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شِدِت

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ARCHAEOMETALLURGICAL CHARACTERIZATION AND CONDITION ASSESSMENT OF ANCIENT ROMAN COINS FROM EGYPT

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ABSTRACT

This paper presents scientific investigations of three ancient Roman coins excavated from Al Sheikh Zuweid, Sinai city in 2002. A punch of examination and analytical techniques consists of stereo microscope, optical microscope, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) and X-ray diffraction (XRD) are used to study the morphological characteristics of the coins patina, to identify the chemical composition of the metallic core, to determine the corrosion products and to understand the corrosion mechanism. The results indicate that copper is the major element of the three coins with small proportion of silver and tin. The presence of tin in the composition of two coins refers to bronze alloy. The identification of the exact corrosion products is determined by XRD analysis. The results reveal that the corrosion products consist mainly of cuprite and tenorite. Also, the results indicate that the coins were buried in a soil rich in chloride ions due to the presence of copper hydroxychlorides such as paratacmite and atacamite. Metallographic investigation is used to reveal the coins manufacture and identify spatial distribution of the alloy components and phases. Also, metallographic investigation indicates pitting corrosion resulted from the attack of chloride and the occurrence of a "bronze disease" phenomenon. The results of this study can provide valuable information that helping in conservation and preservation of the archaeological coins.

KEYWORDS

Coins, copper-based alloy, archaeometallurgy, SEM-EDX, XRD.

الملخص

يتناول هذا البحث فحص وتحليل علمي لثلاث عملات رومانية قديمة تم الكشف عنها في مدينة الشيخ زويد محافظة سيناء عام 2002، تمت دراسة العملات بإستخدام مجموعة من تقنيات الفحص والتحليل وذلك بإستخدام الميكروسكوب المجسم والميكروسكوب الضوئي، والميكرسكوب الإلكتروني الماسح (SEM) المزود بوحدة تحليل العناصر (EDX)، وحيود الأشعة السينية. تشير نتائج التحليل إلى أن النحاس هو العنصر الأساسي للعملات الثلاثة مع نسبة قليلة من الفضة. يشير وجود القصدير في عملتين من الثلاث إلى سبيكة البرونز. تم تحديد مركبات الصدأ بواسطة حيود الأشعة السينية. أشارت النتائج أن مركبات الصدأ تتكون بشكل اساسي من الكوبريت والتينوريت. ايضاً أشارت النتائج أن العملات كانت مدفونة في تربة غنية بايونات الكلوريد وذلك لوجود مركبات الهيدروكسي كلوريد مثل الباراتاكاميت والأتاكاميت. يستخدم الفحص الميتالوجرافي للكشف عن عمليات تصنيع العملات قديماً وتحديد مكونات وأطوار السبيكة. ايضاً يشير الفحص الميتالوجرافي إلى الصدأ الحفري الناتج عن هجوم ايونات الكلوريد وحدوث ظاهرة مرض البرونز. تقدم نتائج هذه الدراسة معلومات مفيدة في علاج وصيانة العملات الأثرية.

الكلمات الدالة

عملات، سبائك النحاس، دراسة فلزية أثرية، الميكرسكوب الإلكتروني الماسح المزود بوحدة تحليل العناصر، حيود الأشعة السينية.

1. INTRODUCTION

Archaeological coins are objects of greatly important value as they reflect the various aspects of ancient civilizations that used them and assist in dating historical events. Excavated coins are usually covered with corrosion products that overlap with soil deposits and may contain active corrosion that could convert the whole coin into corrosion products.

Corrosion reactions are defined as the chemical reactions by which metals convert back to their natural state. The path the reaction takes depends on the metal alloy and the environment conditions in which the artifact exists.[1-2-3] Corrosion mechanisms of copper-based alloys artifacts in burial environment is complex as they are related to both chemical composition of metal alloy and burial conditions which vary according to soil parameters and geographic areas.[4-5] During burial, archaeological coins suffer from different corrosion mechanisms which can lead to the formation of different corrosion layers with variable thicknesses and chemical compositions, and in some cases completely corroded artifacts may be found without any metallic remnant.[6]

Copper and its alloys can form different kinds of corrosion products, depending on the dominant corrosive factor in the burial environment.[7] Corrosion formed on copper-based alloys can be characterized according to the chemical compositions and morphology. Corrosion products can be formed in (thin, medium and thick) layers, in different physical phenomena (cracks, pits etc.) and in different chemical stratification (primary and secondary chemical compounds).[8-9] The formation of an oxide layer on a metallic core is the first stage of corrosion of copper and its alloys (which may take place before burial during manufacturing or during use of a coin).[10] The corrosion products of the secondary level are usual colored and can refer to the preliminary chemical composition of the metal alloy underneath the corrosion and the soil type.[11] When copper and its alloys are present in saline soil environment, chloride ions migrate through the oxide layer or through age cracks forming a greenish compound of nantokite (CuCl). Nantokite forms close to the bulk metal surface and covered with the other corrosion products.[12] At first, growth of the nantokite on the metal surface appears as boils, and then it spreads into the interior parts of the metal artifact forming the secondary corrosion layer.[13-14] In the presence of oxygen and water and under soil burial

[1]Brown et al., Corrosion and metal artifacts: a dialogue between conservators and archaeologists and corrosion scientists, 1-4.
[2]Scott, Periodic corrosion phenomena in bronze antiquities, 49-57.
[3]Roberge, Handbook of corrosion engineering, 142.
[4]Nord et al., Factors influencing the long-term corrosion of bronze artefacts in soil, 309-316.
[5]Sandu et al., Influence of archaeological environment factors in alteration processes of copper alloy artifacts, 1646-1652.
[6]Schweizer, Bronze objects from lake sites: from patina to " biography, 33-50.
[7]Quaranta, On the degradation mechanisms under the influence of pedological factors through the study of archeological bronze patina, 71-75.
[8]Scott et al., Ancient & historic metals., 34.
[9]Sandu et al.,A study on the deterioration and degradation of metallic archaeological artifacts, 180.
[10]Sandu et al.,The liesegang effect on ancient bronze items discovered in Romania, 573.
[11]Ghoniem, The characterization of a corroded Egyptian bronze statue and a study of the degradation phenomena, 103-104.
[12]Al-Zahrani and Ghoniem, A characterization of coins from the Najran hoard, Saudi Arabia, prior to conservation, 150-151.
[13]Scott, Copper and bronze in art: corrosion, colorants, conservation, 125-130.
[14]Sandu et al.,The liesegang effect on ancient bronze items discovered in Romania, 575.

conditions, CuCl (nantokite) produces basic copper chlorides like atacamite and paratacamite.[1-2] The presence of chloride compounds indicates the occurrence of a "bronze disease" phenomenon which appears in a range of green color.[3] Bronze disease is a form of pitting corrosion in which the inner area under the oxide layer is dissolving (anodic area) and the corrosion products (cathodic area) are deposited above the Cu_2O film.[4-5-6]

Due to the complex nature of archaeological coins, research studies have widely performed archaeometallurgical characterization using various analytical methods to study corroded coins. Researchers faced challenges to investigate the composition and the complex structure of copper-based alloy coins and its corrosion products and understand the relation between the corrosion products and the environment, in which coins were buried.[7-8-9-10-11-12]

This work aims to conduct archaeometallurgical characterization of ancient Roman coins to understand the chemical composition and microstructure of the metallic core and the analysis of corrosion products to better understand of corrosion mechanisms. This study was carried out using a set of analytical techniques including stereo microscope, optical microscope, scanning electron microscopy (SEM) coupled with EDX unit (Energy Dispersive X-ray Analyses) and X-ray diffraction (XRD).

2. MATERIALS AND METHODS

2.1 Coin samples

Three ancient Roman coins are selected for the present research (Fig.1), The coins have good metallic states and differ from each other in size, shape, and corrosion status. Coin-1 is the least corroded one from the three coins that makes it possible to see some of the depicted figure on the coin obverse. The coin is almost in a good condition covered with a thin dark brown corrosion layer. The reverse bears some unidentified random depictions and symbols. Although the coin shows some clear inscriptions, they are not readable, and the legend of the coin is mostly disappeared. Coin-2 is the largest one from all the three coins, and it is the most corroded one. The coin is not classified/readable due to the thick and rough corrosion layers. The coin surface is multicolored by corrosion products with black as the predominant color. The edge of the coin has an irregular shape with a small missing part on the upper right edge. Although, coin-2 is completely covered by corrosion products, it looks in a good physical condition with a hard core and no fragments. Coin-3 is similar to coin-1 in the

[1]Scott, Periodic corrosion phenomena in bronze antiquities, 49-57.
[2]Ghoniem, The characterization of a corroded Egyptian bronze statue and a study of the degradation phenomena, 104.
[3]Demidova, Archaeometallurgical characterisation of ancient Roman bronze coins, 64.
[4]Bresle and Arrhenius, Studies in pitting corrosion on archaeological bronzes, 7-8.
[5]MacLeod, Bronze disease: an electrochemical explanation, 16-26.
[6]Scott, Copper and bronze in art: corrosion, colorants, conservation, 125-133.
[7]Vijayakumar et al., A study of Vishnukundin coins, 137-147.
[8]Plattner et al., The Corrosion of Archaeological Copper Alloys. The case study of a coin hoard from the Tenuta Radicicoli-del Bene, Rome, 1-2.
[9]Mata et al., Characterisation of five coins from the archaeological heritage of Portugal, 495-503.
[10]Reale et al., Ancient coins: cluster analysis applied to find a correlation between corrosion process and burial soil characteristics, 1-9.
[11]Allen, A systematic study of the corrosion layers on excavated coins from varying historical periods, 40-74.
[12]Demidova, Archaeometallurgical characterisation of ancient Roman bronze coins, 16-71.

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condition, since its surface is covered by a thin uniform brown and black corrosion layer. On the obverse, the portrait appears clearly. Some letters are visible but not readable, and still, it is possible to make a guess on the origin identification. The legend inscriptions on the reverse were mineralized, thus its details are not readable. The coin milled edge is irregular. In general, the coin is in good condition, in few places, shiny red color appears which likely to be the metal core.

Fig. 1. Shows the obverse and reverse of the archaeological coins (1,2,3 left to right respectively) which is covered with different types and thicknesses of corrosion products

Table 1: Morphological characteristics of the three archaeological coins

Coin	Weight (g)	diameter (mm)	Thickness (mm)
Coin-1	2.89	18.09	~1.65
Coin-2	9.10	27.00-29.27	~2.35
Coin-3	12.15	22.68-24.49	~2.78

2.2 Analytical techniques
2.2.1 Microscopy

The surface morphology of the coins was investigated by stereo microscope ZEISS (Stemi 2000-C), and the scanning electron microscope (SEM) model Quanta 250 FEG (Field Emission Gun, coupled with energy dispersive x-ray spectrometer (EDX), FEI, Netherlands, with accelerating voltage 30 K.V, magnification 14x up to 1000000 and resolution for Gun.1n. The systems used to identify the metallic core elements, corrosion products and assess the surface morphology of the archaeological coins.

To determine the chemical composition of each coin alloy, it has been polished a minute part to remove surface corrosion (about 2mm) at the curved of each coin far away any numismatics information. The coins were placed in the analysis position vertically, since the polishing part was directed towards the electrons for better observation of the metallic core alloy. All images of the coins core have been investigated using backscattered electrons (VCD), which is usually high in contrast and, depends on a chemical composition of a sample.

2.2.2 X-Ray Diffraction

X-Ray Diffraction (XRD) analysis was performed to confirm the corrosion compounds presented on the surface of the archaeological coins. The XRD analysis was conducted using Shimadzu XRD-6100 diffractometer.

2.2.3 Metallography

Metallography is a scientific study that aims at the identification of metal alloy microstructure, spatial distribution of its components, determination of alloy phases and changes, like corrosion. Optical microscope (model ZEISS, Germany) was used to conduct metallography investigation.

Each coin's polished area prepared for SEM-EDX investigation was prepared for the metallographic examination. Firstly, the process implies smoothing the polished area by rubbing the surface using sandpaper in order to the make the surface as smooth as the mirror as much as possible. Secondly, the smoothed area was polished again using a polishing machine (MP-2B Grinder Polisher). Polishing procedure started with 1200 gradually increased to the finer one 2400. The rotation of a polishing disk with a use of silicon carbide papers is usually accompanied with a water supply to increase the efficiency of the process. After that, the etching material was applied to reveal some details that could not be visible when polished. Etching was performed between the microscopic observations several times. The etching solution (Table 2) was applied on the polished surface and kept for certain amount of time (about 3 seconds).[1]

Table 2. The composition of the etching solution

Composition	Proportions
H_2O	120 ml
HCl	30 ml
$FeCl_3$	10 g

3. RESULTS AND DISCUSSION

SEM investigation of the metallic core of coin-1 reveals homogenous structure and morphology. There are some dark patches on the entire surface which may refer to the core degradation (Fig. 2-A). Elemental composition detected from EDX analysis (Fig. 2-B and Table 3) reveals that the basic chemical compositions of the alloy is Cu 92.13 %, Ag 5.61% and Sn 2.26%. White spots refer to silver. The coin-1 surface pattern appears uneven, and covered with a thin corrosion layer (Fig. 3). Brown to black colors can be distinguished in the corrosion layer. Also, a bright yellow color is clearly visible, which most likely indicates the metal core. The appearance of metal core is associated with surface scratches, which most likely resulted from human damage during its lifetime or long-term burial degradation.

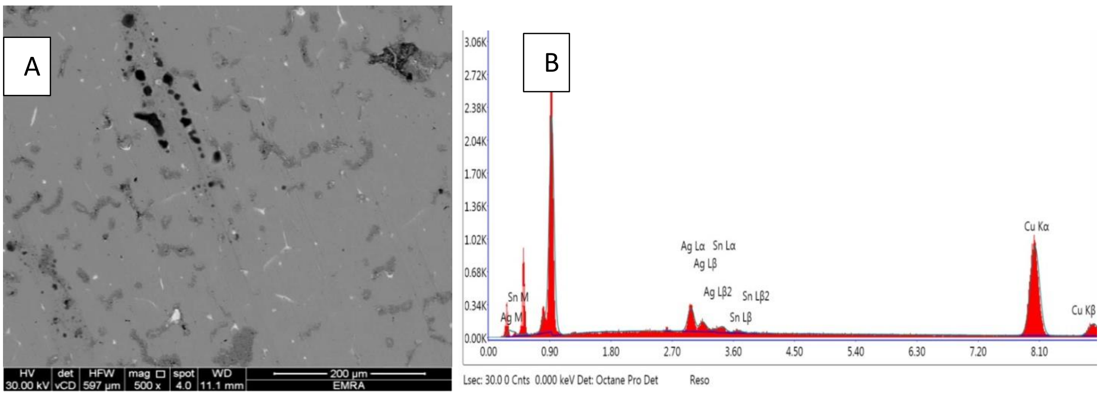

Fig. 2. SEM image of the metallic core of coin-1 (A) and its EDX spectrum (B)

[1]Scott, Metallography and microstructure in ancient and historic metals, 72.

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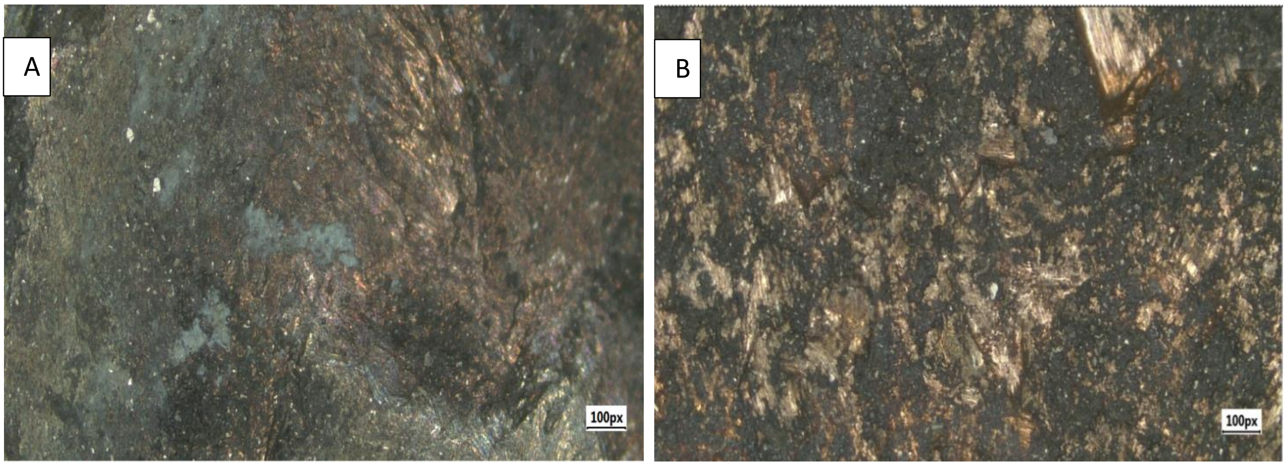

Fig. 3. The coin-1 surface corrosion features; the obverse (A) and the reserve (B).

The coin-1 visually appears in a good condition and has no sign of green corrosion observed by naked eye. However, clearly pale green powdery patches are revealed under stereo microscopy in limited areas on the coin obverse (Fig. 3-A). This illustrate that the main compound in XRD results (Fig. 4) is atacamite ($Cu_2(OH)_3Cl$) and the presence of chloride element in the EDX analysis (Fig. 5-B and Table 3), which represented this pale green corrosion products. Compounds of chloride reveal the presence of bronze disease. Bronze disease does not always appear clearly on the surface, but it is sometimes hidden and it is not easy to identify on time and to assume that a safe artifact. The coin surface under SEM (Fig. 5-A) appears compact and can show some pits and holes, that, most probably, represented corrosion pits which resulted from chloride products.[1] Silver is clearly visible in the form of white clusters. Mg is detected in EDX analysis as a soil contamination.

Also, XRD results show the presence of copper oxides represented in cuprite (Cu_2O) and tenorite (CuO). Moreover, the black patina can be attributed to the presence of silver sulfide (Argentite Ag_2S) in black color which identified in XRD results. The current results suggest that the corrosion products on the coin may be formed because the coin was buried in a salty soil. This soil might contain contaminations active ions such as Cl and S.[2]

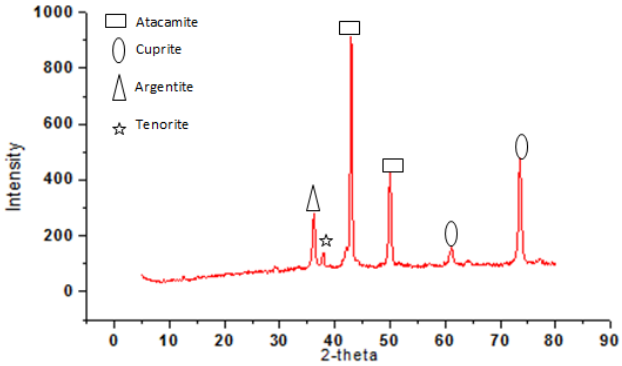

Fig. 4. XRD pattern of the surface corrosion products of coin-1

[1]Pedeferri, Pitting Corrosion, (2018).
[2]Oudbashi, A methodological approach to estimate soil corrosivity for archaeological copper alloy artifacts, 1-15.

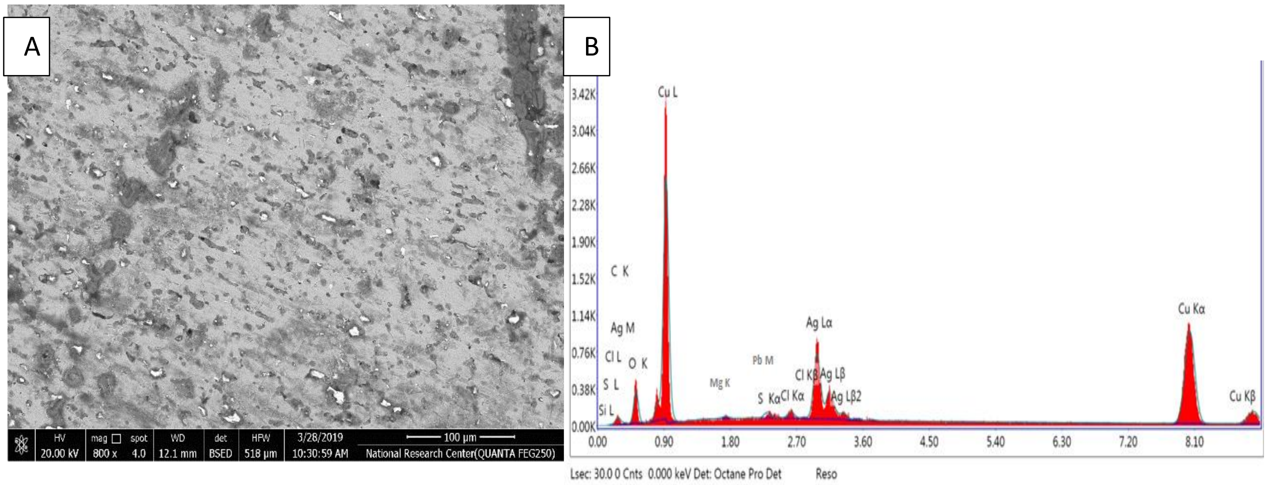

Fig. 5. SEM image of the surface corrosion products of coin-1(A) and its EDX spectrum (B)

Table 3. Chemical composition of the metallic core and the surface of coin-1

Element (wt%)	O	C	S	Mg	Sn	Pb	Cl	Ag	Cu
Metallic core	-	-	-	-	2.26	-	-	5.61	92.13
Surface	7.85	1.1	0.79	1.08	-	3.07	4.62	10.83	70.66

SEM examination of the metallic core of coin-2 (Fig. 6-A) shows a deteriorated structure. The topography of the alloy is rough with some cracks dispersed on the metallic core. Also, black spots appear that indicate pitting corrosion.[1] EDX analysis result (Fig. 6-B and Table 4) of the metallic core reveals that the copper is the main alloy component with low content of silver which appears in the form of bright white clusters.

Corrosion products of coin-2 cover the entire surface except for the upper right edge of the coin, which has a thin brown layer. The SEM image of this layer reveals the tough and rough surface topography with severe pitting corrosion of the metal alloy (Fig. 7-A). This indicates that the coin is severely corroded. EDX analysis (Fig. 7-B and Table 4) of this layer shows a high content of oxygen with copper and low proportion of chloride. High proportion of copper and oxygen indicate the presence of copper oxides that are represented in the brown layer[2]. Also, the fact that chloride is present in this area explains why the morphology in general appears much rougher and coarser and full of pitting corrosion. This is due to when copper exists in an environment rich in chloride ions, it becomes unstable due to the chloride ions break down the oxide layer causing pitting and further damage to the surface as shown here.

[1])Pedeferri, "Pitting Corrosion." (2018): 207-230
[2])Verma et al., "Microstructural characterization of early Twentieth-Century British period Indian copper coins." (2021): 1-9.

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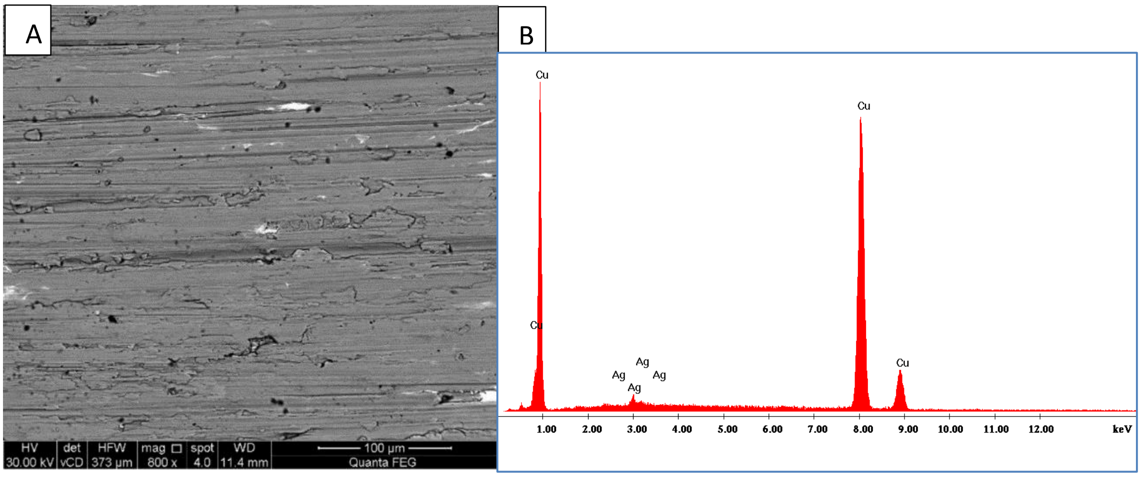

Fig. 6. SEM image of the metallic core of coin-2 (A), and its EDX spectrum (B)

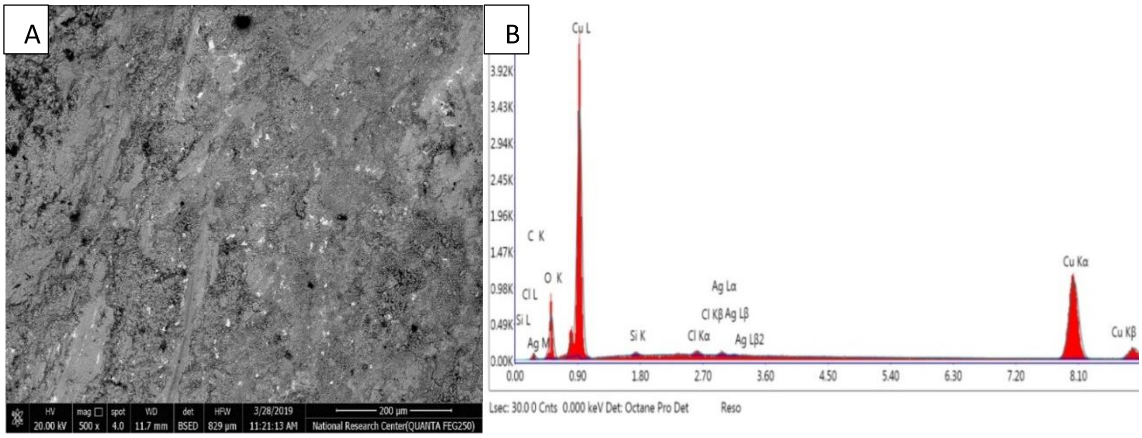

Fig. 7. SEM image of the oxide layer (A), and its EDX spectrum (B)

The coin shows rough and uneven surface that is characterized by compact corrosive layers overlapping with the microstructures from the soil. The coin surface (Fig. 8) is multi-colored of green, pale green, brown, black, blue and gray which all overlap with soil granules, indicating the preliminary chemical composition of the corrosion products. The SEM observation (Fig. 9) of the upper surface shows that the coin is largely corroded with fine grains and shows the rough morphology of the corrosion crust, the distribution of the primary and secondary compounds and the microstructures from the soil, which are well represented by a large range of surface structural formations (microcrust, nodules, etc.)

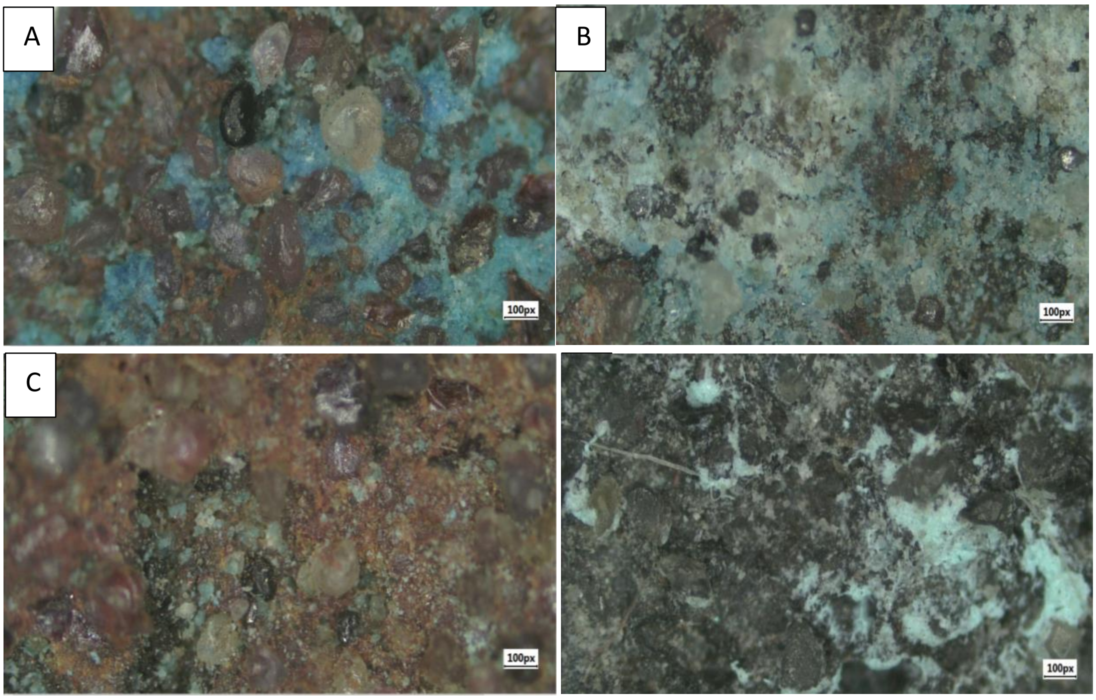

Fig. 8. The surface corrosion products and environmental deposits of coin-2; the obverse (A), (B) and the reverse (C), (D).

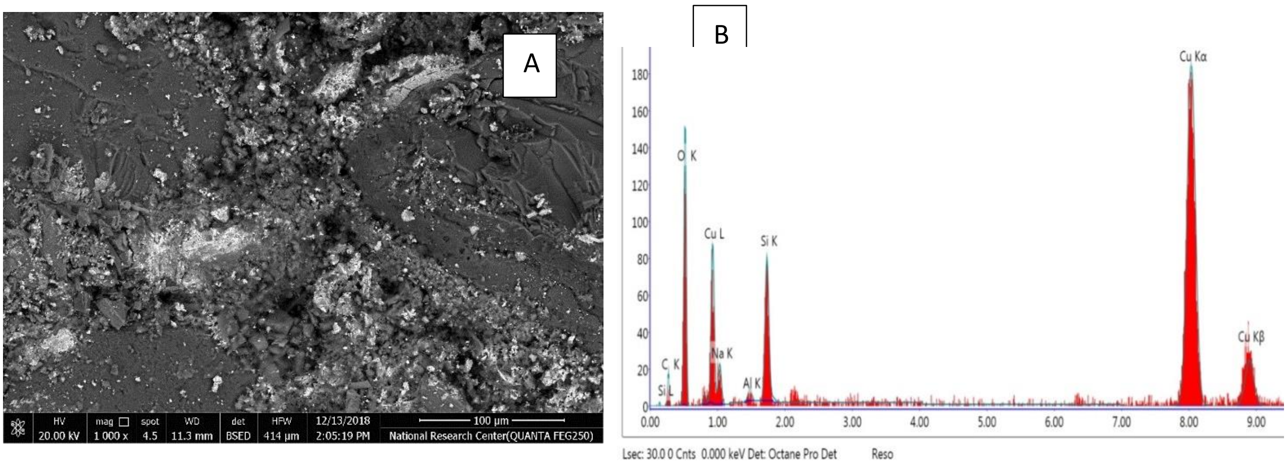

Fig. 9. SEM image of the coin-2 surface (A) and its EDX spectrum (B)

The soil has a great influence on the coin surface confirmed by the presence of large crystalline concretions shown in SEM image (Fig. 10-A). The EDX analysis (Fig. 10-B) of this area shows a high amount of Si. With a high content of silica, there is a high probability that this concretion is quartz from the soil. The results of XRD (Fig. 11) come to confirm this possibility, since quartz (SiO_2), the constituent of the soil, is identified as the major compound in coin-2. The presence of quartz in a large proportion reflects the nature of the burial soil which has to be sandy soil.

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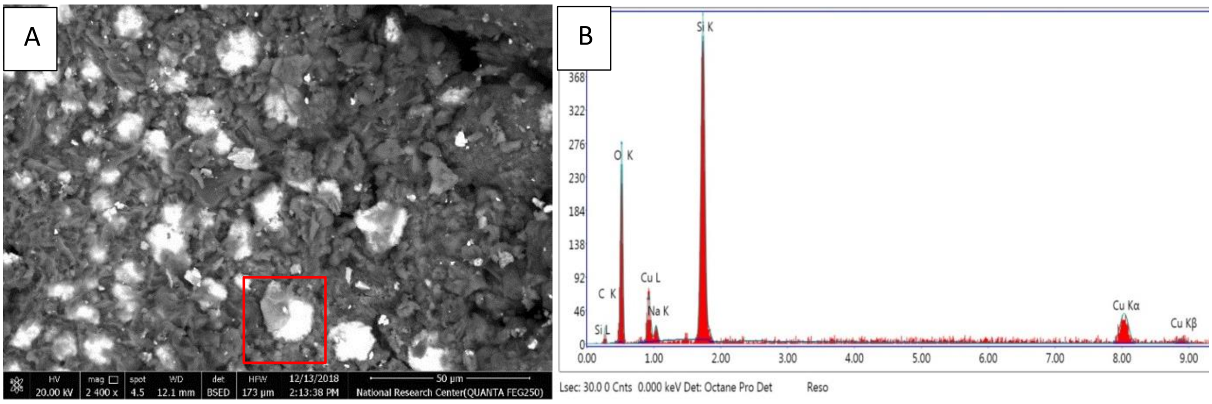

Fig. 10. SEM image of the quartz crystal from the soil (A) and its EDX spectrum (B)

Table 4. Chemical composition of the metallic core, oxide layer and surface of coin-2

Element	C	O	Na	Si	Al	Cl	Ag	Cu
Metallic core	-	-	-	-	-	-	2.75	97.25
Oxide layer	2.39	13.84	-	0.62	-	1.79	0.99	80.37
Surface	5.73	10.62	3.97	4.93	0.73	-	-	74.02

Also, XRD results (Fig.11) reveal that the patina consists of chlorides, oxides and carbonates. All these compounds are of copper, which represent the main compound of the alloy. The detailed corrosion elements characterized by the EDX analysis (Fig. 9-B and Table 4) confirm XRD results, since the presence of oxygen and carbon refers to cuprite and malachite. EDX results do not show chloride, however, paratacamite is clearly identified in XRD results. The absence of the Ag in the spectrum of the surface of the coin assumes that the copper corrosion products with soil deposits covered the coin.[1-2] Si, C and Na can indicate the type of soil where the coin was buried.

The XRD analysis results are not only in a good match with the EDX analysis, but also fit the patinas that can be present in buried archeological objects made of copper alloys. Al and Na can indicate the type of soil where the coin was buried. All analysis results indicate the type of saline sand soil, which is characteristic of the local soil.

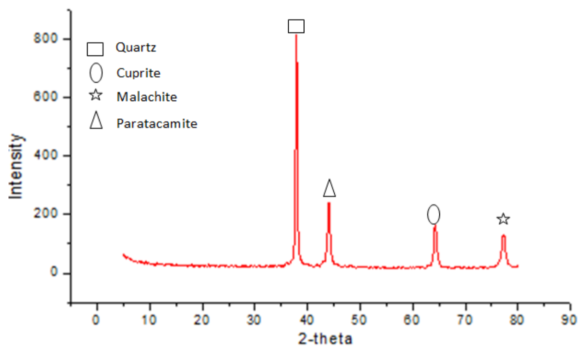

Fig. 11. XRD patterns of the corrosion products of coin-2

[1]Di Fazio et al., "Microstructure and chemical composition of Roman orichalcum coins emitted after the monetary reform of Augustus (23 BC), 1-11.
[2]Cruz et al.,"Surface analysis of corroded XV–XVI century copper coins by µ-XRF and µ-PIXE/µ-EBS self-consistent analysis, 110170.

The SEM investigation of the metallic core morphology of coin-3 (Fig.12-A) seems smooth and flat with thin strips which may be resulting from the coin manufacture or polishing process. Along the entire surface, there are few cracks and one of them is slightly deeper. The elemental composition of the metal alloy (Fig. 12-B and Table 5) reveals that copper is the main element with low content of silver, tin and lead. The presence of tin 2.49% and lead 2.30% refers to bronze alloy.[1] An area of lead particles appears in light gray, while silver appears in white spots (Fig.12-A).

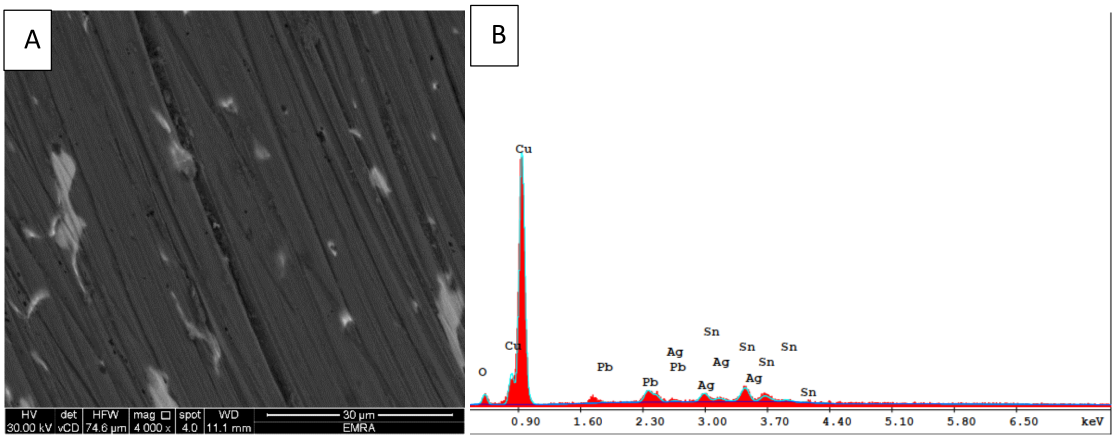

Fig. 12. SEM image of the metallic core of coin-3 (A), and its EDX spectrum (B)

The microscopic examination images (Fig. 13) show that the upper surface of the coin characterizes by different features. It is revealed that the patina presented in some areas is smooth, even, less thick, and in the other most areas, the patina shows an irregular and uneven surface. Also, stratified layers are observed in both sides of the coin surface. SEM observations (Fig.14) show how this coin is strongly corroded, highlighting the secondary patina that its presence is poor overlapping with contamination from soil, which are well represented by a wide range of surface structural formations (deep cracks and crevices, microcrusts, etc.). Deep crack which extends into the inner is usually related to internal stresses in the corrosion layers, or due to the manufacture process. EDX analysis (Fig.15 and Table 5) of the upper surface detects that the soil deposits are mainly consisted of Si with Fe, Al and K as common soil elements.[2]

[1]Van Ham-Meert et al., Sasanian copper and billon coins from the collections of the Royal Museums of Art and History, Brussels, Belgium—insights using semi-quantitative analysis by µXRF, 1-21.
[2]Di Fazio et al., Microstructure and chemical composition of Roman orichalcum coins emitted after the monetary reform of Augustus (23 BC), 5-11.

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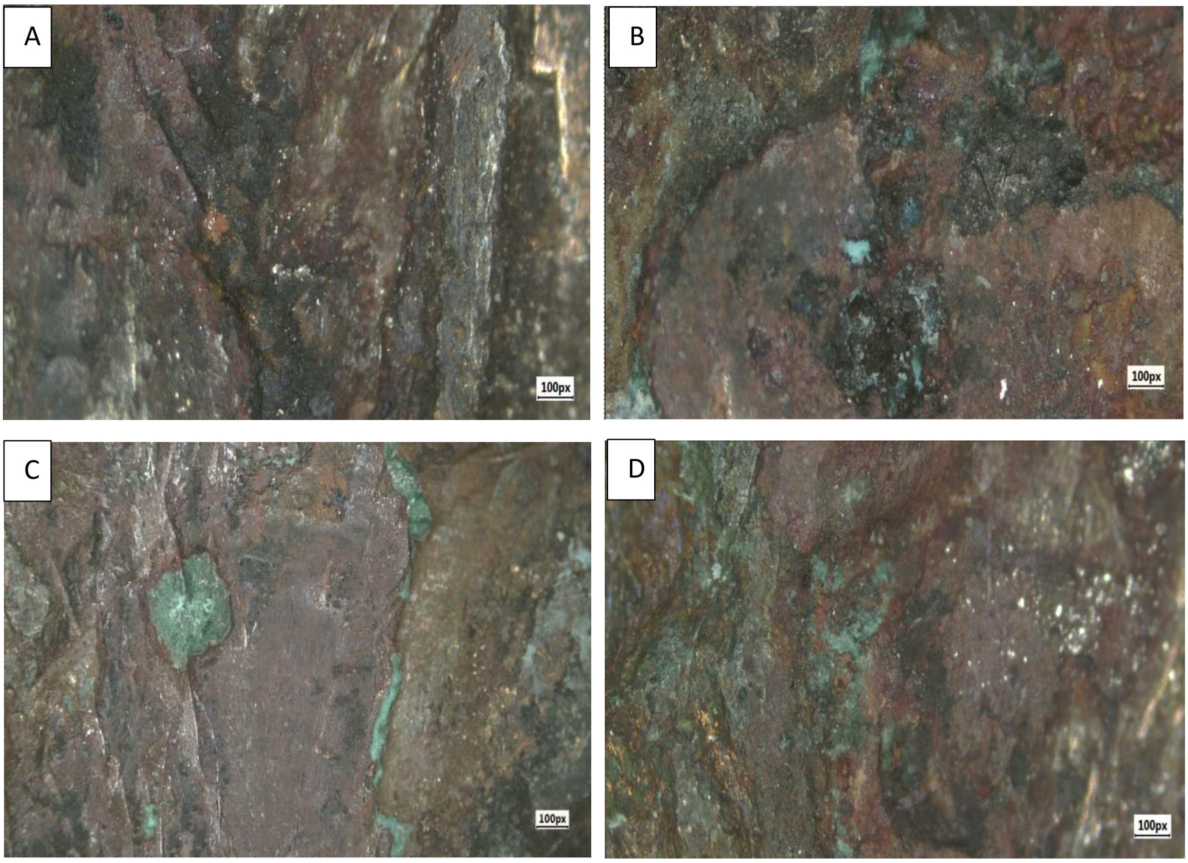

Fig. 13. The surface features of coin-3; the obverse (A), (B) and the reverse (C), (D).

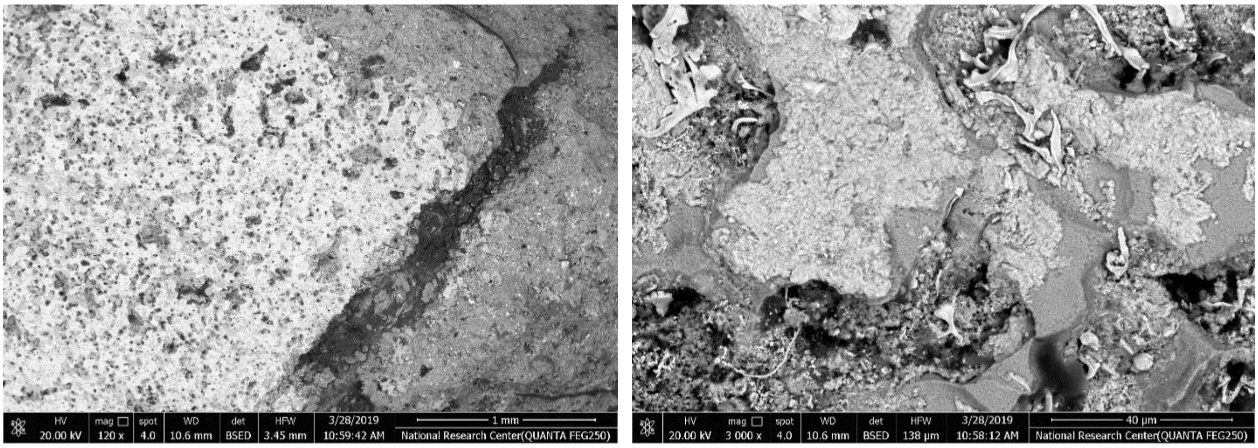

Fig. 14. SEM images of the corrosion products and contamination layer of coin-3

Table 5. Chemical composition of the metallic core and surface of coin-3

Element (wt%)	O	C	Al	Si	Cl	Ag	K	Fe	Cu	Sn	Pb
Metallic core	-	-	-	-	-	4.41	-	-	90.8	2.49	2.30
Surface	26.86	16.86	2.51	22.83	2.14	15.24	2.88	0.98	9.7	-	-

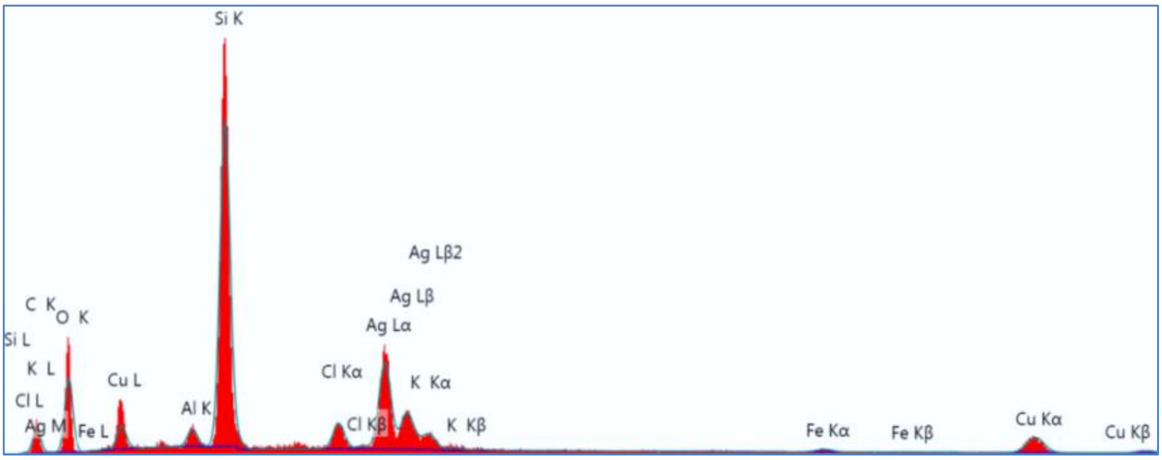

Fig. 15. EDX analysis of the surface of coin-3

EDX analysis results match the results of XRD analysis (Fig. 16) that shows the presence of orthoclase ($KAlSi_3O_8$) as a soil compound. Also, XRD results show cuprite Cu_2O and tenorite CuO, which explains why brown and black are the dominant colors on the coin surface.[1] The basic copper chloride atacamite $Cu_2(OH)_3Cl$ is detected exhibiting secondary corrosion products. Analysis of the corrosion products shows that the coin has bronze disease caused by the corrosive attack by chloride ions coming from the burial soil or the poor storage conditions after its excavation.[2]

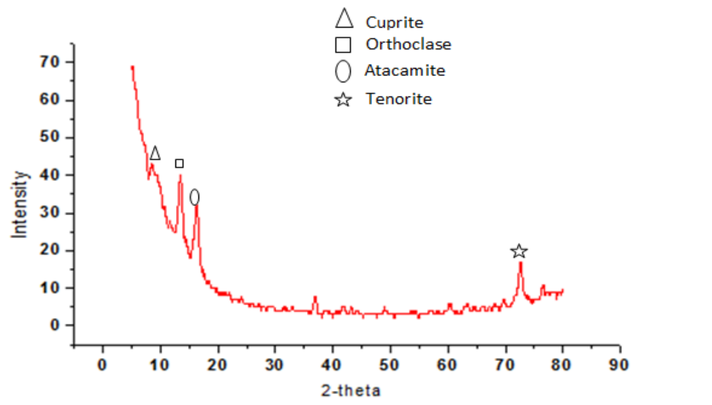

Fig. 16. XRD pattern of the corrosion products of coin-3

[1]Verma and Singh, Microstructural characterization of early Twentieth-Century British period Indian copper coins, 1-9.
[2]Bryan, Copper Alloy Objects Suspected of Bronze Disease: The Burrell 'Bronzes',115-123.

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Metallographic investigation of coin-1 (Fig. 17) shows a hard deformed microstructure. There is no grain boundaries and multiple strained areas. This coin was not subjected to any type of annealing. This coin might be heavily corroded than the other coins. The background is α-Cu where the gray islands are eutectic from (α-Cu +β-Ag+ β-Sn).

Metallographic investigation of coin-2 (Fig. 18) shows cast microstructure, which is slightly visible on the edge of the polished area.[1] The grain boundaries are not clearly obvious. This lead to conclude that this coin was not annealed to mandatory temperature and time. The matrix is α-Cu where the gray islands are eutectic from (α-Cu +β-Ag). Dark holes are attributed to selective corrosion (pitting).

The metallographic investigation of coin-3 (Fig. 19) made from Bronze shows hexagonal grain structure resulted in fully recrystallized and annealing condition. The investigation shows worked and annealed grain structure with variable grain size. Also, dark holes are detected due to pitting corrosion, which is formed at grain boundaries and especially at triple points where three grains are connected. It can also see that the triple eutectic of (Sn-Ag-Pb) are precipitated around grains. Based on the literure,[2-3-4] these features confirmed that this coin was manufactured by cold-working and further annealing that involved casting in the mould to produce a metal piece, placing a blank piece of metal between two dies, and then striking with a hammer with multiple annealing. All the three coins show white spots that refer to silver.

[1]Scott, Metallography and microstructure in ancient and historic metals, 3-6.
[2]Scott, Metallography and microstructure in ancient and historic metals, 6-9.
[3]Salem and Mohamed, "The role of archaeometallurgical characterization of ancient coins in forgery detection, 247-255.
[4]Verma and Singh, Microstructural characterization of early Twentieth-Century British period Indian copper coins, 3-9.

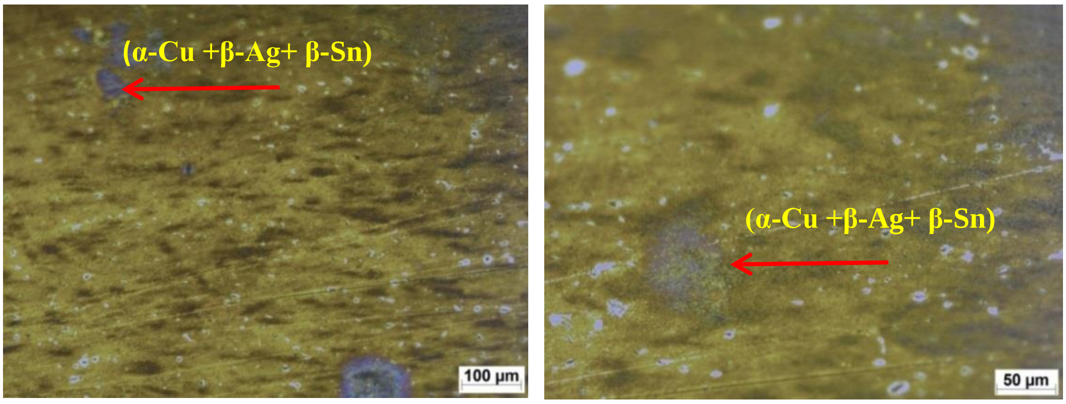

Fig. 17. **Metallographic investigation of coin-1 show the deformed structure**

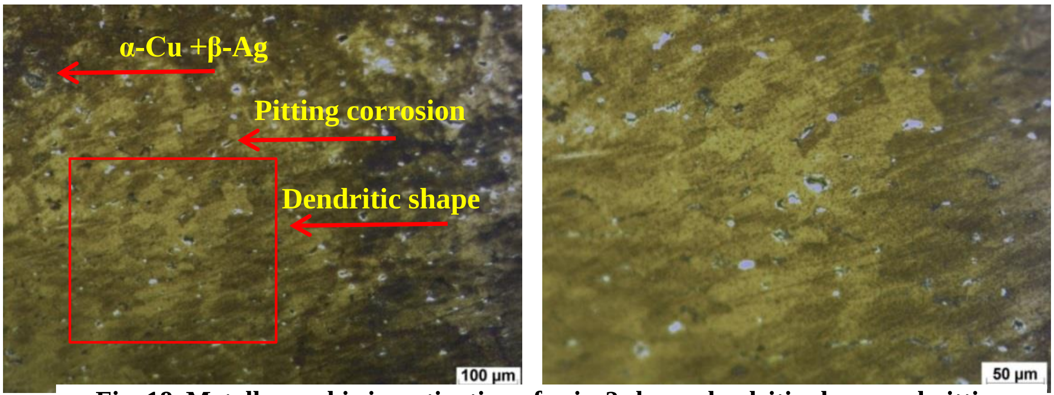

Fig. 18. Metallographic investigation of coin-2 shows dendritic shape and pitting corrosion

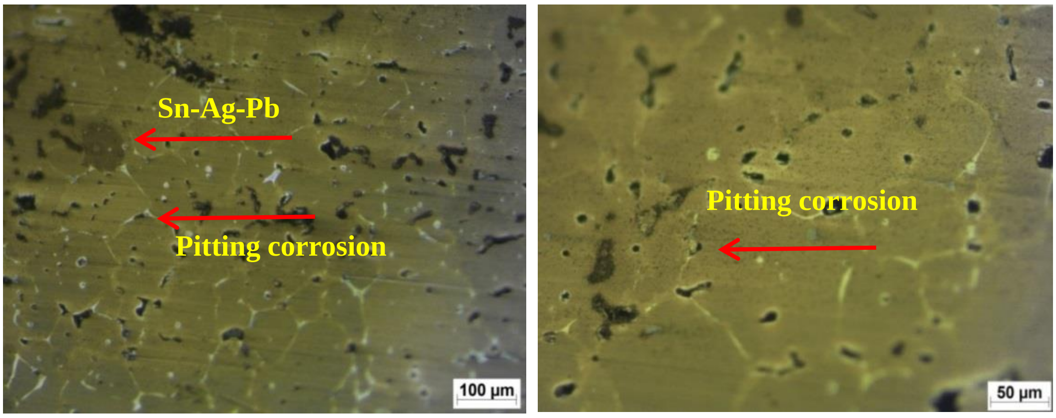

Fig. 19. Metallographic investigation of coin-3 shows hexagonal grain structure and pitting corrosion

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4. CONCLUSION

Three ancient Roman coins selected for investigation and analysis in the present paper were excavated from Al Sheikh Zuweid, Sinai city. Archaeometallurgical characterization of the coins, in question, included a detailed investigation of the chemical composition and microstructure of the metallic core and the identification of the corrosion products. The study was carried out with a combination of investigation techniques consisting of stereo microscopy, optical microscope, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) and X-ray diffraction (XRD). In the present study, the state of degradation of two coins of the three examined is similar. That is, the two coins are covered with thin brown and black corrosion layers, which hide some inscriptions. The third coin, on the other hand, is covered with an alteration layer that consists of corrosion products overlapping with soil particle which formed a hard encrustation that covered all surface details.

The SEM-EDX measurements provide an identification of the chemical composition of the metal bulk of the coins as well as an indication of the composition of the corrosion and soil constituents. The results of the chemical analysis indicate that copper is the major element of the three coins with small proportion of silver. The presence of tin in the composition of coin-1 and coin-3 refers to bronze alloy with the presence of lead, while coin-2 is made from copper-silver alloy.

The microscopic investigation allows the identification of the surface of the three coins. The morphological features present on coin-1 and coin-3 are similar, since uniform corrosion is observed with localized corrosion. The two coins exhibit the initial oxide layer of copper which appeared even and sometimes irregular with green active corrosion spots rich in common soil elements such as Si, Al, Na, Mg and Fe. While coin-2 is characterized by being covered with corrosion products overlapping with soil elements formed a hard encrustation.

XRD analysis is used to determine the exact corrosion products. The results demonstrated the nature of copper corrosion products that mainly consists of cuprite and tenorite. Also, the results showed the presence of copper hydroxychlorides presented in paratacmite and atacamite. The presence of copper hydroxychlorides indicates bronze disease which appears clearly in green powder.

The soil has a significant effect on the outer layer of coin-2 that is confirmed by the hard encrustation. High amounts of silica indicate sand (SiO_2) which represents the concretion covering the coin surface together with corrosion products forming the patina. All analysis results refer to the type of saline sand soil which has active ions of Cl. The results match the normal patterns of patinas present in buried archaeological coins made of copper-based alloys. Because all the coins in this study have a small proportion of silver, the analysis results show silver sulfide (Argentite -Ag_2S) in coin-1.

The metallographic investigations of the three coins show the microstructure transformation resulted from the coin production, taking into account the manufacturing conditions and methods in the past. Coin-2 shows cast microstructure presented in the appearance of the dendritic shape. While coin-3 shows clearly hexagonal grain structure resulted in fully recrystallized and annealing condition and the investigation shows the worked and annealed grain structure with variable grain size. These features confirm that the coin in question was manufactured by cold-working and further annealing. Metallographic investigation of coin-1 showed hard deformed microstructure. The result was that this coin was more corroded than others.

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