Colourful Corrosion: Black Bronze and its Enigmatic Patina

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Introduction

'Black bronze' is a modern term for ancient bronze artefacts that show a fine, black patina. A patina is an external, physical layer that develops on an object, either artificially or naturally, often lending the object a unique colour. The aim of my 2007-2008 research was twofold: (1) to identify the composition of the black patina for different black bronze corpora and (2) to determine whether the patina developed artificially or naturally in each case. This report will discuss my research into the Greek and Roman corpora of black bronze as well as Chinese black bronze mirrors. Besides these artefacts, I explored several other black bronze corpora including Japanese *shakudo* and Egyptian statuettes. Through an examination of black bronze artefacts and an extensive literature review, I have concluded that black patinas arose on archaeological bronze by a variety of methods. Furthermore, scholars must work from artefacts, and not from texts, to draw conclusions about black bronze.

Black Bronze in Ancient Greece and Rome

Several examples of black bronze come from ancient Greece and Rome. Luxurious, non-functional daggers excavated from Mycenaean sites often show a combination of black patina and precious metal foil on their surfaces. The black patina appears in panels with the precious metal as an inlay. The Patras dagger, decorated on its surface with dolphins made of impure gold and silver foil, has edges that are black (Photos *et al*. 1994: 267, 270). These daggers were status symbols for the owners of the tombs in which they were buried (Graziadio 1991: 406). The black backgrounds and edges enhance the brilliance of the gold and silver foil. This aesthetic effect implies the black patina is artificial. However, while scientists have analysed the black panels' substrate – a low-tin bronze with small amounts of gold and silver – they have not studied the actual black patina. Furthermore, the compositional analyses they have performed have not been comprehensive. The fact that their X-ray fluorescence (XRF) analysis could not search for elements like sulphur (see Demakopoulou *et al*. 1995) makes it uncertain whether the black patina is *niello*, a metal sulphide paste. Today, sulphur can still be a crucial component of black patinas on bronzes. The Modern Art Foundry in Queens, New York uses compounds such as ammonium sulphide and potassium sulphide to create a black patina on their bronzes. Moreover, Mycenaean metalsmiths knew how to make and use *niello*; chemical analysis has revealed the presence of *niello* on electrum vessels excavated from Mycenae and Pylos (Ogden 1993: 41).

I examined a Roman *pugio*, a small dagger, in the Princeton University Art Museum (1999-148) that dates to the 1st century AD (see Fig. 1). The dagger has gold and silver inlay, and its black patina is thought to be *niello*. However, when I observed it, I

noted two black patinas: one was a dull black that appeared to form a base for the metal inlay, while the second was a lustrous, black-silver paste that lined the inlay cavities and appeared clumpy in eroded areas. On the handle's reverse, there are two inscribed sinusoids: one contains the black-silver patina, and the other is empty except for the dull black patina as a base. Perhaps there are two methods at work: a chemical treatment to produce the black base and a mechanical application to create the black-silver paste which sits atop the base. Though the dagger is frail, chemical analysis may reveal new complexities in how it was patinated. The presence of two distinct black patinas with different appearances on this one object suggests we should not assume only one artificial process yielded the black colour(s). Furthermore, in addition to the ancient artificial treatment(s), the corrosion processes which happened over time are responsible for what we see today.

Figure 1. While the original thought is that the black patina on this dagger is *niello*, inspection suggests that multiple processes or steps may be responsible for the different layers of black patina[1].

Part of the challenge in this context is to determine how the surfaces of these bronzes appeared to their ancient makers. The surfaces may have undergone numerous changes between then and now. One of the two Riace bronze statues, both of which were made in the 5th century BC and were found in the Ionian Sea, has patches of black patina. This patina appears in areas "better protected from abrasion" (Garbassi and Mello 1984: 176) and it consists of two chemical layers: an upper layer of tin hydroxides, cassiterite (tin oxide), and copper (I) sulphide and a layer closer to the substrate made of iron and magnesium compounds (Garbassi and Mello 1984: 173, 176, 178). The patina is likely to be artificial. As Garbassi and Mello (1984: 178) note, since the

patina – which is perhaps *niello* – occurs in crevices, it was probably peeled away rather than built up while in the sea.

Black Bronze in Ancient China

There is a large corpus of black, circular mirrors from ancient China. These mirrors have one side decorated with complex geometric patterns in relief; the other side is undecorated but highly lustrous. The mirrors were clearly functional: even today, someone holding one can see his or her reflection on the lustrous side. They are made of high-tin bronze: 70 wt% copper, 25 wt% tin and 5 wt% lead (Soto *et al*. 1983: 241). Some mirrors from the Sackler Museum at Harvard University exhibit blistering on their surfaces, caused by corrosion products penetrating the surface and pushing the black patina upwards (see Fig. 2). The black patina consists of two zones: an outer layer of cassiterite (tin oxide) and an inner layer called the "altered zone" made of cassiterite and tin-rich δ-phase (a copper-tin compound) (Taube *et al*. 2008: 219).

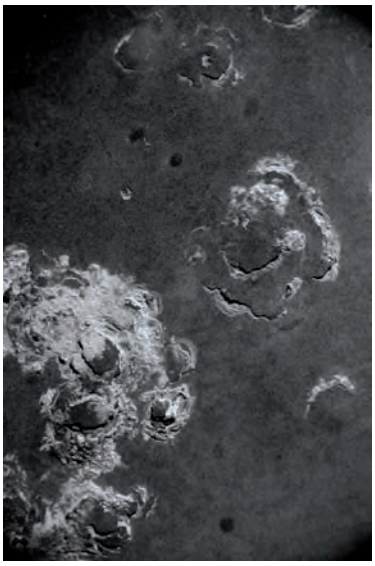

Figure 2. The surface of this mirror shows blistering corrosion, where the corrosion products push up the black patina[2].

However, without further scientific analysis, it is difficult to determine the nature of the patina. An Eastern Han mirror at the Freer Gallery (F1909.275) has a surface that has been patinated black on some parts, silver on others, with no correspondence to the surface's geometric decoration. The black patina does not seem to be aesthetic. On another Freer mirror (F1907.518), the decorated side is entirely black without blistering or blemishes, and the plain side is entirely silver and lustrous. Did the mirror's maker intend for this duality in colour, or is the layer underneath the black patina silver-coloured? In his studies of the black patina, Nigel Meeks detected "ghost…structures"

(1993: 76), the result of a reaction between the substrate and the surface layer, which preserves a map of the alloy's microstructure. This observation suggests the patina may be the product of corrosion, a case of pseudomorphic replacement. Buried in the ground, soil leaches copper from the mirrors' surfaces, the surface tin then oxidizes, a protective layer of cassiterite forms, and ultimately additional corrosion resumes (Robbiola *et al*. 1998). Mirror makers may have made some contribution to the patina – through polishing or by applying some chemical treatment that accelerated the natural patination. Perhaps the patina was artificially developed in order to mimic the black patina on tin-bronze objects buried and unearthed in antiquity, invoking the coloured corrosion for new aesthetic reasons. Besides aesthetic motivations, mirror makers may have favoured the patina for the corrosion resistance it lends the mirrors' surfaces. This attribute owes to the fact that the patina itself, predominantly cassiterite, "is the stable product of a corrosion mechanism" (Meeks 1993: 81).

Textual Black Bronze

In addition to corpora of artefactual black bronze, there are separate traditions of 'textual black bronze.' I have found, however, that scholars tend to mix artefacts and texts when the two should be kept separate. Black bronze artifacts reveal specific information about how a particular object was made. On the other hand, texts mentioning black bronze do not necessarily convey accurate information about technique. In Egypt, texts dating back to the 18th Dynasty refer to 'black copper' (*hmty km*), but there are no references to 'black bronze' (Giumlia-Mair and Quirke 1997: 102). Black copper is included alongside luxury goods like gold and silver in lists of materials used in royal projects and lists of royal dedications (Giumlia-Mair and Quirke 1997).

Is it possible to coordinate these ancient texts with actual artefacts? The scribe who wrote these lists may have been describing a material which we would not consider black or made with copper. The objects that the scribe designated as 'black copper' did not necessarily exist. In short, these texts should have little or no direct bearing on any search to learn about how black bronze was made. The same goes for other textual traditions, such as Corinthian bronze, purported luxury Greco-Roman objects having surfaces coloured gold and/or black, and *zimojin*, a 'purple sheen gold' from China. In trying to understand the technical aspects of black bronze, it is more productive to begin by studying the material artefacts available to us.

Conclusion

In each corpus of artefacts for which the black patina has been analysed, the patina consists of a natural corrosion product of tin-bronze: cassiterite, copper sulphide, or, in the case of Japanese *shakudo* and many Egyptian black bronze statuettes, cuprite. This is true even in cases when the patina was artificially made. In those cases, the ancient makers were able to manipulate the natural corrosion process to generate a desired surface appearance. There is still much to be learned about how the black patina developed on these bronzes. Nevertheless, some scholars have already attempted to draw causal connections between different production regions. Paul Craddock and Alessandra Giumlia-Mair (1993: 124) propose a diffusion of black bronze technology

from the Near East and Levant to Greece and to the Far East. The possibility remains, however, that the regions that intentionally produced black bronze developed a technique independent of other regions. A variety of black bronze techniques may have been at work in the ancient world, and these techniques may have varied within one region.

What then is the value of comparing these different corpora? Studying one corpus can suggest what to look for when studying another. For example, knowing that sulphur is a key component of black patinas for modern bronze foundries, we might analyse the black patinas of Mycenaean daggers for sulphur. Also, examining the techniques employed in these different corpora prevents us from seeing ancient technologies as monolithic. Comparisons are valuable as long as we wield them carefully.

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Notes
1. Roman
Honillius
Inlaid dagger and sheath, signed on the hilt by Honillius.
ca. 1st - 2nd century
Bronze, iron, silver, gold, *niello*
l. 29.2 cm., w. 5.5 cm., d. 1.9 cm. (11 1/2 x 2 3/16 x 3/4 in.)
Princeton University Art Museum
Museum purchase, Carl Otto von Kienbusch Jr., Memorial Collection Fund.
Photo: Bruce M. White
1999-148
(Caption information courtesy of the Princeton University Art Museum)

2. Chinese
Large mirror with foliate rim and with floral décor.
Tang dynasty, 618-907
Bronze
diam. 30.6 cm. (12 1/16 in.)
Harvard Art Museum/Arthur M. Sackler Museum
Bequest of Grenville L. Winthrop
Photo: Dr. Henry Lie
1943.52.169
(Caption information courtesy of the Harvard Art Museum)

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