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White copper: The arsenical coinage of the Libyan revolt 241-238 BC

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Abstract

Arsenic-copper alloys are not common after the Early Bronze Age. The discovery of a group of 3rd century BC coins, probably from Tunisia, with surface metal composition of up to 29% arsenic in the copper prompted this metallurgical examination. The arsenic was found to occur in greatest concentration on the coin surfaces as the result of inverse segregation during casting.

Introduction

A hoard of coins, believed to have come from Tunisia, has proved to be of particular interest both for its historical context and its metallurgy[1]. The hoard belongs to the period of the Libyan War of 241-238 BC. This war was fought in the region of modern Tunisia between the Carthaginians and their former mercenaries, who had recently returned in defeat from the First Punic War against the Romans. The mercenary revolt developed into a major conflict between the Libyan people and their Carthaginian masters. The hoard contained a total of 167 coins which at first sight all appeared to be bronzes. After cleaning, it was revealed that there were both silver and bronze coins and, most interestingly, a group of forty-two pieces whose metal composition was not immediately obvious[2]. The coins of this group have a distinctive design: on one side a head of the goddess Tanit and on the other side a plough and the Punic letter *zayin.* They have no identifying inscription but since they only appear in hoards from Tunisia and in association with other coins signed by the Libyan rebels it seems certain that these coins must also be an issue of the Libyan war. These Tanit/Plough coins have previously been labelled as bronzes, but several examples in this group did not look at all like bronze coins. Some had a silver grey colour and others had a copper coloured core showing through breaks in the

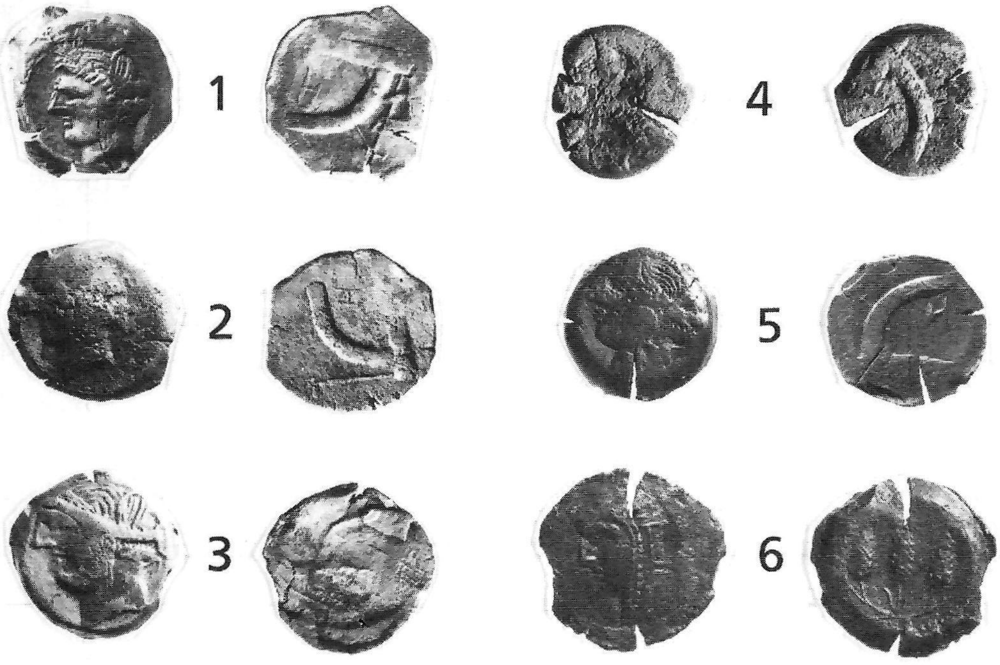


Figure 1 Six arsenical copper coins, analytical results in table 1.

'silvery' surface. These were examined to see if they were base silver or silver plated. However, surface analysis revealed no silver at all, but instead, up to 29% of arsenic in copper.

The Tanit/Plough coins are approximately 20mm in diameter and of variable thickness (2-5mm). The coin flans have a characteristic shape, being flat on one side and convex on the other with one or, more commonly, two casting sprues. Where there are two they occur directly opposite each other. The designs were then struck onto the cast flans. Many of them have deep cracks around their edges (fig 1).

Historical Occurrence of Arsenic-Copper Alloys

Arsenical copper was probably the earliest alloy made by man and its use for tools and weapons was widespread in the Copper and Early Bronze Ages. Early Bronze Age alloys typically have 1-5% of arsenic in the copper which gives improved hardness and strength[3] [4]; when tin was added to copper, bronzes rarely contain more than 0.5% of arsenic. There has been some discussion about the level of arsenic which might be an indication of deliberate addition[5] [6] [7] [8] but it is not possible to fix a precise level unless the total history of treatment, from ore to finished product is known; for example during roasting of sulphide ores and hot working of the metal in oxidising conditions, arsenic is lost to the atmosphere as arsenic trioxide vapour. However, it is difficult, even deliberately, to remove all traces of arsenic from the ore and melting of the metal can be carried out under favourable conditions (i.e. reducing) to prevent significant loss of arsenic, as demonstrated by McKerrell and Tylecote[9]. There are several arsenic rich minerals which are often found in association with copper sulphide ores, e.g. enargite Cu_3AsS_4 and tennantite Cu_3AsS_3, which could have been the source of arsenic in the metal. Other suggestions include the arsenic minerals orpiment (As_2S_3) or realgar (AsS).

During the last two centuries in the West, low levels of arsenic (less than 1%) were added to copper alloys for locomotive fire-boxes, boilers, roofing and condenser tubes because of its properties of raising annealing temperatures and protecting copper and brass from corrosion and wear[10]. However, arsenic is normally rigorously excluded from modern copper because of its deleterious effect of electrical conductivity. Modern metallurgical research into the effects of arsenic and also antimony on copper is generally confined to trace levels of less then 1%, as nothing greater is of commercial interest[3] [11] and therefore there is little metallurgical data on high arsenic alloys.

As well as altering mechanical properties, arsenic can also be used to whiten copper. An interesting case of arsenic plating is reported on a bronze bull statuette from Horoztepe, Anatolia, dating to circa 2100 BC[12] [13] This was purely decorative, the silvery coloured arsenic alloy contrasting with the bronze. Smith[13] has suggested that the arsenical zones on the bull were the result of an *in situ* cementation process, possibly achieved by masking off the body of the bull, except in the areas to be plated, and heating it in a sealed vessel packed with a mixture of white arsenic oxide, an alkali carbonate and charcoal. This has produced a thin plating (less than 0.2mm) of the inter-metallic compound Cu_3As by diffusion of the arsenic, reduced by cementation, into the surface of the bronze. No arsenic was present in the underlying metal and the appearance of the interface between the plating layer and the body suggested a solid state diffusion reaction.

A second example of the addition of arsenic to whiten copper is the base of a small 11-12th century Tibetan brass statuette of Manjusri (fig 2). A drilling of the base analysed by atomic absorption spectrometry contained 7% of arsenic whereas the 30% zinc brass statuette contained only 0.3% arsenic[14]. In this example the arsenical casting alloy was chosen for the visual effect of a golden statue on a silvery base.

Contemporary forgeries of silver coins of the 16th and 17th centuries have been found to contain several percent of arsenic in the alloy[15].

The works of the alchemists contain many versions of recipes for whitening copper with arsenic to transmute

Figure 2 11-12th century AD Tibetan brass statuette on an arsenical copper base.

it into 'silver'. The recipes fall into two groups: in the first, copper is coated or heated with an arsenic compound to give it a surface plating of silvery colour, as in the case of the Horoztepe bull discussed above. In the second, a white casting alloy is prepared by melting copper with arsenic compounds. The recipes are generally obscure, but some were later collected together in a relatively comprehensive form in a handbook of craftsmen's recipes known as the Leyden Papyrus. For example, on whitening copper for casting:

> "Taking some Cyprian copper, melt it, throwing on it one mina of decomposed sandarach, two drachmas of sandarach the colour of iron . . ."[16]

Sandarach is arsenic sulphide and "decomposed sandarach" is probably white arsenic trioxide, (the poisoners' arsenic of common parlance) which can be collected as a sublimate when arsenic sulphide is heated in air. The Leyden Papyrus was written in the late 3rd century AD but quotes works by earlier alchemists of Alexandria. Most of the surviving works are not any earlier than the 1st century AD, but an alchemist writing under the name of Democritos has been dated by some scholars to circa 200 BC. He was interested in transmuting base metals into silver and gold and gave several recipes for whitening copper using arsenic compounds[17].

Until the discovery of these high arsenic Libyan coins it had been thought that high arsenic copper alloys were not made between the Early Bronze Age and the later Medieval period, but as has been pointed out[18], it is surprising that the alchemical literature should indicate a familiarity with the alloy if no actual examples exist. These unparalleled coins therefore merited further investigation.

Analysis

Analysis was done by x-ray fluorescence (XRF) using a Link Systems 290 spectrometer with an air-cooled tungsten target x-ray tube operated at 40 kV and 0.4mA. The x-ray beam is filtered and collimated so that an area approximately 1.5 x 2.2mm is irradiated. The results were standardised using alloys of known composition.

Semi-quantitative XRF analysis of the unprepared surface (i.e. without removing any patina) of the 42 coins of the Tanit/Plough type from the hoard indicated that most were arsenical copper: twenty-three gave high arsenic values (3-29%) allied to low tin (less than 2%). Six coins gave moderately high arsenic values (3-9%) and tin (3-11%). The remaining thirteen coins are bronzes with averages of 8% tin and less than 2% arsenic.

Because of the damage to the coins, however slight, necessary to obtain analyses of the core metal, just four of the high arsenical coins, with conspicuously 'silvery' surfaces, were subjected to detailed XRF analysis. The coins were first analysed on the white metal surface without any preparation of the analysis area. These results are labelled 'surface' in table 1. To obtain an analysis of the core metal of the coins, an area on the edge was abraded to provide a clean flat surface. However, these arsenic rich coins failed to give consistent results after repeated abrasion so a sample of metal was taken from further into the centre of the coin by drilling into the edge (discarding the first turnings). These drilled samples were also analysed by XRF and the results were standardised using samples drilled from alloys of known composition. These are the results quoted in the table as 'core'. In addition to the coins from the hoard, two coins already in the British Museum's collections were picked out as having 'silvery' surfaces and found to have high arsenic contents; coin 5 in the table is of the same type as the hoard coins with head of Tanit and Plough, coin 6 is of a different type with a head of Isis and Three corn ears but it has a noticeably 'silvery' surface and is also associated with the Libyan revolt[1]. These coins are illustrated in fig 1.

From the analyses in table 1, it can be seen that arsenic, antimony and, to some extent, tin are considerably more concentrated on the surface of all six coins, at the expense of copper and that both arsenic and antimony occur in unusually high levels. Tin and lead constitute fairly major additions to the alloy in coin 6. It was clear that although the surfaces of the coins were enriched in arsenic, significantly, arsenic was also present in considerably more than trace levels in the cores. It was also clear from the difficulty in obtaining a reproducible analysis of the core metal, despite abrasion of the surface, that the arsenic rich layer was of variable thickness. What was not at all certain from the XRF analysis was how this arsenic rich surface was formed and whether it was applied as a plating layer after the flan was cast. This could only be determined by detailed metallography.

			XRF Analysis %					
	BM Coin Reg No		**Cu**	**As**	**Sn**	**Pb**	**Ni**	**Sb**
1.	1987, 9-13, 4	Surface	73.9	20.1	1.9	1.9	<0.1	2
		Core	87.9	8.8	0.7	2.1	<0.1	0.4
2.	1987, 9-13, 8	Surface	71.9	18.8	3	2.8	<0.1	3.2
		Core	88.5	7.3	1	2	<0.1	0.9
3.	1987, 9-13, 13	Surface	78	19.4	0.1	0.2	<0.1	2.1
		Core	96.4	3.1	0.1	<0.1	<0.1	0.4
4.	1987, 9-13, 14	Surface	66.2	28.6	0.2	0.7	<0.1	4
		Core	87.1	11.6	<0.1	<0.1	0.2	0.5
5.	1930, 4-27, 9	Surface	71.3	22.9	1.8	3.3	0.1	0.4
		Core	84.4	12.2	0.9	2.2	0.1	0.2
6.	1961, 4-4, 1	Surface	71.5	14.5	6.3	7	<0.1	0.3
		Core	81.4	5.7	3.7	9	<0.1	0.1

TABLE 1

Metallography and SEM Microanalysis

In order to characterise this arsenic-rich surface and its relationship with the core, and to determine how the coins were made, a metallurgical examination of one coin was undertaken. A taper section was polished to a 0.25 micron finish on the edge and it was examined in the scanning electron microscope (SEM) (JEOL 840 SEM with Link Analytical 860-500 series quantitative EDX analysis).

The photograph (fig 3) shows the polished section with the coin edge-on; note the thick, pale, arsenic-rich layer around the convex lower surface of the flan. The other major features are the dendritic structure, casting porosity (black in the photograph) and cracking across the left hand side of the polished area.The cracking is probably caused by striking when cold, though no distortion is visible in this section, which is at the very edge of the coin. A detailed examination (fig 4), at higher magnification, of an area of the polished section near the upper, flat surface of the flan shows the slightly cored dendrites (dark grey in photograph) of alpha solid solution reaching uniformly from the core almost to the surface of the coin and separated from each other by a light coloured interdendritic matrix. The dendrites contain about 5% of arsenic and a trace of tin in the copper; there is of course some variation because of coring. The arsenic-copper equilibrium diagram (fig 5) predicts that the light coloured interdendritic matrix should be the low melting point eutectic of the compound Cu_3As plus alpha, resulting from normal segregation and coring during casting. However, no resolvable eutectic structure could be seen. Micro analysis of this light coloured matrix shows arsenic approaching the eutectic composition (21% arsenic) in some areas with other regions as high as 26% and as low as 10%. However, in addition to arsenic, lead (small white globules in SEM micrographs), tin and antimony are concentrated into this phase so the simple copper-arsenic binary equilibrium diagram cannot be expected to fully explain the phases present and no diagram has been calculated to include these additional elements.

A detail including the convex side of coin 5 is shown at the same magnification in fig 6. On this side the alpha dendrites merge into the arsenic-rich layer, which is of variable thickness, over 100 microns thick at some points. The important point to note is that there is complete continuity between the high arsenic surface layer and the high arsenic interdendritic matrix of the core (fig 7). There is no hint of a physical or analytical boundary separating the surface layer from the body of the coin, unlike the arsenic-rich layer reported on the bull from Horoztepe.

How then was the arsenic-rich layer formed? The answer can be found in the tendency of many non-ferrous alloys to undergo inverse segregation during casting. Inverse segregation is a form of macro-segregation which occurs in alloys which freeze over a long temperature range and which contract during solidification[19]: inverse segregation is commonly seen as tin-sweat on bronze[20]. It is a very complex phenomenon which is governed by a number of factors. Casting conditions are important, particularly a rapid cooling rate causing coring. The lower melting point component of the alloy, which occurs during normal coring, is forced towards the cooling face (e.g. the mould surface) as the still partly liquid casting cools. Experiments by McKerrell and Tylecote[9] have shown that copper-arsenic alloys, chill-cast in non-oxidising conditions, exhibit more extreme inverse segregation even than tin-bronzes. The semi-quantitative XRF analysis of the surfaces of all the high arsenic coins from the hoard revealed that the arsenic content of the convex side was invariably higher than that of the flat side indicating that, like coin 5, they have a thicker layer of arsenic enrichment on the convex side. This is difficult to explain. If a closed mould for mass-producing coin flans was used, as might be expected from the pairs of

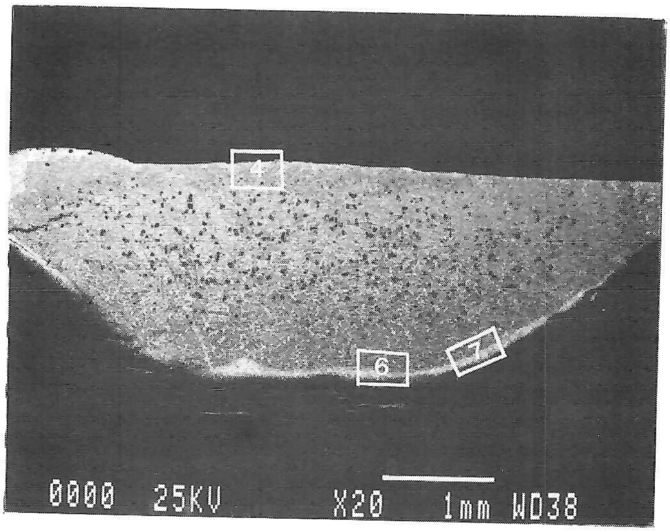
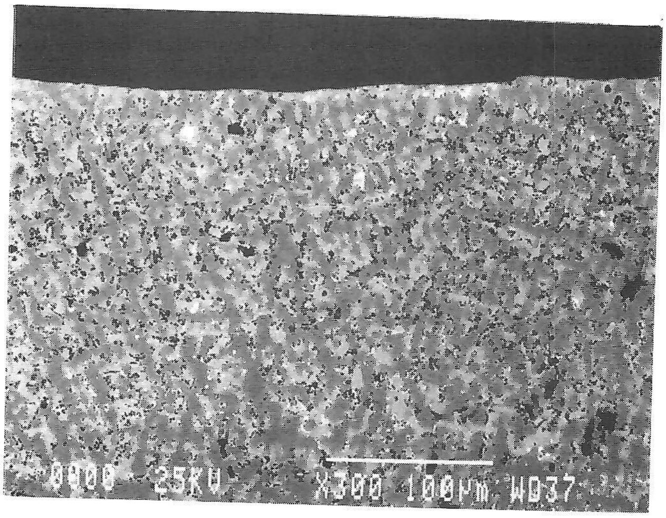


Figure 3 Scanning electron micrograph of polished taper section on edge of coin 5. The positions of figures 4, 6 and 7 are marked. (The white bar is a 1mm scale). Compositional contrast; back scattered electron (B.S.E.) image.



Figures 4 and 6 Scanning electron micrograph details of the polished section (see fig 3 for positions). Unetched. B.S.E. image. Both at same scale: white bar = 100 microns.

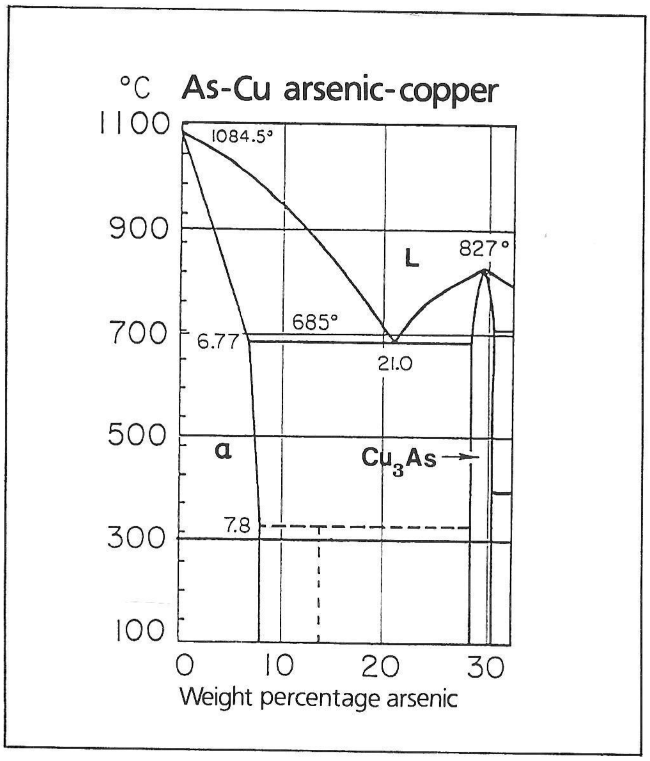


***Figure 5** Equilibrium diagram of the copper-arsenic system (24). A compound with the approximate formula Cu_8As (about 14% arsenic; indicated by the dotted line on the diagram) has been found (25) but this transformation is sluggish and would not be expected to occur under normal casting conditions.*

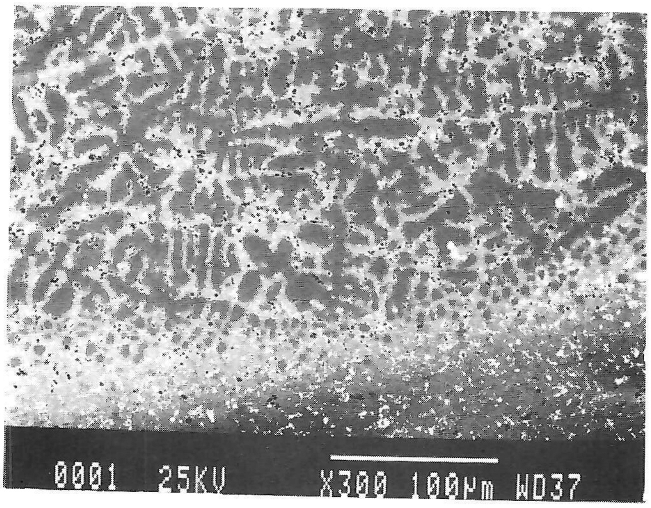


Figure 6 See caption Fig 4.

casting sprues[21], there should not have been a difference in the thickness of the arsenic-rich surface layer on the two sides. If the materials used for each side of the mould had different heat conducting properties such a difference might have occurred. Alternatively an open mould would certainly cause differential inverse segregation, though casting sprues would not normally be expected in an open mould.

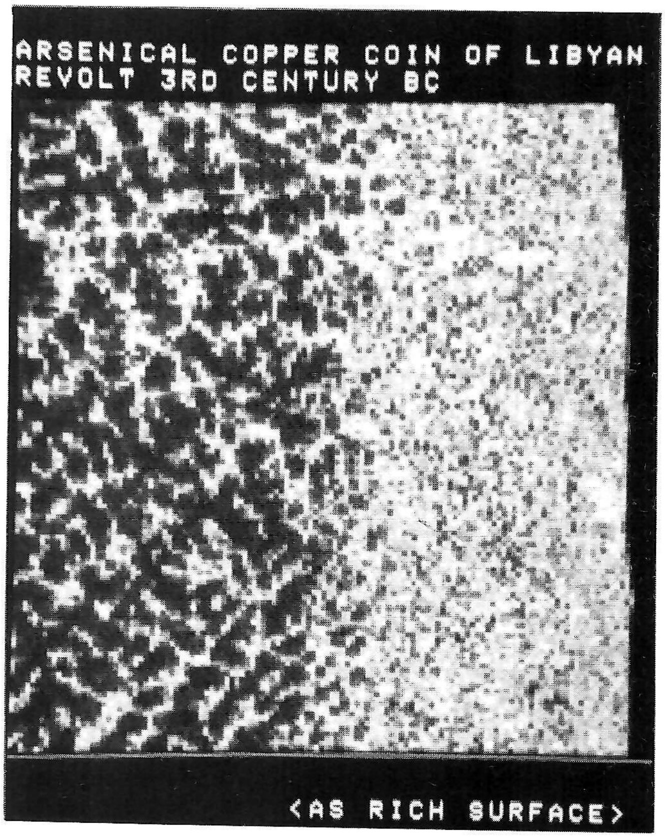


Figure 7 Digital X-ray map of arsenic distribution on the convex side of the polished section; Coin 5. The lightest areas have the greatest arsenic concentration. Note the continuity between the surface and the arsenic rich interdendritic matrix.

Surface analysis of the base of the Tibetan statuette gave an arsenic value of 14%, which is double the arsenic in the sample drilled from the core, confirming that this too has suffered inverse segregation during casting.

Conclusions

It can be stated categorically, on the evidence of the metallographic examination, that these coins were not plated and that the "silvery" surface is the result of inverse segregation during casting. It cannot be proved, but it seems likely, that the craftsmen deliberately encouraged the production of a silvery coloured coin by the selection of the alloy ingredients and casting conditions; they cannot have failed to notice the result. However, as mentioned above, not all the coins of this Tanit/Plough issue are arsenical; thirteen of the forty-two coins are bronze and do not have enough tin on the surface (maximum 15% and most 10% or less) to give a comparable whiteness to the alloy. Also, the physical appearance of the coins, with their dumpy form and visible casting sprues, puts them firmly alongside contemporary bronzes, as opposed to the much flatter and more regular shaped silver issues. Perhaps they were meant to stand out as more valuable than ordinary bronzes, but not to be equated with silver coins. In this period the Carthaginians were producing debased gold (electrum) and silver (billon) issues of coinage and the Libyans used these Carthaginian coins, overstruck with their own designs. Into this system of debased precious metal issues the Libyans might then have added their 'enhanced' bronzes. For a more practical, as opposed to economic, explanation it is possible that the arsenic was used as a substitute for tin, to lower the melting point for easier casting and to harden the alloy. Tin may not have been so easily accessible to the Libyan rebels, but the amount of arsenic present is rather greater than was strictly necessary. Whatever the explanation, the whitening of the copper alloy was almost certainly deliberate but probably not intended to deceive.

Arsenic and copper ores are found in North Africa. In particular there are large enough deposits in Algeria to have been commercially viable in modern times[22] although it is not known if they were exploited in the 3rd century BC. Interestingly, antimony ores are also found in Algeria[22,23]; antimony and arsenic ores do frequently occur together. It is not suggested that the antimony was a deliberate addition to the alloy, rather an accidental inclusion with the ore. No evidence of any other ancient arsenical coinage has been identified either from North Africa or elsewhere in the Mediterranean area. A fairly limited search for other items manufactured of high arsenic alloys from North Africa has so far failed to produce further examples. The alloy may be recognised by its silvery-grey colour, although it is similar to high-tin bronze and the burial corrosion products are not noticeably different in appearance to those on normal bronzes. The most obvious distinguishing feature of the coins is the cracking around the edges of the flans, possibly caused by cold striking. At the moment it seems that these coins are unparalleled, but as the alchemists were familiar with the properties and appearance of copper-arsenic alloys, other examples might be expected to come to light from the Classical world or its fringes.

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Biographies

Susan La Niece read archaeology at Manchester University. After a few years as a field archaeologist she read archaeological science at Bradford University and later studied metallurgy at the City of London Polytechnic. Joined the metals section of the British Museum Research Laboratory in 1977. Areas of research include niello inlays, medieval copper alloys, Islamic metal-working techniques and silver plating in antiquity.

Ian Carradice read History and Archaeology at Liverpool University and gained a PhD from the University of St Andrews for a thesis on the coinage of the Roman Emperor Domitian. He has worked in the Department of Coins and Medals at the British Museum since 1977; his present position is curator of coinages of the ancient Near East. He has published many articles on Greek and Roman numismatics and his books include *Coinage and Finances in the Reign of Domitian.* Areas of current research include Roman provincial, Achaemenid and Carthaginian coinage.