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ANCIENT EGYPTIAN BLACK-PATINATED COPPER ALLOYS*

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This analytical study aims to investigate ancient Egyptian black-patinated copper alloys. The study group was selected from the collections of the Egyptian Museum in Cairo and from the Faculty of Archaeology Museum in Cairo University. Examination and analysis were undertaken using optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDX), X-ray diffractometry (XRD), X-ray fluorescence analysis (XRF) and Fourier transform infrared spectroscopy (FTIR). The analysis results indicated that the black patina contained mainly tenorite (CuO). The study presents evidence of thermal patination and animal glue coating.

KEYWORDS: ANCIENT EGYPT, COPPER ALLOYS, BLACK PATINATION, THERMAL TREATMENT

INTRODUCTION

The colour black has been used as a pigment from prehistoric times. In dynastic times, it was considered to be the colour of the fertile soil of *kmt* (the Black Land), one of the names for Egypt; it therefore carried connotations of fertility and regeneration. It was also the colour of the underworld. The deity Osiris, ruler of the underworld, was referred to in texts as *kmjj* (the black one). During some periods, coffins were given a black ground as a reference to the underworld, to Osiris, and to the renewal of the deceased. Black skin was given to some royal images, to signify the king's renewal and transformation. The association of black with the underworld and its transformatory powers explains the black statues of the king that were buried in the royal tomb of Tutankhamun and in other New Kingdom royal tombs (Redford 2000). Generally, black colours in ancient Egypt symbolized night, death, the underworld and resurrection (Rankine 2006). This, in fact, can explain why many statuettes of kings and gods, funeral objects, and even inlays, metals or wooden objects, have been coloured black (Wilkinson 1994, 109–10). Black-patinated copper alloy objects seem to have been produced in Egypt as early as the Middle Kingdom Period (2040 to 1782 BC) (Giumlia-Mair 1996), and continued until they disappeared after the fall of the Roman Empire (Giumlia-Mair 2005).

For more than a century, efforts have been made to uncover the secrets of ancient Egyptian black-surfaced copper alloy objects. This started with theoretical approaches by researchers (e.g., Pliny 1857; Middleton 1887) and continued with technical investigations and analytical approaches (e.g., Bannister 1929; Craddock and Giumlia-Mair 1993; Ogden 2000; Giumlia-Mair and Lehr 2001; Whyte *et al*. 2002; La Niece *et al*. 2002; Giumlia-Mair 2005; Mathis *et al*. 2009). However, although a mechanism for the formation of what is generally called 'black bronze' has been proposed (see below), there are also black surfaces found on ancient Egyptian copper alloy objects that do not contain gold, most of which have not been fully investigated (Giumlia-Mair

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2001). The fact that black patina covers localized areas of other copper alloy objects suggests that alloy composition is not always the determining factor. Black patina can form easily on any copper alloy surface (Giumlia-Mair 2001). In this context, Laurent and Marc (2001) studied the black patina observed on patrimonial artefacts of different periods. The best known example, they pointed out, is the '*nikomi-chakushoku*' treatment of Cu–Au (0.5–4.0 wt% Au) 'Shakudo' alloys. This patina, a traditional medieval chemical recipe, has been identified as a thin layer of cuprite Cu_2O (Murakami *et al*. 1988), 'but its black color is difficult to explain, as well as the exact importance of gold alloying', they commented. The mechanism of black patina formation on copper alloys is not well understood and still not satisfactorily explained. There may be additional explanations for its formation, so that more analysis and experimentation are required to clarify the matter (Giumlia-Mair 2001).

This paper describes results of recent examination and micro-chemical analysis of ancient Egyptian black-patinated copper alloys from Egyptian collections. It aims to identify the surfaces and investigate the micro-chemical composition and structure to interpret the patination process.

STUDY GROUP

The study group consists of 23 objects. They were selected from the exhibition and storage rooms of the Egyptian Museum in Cairo and from the Faculty of Archaeology Museum in Cairo University. The studied collections came to the museums from the context of archaeological hoards and foundation deposits of controlled excavations. Although there is a lack of documentation in the museum's registration records, the provenance is known for almost all the studied objects. Figure 1 shows a collection of the study group, which contains statuettes, situlas, plaques, fragments and a vase. They date back to different periods of the Egyptian history from the New Kingdom period (*c*. 1550 to 1069 BC) to the Graeco-Roman period (332 BC – AD 640). The description, identification numbers, dates and provenance of the study group are listed in Table 1. The selected study objects have generally dark brown to black surfaces, which were in some cases overlaid with green patina.

EXPERIMENTAL

The surfaces of the objects were examined by optical microscopy. Tiny samples of surface materials, black patina and green patina were removed for analysis. Samples were analysed using a Philips PW 1729 X-ray diffractometer (XRD) and a Jasco-460 plus Fourier transform infrared spectroscopy (FTIR). For the later analysis, samples were ground and pressed in KBr pellets. The analysis has a spectral range from 400 to 4000 cm^{-1}, with a maximum resolution of 4 cm^{-1}. All spectra were recorded in the transmission mode. Non-destructive analytical equipment was not available to the authors at this stage of the research, so cross-section samples containing patina and very small parts of the metal were removed. Sampling was only allowed from fragments. A small black patina chip was removed, as well from the surface of the plaque (JE.35107AF) for imaging and for micro-chemical analysis by a Philips X 130 environmental scanning electron microscope (ESEM) with combined EDX. The samples were embedded in epoxy resin, ground and polished mechanically according to standard metallurgical procedures. The main detection limits of EDX measurement are 0.2% for Cu, 0.5% for Au and As, and 0.3% for Pb, Ag and Sn. Data at or below these limits are not significant.

A Metorex X-Met 2000 XRF was used to analyse the bulk alloys. The reference material used for calculating the results is BCR no. 691 of the Bureau of Certified Reference Materials (BCR).

Figure 1 *The collection of ancient Egyptian black-patinated copper alloy objects that were investigated in the study.*

The precision values for the measurement are as follows: ~ ±1% for Cu, ~ ±1.2% for Sn, ~ ±1.5% for Pb, ~ ±0.03% for Zn, ~ ±0.05% for As, ~ ±0.06% for Fe and ~ ±0.01% for Mn. The accuracies of the analysis should be at similar levels. A Niton XLT 700, version 4, portable XRF was used for the analysis of the body alloy compositions of three objects; the Maat statuette (1615), the

Table 1 *A list of the study group objects with their corresponding description, identification number, date, provenance, analysis results of bulk alloy by XRF, patina sample type, principal crystalline compounds identified by XRD and analysis results by FTIR*

Description	*ID*	*Date and provenance*	*Bulk alloy identified by XRF*	*Sample type*	*Principal crystalline compounds identified by XRD*	*Compounds identified by FTIR*
Maat* Statuette of the goddess Maat, seated squatting on a bronze chair. Her feather crown is missing. Recesses for inlay are present around the head, in the eyes and in the chair. It is 17.2 cm high and 5.5 cm wide.	1615	Graeco-Roman (332 BC – AD 640); Tuna El-Gabal	86.7% Cu, 10.6% Pb, 1.1% Fe, 1.0% Sb, 0.08% Au	Black patina	—	Animal glue + tenorite + copper acetate + acetic acid + calcium carbonate (spectrum no. 1, Fig. 3)
Ibis* Ibis god statuette, body made of gesso while the head, neck, legs and tail feathers are made of black copper alloy. The eyes, the neck and the legs have recesses, which indicate lost inlay. It is standing on a modern base, as it was originally standing on Naoos. The new wooden base was made only for exhibition purposes. It is 27 cm high.	1616	Graeco-Roman (332 BC – AD 640); Tuna El-Gabal	—	Black patina	Calcite + atacamite + calumetite + anglesite + tenorite + copper (II) acetate hydrate	Animal glue + tenorite + copper acetate + acetic acid (spectrum no. 2.1, Fig. 3)
				Black patina	Calcite + cuprite + unidentified material + copper (II) acetate hydrate	Animal glue + copper acetate + acetic acid (spectrum no. 2.2, Fig. 3)
				Coating material	—	Animal glue (spectrum no. 2.3, Fig. 3)
Ptah* Statuette of the god Ptah, depicted with his hands emerging from wrappings in front of his body and holding a sceptre, an ankh and a Djed. It takes the form of a bearded man wearing a skullcap and shrouded as a mummy. It has fine recesses in the eyes and in the necklace, in which original inlays were lost. It is 13.5 cm high and 4.5 cm wide.	2000	New Kingdom (1550–1069 BC); Helopolies	33.2% Cu, 2.6% Sn, 60.5% Pb, 1.7% Fe, 0.5% Sb, 0.9% Zn	Black patina	Cuprite + calcite	Animal glue + tenorite + calcium carbonate + ester of fatty acids (spectrum no. 3, Fig. 5)
Feminine statuette* Gilded wooden feminine statuette wearing a black bronze *atef* crown with two long spiral horns, the sun disc and four dangling cobras. It is 24.5 cm high and 10 cm wide.	1620	Graeco-Roman (332 BC – AD 640); Tuna El-Gabal	76% Cu, 11.5% Sn, 11.5% Pb, 0.05% Au, 0.4% Fe			

Osiris head* Solid cast head of Osiris that is broken around the neck of a large-sized statue of the god Osiris. The eyes were inlaid with electrum. It is 39 cm high.	1619	Graeco-Roman (332 BC – AD 640); Tuna El-Gabal	—	Black patina	Tenorite + cuprite + Cu–Sn + quartz	—
Harpocrates Seated bronze statuette of Harpocrates, with his two hands extended on the knees. It has a hair-band strewn with small rounds by two features; above the right ear, a braid that sticks to it has a bent lower end; on the face, the *Uraeus* was fixed. This bronze is not cleaned yet and it is covered with corrosion crust. There are fine recesses in the eyes and in other parts of the body, from which original inlays were lost. It is 14 cm high. It was found in 1893.	CG.38129	Memphite region; Saqqarah	—	Black patina	—	Animal glue + tenorite + {ester of fatty acids/beeswax} + atacamite (spectrum no. 4.1, Fig. 6)
				Green patina	Malachite + atacamite + clinoatacamite	Animal glue + tenorite + ester of fattyacids (beeswax) + atacamite (spectrum no. 4.2, Fig. 6)
Osiris Seated statuette of Osiris. It is 21 cm high.	CG.38423	Late period (Sais period); San El-Hagar	—	Black patina/ green patina	Quartz + atacamite + cuprite	Esters of fatty acids/wax + antlerite + unidentified organic material (spectrum no. 5, Fig. 4)
				White material	Quartz + gypsum + calcite	—
Kneeling king Bronze statuette of a king making an offering. The figure has fine recesses in the eyes and in other parts of the body: the original inlays are lost. It is 12 cm high. It was excavated by A. Mariette in 1858.	Tr. 8-5-21-2	Memphite region, Saqqara; North Serapeum area	—	Green patina	Quartz + atacamite + clinoatacamite + malachite	—
				Green patina	Quartz + atacamite + clinoatacamite + cuprite	—
Ibis Statuette of the god Ibis. It is 13 cm high.	Tr. 18-1-19-4	Memphite region	—	Green patina	Samplite + atacamite + clinoatacamite + calcite	—
Osiris face Bronze face of Osiris for inlay. There are fine recesses in the face where original inlays were lost. It is 9 cm high.	Tr.8-3-19-2		—	Black patina	—	Antlerite + unidentified organic material (spectrum no. 6.1, Fig. 4)
				Green patina	Calumetite + atacamite + clinoatacmaite + quartz	Antlerite + ester of fatty acids (beeswax) + unidentified organic material (spectrum no. 6.2, Fig. 4)
Vase Miniature bronze vase. It is 4.8 cm high.	Tr. 1-5-26-1	Middle Egypt; Deir El-Bersha	—	Green patina	Unidentified	Antlerite + unidentified organic material (spectrum no. 7.1, Fig. 4)
				Black patina	—	Unidentified organic material (spectrum no. 7.2, Fig. 5)
				Black patina	Tenorite + nantokite + atacamite	Antlerite + unidentified organic material (spectrum no. 7.3, Fig. 4)

Table 1 *(Continued)*

Description	*ID*	*Date and provenance*	*Bulk alloy identified by XRF*	*Sample type*	*Principal crystalline compounds identified by XRD*	*Compounds identified by FTIR*
Situla Bronze situla with a very sharp edge. Light green patina on the outside and internal surface. It is 12 cm high and 4.4 cm wide.	CG.3458	Late period (713–332 BC)	—	Black patina	Cuprite + malachite + tenorite + nantokite	Animal glue + ester of fatty acids (beeswax) + tenorite (spectrum no. 8.1, Fig. 6)
				Black patina	—	Animal glue + ester of fatty acids (beeswax) + tenorite + malachite (spectrum no. 8.2, Fig. 5)
Situla Bronze situla; the handle is broken. It is 17 cm high.	Tr.20-6-17-3	Middle Egypt; Zawyet El-Amwat	—	Black patina	—	Tenorite + mineral wax (spectrum no. 9.1, Fig. 5)
				Black patina	—	Tenorite + calcium carbonate + unidentified organic material (spectrum no. 9.2, Fig. 5)
Plaque Bronze plaque with an inscription of Osiris Wennefer. It is 21 cm high and 8.5 cm wide. Excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	JE.35107V	Memphite region; Mit Rahina	97.4% Cu, 1.4% Sn, 0.4% Zn, 0.7% As, 0.03% Mn	Green patina	Atacamite + clinoatacamite + malachite + tenorite	Animal glue + tenorite + ester of fatty acids (beeswax) + atacamite (spectrum no. 10.1, Fig. 6)
				Black patina	—	Protein + ester of fatty acids (beeswax) + tenorite + atacamite (spectrum no. 10.2, Fig. 6)
Plaque Inscribed bronze plaque: Hapy carrying two vases. It is 25 cm high and 8.5 cm wide. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	JE.35107 Z.2	Memphite region, Mit Rahina	97.1% Cu, 1.7% Sn, 0.4% Zn, 0.8% As, 0.05% Mn	Green patina	Atacamite + cuprite + tenorite	
				Black patina		Animal glue + tenorite + ester of fatty acids + fatty acids (beeswax) + atacamite (spectrum no. 11, Fig. 6)
Plaque Bronze plaque fragment. It is 19.5 cm. high and 9.5 cm. width. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	TR. 28-11-26-9	Memphite region; Mit Rahina	91.2% Cu, 4.1% Sn, 3.6% Pb, 0.4% Zn, 0.7% As	Green patina	Atacamite + clinoatacamite + trace of cuprite	—
				Brown patina	—	Cuprite (spectrum no. 12, Fig. 5)
Plaque Bronze plaque fragment. It is 16 cm high and 9.5 cm. wide. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	JE.37064	Unknown	—	Black patina		Animal glue + {ester of fatty acids/beeswax} + atacamite + tenorite (spectrum no. 13, Fig. 6)

Serpent Bronze serpent fragment, with projections to be used for inlay. It is 7 cm high and 11 cm wide. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	TR. 28-11-26-20	Memphite region; Mit Rahina	96.4% Cu, 2.5% Sn, 0.3% Zn, 0.8% As	Green patina	Malachite + atacamite + clinoatacamite	—
				Black patina		Animal glue + tenorite + ester of fatty acids + atacamite (spectrum no. 14, Fig. 6)
Udjat-eye Bronze Udjat-eye for inlay, with a projection in the back. It is 9.5 cm high and 4.5 cm wide. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	Tr.28-11-26-22	Memphite region, Mit Rahina	96.3% Cu, 2.6% Sn, 0.3% Zn, 0.8% As	Black patina	—	Tenorite + unidentified organic material (spectrum no. 15.1, Fig. 5)
				Green patina	Clinoatacamite + atacamite + malachite + quartz	—
				Black patina	—	Animal glue + ester of fatty acids (ancient animal glue) + atacamite + tenorite (spectrum no. 15.2, Fig. 6)
Arm Bronze statuette forearm. It is 14.5 cm long. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service) in 1901.	Tr 28-11-26-8	Memphite region; Mit Rahina	—	Black patina	Atacamite + clinoatacamite + tenorite + quartz	Animal glue + {ester of fatty acids/beeswax} + atacamite + tenorite (spectrum no. 16.1, Fig. 6)
Arm Bronze statuette forearm. It is 15 cm long.	Tr 30-11-26-31	Memphite region; Mit Rahina	—	Green patina	Atacamite + clinoatacamite + tenorite + digenite	Animal glue + {ester of fatty acids/beeswax} + atacamite + tenorite (spectrum no. 16.2, Fig. 6)
Arm Bronze statuette firearm. It is 12.5 cm long.	JE 35107 AH	Memphite region; Mit Rahina	—	Black patina	Cu–Sn + digenite	Animal glue + ester of fatty acids (ancient animal glue) + tenorite (spectrum no. 17, Fig. 6)
Amun fragment Bronze figure of Amun for inlay. It is 7.5 cm high and 4.5 cm wide. It was excavated by A. Daninos for the EAS (Egyptian Antiquities Service).	Tr.28-11-26-21	Unknown	98.9% Cu, 0.3% Zn, 0.7% As	Black patina	Unidentified	—
				Green patina	Atacamite + clinoatacamite	—

Notes: ID = identification number; CG = *Catalogue general* (Daressy 1905); Tr = temporary registration number; JE = *Journal d'entré*.

*The source of the object is the Faculty of Archaeology Museum, Cairo University. Objects without this symbol are from the Egyptian Museum, Cairo.

ICDD file reference nos.: atacamite $Cu_2(OH)_3Cl$, 02-0146; clinoatacamite $Cu_2(OH)_3Cl$, 25-1427; cuprite Cu_2O, 05-0667; malachite $CuCO_3.Cu(OH)_2$, 10-0399; calumetite $Cu(OH,Cl)_2$, 15-669; quartz SiO_2, 05-0490; anglesite $PbSO_4$, 05-0577; gypsum, 33-0311; calcite $CaCO_3$, 05-0586; digenite, 09-0064; tenorite CuO, 05-0661; nantokite CuCl, 06-0344; brochantite $CuSO_4.3Cu(OH)_2$, 03-0282; Cu–Sn, 02-0713; copper (II) acetate hydrate, 27-0145.

The line in the centre of a column means 'this method was not used on this sample'.

Figure 2 *A photomicrograph of the yellow transparent material that was found covering the Ibis (1616), This coating material is strongly adhered to the black patina. Magnification × 100.*

Ptah statuette (2000) and the Feminine statuette (1620). The analysis was undertaken in two different analysis areas on each object. The obtained results are the average of two measurements. The Certified Reference Material of the measurement is no. 35, EN-04292005-IARM-P. The precision values for the measurement are as follows: ~ ±0.2% for Cu, ~ ±0.4% for Pb, ~ ±0.1% for Sn, ~ ±0.4% for Ag, ~ ±0.09% for Au, ~ ±0.1% for Sb, ~ ±1.6% for Fe and ~ ±0.05% for Zn.

RESULTS AND DISCUSSION

Visual examination of the study objects revealed that they generally have a uniform and compact black patina, with little difference in the appearance and some green patina overlay. Careful examination of the surface of the Ibis statuette (1616) revealed that there is a dry droplet of a yellow transparent material on one of the legs. This material appeared to be covering the whole object as a coating. Optical microscopic examination revealed that this yellow coating is strongly adhered on top of black patina, as shown in Figure 2. The analysis results of the black patina, the green patina, the coating material and the bulk alloy are listed in Table 1.

Black patina composition and formation mechanism

Black patina samples were analysed by both FTIR and XRD. The identification of the patina by FTIR spectroscopy was based on characteristic features related to organic and inorganic constituents. These features are listed in Table 2. The infrared transmission spectra of the analysed samples are shown in Figures 3–6. Tenorite was identified in 19 samples taken from 15 objects, and cuprite was found together with tenorite in black patina samples, as shown in Figure 7.

Table 2 *Analysis data of FTIR spectroscopy of black and green patina samples, wavenumber (cm^{-1}), functional group and the characteristic features of the identified compounds*

Wavenumber (cm^{-1})	*Identified functional groups/characteristics*	*Notes*
~1650	C=O stretching (amide I)	
~155	C–N stretching and N–H bending (amide II)	These features are characteristic for animal glue (Derrick *et al*. 1999)
~1450	C–H bending (amide III)	
3200–3500	N–H stretching peaks on the broader bonded O–H band	
2926 and 2855	Asymmetric and symmetric C–H stretching of aliphatic groups	These features indicated the presence of beeswax (Derrick *et al*. 1999)
1735	C=O stretching of ester group	The presence of C=O group of ester of fatty acids bands at 1735 cm^{-1} in some samples is possibly due to ageing of animal glue. Ancient glues often contain a small amount of lipids, giving a very small ester band, which would not be present in modern glue or gelatin (Skans and Michelsen 1986; Mills and White 1994; Newman and Serpico 2000).
~1464 and 721	C–H bending	
1110–1180	C–O stretching	
600, 510 and 420	Metal–oxygen stretching of lattice vibrations	Characteristic features of Tenorite (McDevitt and Baun 1964; Estep-Barnes 1977; Giangrande 1987).
Very strong band at 615	Metal–oxygen stretching of lattice vibrations	Characteristic features of cuprite (O'Keeffe 1963).
3445 and 3350	Asymmetric and symmetric O–H stretching	
1050–600	Planar deformation modes of O–H group	Paratacamite and atacamite (Tennent and Antonio 1981; Matteini *et al*. 1984).
1110	SO_4^{2-} stretching band	These features are characteristic for antlerite (Omari and Kerr 1963; Hertzberg 1986).
1070	S_2O_5 stretching band	
3480	O–H stretching band	
1155	H_2O deformation band	
1660–1550		These features are characteristic for copper acetate.
1450–1400	Acetate ion stretching and bending bands	
~1050		
~1020		
~925		
3550–3200	Asymmetric and symmetric O–H stretching bands	

The black patina was previously identified by Craddock and Giumlia-Mair (1993) as cuprite. However, tenorite was detected together with cuprite in one of their analysed objects, and gold was generally found in as little as trace amounts (less than 0.06 wt%) in the body metal. It was proposed that the black patina developed on copper alloys containing gold consists of cuprite,

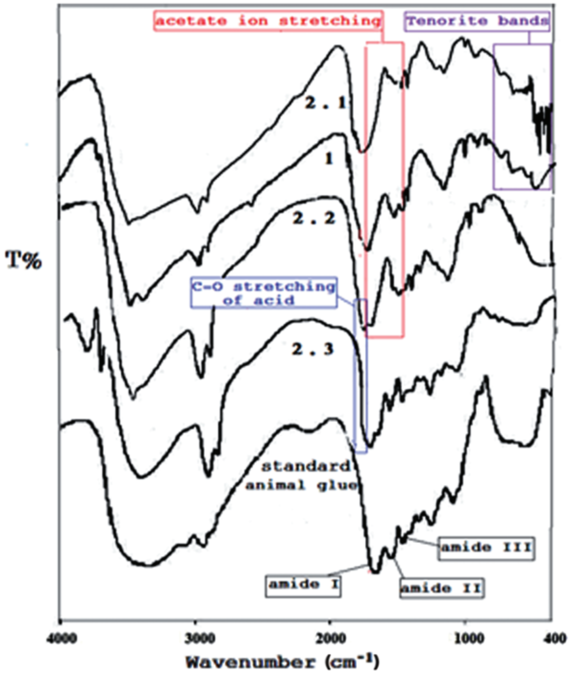

Figure 3 *FTIR transmittance spectra 1–2.3 are compared to the animal glue reference spectrum (prepared standard). The characteristic features of the identified components, animal glue, tenorite, copper acetate and acetic acid are illustrated on the spectra and explained in detail in Table 2.*

with only some interspersed tiny specks of precious metals. But as cuprite normally has a red colour and is rather fragile, and the crystalline compound found on the objects was very dark and very compact, further explanations are required (Giumlia-Mair 2001).

Tenorite forms when copper is slowly heated in air. At first, the copper develops a cuprite film that, as it thickens, exhibits a succession of interference colours up to the fourth order. As the film continues to grow, small black spots of tenorite appear, giving the film a sooty appearance. As the thickness increases beyond the interference colour range, the black tenorite layer spreads over the entire surface of copper. Evans (1960) proposed that a chip of this patina would reveal that the initial red cuprite layer is retained below the tenorite. The existence of both copper oxides cuprite Cu_2O and tenorite CuO in black patina samples (see Fig. 7) and the dominant presence of tenorite indicate that the objects were subjected to heating (Scott 1997; Mathis *et al*. 2009).

The black patina chip removed from object number JE.35107AF was imaged (Fig. 8) and analysed by SEM–EDX at five analysis spots. The analysis data in Table 3 show that copper was detected in a high percentage at spot C, where the cuprite layer was distinguished as a consistent layer (Fig. 8). Carbon was detected at a relatively high percentage (up to 35.4%) in spot (E). This is due to the increasing concentration of the coating material towards the outer surface. The thickness, structure and morphology of the black patina chip (Fig. 8) differ from these of naturally produced copper oxides. Moreover, they differ from those of natural patina formed on copper alloys, as categorized by Robbiola *et al*. (1998).

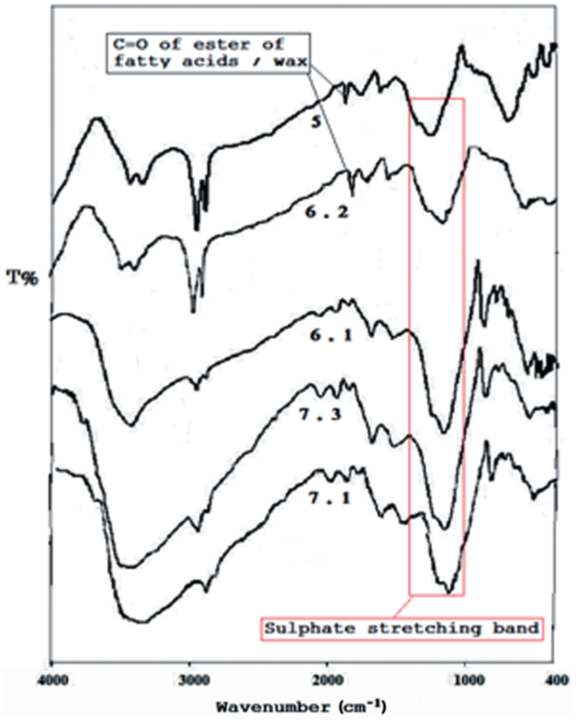

Figure 4 *FTIR transmittance spectra showing SO_4^{2-} containing compounds and beeswax features in addition to unidentified organic material.*

Green patina composition

The presence of green patina, which was identified as atacamite, clinoatacamite, nantokite, malachite and calumetite, overlaying some black-patinated surfaces and within the black patina results from natural mineralization processes that may have taken place before and after excavation. The presence of copper acetate in the patina samples is suggested to result from exposure to vapours of acetic acid (Derrick *et al*. 1999). This may be due to contact with wood in burial or in storage.

Black surfaces that were not overlaid with green patina are suggested to have undergone limited cleaning operations, as some soil residues such as quartz were identified in the black patina (see Table 1). This indicates that the objects have not been stripped and that they still retain their original surfaces. These cleaning operations were unfortunately not documented.

Coating material

The coating material was identified by FTIR as animal glue (see Table 1). Animal glue was identified in 17 black patina samples. This can be explained if the intentionally produced black patina had been given a coating of animal glue to protect the patina against scratching. Animal glue is a strong liquid protein-based adhesive, which is (as other proteins) a rather stable material

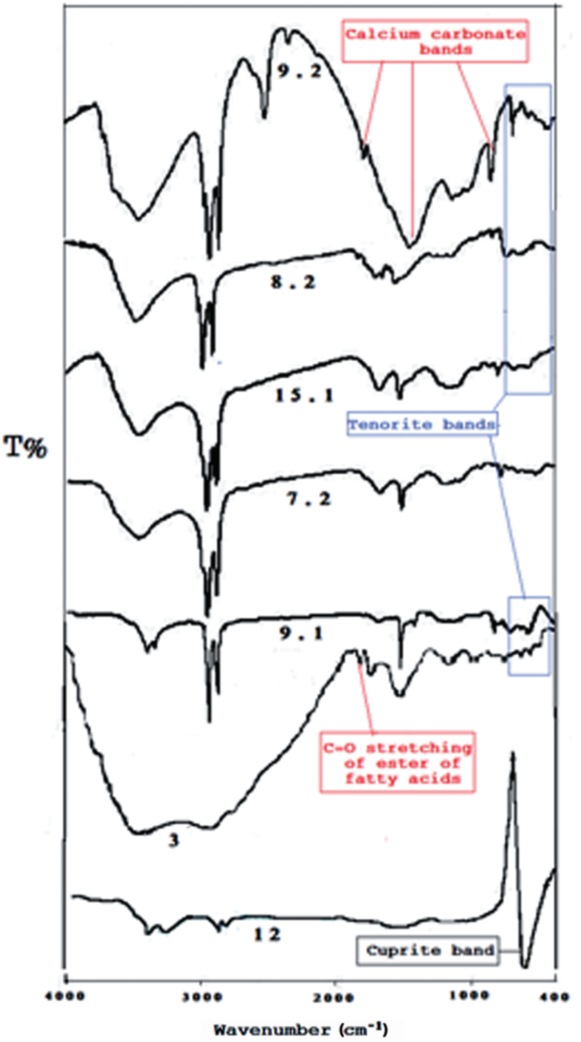

Figure 5 *FTIR transmittance spectra showing characteristic features of the identified components: tenorite is identified in all spectra except nos. 7.2 and 12; animal glue and beeswax are identified in spectra nos. 3 and 8.2; calcium carbonate is identified in spectra nos. 3 and 9.2; mineral wax is identified in spectrum no. 9.1; and cuprite is identified in spectrum no. 12.*

to oxidation and undergoes little chemical change in non-elevated temperature and humidity. Although animal glue is vulnerable to microbial attack, copper and its alloys are natural anti-microbial materials (Dollwet and Sorenson 1985). This fact can explain the survival of animal glue for a long time after burial. In addition, lipids were detected in the analysed samples (see Table 2 and Figs 5 and 6). This small amount of lipid indicates that the glue is ancient, as lipids would not be present in modern glue (Skans and Michelsen 1986, 63; Mills and White 1994; Newman and Serpico 2000). On ageing, the solubility of gelatin glue is diminished (Birstein and Tul'chinsky 1981; Karpowicz 1981): this explains the low solubility noticed by the authors of an

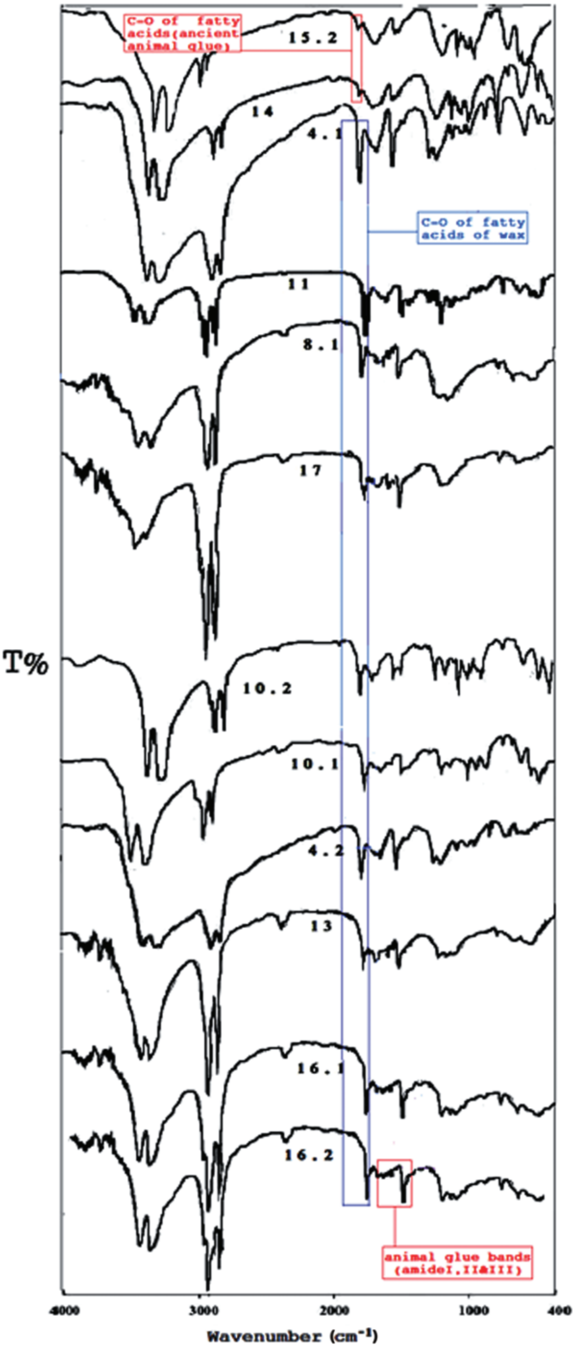

Figure 6 *FTIR transmittance spectra showing characteristic features of animal glue, tenorite and beeswax: esters of fatty acids resulting from ancient animal glue are present in spectra nos. 14 and 15.2, while atacamite and paratacamite are present in all spectra except for nos. 8.1 and 17.*

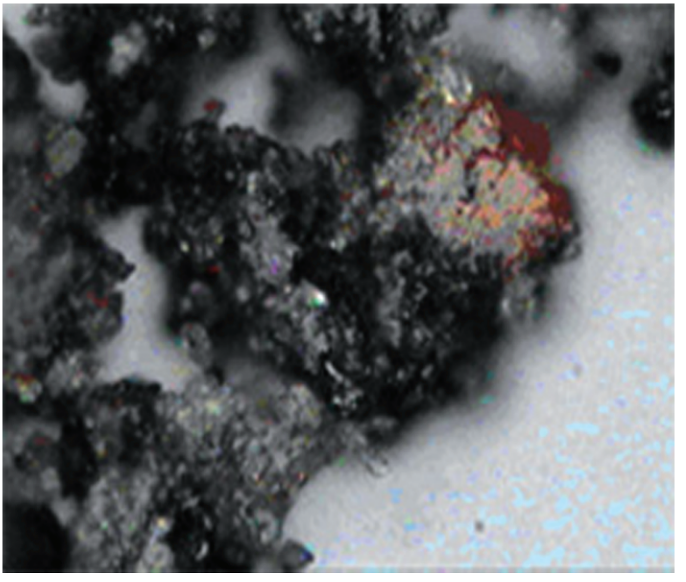

Figure 7 *A photomicrograph showing tenorite overlaying cuprite in a black patina sample. Magnification × 400.*

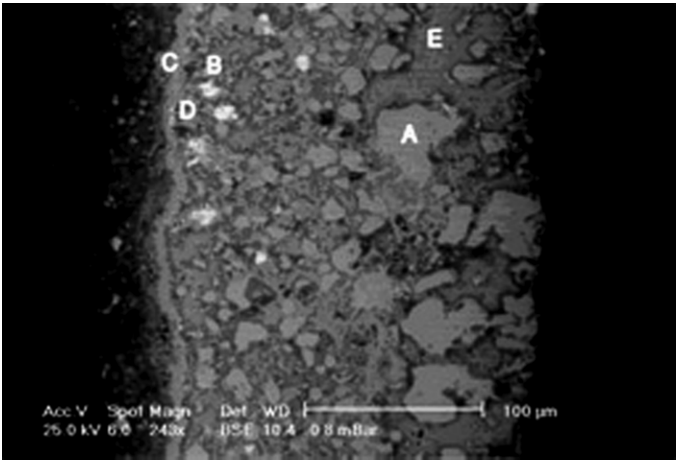

Figure 8 *An SEM photomicrograph of a cross-section of black patina chip removed from plaque (JE.35107AF): A, B, C, D and E are EDX analysis spots. Analytical data are given in Table 3.*

animal glue sample removed from the Ibis statuette (1616). The presence of beeswax and mineral wax may result from post-excavation interventions.

Alloy composition and microstructure

Two objects of the study group were identified as ancient Egyptian *hmty km*, as very little gold was detected in the body metal. Other objects are identified as copper, tin–bronze and leaded

Table 3 *EDX analysis results of the patina chip shown in SEM image of Figure 8*

Element	*Composition (wt%)*				
	Spot A	*Spot B*	*Spot C*	*Spot D*	*Spot E*
C	27.61	29.12	31.49	34.73	35.40
As	0.00	0.00	0.14	0.87	0.00
Al	0.00	0.00	0.00	14.98	0.32
Si	0.00	0.89	0.46	0.30	0.22
P	0.00	0.47	0.05	0.03	0.03
Cl	2.78	4.49	2.78	3.72	16.32
Ag	0.00	0.24	0.17	0.17	0.17
Ca	0.00	0.26	0.06	0.09	0.12
Fe	0.05	0.23	0.12	0.14	0.10
Cu	69.57	33.56	62.21	42.73	46.56
Au	0.00	0.00	0.82	0.62	0.00
Pb	0.00	30.75	1.68	1.62	0.76
Total	100	100	100	100	100

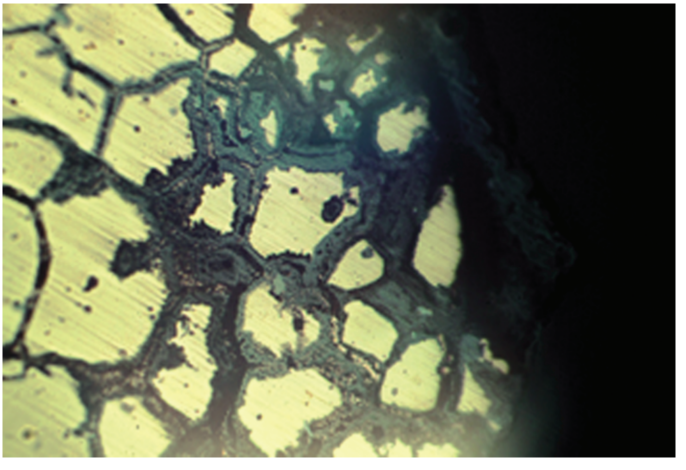

Figure 9 *The microstructure of a cross-section sample of the serpent (TR. 28-11-26-20), showing black patina on the surface and intergranular corrosion of the body metal, Magnification* × *200.*

tin–bronze (see Table 1). This reinforces the suggestion that the alloy composition is not the determining factor for black patina formation. Black patina was produced on a range of copper alloy surfaces.

The microstructure of the body metals revealed intergranular corrosion, as shown in Figure 9. Thermal treatments induce crystallization and could increase the extent of the intergranular corrosion phenomena (Ingo *et al*. 2006). This indicates that the studied objects were thermally treated. The combination of these research findings provides evidence that the black patina on the studied copper alloys was produced by thermal patination.

Other possible mechanisms

Black copper sulphide, digenite Cu_9S_5, was found in the black patina on one of the investigated objects. Sulphur, egg mixture and/or egg yolk could have been used for treating metal surfaces, and this could be the source of the produced black copper sulphide. Staining with sulphur and blackening silver with egg yolk were not uncommon in ancient Egypt (Pliny 1857, 128; Cooney 1966). This gives rise to the suggestion that there are other mechanisms of black patination that have not yet been investigated. There could be more than one recipe applied in ancient Egypt, for instance, according to economic or technical purposes. This suggestion can be evidenced by the poor-quality black-surfaced Osiris statuette (CG 38423), which proved to have a black surface over a gesso layer, giving an example of an unusual black-surfaced appearance over a white ground.

However, a wider survey is needed for the investigation of black patina produced by different recipes, in order to define the recipes that were most commonly applied in ancient Egypt. It has also been noticed through observations that black-patinated objects were less dramatically affected by corrosion attack and seemed better naturally preserved than bare copper alloys. The authors suggest that this is another important point for future study, as experiments are needed to explain this observation.

CONCLUSION

The study suggests different methods and mechanisms for the production of black-patinated copper alloy artefacts in ancient Egypt other than that proposed earlier on copper alloys containing up to 4% gold. The examination and analysis described in this study show that the black patina contains organic and inorganic constituents. XRD and FTIR provided evidence of thermal patination of ancient Egyptian copper alloys. The alloy composition of most of the investigated objects was found to be different from the classic black bronze alloys and does not contain gold. This proves that the alloy composition is not the determining factor for producing artificial black patina on copper alloys.

The morphology, metallurgical features and micro-chemical structure of the black patina/metal interface reinforced the suggestion of thermal patination. FTIR gave strong evidence for the application of animal glue in the preparation of the black patina. It is suggested that it was used as a surface coating.

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