction are able to give a complex characterization of the ancient bronze artifacts that are helpful for the archeological research.

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