

A better shade of black: effects of manufacturing parameters on the development of ancient black bronzes

Agnese Benzonelli, Ian C. Freestone, Marcos Martín-Torres

Keywords: black bronze alloys, artificial patination, colouring, gold, experimental replication.

## ABSTRACT

Alloys with controlled contents of Sn, Ag and Au, were treated with methods and solutions that mimic those used in ancient and traditional procedures for the production of black bronze. Examination of the resulting patinas with colorimetry, SEM-EDS, TEM, Raman Spectroscopy, and XRD revealed no systematic differences according to fabrication method, whereas patina homogeneity and colour in those alloys which did not contain precious metal were affected by superficial work. Patina microstructure determines adherence and coverage, and depends upon solution used irrespective of the alloy composition, but the colour of the patina is mainly related to alloy composition. Gold promotes the development of cuprite, slowing the oxidation to tenorite in the corrosion process. Gold additions produce a more uniform patina as well as a desirable blue-black tone which is likely to have been a factor in alloy selection.

## 1 - Introduction

The term “black bronze” refers to a class of artificially patinated copper-alloys used for high-status objects, which occur sporadically across a wide range of cultures (Craddock and Giumlia-Mair 1996). The technique is thought to have originated in south Anatolia, Syria or Mesopotamia (Craddock and Giumlia-Mair 1993), but the earliest black bronze object has been found in Egypt. This is the crocodile from Fayum, dated to the 19th century BC, now in the Ägyptische Sammlung collection in Munich (Germany; cat. no. AS 6080) (Giumlia-Mair 1997; Giumlia-Mair and Quirke 1997). A hieroglyphic inscription of kings and high officials, dated XVIII Dynasty, 1550-1292 BCE and thus much later than the crocodile of El Fayum, cites a material called *hmty-km*, which literally means “black copper” (Giumlia-Mair & Quirke 1997). The material was later known in Mycenae as *kuwano*, in classical Greece as *kyanos*, and in the Roman world as *Corinthium aes* or Corinthian bronze. The alloy was also used in the early medieval period, for example in Anglo-Saxon Britain (Bayley & McDonnell 2000; Caple 2001; Hamerow & Pickin 1995; Stapleton *et al.* 1995; Whitfield 1997). Similarly black metal objects are made in modern times in China as *wu-tong*, and in Japan as *shakudo*, the latter belonging to the broader category of *irogane* (alloys that are artificially patinated to obtain an infinite number of colours).

The study of black bronzes is typically based on investigating literary sources and analysing artefacts. However, texts mentioning black bronzes are often inaccurate or ambiguous about how they were made and treated. Trying to reconcile historical recipes with modern materials and processes, and with archaeological artefacts, can lead to dubious correspondences (Martín-Torres and Rehren 2008). For this reason, modern literature on the history of black bronze alloys highlights the need for more detailed technical analyses on archaeological or historical artefacts that may allow reverse engineering of their manufacture (e.g. Giumlia-Mair 2001; 2012; Whitfield 2007) as well as for a better understanding of the material in itself and the patination mechanisms, achievable through experimental tests (Mathis *et al.* 2005).

A number of publications have presented the major element analysis of black bronze artefacts (Aucouturier *et al.* 2010; Caple 2001; Craddock 1982; Demakopoulou *et al.* 1995; Giumlia-Mair 1995; 2012; Giumlia-Mair & Craddock, 1993; Mathis *et al.*

2005; 2009; Mohamed & Darweesh 2012; Murakami et al. 1988; S. La Niece 1991; Photos 1994; Stapleton *et al.* 1995; Wayman & Craddock 1993). It is generally agreed that black bronze owes its appearance to a fine, compact and resistant patina developed on its surface. In most cases and notwithstanding exceptions and variants, this was achieved by intentionally using a copper alloy containing small amounts of gold, silver and other elements, and simmering the fabricated artefact in a chemical solution containing copper salts (e.g. Giunlia-Mair 2001; O'Dubhghaill & Jones 2009; Oguchi, 1983; Murakami *et al.* 1988). According to the literature, this process created a network of cuprite ( $\text{Cu}_2\text{O}$ ) in which fine gold particles were dispersed, which gave the film a particular black colour with blue to purple shades. However, the presence of nanoparticles of gold has been confirmed in only a single modern replica (Kitada, 2005) and never in the archaeological material.

A few published papers describe experimental tests undertaken in order to better understand the nature and the properties of black bronzes (Oguchi 1972; 1983; Notis 1988; Murakami *et al.* 1988; Giunlia-Mair and Lehr 1998; 2003; O'Dubhghaill 2009). The majority of these were performed on replicas of *shakudo* alloys, although Giunlia-Mair and Lehr (2003) replicated a broader spectrum of black bronze recipes taken from both modern (Chinese and Japanese) and ancient texts (Pausanias, Zosimos). These experiments produced important information on the development of the patina on a range of alloy compositions and for a range of treatments, but the reports do not provide full information as to the combinations of alloys and solutions and moreover the patinas were subject only to a visual evaluation. A systematic experimental study of the wide range of factors which can affect patina development, coupled with instrumental evaluation of the products is therefore timely.

Many questions still surround black bronzes and their use. Are there alternative recipes for the making of black colour? If so, do they represent independent technical traditions or are there other technical or cultural reasons behind the choice of one over another in a given context? Does gold have a tangible effect in the patina or was its addition based on status-related or other cultural constraints? In order to answer these questions we need a better understanding of the technical parameters behind the patination of black bronzes and, ideally, diagnostic criteria based on reference data that may allow us to discern different recipes in archaeological materials. For

example, the degree to which the development of a successful patina was dependent upon parameters such as alloy and solution composition will have a critical bearing on such issues.

A series of experiments was therefore designed to evaluate the chemical and physical characteristics of black bronzes and the influence of alloy composition, fabrication method, metal surface finish, and patinating solutions used on the colour, adhesion and durability of the patina. Moreover, emphasis was placed on evaluating different methods for the characterisation of black bronze alloys and their patinas, particularly using minimally invasive techniques. It is anticipated that the results will allow an improved understanding of the relationship between the production technologies, alloy composition and physical-chemical characteristics of the patinas, providing a framework within which the archaeological patinas may be studied and interpreted. This should allow a more robust understanding of the choices of the craftspeople and the transmission of the technology.

The present paper reports the results of the first stage of the project, which explores the effects of metal fabrication techniques upon patina development, the effects of different patination solutions, and the presence/absence of precious metals in the resulting patinas. The experimental products are examined with a range of non-invasive instrumentation. This research provides a framework for future work which examines the sensitivity of the patination process to specific alloy recipes involving gold and/or silver.

## 2 - Method

### 2.1 Materials

#### 2.1.1 Alloys

A database of confirmed and suspected occurrences of black bronze alloys was created and formed the basis for the choice of replica alloy compositions. Analyses of 69 ancient black bronzes have been reported. A summary of the literature

compositions is provided in Table a, supplementary material, and full data and references are presented in the in-line material.

Element	Range of content	Mean	Median	Mode	Number of occurrences	Number of times sought
Sn	0.00 – 11.88	2.1	0.0	0.0	30	36
Au	0.02 - 12.81	3.1	2.5	1.0	69	69
Ag	0.00 – 35.00	4.6	1.4	0.0	60	65
Pb	0.00 – 26.42	1.3	0.2	0.0	46	50
As	0.00 – 3.00	0.4	0.0	0.0	30	47
Fe	0.00 – 3.06	0.1	0.0	0.0	18	36

Tab. a: Range of composition of analysed black bronze artefacts from the literature. A total of 69 occurrences of black bronze alloys are recorded in the database. In a few cases more than one black bronze was inlaid in a single artefact. All values are normalised %wt.

On the basis of the previous analyses (Tab. a, supplementary material), the composition of each sample was limited to a maximum of four elements, namely copper, tin, gold, and silver. The occurrence of arsenic in black bronze is sporadic and because of this and for health and safety constraints it has been neglected. Although there have been some suggestions that arsenic may be important in the generation of patina colour (e.g. Giunlia-Mair & Lehr, 2003), the majority of black bronze analysis that we have assembled here do not report the presence of arsenic (Tab. a, supplementary material). Iron is not considered to have been a significant factor, as it is present at low levels in many copper alloys. A series of 27 replica copper alloys was produced based on all the combinations of three alloying constituents added to copper in the concentration levels:

- Gold (Au) content: 0, 1, 3 wt%
- Tin (Sn) content: 0, 2, 5 wt%
- Silver (Ag) content: 0, 1, 3 wt%

Of the twenty-seven replica alloys, four were selected for the range of experiments reported here, aimed to determine the framework for more detailed investigation: pure copper (100Cu) 5% tin bronze (95Cu5Sn), black copper (97CuAu3) and black bronze (89Cu5Sn3Au3Ag).

### 2.1.2 Solutions

Modern texts and papers report a wide number of detailed solution recipes, especially the ones used in Japan to produce *shakudo*. The recipes of the possible solutions described in ancient texts by Zosimos (see Giunlia-Mair, 2002), Plinii (Bostock & Riley, 1855), and Pausanias (Jones, 1918) are often imprecise and unspecific, but they still allow us to infer some of the important reagents. The main ingredients given are copper acetate (*rokushō* in Japan), copper sulphate, water, apple vinegar, alum, and common salt – although not all of them are always mentioned.

Thirteen recipes taken from ancient and modern sources were compiled and recreated with modern laboratory materials. Following initial evaluation, four final representative solutions were selected for detailed experiments on the basis of the frequency of the ingredients, range of pH and formation of precipitates. Two ingredients seem to be the most common: copper acetate anhydrous (verdigris) and copper sulphate pentahydrate. Citric acid was used to lower the pH and mimic those solutions which contain vinegar with, or instead of, water. The solutions chosen for this study were:

- 1) Solution 1: 0.40 g copper acetate in 100 ml of deionised water (pH: 5.94)
- 2) Solution 2: 0.30 g copper sulphate in 100 ml of deionised water (pH: 5.20)
- 3) Solution 3: 0.40 g copper acetate + 0.30 g copper sulphate in 100 ml of deionised water (pH: 5.60)
- 4) Solution 4: 0.40 g copper acetate + 0.30 g copper sulphate + 0.16 g citric acid in 100 ml of deionised water (pH: 3.90)

While solutions 1, 2 and 4 were transparent, solution number 3 was slightly cloudy, indicating the formation of an insoluble compound. This precipitated material was found to be brochantite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ) using X-ray diffraction analysis. However,

since this solution is one of the most frequent in the literature, we decided to proceed to patination, and evaluate its behaviour during the process.

## 2.2 Evaluation of fabrication method and superficial work

Three 40g tokens of each of pure copper, tin bronze and black bronze were cast. For each alloy a token was (1) left as cast (C), (2) cast and hammered for 2 minutes on a steel anvil (C-H) and (3) cast, hammered and annealed at 600°C for 15 minutes (C-H-A).

Each token was cut into four parts, one of which was retained as a control while the remainder were ground using SiC paper of three grades: fine/4000 grit/5 µm (F); medium/1200 grit/15.3 µm (M); and coarse/320 grit/46.2 µm (C).

The grinding was carried out immediately before the patination, and gloves were worn to avoid the transfer of grease onto the tokens. Afterwards the tokens were subjected to an ultra-sonic bath in IMS (Industrial Methylated Spirit) and then dried with a fan heater before patination.

The resulting 27 samples were patinated using a solution of 0.022 M anhydrous copper acetate in deionised water (Solution 1), which is the most typical of all the solutions found in modern and ancient sources. The patination of the alloys was performed in separate beakers on a hotplate, maintaining a stable solution temperature of 80°C for 40 minutes. Afterwards, the patinated tokens were washed in distilled water. The resulting patinas were analysed using colorimetry.

## 2.3 Evaluation of different patinating solutions

Three alloys – Cu, 97Cu3Au and 89Cu5Sn3Au3Ag – manufactured as C-H-A and with a surface finish of 600 grit SiC paper, were patinated in each of the four solutions using the procedure outlined above.

The resulting 12 samples were analysed using optical and scanning electron microscopy (SEM), X-ray diffraction (XRD), portable X-ray fluorescence (pXRF)



and Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM), and colorimetry. Transmission electron microscopy (TEM) was used on two samples.

## 2.4 Instrumentation

SEM analysis was performed using a Hitachi S-3400N operated at 5-25kV, or where improved spatial resolution was required a JEOL JSM-6301F with a field emission electron gun (FE-SEM). Both instruments were equipped with an Oxford Instruments INCA energy dispersive X-ray spectrometer, standardised in the laboratory with pure elements and oxides. Instrumental drift was corrected by the frequent analysis of metallic cobalt. Analyses were carried out on the flat surfaces of the unprepared samples, as well as on an edge ground with 600 SiC paper, without carbon coating. EDS analyses were performed at 20 kV, 10 mm working distance and 100 s counting time.

TEM was used to investigate small particles ( $< 3 \mu\text{m}$ ) detected in some patinas with SEM and FE-SEM techniques. The instrument used is a JEOL J2100, 100 keV system. The usual sample preparation for TEM requires the preparation of an electron transparent specimen (100-150 nm thick) (Sridhara Rao *et al.* 2010), usually in the form of slices or particle suspensions. The patina particles were collected from the sample by wetting the surface with methanol then rubbing with a fingertip in a nitrile glove. The glove was then agitated in a beaker containing 10 ml of methanol. A drop was deposited on a TEM grid (3 mm diameter) and left to evaporate at room temperature.

XRD analysis was performed using a PanAnalytical X'Pert Pro diffractometer with Bragg-Brentano geometry. Instrumental settings: Cu anode ( $K\alpha_1 = 1.5418$ ), 30 mA, and 40 kV, goniometric radius of 240 mm. Analysis was performed from  $5.520^\circ$  to  $79.80^\circ 2\theta$ , with a step size of  $0.0021^\circ$  and at a rate of 10.16 seconds/step. Spectra treatment and qualitative analysis were performed using EVA software and the ICSD database. It was not necessary to prepare the sample for XRD analyses as the sample was thin enough to be inserted in the instrument's sample holder.

Selected samples were analysed using a Renishaw InVia Raman Microscope, equipped with a red laser (785 nm). Analytical conditions were varied according to

the material response; 5 mV laser power was typically 5-10% for exposure times of 10-30 s.

Colour was measured using an X-rite 530 portable reflection spectrodensitometer. Colorimetry is a technique routinely used on paintings and ceramics but less commonly on metals. However, it was considered a fundamental technique given the aims of the project, based on the evaluation of patinas colour. Instrumental settings: D65/10, modality SCI, 5 seconds. Each sample was measured once on the most uniform and representative area, and 3 more times at arbitrary positions on the sample. The first measurement was useful to determine the actual colour of the patinas, while the mean and standard deviation calculated on all four measurements was used to compare the general characteristics of the samples and to evaluate the degree of uniformity of the patinas.

### 3 – Results

#### 3.1 Visual appearance

##### 3.1.1 Fabrication method

Since variable C, H, A treatments create different metal alloy microstructures, a consistent difference in patina colour or degree of reflectance was expected. However, no differences were noticeable visually, and virtually identical VIS reflectance spectra were obtained for each fabrication method (Fig. a, supplementary material), differing only in the overall intensity. The same lack of correlation between fabrication methods and colour was found irrespective of the grade of surface finish. There was no correlation between spectrum intensity and grade of surface finish.

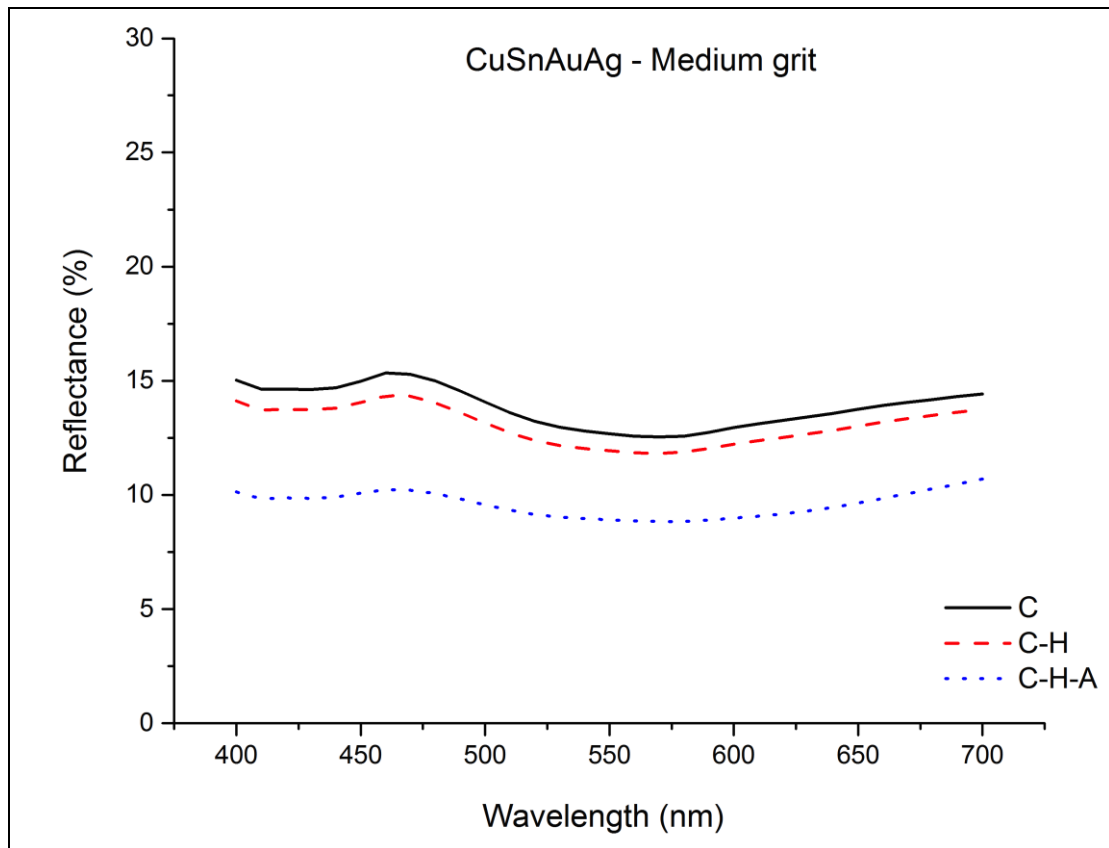


Fig. a: Reflectance in VIS range of the patina on alloy Cu89Sn5Au3Ag3 and surface finish M (medium grit) for different fabrication methods. Each spectrum is a mean of 4 measurements; the scatter was minimal.

### 3.1.2 Superficial working

There were clear variations in patina quality depending on the grade of surface finish. Fig. 1 shows that in copper and bronze alloys with no added precious metal, the patination was less effective. The only acceptable results were obtained on the medium grit finish, which appeared to provide the best adherence and most uniform colour. On surfaces with a finer finish, the patina was loose and washed off during the cleaning stage in distilled water, while on coarser surfaces the patina growth was very uneven. In contrast, patinas on the alloy spiked with gold and silver (Cu89Sn5Au3Ag3) appeared more uniform to the naked eye compared across all grades of surface finish (Fig. 1).

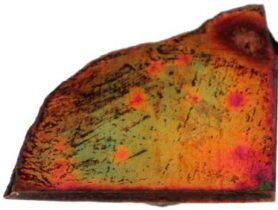








	<b>Cu100</b>	<b>Cu95Sn5</b>	<b>Cu89Sn5Au3Ag3</b>
<b>F-Fine</b>			
<b>M-Medium</b>			
<b>C-Coarse</b>			

Fig. 1: Macrophotographs of samples of different alloys patinated after grinding with different grades of abrasive. Each rectangle is 3.3 x 2.6 cm.

Colorimetric measurements showed a consistent relationship between the underlying alloys and the colour of their patina (Fig. 2).

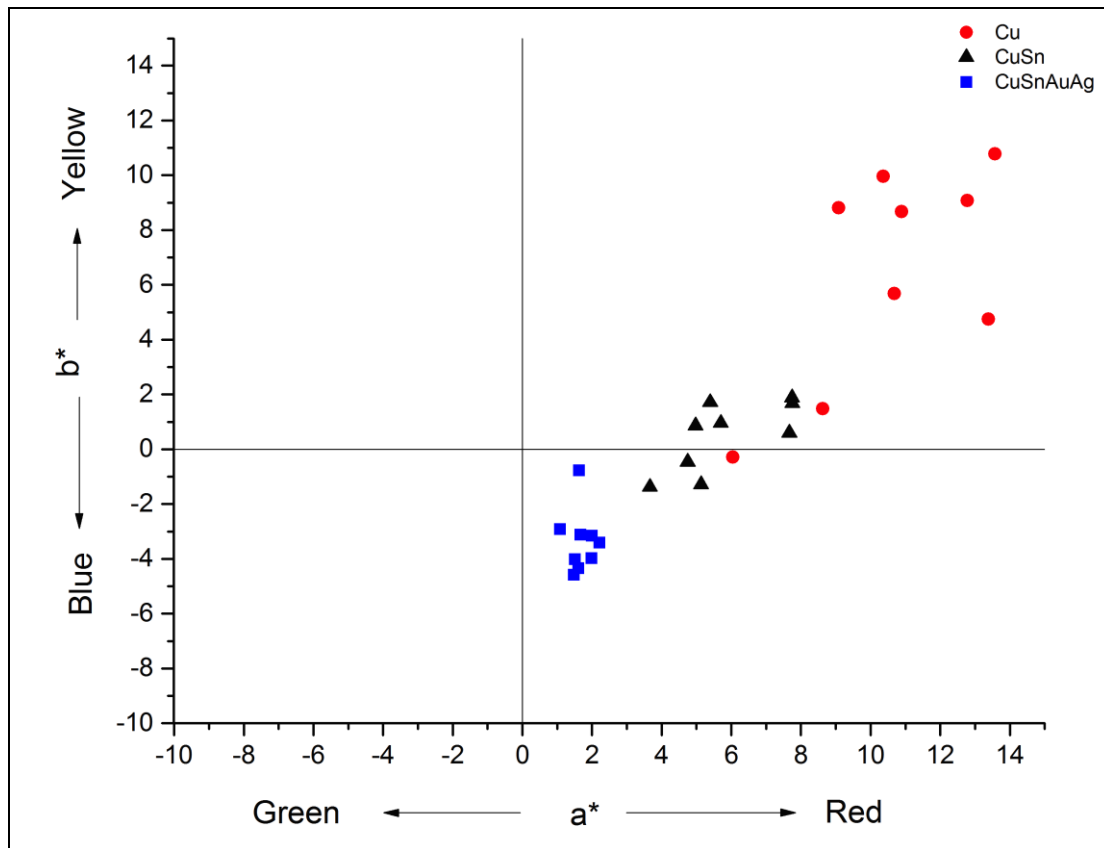


Fig. 2:  $a^*/b^*$  ratio alloy Cu, CuSn, Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub>. N=9 (each alloy) corresponding to 9 samples obtained combining 3 fabrication methods (C, C-H, C-H-A) and 3 superficial workings (F-M-C). Each data point represents the mean of 4 measurements.

The back bronze alloy (Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub>) has more negative values of the “b” colorimetric chromaticity coordinate, which is the yellow-blue coordinate, where negative values indicate blueness and positive values indicate yellowness. The graph also shows a significantly lower dispersion of data from the black bronze sample. This demonstrates that the precious metals additives not only give a specific colour and shade, but also create more consistent results irrespective of the surface finish.

### 3.1.3 Effect of patinating solution

The end products of the patination of the three alloys (Cu<sub>95</sub>Sn<sub>5</sub>, Cu<sub>97</sub>Au<sub>3</sub>, Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub>) in the four patinating solutions are shown in Fig. 3. To the naked eye all the patinas on the gold-bearing alloys, black copper (Cu<sub>97</sub>Au<sub>3</sub>) and black

bronze (Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub>) appeared black. In contrast, those on the bronze without gold appeared reddish brown (Fig. 3).













	<b>Cu<sub>95</sub>Sn<sub>5</sub></b>	<b>Cu<sub>97</sub>Au<sub>3</sub></b>	<b>Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub></b>
<b>Sol. 1</b>			
<b>Sol. 2</b>			
<b>Sol. 3</b>			
<b>Sol. 4</b>			

Fig. 3: Visual appearance of the 3 alloys patinated with 4 different solutions. Each rectangle is 3.3 x 2.6 cm.

The macro scale visual analysis is confirmed by the measurement of the colour as reflectance in the visible range (Fig. b, supplementary material), which corroborates that alloy composition is the main factor affecting patina colour, with solution composition playing a comparatively smaller role. On the gold-free tin bronze (Cu<sub>95</sub>Sn<sub>5</sub>) the patina is reddish and its colour changes slightly according to the solution used to patinate the samples. Solution 1 leads to a black colour, solutions 2

and 3 have higher reflectance in the 600-700 nm region resulting red, and solution 4 has lower reflectance value in the 400-500 nm region. In alloys Cu<sub>97</sub>Au<sub>3</sub> and Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub> the patinas are black and the solutions do not affect the final colour. The colours of the patinas on these two precious metal-bearing alloys differ in the blue/red component ratio: sample Cu<sub>97</sub>Au<sub>3</sub> has low reflectance in the red part of the spectrum; sample Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub> has a low red component, but slightly higher blue reflectance (Fig. b, supplementary material).

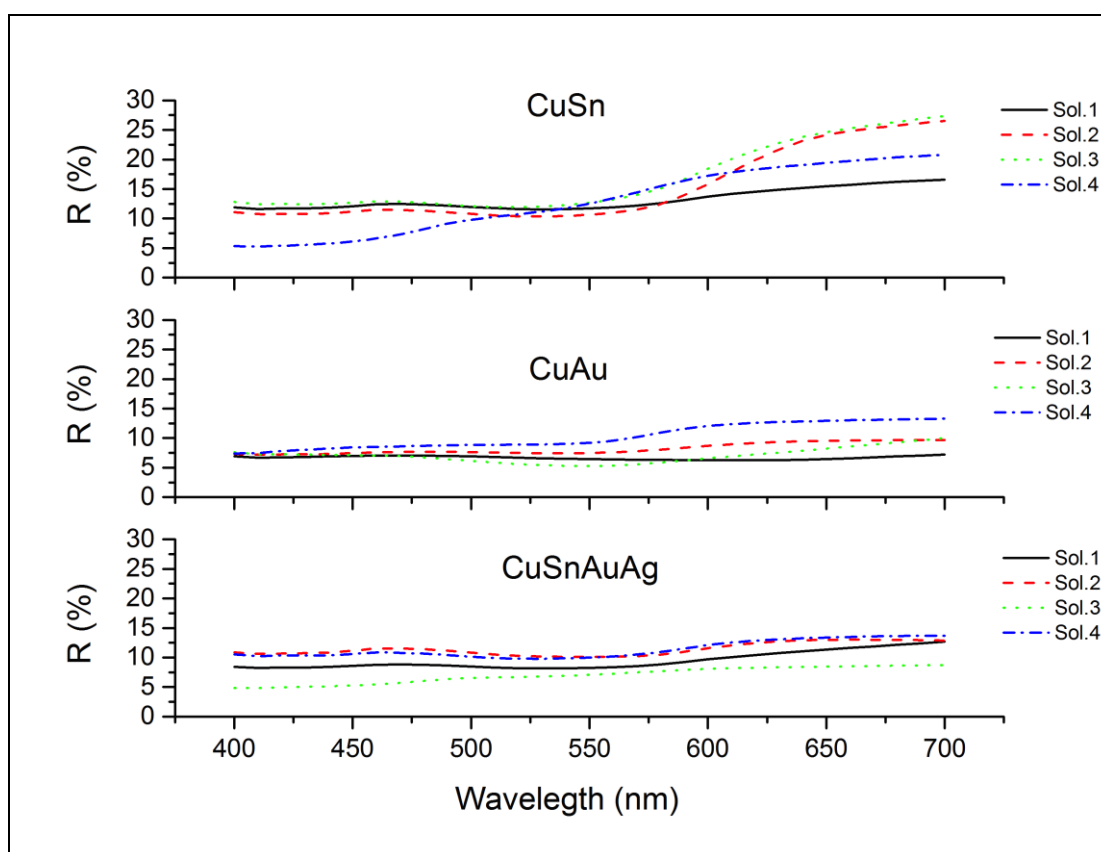


Fig. b: Reflectance in VIS range of the patina on alloys Cu<sub>95</sub>Sn<sub>5</sub> (top), Cu<sub>97</sub>Au<sub>3</sub> (middle), Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub> (bottom). Note that the colour changes mainly according to the alloy and not according to the solution used. Each spectrum is a mean of 4 measurements.

### 3.2 Patina microstructure and composition

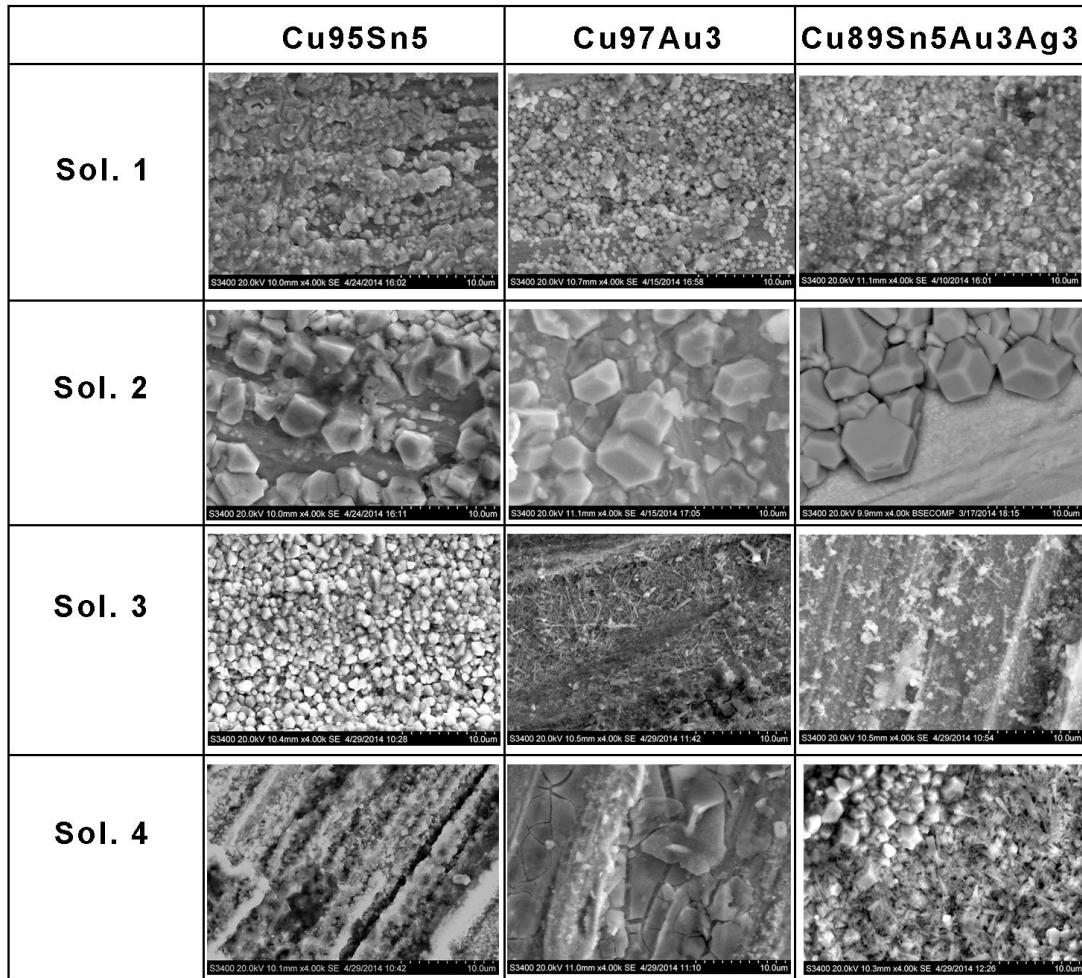


Fig. 4: SEM image. Patina microstructures for 3 different alloys and four different solutions seen at 4000X (area = 1.33 x 0.93 mm).



Sample - solution		O	S	Cu	Ag	Sn	Au
CuSnAuAg – Nominal composition				89.0	3.0	5.0	3.0
CuSnAuAg – Sol.1	Mean	10.51		60.54			
	Std. Dev.	0.22		0.58			
CuSnAuAg – Sol.2	Mean	20.21	0.29	76.21	0.87	1.58	0.84
	Std. Dev.	0.02	0.05	0.77	0.14	0.41	0.18
CuSnAuAg – Sol.3	Mean	20.14	0.73	69.29	3.16	3.73	2.95
	Std. Dev.	0.07	0.06	0.55	0.22	0.21	0.15
CuSnAuAg – Sol.4	Mean	20.79	0.73	77.09	0.46	0.93	0.73
	Std. Dev.	0.17	0.17	0.44	0.06	0.13	0.17

Tab. 1: Surface patina composition on alloy Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub>. EDS analysis at 100 X magnification (area of analysis = 315x220 μm). N=3.

Figure 4 shows the surface microstructures of the bronze, black copper and black bronze alloys, patinated with the four different solutions. All the alloys patinated with copper acetate only (Sol. 1) show a patina with fine (<1 μm), compact, irregular crystals. SEM-EDS directly on the surface did not reveal the presence of Au and Ag, indirectly indicating the patina is relatively thick. The patina obtained using copper sulphate without copper acetate (Sol. 2) is not compact but consists of larger polyhedral crystals (5-10 μm) that lie on the surface of the alloy, and a fine dispersion of sub-micron particles of higher atomic number adhering on the surface of the metal below the polyhedral crystals (Fig. 5). An attempt was made to identify the nanoparticles with EDS but it was not successful due to the relatively large beam size and the interference of the substrate. The polyhedral crystals seem not to cover the whole surface of the sample and, although Ag and Sn were detected in the analysis (Table 1), the possibility that they were detected from the substrate rather from the patina itself cannot be excluded.

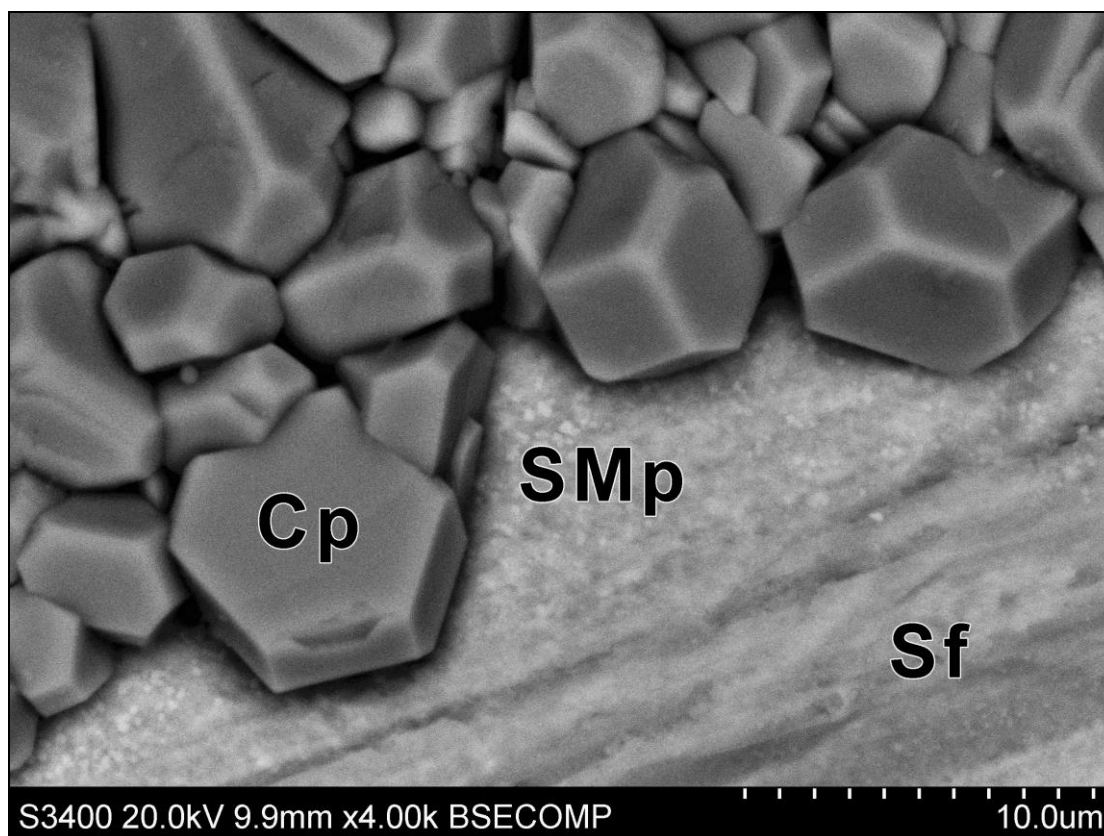


Fig. 5: BSE SEM-EDS image. Microstructure of sample  $\text{Cu}_{89}\text{Sn}_5\text{Au}_3\text{Ag}_3$  after treating with the solution of copper sulphate (Sol. 2). The picture shows large crystals of cuprite (Cp) overlying the metal surface (Sf) with minute sub-micron particles (SMp).

In patinas obtained with both copper acetate and copper sulphate (Sol. 3 and Sol. 4), on alloy  $\text{Cu}_{97}\text{Au}_3$  the solutions seem to have created amorphous patina and, solution 4 has formed a cracked layer on the substrate. In alloy  $\text{Cu}_{89}\text{Sn}_5\text{Au}_3\text{Ag}_3$  treated with the two solutions of copper acetate and sulphate (Sol. 3 and Sol. 4) there are acicular crystals not found in other patinas. Attempts to characterise these crystals by EDS were unsuccessful. Small amounts of Ag, Sn and Au were detected, particularly in patinas formed with solution 3, but these elements could have been detected from the substrate.

Raman spectroscopy and XRD show the presence of cuprite and tenorite in all the samples (Fig. c, supplementary material).

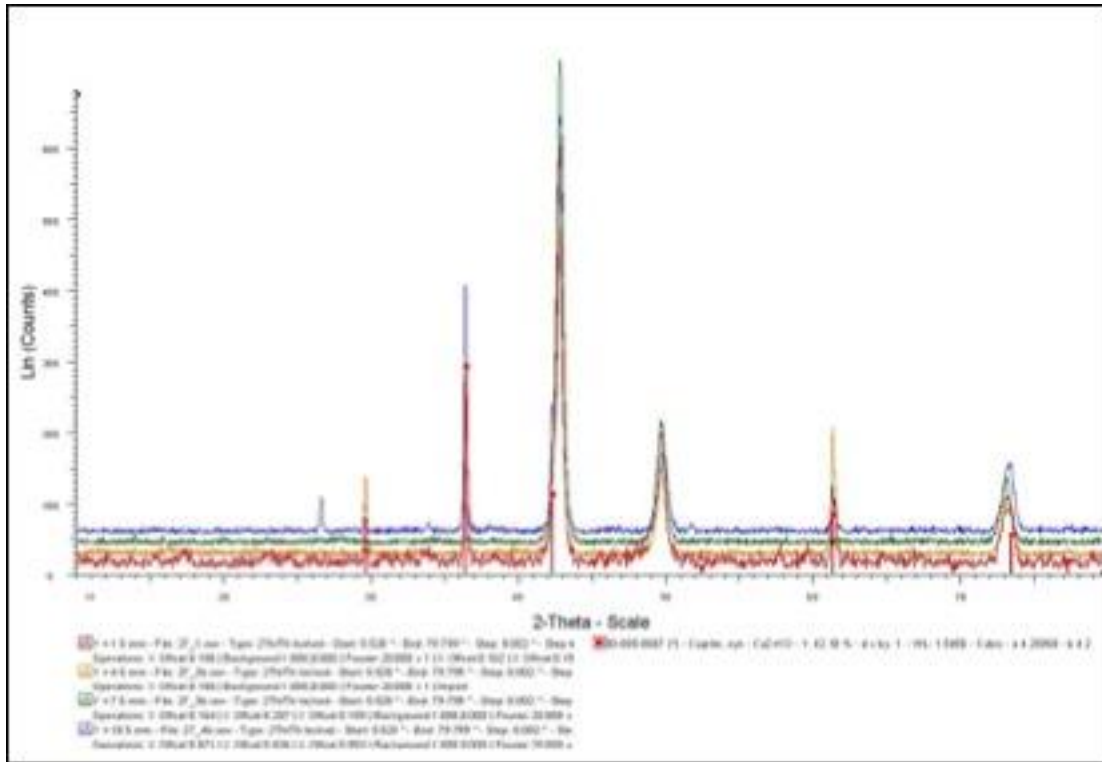


Fig. c: Diffractograms sample Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub>, solution 1 (red), 2 (yellow), 3 (green), and 4 (blue).

In the Raman spectra, cuprite (210 cm<sup>-1</sup>) is revealed in the patinas on all of the alloys but its signal appears higher in alloys containing noble metals. In contrast, a high content of tenorite (294 cm<sup>-1</sup>) is present in the bronze sample without precious metals (Cu<sub>95</sub>Sn<sub>5</sub>). Unidentified reflections and bands are present in both XRD and Raman spectroscopy. However, a cross check with Raman spectroscopy reference spectra from databases (ICDD) and relevant papers (e.g. Colombari *et al.* 2011; Smith & Clark 2004) did not reveal phases typical of copper reaction in a humid environment (malachite, posnjakite, brochantite, antlerite) or tin phases. It is not surprising that chlorine bearing phases were not present, as chlorine was excluded from the experiments.

The SEM and FE-SEM analyses showed gold unequivocally present as an enriched component only in the surface of alloy Cu<sub>89</sub>Sn<sub>5</sub>Au<sub>3</sub>Ag<sub>3</sub> patinated with copper acetate (Sol. 1). In this sample a gold-enriched phase was seen as irregular particles about 100 nm across but observed very infrequently.

Even here it was very dispersed and it would explain the value below the detection limit in the SEM-EDS analysis. Moreover, it is unclear if the density of these Au particles is sufficient to have an effect on the final colour. Analyses of a sample of this patina with TEM to assess the presence of precious metal particles has so far failed to confirm their presence. Furthermore, in the TEM neither gold nor silver were detected with EDS.

On balance, if the intention is the production of a black colour and a homogeneous, fine-grounded microstructure giving an adherent and robust patina, it would seem that solution 1 (copper acetate) is the most successful patination solution of those we have tried.

#### 4 – Discussion

The importance of the superficial work (abrading/polishing) carried out prior to patination is highlighted particularly in the Japanese texts and modern patination recipes (e.g. Sugimori 2004, Hughes & Rowe 1982). This crucial procedure allows attenuation of the surface segregation formed during casting and exposes the underlying alloy. Furthermore, roughening the surface may provide protected areas from which it will be harder to dislodge the patination by abrasion in normal handling. The traditional Japanese texts suggest that the surface should be polished with charcoal powder or clay (Sugimori 2004). O'Dubhghaill & Jones (2009) have measured the surface texture produced by different polishing media. The surface treated with charcoal powder was rougher than that using a 1200 grit paper, while the surface produced by clay was slightly finer (O'Dubhghaill & Jones 2009). The present study confirms that the nature of superficial work affects the homogeneity and colour of the patina formed. In the experiment presented here, the best results were achieved with the intermediate 1200 grit, which is itself intermediate between the traditional materials. Too rough a surface produced an uneven patina, while too smooth a surface resulted in poor adherence. As such, our results would seem coherent with the recommendations made in written sources. Importantly, however, this difference was observed only in those alloys which did not contain precious metals. In the black bronzes (alloys with added Au) the patina was homogeneous regardless of the grade

of finish, as confirmed by both visual and colorimetric analysis. This suggests that not only does the presence of gold in the alloy produce a more desirable colour in the patina, but also it promotes homogeneous formation and better adhesion. Given that the effect of surface treatment on gold-containing alloys seem slight, textual references to the importance of surface finish may simply evoke the thoroughness and attention to detail typically demanded in the traditional craft workshops. Alternatively, they may relate to the persistence of the patina over long periods – a variable which was not tested here.

Giumlia-Mair and Lehr (2003) comment on the role of fabrication method in the development of black patinas, but their comments seem to be a little unclear as on the one hand they indicate that the best patinas were achieved on hammered and annealed pieces, but on the other they say that annealed objects cannot be patinated as easily as fine-grained alloys. However, we did not observe a dependency of patina formation on the fabrication methods of alloys with or without gold. Furthermore, for alloys with gold, we found at most a very limited dependency on surface treatment. It may be that the observation of Giumlia-Mair and Lehr relates to the exceptionally fine surface structure of the rolled alloys they used and possibly the non-removal of surface material where there may have been some segregation effect.

The black patinas tested on the gold-bearing alloys have higher negative “b” colour values than those on the gold-free alloys. This explains and confirms that the particular blue shade of black, described and indicated as a characteristic feature of black bronzes by several modern authors (e.g. Craddock & Giumlia-Mair 1993; Pumpelly 1866), may have been a critical factor explaining alloy selection. Interestingly, in our experiments the colorimetric measurements suggest that the patina formed on the black copper (97Cu3Au) is less blue than that on the black bronze, an observation pointing to the particular role played by tin, which will be explored further in future work. These experiments already show that subtle properties such as colour shades may have had very significant effects in the appreciation and value of different objects. This feature could explain why a black bronze would be preferred to a black bronze simply obtained on an annealed high tin bronze.

It is interesting to note that the solution most frequently recommended in the Japanese texts (e.g. Bisei 1951, Sugimori 2004), made of copper acetate and copper sulphates (Sol. 3 in these experiments), produced precipitates. In fact, the same sources suggest that the solution is constantly agitated or that vinegar is added to the solution to obtain a better colour. Our results show that the same solution of copper salts with lower pH (Sol. 4) does not create precipitates and produces a good patina on gold bronze alloy. Hence our findings appear consistent with the textual evidence.

Solution composition appears to be the main factor controlling patina microstructure. Copper acetate (Sol. 1 in the experiments) seems to be essential to obtain a fine, homogeneous structure while copper sulphate (Sol. 2 in the experiments) creates large crystals, which do not cover the entire surface and appear relatively easily detached. Solution 3 and 4 create cracked patinas with acicular crystals.

Even though the research has been restricted to only four solutions, it appears possible to distinguish the kind of solution used by analysing the superficial microstructure of the objects. If this finding is confirmed, the implications for the study of patinated artefacts would be significant, as it would allow to infer technical behaviour and possibly different technological traditions, by the simple study of the surface of archaeological materials.

In general, when a black bronze is immersed in a hot solution, two competing processes may occur: corrosion and crystal growth. The prevalence of one or the other is likely to be dependent upon the solution used. The fine-grained homogeneous layer developed with copper acetate (Sol. 1) is likely to reflect the predominance of corrosion, while the coarse crystals generated in copper sulphate solution (Sol. 2) are likely to reflect the predominance of crystal growth. As both solutions are acidic it appears to be the anionic composition that is critical, rather than the acidity. The presence of acetate is the common factor in all three solutions in which corrosion appears to be dominant and where a fine-textured layer is produced, and we assume that this increases the solubility of copper in solution, favouring corrosion over crystal growth.

Cuprite is the dominant phase in the patinas on alloys containing gold but its morphology appears to depend upon solution composition. Tenorite is predominant on the bronze without gold. It therefore appears that the presence of gold inhibits the growth of tenorite, allowing the growth of cuprite. The precise mechanism for this effect is unclear. Considering the combined results of imaging, SEM-EDS, Raman and XRD analyses, it is likely that non-stoichiometric  $\text{Cu}_{2-x}\text{O}$  compounds are present, which may account for some of the unattributed Raman bands. A potential contributor to the colour might be sulphur-based compounds like Cu-sulphide but the formation of a black patina in solutions without sulphur and the failure to detect sulphide phases by Raman spectroscopy or XRD make this unlikely.

While patina colour seems to be dependent mainly on the composition of the alloy substrate and is not influenced by the patination solution, the microstructure of the patinas seems to depend mainly on the solution used and not on the composition of the underlying alloy. However, the microstructure is likely to affect the adherence of the patina to the alloy surface. Thus the coarse tenorite crystals, formed in the copper sulphate solution, produce a less satisfactory patina, although it is black, as they are less firmly bound to the surface.

There is general agreement in the literature that the colour of black bronze is due to the presence of gold nanoparticles and several papers report observations of these (Kitada 2005, Murakami 1993, Notis 1988) which, according to the work of Kitada (2005) are in the range 2-5 nm. So far we have not observed gold nanoparticles, but have seen sparse micrometre-sized gold particles in some patinas (Fig. d, supplementary material).

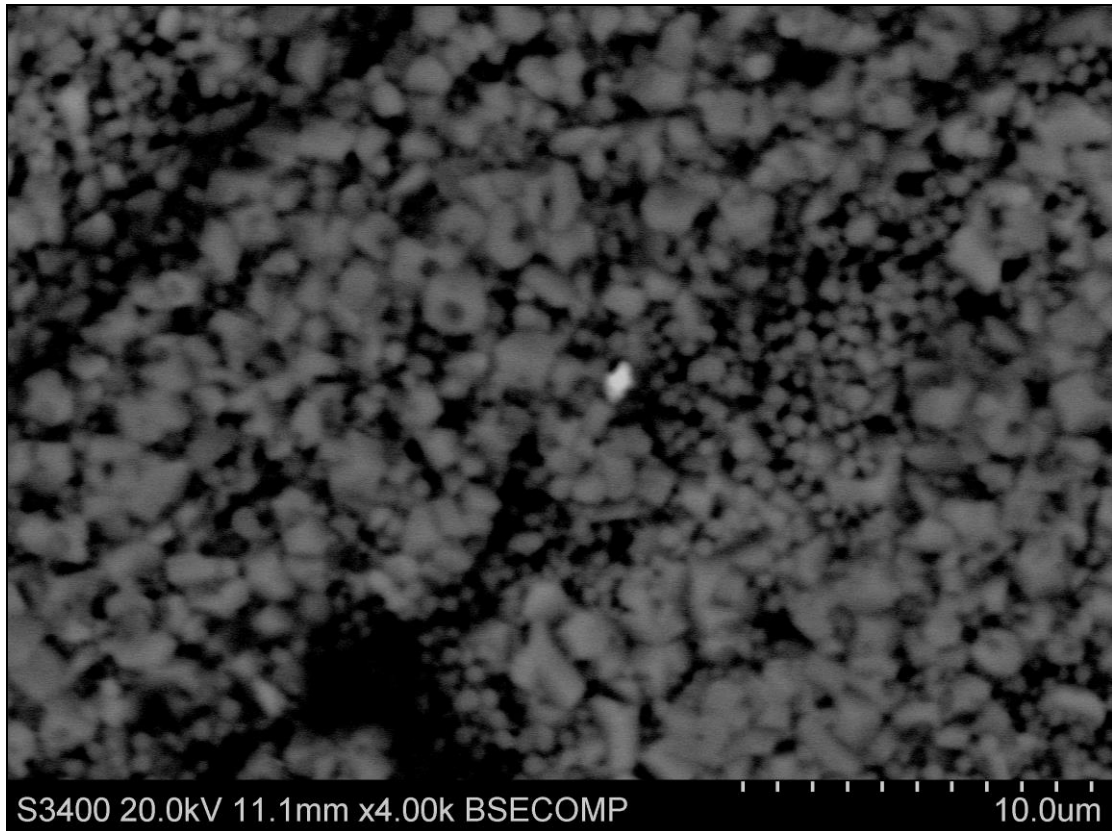


Fig. d: BSE SEM image. Gold-rich particle in the patina on sample  $\text{Cu}_{89}\text{Sn}_5\text{Au}_3\text{Ag}_3$  patinated with solution 1. Note the dispersion (large inter-particle distance) of the particle in the area analysed and its dimension, less than one micrometre.

As the particles observed by Kitada were dispersed in the cuprite layer, further TEM work will be conducted to determine their presence and nature. However, it is of interest that our SEM-EDS analyses of the patina layers detected no gold in several of them, and also failed to detect tin. The presence of these elements in the patinas, or in the interface between the metal and the cuprite-rich layer, is being investigated.

## 5 - Conclusions

These experiments indicate that the development of black bronze is dependent upon the interplay of a number of factors. Colour and appearance of the patina are not affected by the object fabrication method (e.g. casting vs hammering), but they are by the surface preparation. Alloy composition and patination solution are both important parameters, each of them responsible for a different aspect of the final patina. The



alloy composition is the main controlling factor for the colour, while the solution composition is the main controlling factor for the resulting microstructure. Of the two anionic types tested, copper acetate solution seems to be essential to obtain a fine, homogeneous structure, while copper sulphate solution results in the formation of larger crystals, which do not cover the entire surface. This appears to be due to the dominance of a dissolution/corrosion process in the acetate solution, while precipitation prevailed in the copper sulphate. The main phases in the patinas are cuprite and tenorite. However, no tin was found in the black patinas on tin-bearing alloys and the reason for this is presently unclear. The precipitate obtained by filtering the solution was checked by XRD and no tin-bearing phases were detected.

The presence of gold in the alloy promotes homogeneous formation and better adhesion of the patina on the surface. Furthermore, alloys containing precious metals are the least sensitive to variations due to surface finish.

It appears that the presence of gold in the alloy is necessary to promote a desired bluish-black as opposed to a reddish-black colour. As the patinas on gold-bearing alloys develop more cuprite, while those without gold develop tenorite, it is inferred that gold is behaving as an inhibitor, slowing the oxidation of cuprite to tenorite in the corrosion/patination process. Mineral tenorite is also black, but the colour observed on the macroscopic scale on metal patinated by tenorite is more red and arguably less pleasing.

The gold nanoparticles reported in previous studies form as the alloy is corroded by the patination solution and must therefore depend upon the aggregation of gold which had previously been dissolved in the metal on an atomic scale. Development of cuprite should be at a rate sufficiently slow to allow gold to aggregate on the nanometre scale but not so slow that the gold particles become too large, when they would not create the desired optical effect. That this may occur is evidenced by the micrometre-sized gold we have seen in the experiments. The reported observations of silver and lead particles in the corrosion products on naturally corroded copper alloys (e.g. Franke et al. 2015) are another manifestation of this type of process.

These experiments confirm that a determining factor in the development of a blue-black, uniform and homogeneous patina is the presence of precious metals. Gold appears to inhibit the development of tenorite in favour of cuprite, to ensure a uniform development and to promote adhesion. The presence of gold ensures that the development of the black patina is a relatively robust process, which is not as sensitive to variables such as metal fabrication as might have been expected.

Copper alloy artefacts with black-looking surfaces appear throughout the archaeological record, but very few of them seem to contain significant levels of gold. Systematic experiments have been conducted to demonstrate that gold-bearing black alloys were made to ensure the highest quality, not only in terms of appearing black, but black of the finest shade and uniformity, and which was least likely to be lost. Since blacks generated on gold-free alloys by other methods can be argued to be of inferior quality from a number of perspectives, it will be interesting for future work to assess the extent to which this realisation affected the choice of patinating technique in different contexts, depending on the expected quality or status associated to the objects. This may help ascertain the intentionality behind the addition of noble metals to black bronzes, as well as to map different technical procedures in time and space.

### Acknowledgements

The authors are grateful to Harriet White and Kevin Reeves from the UCL Wolfson Archaeological Science Laboratories, Steve Firth from UCL Chemistry, and Matija Strlic and Katherine Curran from the Heritage Science Laboratory for their precious technical assistance, and Philippe Colomban for his useful suggestions on Raman spectroscopy. Finally, we express our gratitude to Gaia Fenoglio, Angelo Agostino and Maurizio Aceto for their valuable comments, suggestions and encouragement during the progress of this paper.

## Bibliography

Aucouturier, M. Mathis F., Robcis D., Castaing J., Salomon J., Pichon L., Delange E., and Descamps S., 2010. Intentional patina of metal archaeological artefacts: non-destructive investigation of Egyptian and Roman museum treasures. *Corrosion Engineering, Science and Technology*, 45 (5), 314–332.

Bayley, J. and McDonnell, J.G., 2000. A bracelet in “Corinthian Bronze”. In Rahtz, P., Hirst, S., and Wright, S. M., *Cannington Cemetery*. 355–359.

Bisei, U., 1951. Japanese techniques. In Wilson, H. (ed.), *Silverwork and Jewellery*. London, U.K.: Ulan Press.

Bostock, J., Riley, H.T., 1855. K: Plinii Secundi: *The Natural History, Books XXXIII, XXXIV*. Taylor and Francis: London, U.K. Vol. 6.

Caple, C. and Clogg, P., 2001. Saxon *Shakudo*. *Durham Archaeological Journal* 16, 27-32.

Colomban, P., Tournié, A., Maucuer M., and Meynard P., 2011. On-site Raman and XRF analysis of Japanese/Chinese bronze/brass patina – the search for specific Raman signatures. *Journal of Raman Spectroscopy, Early View*.

Craddock, P. T. and Giunlia-Mair, A., 1993. Hsmn Km, Corinthian bronze, *Shakudo*: black patinated bronze in the Ancient World. In La Niece, S. and Craddock, P. T. (eds), *Metal Plating and Patination: Cultural and Historical Developments*. Oxford, U.K.: BUTTERWORTH-HEINEMANN, LTD, 102–127.

Craddock, P. T. and Giunlia-Mair, A., 1996. The identity of Corinthian Bronze: Rome’s *Shakudo* alloy. *Proceedings of the 12th International Bronze Congress at Nijmegen, 31 May 4 June 1992, Provinciaal Museum C.M. Kam, Nijmegen, Netherlands*. 137–147.

Craddock, P. T., 1982. Gold in antique copper alloy. *Gold bulletin*, 15(2), 69–72.

- Demakopoulou, K., Mangou, E., Jones, R., E., and Photos-Jones, E., 1995. Mycenaean Black Inlaid Metalware in the National Archaeological Museum, Athens: A Technical Examination. *The Annual of the British School at Athens*, 137–153.
- Franke, K. A., Pigott, V. C. and Nash, S., 2015. The Analysis of Metal Artifacts from Tell al-Raqa'i. In: G. Schwartz (ed.), *Rural Archaeology in Early Urban Northern Mesopotamia: Excavations at Tell Raqa'i*. Los Angeles: Cotsen Institute of Archaeology Press. (Monumenta Archaeologica 36), 521-550.
- Giumlia-Mair, A. and Craddock, Paul T., 1993. Irogane alloys in Classical Antiquity. *Bulletin of the Metals Museum, Sendai, Japan*, 20 (2), 3–17.
- Giumlia-Mair, A. and Lehr, M., 1998. Patinating black bronzes: texts and test. *Proceedings of the 4th International Conference on the Beginning of the Use of Metal and Alloys (BUMA IV), May 25-27, 1998*, 103–108.
- Giumlia-Mair, A. and Lehr, M., 2003. Experimental reproduction of artificially patinated alloys, identified in ancient Egyptian, Palestinian, Mycenaean and roman objects. In *Archeologie Sperimentali. Metodologie ed esperienze fra verifica, riproduzione, comunicazione e simulazione. Comano Terme, Fiavè (Trento, Italy), 13 - 15 settembre 2001*. 291–310.
- Giumlia-Mair, A. and Quirke, S., 1997. Black copper in Bronze age Egypt. *Revue d'Égyptologie*, 48, 95–108.
- Giumlia-Mair, A., 1995. The appearance of black-patinated copper-gold-alloys in the Mediterranean area in the second millennium BC. Material characterisation and problem of origin. *Prehistoric Gold in Europe, Mines, Metallurgy and Manufacture*, Prehistory, 425–435.
- Giumlia-Mair, A., 1997. Early instances of Shakudo-Type alloys in the west. *The Bulletin of the Metals Museum, Sendai, Japan*, 28 (2), 3–15.

Giumlia-Mair, A., 2001. Colouring treatments on ancient copper-alloys. *Revue de Métallurgie*, 98(9), 767–776.

Giumlia-Mair, A., 2002. Zosimos the Alchemist - Manuscript 6.29, Cambridge, Metallurgical interpretation. *XV Congresso Internazionale sui Bronzi Antichi "Produzione e Tecnologia"* (A.Giumlia-Mair ed), 2002, Aquileia e Grado, 22-26 Maggio 2001, 317–323.

Giumlia-Mair, A., 2012. I materiali della coppa di Enkomi (Cipro), ovvero, non è tutto niello quell che è nero. *Actes de colloques Bronzes grecs et romains, recherches récentes — Hommage à Claude Rolley*, INHA.

Hamerow, H. and Pickin, J., 1995. An early Anglo-Saxon Cemetery at Andrew's Hill, Easington, Co. Durham. *Durham Archaeological Journal*, 11, 35–66.

Hughes, H. and Rowe, M., 1982. *The Colouring, Bronzing and Patination of Metals*, New York, N.Y.: Watson-Guptill/Whitney.

Jones, W.H.S., 2014. *Pausanias: Description of Greece*. Cambridge, MA: Harvard University Press, Vol. 2.

Kitada, M., 2005. Microstructures and Physical Properties of Colored Layer of Cu-4 mass% Au Alloy (Shakudou) Fabricated by Japanese Traditional Technique. *Journal of the Japan Institute of Metals and Material*, 69 (12), 1069-1076.

La Niece, S., 1991. Japanese polychrome metalwork. *Archaeometry*, 32, 87–94.

Martinón-Torres M. and Rehren, T. (eds), 2008. *Archaeology, History and Science. Integrating Approaches to Ancient Materials*. Left Coast Press.

Mathis, F., 2005. PhD Thesis, *Croissance et propriétés des couches d'oxydation et des patines à la surface d'alliages cuivreux d'intérêt archéologique ou artistique*.

Matériaux. Université Paris Sud - Paris XI Available online: <https://tel.archives-ouvertes.fr/tel-00011255>

Mathis, F., Descamps S., Robcis D., Aucouturier M., 2005. Original surface treatment of copper alloy in ancient Roman Empire: chemical patination on a Roman strigil. *Surface Engineering*, 21, 346–351.

Mathis, F., Descamps S., Robcis D., Aucouturier M., 2009. HMTY-KM (black copper) and the Egyptian bronzes' collection of the Musee du Louvre. *Journal of cultural heritage*, 10 (1), 63–72.

Mohamed, W. and Darweesh, S., 2012. Ancient Egyptian black patinated copper alloys. *Archaeometry*, 54 (1), 175–192.

Murakami, R., 1993. Japanese traditional alloys. In La Niece, S. and Craddock, P. T. (eds.), *Metal Plating and Patination: Cultural and Historical Developments*. Oxford, U.K.: Butterworth-Heinemann Ltd, 85–94.

Murakami, R., Nijyama, S., and Kitada, M., 1988. Characterization of the black surface layer on a copper alloy coloured by traditional Japanese surface treatment. In Mills, J. S., Smith, P., and Yamasaki, K. (eds.), *The Conservation of Far Eastern art. Proceeding of the IIC Congress, 19-23 September 1988, Kyoto*. London: The International Institute for Conservation of Historic and Artistic Works Publ., 133–136.

Notis, M. R., 1988. The Japanese Alloy *Shakudo*: Its History and its Patination. In Maddin, R. (ed.), *The Beginning of the Use of Metals and Alloys*. Cambridge, MA.: MIT Press, 315–327.

O'Dubhghaill, C. and Jones, A. H., 2009. Japanese irogane alloys and patination, a study of production and application. *Proceeding of the Twenty-Third Santa Fe Symposium on Jewelry Manufacturing Technology*. Albuquerque, New Mexico: Met-Chem Research.

Oguchi, H., 1972. Experimental studies on Japanese traditional coloring copper. *Bulletin of the Faculty of Fine Arts Tokyo University of Art, Tokyo Geidai*, 8, 23–88.

Oguchi, H., 1983. Japanese *shakudo*: its history, properties and production, from gold-containing alloys. *Gold bulletin*, 16 (4), 125–132.

Photos, E., Jones R. E., and Papadopoulos Th., 1994. The black inlay decoration on a Mycenaean Bronze Dagger. *Archaeometry*, 36 (2), 267–275.

Pumpelly, R., 1866. Notes on Japanese Alloy. *American Journal of Science*, 42, 43–45.

Smith, G. D. and Clark, R. J. H., 2004. Raman microscopy in archaeological science. *Journal of Archaeological Science*, 31 (8), 1137–1160.

Stapleton, C., Bowman, S. G. E., Craddock, P. T., La Niece, S., and Youngs, S. M., 1995. Corinthium aes and black bronze in the early medieval period. *The Antiquaries Journal*, 75, 383–390.

Sugimori, E., 2004. *Japanese patinas*. Portland, Maine, USA: Brynmorgen Press.

Wayman, M. and Craddock, P. T., 1993. Wu tong, a neglected Chinese decorative technology. In La Niece, S. and Craddock, P. T. (eds.), *Metal Plating and Patination: Cultural and Historical Developments*. Oxford, U.K.: Butterworth-Heinemann Ltd, 128–134.

Whitfield, N., 1997. “Corinthian Bronze” and the “Tara” Brooch? *Archaeology Ireland*, 11 (1), 24–28.