

## A CHARACTERIZATION OF COINS FROM THE NAJRAN HOARD, SAUDI ARABIA, PRIOR TO CONSERVATION

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### *Abstract*

*This paper presents the results of scientific examinations and analyses carried out on the archaeological coins discovered in Najran, Saudi Arabia. Optical microscopy (OM), scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) and X-ray diffraction (XRD) were used to investigate morphological corrosion features, to clear the nature of the patina and to analyze the elementary composition. Morphologically, it was revealed that there are reniform, coral reef and dendritic shapes of corrosion products and heterogeneous multicolor patina on the studied coins surfaces. It was proven that those coins were made of a silver-copper alloy and were covered by three superficial corrosion layers. The main composition of the coin corrosion compounds was identified as copper carbonate, copper chloride, copper silicates, silver chlorides and silver sulphide. The proposed corrosion mechanism revealed that those coins were characterized by heavy degradation phenomena, induced by corrosive species and soil contaminants. The corrosion processes led to the depletion of copper and the enrichment of silver near the surface, as compared to the core composition. This study provides useful information for the conservation and preservation of the Najran hoard coins.*

**Keywords:** *Najran; Patina; Coins; SEM-EDS; XRD; Corrosion; Silver-copper alloy; Enrichment.*

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### **Introduction**

Coins are objects of great value not only to the historians, but also to numismatists, economists, metallurgists and conservators. Most of the ancient coins are often subjected to various corrosion processes resulting in different corrosion crust products that gradually alter their aspect, shape, nature and resistance, up to a stage where it is impossible to use them as historical evidence of human civilizations, or even up to the complete destruction of the items [1]. A study of the corrosion features and the effects thereof on archaeological coins is greatly important to clarify the corrosive media and the corrosion processes. Such kind of studies helps in selecting the conservation methods, which makes it significant for both corrosion science and the preservation of archaeological objects. Many scientists [2-12] used different analytical methods in this field, to investigate the morphology, structure and nature of the patina, or of the corrosion products on archaeological metallic objects and coins. Those studies concentrated on finding a relationship between the surrounding environment, where they were formed, and their micro-chemical structure.

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This work is the first part of a project aiming to perform the conservation and authentication of the archaeological coins of a hoard discovered in Najran, south of Saudi Arabia. The authors focused on the examination of the surface of the four selected coins and a cross-section of a fragmented coin, representing all the categories of the hoard's coins degradation. The aims of this study are to characterize the corrosion features and the surface morphology of the selected coins and to explore the nature of the patina. Moreover, this study aims to understand the chemical composition of the coins, the elements and their distribution on the surface of the selected coins and on the cross section of the fragmented coin. The corrosion mechanism of these coins was studied, in order to understand their degradation, which will help choose the correct strategy for their conservation. To achieve these aims, we used optical microscopy (OM), scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS), and X-ray diffraction (XRD).

### *Description of the studied Coins*

The studied coins were found covered with a layer of corrosion products, resulted from the degradation that occurred during their long-term underground stay. Their aspect was so distorted that no detail of the original surface could be retrieved. That layer had a nearly composite structure, including metallic remains, mineralized, metallic, insoluble phases and products formed from the interaction between soil components and metal corrosion compounds and also soil particles. The four selected coins represented in Fig. 1, have diameter ranges from 1.3 to 1.5 cm. Coin 1 is covered with a heterogeneous thick crust of different colors and corrosion products coexisted with soil particles. Coin 2 is covered mainly with a dark green, compact patina, as a uniform corrosion crust. Coin 3 is covered with a thin, light greenish layer that has some random spots of greenish-blue corrosion products. Coin 4 is covered with a layer of green corrosion products and whitish, gray or dark gray to brown patina as spots in some areas.



Fig. 1. The selected four coins from the Najran hoard.

### **Experimental part**

Microscopic investigations were carried out by using a Smart-Eye USB Digital Microscope at various magnifications, up to a maximum of 170x fixed magnification, in order to characterize the morphological features of the corrosion products and to explore the nature of the patina.

Scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS), was used to investigate the surface and the metallic core and to detect the distribution of the chemical elements on the corrosion layer and in the core. SEM micrographs and EDS spectra of the selected coins were obtained by using a JEOL/EO, JSM-6380 device, equipped with an EDS link operating up to an accelerating voltage of 20 kV and a working distance of 9 mm. XRD analysis was used to identify the corrosion products and to understand the corrosion mechanism.

The corrosion products analysis was performed with an Ultima IV, multipurpose X-ray diffraction system equipped with a copper anticathode. The measuring conditions were set as

follows: Cu target, 40 kV accelerating voltage, 40 mA current, the scanning range of  $2\theta$  was from 5 to 70° and the scanning speed was 2°/min.

## Results and Discussions

### *Patina Features and Corrosion Characteristics*

Optical microscope observations were primarily carried out without any preparation in order to keep the surface intact. It was revealed that coin 1 presented a rough corrosive surface with cracks and pits. It had multicolor areas of dark green, light green, greenish blue and metallic gray blackish surface covered with soil residues (Fig. 2a). In some parts, there was a green corrosion layer, resembling coral reefs full of pores and cavities (Fig. 2b). The dark green patina on coin 2 was composed of circular grains with different sizes that took a reniform shape (Fig. 3). The surface of coin 3 was covered with an irregular, light green corrosion layer, with little spots of bluish corrosion products and areas of dark gray to blackish and brown patina (Fig. 4). On the fourth coin, the light green layer appeared loose and porous, and took a dendritic shape (Fig. 5a), while the patina of the original surface appeared as gray to blackish areas, and silvery areas (Fig. 5b). The examination of the cross-section sample, represented in figure 6a and schematically represented in figure 6b, showed three irregular layers of corrosion products upon a very thin, adhered, silver layer. The first layer was beneath a thin greenish layer, followed by another internal gray to blackish layer, that had lustrous grains and an external thick layer. This last layer was a loose or compact, green layer, that surely coexisted with soil residues.



**Fig. 2.** (a) Optical observation of coin 1, multicolor areas, 65X, (b) Coral reef-shaped corrosion product, 170X.



**Fig. 3.** Optical observation of reniform shape on coin 2, 120X.



**Fig. 4.** Optical observation of light green corrosion product associated with bluish spots on coin 3, 150X.

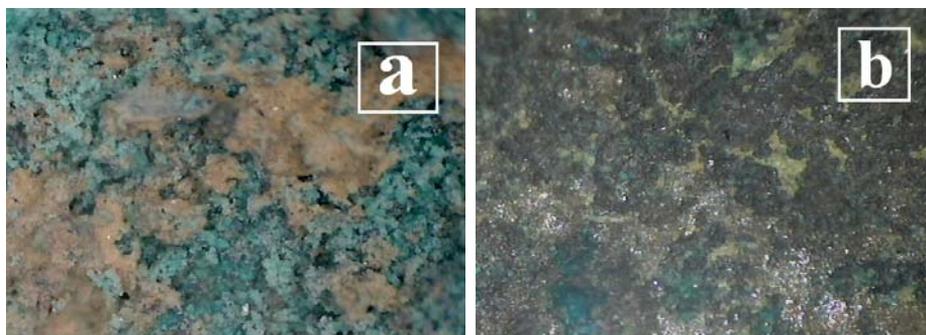


Fig. 5. (a) Optical observation of coin 4, dendritic green corrosion product, 120x, (b) Gray blackish patina, 170X.

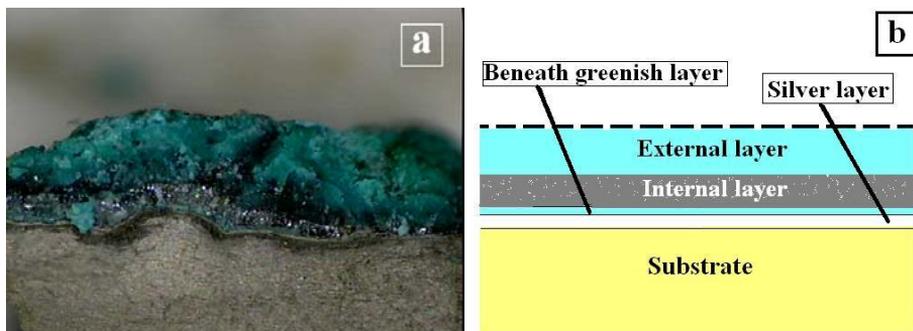


Fig. 6. (a) The optical observation of the corrosion on the cross section sample, 170X. (b) Schematic representation of the corrosion layer

**Chemical Composition**

The chemical composition of the studied coins, detected by our SEM-EDS investigations and analyses are represented in Table 1 and in Figures 7-10.

Table 1. The elemental composition (wt.%) of the studied coins surfaces.

Coin	Ag	Cu	C	O	Cl	S	Ca	Si	Al	Mg
Coin 1	1.37	47.58	30.09	14.97	1.04	-	3.43	0.68	0.83	-
Coin 2	1.52	67.44	8.69	18.99	0.83	-	1.30	1.21	-	-
Coin 3	19.45	25.25	20.02	14.43	7.64	-	8.48	3.02	-	1.71
Coin4	63.01	0.23	9.14	5.22	22.08	0.33	-	-	-	-

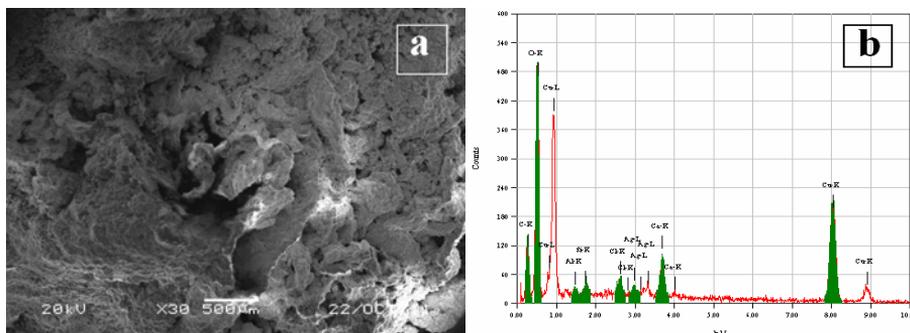


Fig. 7. SEM image of the surface of coin 1 (a), and its EDS spectrum (b).

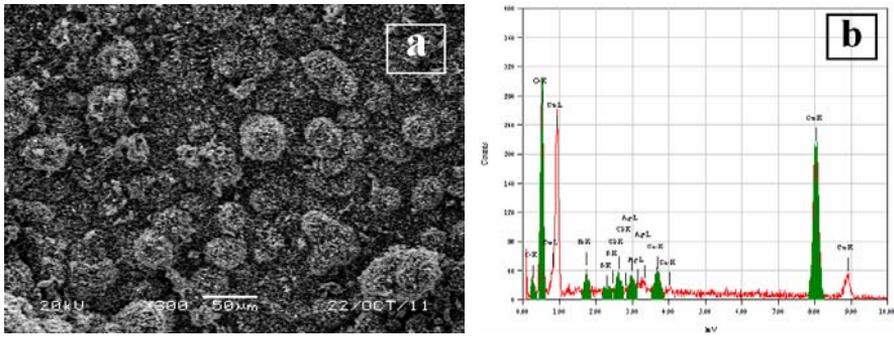


Fig. 8. SEM image of the surface of coin 2 (a), and Its EDS spectrum (b).

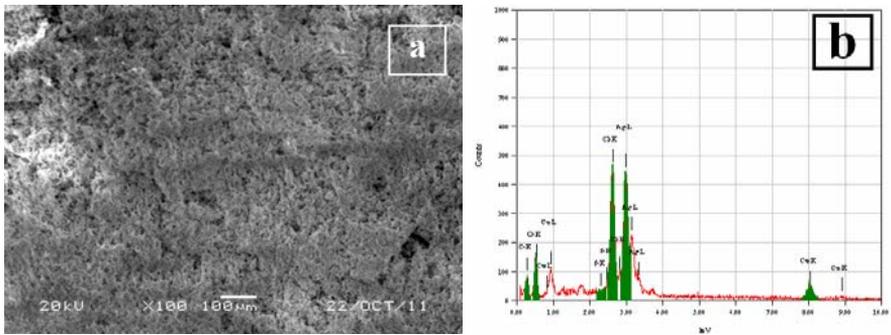


Fig. 9. SEM image of the surface of coin 4 (a), and its EDS spectrum (b)

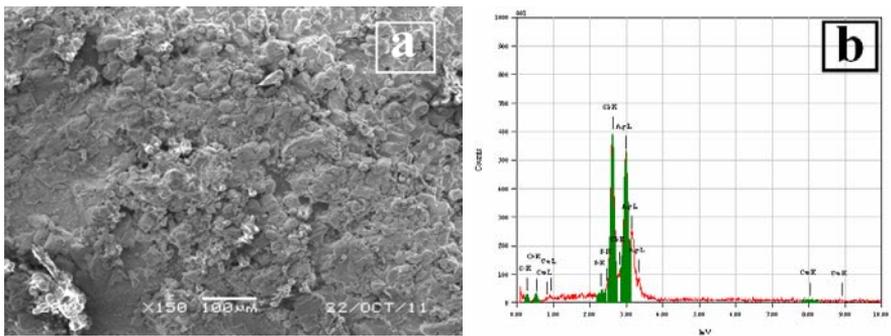


Fig. 10. SEM image of the silvery areas on the surface of coin 4 (a), and its spectrum (b).

The SEM observations clarified many features of the coins surface morphology. Some of those features were detected before, by optical microscopy. Coral-reef shaped corrosion products were observed on the surface of coin 1 (Fig. 7a).

Reniform-shaped corrosion products on coin 2 (Fig. 8a), the dendritic corrosion products on coin 4 (Fig. 9a), and the gray to silvery areas on the same coin (Fig.10a) all were observed.

From the EDS results we deduced that copper and silver were the two major metals detected on the four coins surfaces. Copper contents were high, while high silver contents were found in coin 4 and coin 3. The high concentration of silver predominated in the dark gray patina areas and in the original surface that was observed by optical microscopy. Carbon and oxygen were detected as minor elements. The percentages of the corrosive elements S and Cl vary from one coin to another, but Cl was detected in a considerable amount, especially on the surface of coin 4. The other elements, Si, Ca, Al, and Mg were detected in small weight

percentages that come most likely from the burial soil. We concluded that the coins were made of a silver-copper alloy, covered with their corrosion compounds, especially carbonates, chlorides, silicates and some sulphides, as a result of the interaction between those two metals, or their primary corrosion compounds and the soil components.

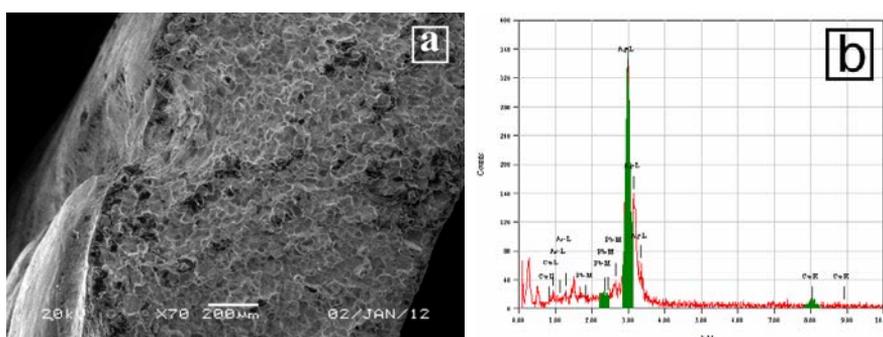
For the investigation and analysis of the metallic core and the original surface of the fragmented coin, we cleaned it chemically with an alkaline Rochelle solution, followed by formic acid solution 10%, washed with instilled water and dried it with acetone [13-15]. The results of our SEM observations and EDS analyses are represented in figures 11-13 and in Table 2. The metallic core was observed in a grainy form, covered with a thin superficial layer (Fig. 11a). The original two surfaces of the fragmented coin had some pores that, most probably, represented corrosion pits.

EDS results indicated that the coin substrate, or the metallic core was constituted of a binary copper-silver alloy, as silver was the major element and copper the minor, whereas the superficial layer was pure silver (table 2 and figures 11b, 12b and 13b).

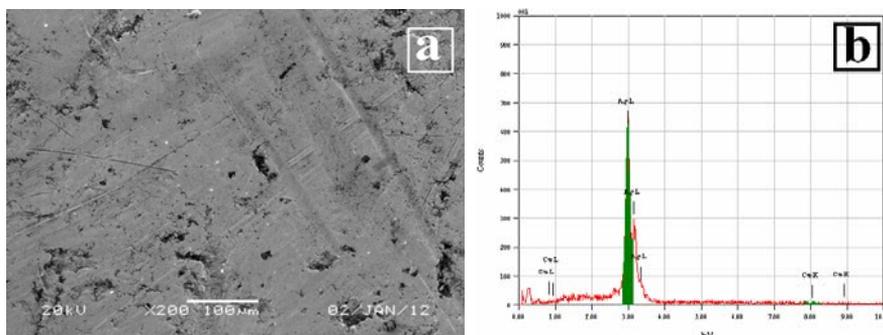
**Table 2.** The elemental composition (wt.%) of the fragmented coin

The fragmented coin	Ag	Cu	Pb	As
Metallic core	89.41	8.10	1.36	1.12
Face 1	100	-	-	-
Face 2	99.67	0.33	-	-

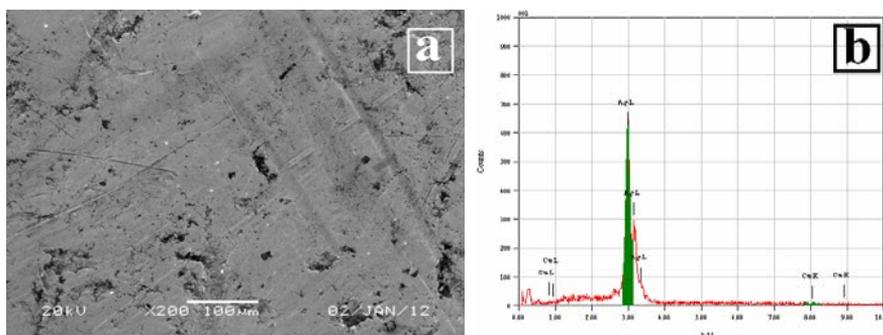
The weight percentage values of the elements on the corrosion layers, identified by EDS, revealed a lower grade of silver than that of the substrate. Additionally, a high content of Cu was present on the corroded areas, in comparison with the one identified in the core. The diffusion of copper particles to the surface occurred due to the tendency of copper to dissolve to the corrosion layers. The silver content increases from the metallic core, to be 100% on the surface, but decreases in the corrosion layers. This superficial silver-rich layer proves that the silver surface was enriched, as usually observed on ancient silver-copper coins, consisting of a silver matrix with less copper content. This phenomenon resulted from the selective depletion or the leaching of copper from the surface to form corrosion products, which resulted in a thin layer of pure silver. In addition to this preferential removal (corrosion) of copper, surface depletion is likely to occur, because copper and silver are only slightly soluble in one another at room temperature [16], or because of their segregation during casting or annealing, by deliberate thermal wearing [2].



**Fig. 11.** (a) SEM image of the cross section sample covered with a thin superficial layer, (b) EDS spectrum of the metallic core.



**Fig. 12.** SEM image of the first face of the fragmented coin (a), and its EDS spectrum (b).



**Fig. 13.** SEM image of the second face of the fragmented coin (a), and its EDS spectrum(b).

### *The Nature of the Patina*

The studied coins surfaces were carefully scraped with a small spatula, to collect the fine patina particles for our X-Ray diffraction analysis. The results for that fine powder are shown in figure 14. The hard crust and the multicolored patina on coin 1 consists mainly of malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), chrysocolla ( $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ ), atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), in addition to paratacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), and cerargyrite ( $\text{AgCl}$ ) (Fig. 14a). The main component of the compact, dark green patina on coin 2 is malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), associated with atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) in minor quantity and nantokite ( $\text{CuCl}$ ), cuprite ( $\text{Cu}_2\text{O}$ ), and traces of metallic silver ( $\text{Ag}$ ) (Fig. 14b). The major compound of the light green patina of coin 3 is paratacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), which coexists with little amounts of malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), chrysocolla ( $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ ) and metallic copper ( $\text{Cu}$ ) (Fig. 14c). The multicolor and greenish patina coexist with soil residues on coin 4 and contain malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), bromyrite ( $\text{AgBr}$ ), paratacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), chrysocolla ( $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ ), quartz ( $\alpha\text{SiO}_2$ ), dipotase ( $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ ) and calcite ( $\text{CaCO}_3$ ) (Fig. 14d). The whitish to dark gray patina on some areas represents metallic silver ( $\text{Ag}$ ) as the major component, besides argentite ( $\alpha\text{Ag}_2\text{S}$ ), cerargyrite ( $\text{AgCl}$ ) and traces of paratacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) (Fig. 14e).

These results are in a good conformity with the EDS results. The spectra are characterized by the presence of corrosion species, such as Cl, S, and soil species, such as C and Si. Extremely fine deposits of copper carbonates, copper and silver chlorides, silver sulphide and copper silicates were revealed by XRD analysis. The data we obtained revealed the composition of the patina and the superficial composition of the alloy. We deduced that the coins were made mainly of an Ag-Cu alloy, which has undergone chemical alterations that resulted in the formation of the identified corrosion compounds.

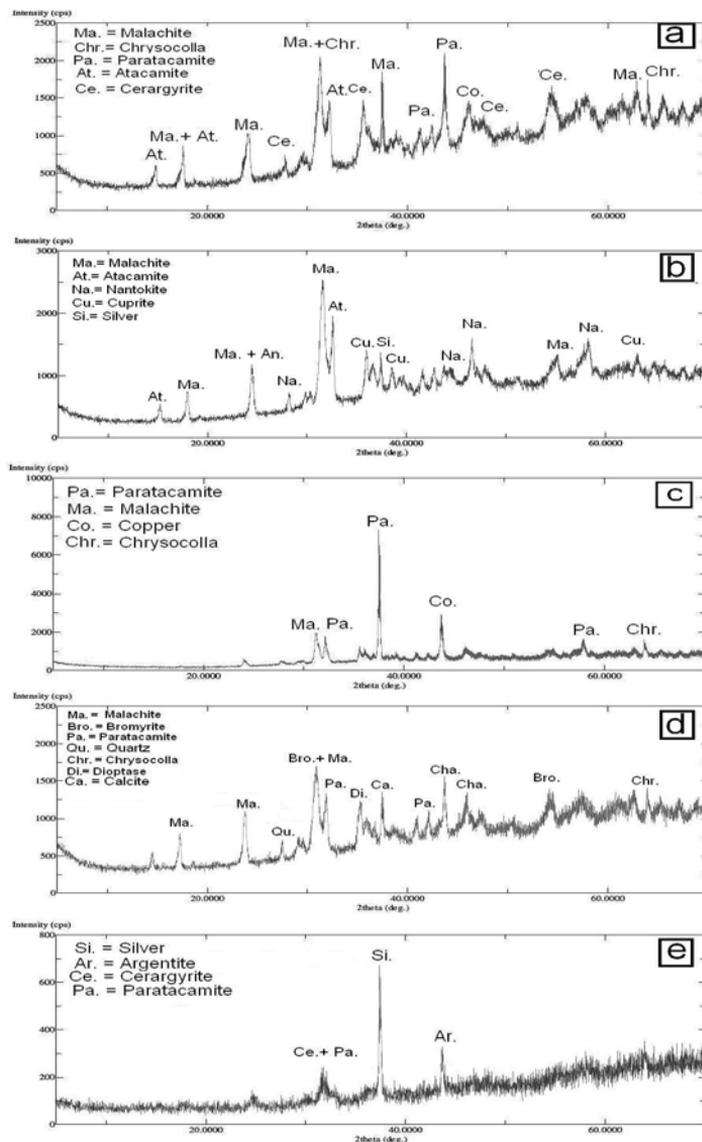


Fig. 14. X-ray patterns of the corrosion products on the studied four coins surfaces, coin 1 (a), coin 2 (b), coin 3 (c), and coin 4 (d and e).

**Proposed Corrosion Mechanism**

Our surface analysis data guided us to conclude that the burial soil was a sandy calcareous soil, as quartz and calcite were detected by XRD analysis. That soil was mixed with organic components and was rich in water, oxygen and carbon dioxide. The investigated coins were made of a silver-copper alloy. Copper in such alloys corrodes preferentially to silver and deposits typical corrosion products both on the surface and between the silver grains. In acidic conditions, where the copper corrosion products are dissolved away, the remaining silver will probably be blackened [17].

The proposed corrosion mechanism for those coins began, most likely, with the leaching out of copper ions from the alloy substrate into the surface layer. That selective depletion of copper, associated with the enrichment of silver on the coin surfaces, happened as a result of the corrosive attack of the surrounded soil ions, or because of the galvanic corrosion with copper acting as the anode and silver as the cathode. In the later case, the less noble component, copper, is more reactive

and copper oxide may be formed, increasing the volume, which may then lead to the migration and diffusion of metallic components. Thus, silver atoms may concentrate in the surface layer of the coin [18].

Cuprous oxide, cuprite, was the first copper corrosion product formed on the coins surfaces, most likely after minting, or in a period prior to their burial, as a result of oxidation. If that was not the case, the oxygen in the soil would soon provide such a layer. The red, cuprous oxide layer, which was adhered to the metal core, usually covered with the other Cu(II) salts. When a coin stays buried in soil for a long time, water, carbon dioxide and chloride ions are the three keys for its corrosion. The porosity of the oxidized compound formed on the coin surface provides the possibility for water movement and other corrosive ions activities, such as that of Cl, O, S, and other ions. Oxygen, carbon dioxide and water were mainly responsible for local cell activity leading to the formation of malachite, which was identified as the main corrosion compound on the coins surfaces. Chloride ions, from the soluble chlorides salts in the soil, may have migrated through the oxide film, stimulating corrosion and forming a greenish compound of nantokite, adjacent to the original metal surface and covered with the other corrosion products. This is most probably found beneath the thin greenish layer that was observed by optical microscopy (Fig. 6). In contact with water, nantokite reacts to produce basic copper chlorides, atacamite and paratacamite [19].

Soluble chlorides, in the presence of copper or its salts from the silver-copper alloy, corrode silver severely, producing cerargyrite (AgCl) [15].

The produced cerargyrite is a very insoluble dark gray compound. Its presence is usually associated with the brown opaque silver bromyrite (AgBr), found in the corrosion compounds of archaeological coins found in deposits rich in organic matter [17].

The blue-green copper silicate, chrysocolla and the vitreous, green to emerald-green dipotase ( $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ ) are resulted from the reaction between copper and silicon dioxide, the main constituent of sandy soils, in the presence of water. In the presence of sulphides, coins are usually attacked, as the contact between the silver cations and the sulphide ions results in forming the blackish, iridescent, silver sulphide, argentite ( $\text{Ag}_2\text{S}$ ) [15].

### Conclusions

The morphological features of the patina were characterized by rough, dendritic, multicolor, reniform and coral-reef shaped features.

The OM observations revealed the stratification of the corrosion products formed after burial and they were based on complex, chemical reaction processes, with cumulative effects.

The corrosion products identified on the coins surfaces resulted from a series of reactions between metallic constituents and soil species that produced precipitations of relatively insoluble corrosion products. The nature of the patina consisted partly of malachite that was the main corrosion product on the tight, dark green surface, while paratacamite was the main component of the light green surface. Cerargyrite, argentite, bromyrite, associated with silver, were the main components of the whitish, dark gray to blackish brown patina.

The analysis results in this work have shown that the coins in the Najran hoard were made of a silver-copper alloy. Silver was detected as the major metal compound in the coin cores, whereas copper was found a high amounts in the corrosion layers.

The elemental distribution indicates the depletion of copper and the enrichment of silver, the phenomenon that usually occurs with archaeological coins made of silver-copper alloys. To conclude, chemical cleaning is a good conservation strategy for removing corrosion products and disclosing the original surface details of coins, without harming the artifacts.

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