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CHARACTERIZATION AND SCIENTIFIC CONSERVATION OF A GROUP OF ARCHAEOLOGICAL BRONZE EGYPTIAN STATUES

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Abstract

Several archaeological bronze statuettes adhered randomly to a bigger statue of goddess Sekhmet as a big mass, which was excavated from Sais and most likely dates to C.600 BC, and was investigated and conserved. They were in a poor condition, retained intact their thick corrosion crust incorporated with residual burial soil. Both the surface corrosion products and the metal substrates were studied to understand the objects corrosion process and to obtain information about their chemical composition before the conservation procedures. Optical Microscopy (OM), X-ray diffraction analysis (XRD), and Scanning electron microscope equipped with energy-dispersive spectrometry (SEM-EDX) were used for disclosing corrosion features, the nature and composition of the patina, and compositional analysis of the study group. The results indicated that the objects have been buried in wet sandy saline soil or were exposed in storage to an environment rich in many aggressive ions such as chloride, sulfur and oxygen. These corrosive conditions reflected on the patina and the composition of the corrosion layers that mostly composed of chlorides, sulfates and oxides. The objects were made by solid casting technique except the statue of Sekhmet that was made using the hollow casting technique. All the objects were made of Lead-bronze alloy, with a lead content ranging from 5.43% to 19.12%. Different approaches of cleaning were adopted according to the condition of the objects, in order to remove the corrosion and soil disfiguring deposits and to reveal the original surface details. The loose, powdery and thick encrustations were removed by subsequent manual cleaning down to the level of the original surface. The hard corrosion crust on the other objects was stripped chemically with a less aggressive alkaline solution. This procedure was followed by successive baths in distilled water and drying cycles, followed by a succession of acetone baths. For stabilization, all the treated objects were placed in 5% w/v benzotriazole in ethanol solution to prevent future outbreaks of corrosion. Finally, the objects were coated with a protective coating of Paralloid B-44 acrylic co-polymer dissolved in toluene and a waxy coating of microcrystalline wax (Cosmoloid H80) as a superficial topcoat barrier against water or water vapor and to offer a more robust protective system

Keywords: *Bronze statues; XRD; EDS; corrosion products; leaded bronze; conservation.*

Introduction

Most of the ancient Egyptian metal statues were produced at temple workshops for rituals, as votive statues or for religious purposes as cult statues [1, 2]. The votive statues are objects dedicated to a particular deity, and some examples of them show groupings of more than one deity. Most of them are statuettes that were usually between twenty and thirty centimeters tall representing gods in standing or enthroned poses [3]. Cult statues that would have been the center of ritual devotion or worship are usually over thirty centimeters in height

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[4]. Furthermore, it is likely that smaller, more portable statues were also used for festivals and processions [5]. The greatest number of these objects was produced during the Third Intermediate Period (ca. 1070–712 B.C.) and the Late Period (712-332 BC.). Majority of them were made of bronze alloy that has many advantages to the manufacturing process of metal and to the actual use of objects; it reproduces every detail of the mould and has high corrosion resistance [6]. The addition of lead to the bronze alloy was also used as it improves the fluidity of the melted bronze alloy and makes it easier to machine. The majority of the discovered bronze statues are frequently found in temples deposits as caches [3, 7-9]. Most of them are votive offerings made at a temple or throne from which they were cleared, as occasion required, and disposed of by burial within sacred precincts or after long periods of use [10-12].

During the long burial periods, bronze statues are subject to corrosive factors that slowly, or perhaps even quickly, transform them back into mineral compounds similar to those from which the metallic components of the bronze alloy originally derived. Due to that, a variety of corrosion compounds may form on the surface of the buried statues, depending on the nature of the objects and the chemical composition of the environment to which they have been exposed. They are usually excavated in poor conditions, have burial concretions and disfiguring, granular or spotted patina with different colored corrosion products. However, some of them, even after long burial, have only superficial corrosion.

A group of deities statues and other metal ritual equipment were excavated from the site of Sais around 93 km western north Cairo (the ruins are to the north of Sa el-Hagar village) [Fig. 1]. It was the capital of Egypt during Dynasty 26 **(**ca. 664–525 BC), and one of the most important regions where many archaeological finds were excavated.

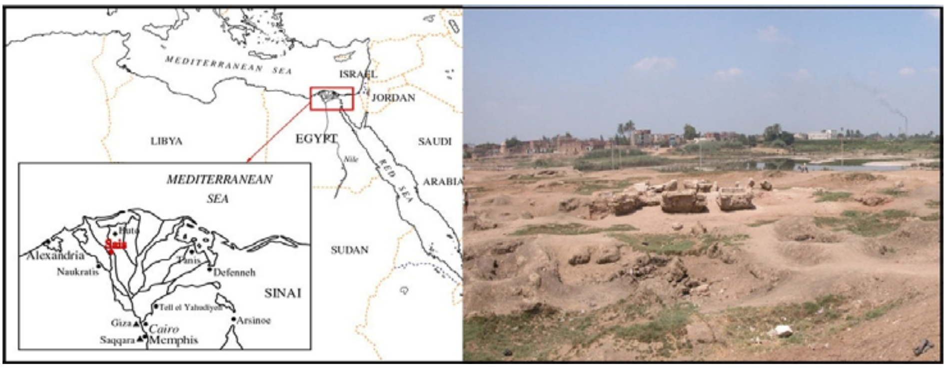

Fig. 1. Map and site of Sias (sa el hagar) where the group of statues were excavated.

They were formally accessioned into the Egyptian Museum in Cairo in 1926 with the temporary register number 31/12/26/11. No more information is given relating to the specific place where it was originated from, i.e. a temple or a tomb. From the time of acquisition, all the objects have been stored in the fifth department of the museum, remained uncleaned and so they retained a burial corrosion concretion till July 2009 when they were subjected to conservation. Two of those items were studied by Ghoniem [13, 14]. A big mass of metal objects from this group taking the temporary register number 31/12/26/11 F (Fig. 2) is the focus of this work. It represents a number of small statuettes adhered randomly to a greater statue of goddess Sekhmet seated on a high cubic chair. Thick burial concretions and corrosion crusts, including blue to green corrosion products incorporated with soil residues cover all the items of this study group. The main aims of this work are: characterization of this mass of bronze statues using investigation methods so as to disclose the nature of the patina, to identify the corrosion compounds and to understand the corrosion process, to do the analysis of the metallic composition of the statues group, as well as their conservation in preparation for their display in the museum.

Fig. 2. A big mass of group bronze statutes depicts a statue of Sekhmet adhered randomly with other statuettes.

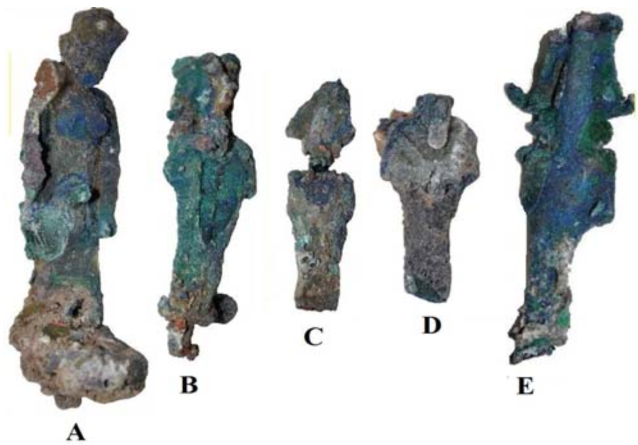

Fig 3. Collective photograph of the five Osiris statuettes.

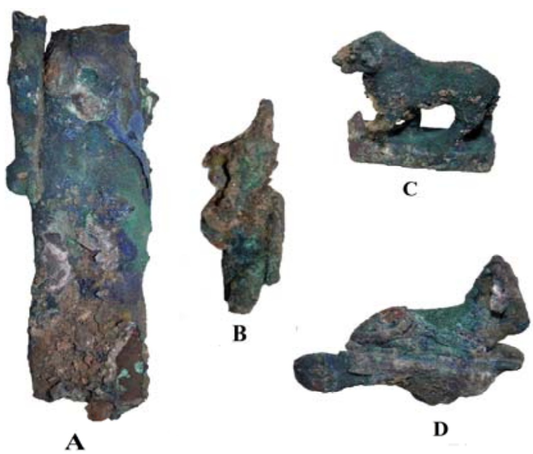

Fig 4. The feminine statuette (A), Horous the Child (B) and the two statuettes of Amun as a standing ram (C) and a seated ram (D).

Experimental Part

The study group

The study group consists of ten objects that were separated mechanically from the badly corroded mass. These objects are:

- The statute of Sekhmet (Fig .2), 60cm high, was depicted as a lion-headed woman seated on a cubic seat. There is a wig with long lappets hanging on the chest; hands are placed near the knees; the right hand is flat while the left is clasped. Without feet, the bottom part was destroyed and there is a deeply crack in the left leg. There is a hole atop of the head, most likely representing the place of the lost uraeus serpent.
- Five Osiris statuettes with the following dimensions: 125 mm high (Fig. 3A), 90 mm high (Fig. 3B), 52mm high (Fig. 3C), 54mm high (Fig. 3D), and 100mm high (Fig. 3E).
- Feminine statuette of 220mm high, without head, chest, feet and the left arm. It most probably depicts the goddess Mut (Fig. 4A).
- A statuette of Horous the Child of 76 mm high, without feet and the lowest part of the legs (Fig. 4B).
- Two statuettes of Amun; one is depicted as a standing ram with curved horns and measures 40mm wide and 45mm high (Fig. 4C), while the other is depicted as a seated ram of about 70mm wide and 50mm high (Fig. 4D).

All the objects are in a very bad heavily corroded condition. Some of them have corroded throughout their depth; others were covered with an extremely disfiguring hard crust up to a 3 millimetres thick. This crust consists of light–dark green and dark blue corrosion products incorporated with soil residues. In some areas, a rather smooth surface showed under the deposits and many spots of bright green patches can be noticed.

Methods

The corroded surfaces of the objects were examined by optical microscope using a Smart-Eye USB Digital Microscope at various magnification degrees, up to maximum 200X. Eight powdered samples were taken gently and mechanically to be analyzed by X-ray diffraction method. Six samples represent the different corrosion products on the group, one sample was removed from the core material inside the statue of Seckhmet and one sample taken from the soil deposits on the objects. The corrosion products were selected with the aim of identifying the causes of the corrosion and understanding its phenomenon. Samples were analyzed using a Philips PW1840.X-ray diffractometer. The operating conditions were: Cu target, 40 kV pressure and 25 mA current.

Tiny specimens of detached fragments containing very small parts of the metallic core covered with a superficial corrosion layer were analyzed by using a Scanning electron microscopy, JSM-6380 LA instrument, equipped with a Link EDS (energy-dispersive spectrometry) operating up to 30 kV. SEM–EDS, was used to identify the elemental composition of the metallic core representing the objects.

Results and discussion

Investigation observations

Visual Examination of the objects revealed that all are freestanding, independent; there are no evidences of inlaying, gilding and any textiles traces or impressions ostensibly. The simple handling of the statues and the appearance of the cracked areas reveal that the lost-wax casting process was the manufacturing technique used to create these statues. It is known that the majority of the Egyptian bronze statues were produced by this technique that allowed for the creation of both hollow cast and solid cast types. Large statues were normally cast in hollow cast technique [15], where a central core of clay with an organic material was shaped to create the intended sculpture and covered with a thin layer of beeswax [4]. Metal support pins or chaplets were often used to hold the form in place [16]. It was then covered with a heat proof mould of clay which was fired, resulting in the wax running out. The blacked clay mould was turned upside down and molten metal was poured into the resulting gaps left between the core and the outer mould. Holes or runners allowed for the mould to be completely filled when molten metal was poured into them [4].

The statue of Sekhmet is most likely made by this technique. Remains of the sandy core can be observed from the crack in the right leg of the statue (Fig. 5A). It represents the central core of the blacked sandy clay mould. During the casting process this core absorbed some of the wax and then burnt, turning black in colour. These cores are typical of Egyptian as well as other ancient hollow-cast bronzes [17].

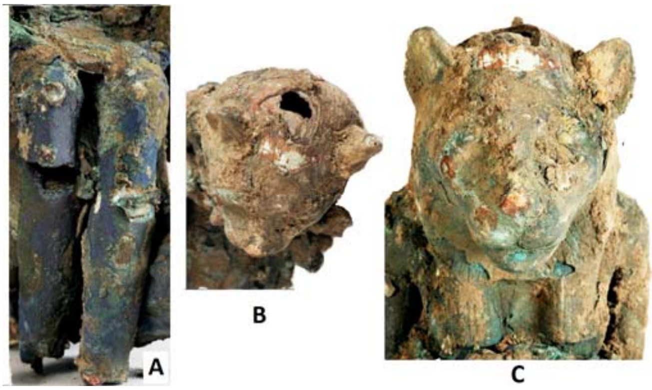

Fig. 5. (A) Remains of the blacked sandy core that can be observed from the crack in the right leg of the Sekhmet statue. (B) The vacuum cavity representing the missing uraeus-cobra solar and disk atop the head. (C) Incised lines of the face and the chest are heavily obscured by uneven encrusting deposits.

The vacuum cavity, which represents the missing uraeus-cobra solar and disk atop the head revealing the internal vacuum and the thickness of the metal, is another indicator to the hollow-cast technique (Fig. 5B). Incised lines of the face, the chest and the wig that were heavily obscured by uneven encrusting deposits of corrosion and soil residues (Fig 5C) have been simply modeled into the wax prototype before encasing in the clay mould. Although some chasing done by hand was added to the finished product, it is believed that most surface details on hollow-cast statues were done before the casting process [18] and after the wax had melted, the incisions remained on the mould were reproduced in the metal casting.

Hollow casting technique had more advantages for metal smiths than solid casting. It was more economical, especially for large works, because it saved metal and on a technological level there was less possibility of distortion or shrinkage inside the mould [4, 18, 19].

There is no evidence that the Sekhmet statue consisted of separate components that were cast onto the statue or were mechanically joined. There are no signs of pegs or mortise and tenon joints that could be used to join areas, connecting arms or legs to the body or to attach the headdress. It is only the missing uraeus-cobra solar and disk atop the head that were likely cast separately and mounted in the empty vacuum atop the head.

The sandy core that was used in the hollow cast technique of Sekhmet was not found inside the other statuettes. Visual examination to the cross section of the cracked areas and the roughly pointed metal tangs in the lowest part of some of them indicates that they were made by solid cast technique. It was the most basic type of casting used in antiquity in Egypt [4], especially for small objects [15]. It was already employed as far back as the Pre-dynastic Period [20].

It is most likely that a model of each statuette was modeled or molded in wax or some other material which is easy to model and has a low melting temperature. Then this model is coated with an investment material, usually clay with an organic binder like dung or chaff and a hole pierced down from the outer surface to the model. When the clay is fired, the wax burns or flows out and molten metal can be poured in. Once the metal has cooled and solidified, it takes the shape of the model and the mould is broken to extract the statuette that typically requires the removal of any surface protrusions or flaws. It is generally given the final surface details and polished [16, 21]. The pouring point of solidified metal that becomes the tang represents protrusion originally used to secure the statute onto a base of wood or stone [16]. The tangs of these statuettes are now lost except one of the Osiris figurines. Roughly pointed metal tangs can be seen underneath some statuettes and can also be helpful indicators on dating the statue. Schorsch [18] believes that before the New Kingdom they appear irregular in shape and size, while afterwards take on a canonical form of being rectangular with a flat end.

Also, this pointed metal tang indicates the possibility of votive or cult function. As representations of deities, cult statues were usually kept inside a portable wooden shrine that was fitted into a slightly larger stone one, located within the sanctuary of the temple [4], and often used for festivals and processions [5],whereas the votive statuettes were probably smaller, often just between twenty and thirty centimeters tall. They are usually dedicated to a particular deity and referred to as votive offerings or dedications and mostly represent gods in standing or enthroned poses [3]. Royalty, official and private individuals would donate such objects to temples or shrines with the expectation that the particular deity would bless them, would provide an answer to their prayers or as a thanksgiving gift [4]. Unfortunately most of the statues tangs have been lost, just the one of the Osiris statues and the one of the two statuettes of Amun still remain. They are regular in shape and size which indicates that they most likely date back to the Late Period. Regarding to the function of the group's statues, we can say from their size and according to what is mentioned above that Sekhmet statue is most likely a cult statue where the other small statuettes are votive statues.

As it is usual in most of the archaeological bronze objects, the corrosion layer on the group surfaces was in strata. Three layers of corrosion deposits can be detected by visual examination. These layers, from down to up are reddish brown layer, covered with a blue-green corrosion layer and a superficial layer of different corrosion products incorporated with soil residues.

The close visual examination reveals distortions and may be faults in many statuettes such as curvature or lack of integrity, cracks and missing parts that appeared clearly after the cleaning procedures. These defects sometimes occurred as a result of impurities in the metal/alloy or uneven temperature if the core retained any moisture during manufacturing process. The thin-walled hollow castings had a tendency for the cores to expand and crack while casting. Therefore such distortions on statutes cannot always be attributed to post-burial corrosion [4, 17].

The microscopic investigation of the corrosion layers revealed the same features that were detected on the previous studied object accompanied with this group by Ghoniem [13]. Micro photos of the surface corrosion layer (Figs. 6A, 7A, 8A and 9A) revealed the corrosion layers color, shape and nature. A variety of light to dark green, blue and gray colors overlapping with soil residues can be distinguished. The surface pattern appears heterogeneous, uneven and disparate. The corrosive features such as rough, powder or compact thick corrosive layer and fissures were detected. It was deduced by X-ray diffraction analysis method that the blue corrosion layer consists mainly of Cumengite mineral (Fig. 6), the dark green corrosion consists mainly of brochantite and atacamite (Fig. 7), the greenish blue consists mainly of cumengite and brochantite minerals (Fig. 8), while the heterogeneous bluish green patina incorporated with soil residues consists mainly of brochantite and calcite representing the soil residues as a trace (Fig. 9).

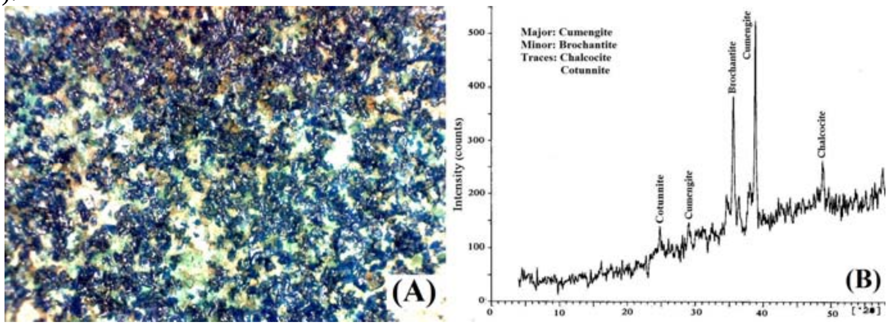

Fig. 6. (A) The blue continuous corrosion crust that was detected on the study objects, 65X; (B) its XRD analysis pattern.

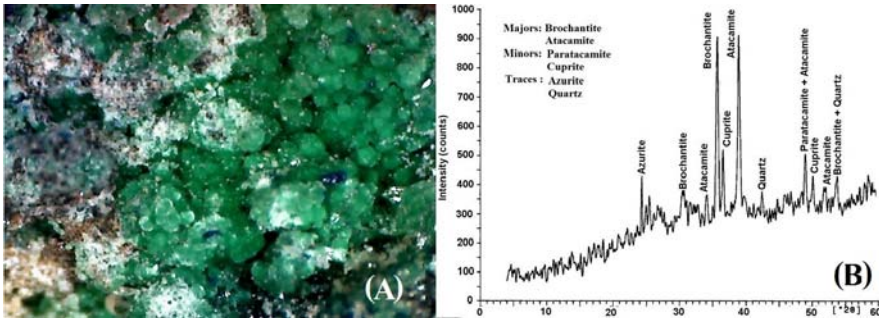

Fig. 7. (A) The dark –light green corrosion product on the study group that takes the roes shape, 180X; (B) its XRD analysis pattern.

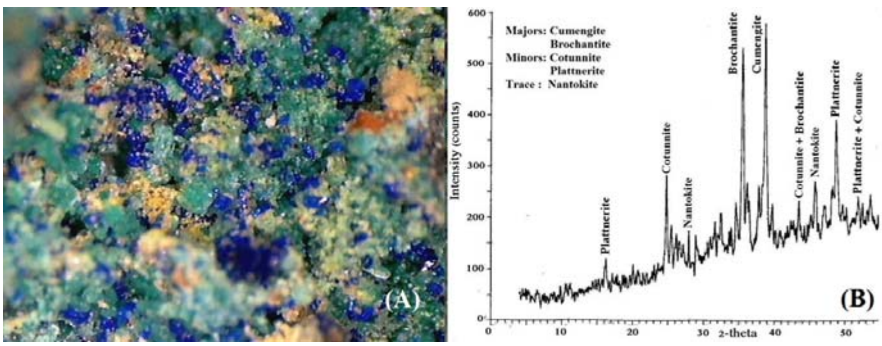

Fig. 8. (A) The greenish blue corrosion layer covering most of the objects 100X; (B) its XRD analysis pattern.

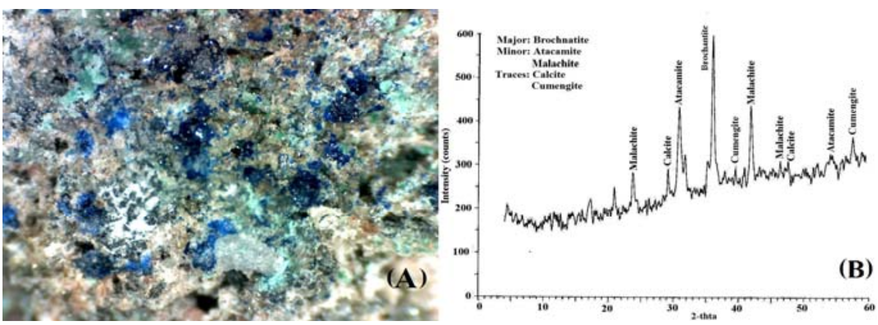

Fig. 9. Heterogeneous bluish green patina incorporated with soil residues, 180X; (B) its XRD analysis pattern.

Chemical composition

The different corrosion products covering the study group, soil granules, and the sandy core of Sekhmet statue were analysed by X-ray diffraction analysis (XRD) to identify their chemical composition. The results of the analysed samples are given in Table 1.

Table. 1. Chemical composition of the corrosion products, soil granules, and the sandy core of Sekhmet statue identified by XRD analysis.

No.	Sample Description	Identified compounds		
		Major	**Minor**	**Trace**
1	Dark to light-indigo blue	Cumengite $Pb_4Cu_4Cl_8(OH)_8 \cdot H_2O$ [ICDD 14-186]	Brochantite $CuSO_4(OH)_6$ [ICDD 13-398]	Cotunnite $PbCl_2$ [ICDD 5-416] Chalcocite Cu_2S [ICDD 12-227]
2	Bluish green	Cumengite $Pb_4Cu_4Cl_8(OH)_8 \cdot H_2O$ [ICDD 14-186] Brochantite $CuSO_4(OH)_6$ [ICDD 13-398]	Cotunnite $PbCl_2$ [ICDD 5-416] Plattnerite PbO_2 [ICDD 8-185]	Nantokite CuCl [ICDD 6-344]
3	Powdered light green patina	Paratacamite $Cu_2(OH)_3Cl$ [ICDD 15-694]	Atacamite $Cu_2(OH)_3Cl$ [ICDD 2-146]	Cuprite Cu_2O [ICDD 5-667]
4	Dark green compact patina	Atacamite $Cu_2(OH)_3Cl$ [ICDD 2-146] Brochantite $CuSO_4(OH)_6$ [ICDD 13-398]	Paratacamite $Cu_2(OH)_3Cl$ [15-694] Cuprite Cu_2O [ICDD 5-667]	Quartz SiO_2 [ICDD 46-1045] Azurite $2Cu_2CO_3$. $Cu(OH)_2$ [ICDD 11-136]
5	Green patina incorporated with soil residues	Brochantite $CuSO_4(OH)_6$ [ICDD 13-398]	Atacamite $Cu_2(OH)_3Cl$ [ICDD 2-146] Malachite $Cu_2CO_3.Cu(OH)_2$ [ICDD 10-399]	Calcite $CaCO_3$ [ICDD 5-586]
6	Reddish brown	Cuprite Cu_2O [ICDD 5-667] Cassiterite SnO_2 [ICDD 5-467]	Atacamite $Cu_2(OH)_3Cl$ [ICDD 2-146]	Atacamite $Cu_2(OH)_3Cl$ [ICDD 2-146]
7	Soil residues incorporated with corrosion products	Quartz SiO_2 [ICDD 46-1045] Brochantite $CuSO_4(OH)_6$ [ICDD 13-398]	Atacamite $Cu_2(OH)_3Cl$ [ICDD 2-146] Cassiterite SnO_2 [ICDD 5-467]	Plattnerite PbO_2 [ICDD 8-185] Malachite Cu_2 $CO_3.Cu(OH)_2$ [ICDD 10-399]
8	Sandy core of the Sekhmet statue	Quartz SiO_2 [ICDD 10-1045]	Malliss clay Ca-Mg-Al-Si-O [ICDD 03-00418]	Anorthite $Al_2Ca(SiO_4)_2$ [ICDD 2-0537]

It is clear from XRD results that the main components of the patina are chlorides, sulphates together with carbonates and oxides. Most of these compounds are of copper and little of them are of lead and tin that indicates the composition of the alloy. The corrosion product, crystalline dark to light-indigo blue taken from the legs of Sekhmet statue (sample 1) and bluish green product taken from the surfaces of the Osiris figurines (sample 2) are composed mainly of cumengite. It is a deep-blue tetragonal mineral consisting of a basic lead-copper chloride $Pb_4Cu_4C_{l8}(OH)_8 \cdot H_2O$. It is most likely found as a result of the interaction of metallic copper and lead with the corrosive chloride anions in the presence of water. It is the first time to be detected as a corrosion product on the Egyptian bronzes. It has been detected by Gettens [22] on the stem of an ancient Persian lam in the collection of the Freer Gallery of Art, and was found as an alteration product od mixed copper-lead chloride on ancient lead and silver slags from smelting operations in Lávrion (ancient Laurion) Greece [23].

This compound, in the form of deep blue highly refracting crystals, is different from the blue corrosion product that has been studied for more than 60 years on the ancient Egyptian bronzes chalconatronite ($Na_2Cu(CO_3)_2 \cdot 3H_2O$). The latter was detected as a greenish blue to pale blue corrosion product by Gettens and Frondel [24] due to the abundance of alkali carbonates in the soil in Egypt [25] or as a result of using some chemical cleaning agents on copper alloy artifacts [26-28]. Sampleite consisting of hydrous phosphate and chloride of sodium, calcium, and copper $NaCaCu_3(PO_4)_4Cl.5H_2O$ was found on objects from Memphis as a pale blue corrosion product [29] as a result of the presence of mixed ions such as sodium, chloride, and phosphate associated with water. Copper acetate, sodium copper carbonate acetate, copper formate and sodium copper formate acetate were also detected as a pale blue corrosion product on copper alloy artifacts in museum collections. Those latter compounds are often associated with the presence of acetic and formic acids emitted from the materials within the display or storage environment [9, 30-33]. All of these compounds were not detected on the surface of the study group statues. Azurite, $Cu_3(OH)_2(CO_3)_2$ that has been detected on some Egyptian bronze objects as a compact continuous dark blue layer or as fine crystal aggregates scattered among patches of malachite [25]. It was not detected as a major compound in the analyzed samples but as a trace compound in sample No. 4. It is formed only from near-neutral or weak acid solutions with high concentrations of the hydrogen carbonate ion HCO_3^-. Its existence, as a hydrated carbonic compound, has not been confirmed [34].

The presence of basic copper and lead chlorides compounds indicates that the objects were preserved in an environment rich of water and chloride anions for a long time before excavation, and had been stored in uncontrolled conditions for more than 85 years. The basic copper chloride atacamite $Cu_2(OH)_3Cl$ was detected as the major compound in the dark compact green patina (sample 4) and as a minor compound in the light powdered greenish patina (sample 3) and in the reddish brown patina (sample 6). The other basic copper chloride paratacamite $Cu_2(OH)_3Cl$ was detected as the major compound of the light powdered greenish patina (sample 3). Lead(II) chloride $PbCl_2$, cotunnite, was detected in sample 2 and sample 1, while cuprous chloride nantokite CuCl was detected as a minor compound in sample 2.

These chlorides compounds result from the interaction between the object's metals and the chloride ions coming from the surrounding environment. Nantokite is the first compound of interaction between copper and chloride ions. Its location of within the patina constituents can vary. In some cases it is adjacent to the metal surface, but in other examples it may overlie cuprite or be sandwiched between cuprite layers [35]. Cuprite Cu_2O was detected as a major compound in sample 6 and as a trace in sample 3. In the presence of moisture and oxygen, cuprous chlorides are hydrolyzed to form hydrochloric acid and basic cupric chloride [36]. The hydrochloric acid, in turn, will attack the metal to form more cuprous chloride the main compound of the process that is commonly referred to as 'bronze disease'. The produced basic copper chloride will be as a pale green powdery paratacamite or as a dark green crystalline phase atacamite. Those two basic copper chlorides are identical in chemical composition but differing in crystal form. Paratacamite takes the rhombohedral crystalline form while atacamite takes the orthorhombic crystalline form [37]. Atacamite appears to occur on the surface in two modifications, firstly as thick sheets of corrosion, and secondly, as eruptions of atacamite in the form of small pustules over this surface, which are covered with a thin layer of cuprite, which accounts for their brown/black appearance, as the thin skin of red cuprite is underlain by the dark green of the atacamite [38].

All of these chloride compounds are the predominant corrosion products on many Egyptian bronze objects [6, 25, 38, 39] and were identified on the two studied objects that have been accompanied to these objects in the cache discovered in Sais in 1926 and accessioned into the Egyptian Museum in Cairo with the temporary register number 31/12/26/11 [13, 14]. They are formed as a result of exposure to a long contact with saline soil richer with chloride content at high moisture level. It is known that the Egyptian soil is rich in sodium chloride that is highly reactive toward copper and its alloys.

The basic copper sulfate brochantite, which was detected as a major compound in samples 2, 4, 5 and 7, is usually formed on copper objects during prolonged exposure to humid atmospheric conditions through adsorption and oxidation of sulphur dioxide SO_2 [23, 40, 41]. In soil, it is formed as a result of burial oxygenated conditions, where hydrogen sulphide is evolved as a consequence of bacterial reduction of sulphates that utilize the oxygen for oxidative enzymatic activity from the microfauna present in the humus found in the soil sediments. Under this condition, sulfide ions are produced, thus giving rise to the formation of copper sulfides via the interaction with copper ions [23]. These copper sulphide formations oxidize to copper sulphate [40]. Chalcocite Cu_2S that was detected as a trace component in sample 1 is one of these sulphide formations. Brochantite was identified as a major compound in corrosion samples taken from a bronze Osiris statuette by Ghoniem [14] and was detected associated with chalcocite and digenite Cu_9S_5 on a Sekhmet statue by Ghoniem [13] from the same cache that these objects belonged to. There is no evidence regarding to the source of sulphide ions, i.e. hydrogen sulphide in the burial soil before excavation or the polluted atmospheric conditions during the long storage period.

The dark green basic copper(II) carbonate, malachite $Cu_3(CO_3)_2(OH)_2$, was detected as a trace compound in samples 5 and 7 and the blue basic copper(II) carbonate, azurite $2Cu_3(CO_3)_2(OH)_2$, was also detected as a trace amount in sample 4. The two compounds usually develop during the corrosion process of copper alloys buried in soil or in atmospheric condition after initial forming of cuprous oxide adjacent to the metal surface. This usually happens in the presence of oxygen, carbon dioxide and water [42]. Three oxides were detected; cuprous oxide, cuprite Cu_2O, as a trace compound in sample 3, lead dioxide, palttnerite PbO_2, as a minor compound in sample 2, and tin oxide, cassiterite SnO_2, as a trace compound in sample 7. The presence of those three oxides indicates that the objects are made of bronze (Cu-Sn-Pb) alloy. Usually oxide layer is the first layer formed on the metal surface in most environments. It is probably developed on these objects in a period prior to the burial. If this is not the case, oxygen in the soil will soon procure such a layer that on it the corrosion mechanism is dependent. The flaws, fissures or cracks in this oxide layer favour local cell activity leading to the amassment of other compounds depending on the corrosive factors in the surrounded environment such as Cl^-, S^{--}, soil elements, carbon dioxide and water. It is known that the composition of the corrosion layers is relative to the composition of the soil, the composition of the alloy and the case of the oxide layer.

Quartz, SiO_2, the constituent of the soil, was detected as the major compound in sample 7 and as a trace in sample 4. It reflects the siliceous nature of the burial soil that has to be sandy soil. While the other identified corrosion compounds indicates that it was salty moist soil. In such soil, copper and its alloys corrode intensively as compact sand grains give rise to a structure of wide pores through which water and air may percolate at random [40].

The sandy core found inside of Sekhmet statue and surely used in the hollow cast production process included mainly sand, clay as a minor compound and anorthite as a trace. It could include other organic materials that were not detected by X-ray diffraction method. Many scholars described the discovery of such core material inside Egyptian bronzes [20, 43]. A similar core material was discovered inside a small Egyptian bronze statuette of the Child Horus in the collection of the Ditsong: National Museum of Cultural History in Pretoria after the bronze accidentally broke into two pieces. Analysis of the core samples revealed a composition of clay also but two types of clay; which may indicate layering of the core material that took place during its manufacture [43].

The elemental composition of the objects was analyzed by EDX on tiny specimens taken from detached fragments from the statuettes. Eight metals were detected; three of them are the main elements while the other fifth elements are considered impurities. Copper, tin and lead are the main alloying elements while arsenic; zinc, silver and gold are traces. It can be deduced that the study objects made of leaded bronze alloy. The analyses data in Table 2 show that copper content varies from 75.14% in the specimen of Osiris statuette (52mm high) up to 85.22% in the specimen of Sekhmet statute, Tin content varies from 4.23% in the specimen of Osiris statuette (52mm high) up to10.59% in the specimen of Amun seated ram, while the lead content varies from 5.43% in the specimen of Sekhmet statute up to 19.12% in the specimen of Osiris statuette (52mm high). These results are compatible with the results of SEM-EDS investigation of the Sekhmet bronze statue and the statue of Osiris that were excavated with the same study group and were investigated by Ghoniem [13, 14]. The latter two objects were also made of leaded bronze alloy, where the content of lead in Sekhmet statue amounted to 9.4% and in Osiris statuette up to 10.58%.

Recently, Gouda et al. [6] investigated ten bronze statues displayed at the Egyptian museum in Cairo by X-ray fluorescence. These statues are from the Late Period of the ancient Egyptian history the same period that most likely the study group are dating back to it. The lead content in these ten statues ranged from 3.43% to 20.84%. All of these results assure that the leaded bronze alloy was used extensively in making statues and statuettes in this period of ancient Egypt. The high level of lead was characteristic of copper-alloy statues made during it [4], and over 30% of lead is reported in some instances [17]. One of these instances is the bronze statuette of Osiris dating to C. 600 BC that was excavated with many other bronze objects from the site of the sacred animal necropolis at Saqqara where the lead level arrives to 32% [9]. The high level of lead has many advantages for the casting process of copper alloy artifacts as it increases the fluidity of the alloy where it lowered the melting point of the metal and limited porosity [17]. It also improves the corrosion resistance when exposed to the mild soil, moist air, and also when exposed to near neutral solutions [6].

Table 2. The elemental composition of the study group statues.

	The elemental composition (wt.%)							
Fragment's origin	**Cu**	**Sn**	**Pb**	**As**	**Zn**	**Fe**	**Ag**	**Au**
Sekhmet's statute	85.22	6.50	5.43	1.50	0.46	0.30	0.45	0.12
Feminine statuette	78.62	5.55	13.49	1.19	0.26	0.24	0.44	0.20
Osiris (125 mm high)	80.97	5.78	10.90	0.73	0.81	0,63	0.10	0.04
Osiris (90 mm high)	81.99	6.70	8.90	0.34	0.62	0.35	0.18	0.00
Osiris (52 mm high)	75.14	4.23	19.12	0.34	0.60	0.23	0.20	0.12
Osiris (54 mm high)	80.89	5.64	11.64	0.59	0.45	0.68	0.00	0.10
Osiris (100 mm high)	83.13	5.53	8.85	0.69	0.22	0.31	0.21	0.07
Amun standing ram	78.36	8.30	11.25	0.80	0.24	0.51	0.50	0.00
Amun seated ram	79.66	10.59	7.54	0.66	0.40	0.62	0.31	0.20
Horous the Child	80.65	6.10	12.35	0.40	0.35	0.00	0.11	0.04

Conservation methodology

The first stage of the conservation work involved separating or detaching the statuettes from the statute of Sekhmet that was done mechanically and gently. The main purpose of the objects treatment and conservation was to remove the superficial deposits/encrustations so as to reveal the hidden original surfaces and unveil the incised decoration's details. Treatment procedures varied according to the physical condition and any intervention was balanced by an evaluation of the risk of losing any evidence contained in the corrosion layers.

The first step was the preliminary examination, done using binocular microscopy that was followed by investigative cleaning to establish the condition and the extent of any hidden details. The range of treatments included removal of the compact soil deposits and the hard corrosion encrustation.

Mechanical cleaning was carried out by the use of small hand tools under magnification to the level of the original surface at the red cuprite layer. Laser, as a modern cleaning technique, is not suitable with this hard thick crust of corrosion concretion and the microplasting technique was avoided as it may damage the surface. Soft to firm glass-bristle brushes and small hand-tools were preferred with the statute of Sekhmet (Fig. 10) and the feminine statuette (Fig. 11). These hand tools were used in removal the residual loose, powdery disfiguring deposits and the incoherent upper corrosion layer. The hard green corrosion products were removed with scalpel and vibrotool, while the thick voluminous corrosion crusts were removed with a small chisel and a small wood mallet. Mechanical cleaning, by using Micro-drill with different heads was adopted to grind the hard crust of corrosion products in specific areas. Bamboo skewers, pins and needles were used delicately under magnification to remove all corrosion products from pits and cavities [44].

Fig. 10. The statue of Sekhmet after mechanical cleaning.

Fig. 11. The feminine statuette after mechanical cleaning.

Cleaning of Sekhmet statute revealed the incised lines of the kilt and the mane or the hair around the neck and the face. Incised figures of Lotus flowers were revealed on one side of the throne representing the plant of Upper Egypt whilst the other side most likely has jungles of papyrus representing the plant of the Lower Egypt. The presence of the two plants on the other sides of the throne reflects a representation of the Upper and Lower Egypt's unification. Cleaning of the feminine statuette revealed the features of the female torso clearly where there are not any details, incised lines, or texts on the surface (Fig. 11).

Chemical cleaning was preferred for the other statuettes as the mechanical techniques can be destructive with these smaller objects. The galvanic and electrolytic methods were avoided with these disfigured objects as a layer of elemental copper may be reduced on the surface [45]. First, surface dirt and loose soluble corrosion products were softened by immersion of the objects in tap water for a minimum of one hour associated with using soft and firm brushing. These layers were removed by brushing using soft to firm toothbrushes. For striping the hard insoluble corrosion products, alkali treatments are believed to be less aggressive to these objects. Sodium sesquicarbonate, commonly used in the past for the stabilization of bronze, can tarnish unleaded bronze. It also can promote faster corrosion of leaded bronze as it encourages acid attack on copper in leaded bronze; as well sodium from it contributes to the formation of sodium copper carbonate as a secondary corrosion [33]. Ethylene Diamine Tetra-acetic Acid (EDTA) can be applied as a based chelating agent to soften the hard green corrosion and to facilitate its mechanical removal but it can be a source in producing acetate reactions [33].

Alkaline Rochelle salt solution containing 5% sodium hydroxide (NAOH) and 15% potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$) was preferred for stripping archaeological bronzes [40]. It is still applied in the field for cleaning of ancient metals objects especially coins in order to reveal the surfaces details inscriptions and figures. The studied objects surfaces are obscured by a hard crust of corrosion layer that may hide details that could be exist such as symbols, texts and incised lines or inlaid areas with precious metals such as gold or silver. For these reasons this technique was chosen for the treatment of those statuettes to reveal any possible details.

Chemical stripping by soaking the objects for extended periods in this sequestering solution associated with brushing delicately with glass-bristle brushes guaranteed complete removal of chlorides. Thirty successive baths, two baths daily for up to 15 days, every bath for 30 minutes followed by washing in water and drying thoroughly were applied. These baths succeeded in dissolving cupric compounds without attacking cuprite layer. At the end of this procedure, the objects were rinsed intensively in distilled water to remove any chemical solution residues, and dried in a succession of acetone baths. For stabilization, all the treated objects were placed in 5% w/v benzotriazole in ethanol solution so as to arrest any existing active corrosion and to prevent future outbreaks of corrosion [46]. Benzotriazole is an effective corrosion inhibitor for most copper-base materials by preventing undesirable surface reactions. It produces a passive layer, consisting of a complex between copper and benzotriazole which affords protection in aqueous and gaseous environments polluted with sulphur dioxide, hydrogen sulphide and salt mist [47, 48].

Finally, the objects were coated with a protective coating of paralloid B-44 (Methyl-Methacrylat-Copolymer, Tg 60ºC) in toluene. Paraloid B-44 performs well on copper alloys compared to other coatings [49] as it supplies a good adhesion and toughness to the coating film together with clarity transparency and good resistance to UV ageing and yellowing. It was applied by brush in two coats, eight hours between each coat to allow polymerization of the film. A waxy superficial topcoat of microcrystalline wax (cosmoloid H80) was applied to protect the underlying paralloid layer from degradation. This latest waxy coating functions as a barrier against water or water vapor and offers a more robust protective system. The statuettes that can be seen in figure 12 after treatment and conservation were packed in acid free tissue and placed in polyethylene boxes with silica gel as a preparation for their display or storage.

Fig. 12. Eight statuettes of the study group after cleaning and conservation.

Conclusions

The examination of the all study group objects revealed that they are made using casting techniques; the statute of Sekhmet was cast over sand core, while the other statuettes were made by solid-cast technique. The roughly pointed metal tangs in some of them assure that they were made by solid-cast technique and refer to the possibility to date back to the Late Period (712-332 B.C.). Depending on the visual examination and the size of the objects, it can be said that the statue of Sekhmet is most likely a cult statue where the other statuettes are most likely votive statuettes.

Analysis of the corrosion products indicated that the objects were subjected to corrosive attack as a result of the interaction between their components and the corrosive chloride, sulfate ions coming from the surrounding environment either the saline sandy moist burial soil or the poor storage conditions over many decades. The blue corrosion layer covering most of the objects was analyzed and found to contain mainly of basic lead-copper chloride cumengite. The dark green corrosion product consists mainly of basic copper sulphate brochantite and basic copper chloride atacamite, while the greenish blue corrosion layer consists mainly of cumengite and brochantite minerals. Sand and clay are the main compounds of the sandy core found inside of Sekhmet statue and surely used in the hollow cast production process, while the main compound of the burial soil is quartz.

The identification of copper, lead and tin compounds in corrosion layers gives an indicator that the objects made of bronze alloy, fact that was confirmed by elemental EDX analysis. The analysis results clearly assured that they are made of leaded bronze alloy. Copper content varies from 75.14% up to 85.22% in the specimen of Sekhmet statute, the tin content varies from 4.23% up to10.59%, while the lead content varies from 5.43% up to 19.12%. This analysis assures that the lead bronze alloy is the preferred alloy for casting metallic statues and statuettes in the Late Period.

Conservation methodology comprised cleaning, stabilization and lacquering. Different approaches of cleaning were adopted according to the condition of the objects. Hand tools succeeded in removal residual loose, powdery disfiguring corrosion and soil deposits. The hard corrosion encrustation was removed by careful mechanical cleaning to reveal the preserved surface of the metal. Hand and mechanical cleaning procedures were adopted on the statue of Sekhmet and the feminine statuette. The other statuettes were cleaned chemically for stripping the corrosion layer by soaking in chemical reagent that followed by successive baths of distilled water and acetone. Conservation cleaning of the objects has revealed the original surfaces and the original decorative details in some cases.

Regardless of cleaning procedures, stabilization and protective lacquering should be inherent steps in the conservation of all treated bronzes objects. After their stabilization and conservation, the study group objects are considered suitable for display in the Egyptian Museum.

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