Bronzes from the Sacred Animal Necropolis at Saqqara, Egypt: a study of the metals and corrosion

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Summary More than 1800 bronze objects dating to *c*.600 BC were excavated from the site of the Sacred Animal Necropolis at Saqqara, Egypt between 1969 and 1971. While the important pieces had been accessioned by the Department of Ancient Egypt and Sudan and had been routinely cleaned using alkaline and/or acidic reagents in the 1970s, the residual group considered here, which includes numerous figurines and parts of sculpture, situlae and jewellery, had remained unregistered and uncleaned and so retained a burial corrosion crust. Both the metal substrates and the surface corrosion were studied to obtain information about objects that were under consideration for accession and to contribute to the wider study of this important site.

Microscopy, scanning electron microscopy with energy dispersive X-ray spectrometry, X-ray diffraction and Raman spectroscopy were used for the microstructural and compositional analysis of metals and for the identification of the corrosion products on the surface. Of the five objects selected for metallographic study, two are tin bronzes and the others are leaded tin bronzes; four have as-cast structure while one (a ring) was cast and had been subjected to working and annealing. The pale blue corrosion on the surface was identified as a mixture of chalconatronite ($Na_2Cu(CO_3)_2 \cdot 3H_2O$) and copper sulphates, with smaller quantities of acetates, including sodium acetate trihydrate and sodium copper carbonate acetate. Chalconatronite and copper sulphates are likely to be part of the original burial concretion, while the acetates have probably resulted from the alteration of the original corrosion and the formation of new corrosion in the presence of acetic acid during storage, as these objects have been stored in wooden trays since excavation. In the case of a composite bird figure, the wooden body of the object may have been the cause of localized formation of the acetates on the bronze foot.

In parallel to the scientific investigation, corrosion removal was carried out to reveal hidden decoration. Some of these objects have been cleaned and the unsuitable storage media have been replaced.

INTRODUCTION

The ruins of Memphis, known as the first city of pharaonic Egypt, are on the west bank of the Nile, around 30 km south of Cairo. To the west of the city is Saqqara, the great necropolis of Memphis, and on the west side of the bluff of North Saqqara lies the site of the Sacred Animal Necropolis (SAN). From 1964 to 1976, excavations were conducted by the Egypt Exploration Society (EES) at SAN and more than 1800 bronze objects were found. The finds included statuettes and other ritual equipment, including altars, stands, censers, tongs, razors, ladles, skillets, strainers, ewers, jars, basins, dishes and situlae [1].

In the 1970s, some of the bronze finds from SAN were donated to the British Museum by the EES and the majority of them were formally accessioned into the Museum collections. Many of these bronzes were routinely cleaned at the time of acquisition and some have been displayed in the public galleries. The residual group studied here had been considered in poor condition and remained unregistered while stored in the reserve collections of the Department of Ancient Egypt and Sudan. The items in this group are all made from copper alloys and include 26 single objects and three groups of miscellaneous fragments; among the objects are numerous figurines and parts of sculptures, situlae and jewellery; most of the small bronzes discussed here can be dated to approximately 600 BC.

Apart from a few objects that had been cleaned on site in Egypt, using methods for which no details are available, the group retained their burial corrosion concretion. It would appear that they had been kept in a wooden cupboard on a wooden tray padded with cotton wool since the time of their acquisition. Thick burial concretions including pale blue corrosion products, which were said to have been present

FIGURE 1. Four objects from which samples were taken for metallographic study in cross-section: (a) torso of Osiris, No. 8; (b) ring, No. 11; (c) Osiris, No. 12; and (d) Osiris, No. 14. Scale bars show 1 cm divisions

at the time of excavation, were observed on some objects [2]. However, the formation of new pale blue corrosion efflorescences, identified as copper compounds containing acetate (ethanoate) and/or formate (methanoate) has often been associated with the side effects of certain display or storage environments [3–6]. Previous chemical treatments have also been reported as responsible for the formation of these types of corrosion products on copper alloys [7–10]. Here, the identification of corrosion products was carried out for the group of unaccessioned objects and the causes of corrosion are discussed.

Metallographic samples were taken from a small number of the objects to enable studies of metalworking technology to be made and to assist in an understanding of the development of corrosion on the surfaces. It was hoped that this technical investigation would also contribute to the wider study of the important site of Saqqara.

SAMPLING AND EXPERIMENTAL

The pale blue corrosion products were taken for analysis from five objects and an unidentified 'lump' of corrosion. The corrosion products were selected with the aim of identifying the causes of the corrosion, which in this instance derive either from burial or from the conditions in which the objects were stored (or a combination of both). The corrosion products were identified using X-ray diffraction (XRD) combined with elemental analysis using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyser (EDX). Raman spectroscopy was also used to detect any organic salts present, as XRD is not very sensitive to copper formate or acetate. Cross-sections were taken from four objects (Figure 1) and two fragments to allow metallographic study of the metals using microscopy and SEM-EDX. These objects were selected in order to

obtain maximum technical information while minimizing damage; the sample preparation and analytical techniques are described in the experimental appendix.

COMPOSITION AND MICROSTRUCTURE OF THE METALS

The condition of the objects varied, with some being partially corroded and others having corroded throughout their depth, leaving little metal remaining, Table 1. It was found by EDX analysis that five objects were tin bronzes of which three were leaded tin bronzes. The tin content was found to be in the range 1.6–7.0 wt%, with a lead content in the range 8.4–32.0 wt%. The lump of corrosion (No. 29) was probably originally part of a wire or ring (Figure 2); EDX analysis suggested it was a leaded tin bronze.
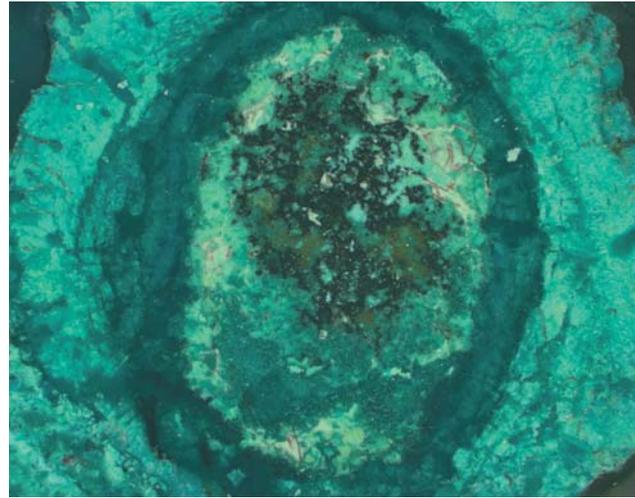

FIGURE 2. Photomicrograph of a lump of corrosion (No. 29), suggesting that the original object was a wire or ring. Image width: 3.45 mm

FIGURE 3. Photomicrograph of a polished section of the ring (No. 11) showing an annealed structure; etched with ethanolic iron(III) chloride. Image width: 0.27 mm
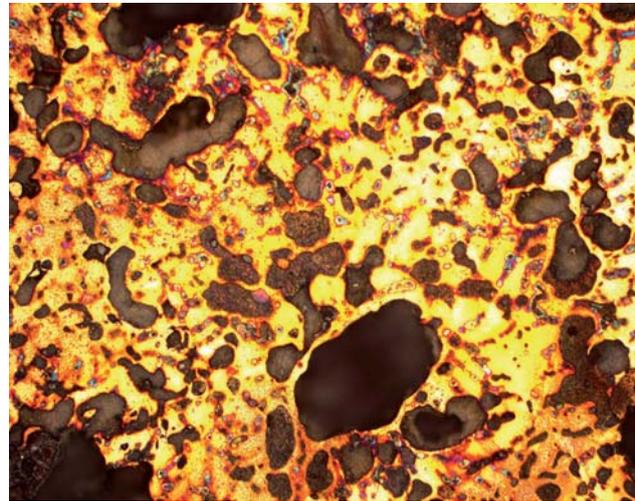

FIGURE 4. Photomicrograph of a polished section of an Osiris figure (No. 14) showing a dendritic structure; etched with ethanolic iron(III) chloride. Image width: 0.68 mm

TABLE 1. The composition and microstructure of the bronze objects studied

Sample No.	Object	Metal thickness (mm)	Cu wt%	Sn wt%	Pb wt%	As wt%	Other elements wt%	Microstructure	Comments
8	Osiris torso	4.1	80.2	3.1	15.9	0.8		As-cast equiaxed with eutectoids on grain boundaries	Corrosion penetration is 1.1 mm. Pitting corrosion and large voids due to loss of Pb globules were observed
11	Wire or earring	1.3	91.6	7.0	–	0.8	0.6 S	Recrystallized structure with annealing twins	Metal remained in most areas, but corrosion penetrated through in some areas
12	Osiris	2.4	88.4	1.6	8.4	–	1.6 Cl	As-cast equiaxed without eutectoids	Corrosion has penetrated through the metal with a small area of metal remaining
14	Osiris	3.0	64.4	2.1	32.0	0.8	0.2 Cl	Dendritic structure	Corrosion penetration is 0.8 mm with large voids due to loss of Pb globules
18	Fragment	1.4	94.6	3.1	–	–	1.5 Si 0.6 Cl 0.2 Fe	As-cast equiaxed without eutectoids	Corrosion has penetrated through the metal with islands of metal remaining
29	Fragment	3.0	*	*	*			Pseudomorphic dendritic structure	Probably a wire that has completely corroded

Note: * indicates detected but not quantified

All the samples examined except for the ring (No. 11) showed an as-cast structure; the ring has a recrystallized equiaxed structure with annealing twins, Figure 3. All the samples with an as-cast structure had less than 5% tin, which is normally the level at which the (α+δ) eutectoid phase begins to appear, but this depends on the cooling rates of the alloy [11]. It is notable that eutectoids were present in some samples (e.g. No. 8 and No. 14), but not in others that had similar levels of tin. Although samples No. 8 and No. 18 both had equiaxed structures and contained the same amount of tin, eutectoids were found in No. 8 but not in No. 18. Prior to etching for metallographic examination, sample No. 14 appeared to have a granular structure but, although it contains only 2.1% tin, after etching it showed a dendritic structure with eutectoids in the interdendritic regions, Figure 4. This suggests that these objects cooled at different rates after casting; those with eutectoids or dendrites must have been cooled quickly [12]. The ring or earring had a recrystallized granular structure with annealing twins, indicating a cycle of casting, working and annealing. The last two processes in the cycle could have been repeated several times and the final step was annealing, which is evident from the presence of annealing twins in the grains, Figure 3.

Lead is immiscible in copper and is present as globules in the alloy, Figure 5. These lead globules are sometimes corroded and replaced by lead carbonate (cerussite) and copper(I) oxide (cuprite) [13], which is the case here, see Figure 5. The addition of lead does not affect the structure of the bronze but it makes the bronze easier to cast because it improves the fluidity of the metal in the melt. Of note is that lead was found in these three cast Osiris figures but not in the earring or the fragment that was analysed. As would be expected at this late period, the Egyptian craftsmen were clearly aware that lead made the casting easier [14, 15].
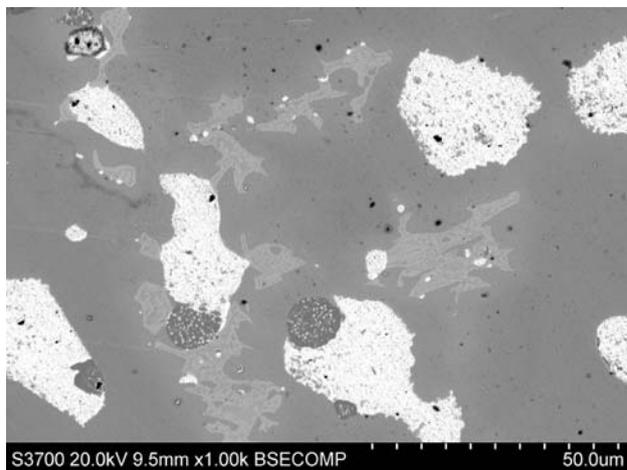

FIGURE 5. Backscattered electron image of a sample from the torso of Osiris (No. 8) showing the presence of a copper eutectoid (α+δ) and lead globules (which appear light); some of the globules have partly corroded

CORROSION PRODUCTS ON THE COPPER ALLOYS

Background

Blue corrosion products on copper alloy artefacts have been studied by conservators and scientists for more than 50 years. Chalconatronite (sodium copper carbonate hydrate: $Na_2Cu(CO_3)_2 \cdot 3H_2O$), which is greenish blue to pale blue, has often been found on archaeological copper alloys. It was first discovered on ancient Egyptian objects in 1955 by Gettens and Frondel [16]. It can be a natural corrosion product on Egyptian bronzes due to the abundance of alkali carbonates in the soil in Egypt [17]. It can also be a result of conservation treatments that include sodium sesquicarbonate (trisodium hydrogendicarbonate: $Na_2CO_3 \cdot NaHCO_3$), which was used in the past as a standard stabilization process for archaeological copper objects [7–9]. Some chemical cleaning agents used on copper alloy artefacts, including Calgon (a proprietary water softener), zinc and sodium hydroxide, alkaline solutions of Rochelle salt (potassium sodium tartrate) and alkaline glycerol, are also the sources of sodium for the formation of chalconatronite [10]. Apart from the sodium copper carbonates, other pale blue corrosion products, for example sampleite ($NaCaCu_5(PO_4)_4Cl \cdot 5H_2O$), have also been found on objects from Memphis [18].

In recent years, unusual pale blue corrosion products, including copper acetate, copper formate, sodium copper carbonate acetate and sodium copper formate acetate, have been reported on copper alloy artefacts in museum collections [3–6]. These corrosion products are often associated with the presence of acetic and formic acids emitted from materials within the display or storage environment and it appears that the phenomenon of pale blue corrosion is far from rare in museum collections [19]. Trentelman *et al.* discovered a new pale blue corrosion product of copper containing sodium, formate and acetate ions on Egyptian, Greek, Assyrian and Chinese artefacts [6]. This corrosion product was also found on a silver *kantharos* in the British Museum collection (GR 1962,1212.1) that contains very little copper [20]. In this instance the new corrosion was clearly associated with incomplete removal of a reagent containing formic acid that reacted with the sodium-containing mild abrasive used to clean the object in a later treatment. Since all the pale blue corrosion products analysed here were from untreated objects, the effect of past conservation treatments on the formation of this type of corrosion product can be eliminated and they must have formed either in burial or during storage.

Identification of the corrosion products

Samples of the pale blue corrosion products were taken for XRD analysis from four objects, including an arrowhead (No. 2), a foot (possibly of an ibis: No. 5, Figure 6),

TABLE 2. XRD results for the corrosion products from the Saqqara bronzes compared to chalconatronite and published data for the pale blue corrosion termed 'sodium copper carbonate acetate' [4]: d = d-spacing; I = relative intensity

Chalconatronite ICDD 22-1458		'Pale blue' [4]		Sample from No. 2		Sample from No. 5		Sample from No. 6		Sample from No. 8		Sample from No. 29	
d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)
		10.50	100	10.71	100	10.71	100	10.71	100			11.62	75
		10.00	40	10.04	25	10.04	25	9.98	25				
		9.00	20					9.63	20				
8.06	30	8.00	70	7.96	50	7.96	45	7.96	35	8.04	10		
7.82	50			7.69	20	7.69	55	7.72	30	7.76	80	7.76	100
		7.20	60	7.13	30	7.13	25	7.11	30				
6.90	100			6.91	65	6.91	90	6.88	75	6.92	100		
				6.70	30	6.70	45	6.68	100	6.71	30	6.70	90
		6.50	50	6.41	20	6.41	25	6.41	20				
		5.80	10									5.82	25
5.59	40	5.50	20	5.34	20	5.43	15	5.43	20			5.64	30
		5.40	20										
5.18	70			5.24	20	5.21	25	5.21	25	5.25	15		
		5.00	10	5.18	15	5.15	20	5.15	25	5.17	15		
4.85	30												
4.81	30												
		4.70	10	4.64	20	4.64	25	4.64	30	4.58	25		
4.57	40			4.55	15	4.55	20	4.55	20	4.55	25	4.72	25
		4.30	30	4.33	15	4.31	20	4.31	30	4.33	25		
4.21	40			4.21	20	4.19	20						
4.18	80			4.17	25	4.16	30	4.19	25	4.17	30		
4.10	50			4.09	20	4.09	25	4.13	30	4.10	10	4.09	15
4.05	20	4.00	20					4.07	25			4.02	20
3.91	30			3.93	20	3.93	50	3.91	30	3.95	10	3.85	65
3.80	30											3.77	20
3.68	90	3.72	10	3.66	20	3.65	30	3.64	30	3.67	30		
3.63	40	3.65	10									3.60	40
3.45	40	3.52	30	3.48	25	3.55	30	3.52	25	3.44	20	3.48	20
3.41	30			3.44	20	3.42	25	3.41	25				
3.37	40									3.36	20	3.34	25
3.29	10	3.31	10			3.31	20	3.31	55				
3.17	20	3.23	10	3.20	20	3.17	30	3.17	40	3.20	60		
3.12	40	3.10	30									3.08	35
3.04	10	3.03	30									3.06	30
3.00	50			2.99	80	2.99	55			3.00	10		
2.98	40			2.98	45	2.98	45	2.97	45				
2.91	50	2.92	10										
2.89	60			2.87	15	2.87	20	2.87	25	2.88	10	2.88	30
2.852	70												
2.847	50	2.84	10	2.84	15	2.86	20	2.86	20	2.86	10		
2.780	30	2.75	10	2.76	15	2.73	20	2.74	30	2.78	10		
2.690	30											2.71	25
2.673	50	2.67	10							2.67	10		
2.630	20			2.65	20	2.64	25	2.63	25	2.66	30		
2.612	40			2.62	15	2.62	25						
2.605	40							2.60	30				
2.590	20												
2.530	60	2.55	10									2.56	35
2.510	60									2.51	10		
2.460	40											2.47	20
2.450	20	2.44	10	2.45	25	2.44	25	2.43	20	2.45	10		

a broken situla (No. 6), an Osiris torso (No. 8) and a fragment (probably a lump of corrosion: No. 29), see Table 2. The diffraction data for chalconatronite, a common natural corrosion product often found on bronzes buried in sandy soils, and sodium copper carbonate acetate, a pale blue corrosion product found on copper alloy artefacts in museum collections in recent years, are also listed in Table 2 for comparison.

TABLE 3. Analytical results for the pale blue corrosion products

Sample No.	Object	Elements identified by EDX	Corrosion products identified by XRD	Corrosion products identified by Raman spectroscopy
2	Arrowhead	Cu, Na and O	Chalconatronite, copper sulphate hydrates, sodium acetate trihydrate and sodium copper carbonate acetate (?)	Not analysed
5	Foot of Ibis (?)		Chalconatronite, copper sulphate hydrates, sodium acetate trihydrate and sodium copper carbonate acetate (?)	Sodium copper carbonate acetate
6	Broken situla	Cu, Na, Ca, Si, O and S (Pb, Cl and P in 'spots')	Chalconatronite, copper sulphate hydrates, quartz, sodium acetate trihydrate and sodium copper carbonate acetate(?)	Sodium acetate trihydrate and sodium copper carbonate acetate
8	Torso of Osiris		Chalconatronite	Sodium acetate trihydrate
29	Lump of corrosion	Cu, Na, O, Si, Al, Ca and S	Zapatalite	Not analysed

The diffraction patterns for these samples are very complex; those for sample Nos 2, 5 and 6 seem similar and contain mainly chalconatronite. A conclusive identification of such a complex mixture by XRD alone was difficult, so SEM-EDX was used to provide elemental analysis for the corrosion products to complement the XRD analysis. It was found that the corrosion products contained mainly copper, sodium and oxygen, with silicon, calcium, sulphur and chlorine present in some of the samples, Table 3. It is likely that most of the samples contain copper sulphate hydroxides, for example $Cu_5(SO_4)_2(OH)_6 \cdot 5H_2O$, for which the main peaks listed in the International Centre for Diffraction Data (ICDD) data file (41-7) are 10.72, 5.37 and 3.59 Å. Quartz was also identified in some of the samples, including that from No. 6.

Some of the d-spacings, particularly those for very small diffraction angles, gave a match with the pale blue corrosion products found in the British Museum collection by Thickett and Odlyha, which had been described as sodium copper carbonate acetate ('pale blue' in Table 2) [4]. This pale blue corrosion product had also previously been analysed by Raman spectroscopy and the data were therefore already stored in the British Museum in-house Raman database. As there are no ICDD data for sodium copper carbonate

FIGURE 6. A bronze foot (No. 5), showing the pale blue corrosion on the upper part, which was inserted into a bird-shaped body that was probably made of wood
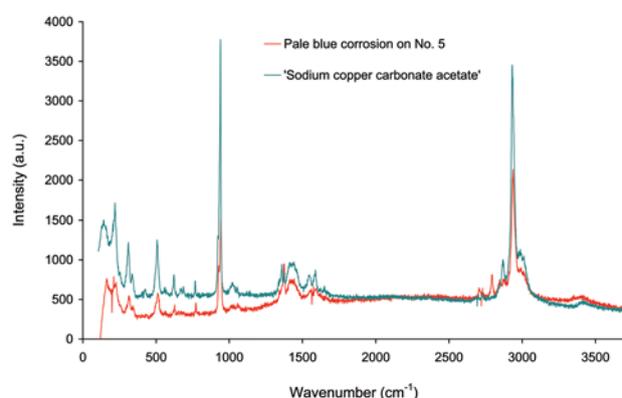

FIGURE 7. Raman spectrum of the pale blue corrosion from the foot shown in Figure 6. A reference spectrum of 'sodium copper carbonate acetate' from the British Museum in-house database is shown for comparison
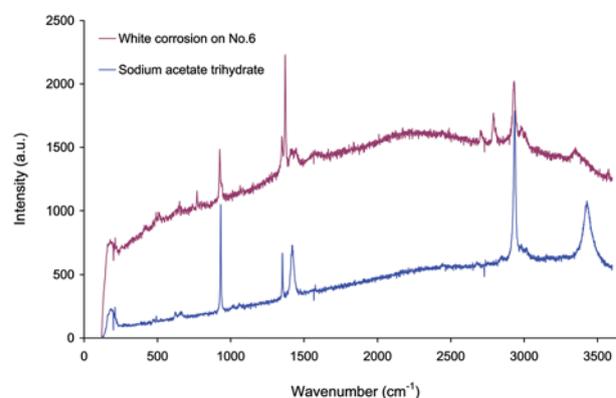

FIGURE 8. Raman spectrum of the pale blue corrosion from a broken situla (No. 6). A reference spectrum of commercial grade sodium acetate trihydrate is shown for comparison

acetate, the pale blue corrosion products from these Saqqara bronzes were investigated using Raman spectroscopy; some of their Raman spectra matched that for a 'pale blue' material described in the database as sodium copper carbonate acetate (Figure 7), while others gave a better match with reference spectra for sodium acetate trihydrate, Figure 8. Those particles identified as sodium acetate trihydrate were white in colour when seen under magnification, but when seen in bulk alongside other corrosion products appeared pale blue. The XRD results (Table 2) showed the presence of sodium acetate trihydrate (ICDD 28-1030: d (Å) = 3.00, 7.73 and 4.65) in some samples, including Nos 2, 5 and 6. Sodium acetate trihydrate has been reported on Egyptian bronzes in the British Museum collections [21], and on objects in other collections [3, 10]. However the identification of the 'pale blue' as sodium copper carbonate acetate warrants further study, as its characterization by Thickett and Odlyha was based on the examination of a physical mixture of malachite, copper acetate, sodium acetate and sodium carbonate, rather than a synthesized single phase compound [4].

Two samples of the corrosion products from No. 8 were analysed, including a surface sample of pale blue material and a sample of the greenish blue/pale blue materials beneath. The pale blue sample had been studied using XRD by Paterakis [22], and identified as sodium copper carbonate acetate by comparing the d-spacings with those published by Thickett and Odlyha [4]. Further examination of this pale blue sample by one of the authors (QW) using Raman spectroscopy has subsequently revealed that it contains mainly sodium acetate trihydrate. As noted above, samples that appear pale blue to the naked eye are often found to comprise a mixture of transparent white and blue particles when examined under a microscope. Such mixtures of sodium copper carbonate acetate and sodium acetate trihydrate were confirmed to be present in some of the pale blue samples (e.g. No. 6) by Raman spectroscopy. The greenish blue/pale blue subsurface sample from No. 8 was identified by XRD as mainly chalconatronite, Table 2. This confirms that corrosion is frequently complex and localized, and that there is often more than one corrosion product present within thick crusts that have formed over the long history of an object: care needs to be taken in the interpretation of corrosion on museum artefacts.

The diffraction patterns for the sample taken from No. 29 were similar to that for zapatalite, $Cu_3Al_4(PO_4)_3(OH)_9 \cdot 4H_2O$ (ICDD 25-261), although the match is not perfect. Zapatalite is a pale blue mineral that has been identified as a corrosion product on outdoor bronze statues [23], although it has rarely been reported as a corrosion product on other types of copper alloy objects.

As discussed previously, the burial environment and conservation treatments are two possible sources for the sodium present in chalconatronite, sodium acetate trihydrate and sodium copper carbonate acetate. The four objects from Saqqara selected for analysis have not been treated previously, so the sodium is likely to be from the soil. Sodium was detected by EDX in a soil sample taken from the inside of object No. 6 (situla). The acetate ion in some of the corrosion products probably comes from one of two sources, from the wooden trays and cupboards used to store many objects after excavation, or from wood in the burial environment – either wooden parts or bases in composite sculptures, or the wooden boxes that were sometimes used for the burial of groups of statuettes. For example, the pale blue corrosion on the upper part of the bronze foot (Figure 6) could have derived from interaction of the metal with the wooden body of the original composite bird figure. Other sculptures show basal tangs, which may indicate that they were originally associated with wooden bases that could have been a factor in the formation of these corrosion products.

In cases where acetate-containing corrosion products are present on objects that have not known association with original material containing acetic acid, it seems more likely that they have formed during storage. These acetates are probably alteration products of chalconatronite resulting from the absorption of acetic acid [5], but they could also be new corrosion products formed by direct interaction between copper and the acetic acid emitted from wooden trays, etc.

CONSERVATION TREATMENTS

Parallel to the scientific investigation reported here, new work was carried out to investigate, and where necessary remove, burial concretions on a proportion of the bronzes. The objects from Saqqara are the last major group of recently excavated bronzes accessioned by the Department of Ancient Egypt and Sudan, and many of these bronzes had already been routinely cleaned in the 1970s [24]. As has been noted, the residual group studied here was interesting for both metals scientists and conservators as, although they had been considered unpromising and remained unregistered, they retained their intact burial corrosion crust and only a few items had been cleaned on site.

Current approaches to conservation reflect the changes since earlier, radical cleaning of collections of ancient Egyptian bronzes, which was an almost routine process carried out at the British Museum and elsewhere; the accession of a large volume of material from Saqqara led to a particularly intense period of cleaning activity at the Museum in the 1970s. The main purpose of all cleaning of bronzes has been to remove the visually incoherent upper corrosion layers to reveal hidden detail of original surfaces and unveil any decoration, Figure 9. Present methods are more conservative and predicated on careful rationalization of any intervention that may remove material or change appearance. In terms of treatment choices, there are more options available to a metals conservator, particularly in the stabilization of corrosion by the use of benzotriazole [25]. Passive approaches to stabilization may also be adopted by the control of the environment, with the aim of reducing

FIGURE 9. The torso of Osiris (No. 6) seen: (a) before conservation (the scale bar shows 1 cm divisions); and (b) in detail after treatment

relative humidity in the vicinity of the bronze. Careful selection of materials used in the display and storage of bronzes is also essential in order to screen out those that might promote the deterioration of the alloy.

In this instance, it was necessary to conserve some of the objects from this group as the loose corrosion on their surfaces meant that they could not easily be handled. An improvement in their storage conditions was also essential to facilitate access to the collection. New storage throughout the Museum is based on metal storage modules that are gradually replacing those made of wood that may have caused damage to objects in the past. Inert packing materials such as polythene foam have also largely replaced cotton wool as a cushioning layer beneath and between objects within the metal drawers.

Treatment of these Saqqara bronzes varied in degree according to their surviving physical condition and any intervention was balanced by an evaluation of the risk of loss of evidence contained in the residual corrosion. In every case preliminary examination using binocular microscopy was followed by investigative cleaning to establish condition and the extent of any hidden detail. In addition, X-radiography and technical recording preceded any corrosion removal and selective desalination. The range of treatments included the removal of compacted sand and hard corrosion products using small hand-tools operated

under magnification. In some cases where corrosion was particularly disfiguring, preliminary softening by soaking in successive baths of distilled water was carried out. In these cases residual loose, powdery and disfiguring deposits were removed by subsequent manual cleaning to either the level of the original surface of the bronze at the upper green copper carbonate or the underlying red cuprite (copper(I) oxide) layers.

In terms of interventions, not all objects from this group were treated in the same way; as mentioned above, corrosion was left in place where it was important to retain contextual evidence such as corrosion or other burial-related stratigraphy, unusual patterns of surviving corrosion or associated mineral-preserved organic remains. A good example from this small group of untreated bronzes was an avian foot (No. 5), which was examined by X-radiography, but apart from the removal of sand accretions, was not cleaned of corrosion. An unusual corrosion pattern indicated it had formerly been part of a composite object and, in addition, mineral-preserved woven linen textile remains were present on areas of the object. The surviving corrosion on this object is unsightly and although the object would not be selected for display on these criteria, evidentially it certainly has a value for the interpretation of an object now separated from its immediate context. Both the textile and upper corrosion layers would have been permanently removed from

the surface of the object if strong reagents had been used to 'clean up' the object by improving its appearance and making the surface more visually coherent. Analysis of the unusual corrosion pattern on the lower legs of the bird foot supports the suggestion that wood had formerly been present in this localized area of the object and that this had induced corrosion in antiquity. Both falcon and ibis sculptures have been found among the bronze finds from Saqqara [1]; the form of this foot indicates that it is more likely to have been part of an ibis than from the raptor family.

CONCLUSIONS

The condition of the objects varied from light surface corrosion to more advanced corrosion with little residual metal remaining. All the objects examined, except for the ring (No. 11), showed an as-cast structure, while the ring has a recrystallized equiaxed structure with annealing twins. All of the metals were tin bronzes and the objects with thick walls were made of leaded tin bronzes. The differences in microstructure between the metals with similar tin contents indicate different cooling rates during casting.

The pale blue corrosion products on the surface of the untreated objects were analysed and found to contain mainly chalconatronite and copper sulphate hydroxides which were formed during burial. Organic copper salts, including sodium acetate trihydrate and sodium copper carbonate acetate, which are often associated with the presence of acetic acid vapour in display and storage environments, were also identified in the corrosion layers studied here. The presence of sodium acetate trihydrate suggests that the existing burial corrosion is likely to have been subject to further changes once in the Museum, although a direct interaction between the metal and acetic acid emitted by wooden storage trays or cupboards cannot be ruled out. Additionally, the localized, specific burial conditions at the Sacred Animal Necropolis at Saqqara (such as the role of composite objects, wooden funerary items and mass burial of mummified ibis) were undoubtedly unusual and their effects on the corrosion of objects have not yet been interpreted fully.

Conservation cleaning of the bronzes has revealed new evidence for original surfaces and in some cases original decorative effects. The remains of contextual evidence, such as textile wrappings found on objects, were left undisturbed to ensure their preservation, even though this has the effect that details of the original surfaces may still be obscured. As part of a general programme of improving storage across the Museum, unsuitable storage media have been replaced. It is hoped that a proportion of the cleaned objects are now more accessible by those interested in the many bronzes from this site. Following cleaning some objects may now be considered suitable for inclusion in the permanent registered study collections of the Department of Ancient Egypt and Sudan.

EXPERIMENTAL APPENDIX

Microscopy

The stereomicroscope used for the investigation of surface corrosion was a Leica Wild M8. A Zeiss AXIOVERT 100A microscope was used for the metallographic study of the polished sections.

Raman spectroscopy

Raman spectroscopy was carried out using a Jobin Yvon Infinity spectrometer with a green (532 nm) laser, using a maximum power of 2.4 mW at the sample. The corrosion products were measured using a power of 0.6 mW to avoid 'burning' the samples and to allow a comparison to be made with the reference spectrum in the British Museum in-house database for the 'pale blue' described as sodium copper carbonate acetate by Thickett and Odlyha [4].

XRD

X-ray diffraction was carried out with a Philips PW 1120/90 diffractometer using Cu Kα radiation. The samples were run at 40 kV, 15 mA for about an hour. Diffraction lines were identified by matching them with ICDD standards.

Preparation of metallographic sections

The cross-sections were mounted in epoxy resin, ground and then polished using diamond paste to a finish of 1 μm. After examination of the corrosion layers, the polished sections were etched using ethanolic iron(III) chloride to reveal the metallographic structure of the metals.

SEM-EDX

A Hitachi S-3700N Variable Pressure SEM with an Oxford INCA Energy system was used for elemental analysis and mapping. The analyses were run at an accelerating voltage of 20 kV at a pressure of 50 Pa and with a working distance of 10 mm. The detection limits for each element are variable but typically 0.1–0.3%. The relative precision (reproducibility) is about 2% for the major elements, 10% for concentrations in the 5–20% range and deteriorates as the detection limits are approached.

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REFERENCES

1. Davies, S. and Smith, H.S., *The Sacred Animal Necropolis at North Saqqara: the Falcon Complex and Catacomb: the archaeological report*, Egypt Exploration Society, London (2005).

2. Spencer, J., Department of Ancient Egypt and Sudan, the British Museum, personal communication, 30 October 2007.

3. Tennent, N.H. and Baird, T., 'The identification of acetate efflorescence on bronze antiquities stored in wooden cabinets', *The Conservator* 16 (1992) 39–43.

4. Thickett, D. and Odlyha, M., 'Note on the identification of an unusual pale blue corrosion product from Egyptian copper alloy', *Studies in Conservation* 45 (2000) 63–67.

5. Paterakis, A.B., 'The hidden secrets of copper alloy artifacts in the Athenian Agora', in *Metals 2001: Proceedings of the International Conference on Metals Conservation*, ed. I.D. MacLeod, J.M. Theile and C. Degrigny, Western Australian Museum, Welshpool (2004) 232–236.

6. Trentelman, K., Stodulski, L., Scott, D., Back, M., Stock, S., Strahan, D., Grews, A.R., O'Neill, A., Weber, W.H., Chen, A.E. and Garrett, S.J., 'The characterization of a new pale blue corrosion product found on copper alloy artefacts', *Studies in Conservation* 47 (2002) 217–227.

7. Oddy, W.A. and Hughes, M.J., 'Stabilization of "active" bronze and iron antiquities by the use of sodium sesquicarbonate', *Studies in Conservation* 15 (1970) 183–189.

8. Horie, C.V. and Vint, J.A., 'Chalconatronite: a by-product of conservation?', *Studies in Conservation* 27 (1982) 185–186.

9. Pollard, A.M., Thomas, R.G. and Williams, P.A., 'Mineralogical changes arising from the use of aqueous sodium carbonate solutions for the treatment of archaeological objects', *Studies in Conservation* 35 (1990) 148–152.

10. Paterakis, A.B., 'The influence of conservation treatments and environmental storage factors on corrosion of copper alloys in the ancient Athenian Agora', *Journal of the American Institute for Conservation* 42 (2003) 313–339.

11. Scott, A.D., *Metallography and microstructure of ancient and historic metals*, Getty Conservation Institute, Los Angeles (1991).

12. Wang, Q. and Ottaway, B.S., *Casting experiments and microstructure of archaeologically relevant bronzes,* BAR International Series 1331, Archaeopress, Oxford (2004).

13. Wang, Q., *Metalworking technology and deterioration of Jin bronzes from the Tianma-Qucun site, Shanxi, China*, BAR International Series 1023, Archaeopress, Oxford (2002).

14. Cowell, R.M., 'Scientific appendix I: chemical analyses', in *Catalogue of Egyptian antiquities in the British Museum: VII tools and weapons I: axes*, ed. W.V. Davis, British Museum Press, London (1987) 96–118.

15. Ogden, J., 'Metals', in *Ancient Egyptian materials and technology,* ed. P.T. Nicholson and I. Shaw, Cambridge University Press, Cambridge (2000) 148–176.

16. Gettens, R.J. and Frondel, C., 'Chalconatronite: an alteration product on some ancient Egyptian bronzes', *Studies in Conservation* 2 (1955) 64–75.

17. Gettens, R.J., 'Mineral alteration products on ancient metal objects', in *Recent advances in conservation*, ed. G. Thomson, Butterworths, London (1963) 89–92.

18. Fabrizi, M., Ganiaris, H., Tarling, S. and Scott, D.A., 'The occurrence of sampleite, a complex copper phosphate, as a corrosion product on copper alloy objects from Memphis, Egypt', *Studies in Conservation* 34 (1989) 45–51.

19. Paterakis, A.B., 'Corrosion of archaeological bronze by acetic acid', in *Metal 07: Interim Meeting of the ICOM-CC Metal WG Amsterdam*, ed. C. Degrigny, R. van Langh, I. Joosten and B. Ankersmith, Rijksmuseum, Amsterdam (2007) 94–99.

20. Wang, Q., 'Identification of blue corrosion on silver head vase (1962,1212.1)', *British Museum CDS analytical request No. AR2007/60*, British Museum, London (2007) (unpublished).

21. Bradley, S. and Thickett, D., 'The pollutant problem in perspective', in *Indoor air pollutants: detection and mitigation of carbonyls* (1998): http://iaq.dk/iap/iap1998/1998_05.htm (accessed 14 May 2009).

22. Paterakis, A.B., University College London, personal communication, 17 November 2008.

23. Selwyn, L.S., Binnie, N.E., Poitras, J., Laver, M.E. and Downham, D.A., 'Outdoor bronze statues: analysis of metal and surface samples', *Studies in Conservation* 41 (1996) 205–228.

24. Shearman, F., 'Patina and polychromy: reconstructing some technical histories for small Egyptian bronze sculpture in the British Museum', in *Decorated surfaces on ancient Egyptian objects: technology, deterioration and conservation*, ed. J. Dawson, C. Rozeik and M. Wright, Archetype Publications, London (forthcoming).

25. Madsen, H.B., 'Benzotriazole: A perspective', in *Corrosion inhibitors in conservation, UKIC Occasional Paper 5*, ed. S. Keene, UKIC, London (1985) 19–21.