

Microchemical Investigation and Conservation of a Lion Figurine and Two Coins from Al-Kheraibah Excavation, Saudi Arabia

Abdulnaser Al-Zahrani & Mohamed Ghoniem

Abstract: A bronze lion figurine and two coins were discovered at the archaeological site of Al-Kheraibah located within Al-‘Ula in northwestern Saudi Arabia during the excavation seasons 2005 and 2012. They were heavily deteriorating and were completely covered with corrosion output mixed with hardened soil and dirt calcification to such a point that no detail of the original surface could be observed. They needed to be investigated and conserved to understand their surface details.

They have been investigated to analyze the chemical composition, and to identify the nature and features of the corrosion layer. Physical, chemical, and structural characterization was performed using Optical Microscopy (OM), X-ray Radiography, X-ray diffractometry (XRD) and Scanning Electron Microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). The nature of the patina was detected by SEM and OM. The surfaces of the objects were covered with a multicolored patina that incorporated or was covered with soil particles, and had many micro-cracks, pits and cavities. EDS and XRD analyses revealed that these objects are made of a Cu-Sn-Pb bronze alloy. They have been buried a long time in sandy soil that allows movement of oxygen and water charged with chloride ions and carbon dioxide, thus contributing to their corrosion. Treatment, inhibition and conservation procedures were carried out to protect the objects against further deterioration.

1. Introduction

Archaeological metals buried in ground for centuries are usually covered with corrosion products and soil particles. The corroded layer arises from the interaction between soil components and the metal relics, or from complex interactions with metal corrosion

compounds during long-term burial. Knowledge of archaeological objects (their structure and the chemical composition of the corrosion products) is important to identifying the origin of degradation, its relation to the archaeological environment, and to selecting the suitable treatment and conservation procedures.

Optical microscopy (OM), Scanning electron microscopy (SEM), X-ray diffractometry (XRD) and energy dispersive spectrometry (EDS) have been used to investigate the structure and composition of the corrosion products, their metallurgical features and their elemental composition and distribution (Cura et al., 2007; Ingo et al., 2004; Mantler et al., Robbiola et al., 1998; 1992; Sandu et al., 2004; Schreiner et al., 2004; Schreiner et al., 2007; Spoto and Giliberto, 2000; Stuart, 2007; Velraj et al., 2010). Such methods are of great importance for scientists and conservators; they help experts to understand corrosion mechanisms and the micro-chemical structure of the original metal composition before undertaking conservation actions. In the present work, investigation and micro-chemical surface analyses were focused on a bronze lion figurine and two coins discovered at the archaeological site of Al-Kheraibah located in Al-‘Ula in northwestern Saudi Arabia. It was the southernmost part of

the Nabatean kingdom and, after Petra, the largest capital of the Lihyanite kingdom. The majority of the vestiges date from 1st century AH. Isolated mud-walls with stone foundations, beads, pots, metals, as well as ancient coins and various kinds of potteries were found.

The lion figurine(1) (Find # 65) is 3 cm long, 2 cm high and weighs 24 g (Fig. 1A). It was completely covered with green to greenish blue corrosion layer covered with an outer cracked layer of adhering soil.

The first coin,(2) ("Coin 1"; Find # 1003), has a diameter of 1.6 cm, an irregular oval shape, and weighs 8 g. It is almost completely covered with a thin layer of light to dark green corrosion product incorporated with soil particles on both sides (Fig. 1B).

The second coin(3) ("Coin 2"; Find # 150) has a 2 cm diameter and has an irregular quasi-circular shape; it weighs 7 g. It too is covered with a non-uniform layer of light green corrosion product and soil residues with a small area of bare metal surface (Fig. 1C).

The lion figurine and the two coins were discovered in the same place; therefore, they most likely have been exposed to the same burial conditions and same corrosive factors. Their investigation will help identify the effects of corrosion on these objects, as opposed to differences in manufacturing and composition.

The present work aims to characterize the corrosion features, identify the chemical composition and distribution of the corrosion products, and treat and protect the objects against further corrosion. Before applying restoration or preservation procedures, the chemical composition of the objects must be established to help understand their deterioration mechanism. This is done by means of optical microscopy (OM), scanning electron microscopy (SEM) equipped with energy dispersive spectrometry

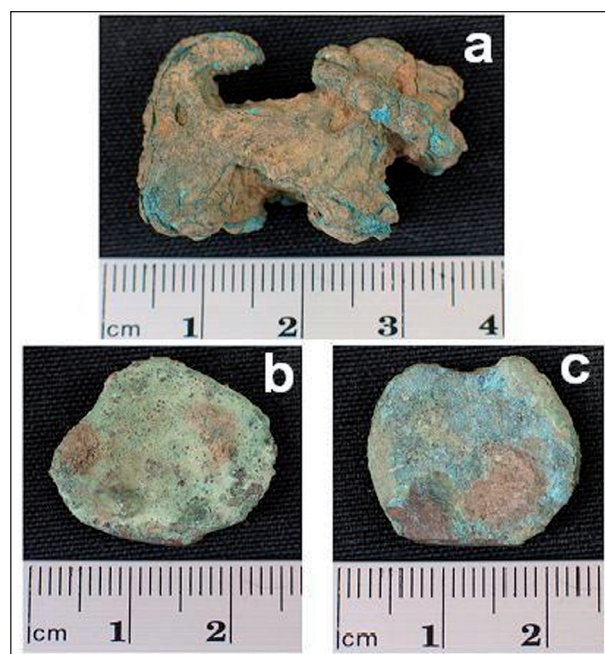


Fig. 2. The lion figurine (A) and the two coins (B and C) covered with dull corrosion products layer incorporateExperimental with soil material.

(EDS) and X-ray diffractometry (XRD). This approach is expected to be significant for understanding corrosion processes and preservation of archaeological metal objects.

2. Experimental

Analytical techniques have been applied to provide specific information about the features and composition of the corrosion layer, and the composition of the original cleaned metal.

The characteristics of the corrosion products on the objects were identified by using a Smart-Eye™ USB Wireless Microscope with adjustable focus and Magnification from 10X-200X.

Radiographic investigation was conducted to evaluate the structural homogeneity of the objects and to help reveal corrosion areas. The exposure conditions were: tension 74 kV; anodic current 5 mA; exposure time 300s.

The structural identification of corrosion compounds was determined by using Ultima

IV X-ray diffractometry provided with copper anticathode. The measuring conditions were: Cu target, 40 kV accelerating voltage, 40 mA current, and the scanning range of 2θ was from 5 to 70° and the scanning speed was $2^\circ/\text{min}$.

A JEOL/EO, JSM-6380 LA scanning electron microscope equipped with an Energy Dispersive Spectrometer (EDS Link Analytical) was used to inspect the features of the patina, the clean original surface of the object, and the chemical composition. The operation procedures of SEM were an accelerating voltage of 0.3 to 30 kV. Energy dispersive spectrometry (EDS) was used in order to study the spatial distribution of major and trace elements composition in the corrosion layer and in the cleaned original surfaces. This analysis was performed with a live time of 100s, a pulse-counting rate of about 4000 cps, a working distance of 23 mm and an accelerating voltage of 20kV.3. Results and Discussion

3.1. The Corrosion Characteristics

The lion figurine is thoroughly covered by corrosion products and soil residues. Two layers of deposits could be characterized; an outermost layer of soil material, with many micro-cracks, holes and cavities, and an inner layer of powdery bluish green corrosion compounds between the outermost layer and the original surface (Fig. 2a and b). These micro-cracks in the outermost layer are attributed either to internal stresses in the corrosion layer, or the long-time corrosion caused by the periodic hydration and dehydration in soil. In normal circumstances, the extension of the internal layer would be accompanied by the incorporation of corrosion species (He et al., 2011: 206).

The surface of coin 1 is covered with a thin, rough and compact light green patina that incorporated soil granules (Fig.3a and b). The surface of coin 2 is covered with a light-dark

green and gray-blackish patina characterized by multicolor areas interwoven with soil residues that have many pits and microscopic non-interconnected fissures (Fig. 4a and b).

Radiography for the three objects indicated that the lion figurine was made via a solid cast technique, and has a layer of thick corrosion products covering its core, looking soft and has many cracks and fissures (Fig. 5 a). The two coins have an outer layer of corrosion products that are thick on the edges, lacking the circular shape of coins (Fig. 5 b and c).

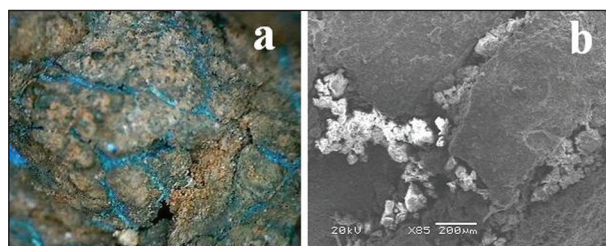


Fig. 2. OM image, 65X (a) and SEM image of 2mm across, 85X (b) of the outer layer on the lion figurine that has many micro-cracks and cavities.

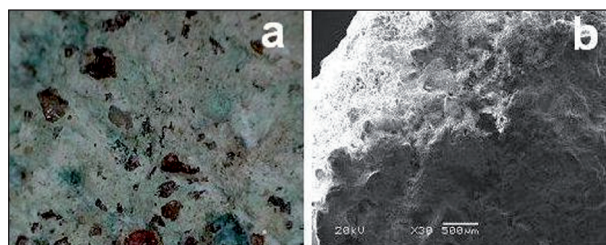


Fig. 3. OM image, 65X (a) and SEM image, 30X (b), of the rough compact light green corrosion layer incorporated with soil granules on the surface of coin 1.

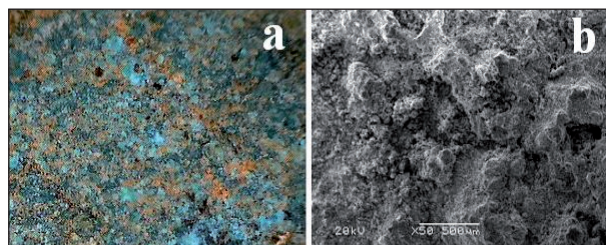


Fig. 4. OM image, 65X (a) and SEM image, 50X (b) of the multicolored layer interweaved with soil residues, many pits and microscopic non-interconnected fissures on the surface of coin 2.

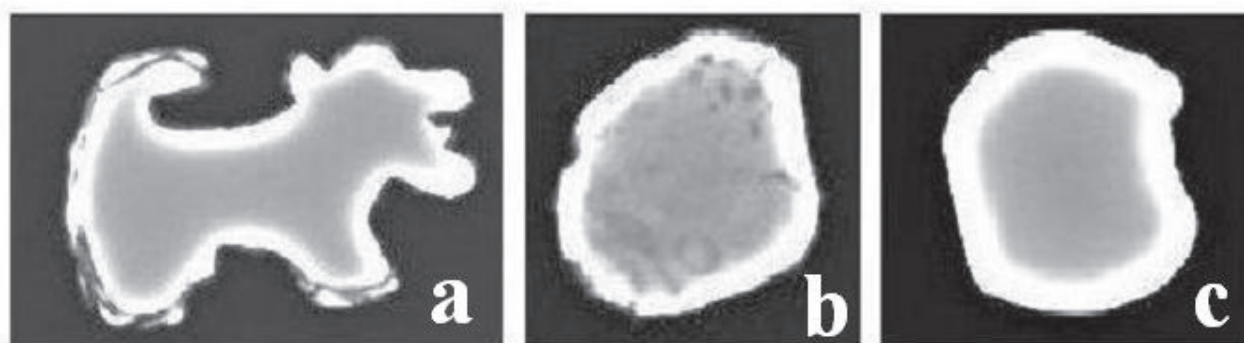


Fig. 5. X-ray radiography for the lion figurine (a), Coin 1 (b) and Coin 2 (c).

3.2. The Chemical Compositing of the Corrosion Layers

The detailed elemental chemical compositing of the corrosion layers on the lion figurine and the two coins was characterized by EDS analysis (Fig.6 and Table 1). Many chemical elements were detected on the outermost layer of the lion figurine's surface. C, O, Cu, and Si were found in high weight percentages while Al, Cl, K, Ca and Fe were in small weight percentages. This microanalysis shows that this layer must have been formed by a mixture of soil quartz, and metal corrosion compounds of copper such as chlorides and oxides, all of which were confirmed by XRD analysis in this paper (Figs 8-11. Table 2).

The outer layer of the lion figurine consisted of the major (>5 wt%) elements C, O, Si, and Cu, with the minor (0.1-5 wt%) elements Al, Cl, K, Ca and Fe (Table 1. Fig. 6a). In contrast, the interior coloured layer of the lion consisted of the major elements C, O and Cu, minor elements Al, Cl, K, Ca, Sn and Pb, and trace (<0.1 wt%) element Mg (Table 1. Fig. 6b). It is most likely that this layer is made of copper carbonate.

EDS analysis of the corrosion layer on coin 1 (Table 1. Fig.7a) reveals the major elements C, O, Si and Cu, with minor elements Mg, Al, Cl, K and Ca. This corrosion layer must have been

made of a mixture of copper corrosion products and soil compounds.

The corrosion layer on coin 2 is characterized by the major elements of C, O, Cl and Cu, with minor elements Al, Si, K, Sn and Ca as shown in Table.1 and Fig.7b.

This EDS analysis of the corrosion layer on the three objects indicates that C, O, Mg, Al, Si, Cl, K, Ca, Fe and Mg were derived from the soil where these objects have been buried. The presence of Cu, Sn and Pb indicates that these three objects were made of copper-based alloys.

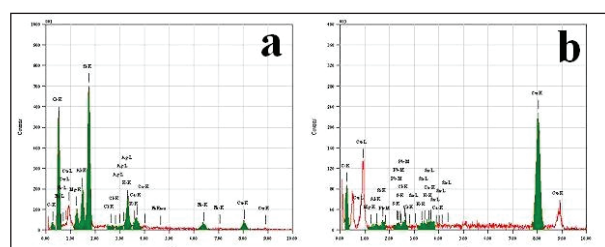


Fig. 6. (a) EDS spectrum of the outermost layer on the lion figurine surface. (b) EDS spectrum of the inner colored powdery corrosion layer on the lion figurine's surface.

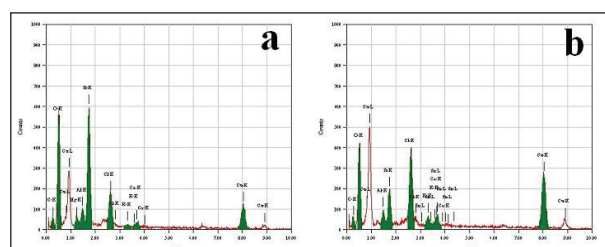
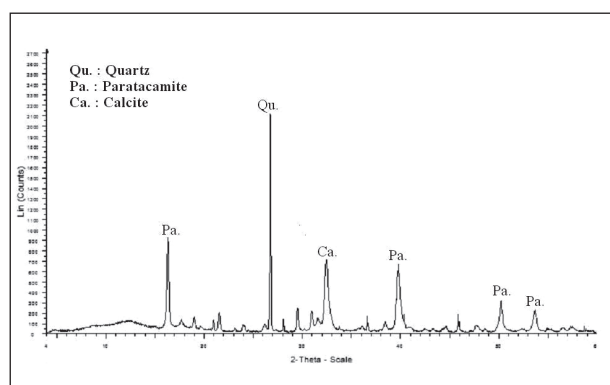
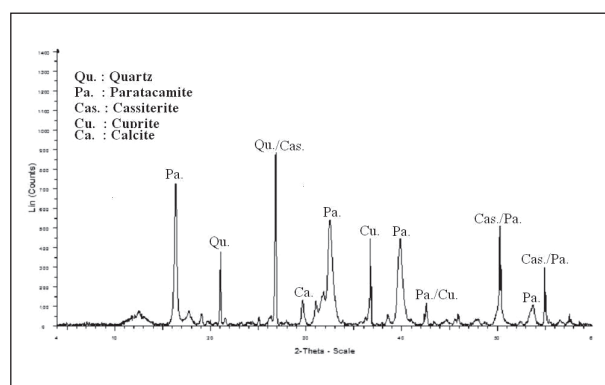
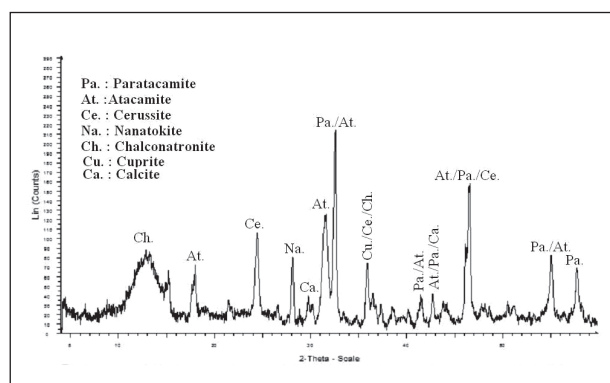
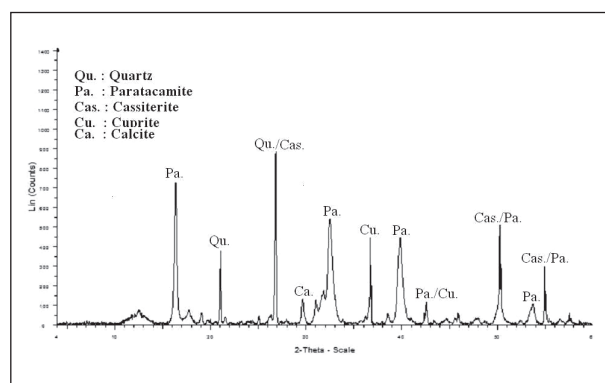


Fig. 7. (a) EDS spectra of the corrosion layer on coin 1. (b) EDS spectrum of the corrosion layer on coin 2.

Table 1: EDS analysis results of the corrosion layers on the three objects.

| Description of analyses points | The elemental composition (Wt.%) | | | | | | | | | | | |
|---|----------------------------------|------|------|------|------|------|-------|------|------|-----|------|------|
| | Cu | Pb | Sn | Si | Cl | C | O | Al | K | Fe | Ca | Mg |
| The outer layer of lion figurine surface | 16.2 | - | - | 7.69 | 4.77 | 37.4 | 19.8 | 4.24 | 2.58 | 2.5 | 4.83 | - |
| The colored inside layer of the lion figurine's surface | 58.9 | 0.14 | 0.43 | 0.41 | 0.24 | 23.3 | 15.8 | 0.29 | 0.25 | - | 0.13 | 0.07 |
| Coin 1 | 25.1 | - | - | 15.4 | 4.47 | 22.6 | 27.45 | 2.77 | 0.38 | - | 0.67 | 1.17 |
| Coin 2 | 48.24 | - | 0.40 | 4.15 | 8.41 | 13.7 | 19.9 | 2.19 | 1.38 | - | 1.69 | - |
| | | | | | | | | | | | 1.69 | |
| | | | | | | | | | | | 1.69 | |

The structural characterization of corrosion products grown on the surface of the lion figurine and the two coins was determined by XRD analysis (Figs 8-11. Table 2).

**Fig.8. XRD pattern of the outermost layer on the lion figurine's surface.****Fig. 10. XRD pattern of the corrosion layer on coin 1.****Fig. 9. XRD pattern of the inner layer of the corrosion layer on the lion figurine's surface.****Fig. 11. XRD pattern of the corrosion layer on coin 2.**

The XRD analyses are consistent with the EDS analyses. They are also consistent with the composition of the patinas in other buried archaeological objects of copper alloys, such as chlorides, carbonates, oxides of the metals copper, tin and lead (He et al., 2011: 209). XRD also showed the presence of copper, tin and lead species suggesting the objects were made of bronze alloy, and the corrosion products resulted from an interaction between different soil constituents, such as C and Cl and the bronze alloys components.

Quartz (SiO_2), the main constituent of many sandy soils, was detected as the major component in the outermost layer of the lion figurine and on the corrosion layer of coin 1 and of coin 2. This indicates that the burial soil in which these objects were found is a quartz-rich soil. In such soil, the compact sand grains give rise to a structure of wide pores which allow water and air to infiltrate, leading to the deterioration of the buried bronzes.

Cuprite (Cu_2O) and cassiterite (SnO_2) were detected by XRD analysis as minor components in the inner corrosion layer of the lion figurine and on the corrosion layer of coin 1. The corrosion mechanism starts with oxidation that begins after manufacturing and long burial time. Different oxides form initially as protective layers. The porosity of these oxidized layers allows for movement of water, carbon dioxide and solutes such as chloride ions. In humid environment where soil water is charged with carbon dioxide, produced carbonic acid may attack metals directly to form cupric ions of basic carbonate [$\text{Cu}_2\text{CO}_3(\text{OH})_2$].

Malachite [$\text{Cu}_2\text{CO}_3(\text{OH})_2$] was detected as minor compound on the outer layer of the lion figurine and on the corrosion layers of coin 1 and of coin 2. Cerussite (PbCO_3) was detected as a minor compound in the outermost layer and the inner layer of the lion figurine. These compounds may be formed also as a

result of combination of carbon dioxide with oxygen on the cuprous oxide (Cu_2O) layer. The chalconatronite, the blue green sodium-copper carbonate [$\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$] that was detected as minor compound in the inner layer on the lion figurine surface, may be formed by direct precipitation from saturated solutions of the highly soluble mineral juangodoyite [$\text{Na}_2\text{Cu}(\text{CO}_3)_2$]. The presence of this compound prevents the precipitation of malachite, creating instead an alteration of the reaction process from malachite to chalconatronite (Scott, 2002: 111).

Nantokite (CuCl) was detected as a minor compound in the inner corrosion layer of the lion figurine. It was formed during the burial via the interaction between copper and Cl-anions coming from the soil. The presence of CuCl is detrimental to the stability of the bronze artifacts since it activates the most dangerous form of post burial active corrosion, commonly known as “bronze disease”. Nantokite (CuCl) cyclically reacts with oxygen and water giving rise to one or more hydroxydicopper chlorides [$\text{Cu}_2(\text{OH})_3\text{Cl}$] such as paratacamite or atacamite.

Paratacamite, which is found as a light or pale green powdery trigonal crystal, was detected as major compound in the inner corrosion layer on the lion figurine's surface and on the corrosion layers of coin 1 and of coin 2. Atacamite, usually presenting as dark green orthorhombic crystals, was detected as major compound in the outermost layer on the lion figurine's surface and as minor component in the inner corrosion layer.

3.3. Treatment and Conservation Procedures

Treatment and conservation of bronze artifacts are undertaken to restore the surface features which are obscured under thick mineralization or deposits, and to stabilize the patina against change under the influence of an adverse

Table 2: Micro-chemical composition and crystalline phases present in the lion figurine and the two coins obtained by XRD.

| Sample's source | Minerals | Formula | ASTM file No. |
|--|-----------------|---|---------------|
| The outermost layer on the lion figurine | Quartz | SiO_2 | 46-1045 |
| | Atacamite | $\text{Cu}_2(\text{OH})_3\text{Cl}$ | 2-146 |
| | Malachite | $\text{Cu}_2\text{CO}_3(\text{OH})_2$ | 10-399 |
| | Cerussite | PbCO_3 | 5-417 |
| | Calcite | CaCO_3 | 5-586 |
| The colored inner corrosion layer on the lion figurine's surface | Paratacamite | $\text{Cu}_2(\text{OH})_3\text{Cl}$ | 15-694 |
| | Atacamite | $\text{Cu}_2(\text{OH})_3\text{Cl}$ | 15-694 |
| | Cuprite | Cu_2O | 2-146 |
| | Cerussite | PbCO_3 | 5-667 |
| | Nantokite | CuCl | 5-417 |
| | Chalconatronite | $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ | 6-334 |
| Coin 1 | Calcite | CaCO_3 | 10-442 |
| | | | 5-586 |
| | Quartz | SiO_2 | 46-1045 |
| | Paratacamite | $\text{Cu}_2(\text{OH})_3\text{Cl}$ | 15-694 |
| | Cuprite | Cu_2O | 5-667 |
| | Cassiterite | SnO_2 | 2-1337 |
| Coin 2 | Malachite | $\text{Cu}_2\text{CO}_3(\text{OH})_2$ | 10-399 |
| | | | 5-586 |
| | Quartz | SiO_2 | 46-1045 |
| | Paratacamite | $\text{Cu}_2(\text{OH})_3\text{Cl}$ | 15-694 |
| | Calcite | CaCO_3 | 5-586 |
| | Malachite | $\text{Cu}_2\text{CO}_3(\text{OH})_2$ | 10-399 |

environment. There are perhaps only two classes of corroded bronze objects in which stripping of the natural patina are justified. In the first class, there are those that have granular patina and areas of bronze disease which is applicable to the condition of the lion figurine. In the second class, the patina covers or obscures details of design, coating, or modeling. Coins can be of the second class objects where the requirements of the archaeologists, the numismatists, and the art historians are naturally concerned with the maximum possible information that can be recovered from their corroded surfaces. This indicates that the inscriptions, figures and die stamps that were originally on the coins must

have been preserved in the treated coins.

Prior to stripping treatment, careful mechanical cleaning was performed by using nylon brushes and gentle scalpel movement parallel to the corroded surface to remove the outermost deposits of gross encrustation and the corrosion products incorporated with soil residues. This assisted in exposing the preserved surface of the lion figurine and the two coins.

For stripping the corrosion products, a chemical method enhanced with mechanical treatments was applied. This procedure guaranteed a safe cleaning process of the surface and the removal the corrosion layers. The objects were put in

successive baths of alkaline Rochelle solution to dissolve cuprous compounds and to remove cupric salts (Plenderleith and Werner, 1971: 247; Stambolov, 1985: 106)

The lion figurine and the two coins that were treated with this reagent had the pink appearance of freshly exposed cuprous oxide. This washing process was carried out by a thorough light brushing to remove any secondary deposits. Then, the objects were rinsed repeatedly with hot deionized water and thoroughly dried. After finishing these treatments, the surface of the lion figurine appeared smooth with small corroded areas (Fig. 12). Coin 1 has a profile of a human face on the obverse and an unknown figure on the reverse. This surface has also a smooth surface and has large eroded areas on the two sides of the coin (Fig. 13). The surface of coin 2 is heavily eroded and etched, and no recognizable figures can be detected (Fig. 14).

The conservation procedure included degreasing the objects with acetone, and treating them with Benzotriazole (BTA; a corrosion inhibitor) preceding the final sealant to ensure long-term stability. The three objects were brushed with a solution of 3% BTA in ethanol as an inhibitor against further attack. The final protective coating, a 3% solution of Paraloid B-72 dissolved in acetone, was applied by brushing the surface of the aforementioned objects.

The elemental compositions of the lion figurine and the two coins were determined on the cleaned original surfaces by SEM-EDS after treatment and before conservation. The analysis results of the three objects are listed in Table 3.

It was observed from the SEM-EDS results of the lion figurine's cleaned surface represented in Fig.15 a and b that it contains 75.1 wt% Cu, 20.0 wt.% O, 3.56 wt.% Sn and 1.35 wt.% Pb. This indicates that the lion figurine is made of bronze alloy with little amounts of tin and



Fig. 12. The lion figurine after treatment.



Fig. 13. The obverse (a) and reverse (b) of coin 1 after treatment.



Fig. 14. Coin 2 after treatment.

3.4. Elemental composition
lead. The surface has many pits; the elemental composition for one of these pits indicates the presence of a higher amount of lead (23.2 wt

Table 3: Elemental composition of the lion figurine and the two coins.

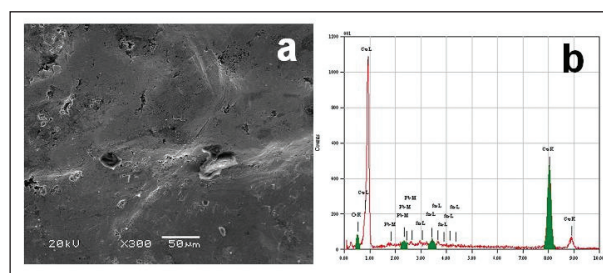
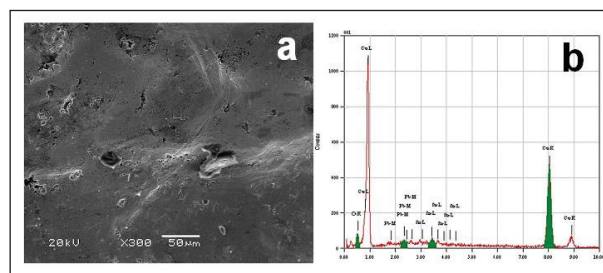
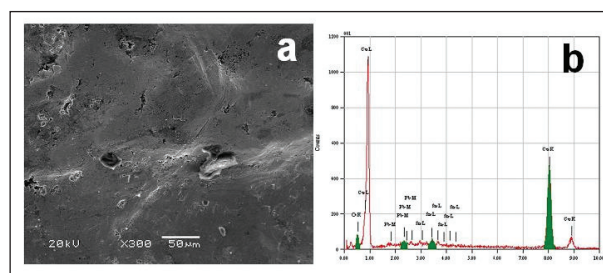
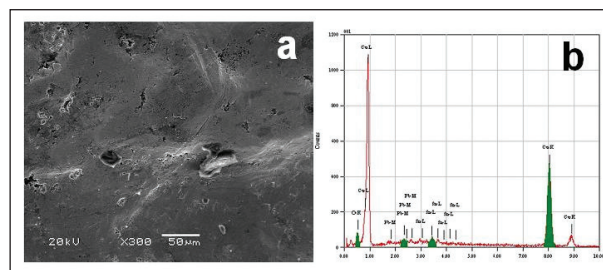
| Areas of analysis | Elemental composition (Wt%) | | | |
|------------------------------------|-----------------------------|------|-------|-------|
| | Cu | Sn | Pb | O |
| Lion figurine's surface | 75.1 | 3.56 | 1.35 | 20.0 |
| One pit on lion figurine's surface | 55.3 | 4.56 | 23.20 | 16.94 |
| Surface of coin 1 | 73.8 | 4.27 | 2.02 | 19.9 |
| Surface of coin 2 | 66.8 | 8.54 | 5.15 | 19.5 |

%) and tin (4.56 wt. %), and the amounts of Cu (55.3 wt %) and O (16.94 wt %) as shown in Figs 16a and b.

The main elements of the cleaned original surface of coin 1, characterized by gray to whitish small pits, are 73.8 wt.% Cu, 19.9 wt.% O, 4.56 wt.% Sn and 2.02 wt % Pb (Figs 17 a and b). The elemental compositions of coin 2 which is characterized by a rough surface, were 66.8 wt % Cu, 19.5 wt %, 8.54 wt % Sn and 5.15 wt % Pb (Figs 18 a and b).

The main metallic elements in the three objects are copper, tin and lead which indicate that the three objects are made of a bronze alloy. Copper is the major component of the bronze alloy, tin is the main alloying element for producing bronze, while lead is a common addition to bronze for producing objects characterized by low mechanical properties to be utilized at room temperature. Oxygen on the cleaned original surface is partly contained within the superficial cuprous oxide layer on the objects' surfaces. Its value is nearly the same in the three objects' surfaces. The values of tin and lead in coin 2 are higher than they are in both coin 1 and the lion figurine which most likely resulted in the heavy erosion on

its surface. The increase in the amount of tin increases the mechanical properties of the bronze. However, bronze that contains greater amounts of tin is more susceptible to breakage due to the formation of the hard and brittle ($\alpha +$

**Fig.15. SEM image, 300X (a) and EDS spectrum (b) of the lion figurine's cleaned original surface.****Fig.16. SEM image, 1000X (a) and EDS spectrum (b), of a pit on the lion figurine's cleaned original surface.****Fig.17. SEM image, 200X (a), and EDS spectrum (b) for the cleaned surface of Coin 1.****Fig.18. SEM image, 200X (a), and EDS spectrum (b) of the cleaned original surface of Coin 2.**

η) eutectoid phase in bronze (Ingo et al., 2006: 515). Increasing the amount of lead up to 2% improves the fluidity of the melted bronze alloy (Craddock, 1976: 93–113; Craddock, 1977: 103–123) although the loss of the mechanical properties could be induced if the lead amount is increased up to 3–4.5 wt%. With higher amounts of lead, a remarkable deterioration of mechanical properties results. Indeed lead has substantially no solid solubility in copper and copper-base alloys. If the percentage of lead in bronze is higher than a few percent, lead occurs as a dispersion of fine particles throughout the bronze (Ingo et al., 2006: 516). This dispersion of fine particles of lead can be observed by SEM examination in the surface of the three objects (Figs 15a, 16a, and 16a) and was indicated by EDS analysis of one of them on the lion figurine's surface (Fig.16 b).

Comparing the values of Cu in the corrosion products layer and in the cleaned original surface of the three objects, may show that the amounts of copper are higher on the cleaned original surfaces than on the corrosion products layers. This results from an interaction between copper and other soil elements forming different copper salts. It can also be deduced that the undetected, or small, amounts of tin and lead in the corrosion products layers compared to their amounts on the cleaned surfaces is due to the ability of their products to be leached from the surface in spite of their richness on the cleaned original surface.4. Conclusions

The combined use of OM, XRD, and SEM-EDS can be useful to identify corrosion agents and mechanisms for archaeological metal objects, and then suggest the most reliable strategies for treatment and conservation of these archaeological objects.

The detailed investigation of the features of

the patina and the corrosion layer of the lion figurine and the two coins indicates that they have a thick corrosion layer mainly composed of copper compounds incorporated and/or covered with soil residues as an outermost layer on the lion figurine.

Corrosion layer analyses indicate that the chloride ion and water, as well as oxygen and carbon dioxide, can be regarded as the powerful corrosion agents for the three objects. Analysis of the outer layer indicated that it formed via interaction between the soil constituents (C, Mg, Al, Si, Cl, Ca, and Fe) and metal corrosion, and products of long-term corrosion.

The many micro-cracks, pits and cavities in the corrosion layers or in the outermost layer are attributed to the internal stresses in the corrosion layer, or due to the long-term corrosion caused by the periodic hydration and dehydration in soil. The burial soil was a quartzose sandy soil that helped in the deterioration of the three objects. The lion figurine and the two coins were made of cast bronze (Cu, Sn and Pb) alloy. Lead has little solid solubility in copper and copper-based alloys which resulted in a dispersion of fine particles throughout the bronze, appearing as pits on the surfaces of the three objects.

Stripping of the corrosion deposits and products can be successfully used for cleaning the archaeological corroded coins to reveal their detailed surfaces and for cleaning the bronze objects suffering from bronze disease and covered with chloride compounds especially the active nantokite (CuCl). Inhibition and protective coating protection of bronze objects against further corrosion is a necessary procedure in the conservation and protection processes of the archaeological objects.

Dr. Abdulnaser Al-Zahrani: Dep. of Heritage Resources Management, College of Tourism & Archaeology, King Saud University,

Dr. Mohamed Ghoniem: Conservation Department, Faculty of Fine Arts, Minia University, Egypt. King Saud University- College of Tourism & Archaeology, KSA.

ملخص: تمثال صغير لأسد وعملتان عشر عليهما في حفائر موقع الخريبة (دادان) الأثري في مدائن صالح بالمملكة العربية السعودية في موسمي الحفائر الثاني والتاسع ١٤٢٦هـ / ٢٠٠٥م و ١٤٣٣هـ / ٢٠١٢م، وهي في حالة تلف شديدة، إذ تغطيها تماماً نواتج الصدأ المختلطة ببقايا التربة، وتكلسات من التربة تشوه شكلها بحيث لا يمكن إدراك تفاصيل السطح الأصلي لها. وهي في حاجة إلى فحص وصيانة لكشف تفاصيل أسطحها. وقد تم فحصها وتحليلها لمعرفة تركيبها الكيميائي، والتعرف إلى طبيعة طبقة الصدأ، وتشخيصها فيزيائياً وكيميائياً، وذلك باستخدام أساليب فحص وتحليل مختلفة، مثل: الميكروسكوب الضوئي (Optical microscope) فيزيائياً وكيميائياً، والتصوير بالأشعة السينية (X-ray Radiography)، والتحليل بحيود الأشعة السينية (X-ray diffraction)، والميكروسكوب الإلكتروني الماسح الملحق به وحدة مطياف الطاقة المشتتة (SEM-EDS «equipped with energy dispersive spectroscopy»).

Notes:

1. This object has been discovered by the excavation of the archaeology department, College of Tourism & Archaeology, King Saud University, season 2012. It was found in square No.5, and given the temporary excavation number 65.
2. This coin was found on the ground surface through the excavation season 2005 of the archaeology department, College of Tourism & Archaeology, King Saud University. It was given the temporary excavation number: 1003.
3. This coin was found on the ground surface through the excavation season 2005 of the archaeology department, College of Tourism & Archaeology, King Saud University. It was found in square No. 16, and given the temporary excavation number 190. References Craddock, P.T., 1976. "The Composition of the Copper Alloys Used by the Greek, Etruscan and Roman Civilizations 1". The Greeks Before the Archaic Period, Volume 3, Issue 2, pp.93-113.

References:

- Craddock, P.T., 1976. "The Composition of the Copper Alloys Used by the Greek, Etruscan and Roman Civilizations 1". **The Greeks Before the Archaic Period**, Volume 3, Issue 2, pp.93-113.
- Craddock, P.T., 1977. "The Composition of the Copper Alloys Used by the Greek, Etruscan and Roman civilizations: 2". **The Archaic, Classical and Hellenistic Greeks**, Volume 4, Issue 2 pp.103-123.
- Cura, J., Junior, D.F., Freitas, V., Lins, C., 2007. "Surface Characterization of a Corroded Bronze-led Alloy in Salt Sprays Cabinet". **Applied Surface Science** 253, pp. 1104-7107.
- Ingo, G.M., Angelini, E., de Caro, T., Bultrini, G., Calliari, I., 2004. "Combined use of GDOES, SEM-EDS, XRD and OM for the Microchemical Study of the Corrosion Products on Archaeological Bronzes". **Applied Physics. A, Materials Science & Processing**, 79, pp. 199-204.
- MacDowall, D.W., 1978. "Coin Collections: Their Preservation, Classification, and Presentation". Paris, UNESCO.
- Mantler, M., Schreiner, M., Weber, F., Ebner, R., Mairinger, F., 1992. "Advances in X-ray Analysis". 35,

pp. 987 - 993 and pp.1157 - 1163.

Plenderleith, H. J., Werner, A. E. A., 1971. **"The Conservation of Antiquities and Works of art"**. Revised Edition, Oxford University Press.

Robbiola, L., Blengino, J.M., Fiaud, C., 1998. "Morphology and Mechanism of Formation of Natural Patinas on Archaeological Cu-Sn alloys". **Corrosion science** 12 2083-2111.

Sandu, I., Mircea, O., Sandu, A. V., Sarghie, I., Sandu, I. G., Vasilache, V., 2010, "Non-invasive Techniques in the Analysis of Corrosion Crusts Formed on Archaeological Metal Objects". **Rev. Chim. (Bucharest)**, 61, Nr. 11.

Schreiner, M., Frühmann, B., Jembrih-Simbürger D., Linke, R., 2004. "X-Rays In Art And Archaeology – An Overview, Jcpds - International Centre for Diffraction Data" **Advances in X-ray Analysis**, Volume 47.

Schreiner, M., Melcher M., Uhler, K., 2007. "Scanning Electron Microscopy and Energy Dispersive Analysis: Applications in the Field of Cultural Heritage. **Anal**

Bioanal Chem., pp.387:737–747.

Scott, D. A., 2002. **"Copper and Bronze in Art, Corrosion, Colorants, Conservation"**. The Getty Conservation Institute, Los Angeles.

Spoto, G., Giliberto, E., 2002. **"Modern Analytical Methods in Art and Archaeometry"**. John Wiley, New York.

Stambolov, T., 1985. **"The Corrosion and Conservation of Metallic Antiquities and Works of Art, Amsterdam"**, Central Research Laboratory for Objects of Art and Science.

Stuart, B. H., 2007. "Analytical Techniques in Materials Conservation". John Wiley & Sons Ltd, England.

Velraj, G., Sudha, R., Hemamalini, R., 2010. "X-Ray Diffraction And Tg-Dta Studies Of Archaeological Artifacts Recently Excavated In Salamankuppam Tamilnadu". **Recent Research in Science and Technology**, 2(10), pp.89-93.