

# Chinese Bronzes: Casting, Finishing, Patination, and Corrosion

W . T . C H A S E

Why is the topic of the present conditions of Chinese bronzes of interest? From a historical point of view, conservators would like to know what the bronzes looked like when they were in use. Study of historical texts has proven to be difficult and fraught with problems, even in the case of modern outdoor sculptures (Weil 1977; Weisser 1992). Research is much more difficult regarding ancient Chinese texts, where the names of the metals have changed over centuries, and the interpretation of a 2,000-year-old language presents problems. It would be best to have some confirmation and indication of possible surface appearances from technical studies.

Trying to figure out what the bronzes looked like when they were made, and attempting to draw convincing inferences from the physical evidence that remains, is a stimulating intellectual exercise. To quote from a source in English rather than one in Chinese (Bowen [1959] 1989:45; Chase 1991:36):

To re-create, even for an instant, what is laid low, dishevelled, or altogether gone into thin air is exciting. The study of anything that has disappeared is a call on faith. What is totally vanished raises peculiar questions.

Also of interest are the processes used to make and finish the bronzes, both from the view of the history of technology and from a more utilitarian perspective. Some of the bronzes are amazingly corrosion resistant, and knowing how to reproduce them would be very useful. The quality of some of the castings and their finishing is very high; casting and finishing methods used by the ancient Chinese can be adapted for modern use.

The study of corroded ancient Chinese bronzes is also of great interest to the study of long-term corrosion phenomena. Learning more about the processes of deterioration can enable conservators to control these processes in modern applications and to assess the deteriorated metal objects in museum collections. This paper focuses on the manufacture of ancient Chinese bronzes and the processes of their

deterioration and corrosion. (For a discussion of the cleaning and stabilization of Chinese bronzes, see Bassett and Chase, herein.)

## TERMINOLOGY

The Chinese bronzes of concern here are ancient vessels, weapons, and mirrors from the beginnings of bronze metallurgy in China, dating from about 1500 B.C.E. up through the Tang Dynasty. Most of these are corroded, following Gettens's (1969:171) use of the terms *patina* and *corrosion products*:

Often the collectors' interest in ancient bronzes is quickened by the colored corrosion products or patina of their surfaces. The term patina . . . was used originally to describe the green, blue and red corrosion products of copper and bronze, but by extension is now used to describe any surface on wood, ivory, or marble or other materials resulting from age and exposure. Chemists use the terms "corrosion" and "corrosion products" to describe the salts and oxides that form during burial or long atmospheric exposure, while mineralogists prefer to call them "mineral alteration products." Patina, however, is a good term even if it implies artistic enhancement by corrosion, which is not always the case. Patina . . . connotes not merely a specific color but also a continuous surface layer of measurable thickness. . . .

For convenience and because of its wide acceptance by collectors, we will often employ the term patina; but in purely technical discussions, we will speak as a chemist of corrosion and corrosion products.

In terms of the changes caused by time and their amelioration by conservators and archaeologists, one should also consider terminology from the field of conservation of paintings. Based on the work of Sheldon Keck at New York University, the concepts of original condition, present condition, and actual condition may be adduced. Original condition is a simple concept: the condition of the object when it was new. With bronzes one has a series of original conditions. It's useful to think about this in terms of particular objects. With a mirror or a black sword, there is an "as cast" condition, a finished (polished) condition, a patinated condition, and the condition after use. In fact, mirrors that were in use underwent constant repolishing (Chase and Franklin 1979:239). Bronzes in ritual use in China and Japan today are usually tarnished; even the mirrors in the temples are rarely bright, and bronze *ding* incense burners, etc., are usually less so.

The term present condition indicates what the object looks like at the present time. In some cases, bronzes are much restored or covered with compensating layers of paint. Whole sides or parts can be restored, designs can be enhanced, inscriptions can be added, and so on (Gettens 1969).

Actual condition means how much of the original is left and what its state of preservation is. The mirror from the University of Michigan discussed in this chapter is in a cleaned and repaired state with heavy surface corrosion, much of which has been removed from the decorated back to reveal design. A sample was taken from

the rim next to a crack, and the area and crack were compensated before returning the mirror to its owner. Without the restoration, however, the actual state of the mirror is corroded and cracked.

The actual condition is determined by what has happened during the corrosion process. The corrosion process is affected by a number of factors, as follows:

1. The composition of the bronze
2. Microstructure
3. Surface finish, including (a) smoothness, (b) change from structure of substrate, and (c) corrosion-resistant surface coatings
4. Environment, including (a) moisture, (b) pH, (c) access to oxygen, and (d) other corrosive ions, especially  $\text{Cl}^-$  and  $\text{PO}_4^{=}$
5. Mechanical and thermal damage
6. Events in recovery of archaeological material, including (a) change in environment and (b) physical damage
7. Later cleaning and stabilization measures
8. Present environment

## C A S T I N G

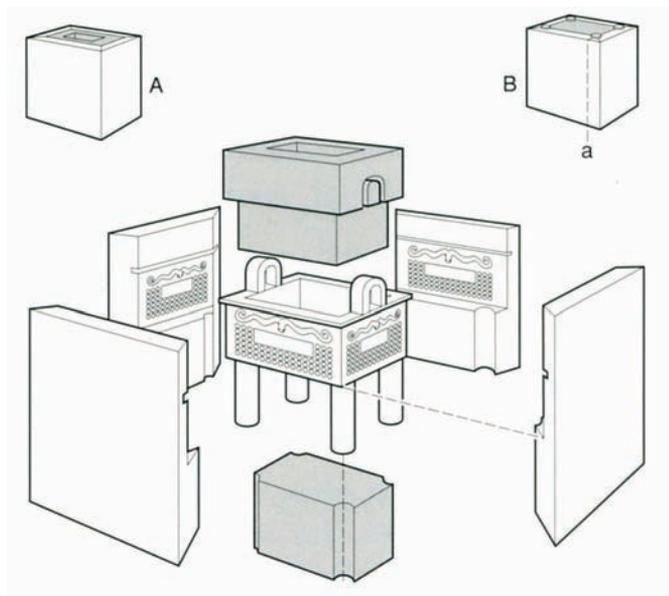
Until the Han Dynasty, Chinese bronzes were cast. There is no evidence of hammering bronze sheet at all until the appearance of a riveted bronze sheet repair in the Man-cheng tombs of about 170 B.C.E. (Barnard and Sato 1975:73). While other metals (gold, silver, and later iron) were worked by hammering, bronze was universally cast.<sup>1</sup>

### Mold Material and Construction

Usually the casting was done into ceramic piece-molds fashioned from the local earth, which in many areas was typical windblown loess or yellow earth (Gettens 1969:107–14; Freestone et al. 1969; Holmes and Harbottle 1991). Loess has a high content of small, sharp, fractured silica grains and—with some levigation or treatment to separate coarser from finer material—forms the basis for the ceramic technology to create the bronze molds. The inner side of the mold is the surface that makes contact with the molten bronze and defines the decoration and detail of the casting. The mold construction for a *fang ding* is shown in Figures 1 and 2 (Chase 1991:24–25).

Molds were made in pieces so that the inner side of the mold could be directly retouched by the foundryman. This practice, plus replication techniques that became more sophisticated as time went on, forms the basis for the striking detail and sharpness of the decoration on the bronzes. A great deal has been written about ancient Chinese casting processes. Of more interest here are the finishing and patination processes.<sup>2</sup> The fact that nearly all the bronzes were cast into ceramic piece-molds is sufficient information about their manufacture.

FIGURE 1. Diagram of mold for casting a fang ding. The four outer mold pieces surround the model; above the model is the inner core, and below the model is the inter-leg core piece. After the exterior mold pieces were made and fired, they could be used to produce the core pieces, which were then thinned down to make the casting space and lightly fired to drive out moisture. The cores and the mold pieces were then reassembled (insert A) and inverted (insert B) so that the metal could be poured in through the opening for one leg. A cross-sectional view of insert B on line a is shown in Figure 2.



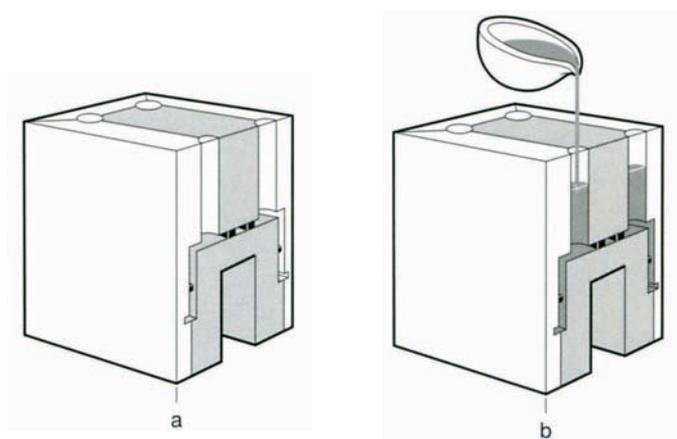
The question of mold temperature at the time of pouring is, however, of interest in the development of the microstructures. While one may suppose that the molds would have been preheated, as is common in modern practice, no evidence has been found of this in the Chinese objects studied. Sections through chaplets (the metal spacers which separate the inner core from the outer mold) usually show a chilling effect in which the molten metal impinges on the cold chaplet (Gettens 1969:132).

One modern technique very similar to that of the ancient Chinese is the Japanese *morokome* process shown in the film *The Enjo Foundry*.<sup>3</sup> Here the outer molds are decorated and fired to a high temperature. The core is then made from an impression taken from the outer mold and is lightly warmed until dry. The final assembly and placing of the chaplets is done just before casting with the molds totally cold. Professor Totsu of the Tokyo National University of Fine Arts and Music has been observed casting an iron teakettle by the *sōgata* (swept-mold) process, in which the iron chaplets were incorporated into the cold-mold assembly just before casting (Totsu, personal communication, Tokyo University, 1991). The chaplets were placed on the inner core of the mold, each on its own small pile of sand. The outer mold was put in place and some pressure exerted. Then the outer mold was removed. The sand had extruded out from under each of the chaplets, showing that each was in contact with the outer mold. Having determined that everything was fitting well, the sand was blown away and the mold reassembled and cast. The whole process of chaplet placement and checking took less than a minute; since the mold was cold, it could easily be handled.

Further discussion with Totsu (personal communication, 1991) leads to the conclusion that there are great similarities between chaplet use in ancient Chinese casting and modern Japanese art-foundry practice.

Another feature of the piece-mold casting technique, and one which is important to this discussion, is that *casting flash*, or mold flash, occurs at the joints where the molds butt up against one another. These are often called “mold marks,” but casting flash is the more precise term. The casting flash indicates where the mold joints are, but it is often finished down. Careful examination of the condition of the mold flash

FIGURE 2a, b. Casting the fang ding. The cross section of the mold assembly (a) shows how the pieces fit together. Chaplets (or spacers) are used to make sure that the casting space does not shift or close during pouring. The chaplets in the bottom of the vessel need to be larger, to counteract the upward hydrostatic pressure on the inner core when the metal is poured in. The bronze is poured in through one leg (b). The other three legs serve as air vents.



can show where finishing took place. Some mold flash is unavoidable in the piece-mold casting method, and it can be very helpful in technological detective work, as will be discussed further.

## C O M P O S I T I O N

Since the ancient Chinese do not seem to have worked or hammered cast bronzes (in fact, many of the Chinese bronze compositions are difficult or impossible to work by hammering), the only method available to them for changing the properties of the bronze was altering its composition. The *Kaogongqi* section of the *Zhou Li* (The Rites of Zhou), dating from the Zhou or Han Dynasty (ca. 400–100 B.C.E.) mentions six different compositions and their uses, ranging from 14.3% tin for vessels and bells up to 33.3% tin for mirrors. Lead is not mentioned. Every author on Chinese metallurgy has his or her interpretation of this enigmatic text (Chase 1983:108; Hua 1985:511; Chase and Chen 1992). Regardless of its exact meaning in terms of percentages, this primary Chinese source does clearly imply that the way to adjust the properties of bronzes (hardness, ability to hold an edge, reflectance) is to change the composition.

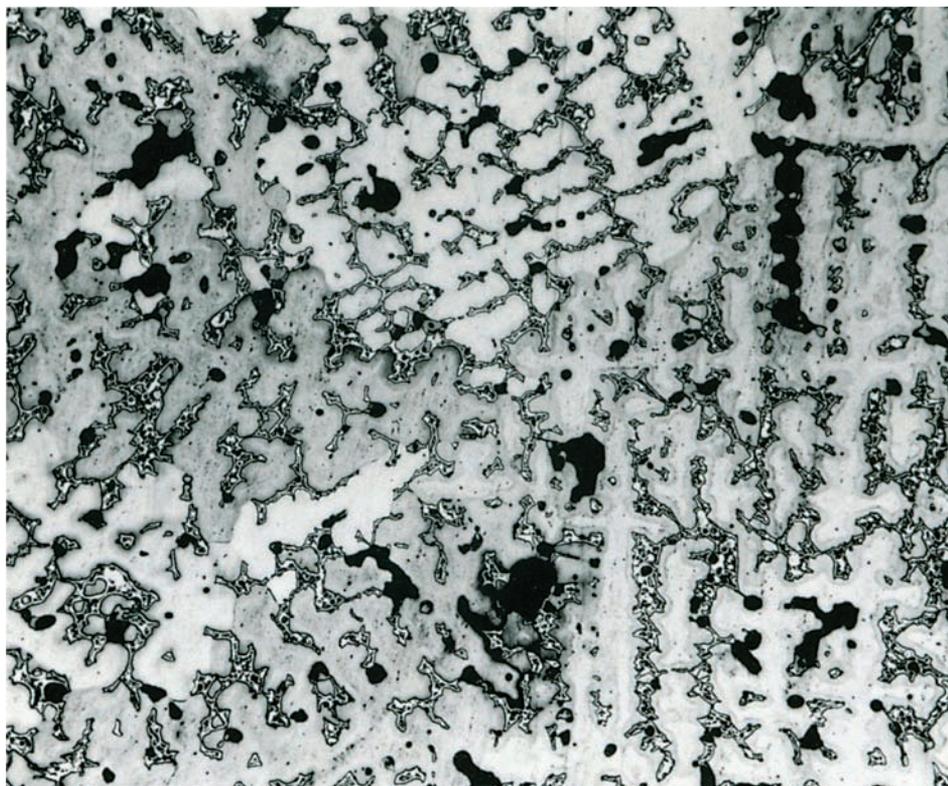
Chemical analyses of the bronzes also demonstrate clearly that this approach was used (Chase and Ziebold 1978; Chase 1983:102ff). Vessels and bells do form a distribution around 15% tin, with lead acting as a diluent. Weapons (except for “parade pieces”) are low in lead. Mirrors center around 27% tin and 5% lead. (The reasons for this will be discussed later.) Belt-hooks, a type of object not mentioned in the *Zhou Li*, were clearly made of a high-copper composition when they were intended for fire-gilding (Oddy 1985:70).

Differences in composition show up as differences in the color of the finished alloy. The relationship between color and composition will be discussed after considering the finishing.

## M E T A L L O G R A P H I C S T R U C T U R E

The usual structures of Chinese bronze vessels, bells, and many weapons (composition around 15% Sn) show columnar crystals. The chill zones are usually not apparent,

FIGURE 3. Microstructure of a typical Chinese bronze,  $\times 260$ , from a cast Chinese bronze dagger.



confirming the lack of a chilling effect of the ceramic mold. Solidification proceeds according to the phase diagram (Johnson 1973:299; Saunders and Miodownik 1990:279), but the transformations shown below 350 °C do not take place. The low-temperature reactions proceed very slowly, and the normal rate of cooling, even in ceramic molds, prevents the transformation from alpha plus delta to alpha plus epsilon (Gettens 1969:122ff; Scott 1991:25). A typical Chinese bronze structure is shown in Figure 3. The usual alpha plus alpha-delta eutectoid with delta fringe can be seen. These structures have been tested, using both the scanning electron microscope and the electron microbeam probe, and they show considerable segregation of tin, with the highest concentration of tin in the delta fringe surrounding the alpha-delta eutectoid. Larger, thicker bronzes have a more equilibrated structure, and this will be illustrated later in this chapter with micrographs of the bell from the tomb of the Marquis of Cai.

Lead does not really affect the solidification structures; since it does not go into solution in copper, it remains in globules, which can be small and well distributed in low-lead bronzes or large and irregular in highly leaded bronzes. Some of the Chinese bronzes contain more than 50% lead. These have usually been solidified rapidly (Chase 1979:96); the highly leaded alloys were used for casting objects such as coins, which could be cast thin (for rapid solidification) and which did not require good physical properties, such as high tensile strength. In lower proportions, the lead adversely affects the physical properties of the final casting (Chase 1983:105), but also makes the melt less viscous and facilitates casting. Experiments by Li Gunsheng of the Archaeometallurgy Group of the University of Science and

Technology, Beijing, show that the fluidity of the molten bronze is greatest at 13% lead. This is exactly the proportion that was used to cast many of the large and thin-walled Han Dynasty bronze drums of south China (Wu and Li 1988:17).

The as-cast surface of an ancient Chinese bronze must have looked exactly like that of a modern bronze cast into fine sand or a loess mold (I have done both and could see no difference). The metal surface is shiny with a very fine roughness, almost like a finely shot-peened surface. On mirrors (a type of bronze often cast with extremely fine detail), the high points of the surface are often finished, while the low parts are simply left in the as-cast condition. The as-cast parts have the same sort of sheen as a good aluminum paint; they look like finely divided, silvery metal. This may come not only from the nature of the mold surface but also from the ends of individual crystals. One can see a fine pattern of raised dots under high magnification.

The ancient Chinese probably used a mold dressing to make the metal flow well into the mold and reduce the surface tension of the molten metal against the mold surface. Carbon is a traditional mold dressing and can be applied by smoking the mold using a smudgy fire (such as that of a candle with a badly trimmed wick) or by applying the carbon in a finely divided state in water. Chinese ink is used at the Enjo foundry. Remains of mold dressing can often be seen as a layer of black material between the foot core and the bronze in vessels where some core has been left in place.

## F I N I S H I N G

Many Chinese bronzes now exhibit a nice, shiny surface, often composed of tin oxide. Some of the mirrors are either black or silvery in appearance, with very shiny surfaces; mirrors that have a contrast of very shiny and not-so-shiny surfaces on the back have already been considered. In all cases (except those in which the bronzes have been refinished since excavation, and are thus easily detectable), the shiny surface is clear evidence of very good surface-finishing techniques in antiquity. Corrosion will often preserve a well-finished surface, and good surface finishing may also alter or slow the progress of corrosion. Corrosion will not, however, make a nice, smooth, shiny surface where one did not exist before; it can turn a nice, shiny surface into a rough, pitted one, but not the other way around. The nice, shiny surfaces we now see are not only good examples of beautiful patinas from corrosion but also a tribute to the skill of the ancient Chinese craftsmen in finishing the bronzes.

Finishing marks can often be seen on Chinese bronzes, but those that are clearly visible are often in areas not normally seen by the user. Rougher finishing marks can be viewed on the flat or concave bottoms of *ding* vessels. The bottoms of these vessels often have large areas of casting flash where the interleg core piece butts up to the molds for the vessel sides. The flash is often roughly finished off; these areas show deep abrasive scratches. Other areas can be quite smooth and show no finishing marks, even though there must have been mold flash there initially. On a Shang Dynasty *zun* in the Freer Gallery of Art (FGA55.1; Pope et al. 1967:79; Gettens

1969:117), the mold flash must have run down between the F-shaped decoration elements. There was also some mold slippage, so in addition to the mold flash there was a difference in levels between the two sides of the vessel. Finishing had to go so far that some of the F-shaped elements were totally abraded away. On some bronzes, notably a *chi* broadaxe in the Freer collection (FGA46.5; Brown et al. 1977:214), the metallographic structure can be seen, preserved in the corrosion products, right up to the cutting edge.

In fact, a lot of Chinese bronzes look just like heavily etched metallographic specimens (Gettens 1969:126), which, along with evidence of rougher scratch marks from finishing in less-visible areas of vessels, points to abrasive finishing. This technique was done with natural stones and grits, just as we do it today with abrasive papers, working down through decreasing sizes of grit. Each successive grit removes the scratches from the previous surface, until the desired degree of finish is achieved. It is a simple technique, though labor-intensive, which was presumably no impediment to the ancient Chinese.

Abrasive finishing must have originated with the lithic industries, particularly jade. Among the late-Neolithic jades from Jiagsu, near Shanghai, hundreds of jade ornaments were found in one tomb alone; their manufacture must have required a prodigious expenditure of effort in carving and polishing. The ancient Chinese also polished agates in the Neolithic period, as recent discoveries from Hefei attest. The surface polish on the jades was important not only for obvious aesthetic reasons, but also to show off fine so-called scratched designs (Bagley 1980:73). While there is no direct evidence from the ancient Chinese as to how long jade polishing took, we do have one interesting bit of information from the premetallic culture of New Guinea, where the author (Harrer [1963]1964:128, 142ff) attests to having seen jade axes ground and finished by primitive methods. One axe took three months to sharpen.

The results of abrasive finishing are clearly shown on a *dui* (FGA32.13) from the fifth century B.C.E. This piece is said to have been unearthed at Li-yü in northern Shansi province (Lawton 1982:32; Pope 1967:528), and it shares with other Li-yü bronzes a nicely preserved surface (Chase 1991:60). The mold mark occurred halfway between the handles, and seems to have been very well finished indeed (Fig. 4a). Were it not for the dislocation in the decoration band, this feature would not be visible at all. The scratches on the body below the decoration might also be a result of abrasive finishing, although they are fairly rough. Figure 4b shows an area on the body near one handle. The shininess of the metal is clearly visible, as are the finishing scratches running vertically parallel to the side of the handle.

The inside of the *dui* is a beautiful bronze color (Fig. 4c). As Gettens says, "On the inside the bronze surface has an untarnished and satinlike finish, as it must have had when it left the hands of its maker" (Pope 1967:531). The satin finish is the result of directional scratching that runs parallel to the major axis of the vessel on the bottom and around the vessel in the area just within the rim. The visual effect is to make the vessel appear to be stepped on the inside, although it is actually quite smooth. In some areas, the fine scratches appear under the edges of the corrosion in such a way as to indicate quite strongly that the shiny surface is not the product of

FIGURE 4a-d. Four views of an Eastern Zhou (ca. 450 B.C.E.) *dui*, FGA32.13: (a) the vessel side, midway between the handles, shows the mold mark; (b) finishing marks run vertically next to the handle; (c) a color view of the interior shows the shiny yellow color of the metal as well as the effect of controlled surface scratching in the finishing; and (d) an overall view of the vessel shows the grayish color of the exterior surface.

some cleaning process. It is also of interest that the majority of the interior corrosion occurs in the bottom of the vessel, just where water from condensation would have run down. Drips and streaky corrosion, possibly from condensation, are fairly common occurrences on ancient Chinese bronzes, especially from the Li-yü and Hou-ma areas. In any case, this bronze may be a good example of what these vessels originally looked like, although the difference in color between the pewterlike outside (Fig. 4d) and the warm yellow-bronze inside gives one pause. Perhaps it was plated or pickled on the outside; this would provide an interesting subject for later study.

In terms of the evolution of finishing techniques, the earlier Shang (ca. 1100 B.C.E.) and perhaps pre-Shang (ca. 1500 B.C.E.) vessels appear to be rougher than the Zhou vessels (ca. 1000 B.C.E.), with the height of perfection being attained at the time of the late Eastern Zhou (ca. 350 B.C.E.) when color of bronze, inlay, gilding, cast iron, bronze mirrors, and other bronze objects all came into prominence (Chase and Franklin 1979:256). Production of marvelously finished, colored, or inlaid bronzes continues into the early Han period (ca. 150 B.C.E.), when reaction against such “conspicuous consumption” occurred (Gale 1931:14–15).



a



b



c



d

## APPEARANCE, COLOR, TARNISH, AND CORRODIBILITY

From the examples above, it is clear that at least some bronzes would have had the color of the finished metal alloy. In the finished (but not patinated) state, the color of the bronze depends solely upon its composition. (Heat-treated alloys do not seem to have been used in early periods in China, so the beta bronzes, heat-treated from 700 °C, do not enter into the picture, nor do other recrystallized bronzes.) The color of the finished metal was the way the ancient Chinese controlled their alloys. A short digression into color and appearance may be useful at this point and draws heavily on previous work (Johnston-Feller n.d.; Chase and Veloz 1989).

It is well known that the appearance of the metal depends on its degree of finish. Consider a flat piece of metal taken to a mirror finish, as in metallographic polishing: it will cleanly reflect an incident beam of light. The incident beam and the reflected beam will each form the same angle perpendicular to the surface. The reflected beam will not be scattered but will reflect off the surface as a perfect, clean image of the incident beam. The closer metal objects come to a perfect mirror finish, the more perfectly reflective and deeper they look.

The reflected beam does, however, change in color. The color change comes from the fact that the absorption index of the metal varies with wavelength. At the metal-air interface some wavelengths are reflected more than others. One can see that, in the case of a perfect mirror surface, there will be no diffuse reflectance. One must measure the color of the specularly reflected beam.

Most colorimeters are set up with geometries (such as 45°/0° illumination/viewing angles) and cannot include the specularly reflected beam. The work presented here was done on a Kollmorgen Color Eye, with an integrating sphere that can measure either total reflectance with specular component included (SCI), or diffuse reflectance with specular component excluded (SCE). The specular reflectance (S) can be determined by subtracting the diffuse reflectance from the total reflectance ( $S = SCI - SCE$ ). For a perfect mirror, the ratio  $SCE/S$  is zero.

The colors of ten samples of bronzes supplied by various workshops (Chase et al. at the Freer Gallery, Rob Pond in Baltimore, and Harold J. Plenderleith at the British Museum) were measured. The compositions, tristimulus values, values in Munsell notation, Sn/Cu ratio, and  $Y_{SCE}/Y_S$  are shown in Table 1 (Johnston-Feller, n.d.).  $Y_{SCE}/Y_S$  is used for the SCE/S ratio mentioned above (see note to Table 1).

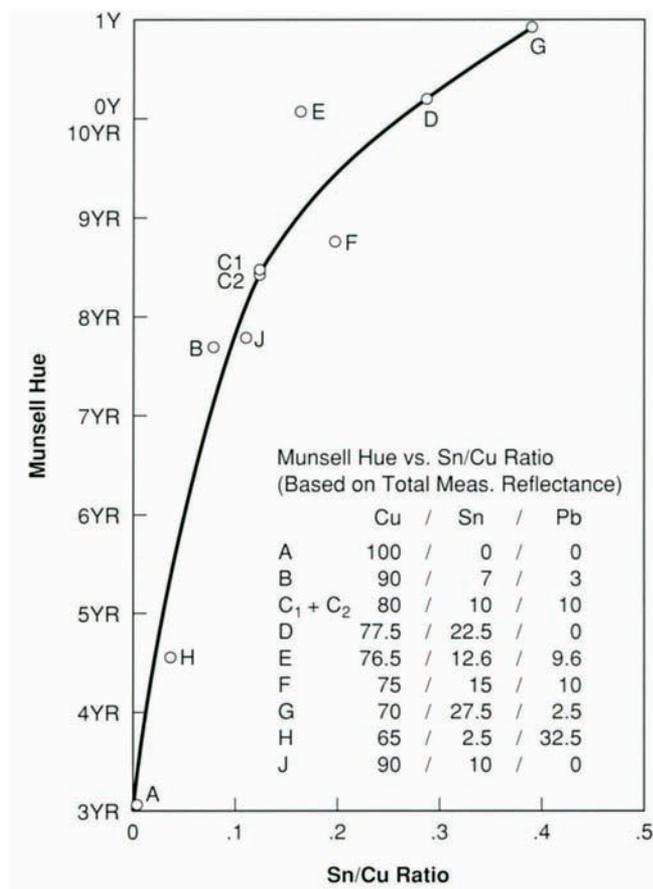
Color is directly related to tin content, as can be seen in Figure 5, where the Munsell hue is plotted against the Sn/Cu ratio. Two other studies of colorimetry of bronzes agree in the shape of the spectral-reflectance curves (Guiver et al. 1988) and in the dependence of color on the tin-copper ratio (Uchida et al. 1988), although the dependence is not so clearly demonstrated. Lead seems to have no effect on hue, as can be seen from the position of sample H, an extremely highly leaded bronze (Pb 32.5%). The lead does lower the chroma, although the relationship is not as clear. We hope to redo this work and extend it to include arsenical bronzes and brasses as well.

TABLE 1. Composition and colorimetric properties of various bronze alloys (data from Johnston-Feller n.d.).

Sample	Cu/Sn/Pb	X	Total Reflectance				Hue	Munsell Notation		
			Y	Z	x	y		Value/Chroma	Sn/Cu	$Y_{SCE}/Y_S^*$
A	100/0/0	56.96	51.57	36.85	.3918	.3547	3.01YR	7.55/5.44	.00	0.277
B	90/7/3	69.34	67.73	54.31	.3623	.3539	7.73YR	8.47/3.56	.08	0.052
C <sub>1</sub>	80/10/10	69.85	69.23	57.18	.3559	.3527	8.49YR	8.54/3.15	.13	0.064
C <sub>2</sub>	80/10/10, old	65.33	64.49	51.89	.3595	.3549	8.47YR	8.30/3.35	.13	0.125
D	77.5/22.5/0	63.15	63.58	55.86	.3458	.3482	0.19Y	8.25/2.38	.29	0.028
E	76.5/12.6/9.6	63.19	63.63	56.48	.3447	.3471	0.09Y	8.25/2.31	.17	0.094
F	75/15/10	63.35	62.89	51.22	.3570	.3544	8.79YR	8.21/3.17	.20	0.077
G	70/27.5/2.5	61.21	62.19	62.86	.3286	.3339	0.91Y	8.17/1.22	.39	0.038
H	65/2.5/32.5	66.44	63.52	53.44	.3623	.3463	4.59YR	8.24/3.64	.04	0.126
I	71/26/3	63.18	63.99	63.12	.3320	.3363	0.28Y	8.27/1.45	.37	0.126
J	90/10/0	65.33	63.88	50.58	.3633	.3552	7.82YR	8.20/3.63	.11	0.020

\*The ratio of the tristimulus value (Y) for the measurement made with the specular reflectance excluded, SCE (diffuse reflectance) relative to the specular reflectance (S), obtained by subtraction of the measurement made with the specular component excluded (SCE) from the measurement made with the specular component included (SCI). Thus,  $S = SCI - SCE$ , and the ratio indicates how near to a perfect mirror the sample appears to be; if perfectly mirrorlike, the ratio would be zero.

FIGURE 5. Colors (Munsell hues) versus Sn/Cu ratio for various polished tin bronzes (Johnston-Feller n.d.).

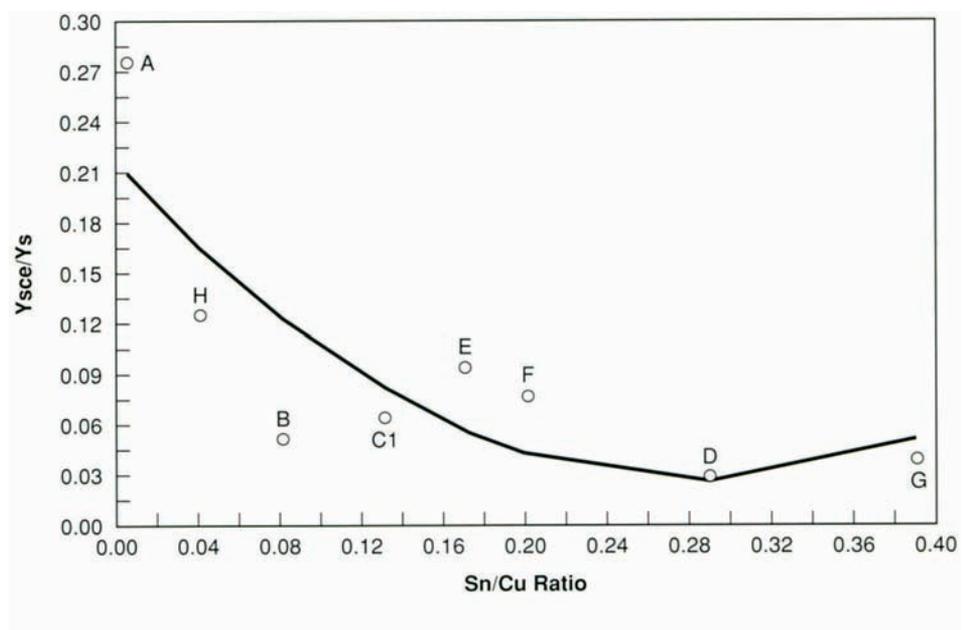


Most of these samples were polished at the same time—a week or so before the test—and then wrapped in tissue and stored in cardboard boxes for transport to Pittsburgh, where the tests were done. It is interesting to look at the plot of the  $Y_{SCE}/Y_S$  ratio against the Sn/Cu ratio (Fig. 6). While this is not a well-controlled experiment in terms of tarnishing rate, there does seem to be a relationship between the tin content and the  $Y_{SCE}/Y_S$  ratio, which can be used here as an index of the corrosion or surface tarnishing. Samples C<sub>2</sub>, J, and I were repolished just before the test in Pittsburgh and have been excluded from the plot. The data are much more scattered than one would like, but it does appear that the higher-tin bronzes tarnish less rapidly. The pure copper (sample A) tarnishes much more rapidly than any of the others; this was the only change in surface appearance on the samples which was clearly visible to the naked eye. This method can detect growth of tarnish films in a very sensitive way. It is, in fact, so sensitive that it was used as the best indicator of the stability of organic coatings on copper alloys (Copper Development Association 1974:3).

### Polarimetric Curves from Robbiola

The finding that tin bronzes are less corrodible with increasing tin content is also borne out by the pioneering polarization measurements on bronzes in aqueous conditions by Luc Robbiola (1990). In his doctoral thesis he reviews the current state of knowledge of the long-term corrosion of copper alloys, analyzes in detail the corrosion on bronzes from the French archaeological site of Fort-Herrouard, publishes some important fundamental corrosion experiments on bronze alloys, and propounds a new theory to explain archaeological corrosion (Robbiola et al. 1988). Looking first at the evidence for corrodibility, Robbiola was not able to find polarization curves for the copper-tin bronzes in the literature, so he performed the experiment, both by standard direct-current (dc) polarimetry and alternating-current (ac)

FIGURE 6. Corrodibility as shown by  $Y_{SCE}/Y_S$  index for bronzes (date from Johnston-Feller 1991).



impedance measurements. Pure copper and tin were used, along with two bronzes with two different heat treatments, as shown in Table 2.

The polarization curves are very interesting. “The bronzes show an overvoltage for oxidation with regards to pure copper: the film previously formed on the surface is more resistant to corrosion than the film of cuprous oxide on pure copper” (Robbiola 1990:160). The heat treatments, though low enough for no visible changes to have taken place in the microstructure, do make a difference on the polarization curves, with the chill-cast bronzes being more resistant to corrosion. As one would expect, the presence or absence of air (dissolved oxygen in the solution) makes a large difference in the polarization curves. The presence of chloride has a destabilizing effect, especially on the cuprous oxide film. The corrodibility of the alloys also changes, with the chill-cast samples corroding more rapidly than the reheated ones.

The most important aspect of Robbiola’s thesis is his emphasis on ion migration as the unifying theme in corrosion investigations. He states that conservators should not be concentrating on chemical reactions nor on environment, microstructure, or any of the conventional factors previously discussed, but rather on ion migration, transport, and movement. This is a very powerful concept, and it is probably correct in its emphasis.

## CUPRITE MARKER LAYERS ON COPPER OBJECTS

Many earlier studies confirm that the tarnish film in atmospheric corrosion of pure copper is  $\text{Cu}_2\text{O}$ , or cuprite. The other bronzes in the colorimetric study discussed here (in which tarnish was not detected visually) may be growing mixed or substituted copper and tin oxides. Those in Robbiola’s polarimetric study are certainly growing films other than pure  $\text{Cu}_2\text{O}$ .

The phenomenon of a marker layer of cuprite,  $\text{Cu}_2\text{O}$ , or copper (I) oxide lying at the original surface of the antique metal is well known. A particularly good demonstration in this study came from fibulas and other small bronzes that were received as surplus material from an excavation in the Near East (Gettens 1970:72; Chase 1974:52). On these objects, a nice, compact dark cuprite lies where the original surface was. These are recrystallized 11% tin bronzes, and the marker layer appears to be cuprite. The phenomenon is also seen on Classical bronzes (Born 1985a),

TABLE 2. *Bronzes used for corrodibility studies by Robbiola (1990).*

	Cu	Sn	Pb	S	Heat Treatments	
Cu7Sn	91.5%	7.0	1.0	0.5	a:CuSn7	chill-cast
					b:CuSn7	reheated 1 hour @ 490 °C
Cu14Sn	84.5	14.0	1.0	0.5	1:CuSn14	chill-cast
					2:CuSn14	reheated 1 hour @ 490 °C

Egyptian bronzes (Eichhorn 1985), bronzes from the sea (Formigli 1990; although the layers here may be copper sulfides), Chinese bronzes, and many objects of pure copper. Cuprite marker layers may be used as evidence for the authenticity of the object (Eichhorn 1988). On modern metal, the phenomenon has been much studied because of the use of copper for electrical conductors.

All the evidence here suggests that the cuprite marker layer is initially formed by the oxidation of copper in (moist) air. Studies have shown that the apparent cuprite layers are not stoichiometrically  $\text{Cu}_2\text{O}$ , but actually  $\text{Cu}_{2-x}\text{O}$ , a lattice with holes. This material is a semiconductor (McNeil and Little 1991) and can act as a membrane for transport of ions across the layer,  $\text{O}^-$  and  $\text{Cl}^-$  inward and  $\text{Cu}^+$  (or  $\text{Cu}^{++?}$ ) outward. While the evidence is not yet complete for the transport of  $\text{Cl}^-$  inward across the cuprite layer, one may well find that this is a convincing explanation for some of the phenomena observed, especially in bronzes with very even layers of cuprous chloride.

One should, however, look a little further to explain the transport of  $\text{Cl}^-$  ions deeply into the bronze substrate. This recalls the idea propounded by Smith (1975, 1959) concerning the transport of chloride being driven by differences in the interface-energy balance: If the  $\text{Cl}^-$  bearing material has a lower interfacial energy than that of cuprite or the metal, it can drive itself inward between the two just as a liquid metal (such as mercury or molten tin) will drive itself between the grains of cast aluminum, rendering the cast aluminum totally brittle in a very short time. This is consistent with the ideas of MacLeod (1981; see also Scott 1990).

It is important to carefully consider the formation of the cuprite layer. In many cases the layer is formed by initial tarnishing and may have even formed while the object was actively in use. It also forms in underground burial chambers, especially where the tomb has not caved in and the vessel has been sitting in moist air. In atmospheres containing sulfides (at about 100 ppm or above) the cuprite layer will not form. Discussions with Joe Payer (personal communication, Case Western Reserve University, Cleveland, 1991) indicate that if one puts an object with a cuprite layer into these atmospheres, the cuprite layer will be disrupted and eventually destroyed.

The model of corrosion that is proposed for pure coppers is as follows: first, the formation of a marker layer of cuprite on the surface of the copper; second, ionic transport through this membrane, with anions migrating inward and cations outward. The membrane remains intact in the absence of disrupting agencies (mechanical damage, sulfides, etc.) and serves to delineate the original surface of the object.

The question of intentional patination versus natural corrosion should also be raised here. Cuprite patinas are used (though rarely) on artistic objects. Two particular examples come to mind: a nineteenth-century Turkish water jug in the British Museum with a bright-red (almost cherry-red) patina, and the bronze maquettes in the Gorham Foundry in Providence, Rhode Island, which were finished around the turn of the century.<sup>4</sup> Formulas for reddish (probably cuprite) patinas are given in Hughes and Rowe (1983). Cuprite patina has also been used in the protection of an outdoor statue in Poland (Socha et al. 1988). If the cuprite patina is formed by chemical or electrochemical techniques, it may not be distinguishable from a natural corrosion product. The question of intentional patination versus corrosion by natural

agencies is a recurrent one; this can be a difficult problem and must be dealt with on a case-by-case basis.

## M A R K E R L A Y E R S O N O T H E R B R O N Z E S

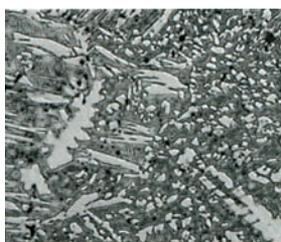
The cuprite marker layer will probably form more easily (and thickly) on the higher-copper alloys in normal indoor atmospheres. In regard to the bronzes and leaded bronzes, one may logically assume that the single-phase structures (up to about 6% Sn) will exhibit the  $\text{Cu}_2\text{O}$  uniform marker-layer growth. Above this, where duplex structures are present, the films could be less coherent and probably consist of patches of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O-SnO}_2$ -mixed oxide over the alpha and delta areas, respectively. This may be a less corrosion-resistant structure. In looking at cross-sections of bronzes with both a duplex structure and a marker layer, however, one does not see any evidence of differences in the marker-layer formation over the alpha and delta phases where they lie on the surface of the object.

The experiments of Robbiola on polarimetry also show that coherent and corrosion-resisting films *are* forming on the higher tin alloys. Since these oxides are difficult to analyze by X-ray diffraction, and since they form very thin films, one does not yet have the quantitative data to predict the behavior of the films or even to see what their composition is. Perhaps a combination of X-ray fluorescence, Moessbauer spectrography, and colorimetry combined with electron optical techniques will provide the tools necessary for understanding these films. Serious questions exist about what is happening on the surfaces of these alloys and whether the oxide formation has components of sideways migration; one should not forget the migration of sulfide corrosion products across the surfaces of objects and even through holes in other materials.

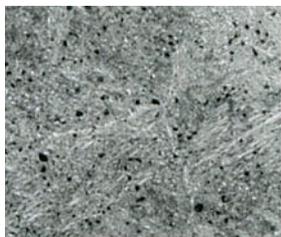
When examining the 22% Sn hot-forged and quenched bronzes, or even the Japanese *sahari*, one finds that these are more corrosion resistant. Increased corrosion resistance may be coming from the structure of these alloys, which are mostly composed of fine needles of beta or beta prime (Goodway and Conklin 1987:8, 9; Scott 1991:95, 98); it is possible that a surface-oxide film of mixed oxides forms. This film is much more corrosion resistant than a film formed on the bronzes containing less tin.

This finding raises the concept of equipotentialization of the surface, meaning that corrosion is driven by differences on the surface that can be reflected in potential (voltage) differences when the object is immersed in an electrolyte (Gettens 1969:182). If one can equipotentialize a surface—for instance, by putting a perfect tin plating on it—the corrosion will have no differences in potential to attack, and the corrosion will slow or stop. This is also the concept of passivation of the surface by oxide films as discussed by Pourbaix (1966, 1973), and works for high-quality paint and lacquers as well. One now-classic method of equipotentialization is to make amorphous or glassy metals; in this technique the corrosion rate drops off dramatically.

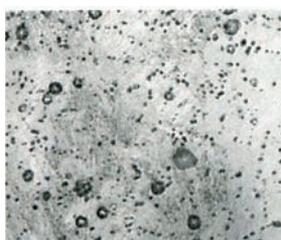
In the case of the hot-forged and quenched high-tin bronzes, it seems that, in going from an alpha plus alpha-delta eutectoid structure to the beta needles, one is



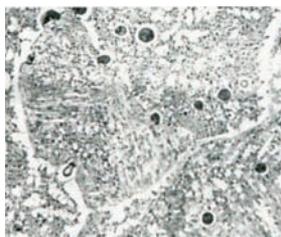
a



b



c



d

FIGURE 7a–d. Microstructures of sand-cast bronzes with 22–26% Sn. All contain 3% lead, and all of the metallographs were taken in bright field at a magnification of  $\times 320$  after etching the sample with potassium dichromate. (Magnifications above are  $\times 112$ .) Note remains of grain boundaries, particularly in c and d.

taking a step toward equipotentialization; the corrosion rate dramatically slows. These alloys seem to form a natural, black-tin-oxide surface film that passivates the surface and inhibits further tarnish. It has been proposed that these surface films were put on intentionally, and some of them may have been. Others appear to have corroded naturally. A covered Korean high-tin bowl in the collection of the Honolulu Academy of Arts has the typical black appearance that could have been intentionally applied; there is, however, a rather distracting slanted line where the cover meets the bottom. This is probably evidence of corrosion during burial rather than artificial corrosion (intentional patination).

Turning to examples of alloys with an even higher tin content, the Chinese mirrors contain around 26% Sn and variable amounts of lead (about 1% to 6%). Twenty-six percent of tin is only 1.6% above the eutectoid transformation (24.6% Sn, 586 °C) where beta decomposes into alpha; it is also only 1% below the eutectoid transformation (27.0% Sn, 520 °C) where gamma decomposes into alpha and delta (Saunders and Miodownik 1990). The microstructure is extremely sensitive to small differences in the tin content, as can be seen in Figure 7. The same types of structures were seen by Mooradian and Gettens (1936) in the 1930s and called by the prevailing terminology *hypo-eutectoid*, *eutectoid*, and *hyper-eutectoid* structures (Chase and Franklin 1979:216ff3). The eutectoid can be extremely finely divided, with a composition of 26% Sn (from SEM and EPMA determinations). The tin differences may be beyond the sensitivity of many chemical techniques of analysis, but they are clearly visible in the microstructures shown in Figure 7a–d, as follows:

- (a) 75% Cu, 22% Sn, 3% Pb; structure alpha + alpha/delta eutectoid. The alpha is large and light grey. Remains of a dendritic structure can be seen.
- (b) 73% Cu, 24% Sn, 3% Pb; structure alpha/delta eutectoid + alpha. The alpha is much smaller and appears to have formed as a result of the eutectic phase transformation. Grain boundaries are partially outlined by alpha.
- (c) 72% Cu, 25% Sn, 3% Pb; structure alpha/delta eutectoid. The structure of the individual alpha and delta is so fine that it is difficult to resolve in the optical microscope. Lead (the dark dots) appears to be more prominent in this section.
- (d) 71% Cu, 26% Sn, 3% Pb; structure delta + alpha/delta eutectoid. Delta can be seen at the edges of the old grain boundaries, as small dendrites forming around the lead globules, and within the eutectoid.

Remains of the grain boundaries from initial solidification can be seen on all four metallographs, most clearly on Figure 7d where the original grains are now delineated with a line of the white delta phase. At this magnification, three or four grains appear in the field, with five showing up in Figure 7c.

One wonders if the presence of the finely divided eutectoid contributes to the corrosion resistance of the Chinese mirrors. Work has been proceeding on the corrosion phenomena on these alloys, and a particularly stable form of the mixed oxide

( $\text{Sn}_{1-x}\text{Cu}_x\text{O}_2$ , where  $x =$  about 0.16) has been found to exist on some ancient Chinese mirrors (Wu et al., in press). In other words, these alloys are corrosion-resistant because of the formation under normal atmospheric conditions of a particularly stable form of the mixed oxide on the surface. It is possible, although not yet proven, that a similar stable oxide film could be produced by intentional patination techniques. Experiments are proceeding. One should note that these experiments *must* be done on the correct alloys. Even a few percentages of difference in tin will drastically alter the behavior of the alloy.

If one moves on to even higher tin alloys, speculum metal (32.5% Sn) is essentially pure delta and is also quite corrosion resistant, probably also due to formation of a stable oxide film.

## I O N M I G R A T I O N : A U N I F Y I N G T H E M E

At least some information now exists on the behavior of cuprite films in terms of ion migration, and one can, for the moment, postulate that there will be movement of cathodic ions outward and anodic ions (oxygen and chloride) inward. However, one cannot conclusively say much about the tin-oxide films and even less about the mixed-oxide films, which may be more common on bronzes than previously suspected. For the purposes of this paper, it seems reasonable to assert that ion migration through tin-oxide films will be much slower and less prevalent than through cuprite films.

Robbiola (1990) places a great deal of stress on considering ion migration as the unifying theme with which to examine corrosion processes. To state his qualitative model simply, he believes that corrosion starts by formation of a layer of tin oxide on the higher-tin bronzes, followed by corrosion controlled by either of two processes:

1. In cationic control, the cations diffusing to the surface control the rate of the process, which is generally slow and leads toward compact corrosion layers maintaining the object's shape. Thicker layers, especially of copper II compounds, may form on the outside.
2. Under anionic control, the process proceeds with more change of volume at the corrosion interface; thicker, less coherent corrosion layers may be the result, with the loss of the original shape. Chloride plays an important role in many instances of the second process.

The idea of concentrating attention on ion migration is a powerful one and may help to explain some phenomena hitherto not understood. To be fully applicable to Chinese bronzes, however, this approach also needs to be coupled with some understanding of the initial corrosion films.

One phenomenon seen fairly often on Chinese bronzes is the formation of fibrous malachite, as shown on a Shang Dynasty *gu* in the Freer Study Collection (Fig. 8). This looks just like a cuprite plus malachite analog of electrolytically deposited copper, the same long needlelike morphology that occurs when making

copper electrotypes. The  $\text{Cu}^+$  ions migrate outward through the superficial cuprite film and are further oxidized to  $\text{Cu}^{++}$  when they get closer to the air, continuing to travel in a direction generally normal to the original surface. This may explain the formation of fibrous malachite as being similar in terms of ion transport to electrodeposition. In this case, though, the ions are moving outward from the surface and not inward toward it.

The second phenomenon—which needs a much more comprehensive look—is that of the corrosion of outdoor bronzes. The lack of cuprite layers due to the destruction of the cuprite by sulfides coupled with ion migration by dissolution of the copper in rainwater is illustrated by the condition of a bell erected outside of Washington’s Union Station in 1981. The bell has a definitely silvery sheen. When observed in detail (Fig. 9), it is apparent that after ten years of outdoor exposure, the high-copper centers of the alpha dendrites are dissolving away and the products are being removed by the rain, leaving a finely etched crystalline surface. Other outdoor sculptures, in statuary bronze rather than in bell metal, sometimes show crystalline structures in their corroded surfaces, especially on the flatter planes where rainwash is not so rapid. The more rapidly flowing solutions tend to wash away a greater proportion of the corrosion products and promote a more general attack. It may be useful to go back and examine some models of corrosion of outdoor sculptures with ion migration (and solubility effects) in mind.

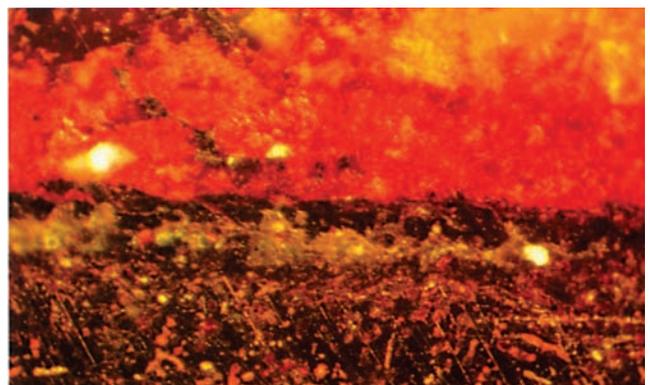
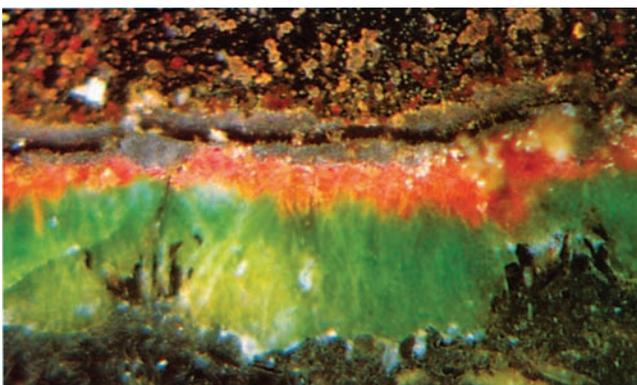
FIGURE 8. *Fibrous malachite on the surface of a Shang Dynasty gu, below left, dark field,  $\times 132$ .*

FIGURE 9. *Surface of a bronze bell, below right, Washington, D.C., Union Station Plaza, after outdoor exposure for ten years. The high-copper centers of the alpha dendrites are being etched away, leaving the high-tin phase behind.*

#### Chinese Bronze Corrosion: Type I

The normal type of corrosion seen on Chinese bronzes, or at least what we think of as normal, is the removal of the tin-rich phase to form tin oxide or mixed tin-oxide and cuprite corrosion products on the surface (sometimes with malachite or azurite being formed as well<sup>5</sup>), leaving behind the alpha phase of the alloy as the last to corrode. This sort of corrosion is well documented in Gettens (1969:171ff). It has been seen on many Chinese bronzes, including those from the original Anyang excavations (Carpenter 1933).

This sort of corrosion can be associated with a cuprite marker layer, although it would be desirable to go back and examine more samples before becoming dogmatic on this point. This corrosion type is often associated with chlorides. The question of amounts of chlorides in the burial environment versus the types of corrosion seen



on the objects has not yet been satisfactorily resolved. However, from the examination of samples from the tomb of the marquis of Cai (Fan et al. 1991), along with others from both China and Japan, one concurs with the ideas of MacLeod (1981) that the electrochemistry will drive the  $\text{Cl}^-$  ions deeply into the bronze. Even a small amount of  $\text{Cl}^-$  in the burial environment will evince itself in  $\text{Cl}^-$  ions at the corroding front, deep within the intergranular corrosion cracks in the bronze. Here is an example of Robbiola's "anionic control," and these bronzes normally do not have beautiful tin-oxide patinas. One also wonders if these were patinated in antiquity, or if this sort of corrosion only occurs on bronzes that were simply naked bronze when they were buried.

## Chinese Bronze Corrosion: Type II

The other sort of corrosion, often seen on later bronzes and mirrors, can be detected visually by a nice, smooth, so-called water patina of tin oxide. In cross section, one can see that the alpha phase of the alloy has dissolved and the delta remains in an uncorroded state. Type II corrosion corresponds to Robbiola's "cationic control" type of corrosion and can lead to very beautiful and stable bronzes. In some cases, at least, one suspects that these bronzes have been intentionally patinated in antiquity. This is certainly the case with the two-colored mirrors, where the color differences do not manifest themselves in a difference in surface level, but rather in a difference in the color of the surface itself. They are still a mystery (Chase and Franklin 1979:238; Chase 1991:75).

This sort of corrosion is believed to start with a layer of intentional patination, because subsequent corrosion (on cracks or pits) often proceeds as Type I corrosion, with the alpha remaining behind (Chase and Franklin 1979:248ff). One hypothesis is that the bronzes were put into the burial environment with some sort of protective patina layer, which determined the progress of corrosion. Later, when the bronzes broke or cracked due to soil pressure or movement and fresh surfaces were exposed, corrosion took place by more normal means. This hypothesis is strengthened by the fact that the heavier corrosion of Type I often occurs at sharp edges or changes in direction of the surface; corrosion often appears like that on chromed white-metal automotive trim parts, where edges are usually the first to go.

With these ideas in mind, the following case histories will examine some cross-sectional samples from Chinese bronzes to see if more sense can be made of their corrosion structures than heretofore.

## CASE HISTORIES

### Corroded Chinese Bronzes

#### BELL FROM THE TOMB OF THE MARQUIS OF CAI

The first example is an excavated Chinese bronze bell from the tomb of the Marquis of Cai, who was buried about 450 B.C.E. in the region of modern Shou Xian, near the Huai River in Anhui province (Institute of Archaeology 1956). The corroding

conditions are rather extreme and the burial environment damp; from the evidence of bronze disease, chlorides are elevated, although there are no soil measurements to back this up. Another sample from the same object has already been examined and published in some detail (Wang et al. 1990; Fan et al. 1991) but without extensive optical microscopy.

The bronze is extremely corroded. Even though it is almost a half-inch thick, it can be broken easily. A cross section reveals deep corrosion (Fig. 10). This sample has more transgranular cracking than is normally seen in Chinese bronzes. The microstructure is that of a moderately high-tin bronze, without the coring and segregation in the delta phase (delta fringe) normally seen in sections from Chinese bronzes. Perhaps, due to its size and great thickness, this object naturally solidified more slowly and the metal was able to form a structure closer to equilibrium. A number of corrosion features can be seen—notably redeposited copper—and both alpha- and delta-removal corrosion (Types I and II) are present (Figs. 11, 12).

Intentional patination might explain the Type II corrosion and a cuprite marker layer might indicate the original surface of the object. All four of the bell's available sections (two each, from two fragments) were carefully inspected for these marker layers. Areas that look like original surface were found, but instead of resembling red cuprite, they were composed of two layers, one red and one black (Figs. 12, 13). No analysis of these layers has yet been performed with electron optical techniques; it would not be surprising to find that they are copper oxide and copper sulfide. The layers are badly broken up by subsequent corrosion, and it appears that the protective nature of the surface layers did not last too long, possibly because of the aggressive nature of the burial environment.<sup>6</sup>

Incidentally, black preservative layers were found not only on the bells but also on other bronzes from the tomb of the Marquis of Yi; the bronzes are now in the Museum in Wuhan. The surface layers were evidently reported as being sulfides. With this section of a contemporary piece tending to confirm black layers on Chu bronzes, it would be desirable to go back and open the question of marker layers again. A large amount of redeposited copper is also seen on the section from the Cai

FIGURE 10. *Sample from a bell from the Tomb of the Marquis of Cai, below left. Overall view, bright field,  $\times 4.8$ , showing deep penetration of corrosion on outside and intergranular cracking running right through the section.*

FIGURE 11. *Same sample as Figure 10, below right, bright field,  $\times 82$ , showing Type II corrosion at the upper left and Type I corrosion along the deep crack. The outer surface of the sample is upward.*

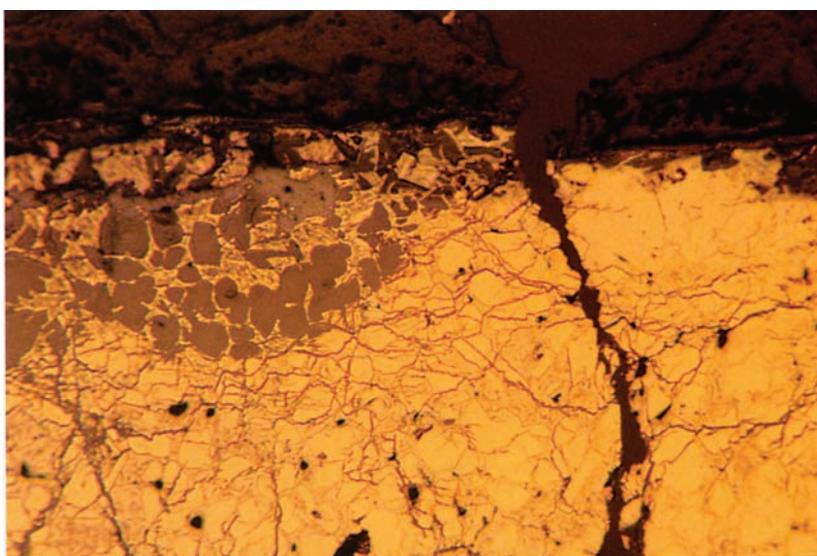


FIGURE 12. Same sample as Figure 10, bright field,  $\times 88$ , near right, showing Type II corrosion under a two-part marker layer.

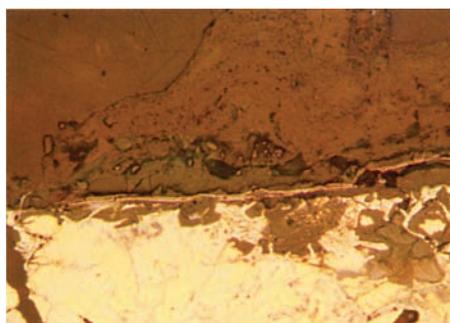


FIGURE 13. Same sample as Figure 10, dark field,  $\times 88$ , far right, showing the marker layer to be red on the top (outside) and black on the bottom.

Hou bell. Redeposited copper will be considered below in the discussion of the Michigan mirror.

#### A WESTERN ZHOU GUI

The existence of what appeared to be a cuprite marker layer was discovered on a Western Zhou gui (FGA24.11) in the Freer Gallery of Art. A sample from the handle shows brazing metal, the metallography of which was well examined by Gettens (1969:135, 181). The Freer Technical Laboratory was interested in reexamining the sample to see if such a marker layer was indeed present. A black layer is clearly evident at the level of the original metal (Figs. 14, 15). The layer has only been identified visually thus far, and one cannot even guess as to whether it is oxide or sulfide. The appearance of the vessel where it has been cleaned, though, argues that it is a cuprite marker layer.

#### MIRROR FROM THE UNIVERSITY OF MICHIGAN

This typical Sui Dynasty (ca. 600 C.E.) zodiacal animals mirror was so corroded that it was difficult to read the design (Fig. 16). The mirror was also cracked at the rim, and it was agreed with the University of Michigan that the Freer's conservators would clean the mirror if they could take a sample from the rim. After sampling, cleaning was done mechanically using fine-steel chisels, a Vibrotool with a sharp needle, and various brushes, including a small glass-bristle brush. The cleaning markedly improved the readability of the design (Fig. 17).

Although the cleaning was completed about ten years ago, the sample was not examined metallographically until recently. The sample, taken from the thick rim, reveals that the mirror is heavily corroded, with somewhat less corrosion on the reflective face (Fig. 18a, b). The metallographic structure is typical of Chinese mirrors, an as-cast structure of high-tin bronze, probably about 24% tin with some lead.

FIGURE 14. Cross-sectional sample, below left, from a Western Zhou gui, FGA24.11, showing dark marker layer on outside (upper surface), dark field,  $\times 3.7$ . The marker layer runs straight along the original surface under the overlying thick corrosion products. Area indicated by small rectangle is shown in Figure 15.

FIGURE 15. Detail, far right, of Figure 14, showing the dark marker layer under an overburden of red cuprite; dark field (Leitz Ultrapak Objective),  $\times 62$ . Area of magnification is indicated in Figure 14.

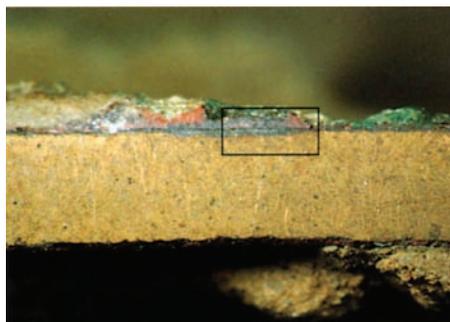


FIGURE 16. Sui Dynasty Chinese zodiacal mirror from the University of Michigan, showing the decorated back before cleaning.



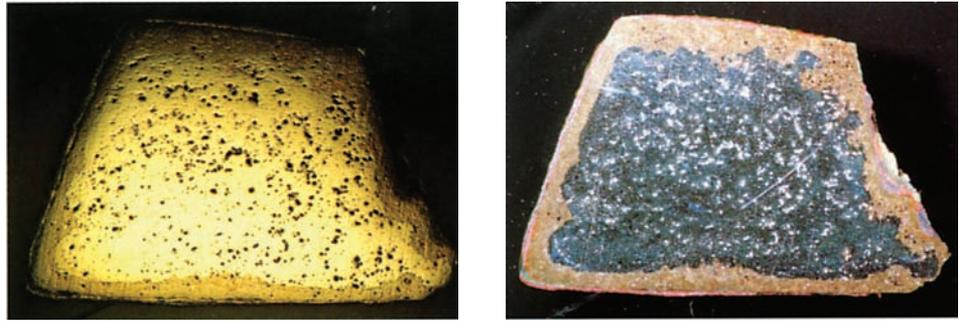
FIGURE 17. Sui Dynasty mirror, shown after mechanical cleaning. The design can be read much more clearly.



Surface layers can be seen to be preserving the original shape of the piece, with a totally corroded area and an interpenetration zone between the metal and the original surface (Fig. 19a, b). Much of the corrosion appears to be tin oxide, although a cuprite marker layer is seen at some spots on the surface.

The other notable factor on the cross section is the great proportion of redeposited copper in the corrosion zone (Fig. 20). Redeposited copper is present in holes left by corroding lead, throughout the structure as stringers, and also on the surface as a discontinuous surface layer lying at or near the original surface of the metal; in all cases, it is probably replacing earlier corrosion products of cuprite. Undisturbed inclusions of sulfides can be seen throughout the metal, the interpenetration zone, and even in contact with the original surface (Fig. 21). These, plus the ghost structures in the corroded zone, lead to the conclusion that there has not been

FIGURE 18a, b. Cross section from the rim of the mirror (a) near right, in bright field,  $\times 4.8$ ; (b) far right, dark field,  $\times 4.8$ . The thinner part of the mirror continues toward the right. The deep but fairly even penetration of corrosion can be seen, along with good delineation of the original surface.



much (or any) dimensional change during corrosion. This mirror is, however, much more heavily corroded than the usual Chinese mirror in the Freer collections.

The presence of the large amount of redeposited copper in this mirror and in the bell from the tomb of the Marquis of Cai suggests a new explanation of the phenomenon. Earlier explanations of “a localized electrolytic process” (Gettens 1969:130), copper prills left over from casting (Barnard and Kennon 1986), and rapid change in the burial environment (Wan 1989) all seem rather unconvincing in light of the prevalence of the phenomenon and its occurrence throughout the sections where it is observed. One possibility may be that this mirror had only a light surface tarnishing when it was buried. Corrosion layers (perhaps oxides or other compounds) would have built up on the surface, and intergranular corrosion would have taken place as well. While there is little evidence of bronze disease on the surface, the underlying layers may contain some chloride. As was previously mentioned, MacLeod thinks that any  $\text{Cl}^-$  in the burial environment will be forced down toward the corrosion front by electrochemical forces.

Thus, there are two ongoing phenomena: increased  $\text{Cl}^-$ , which lowers the pH in the corrosion zone, and the build up of overlayers of corrosion products, which makes it more difficult for oxygen to penetrate. The oxygen in the underlayers also

FIGURE 19a, b. The mirror section at a magnification of  $\times 70$  in (a) near right, bright field; and (b) far right, dark field, shows a corrosion overburden outside the original surface of cuprite, the original surface, heavy corrosion just within the original surface, an interpenetration zone with redeposited copper (mostly round structures), and remnant alpha phase from the original bronze (linear structures). A little uncorroded metal shows at the upper right.

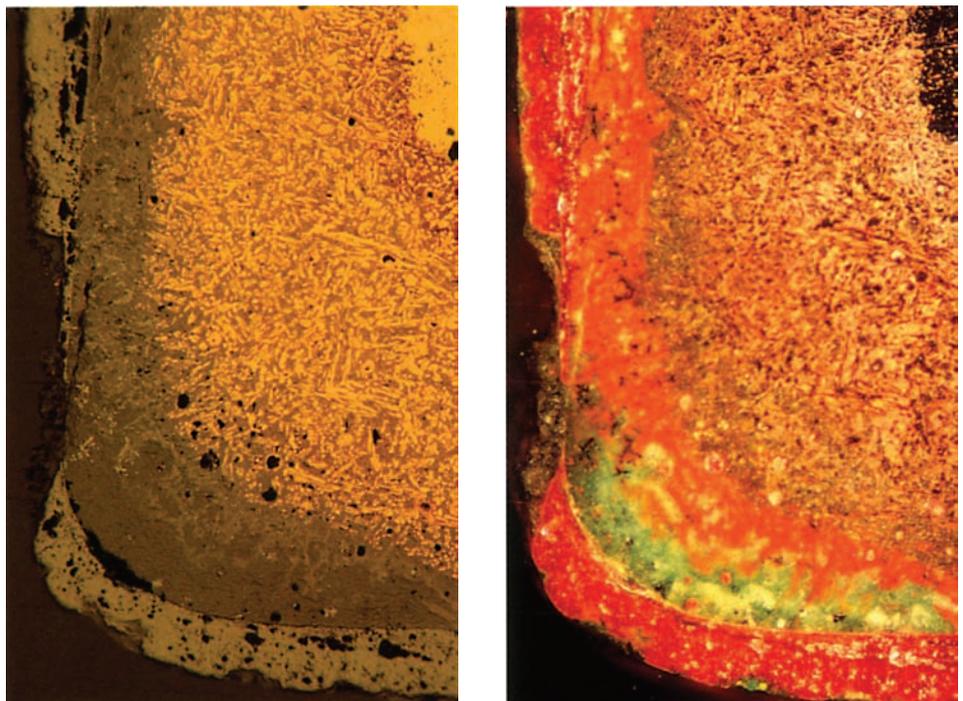


FIGURE 20. Another area of the mirror, near right, bright field,  $\times 65$ , shows large amounts of redeposited copper, both as round structures where redeposited copper is replacing cuprite formed in place of lead globules, and a linear area at the upper left, where redeposited copper is replacing cuprite in the outer layers of corrosion.

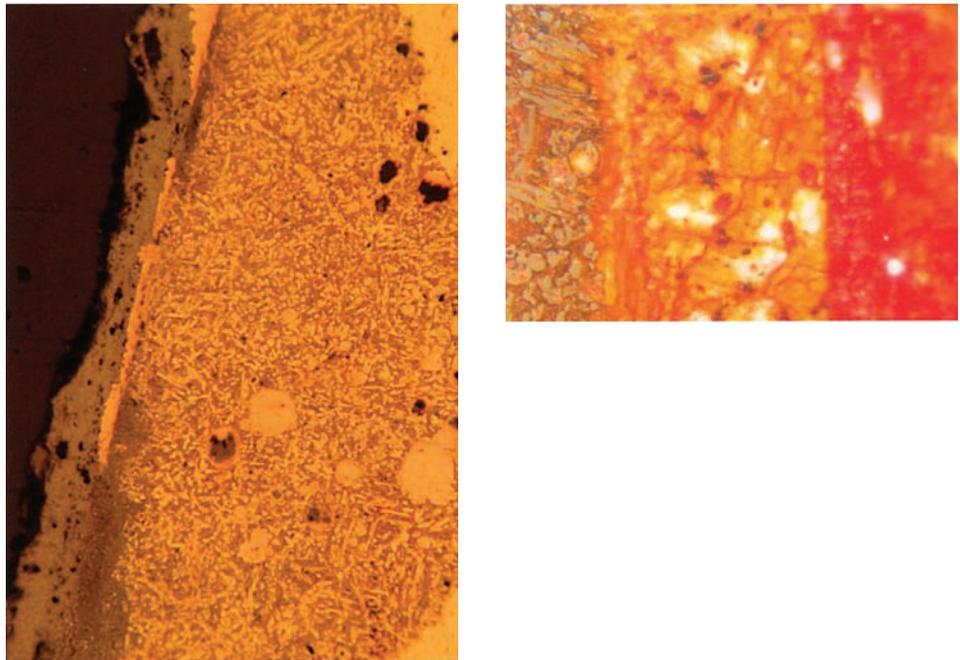


FIGURE 21. The mirror section in dark field illumination, above right, at a magnification of  $\times 223$ . The interpenetration zone is seen at left, the totally corroded zone at center, the sharp demarcation of the original surface at the center right, and cuprite overburden at the far right. Dendritic black-sulfide crystals can be seen in the first two zones, right up to the original surface.

tends to be used up by oxidation processes, which take place on the surface of the sound metal, well within the corrosion zone. The layers away from the metal-corrosion interface could be depleted in oxygen.

If one looks at an Eh-pH diagram for copper in the presence of carbonate, chloride, and sulfur, one sees that at a pH of 7 and oxidation potential of 0.1 V, cuprite is the stable phase (Pourbaix 1973:267; Brookins 1988). If the pH or the oxidation potential drop, the locus moves into a region where copper metal is the stable phase. Taking into account the possible slowness of the growth of the external corrosion layers and the probable gradual intrusion of  $\text{Cl}^-$ , these processes may be very prolonged. The low rate could explain the nice, uniform transformations of cuprite to copper and also the common phenomenon in which the cuprite in the external part of one of the spheres has transformed to redeposited copper while the internal part remains as cuprite. The hypothesis is that the corrosion sequence is metal to cuprite to redeposited copper, the second step taking place gradually as a response to slowly changing oxidation and pH conditions within the corrosion layers, particularly to the reduction in available oxygen as the corrosion layers grow thicker over time.

It would have been worth the trouble to mount, polish, and observe this section before doing the mechanical cleaning; some areas may yield well to mechanical cleaning, but others, where the redeposited copper appears on the surface and is rooted in the inside, are impossible to clean mechanically. The piece may end up with a layer of redeposited copper showing, or with a breakthrough to the weaker, heavily corroded layer that underlies the redeposited copper. Mechanical cleaning should proceed slowly here, and one should not try to force a good outcome in areas that do not seem to clean well; in such areas it would be best to leave well enough alone. While the mirror looks quite good in its cleaned state, a look at the cross section would have indicated the inadvisability of proceeding so far in some spots and might have yielded a better result.

## Intentionally Patinated Objects

Sections of intentionally patinated objects are difficult to find. The ones studied most by the author derive from the Freer study collection (Chase and Franklin 1979:245; Brown et al. 1977:197–207). These objects share the characteristics mentioned above: a well-preserved oxide surface on the outside, usually with Type II corrosion underneath; chloridic corrosion in areas of cracks or abrasions, or on the inside of the closed objects, with Type I corrosion proceeding in these areas; and a shiny and/or decorated surface.

At this point, there is no coherent explanation of the technique used to make intentionally patinated objects; an entire group of techniques may have been used. The possibility that pickling was used to promote Type II corrosion (easily done with ammonia) and that the tin-oxide layer was subsequently applied by a heating process or some other process is the best explanation at the moment. Further study of the question is planned. A more definitive explanation of corrosion phenomena and tarnishing phenomena above will greatly aid in this study.

Nevertheless, the question remains whether intentional patinas may have been even more prevalent on Chinese bronzes than was previously thought (Ma and Han 1988; Meeks 1986, 1988). These layers are subtle and easily lost in cleaning, and usually need to be seen on the actual object before they can be perceived to be legitimate subjects of inquiry. The difference in color on the Li-yü vessel mentioned above is a good case in point. The vessel has not yet been examined to see if there is an actual material difference between the inside and the outside. The bronzes from the tomb of Lady Meng Ji in Baoxiangsi in Henan province (Thorp 1988:52–55), which all have a peculiar, shiny, purplish-brown patina, are among many other objects that could use close investigation.

Seeing the red and black layers in the cross section from the bell from the tomb of the Marquis of Cai, coupled with the bronzes in the tomb of the Marquis of Yi, many of which are black, raises the question of whether blackened bronzes were more common than heretofore believed.

Finally, one may consider the bronzes from the tombs of Liu Sheng and Dou Wan (the tombs of the jade body suits with gold-wire attachments), Han Dynasty (ca. 175 B.C.E.), from Man-cheng, just to the northwest of Beijing. The tombs were cut into the mountain rock, and cast iron was poured in to seal them. The chambers were never filled in with earth, so these are examples of ancient bronzes that were not buried. The bronzes, as pictured in the archaeological report (Institute of Archaeology 1980) and as seen at various times on exhibition (Brown 1977:192–93), have a large number of different patinations: One sword has what looks like a transparent, shiny patina over deep-yellow, bronze-colored metal (Institute of Archaeology 1980:no. 1:5046, plate XLIV, 2). Another (which the author has not seen) appears to have silvery edges and a black center (Institute of Archaeology 1980:no. 1:5051, plate XLIV, 1). A *ge* dagger-ax has a surface pattern of black dots on a bronze-colored background; the mount is gilt bronze (Brown 1977:193; Institute of Archaeology 1980:plate XII). The famous tigers with carnelian eyes (Institute of

Archaeology 1980:plate XXVI) are inlaid with gold and silver, but the bronze color looks very much like a thick, dark-red cuprite patina. The mirrors are three different colors (Brown 1977). Many of the bronzes are dark and shiny, but the famous Boshanlu censer is a matte black, which sets off the gold inlay very well (Institute of Archaeology 1980:plate IX).

The best working hypothesis concerning these bronzes is that they had a variety of different patinas when they were put in the tombs. The closed environment in the rock-cut tombs has preserved the bronzes extremely well. The whole suite of bronzes and their surfaces are worth serious study.

## C O N C L U S I O N

Close study of ancient Chinese bronzes, the materials from which they are made, and the technology of their manufacture, coupled with study of the deterioration mechanisms they have undergone, has yielded some intriguing results. Probably the most interesting part of the whole study is that of patina and corrosion products. The patinas come from initial treatment, use, burial, and later events. Much information is encoded in the patinas of these objects, and it is important for conservators to try to read and understand it. There is also no point in trying to bring these bronzes back to their original condition, for their original condition has been altered totally by corrosion and, in some cases, subsequent treatment. Robbiola makes the additional point that removal of patina layers will probably be destabilizing, especially if the bronze has bronze disease. One should, at the very least, exercise a great deal of restraint in cleaning or altering the surface (Bassett and Chase, this volume).

Additional observations may be made here about conservation treatments of ancient bronzes. Sometimes conservation should go beyond just preserving the present condition; revealing design, removing old and possibly deceptive restoration, and cleaning down an ugly surface to a more attractive surface are all possible reasons for extensive treatment. These treatments are, however, irreversible. Conservators should act from a position of knowledge before beginning any of them. An understanding of the piece needs to come before the treatment of a bronze and, in many cases, the best understanding comes from metallographic study of cross sections.

Perhaps the implications are even more important for archaeologists. More information on the burial environment that bronze objects encounter would be very helpful indeed to those of us trying to interpret corrosion phenomena. The measurement of the soil moisture (often saturated, sometimes waterlogged), pH, Eh,  $\text{Cl}^-$  ion concentration, and carbonate concentration would be extremely helpful in trying to reconstruct the corrosion processes.<sup>7</sup> Measurement of cation concentrations in the soil (especially Cu, Sn, Pb, and Fe) in addition to the anions would be useful. Cross-sectional samples from excavated bronzes and their intensive study are also particularly vital to our understanding of long-term corrosion phenomena, and this work is now proceeding or beginning to proceed in various centers in China and Japan. Cleaning or chemical treatment in an indiscriminate fashion of all bronze finds from a site should be avoided until the finds have been carefully studied. At the least, some finds could be retained in an untreated state for study. If consolidation is nec-

essary, reversible consolidants should be used. Bronze disease should be, at least initially, treated by keeping the objects dry and not by chemical means.

The maintenance of excellent and thorough records on what has been done to the objects in terms of recovery and treatments is also extremely important. In order to reconstruct what has happened or proceed to improve the condition of a deteriorating object, one really needs to know what has been done to it previously.

Study of the corrosion phenomena and the environments and initial treatments that have brought the object to its present condition is intellectually interesting and challenging, but more important, these phenomena enable us to appreciate the skill of ancient craftspeople and the beauty of what they made.

## N O T E S

1. Recently, however, evidence of worked and annealed bronzes dating from the late Zhou period has come to light (He Tangkun 1993). We have also found evidence of worked and annealed bronze in a sample from the Jinsheng Tomb near Taiyuan in Shanxi (personal communication, Tao Shenggang, Shanxi Institute of Archaeology, 1992). Both of these are extremely thin bronzes, but they do illustrate that the process of working and annealing bronze was known before the Han Dynasty. It is, however, still fair to say that the vast majority of early Chinese bronzes were cast.
2. For example: Chase 1991; Bagley 1987; Bagley 1990; Keyser 1979; Han 1986; Huang 1991.
3. Produced by Bill Debold and Ed Yates in Matsue with a grant from The Desert Research Institute of Reno, Nevada.
4. When these maquettes were seen by the author in 1971 at Gorham, he was told that the foundry had lost the secret of this bright-red patina.
5. I will not attempt here to deal with the question of the formation of azurite versus malachite; it seems to be related strictly to local conditions and may well be due to local increases in CO<sub>2</sub> concentration from microbial action on decaying organic matter (McNeil and Little 1991).
6. It has recently come to my attention (personal communication, Zhou Baozhong, 1993) that all of the bronzes from the tomb of the Marquis of Cai were immersed in distilled water for a year prior to any treatment. Some of the swelling of the outer layers may have come from the prolonged corrosion, which did not, however, remove the chlorides deep in the structure.
7. Eh is difficult to measure; perhaps Eh measurements should be made before digging by a probe of some sort.

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# The Corrosion of Bronze Monuments in Polluted Urban Sites: A Report on the Stability of Copper Mineral Species at Different pH Levels

A N D R E W L I N S A N D T R A C Y P O W E R

Copper oxide (cuprite) and basic copper sulfates are the predominant crystalline corrosion products found on outdoor bronze and copper monuments in the United States. In urban-industrial areas, copper sulfates are readily formed and result in the streaked blue or blue-green color evident on many such structures. Caused primarily by acid deposition (dew, fog, rain, particulates, or dry deposition), this discoloration indicates degradation of the metal surfaces, usually manifested as extensive surface pitting. While this discoloration does not typically portend structural damage to well-executed castings, the aesthetic alteration of the surfaces may be profound and irreversible. The partially soluble corrosion products usually formed do not protect the underlying surfaces from attack, as typical exposure conditions do not produce even film growth. In some circumstances, however, thick and closely adherent corrosion crusts may retard the rate of degradation (Mattsson 1982:19; Graedel 1987a:730; Costas 1980:106–15).<sup>1</sup>

Found in lesser quantities than cuprite, brochantite— $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$  or  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ —has long been noted as a very common component of the corrosion films on commercial copper and bronze alloys in polluted urban-industrial environments (Table 1).

The presence of antlerite— $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$  or  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ —in the corrosion films on bronze monuments has been noted several times in recent years. Earlier studies of copper alloy and copper corrosion in the atmosphere seldom cite this corrosion form. The works of art on which this latter, more sulfate-rich species has been reported include some well-known sculptural monuments: the Statue of Liberty by Eiffel in New York Harbor (Baboian and Cliver 1986:74, 80; Nassau, Gallagher et al. 1987:671, 675, 684), The Horses of San Marco in Venice (Marchesini and Baden 1979:200–10), Lorenzo Ghilberti's Baptistry Doors in Florence (Garbassi and Mello 1984:174), and the equestrian monument of Marcus Aurelius in Rome (Leotta and Marabelli 1984:81; Marabelli 1987:214). In Philadelphia, where the following work was undertaken, two of the city's most prominent and best-known outdoor

TABLE 1.<sup>2</sup> Basic copper salts in green patina from various atmospheres, defined by the anions ranked with respect to content.

Reporter	Object	Time of exposure (years)	Country	Type of Atmosphere			
				Rural	Urban or industrial	Marine	Mixed urban-marine
Vernon & Whitby	Copper roofs; copper conductor in marine atmosphere	12–300 13	U.K.	1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup>	1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup> 3. Cl <sup>-</sup>	1. Cl <sup>-</sup> 2. CO <sub>3</sub> <sup>2-</sup> 3. SO <sub>4</sub> <sup>2-</sup>	1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup>
Vernon	Copper roof on church spire on the isle of Guernsey	33	U.K.			1. Cl <sup>-</sup> 2. CO <sub>3</sub> <sup>2-</sup> 3. SO <sub>4</sub> <sup>2-</sup>	
Freeman, Jr.	Copper roofs	16–78	U.S.				1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup>
Thompson, Tracy, & Freeman, Jr.	Copper panels from field test	20	U.S.	1. SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> 2. CO <sub>3</sub> <sup>2-</sup>	1. CO <sub>3</sub> <sup>2-</sup> 2. SO <sub>4</sub> <sup>2-</sup>	1. Cl <sup>-</sup> 2. SO <sub>4</sub> <sup>2-</sup> 3. CO <sub>3</sub> <sup>2-</sup>	
Aoyama	Copper conductor for railway		Japan	1. NO <sub>3</sub> <sup>-</sup> 2. CO <sub>3</sub> <sup>2-</sup>	1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup>	1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup>	
Mattsson & Holm	Copper-base materials from field test	7	Sweden	1. SO <sub>4</sub> <sup>2-</sup> 2. NO <sub>3</sub> <sup>-</sup> 3. CO <sub>3</sub> <sup>2-</sup>	1. SO <sub>4</sub> <sup>2-</sup> 2. CO <sub>3</sub> <sup>2-</sup>	1. Cl <sup>-</sup> 2. SO <sub>4</sub> <sup>2-</sup>	
Scholes & Jacob	Copper-base materials from field test	16	U.K.		1. SO <sub>4</sub> <sup>2-</sup> 2. Cl <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>	1. Cl <sup>-</sup> 2. SO <sub>4</sub> <sup>2-</sup>	

sculptures, William Penn (Fig. 1) by A. M. Calder and the Swann Fountain by A. S. Calder (Alexander Calder's grandfather and father, respectively), show significant amounts of antlerite (>10%) in parts of their corrosion crusts (Lins 1990). Figures 2–4 depict examples of corrosion in the Penn sculpture. Differences of opinion have been expressed about whether the appearance of antlerite indicates the emergence of a more acidic, more soluble corrosion form produced by increasing levels of pollution and acidity in urban-industrial environments, perhaps presaging a more rapid deterioration of such works of art in the future (Nielson [1981] 1984:78; Baboian and Cliver 1986:80; Nassau, Miller et al. 1987:716–17, 773).<sup>3</sup>

In urban regions, many variables determine the corrosion process at a particular site, among the most important of which are (1) atmospheric effects, primarily ambient temperature, relative humidity, and pollution levels; the amount, frequency, and duration of rain, wind, fog, mist, and freeze-thaw events, complicated by wind and aerosol erosion effects that influence the time of wetness on a given surface; organic deposition; photochemically induced reactions; and (2) the composition of the metal, the distribution of primary and secondary phases in the microstructure, defects, and porosity, especially due to casting and soldering in the case of bronzes, surface roughness, shape and position with respect to prevailing atmospheric factors, intentional patination, and coatings.<sup>4</sup> Accepting the impossibility of duplicating

FIGURE 1. A. Milne Calder, bronze statue of William Penn, cast 1889–91, City Hall Tower, Philadelphia.



FIGURE 2. BF  $\times 96$ , near right, from the William Penn figure: a complex, multilayer corrosion crust can develop on bronzes after long exposure to urban-industrial atmospheres—in this case 97–98 years. The corrosion is approximately 200 microns thick and partly follows microstructural features, especially casting pores located near the surface.

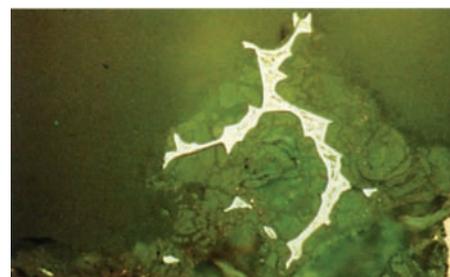
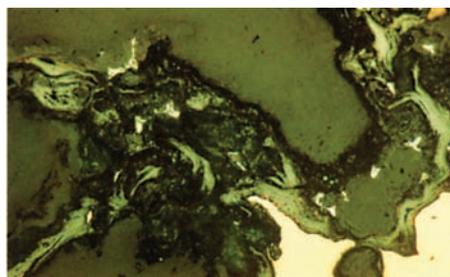


FIGURE 3. BF  $\times 240$ , above far right, also from the William Penn figure, illustrates that the delta phase is not as rapidly attacked as the alpha phase at this particular site.

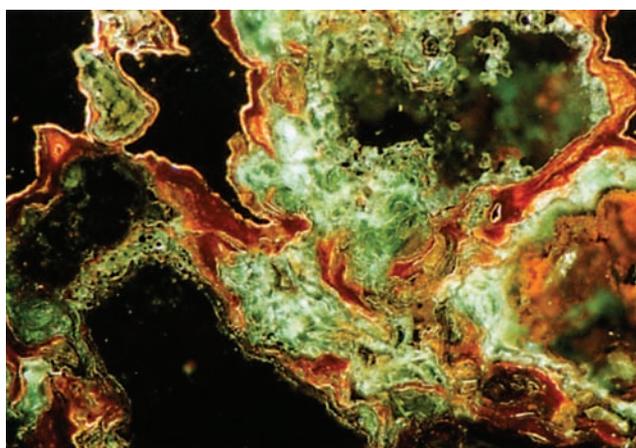


FIGURE 4. BF  $\times 310$ , above near right, shows the irregular, porous nature of the mineral formations within the crust.

more than a few of these variables in the laboratory, the following experiments attempted to measure with simple means the relative stability of some of the principal species involved in the system  $\text{Cu-H}_2\text{O-H}_2\text{SO}_4\text{-O}_{2(g)}/\text{CO}_{2(g)}$  at 20–22 °C. These analyses also attempted to assess the validity of antlerite as a pollution indicator, as well as to study more closely the predominant factors involved in the deterioration of bronze monuments, using concentrations of reactants not grossly different from those found in the environment.

## BACKGROUND

### Thermodynamics

Much of the work on the phase boundaries of the system  $\text{Cu-SO}_3\text{-H}_2\text{O}$  has been based on the thermodynamic properties of the substances involved.<sup>5</sup> The results of this research may be conveniently summarized in five graphs, in which pH and anion concentrations approach those found in the environment. The boundaries of antlerite stability are shaded for ease of visualization.

Based on Figures 5–9—derived primarily from thermodynamic values of  $E^\circ$ ,  $G^\circ$ ,  $H^\circ$ , or  $u^\circ$  at different pH values—one could predict that antlerite is formed under more acidic conditions in aqueous sulfate solutions than is brochantite, the most common sulfate corrosion product on copper and copper alloys in the atmosphere. If this theoretical thermodynamic situation is demonstrated to occur in a reproducible way under typical atmospheric conditions of moisture and pH and at a measurable rate with respect to a time scale of months or years, the ratio of antlerite to brochantite in a corrosion crust should serve as a measure of atmospheric aggressiveness.

FIGURE 5. This is a standard plot of  $E$  vs  $\text{pH}$  for  $\text{Cu}$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ ; for the specific condition that  $10^{-3.24}$  M  $\text{SO}_3$  (or 46 ppm) are dissolved per liter, from M. Pourbaix's work "to show the patina formed on copper in an atmosphere polluted by  $\text{SO}_2$ " (1977:13). Note that while the activity of  $\text{Cu}^{++}$ ,  $\text{H}^+$ , and other charged species in solution vary, this plot is strictly confined to the stated  $\text{SO}_3$  concentration. Changes in the activity of  $\text{SO}_3$  would necessitate redrawing the graph.

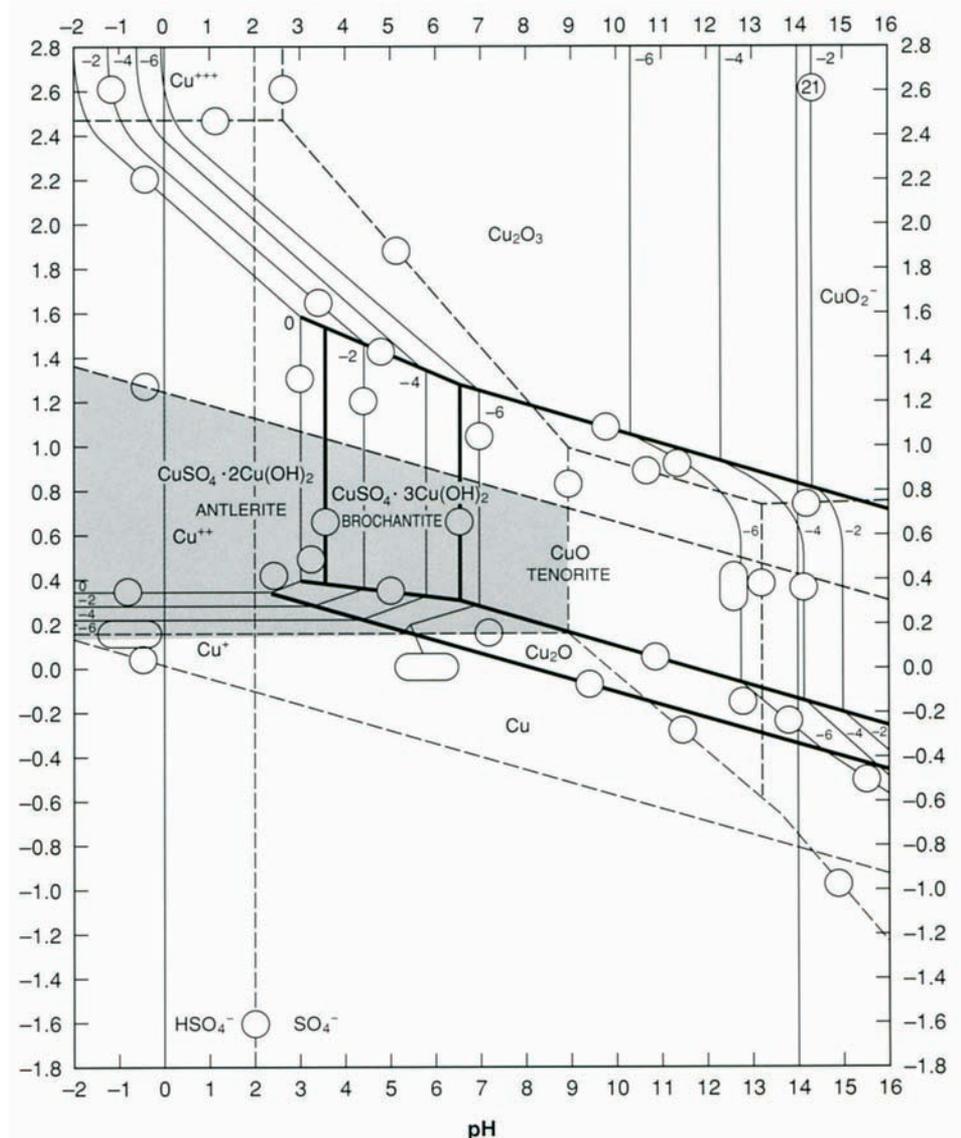


FIGURE 6. This three-dimensional plot, and those below, show the stability of different copper minerals in water at 25 °C. At right are oxidized copper species found in rain or natural waters. The x axis shows pH, the y axis shows sulfate ion activity, and the z axis shows total CO<sub>2</sub> activity (including CO<sub>2(g)</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>=</sup>) based on work of Silman and of Garrels (Garrels and Christ 1965:374–75). Zone of conditions favoring antlerite formation is shaded.

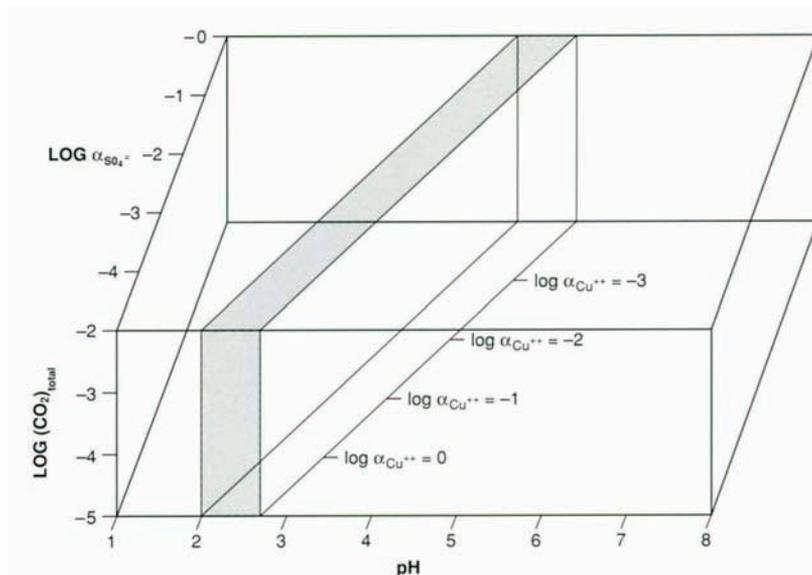


FIGURE 7. Plot emphasizing the calculated lower limit of cupric ion activities ( $a_{ant \ v \ broch}$ ) which would allow antlerite rather than brochantite to form, based on the work of Silman (Schmitt 1962:110–26).<sup>6</sup>

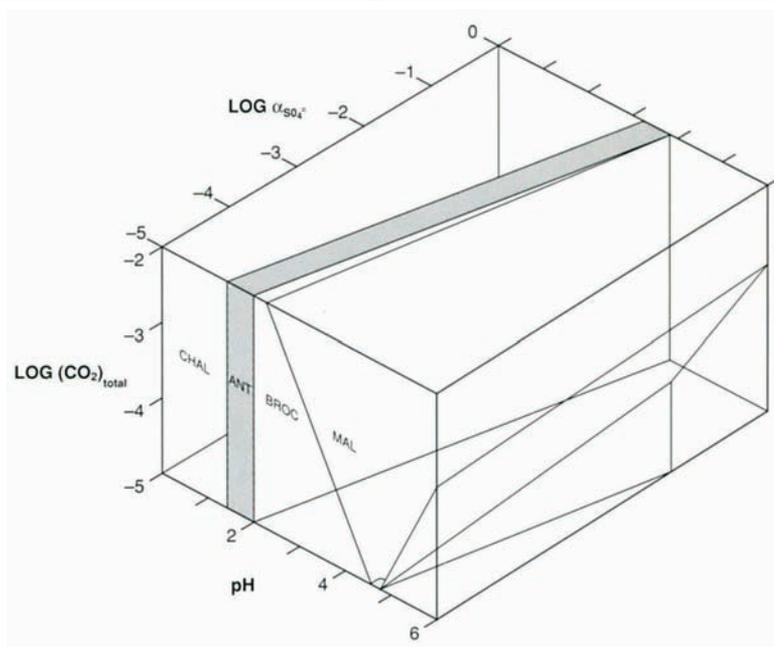


FIGURE 8. Plot showing the solubility of different copper sulfate and oxide species in dilute sulfuric acid solutions. Data based on thermodynamic and other calculations at 25 °C, after Mattsson (1982:18) and Graedel (1987a:731). Zones for acid rain and fog are displayed, overlaps indicating which minerals are likely at particular pH levels and sulfate concentrations. The left side shows no stable mineral forms, only Cu<sup>2+</sup> in solution.

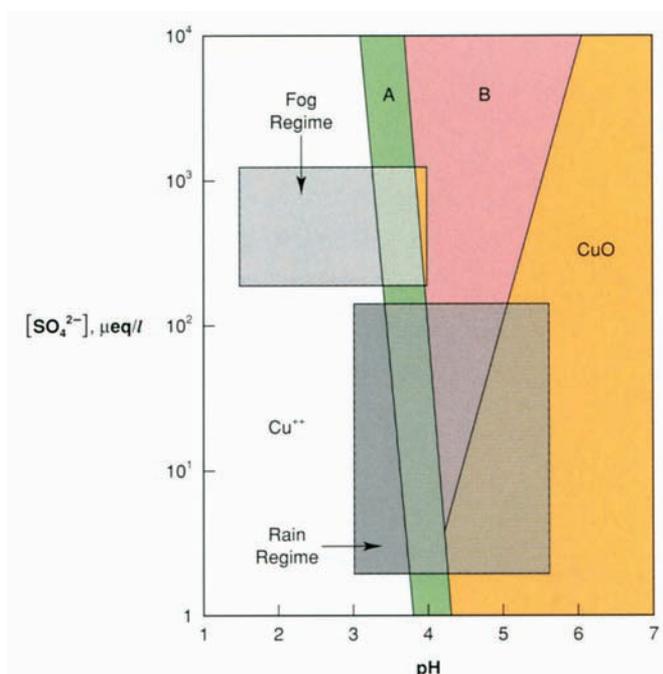
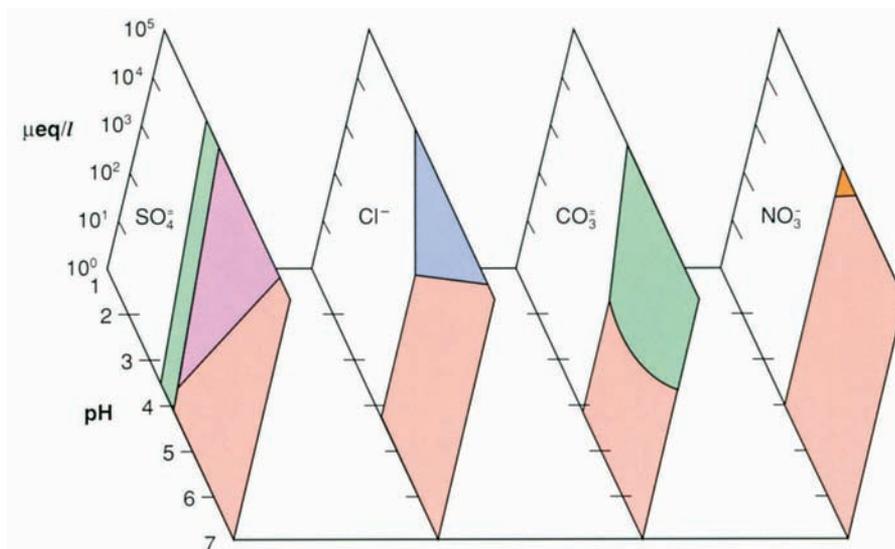


FIGURE 9. Diagram comparing basic copper sulfate stability with that of basic copper carbonates, chlorides, and nitrates. It shows the relative insolubility of basic copper sulfates, and conversely, the solubility of the copper nitrates, as well as the high concentration of anion required for them to precipitate. The x axis is pH. The separate z axes give anion activity in micro-equivalents per liter. Each plot is separate and based on specific and different anion concentrations. The y axis is an arbitrary axis, necessary only for the sense of overlay in the diagram. The range of values on the z axis reflects concentrations that might be found in an average rain or fog-dew event, for each anion species.<sup>7</sup>



### The Behavior of Copper in Sulfuric Acid Solutions

Fundamental to any study of sulfate-film formation on copper substrates in the atmosphere are studies of Cu reactions in dilute H<sub>2</sub>SO<sub>4</sub> and acidic salt solutions. These topics have been extensively investigated.<sup>8</sup> Space does not permit more than a brief summary of the results relevant to the present study:

In dilute sulfuric acid solutions, oxygen is necessary for copper dissolution or for cuprite formation to reach readily measured values. In very dilute sulfuric acid solutions and nearly pure water, cuprite formation is influenced by the concentration of gases dissolved in solution, enhanced in particular by oxygen. If oxygen is rigorously excluded from the reaction vessel, even at pH levels as low as pH 2, copper dissolution is difficult to measure reproducibly, and the growth of a cuprite layer is not demonstrated. In concentrated sulfuric acid solutions (>0.5 M), however, copper dissolves with or without oxygen present, but cuprite is not formed if the pH is kept low. During dissolution reactions with fixed amounts of reactants, the pH rises according to the general equation:

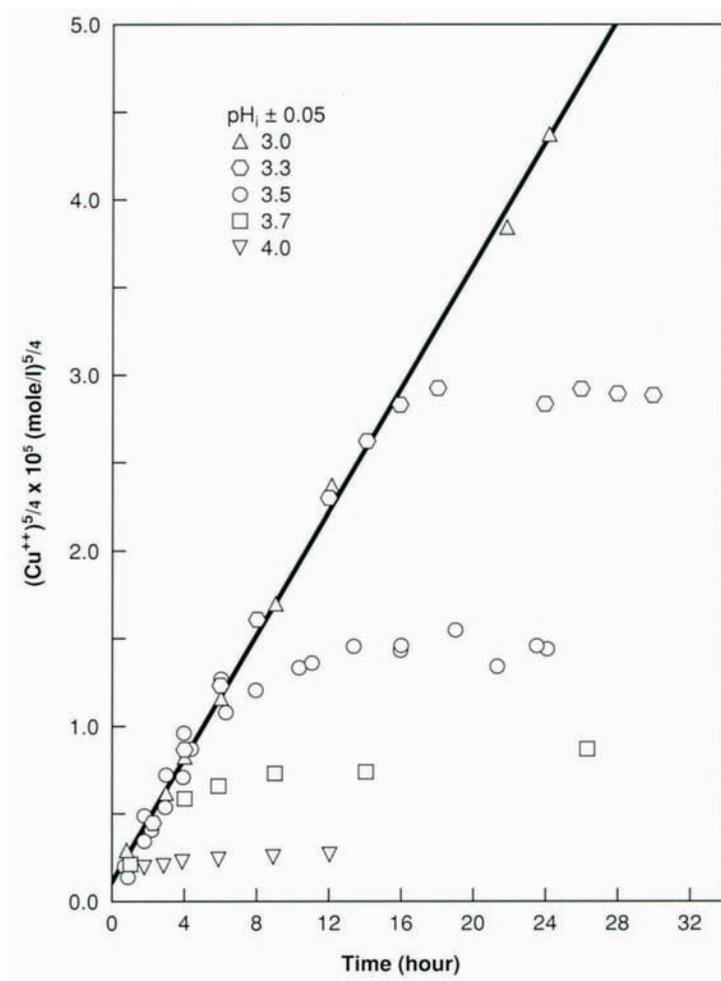


Two H<sup>+</sup> are consumed for each Cu<sup>++</sup> that is put into solution. The equilibrium constant for this electrochemical reaction shifts to the left as more copper ions go into solution. At higher pH (>2.5), relatively small concentrations of Cu<sup>++</sup> shut down the dissolution reaction. As the pH rises in unreplenished solutions, OH<sup>-</sup> concentration increases and with it the likelihood of producing cuprite (Yoon 1971:38; Gregory and Riddiford 1960:950–56).<sup>9</sup>

In sulfuric acid solutions open to air at pH below 3.5, the initial rate of dissolution of copper is independent of pH if sufficient mixing is provided in the solution, as Yoon (1971:53) indicates.

In the absence of rapid stirring (typically above 1000 rpm for the copper disc electrodes employed in such analyses), the rate of dissolution is transport-controlled. In poorly stirred or quiescent H<sub>2</sub>SO<sub>4</sub> solutions below pH 2.8, cuprite has not been observed to form. Above this pH, however, cuprite is formed, and the thickness of

FIGURE 10. Plot of  $\text{Cu}^{++}$  versus time for different initial pH values, after Yoon (1971:53).



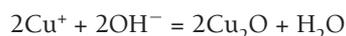
the layer formed depends on the relative quantities of solid and aqueous reactants present (Yoon 1971:47).

In sulfuric acid solutions containing  $\text{CuSO}_4$ , cuprite has not been observed to form below pH 3.1. The rate of formation of cuprite depends on the amount of exposed copper surface available for the reaction:



Near the surface of copper in such reactions, the pH decreases. The cuprite layer thus formed (above pH 3.1) grows at the copper-solution interface without extensive pitting or roughening of the substrate at the immediate interface, though etch pits are noted on adjacent exposed copper surfaces.

The following reaction is *not* favored in acid environments;  $\text{Cu}^+$  is not stable in oxygen-rich solutions (Jenkins and Bertocci 1965:519, Scott and Miller 1966:884, 886, Miller and Lawless 1959:857):



The presence of particular oxidants or depolarizers ( $\text{HNO}_3$ ,  $\text{FeCl}_3$ ,  $\text{Cl}^-$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CrO}_4^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$ ) increases the rate of dissolution of copper in sulfuric acid solutions and solutions containing copper sulfate that are well stirred. In less well-stirred solutions, the initial dissolution of copper—often measured as the weight loss for copper coupons—also appears to increase as the concentration of the oxidant

increases, typically up to a limiting value determined by the relative quantities of copper, sulfuric acid, and oxidant/depolarizer present. Following dissolution in these solutions, in the absence of stirring and resupply of  $H^+$ , corrosion films form. The composition of the films is determined by the components of the salt-acid solution. In some simple salt solutions ( $NaCl$  and  $Na_2SO_4$ ), cuprite growth is not favored below a limiting pH level, for example, pH 5 for 0.1 N  $NaCl$  (Davenport et al. 1959:108–9; Miller and Lawless 1959:854; Ives and Rawson 1962d:462).<sup>10</sup>

Whether salts, oxidants, or depolarizers are present, the cuprite layer formed on copper in  $H_2SO_4$  solutions is discontinuous. If formed rapidly or in poorly mixed solutions, the cuprite layer contains numerous voids and flaws that yield a nonprotective surface susceptible to further corrosion. Soluble aggressive anions (especially  $NO_3^-$ ,  $Cl^-$ ,  $ClO_3^-$ , and  $SO_4^{2-}$ ) trapped in the cuprite layer during film growth determine the susceptibility of the cuprite to subsequent dissolution. In bronzes and other copper alloys commonly used in monuments, secondary phase materials and their corrosion products ( $Sn$ ,  $Zn$ ,  $Pb$ , etc.) may increase the porosity of cuprite films.<sup>11</sup>

### Gas-phase Reactions Between $SO_2$ and Copper Substrates

Also basic to any work on the mechanisms by which copper sulfate corrosion layers develop in the atmosphere are studies of the initial reactions between gas-phase  $SO_2$ ,  $SO_3$ , and  $H_2SO_4$  and Cu substrates. While the pioneering work by Vernon, Whitby, and associates in London in the late 1920s and 1930s described with great thoroughness the components of weathered patinas from copper roofs (Vernon and Whitby 1930:389–96; 1929:181–94; Vernon 1931:255, 582; 1932:153–61), laboratory work did not produce a close simulation of naturally weathered corrosion crusts. Very concentrated  $SO_2$  atmospheres were used, up to and greater than 1%  $SO_2$ .

One important finding of their laboratory simulations was that the rate of corrosion induced by  $SO_2$  dramatically increased as the RH rose to 65–75%, though rate increases above 75% RH were not as marked. Later work by Kosting (1937) and by Ericsson and Sydberger (1977) was also conducted under conditions much more concentrated with respect to gaseous sulfur oxides than are found in typical urban-industrial environments (Kosting 1937:18–19; Ericsson and Sydberger 1977:755–57; Nassau, Miller et al. 1987:703–19).<sup>12</sup> As a consequence, their findings of antlerite—the only listing for antlerite as a result of gas-phase reaction—do not relate to natural weathering phenomena, in view of the fact that the antlerite formed “directly” on the copper without the interposition of a cuprite layer and did not show a stratigraphy similar to what is found on monuments after decades or even centuries of exposure.<sup>13</sup>

### Water in Thin Films

The presence of water on metal surfaces is essential for most corrosion reactions to develop at 20–25 °C. For most metal surfaces exposed outdoors, therefore, the rate of corrosion formation will be substantially affected by the RH. When a thin film of

water is prevented from forming by very low RH, corrosion processes will become extremely slow despite the presence of relatively aggressive corrosion species in the air. On the other hand, as RH increases, the thickness of the water layer increases. The water layer becomes much thickened by dew, fog, mist, or rain; the chemical behavior of the water film, which includes absorbed and adsorbed gases, begins to approach the chemical behavior of bulk solutions. Some values for the weight and thickness of water films are shown in Table 2.

The processes of water-film formation are complicated during normal weathering by a myriad of factors, including those listed in Table 2: temperature and temperature change, RH and RH change, wind, ambient pollution levels, surface roughness and porosity, surface shape, and particulates, to list just a few (Schmidt 1970:2589<sup>14</sup>; Leidheiser, Jr. 1971:74). On already corroded surfaces, the presence of different minerals in the corrosion crust may enhance water absorption and retention. In the case of copper sulfates, there are a number of hygroscopic species which are likely to be present on corroding copper surfaces in urban-industrial atmospheres and which can absorb water from the air even at comparatively low RH levels (around 35%), thus promoting corrosion reactions. These include: chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), bonatite ( $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ),  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{CuSO}_4$ .

In view of the many factors involved in copper corrosion and the many parameters to be taken into account in any study of atmospheric weathering, only a few of which are described here, it is not surprising that the study of thermodynamic stability regions and the kinetics of thin-film aqueous-phase reactions in the laboratory has not been combined, in particular for copper substrates with sulfate-rich films of little commercial value. Further thwarting any attempt to simulate outdoor exposure conditions is the fact that nonequilibrium reactions predominate in typical wetting events: there are never sufficient reactants (including water) nor time for true equilibrium to be established. The paucity of hydrogen and sulfate ions above pH 2.5 in sulfuric acid solutions is evident in Table 3. The majority of rain events result in only small volumes of rain per unit area of exposed copper or bronze surface, perhaps milliliters per square centimeter or less. In such hypothetical average rainstorms, the concentrations of hydrogen and sulfate ions that will be delivered to a square centimeter of exposed surface are expected to be only a small fraction of the values listed.

TABLE 2.<sup>15</sup> Values of weight and thickness of water films on metal surfaces.

Condition	Deposited weight (g/cm <sup>2</sup> )	Water thickness (nm)	Water monolayers
Clean copper, 60% RH, 20 °C	0.0055	5.5	15
Clean copper, 90% RH, 20 °C	0.0095	9.5	27
Copper with deposited particles, RH <sub>critical</sub>	0.01	10	30
Copper at 100% RH	1.0	10 <sup>3</sup>	3 x 10 <sup>3</sup>
Copper covered by dew	10	10 <sup>4</sup>	3 x 10 <sup>4</sup>
Copper wet from rain	10 <sup>2</sup>	10 <sup>5</sup>	3 x 10 <sup>5</sup>

TABLE 3. Calculated concentrations of  $H^+$ ,  $HSO_4^-$ , and  $SO_4^{=}$  per liter in dilute sulfuric acid solutions from pH 0.9 to 7.0 at 25 °C, based on  $K_2 = 1.20 \times 10^{-2}$  for  $HSO_4^- = H^+ + SO_4^{=}$  (CRC Handbook of Chemistry and Physics 1989).

pH	$\frac{[H^+]}{\text{liter}}$	$\frac{[SO_4^{=}]}{\text{liter}}$	$\frac{[HSO_4^-]}{\text{liter}}$	$\frac{SO_4^{=}}{HSO_4^-}$
0.9	126 mM	10.5 mM	105 mM	0.1
1.5	31.6 mM	7.0 mM	17.6 mM	0.40
1.9	12.6 mM	4.2 mM	4.2 mM	1.00
2.00	10.0 mM	3.60 mM	2.80 mM	1.26
2.50	3.16 mM	1.40 mM	0.35 mM	3.98
2.75	1.78 mM	0.83 mM	0.12 mM	7.08
3.00	1.00 mM	0.48 mM	0.038 mM	12.6
3.25	562 $\mu$ M	275 $\mu$ M	12.3 $\mu$ M	22.4
3.50	316 $\mu$ M	156 $\mu$ M	3.9 $\mu$ M	39.8
3.75	178 $\mu$ M	88.4 $\mu$ M	1.2 $\mu$ M	70.8
4.00	100 $\mu$ M	49.8 $\mu$ M	0.395 $\mu$ M	126
5.00	10 $\mu$ M	4.99 $\mu$ M	0.04 $\mu$ M	1260
6.00	1 $\mu$ M	499.9 nM	0.04 nM	12600
7.00	0.1 $\mu$ M	50 nM	$<10^{-4}$ nM	126000

Added to the list of variables that complicate laboratory simulation of weathering reactions are solid-phase phenomena involving crystallization, hydration, resolidification, aggregation, and precipitation of mixed phases.

The following work concentrates on the primary phases detected in sulfate-rich films on copper substrates—principally copper, cuprite, brochantite, antlerite, posnjakite, chalcantite, bonatite, and hydrated copper sulfates—as a first approach to understanding the sequence and mechanisms of mineralization.

## EXPERIMENTAL PROGRAM

### Initial Aging

Initial aging experiments were conducted in which corrosion rates were measured for 90Cu10Sn bronze exposed to sulfuric acid solutions, and 85Cu5Zn5Pb5Sn coupons exposed to acidic gas environments, at levels close to those given in the literature for urban-industrial environments with rain and fog to determine how closely those concentrations could be approached in subsequent experiments. A primary motivation was to avoid concentrations that would produce results skewed so far from conditions of natural weathering that they became meaningless in terms of investigating the processes involved.<sup>16</sup>

The most pertinent results may be briefly summarized as follows: (1) on coupons exposed in and over dilute sulfuric acid solutions (pH 2.8–5.0)—with and without oxidant ( $H_2O_2$ ) but with sufficient acid to cause attack—the copper dissolution rate was very low over a period of six months, as was the rate of corrosion-film formation; and (2) in atmospheres with constant RH  $\geq$ 75% containing  $HNO_3$ , 1 ppm  $SO_{2(g)}$  ( $81\times$  the level in typical Philadelphia air<sup>17</sup>), rapid corrosion did not develop

on the 85-5-5-5 bronze coupons over a period of seven months, despite condensate being maintained at pH 2, 3, 4, and 5. Only cuprite was detected by XRD analysis (Philips 1840 diffractometer), except in the SO<sub>2</sub> gas-phase experiment with condensate at pH 2, where a very small amount of posnjakite was found initially.<sup>18</sup>

## Phase Change

Analysis of phase change was conducted by wet-and-dry cycling using XRD. Based on observations from the initial simulated weathering experiments, it is clear that cyclic wetting and drying enormously increases the rate of corrosion formation on copper substrates, even when the concentration of reactants are not pushed many orders of magnitude above ambient levels.

Samples of antlerite<sup>19</sup> and brochantite<sup>20</sup> were sorted and scraped under the binocular microscope by scalpel and fine needle to eliminate unwanted impurities; the minerals thus cleaned were >95–98% pure, though optical inhomogeneities were evident under the microscope. The samples were analyzed elementally by atomic absorption spectrometry and XRF analyses and emission spectroscopy.

Semiquantitative XRD powder analysis was undertaken on the materials, using the following 2 $\theta$  lines: cuprite 42.3°, brochantite 35.6°, antlerite 18.3° and 24.8°.

Samples of bronze (85-5-5-5), copper, cuprite, antlerite, and brochantite, and a mixture of bronze and cuprite (equimolar with respect to Cu) were wetted for two different periods of time (500 and 10,000 hours) at regular intervals with well-controlled volumes (250 and 500  $\mu$ L, respectively) of: (1) H<sub>2</sub>SO<sub>4</sub> solutions of pH 2.50, 3.00, 3.50, 4.00, and 4.50; and (2) synthetic rain solutions<sup>21</sup> of pH 3 and 4 blanks that were wetted with deionized water in equivalent volumes. The samples were allowed to dry between wettings. The results of the cycling (drying/rewetting with temperatures between 15 and 40 °C) were compared to unexposed samples and the blanks, using XRD analysis to determine the extent of phase transformation or conversion. All samples were run in duplicate.

## Dissolution

Dissolution studies were based on the authors' observations that the well-crystallized copper sulfate minerals antlerite and brochantite appear to have different stability in dilute sulfuric acid than is described in the corrosion literature (Graedel 1987b:760). Studies of the stability of the minerals—and of cuprite and copper for comparison—in sulfuric acid were undertaken, including some simple kinetic analyses of the relative rates of dissolution of the four substances in dilute sulfuric acid and synthetic-rain solutions based on Environmental Protection Agency data for the Philadelphia region.

Copper (99.999% Aesar), cuprous oxide (99.95%, Alfa), brochantite, and antlerite were separately exposed in three different procedures:

1. To 500 ml deionized water—open to the air—into which 0.002 N, 0.01 N, 0.05 N, and 0.1 N H<sub>2</sub>SO<sub>4</sub> (ACS grade) were admitted in order to

reach different pH levels (from 6.20 to 2.50) with slow stirring (100–300 rpm). Samples were withdrawn at intervals for atomic-absorption analysis; each initial solution contained 100  $\mu\text{M/L}$  solid.

2. By introducing the solids into: (a)  $\text{H}_2\text{SO}_4$  solutions at different pH levels [2.50, 2.75, 3.00, 3.50, 4.00, 4.50, and 5.00]; (b) synthetic-rain solutions over the same range of pH, adjusted by addition of sulfuric and nitric acid [0.2 N  $\text{H}_2\text{SO}_4$  : 0.1 N  $\text{HNO}_3$ ], and (c)  $\text{H}_2\text{SO}_4$  solutions over the same range of pH, to which was added 1 ml of ionic strength adjustor [0.5 N  $\text{NaNO}_3$  : 0.5 N  $\text{Na}_2\text{SO}_4$ ] per 100 ml of solution. The solutions were continuously monitored for  $\text{Cu}^{++}$  by ISE measurements.
3. By following the increase of  $\text{Cu}^{++}$  in solution over time (1,800 minutes) for the above four solids exposed to (a) a solution of pH 3 sulfuric acid, and (b) a solution of synthetic rain at pH 3. The solutions were continuously monitored for  $\text{Cu}^{++}$  by ISE measurements.

All solutions were maintained at 20–23 °C, and all pH measurements were corrected to 20 °C.<sup>22</sup>

## Precipitation

Precipitation studies were initiated by the lack of evidence for antlerite formation or stability in the preceding work. The goal of these studies was to form antlerite at room temperatures (20–23 °C).

In the first precipitation study, varying amounts of anhydrous  $\text{Cu}(\text{OH})_2$  (Aldrich no. 28,978-7, technical grade, Cu content 57%) and anhydrous  $\text{CuSO}_4$  (Aldrich no. 20,917-1, 98%) were mixed dry. Over these were introduced 100 ml  $\text{H}_2\text{SO}_4$  solutions of varying pH (2, 3, 4, and 5). At intervals of one month and seven weeks any new phase material was collected and analyzed by XRD. A constant volume of solution (100  $\pm$  3 ml) was maintained over the two months by adding deionized water. In the second precipitation study, varying amounts of Cu (Alfa, 99.95%) and anhydrous  $\text{CuSO}_4$  (as above) were mixed in sulfuric acid solutions of pH 2, 3, 4, and 5 initially, and the new phase development monitored by XRD. The pH levels were measured over the course of each precipitation study.<sup>23</sup>

Quantitation studies were also carried out for cuprite:antlerite and cuprite:brochantite mixtures totaling 50  $\mu\text{M}$  in the ratios of 90/10, 75/25, and 50/50. Ternary mixtures of cuprite:antlerite:brochantite (50/25/25 and 50/10/40) were also prepared and analyzed quantitatively, as were cuprite:covellite and cuprite:chalcocite mixtures.

## EXPERIMENTAL RESULTS

### Wet-dry Cycling

The results of the wet-dry cycling experiments are given by the accompanying XRD plots of counts per second versus  $2\theta$  (Figs. 11–14). Briefly, the data indicate that for the longer exposure period (10,000 hours), all samples were converted at pH 2.5 to

FIGURE 11. Overlay of normalized XRD patterns for brochantite, showing changes at lower pH levels (2.5 and 3.0) in the long exposures (top) and less developed changes for the short exposures (bottom). The y axis gives normalized counts for the samples, overlaid for comparison.

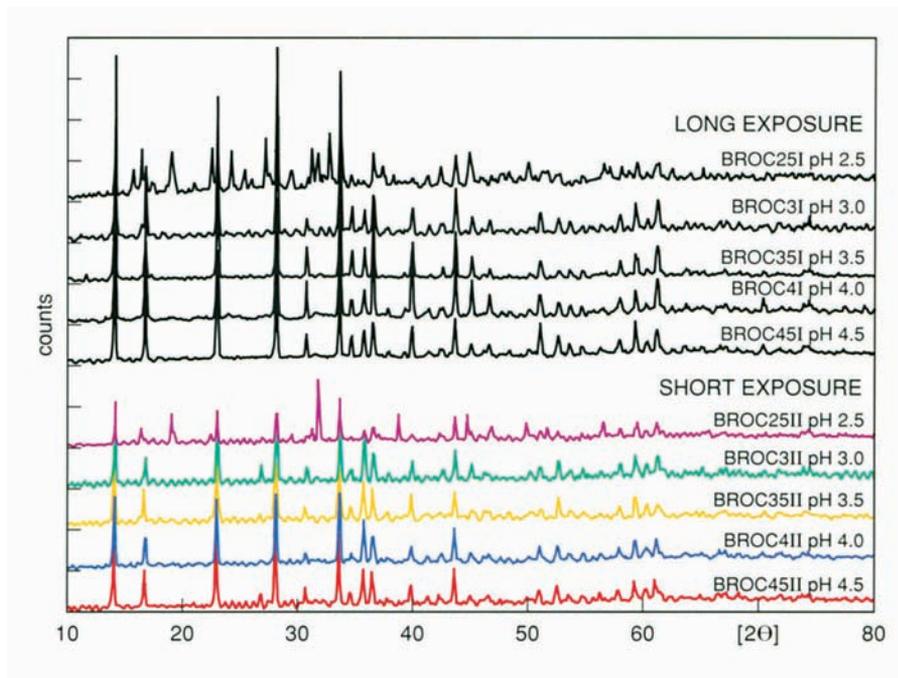
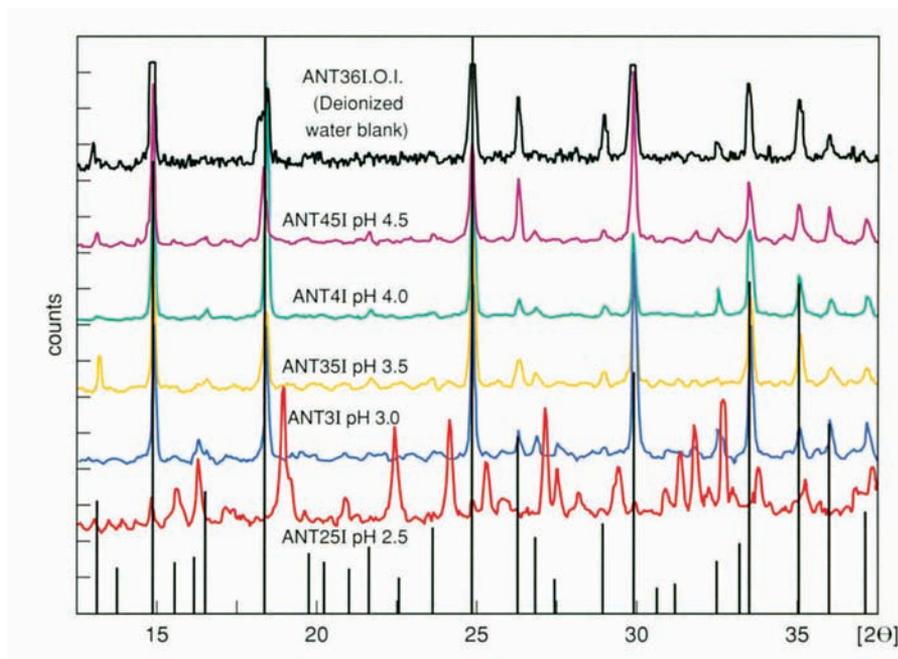


FIGURE 12. Overlay of normalized XRD pattern for antlerite, on long exposure. The lines indicate the peak locations and relative heights for the unexposed antlerite “standard.” The y axis gives normalized counts for the samples, overlaid for comparison.



soluble copper sulfates—primarily chalcantite and, to a lesser extent, bonatite. Over the shorter exposure period (500 hours), the low pH environment did not produce a conversion of brochantite to antlerite. Instead, antlerite, brochantite, copper, and cuprite all converted to more soluble copper sulfates. At pH 2.5, cuprite and copper formed chalcantite rather than antlerite or brochantite.

At pH 3, antlerite and brochantite show much more conversion to soluble sulfate at the long exposure than at the short one; the peak heights for equivalent weights of sample are much reduced for these two species compared with higher pH levels (3.5) and show some alteration of the relative peak heights for each sample, suggesting that some dissolution and reprecipitation is occurring at the outside of the crystals and that a certain amount of noncrystalline or cryptocrystalline precipitation may be occurring. At pH 3, copper undergoes the only clearly observed alteration to antlerite

FIGURE 13. Alteration of brochantite is shown over short and long exposure periods, at pH 2.5 and 3.0. The vertical lines give the position of the primary chalcantite peaks over this range of  $2\theta$  angles. The counts are normalized for overlay on the y axis.

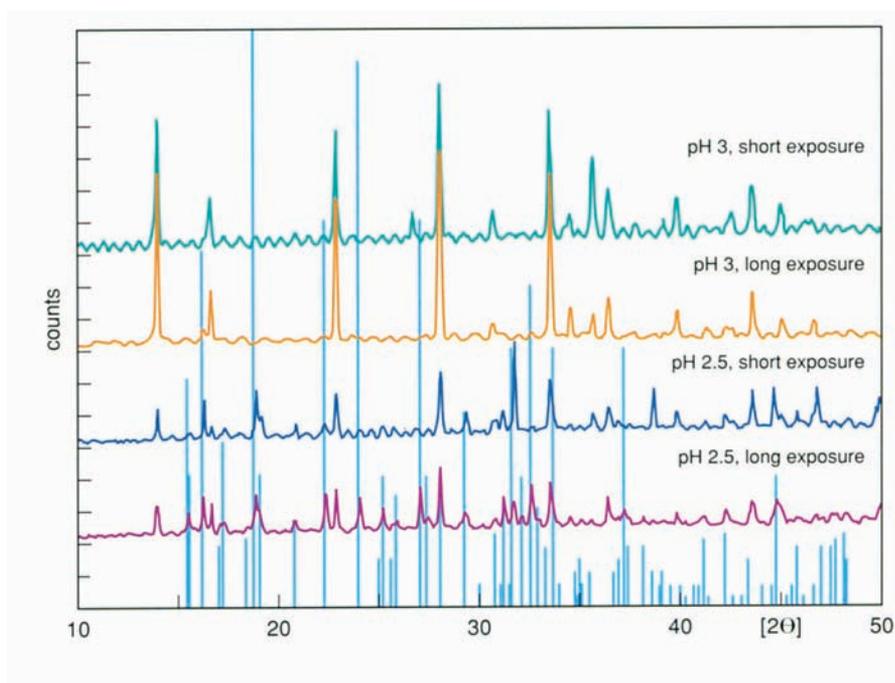
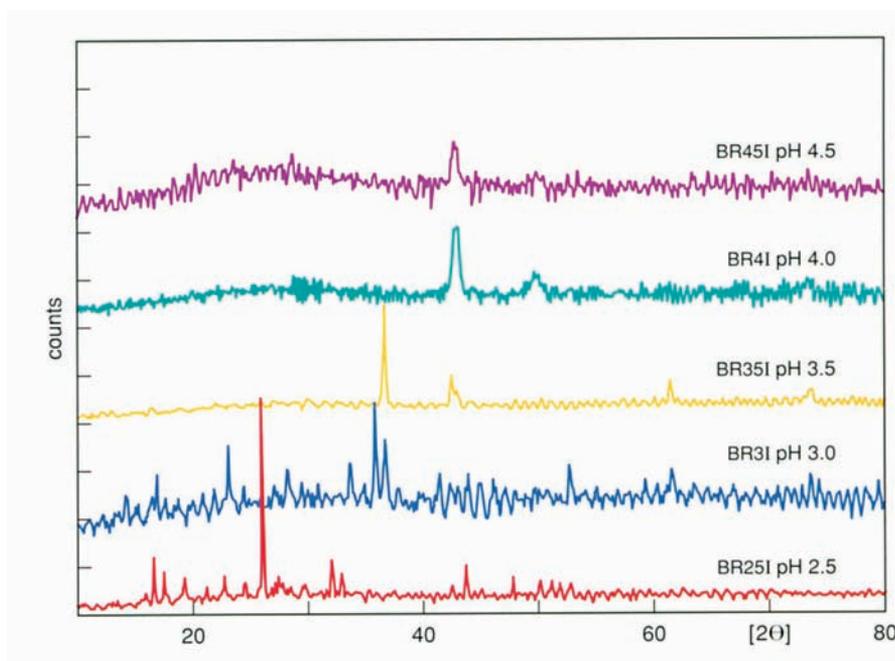


FIGURE 14. Alteration of bronze is given for the long exposure period, illustrating the development of mostly cuprite at pH 3.5, mixed cuprite and brochantite at pH 3.0, and predominantly chalcantite at pH 2.5. The counts are normalized for overlay on the y axis.



in the course of all the experiments to date, brochantite is also produced, and cuprite underlies the sulfate layers. Curiously, both the bronze and the mixture of bronze and cuprite failed to develop antlerite under similar exposure conditions. Cuprite itself at pH 3 tended to develop into brochantite and later chalcantite.

At pH 3.5, the rate of transformation is considerably slower than at the lower pH levels. The net (low) concentration of reactants available is in part responsible.

Table 4 sets out the theoretical yields for each run: The first figure is for a conversion dependent on  $H^+$  only, the second for a conversion dependent on sulfate ion only. In run 1, where a total of 25 ml of synthetic acid rain solution (L/40) was delivered over the period from July 17 to October 25, 1990, in 250–500  $\mu$ l portions (54 $\times$ ), the theoretical conversion or dissolution of the various samples—all at 50  $\mu$ M—is given for each pH:

TABLE 4. Theoretical yields for brochantite and antlerite samples at various pH levels, the first figure in the theoretical yield being based on H<sup>+</sup> dissolution only and the second figure being based on SO<sub>4</sub><sup>=</sup> as the primary reactant in the dissolution process.

pH level	RUN 1		RUN 2	
	Available H <sup>+</sup> per 25 ml	Maximum theoretical yield	Available H <sup>+</sup> per 15 ml	Maximum theoretical yield
2.5	3.2mM/40	100 / 88	3.2mM/66.7	93 / 46
3.0	1.0mM/40	50 / 25	1.0mM/66.7	30 / 16
3.5	0.3mM/40	16 / 8	0.3mM/66.7	9 / 5
4.0	0.1mM/40	5 / 2.5	0.1mM/66.7	3 / 1.5
4.5	0.03mM/40	1.6 / 0.8	0.03mM/66.7	0.9 / 0.5

In run 2, where a total of 15 ml (3L/200) of synthetic rain was delivered in 500  $\mu$ l portions over the period from August 23 to October 25, 1990 (30X), the theoretical conversion or dissolution of antlerite, brochantite, bronze, copper, and a mixture of bronze and cuprite—all 50  $\mu$ M initially—is given at each pH. In run 2, the cuprite sample was increased to 200  $\mu$ M; the yield at each pH level should thus be divided by 4 in Table 4. The data in this table suggest that at higher pH, little H<sup>+</sup> is available to drive the conversion of these samples with the small volume delivered.

It would appear from the data that more reprecipitation or recrystallization occurs at pH 3.5 and to a lesser degree at pH 4 for antlerite and brochantite. This is in keeping with the dissolution data above, which show that both basic sulfates are soluble to a degree at these intermediate pH levels.

At pH 4.5, little change from the blanks and the standards is evident in either the long or the short run, suggesting that the changes are below the readily detectable limits for the XRD technique employed, probably about 3% for these particular materials.

## Dissolution and Kinetic Studies

Results of dissolution and kinetic studies show that both antlerite and brochantite begin dissolving in very dilute acid solutions. The amount of Cu<sup>++</sup> produced is a direct function of the amount of available H<sup>+</sup> in solution. For simplicity, some of the results are summarized in graph form as often as possible.<sup>24</sup>

Figures 15–24 indicate the direct dependence of antlerite and brochantite dissolution on H<sup>+</sup> concentration. At low pH (<3), the distinction between the rate of basic sulfate dissolution and of cuprite dissolution becomes indistinct under the given conditions of the experiment. At pH levels above 4, cuprite dissolution is notably slower than that of the basic sulfates.

Table 5 gives the results of a stability-dissolution study of antlerite, brochantite, cuprite, and copper in H<sub>2</sub>SO<sub>4</sub> solutions. The pH, ppm Cu<sup>++</sup> found in solution, and H<sup>+</sup> in mM/L added to reach each pH point are given for each substance. Each solution contained 100  $\mu$ M/L of solid initially, except for copper, which contained 200  $\mu$ M/L (weights were: antlerite 17.99 mg, brochantite 23.55 mg, and cuprite 7.10 mg). The initial volume of each solution was 500 ml (deionized water; the temperature was 20–22 °C). The solutions were stirred during each measurement period (5–10 m)

FIGURE 15. Dissolution of brochantite showing dependence on available pH.

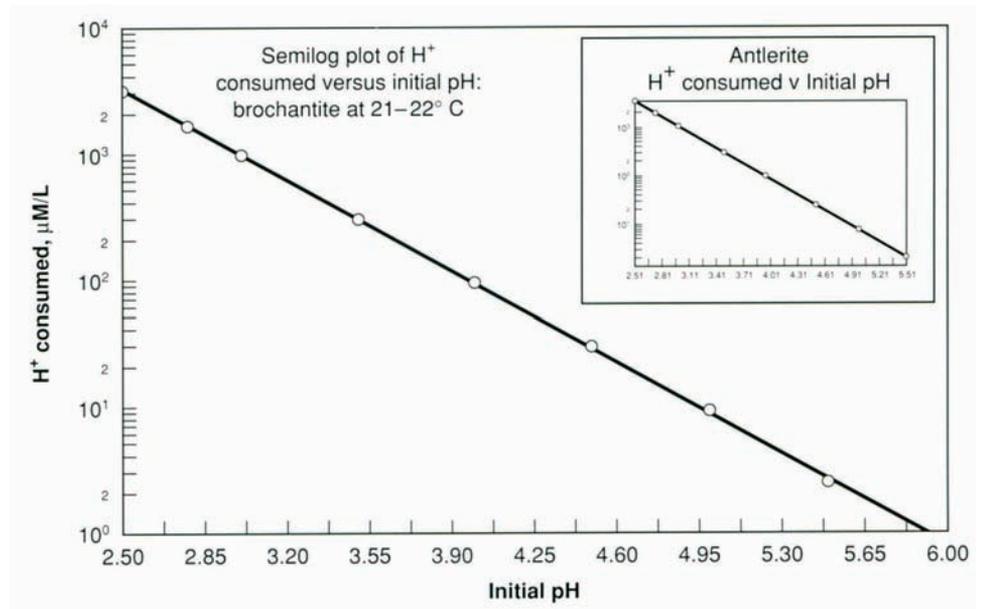


FIGURE 16. Dissolution studies for antlerite showing linear relationship between  $\text{Cu}^{++}$  in solution and  $H^+$  consumed.

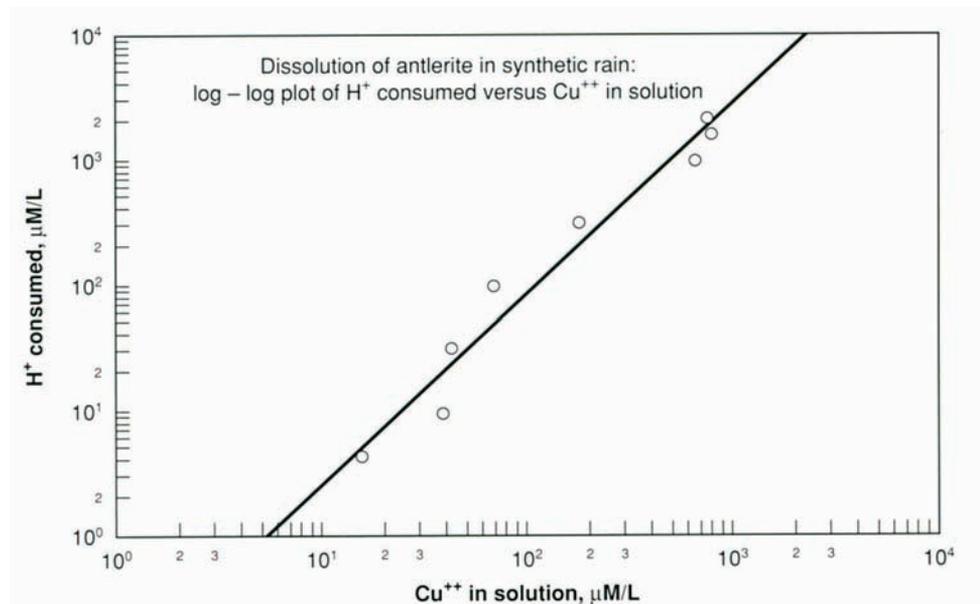


FIGURE 17. Kinetic dissolution study in sulfuric acid.

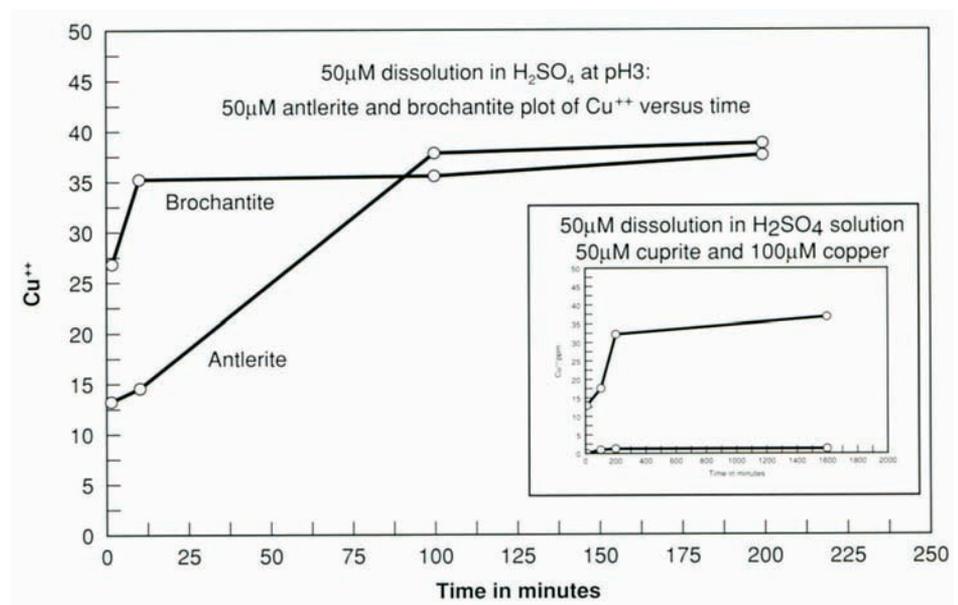


FIGURE 18. Kinetic dissolution study in synthetic rain. Note that antlerite dissolves more slowly than brochantite.

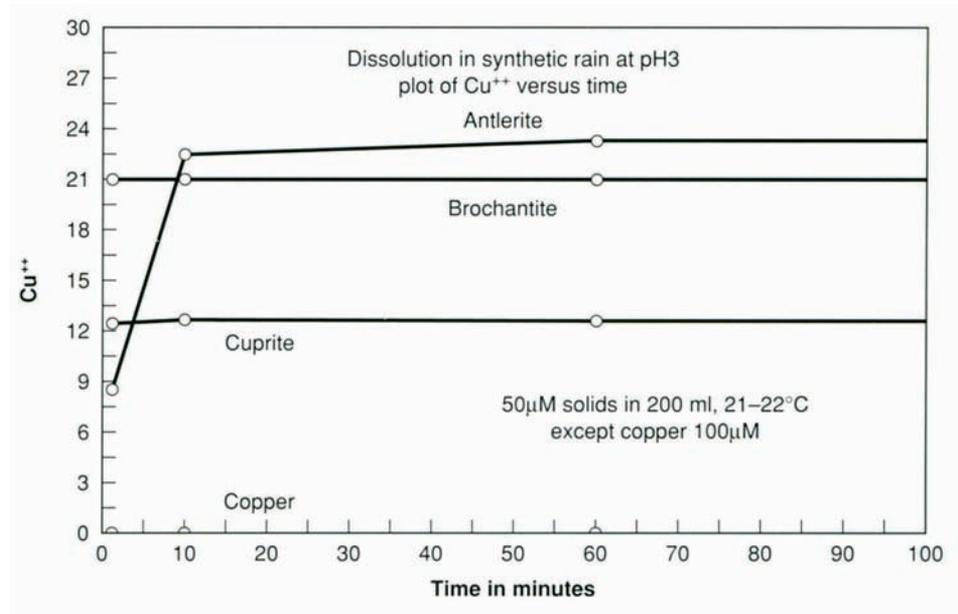
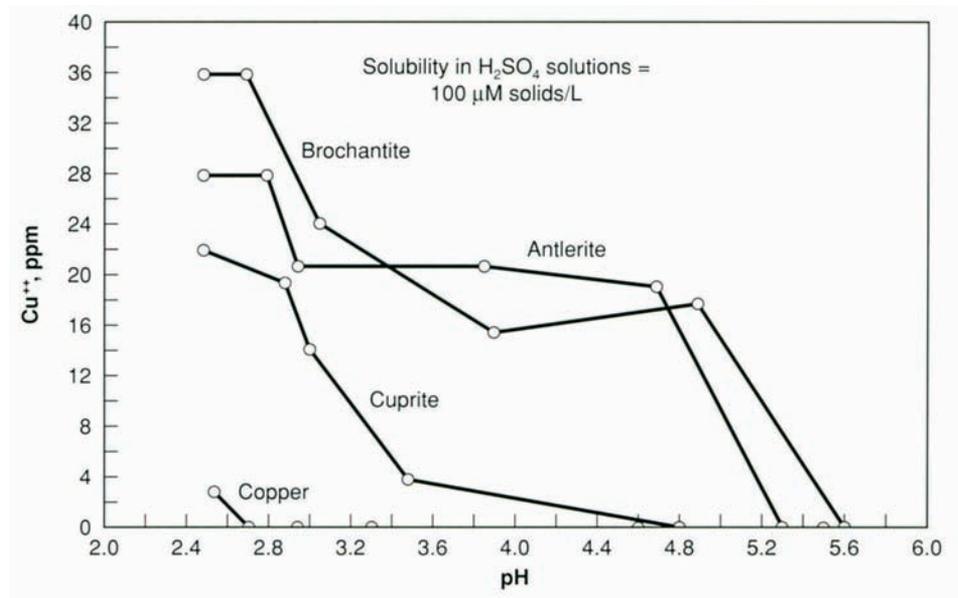


FIGURE 19. Relative solubilities in H<sub>2</sub>SO<sub>4</sub> solutions of different pH.



at 100–300 rpm. Regular volumes of sulfuric acid (0.002, 0.01, and 0.1 N) were introduced by burette into the solution. Following pH measurement, equivalent volumes of solution were extracted for atomic absorption analysis.

The kinetics of dissolution at pH 3 in H<sub>2</sub>SO<sub>4</sub> solutions is shown in Table 6. The heading of each column indicates the time in minutes at which the pH and ppm Cu<sup>++</sup> measurements for the given sample was made. The samples were 200 μM/L—Cu<sub>3</sub>SO<sub>4</sub>(OH)<sub>4</sub> 17.89 mg; Cu<sub>4</sub>SO<sub>4</sub>(OH)<sub>2</sub> 23.01 mg; and Cu<sub>2</sub>O 7.55 mg, except for copper, which was 452 μM/L (7.23 mg). The volume of the solution in each case was 250 ml; the temperature was 20–22 °C.

Table 7 shows the kinetics of dissolution at pH 3 in synthetic-rain solutions. The heading of each column indicates the time in minutes at which the pH and ppm Cu<sup>++</sup> measurements for the given sample was made. The samples were 250 μM/L—Cu<sub>3</sub>SO<sub>4</sub>(OH)<sub>4</sub> 18.34 mg; Cu<sub>4</sub>SO<sub>4</sub>(OH)<sub>2</sub> 23.35 and 20.02 mg; and Cu<sub>2</sub>O 9.53 mg, except for copper, which was 500+ μM/L (7.53 mg). The volume of the solution in each case was 200 ml; the temperature was 20–22 °C.

TABLE 5. Data from stability-dissolution study of sulfates in  $H_2SO_4$  solutions, given as pH/ppm  $Cu^{++}/H^+$  added in mM/L for each sample.

Antlerite	Brochantite	Cuprite	Copper
5.30/nd/.02	5.60/1.0/.02	5.50/nd/.002	5.30/nd/.002
3.85/6.2/.12	3.90/4.6/.12	3.48/1.1/.088	3.30/nd/.088
2.95/6.2/.52	3.05/7.2/.52	3.00/4.2/.49	2.94/<<1/.49
2.80/8.4/1.02	2.70/10.8/1.02	2.88/5.8/.99	2.70/<1/.99
2.50/8.4/3.02	2.49/10.8/3.02	2.49/6.6/2.99	2.53/1.0/2.99

TABLE 6. Kinetics of dissolution at pH 3 in  $H_2SO_4$  solutions. For each sample pH/ppm  $Cu^{++}$  figures are given for the stated time.

Sample	1.2 min.	10 min.	100 min.	200 min.
Antlerite	3.05/13.2	3.18/16.8	3.90/38.4	4.05/39.6
Brochantite	3.10/27.0	3.27/35.4	3.80/36.0	4.20/39.2
Cuprite	2.87/10.4	2.91/13.2	3.30/17.0	3.20/10.6
Copper	3.00/nd	3.05/nd	3.05/0.6	3.05/0.8

TABLE 7. Kinetics of dissolution at pH 3 in synthetic-rain solutions. For each sample pH/ppm  $Cu^{++}$  figures are given for the stated time.

Sample	1 min.	10 min.	60 min.	1080 min.
Antlerite	3.30/8.4	3.90/22.5	4.05/23.4	4.70/22.8
Brochantite	3.10/21.0	3.70/21.0	4.60/31.2	4.70/21.0
Cuprite	3.10/13.2	3.35/13.2	3.30/13.2	3.70/13.2
Copper	3.10/nd	3.10/nd	3.20/nd	20/nd

### Precipitation Studies

The precipitation results were produced as follows: Mixtures of anhydrous  $CuSO_4$  and  $Cu(OH)_2$  at 20–23 °C were dissolved in acidified sulfuric acid solutions of different pH; 0.01 M ratios by weight, measured on a microbalance to 0.1 mg, solution volume of 100 ml. The maximum theoretical concentration of  $Cu^{++}$  species was 0.4 M/L. Solution volumes were maintained with deionized water to within 5 ml of initial volume for two months and covered with plastic film during standing. The capital letters in Tables 8 and 9 indicate new phases being formed: A=antlerite; B=brochantite; C=cuprite, L=langite— $Cu_4SO_4(OH)_6 \cdot H_2O$ ; P=posnjakite— $Cu_4SO_4(OH)_6 \cdot H_2O$ ; and R=ramsbeckite— $Cu_{15}(SO_4)_4(OH)_{12} \cdot 6H_2O$ .

## EXPERIMENTAL PROCEDURES

During the course of laboratory work, features of aqueous mixtures containing hydrated  $CuSO_4$  basic copper sulfates and cuprite-copper  $H_2SO_4$  became more apparent and certainly influenced the results of the quite simple empirical tests described above.

The hygroscopicity and reactivity of the copper sulfates (anhydrous as well as antlerite and brochantite) contrasted strongly with the poor wettability of purified

TABLE 8. Predominant new-phase growth and pH change of solutions are shown after one month and after seven weeks.

Molar ratio initial pH 1 month/7 weeks	pH 2	pH 3	pH 4	pH 5
2 CuSO <sub>4</sub> :1 Cu(OH) <sub>2</sub> pH change	B 4.22/4.18	B 4.19/4.17	B, ?L, P 4.28/4.23	B, ?L, P 4.24/4.19
1 sulfate:1 hydroxide pH change	B 4.39/4.39	B 4.42/4.41	B 4.42/4.40	B 4.38/4.37
1 sulfate:2 hydroxide pH change	B 4.50/4.42	B 4.51/4.48	B 4.55/4.53	B 4.48/4.45
1 sulfate:3 hydroxide pH change	B ≥ P, L 4.64/4/59	B + P 4.71/4.68	P > B 4.76/4.70	P >> B 4.76/4.68

TABLE 9. The predominant new-phase development after one month is shown for mixtures of copper and anhydrous cuprous sulfate.

Molar ratio initial pH	pH 2	pH 3	pH 4	pH 5
3 Cu:1 CuSO <sub>4</sub> pH change	C	C	C	C
2 copper:1 sulfate pH change	C	C	C	C, ?B
1 copper:1 sulfate pH change	C	C >> B	C > B	C > B *?R
1 copper:2 sulfate pH change	C	C	C > B	C > B
1 copper:3 sulfate pH change	C	C	C > B	C

cuprite, copper, or bronze. The rate of wetting and mixing of the finely powdered samples in the dissolution studies was affected by these differences. For the atomic-absorption and ISE measurements, data for the first 10 minutes of dissolution must have been determined in part by these differences, complicated by problems of extracting samples for atomic-absorption analysis while solids floated on the surface of the solution or adhered to the surface of the ISE electrode. Later measurements are less susceptible to variations produced by clumping and uneven distribution of solids, as more effective mixing had occurred and small clumps were broken by stirring rods.

The longer exposures of the drop experiments eventually produced films on the copper, cuprite, bronze, and bronze-cuprite samples that modified and improved the wettability of the samples: in short-term exposures the differences in hydrophilic-hydrophobic mixing were more apparent. Mounting the samples for XRD analysis with deionized water also revealed the differences between samples on the basis of wetting, which are significant in corrosion phenomena.

In the precipitation studies, the mobility of simple copper sulfates in water resulted in the easy separation of the copper sulfates from the newly formed basic copper sulfates, or cuprite, on drying. The simple sulfates moved to the evaporation

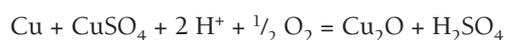
fronts. Of interest to those collecting samples from outdoor monuments was the observation that thin film and very finely divided deposits of simple copper sulfates are often transparent and colorless, in contrast to the strong blue transparent examples of these compounds found in textbooks; in very thin films they may be easy to overlook during collection from a weathered surface.

As the various phases underwent dissolution or conversion in the drop and in the precipitation experiments, the size and shape of the remaining and newly formed solids became more varied with the passing of time. On slow drying, as one might predict, the crystalline structures that developed on some faces tended to grow into solution or into the air, while the faces that pointed toward the bottom and sides of the glass vessels were not easily distinguished and tended to grow together in the constrained space, perhaps analogous to their growth and recrystallization within a corrosion crust. The more rapid drying in the drop experiments produced some new-phase growth near the evaporation fronts; this was very finely divided and approached the appearance of naturally weathered solids (Hemming 1977:98–99, figs. 3, 4), in which erosion and particulate abrasion play significant roles in reducing and rounding crystalline forms.

The results of the dissolution studies indicate that antlerite may be slightly slower to dissolve near pH 3 than is brochantite, but it is not clear how this kinetic difference plays a significant role in the long-term development of a corrosion crust.

## C O N C L U S I O N S

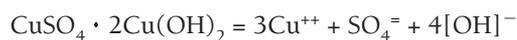
The kinetics of the acid dissolution of well-crystallized copper sulfates indicates that in low pH environments common to polluted urban-industrial environments, acidified copper-sulfate solutions are readily produced from the corrosion crust of bronze and copper substrates, in particular from brochantite and antlerite. These aggressive  $\text{CuSO}_4$  solutions are likely to be responsible for part of the growth of the cuprite crust based on the reaction:



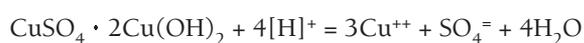
This finding is similar to the findings of Miller and Lawless (1959) and Robertson et al. (1958) in their tightly controlled investigations of systems in which  $\text{CuSO}_4$  was present.

Dissolution of the copper-sulfate-rich materials on the crust exterior is initially accompanied by a rise in pH:

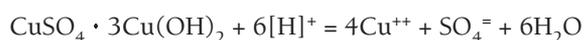
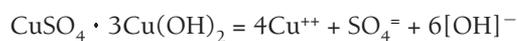
for antlerite:



or



for brochantite:



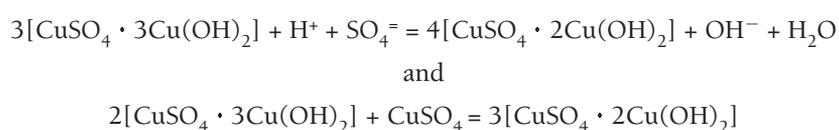
Certainly during rainstorms and other periods of substantial wetness, the surface copper-sulfate films modify the pH of the aqueous phase that reaches the metal-corrosion crust interface, raising the pH while supplying  $\text{Cu}^{++}$  and  $\text{SO}_4^-$  ions. The modification of the pH of atmospherically deposited solutions in the crust is not a simple process. For instance, as the thin film of the aqueous phase dries out on the corroded metal surface, the pH is expected to fall. A 10:1 reduction in volume by evaporation of water should drop the pH one unit. Opposing this pH lowering, the activity of the  $\text{Cu}^{++}$  and  $\text{SO}_4^-$  ions rapidly decreases as their concentration exceeds 0.05 M in concentrated solutions. The precipitation studies, moreover, indicate that after long wetting of solids typically found in corrosion crusts, the initial pH of the aqueous phase is overwhelmed by the copper sulfate material—solids and ions in solution—and reaches intermediate values, perhaps in the region of pH 4–5.

At the surface of weathered sulfate-rich crusts on copper alloys, it would appear that ionic dissolution reactions predominate, rather than electrochemical reactions such as the dissolution of cuprite or copper. The direct electrochemical dissolution of copper or cuprite, which is usually found near the metal interface, is hindered by the thickness and convoluted nature of the crust. At the metal-corrosion interface, however, a different series of reactions takes place, modified by the chloride ions which appear to concentrate often in this zone, and by the available copper-sulfate-rich solution that has permeated through the crust.

Past models for these phenomena have suggested that bulk aqueous-phase reactions occur throughout the corrosion films on copper alloys. The present work indicates that the outermost sulfate-rich layers will supply ions to the aqueous front from heavy rain or other condensation and then serve as sites for solidification as the aqueous phase dries out and evaporates at the surface.

This work also suggests that the reactions and transformations that occur during the relatively dry periods of exposure, when the main mass of pollutant anions and cations are deposited, are equally important. In these situations, the extensive regions of hydration that form around basic copper-sulfate crystals would include (in their outer, last-to-solidify faces) the very soluble chlorides and nitrates. These outer zones would then be the first to redissolve in the presence of additional water. While one would expect some of this material—which is mechanically soft and friable—to be eroded in rainstorms, hydrated and disordered crystalline forms would allow for the accumulation of anions on drying, increasing with time, and providing the copper-rich and anion-rich solutions that stabilize and build the cuprite layer.

It is clear from the wet-and-dry cycling experiments and from the precipitation experiments that the transition of brochantite + acid = antlerite does not easily occur in corrosion crusts by gross aqueous-phase reaction, even over periods of several months. Rather, it would appear that the transformation of brochantite to antlerite



is not kinetically favored at 20–23 °C. Similarly, the transformation of  $\text{Cu}_2\text{O}$  to antlerite does not appear to be favored near 20 °C. This transformation would be:



In the authors' work to the present, which has not strictly duplicated the full range of conditions described in typical Pourbaix-type diagrams at 20 °C, the only laboratory evidence for antlerite formation appears in the cycling experiments, where in low-pH solutions (pH 3) antlerite was found to grow in association with brochantite on copper substrates. In these samples, the presence of a cuprite layer over the copper is evident under the microscope. At lower pH (2.75 and 2.5), with the initial absence of  $\text{Cu}^{++}$  ions in solution, both chalcantite and bonatite develop with time.<sup>25</sup> Using the precipitation experiments described, further aging experiments are currently underway to determine whether much longer periods (six months to one year or more) are necessary for the development of antlerite at 20 °C, as well as experiments at higher temperatures (35–40 °C), which appear to favor antlerite formation.

In summary, the zones of stability predicted for antlerite and brochantite at 20 °C by thermodynamic calculations for the  $\text{Cu}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$  system have not been observed for well-crystallized mineral specimens. It is likely that weathered corrosion films in polluted atmospheres are even less well behaved, particularly with respect to the observable (real-time) events of dissolution and precipitation in a corrosion crust. In the analysis of corrosion processes in sulfate-rich environments, strict adherence to thermodynamic considerations appears to produce a misleading picture of the sequence and nature of the precipitation and dissolution of the corrosion layers, in which a number of complex hydrated species may exist. This complexity discourages the usefulness of antlerite as an indicator of corrosion aggressiveness, though its existence cannot be denied in corrosion films from monuments sited in polluted urban atmospheres (in temperate zones), nor can its high sulfate content be overlooked.

## A C K N O W L E D G M E N T S

The authors gratefully acknowledge that part of this work was conducted with the support of the National Park Service (NPS Bronze Statues subcontract no. B104985-3) administered by Susan Sherwood and Jan Meakin, the latter at the University of Delaware. Also we want to especially thank Karen Fried for her tireless work in quantifying the XRD data; and Elizabeth Pirrotto, Nancy Heller, and Michelle Barger for their help in running samples.

## N O T E S

1. See also Holm and Mattsson 1980:85–104.
2. After Mattsson 1982:16.
3. See also Mattsson 1982:17. No antlerite region is drawn in his  $E_{\text{H}}$  versus pH diagram. Also Leidheiser, Jr. (1971:3–24) omits antlerite as a stable corrosion species in his discussion of long-term atmospheric corrosion.

4. The role of dry deposition has until recently been understated in analyses of corrosion processes in the atmosphere (Dolske and Meakin 1991:A-13). The graph from Graedel 1987b:759 indicates that dry deposition may account for two-thirds of the sulfur dioxide that comes in contact with a metal surface. In urban-industrial environments, the surfaces of copper-sulfate corrosion crusts are hygroscopic, a property that probably facilitates SO<sub>2</sub> incorporation into the crust. In and near marine sites, chlorides play an important role in the rate and formation of corrosion crusts on copper-based metals. At marine sites, chloride deposition rates of 0.3–300 mg Cl<sup>-</sup>/m<sup>2</sup>/day have been cited by Mattsson (1982:10) in comparison with the following SO<sub>2</sub> rates in mg/m<sup>2</sup>/day: rural 0–30, urban up to 100, and industrial up to 200. Some esoteric but less dominant factors are described by Cobb and Gross (1969:796–804) and Leidheiser (1971:71–75), including thermogalvanic effects.
5. The selective attack on the alpha phase in bronzes exposed to the atmosphere has been previously noted by Leoni (1977:245) and by Lins (1992). The phase boundaries of the system Cu–SO<sub>3</sub>–H<sub>2</sub>O have been studied repeatedly in work by Tunell and Posnjak (1929:1ff), Pourbaix and his colleagues (1966:385–92; 1949:53–81; Bustorff and van Muylder 1964:607), Silman (1958), Garrels (1960:50–71), Yoon (1971), and more recently by Graedel et al. (1987), Woods and Garrels (1986a, 1986b), Williams et al. (1990), and Livingston (1991).
6. Silman indicated that within the parameters of the system he considered a stability zone for antlerite as only one log (a<sub>Cu<sup>++</sup></sub>) unit wide. For example, the limiting activity for cupric ions at the boundary between antlerite and chalcantite at point \* (where log SO<sub>4</sub><sup>=</sup> = 24, log CO<sub>2</sub> = 25, and log a<sub>Cu<sup>++</sup></sub> = 0) is: (log a<sub>Cu<sup>++</sup></sub>) + 1 = (0) + 1 = 1.
7. Values given for the range of H<sup>+</sup> and principal anions in rain, fog, and dew are numerous and show considerable variation (Graedel and Schwartz 1977:17–25).
8. Among the most relevant references for this study are: Bockris and Enyo 1962:1187; Elwakkad 1950:3563; Fenwick 1926:860; Giles and Bartlett 1961:266; Guthrow and Miller 1966:415; Halpern 1953:421; Hill 1953:345; Hurlen 1961a–c; Ives and Rawson 1962a:447; Ives and Rawson 1962b:452; Ives and Rawson 1962a–d; King and Weidenhammer 1936:602; Kruger 1959:847; 1961:503; Kruger and Calvert 1964:1038; Lal and Thirsk 1953:2638; Lambert and Trevoy 1958:18; Lu and Graydon 1954:153; Mattsson and Brockis 1959:1586; Miller and Lawless 1959:854; Näsänen and Tamminen 1949:1995; Petit 1965:291; Porterfield and Miller 1966:528; Robertson et al. 1958:569; Royer, Kleinberg, and Davidson 1956:115; Russel and White 1927:116; Scott and Miller 1966:883–86; Topham and Miller 1966:421; Tourky and Elwakkad 1948:740; Wadsworth and Wadia 1955:755; and Weeks and Hill 1956:203.
9. Kruger (1961) suggests that near neutrality CO<sub>2</sub> may allow soluble tenorite to be reduced to cuprite in very pure water solutions.
10. See also Yoon 1971:9, 41, 48–49; Gregory and Riddiford 1960:952; Cocleugh and Graydon 1962:1370–72; Bjorndahl and Nobe 1984:82–87; and Hurlen 1961c:1246.
11. This is the authors' observation, illustrated repeatedly in conservation work. See also Miller and Lawless 1959:859; Cathcart and Peterson 1968:595–97; Bambulis 1962:1130–34; Marchesini and Badan 1979:206; Marabelli 1992; Langennegger and Callahan 1972:252–53; and Finnegan et al. 1981:256–61. The authors found that thin films of cuprite on very short-term exposures retarded the rate of dezincification. It is

clear that near 20 °C the rate of cuprite growth is many orders of magnitude greater in solution than in air. See also Krishnamoorthy and Sicar 1969:734–36, and Roennquist and Fischmeister 1960:65–75.

12. See also City of Philadelphia Department of Public Health 1987.
13. Additional work has been carried out in this area in recent years. Among the most pertinent studies for the weathering of monuments has been the work carried out at the Bell Laboratories, summarized in part in Franey 1987:306–14.
14. Few differences were observed in a seven-year exposure test between samples ranging in hardness from 45 to 120 HV and of varying surface roughness. The time of wetness, determined by the angle of exposure, was more significant, the more horizontal and slow-drying coupons corroding faster than the vertical ones.
15. After Graedel 1987:728.
16. In one experiment, 1.0 cm × 7.5 cm coupons of 90 Cu 10Sn bronze were suspended in excess sulfuric acid solutions (pH 5), with and without oxidant in the form of hydrogen peroxide (5% by weight), at 20–23 °C. The solutions were replenished weekly; the spent solutions were saved for atomic absorption analysis. In addition, coupons of 85-5-5-5 bronze (analyzed by XRF, Kevex Analyst 8000 System, data shown in table below), both patinated and polished to 400 grit, were suspended in research-grade air (MG Scientific Ultra Zero Grade, less than 0.1 ppm THC) raised to 75% RH by bubbling through deionized water to which nitric acid at pH 2, 3, 4, and 5 were added. The exposure chamber, divided into four equivalent volumes of 20 × 20 × 20 cm, was fitted to a permeation tube (Kin-Tek) that delivered 1.0 ± 0.1 ppm sulfur dioxide gas under flow conditions of 2.4 L per minute at 20–20 °C. Initial composition of coupons suspended in acidic atmosphere:

<i>XRF analysis</i>	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Sn</i>	<i>Fe</i>	<i>Sb</i>	<i>Ag ppm</i>
as polished	85.42	5.58	4.35	5.12	0.14	0.11	443
patinated	85.28	5.49	4.57	5.15	0.14	0.13	525

The coupons were all examined directly by insertion into an X-ray diffractometer (Phillips 1840). Those immersed in acid solutions were examined after 25 days, 69 days, and 7 months of exposure. Those exposed to the acidic gas environment were examined after 500 hours and after an 8-month interval. The solutions were analyzed for copper ions by atomic absorption spectrometry (Perkin-Elmer 303). The calibration standards were prepared by dissolving 99.999% Cu in ACS-grade nitric acid and diluting with deionized water (>2MW resistivity, from Continental dual-bed cartridges with carbon filter) to 1, 2, 4, 8, 10, and 12 ppm for the atomic absorption work, with deionized and synthetic-rain blanks. The pH measurements were made with a glass electrode (Orion research-grade 910100) and the double-junction-reference electrode on a Fisher 910 meter and on a Fisher 800 meter.

17. Much of Vernon's work was undertaken at 500,000–1,000,000x the ambient level of SO<sub>2</sub> (12 ppb) in Philadelphia air (City of Philadelphia 1987). Graedel and Schwartz (1977:17–25) state that in 17% of 447 measured sites, the SO<sub>2</sub> concentration was found to average 0.020 ppm or higher.

18. After storage for one year (45–55% RH and 70–76 °F), basic copper nitrate had crystallized on the surface of the pH 2 sample, though this very soluble form was not detected as a crystalline phase immediately after exposure in the chamber.
19. Courtesy of Ward's Scientific Department.
20. Courtesy of the University of Delaware Department of Geology, Mineral Collection.
21. Taken by averaging the data for 31 rain events recorded in the Philadelphia area varying in pH from 3.40 to 5.91 with average pH of 3.84 and the following concentrations of ionic species in microequivalents per liter: H<sup>+</sup> 143, NH<sup>4+</sup> 58, Ca<sup>++</sup> 73, Mg<sup>++</sup> 30, Na<sup>+</sup> 31, K<sup>+</sup> 11, Zn<sup>++</sup> 8; SO<sub>4</sub><sup>=</sup> 219, NO<sub>3</sub><sup>-</sup> 98, Cl<sup>-</sup> 24. The synthetic-rain solution was composed of the following in micromole/l: zinc sulfate 4, calcium sulfate 36.5, ammonium sulfate 29, sodium sulfate 9, magnesium nitrate 15, potassium chloride 11. All salts were 3 N or purer. The pH was adjusted by adding a 1:1 volume mixture of 0.02 N sulfuric and 0.01 N nitric acids (ACS grade).
22. The solutions in Section 1 were analyzed for copper ions by atomic absorption (Perkin Elmer 303). Sections 2 and 3 used cupric ISE measurements for Cu<sup>++</sup> assays (ISE Orion 94-29 with a double-junction Ag/AgCl reference electrode Orion 900200 on a Fisher 910 Isomet meter with digital readout to ±1 mV). The calibration standards were prepared by dissolving 99.999% Cu in ACS-grade nitric acid and diluting with deionized water (>2 MW resistivity, from Continental dual-bed cartridges with carbon filter) to 1, 2, 4, 8, 10, and 12 ppm for the atomic-absorption work, with deionized blanks and synthetic-rain blanks. The standards were to 0.1 ppm, 1 ppm, 10 ppm, 100 ppm, and 1000 ppm for the ISE analysis; for ISE measurements, calibration curves including blanks were run before and after each measurement. The pH measurements were made with a glass electrode and the double-junction-reference electrode mentioned previously.
23. Prior to use, all solids were assayed by atomic-absorption and emission spectroscopy, optical microscopy, and XRD. The emission spectroscopy results (Baird Spectrograph, 3m path length with 15,000 lines per inch grating, alternating-current [ac] arc at 1,100 V and 3–4 A for 30 seconds, plate set for the range 230–375 nm) indicated that the Cu and Cu<sub>2</sub>O were primarily copper with impurities at less than 10 ppm, while the principal contaminants for antlerite were Si and Al at or below 1% by weight, and for brochantite Ag (1–5%), Fe (0.1–1%) and Mg and Si at less than 0.1%. The atomic-absorption yields for Cu and Cu<sub>2</sub>O were 95% or better following digestion in hot, concentrated HNO<sub>3</sub>; the yield for the cleaned antlerite samples was 95 ±3% and for cleaned brochantite 96 ±3%. Copper (alpha copper, JCPDS no. 4-667) was identified in the cuprite sample at a level below 3%. The copper sample did not show an oxide layer in the analysis, indicating only that the layer was below the level of detection by the instrument. Prior to cleaning, the detectable contaminant phases in the antlerite were alpha quartz, beta-CuAlO<sub>2</sub>, kyanite, alumina, pyrope (Mg<sub>3</sub>Al<sub>3</sub>[SiO<sub>4</sub>]<sub>3</sub>), and cuprite; the brochantite sample contained detectable amounts of cuprite, chalcopyrite, covellite, and stromeyerite.
24. An example of the raw data is included in Table 10.
25. Which phase was detected was probably an artifact of preparation caused by gentle warming of the samples (usually <40 °C) to drive off excess moisture prior to XRD analysis.

TABLE 10. Raw data from dissolution and kinetic studies of antlerite.

Species/pH	Date	Titration		Intermediate	Final	H <sup>+</sup> consumption		Cu <sup>++</sup> μM/L
		1°	15m	8 m	1 y	15 m	1 y	15 m
Ant 2.5	(5/90)	2.51	3.01	4.88	4.94	2.16 mM	3.15 mM	790
Ant 2.75	(5/90)	2.75	5.2	5.24	5.15	1.77 mM	1.77 mM	830
Ant 3	(5/90)	3.0	5.4	5.56	5.51	996 μM	997 μM	690
Ant 3.5	(5/90)	3.5	5.6	5.71	5.61	313 μM	313 μM	190
Ant 4	(8/1)	4.0	5.65	6.49	6.23	97 μM	99.5 μM	85
Ant 4.5	(8/1)	4.5	6.10	6.35	6.23	30.8 μM	31.0 μM	40
Ant 5	(8/1)	5.0	6.18	6.43	6.42	9.3 μM	9.6 μM	40
Ant 5.5	(8/1)	5.5	6.34	6.44	6.49	2.7 μM	2.8 μM	15
AntAR 2.5	(8/6)	2.50	3.01	4.82	4.81	2.18 mM	3.14 mM	535
AntAR 2.75	(8/6)	2.75	3.81	5.10	4.95	1.6 mM	1.77 mM	771
AntAR 3	(8/6)	3.00	5.08	5.30	5.05	992 μM	991 μM	425
AntAR 3.5	(8/6)	3.50	5.53	5.89	5.40	313 μM	312 μM	165
AntAR 4	(8/6)	4.00	5.84	6.40	5.47*	99 μM	97 μM	42
AntAR 4.5	(8/3)	4.50	6.20	6.27	6.10	31 μM	30.8 μM	37
AntAR 5	(8/3)	5.00	6.27	6.46	6.41	9.5 μM	9.6 μM	19
AntAR 5.5	(8/3)	5.32	6.28	6.37	6.38	4.3 μM	4.4 μM	14
AntISA 2.5	(8/3)	2.52	3.27	4.84	4.89	2.48 mM	3.02 mM	1071
AntISA 2.75	(8/3)	2.75	4.36	5.36	5.46	1.73 mM	1.77 mM	818
AntISA 3	(8/3)	3.00	5.13	5.54	5.52	998 μM	997 μM	661
AntISA 3.5	(8/2)	3.50	5.43	6.31	6.03	312 μM	315 μM	212
AntISA 4	(8/2)	4.00	5.87	6.16	6.03*	98.4 μM	99.2 μM	66
AntISA 4.5	(8/2)	4.50	6.07	6.42	6.43	30.7 μM	31.2 μM	34
AntISA 5	(8/2)	5.00	6.35	6.55	6.56	9.6 μM	9.6 μM	14
AntISA 5.5	(8/2)	5.50	6.44	6.37	6.65/.49	2.8 μM	2.8 μM	19

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# The Technology of Medieval Jewelry

J A C K O G D E N

Despite the extensive research carried out on ancient goldsmithing technology over the last half century, the techniques of medieval goldsmiths have been largely ignored. The following is a preliminary examination of various technical aspects of medieval goldwork, including a comparison of medieval technology with that of Roman and earlier periods. In general, most techniques remained constant. One major exception, however, is the widespread use of drawn gold wire by about the ninth or tenth century C.E. This technique opened up new possibilities for decorative filigree methods which were used to advantage by medieval goldsmiths. Thus an understanding of technological developments is of primary importance for the stylistic study of medieval European gold jewelry.

## E A R L Y M E D I E V A L P R A C T I C E S

Until about 1500 C.E., medieval jewelry techniques in Western Europe, particularly Britain, were related in a multitude of ways to the techniques of their Classical and Byzantine predecessors. Although the stylistic development of jewelry is not the principal concern here, it is important to note that material and technique do influence style to a considerable extent. For example, changes in the style of filigree work—of paramount importance in characterizing jewelry development in the medieval period—cannot be fully considered without understanding the various manufacturing options available to the goldsmith.

From the point of view of the jewelry historian, the distinction between ancient and medieval is based more on terminology than any real discontinuity. A Hellenistic goldsmith could pick up a medieval jewel and be familiar with most of its technology and the sequence of manufacture; the goldsmith might be surprised mainly by the novelty of design and the use of drawn wire. Even the workshops would have been comparable. Wall paintings of jewelers' workshops as seen in the houses of the Vetii at Pompeii, for example, differ little in their essentials from Renaissance or even

more recent depictions; the same types of tables, furnaces, anvils, and scales are present.

The medieval period has provided a range of representations of goldsmiths and jewelers at work. Some are religious paintings, such as Taddeo Gaddi's fourteenth-century *St. Elgius as a Goldsmith*, now in the Prado, Madrid. Others illustrate technical treatises, such as the mid-fifteenth-century manuscript of Pliny's *Natural History* preserved in the Victoria and Albert Museum, London (Whalley 1982). This latter manuscript, for example, has a rare depiction of a lapidary drilling precious stones with a pump drill. Representations of jewelers' shops are less common; however an engraving of a jeweler selling rings, plus some rather unorthodox gemmological tests, may be seen in a late-fifteenth-century work by Johannis de Cuba (Kunz [1917: facing 343] 1973). Representations of workshop scenes are far more prevalent from the sixteenth century onward.

Medieval documentary references to goldsmiths are quite common. The prime source is the German monk Theophilus, who compiled a comprehensive account of goldsmithing procedures in the first half of the twelfth century C.E. The third book of his *Treatise on Divers Arts* begins with details on how to construct a workshop and equip it with tables, seats, and forges, and then describes the individual tools and their use. Theophilus is now generally taken to be the pen name of Roger of Helmarshausen, a goldsmith-monk who actually left samples of his work, such as a book cover now in the Domschatz Trier (Ronig 1984: cat. no. 65; Hawthorne and Smith 1979: pl. 8). The identification of Theophilus with Roger of Helmarshausen and the dating of the treatise have been most recently discussed by Dodwell ([1961] 1986) and Hawthorne and Smith (1979).

Near-contemporaries of Theophilus include Jean de Garlande of about 1200, who briefly mentions goldsmiths. He writes that "the craft of these goldsmiths consists of hammering with little hammers on the anvil thin sheets of gold and silver and in setting precious stones in the bezels of rings for use by barons and noblewomen" (Cripps 1880:9). The Englishman Alexander Neckham (1157–1217) describes the necessary tools of a twelfth-century goldsmith (Neckham 1867). These include a forge with top chimney; bellows worked with one hand evenly and with light pressure; an anvil; forceps to hold metal during beating; a hammer for shaping gold; very sharp chisels and another chisel (possibly) for cutting stones, a touchstone to test metal; a whetstone to sharpen iron tools; a hare's foot (*pedem leporarium*) to smooth, polish, and clean gold; a leather bag around the waist to collect grains of metal "lest they vanish away"; a toothed saw (*serram dentatum*); and a file for gold (*limam aurifrigium*). It is interesting that there is no mention of wiredrawing equipment. A hare's foot seems an unlikely implement to use for polishing gold, but perhaps it was really used to clean the bench. Earlier this century Maryon advocated the use of the same implement: "The bench is swept several times a day with a hare's foot, which forms a convenient little brush to which the gold will not adhere" (1971:1).

Theophilus describes how different tools were made and shows that goldsmiths made their own equipment. This was true in antiquity and right up to modern times in many parts of the world. A regulation of the year 1513 states that goldsmiths should not work copper or brass apart from making their tools of the trade (Prideaux

1896–97:39). On this basis, many of the more complex or sophisticated implements, such as elaborate wiredrawing equipment or rolling mills, would be out of the question for small craftshops. The large, fully staffed, and impressively equipped workshops seen in Renaissance and later engravings could hardly have existed earlier outside of royal patronage or the main urban centers.

It was a common practice for goldsmiths to bequeath their tools to their sons, friends, or fellow goldsmiths. Sometimes wills list the tools in some detail. For example, the will of John Colan, a goldsmith of York who died in 1490, contains a comprehensive list of the goldsmith's equipment (Cripps 1914). It enumerates several varieties of hammers, stamps, swages, stakes, files, tongs, wiredrawing implements, a gold balance, and more. But one must not forget a vital truth about any craft: Tools are worthless unless manipulated by someone with skill and experience. As Biringuccio said at the end of his discussion of goldwork, "Having told you the general facts concerning the art of working gold and silver I think I have said enough about it. All the rest that is necessary depends entirely on ingenuity and practice" (Smith and Gnudi 1943).

Much documentary evidence for the medieval jeweler's trade derives from regulations defining their working practices and the limitations on the material they could use. Fraud by means of debased gold, plated base metals, filled hollow-sheet objects, and imitation stones were potential problems for the jewelry-buying public throughout history. Neckham said that the goldsmith should be able to "discern well the pure gold from the latten [brass] and copper lest he buy latten for pure gold" (1867).

Medieval English regulations stipulated that jewelers had to work in certain main streets, not in "lanes or alleys"; only very seldom was work in private houses allowed. Similar restrictions are laid down in the tenth century *Book of the Prefect* from Constantinople (Hendy 1985), and similar rules might well have been widespread. Goldsmiths should be visible, but the actual secrets of the craft should not be divulged (Prideaux 1896–97:doc. no. 44; 150). There are references to goldsmiths being punished because they allowed strangers to "see the privities of the trade" (Prideaux 1896–7:15–16; 22). In the early sixteenth century we are told that no goldsmith could work at night by candlelight or on Sundays.

There was clearly rivalry between goldsmiths. One was punished because he told a customer that a competitor's work was overpriced; another was castigated because he alleged that a rival did not know how to make a cup (Prideaux 1896–97:15–16). Successful goldsmiths could certainly become rich, and this meant they could also amass some gold and silver as stock in trade, rather than just working their patrons' materials.

It has been assumed that a master goldsmith would be skilled in all aspects of the trade (Lightbown 1978:84), but Biringuccio points out that such wide mastery was rare, and that in practice "one has his profession in engraving, another in the hammer, and another in mounting or setting jewels, and in making a ring well" (Smith and Gnudi 1943). There is little evidence for medieval specialization apart from mention of gold beaters in thirteenth-century Paris and enamellers, seal cutters, and burnishers in fourteenth-century London; the burnishers included women (Prideaux 1896–97:8).

In the sixteenth century, however, there is more evidence for specialization. Cellini lists several of his contemporaries and gives their specializations (Ashbee 1967:1–6). Gold wiredrawers are mentioned in 1512 (Prideaux 1896–97:38). In general, the specialized manufacture of components for the jewelry industry is a relatively recent innovation. The 1884 *Fifteenth Annual Report of the Royal Mint of London* states, “A new industry, moreover, is springing up for the supply of rolled or drawn metals to jewelers and dentists.”

By the early fourteenth century some distinction is made between wholesale and retail goldsmiths in Paris, and some English regulations appear to distinguish between a goldsmith selling to a merchant and selling to a member of the public. The cost of gold jewelry depended on the materials and labor costs, and these would usually be calculated and listed separately. This is an ancient practice. Plautus, in his play *Menaechmi*, written in about 190 B.C.E., has a dialogue between Menaechmus and a maid. The maid wants a pair of earrings as a gift, and Menaechmus says “sure, you provide the gold, I’ll pay for the workmanship.” The distinction continued through the medieval period and into the Renaissance. French documentary references to medieval jewelers often mention both the material cost and *la façon*. This is the same as the “fashion” we find in medieval and Renaissance English documents. Shakespeare reworked *Menaechmi* for his play *A Comedy of Errors*. In Shakespeare’s version, the plot involved the manufacture of a gold chain, the invoice for which lists everything including the “fashion.” Stubbes, writing in the 1580s, gives much of the same information in his description of goldsmiths’ tricks: “If you buy a chain of gold, a ring, or any kind of plate, besides it you shall pay almost half more than is worth (for they will persuade you that the workmanship of it comes to so much, the fashion to so much, and I cannot tell what)” (Stubbes 1583). This might seem to imply that workmanship and “fashion” were distinct, but all other indications are that they were one and the same.

Medieval French regulations actually stipulated that workmanship and materials costs should be distinguished on invoices and receipts (Cripps 1880:32–34). Stubbes indicates that the workmanship would be about 50 percent of the cost of the materials. We can obtain some idea of medieval equivalents. For example, a gold ring made for the Duke of Orleans in the mid-fifteenth century cost 14 pounds for the materials and 13 shillings for the manufacture; this means that the goldsmith received less than one-twentieth of the value of the materials he was working. Though low by modern jewelers’ standards and even by Stubbes’s margin, this is far higher than the goldsmiths’ profit margins defined in the maximum-price edict of Diocletian a millennia earlier (Ogden n.d.). On the other hand, other medieval documents show that manufacturing costs could easily be up to Stubbes’s level of 50 percent or more of the materials cost. Presumably, fees depended on the nature of the materials, the complexity of work, and the prestige of the individual goldsmith.

## C O M P O S I T I O N

Analyses of Anglo-Saxon and other Dark Age metalwork of the seventh century show that after about 625 C.E. coinage and jewelry alloys were sometimes debased to an

extraordinary degree; an alloy containing less than 10% gold is not unusual (Hawkes et al. 1966). There is little published information on the composition of Western European goldwork after this date. Farther east, analysis of Byzantine jewelry shows that a high purity of around 91–92% (perhaps intended to be 22 carats) lasted through the late tenth century, at least. In addition, several gold objects from the tenth to twelfth centuries were found to contain about 80% gold—possibly relating to the gold hyperperon coin of that purity, which was introduced in 1092 and survived almost through the twelfth century (Oddo and la Niece 1986).

In early medieval Western Europe, a wide range of gold purities were used. The goldsmith would refine or debase the gold depending on a variety of factors; at one end of the scale were official purity requirements, at the other the whim or dishonesty of the goldsmith. Goldsmiths would have generally refined their own gold as and when needed. Medieval and early Renaissance sources such as the “Mappae Clavicula” and Theophilus (Smith and Hawthorne 1974), Cellini (Ashbee 1967), Pegolotti (1936), and Biringuccio (Smith and Gnudi 1943) all describe the refining of gold. However, a statute of 1488 says that “finers [refiners] and parters dwell abroad in every part of the realm,” which suggests that there were specialist refiners—perhaps mainly for silver—by the end of the medieval period (Cripps 1914).

Some tenth- to twelfth-century Western European goldwork certainly has the color of quite high purity gold, and gold is often referred to in contemporaneous documents as being of high purity. For example, objects are sometimes described as made of *aurum purissimum* (Lehmann-Brockhaus 1938). One may also find Western medieval and even Renaissance use of the Byzantine Greek term *obrysus* and its variants (e.g., *obrize*) as a description of pure gold. The tenth-century *Alfric's Vocabulary* defines *obrizum aurum* as “real gold.”

On the other hand, debasement was acceptable. The “Mappae Clavicula,” for example, describes an alloy suitable for making male figures that consisted of 67% gold and 33% silver (Smith and Hawthorne 1974). Female figures were apparently better suited to an alloy of just 20% gold with 80% silver. Even the purer of these two alloys has a high enough silver content to be described as electrum. Other recipes for electrum have survived (Gay [1887] 1928). In general, medieval texts clearly distinguish between gold, electrum, and silver, but one reference to “purest electrum” (*electrum purissimum*) might suggest that not all recordkeepers had a deep understanding of the nature of the alloy (Lehmann-Brockhaus 1938:no. 2551). Analysis of one English gold ring of twelfth century date showed that it was of 60% gold, 30% silver, and 10% copper—a precise ratio that might not be coincidental (John Cherry, personal communication, 1991).

The “Mappae Clavicula” also describes a red alloy with about 57% gold, 29% silver and 14% copper (Smith and Hawthorne 1974:ch. 54). Red gold, or gold alloyed with copper, is quite frequently mentioned in medieval European literature (Kuhn and Reidy 1963) and several extant early medieval ornaments are of distinctly reddish color. In the twelfth century Theophilus describes Arabian gold as having an exceptional red color, and says that workmen imitated its appearance by alloying a fifth-part copper to pale gold (Hawthorne and Smith 1979:ch. 47). Theophilus appears not to have realized that the natural alloy contains copper, and he notes that

the presence of copper was a sign of the spurious alloy. On the basis of the admittedly small number of medieval English gold rings studied, the copper content seems to exceed the silver content far more frequently than it does in ancient goldwork. Possibly the red Arabian gold was derived from Crusader gold coins, some of which contain almost 15% copper. On the other hand, the exploitation of Arabian mines is also certain. Al-Hamdani reveals that Arabian mines were exploited in the tenth century (Dunlop 1957), and European corroboration includes the “Song of Roland” which refers to “ten mule loads of gold dug from Arabian mines.”

The medieval jeweler generally obtained raw materials from a patron or with money provided by the patron; only rarely did a goldsmith amass enough capital to hold his own stock of precious metal. Gold sources usually included damaged or unfashionable objects returned for remaking. Medieval texts refer to goldsmiths purchasing gold jewelry for resale or reworking. An English charter of 1327 described goldsmiths “who keep shops in obscure streets, and do buy vessels of gold and silver secretly without enquiring whether such vessels were stolen or come lawfully by, and immediately melting it down, make it into plate, and sell it to merchants trading beyond the sea” (Jackson 1905:35). There were less conventional ways in which even the crown could obtain gold. In the fourteenth century “the gold from which the nobles of Edward III were coined was said to have been produced by occult sciences” (Freemantle 1870).

Coinage has long been a major source of gold for goldsmiths. There is documentary proof of this in Byzantine and early medieval times, if not earlier. Even in the nineteenth century, the annual report of the Royal Mint of London noted that “working jewelers are in the habit of making use of large quantities of sovereigns [a British gold coin of 22 carat gold] in the business of their trade, owing to the convenience of being able to obtain by this means gold of a known standard” (Freemantle 1870:24). There appears to have been no British law prohibiting the melting down of gold coinage to make jewelry prior to 1920.

Even if coinage was a main source of gold, the goldsmiths of medieval Europe could still have had to contend with widely differing purities. In the early fourteenth century, for example, Pegolotti of the great Florentine banking house of the Bardi, which had offices across Europe from London to Constantinople, produced a merchants’ handbook giving prices and trade details of many countries (Pegolotti 1936). The author lists no fewer than thirty-nine different gold coins that a fourteenth-century merchant might encounter (Pegolotti 1936:287–89). He lists their purity in carats, ranging from debased Tripoli coins of just 11 carats (45.8% gold) up to high purities such as French coins of 23.75 carats. (This is perhaps the earliest recorded European use of the term carats as applied to purity rather than weight.) The Troy ounce was divided, like the Byzantine solidus before it, into 24 carats, which was thus equated with pure gold; 18 carat is 75% gold, and so on. The carat standard of gold makes no distinction between the possible alloying materials. In ancient and medieval times these were typically silver and, to a lesser extent, copper. Today all manner of metals are added, some of which cause problems for goldsmiths.

Other coins listed by Pegolotti include Saracen bezants at 15 carats and *Bisanti vecchi d’oro d’ Alessandrie* at 23 carats. Recent analyses have indeed shown that

Islamic and Crusader bezants had a wide range of purities (Gordus and Metcalf 1980). In many ways, little has changed. The 1884 report of the Royal Mint published a list of the various purities of gold coinage issued by contemporary European mints (Royal Mint 1884) revealing variation even within countries—for example, the Austro-Hungarian 8 florin piece was 90% gold, the ducat of the same country was 98.5% gold.

It is hardly surprising that by the thirteenth century some of the authorities in Western Europe had seen the need to control the quality of gold worked and sold by goldsmiths. Such regulations could best be enforced through the goldsmith guilds that had existed in England at least since the twelfth century. In England the “Close Roll 22” of Henry III in 1238 concerning *de auro fabricando civitate Londiniarum* ruled that no one should use gold under a certain purity (defined by price) and that all work was to be carried out in the public street, “not in secret.” The same ordinance includes provisions about counterfeit and precious stones plus a ban on the gilding of copper and other base metals. In France, a regulation of 1268 states that “no goldsmith may work in Paris, unless it be of the touch of Paris or better: which touch surpasses all the gold of every part worked on the earth.” The “touch of Paris” was actually only 19.2 carats pure, that is, 80% gold. Perhaps the origin of this 80% standard is related to hyperperon coinage of similar purity, as well as goldwork from medieval Constantinople. The French regulations, like the English, include a ban on working at night (except on commissions for Royalty or the Bishop of Paris) and rule against the use of glass-imitation stones and doublets (Boileau 1837:38–39). The “touch of Paris” was also the minimum standard for gold jewelry and other wares allowed in a 1300 English statute of Edward I (Jackson 1905:7–8). According to the same source, goldsmiths were allowed to complete any work in hand made from poorer-quality gold, but if in future they purchased such objects, they had to be melted down and refined, not resold. Later the same century regulations of Edward III in England and John II in France reiterate that no goldsmith could work “gold worse than the touche of Paris” (Prideaux 1896–7:doc. no. 43; Cripps 1914).

A series of analyses of seventeen gold rings from thirteenth- and fourteenth-century Britain shows a wide variation in purity, from about 64 to 96% gold. There are, however, definite clusters at around 80 and 90% gold (both  $\pm 2.5\%$ ; John Cherry, personal communication, 1991). Clearly this could be a fertile area for research.

Gold standards were by no means uniform or necessarily followed. One English document of 1339, refers to “parti-gold” (debased gold). Apparently, various debased alloys were also allowed in certain regions of France. For example the Montpellier goldsmiths were evidently allowed to work 14 carat (58.3%) gold (Cripps 1914:22), and in Put-en-Velay, both 14 and 16 carat gold are found (Cripps 1880:16). It appears that itinerant dealers were still selling debased and unmarked goldwork all over France in the late fifteenth century (Cripps 1880:19). A Scottish statute of 1457 gives 20 carat (83.33%) gold as the minimum gold standard for coins (Cripps 1914:161).

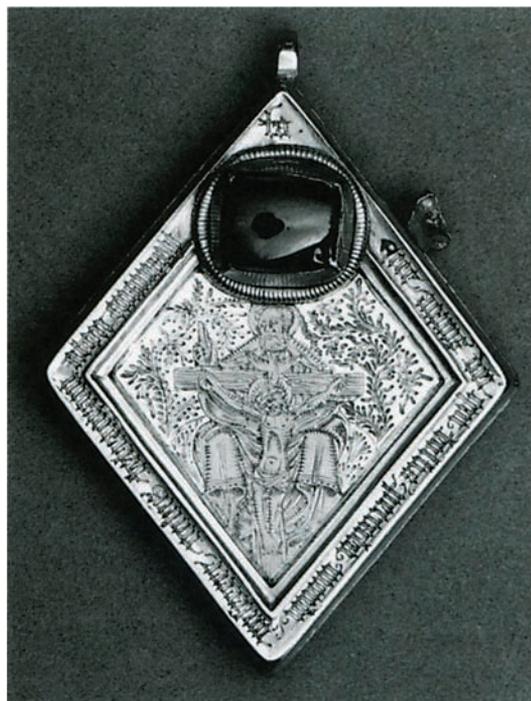
The jewelry standard was thus far lower than the contemporary English and French coinage standard of 23 carats, 3.5 grains (99.5%) that survived through the remainder of the medieval period. This is the defined purity of the gold trial piece

made as an assay standard in 1477 (during the reign of Edward IV) and described as being of 23 carats 3.5 grains of “perfect fine gold” (Ruding 1812). Chemical analysis of this same trial plate carried out in the nineteenth century showed it to be 99.35% gold, 0.5% silver, and 0.14% copper (Royal Mint 1874).

The minimum gold purity for jewelry was lowered in 1477 when a new regulation stated that “no goldsmith . . . shall work, sell or, set to sale any manner of base gold under the fineness of eighteen carats”; that is, 75% gold (Jackson 1905:12–13). Nevertheless, later in the century an Act of Parliament of Richard II made every goldsmith put his mark on his wares “because gold and silver, which is wrought by goldsmiths in England is often times less fine than it ought to be, because the goldsmiths are their own judges” (Jackson 1905:8–9). Too few analyses have been carried out so far to tell whether the new official 18 carat standard is reflected in the composition of late fifteenth-century gold jewelry from Britain. However, it should be noted that Middleham jewel (Fig. 1) is composed of an alloy with about 75% gold, although there is also [deliberate] gold enrichment up to about 86% in certain areas of the surface (John Cherry, personal communication, 1991). This can be seen in the darker color of the Trinity figures, compared to that of the design on either side. The next change in the gold standard—up to 22 carat (91.7%)—was not introduced in England, Scotland, or in France until the mid-sixteenth century.

The English statute of 1300 had included legislation to ensure compliance with the rules regarding gold purity: “Wardens of the crafts shall go from shop to shop among the goldsmiths to assay if their gold be of [that] touch” (Jackson 1905:7–8). “If gold found in the hands of a goldsmith or dealer is not worth the assay, in buckles, rings or other articles . . . these should be broken, and the man loose his work and rectify his gold” (Prideaux 1896–97:doc. no. 44). The purity of the gold was ascertained by “fire or touch,” that is by fire assay or by touchstone. The latter was

FIGURE 1. *The so-called Middleham jewel, a magnificent late fifteenth-century English gold pendant set with a sapphire, found near Middleham Castle in Yorkshire in 1985. The front of the pendant is engraved with a depiction of the Trinity, the back with the Nativity.*



the simplest and “good stones and good needles for to touch be always there ready . . . to make assay of gold of the carat between the merchants and the said master” (Combe 1806). If the gold was not up to standard, it should be “new molten and reformed until it be put to point.” Similar rules also applied to stones. Real stones could not be set in base metal, while false (i.e., glass) stones found set in gold were to be broken up and “ground in a mortar” (Prideaux 1896–97:doc no. 44). Notes in the records of the Worshipful Company of Goldsmiths refer to goldsmiths who produced substandard goldwork; this must have been a perennial problem.

We can imagine that similar regulations—in particular restrictions on the manufacture and sale of substandard gold objects—would be enforced as universally as local circumstances allowed. The tenth-century *Book of the Prefect*, dealing with bankers and precious-metal merchants in Constantinople, ruled that those who debased bullion and worked and sold it would have their hand cut off (Hendy 1985:251–53). This set of regulations from Constantinople also contains similar limitations as to places and times of work as found in the later English and French regulations. Possibly the Western regulations derived from the East.

The purity standards were, of course, minimum levels and quite possibly some goldsmiths might have preferred to use gold of higher purity. Certain types of work might have demanded certain purity levels. In the early sixteenth century Cellini notes that gold under 22.5 carats was too hard for fine work and dangerous to solder, while gold over 23 carats was a bit too soft (Ashbee 1967). In recent times jewelers have considered 22 carat gold ideal for fine work. Cellini’s ideal was between about 92.5 and 96% pure; this is a fairly precise demand, but within the level of accuracy possible with experienced use of the touchstone. A common purity range for much Hellenistic, Roman, and Byzantine goldwork is 92.5–96%. Some medieval Byzantine goldwork seems to vary in composition depending on function. For example the ninth-century Byzantine gold cross in Tournai is made of sheet gold which is between 90 and 92% gold, whereas the bordering beaded wire, more prone to wear, has a slightly higher silver content (de Cuyper et al. 1987). Biringuccio in his *Pirotechnia*, book 5, chapter 2, noted that silver added to gold will harden it, but in general he seems to have had a cavalier approach to debasement. He notes that if you were a goldsmith you might debase gold with silver if you “begrudge the expense of having it fine, or if you find that you do not have enough, or if you do not care about such fineness” (Smith and Gnudi 1943).

## T E C H N O L O G Y

### Sheet Gold

Goldwork was characteristically manufactured from hammered sheet gold and rarely by casting. Hammering has thus always been one of the trademarks of the goldsmith and the most commonly illustrated and described of the goldworker’s skills. Changes in the process include the introduction of the hafted hammer for metalwork in the first millennium B.C.E. (Ogden 1982:34). This can probably be linked to the recent research by Nicolini and Bouchet (1990), who used the scanning electron microscope

to distinguish between “primitive” or “vertical” hammering of ancient gold and the “progressive” hammering that they contend gradually replaced it.

The greatest potential change in the manufacture of gold sheet came after the period considered here, with the invention of the rolling mill, which rolls the metal between two iron or steel rollers. The invention is accredited to Leonardo da Vinci, who provided a sketch for one (Uccelli 1948). There is no evidence for rolling mills prior to the Renaissance, and these devices were probably rare in ordinary jewelry workshops for several centuries afterward. The earliest apparent documentary reference to rolling sheet gold dates from the seventeenth century (Singer et al. 1957:342). The eighteenth-century *Encyclopédie* of Diderot shows a simple hand-rolling machine for use by jewelers (Diderot and d’Alembert 1751–57:pl.6:25), but his and other contemporaneous workshop scenes are still filled with workers hammering out gold and silver sheet.

The various methods of raising and shaping sheet gold have been described in detail elsewhere; the medieval smith had no major new process at his disposal. Numerous tools, including dies and punches, have survived from the Viking and later worlds. Cellini describes the casting of copper-alloy dies and formers and the use of simple tools of wood and bronze for working sheet gold (Ashbee 1967).

Hollow sheet gold often needs to be filled to provide support and weight. Sulfur was typically used in late Hellenistic, Roman, and early Byzantine gold jewelry but does not appear to have survived into medieval times in Europe, although it is possibly present in some medieval Islamic goldwork. The suitability of the melting temperature and flow properties of sulfur are noted by Biringuccio. Pitch or a pitch-like substance was also used as a filler in early Islamic jewelry (Ogden 1987) but has not been recorded so far in medieval European goldwork. However, pitch or resin might well be expected since pitch is still a common filling material in flimsy modern sheet silver objects. From around the twelfth century onward, filled hollow sheet-gold jewelry was often forbidden in Western European statutes; thus filled hollow work became far rarer than it was in Byzantine or earlier times.

## Cutting

Sheet gold was normally cut with chisels, as in antiquity, or with small shears or scissors. The use of scissors or small shears for goldwork in antiquity is generally doubted, and the presence of the tool marks from such implements on purported ancient goldwork is usually taken as a warning sign. However, fine cutting implements of this type came into common use during the course of the early medieval period. Theophilus describes the use of both scissors and shears for cutting metal in his chapters 23, 52, and 76 (Hawthorne and Smith 1979); and a fifteenth-century Greek manuscript, derived from earlier texts, refers to the use of small scissors to cut small pieces of solder (Berthelot 1888:no. 39). Shears are shown being used by a metalworker in an illustration from a mid-fifteenth century manuscript of Pliny’s *Natural History* (Whalley 1982).

The fine almost lacelike pierced work of the late Roman and early Byzantine periods does not survive long into the medieval period. Some cruder pierced goldwork may be found, such as that around the side of the Alfred jewel and on several elements of the Egbert Shrine in Trier (Westermann-Angerhausen 1973:figs. 60–64, 66–69, etc.). Theophilus describes a type of pierced work using a chisel and small files which he terms *opus interrasile*. This term, found only in Theophilus, has also been used by modern historians to describe the finer Roman and Byzantine varieties of pierced goldwork. This terminology has its critics, however (Ogden and Schmidt 1990).

Files are mentioned by Theophilus many times, in relation both to their manufacture and use. His near-contemporary Alexander Neckham includes them in his list of essential goldsmith's tools. Files were used in the manufacture of tools and also in some shaping and fitting operations, though perhaps more commonly for silver rather than gold. By their very nature, files remove metal, and thus are to be avoided where possible when working gold. The use of files on goldwork in antiquity is usually doubted, while sure indications of the employment of such a tool is often taken as an indication of a post-ancient origin. In his chapter 26, Theophilus describes the use of a file to smooth the surfaces and edges of a silver chalice (Hawthorne and Smith 1979) and for similar purposes on other silver components, including niello work and openwork. Theophilus's "very small files—square, round, half-round, three-cornered, and flat and thin" do sound like the files found in modern jewelers' workshops (Hawthorne and Smith 1979:94). Cellini describes numerous small files and engravings of jewelers' workshops of the sixteenth century and later can show an assortment of such tools (Ashbee 1967).

The only saw mentioned by Theophilus is an iron saw, fed with sharp sand, used to cut rock crystal. The twelfth-century "Mappae Clavicula" manuscript similarly mentions a copper saw fed with saliva and emery powder for cutting gemstones (Smith and Hawthorne 1974:ch. 191a). In neither of these cases would a toothed saw be implied. Saws with teeth, probably used mainly for cutting wood, were thought by the Romans to have been invented by Daedalus but actually date back to the early Bronze Age in the Near East. For example, copper saws have survived from the First Dynasty of ancient Egypt (Lucas and Harris 1962:449). The use of a toothed saw for cutting gold is highly unlikely in medieval times, as it would result in lost metal and almost certainly would be too coarse for fine work. Nevertheless, Alexander Neckham, writing in the twelfth century, does include a toothed saw (*serram dentatam*) among the equipment to be found in a goldsmith's workshop (Neckham 1867). The jeweler's saw used by craftsmen today would no doubt have been appreciated by medieval goldsmiths, but it is hard to imagine that fine, handmade iron-piercing saws would have been worth the time and effort prior to their mass production and resulting affordability. They were difficult to make by hand and, like their modern mass-produced counterparts, all too vulnerable to fracture. Until good evidence exists to the contrary, the presence of characteristic parallel-sided, fine saw marks on gold or silver work purported to date from the Renaissance or earlier times should be viewed with great caution.

The early medieval period saw the introduction of wiredrawing—an innovation that was to have a widespread effect on both the construction and design of jewelry. Prior to this period, gold wire was generally formed by hammering—a process better suited to relatively large-diameter wires such as earring hooks—or by twisting narrow gold strips and then rolling the twisted wires to compact them. Wires of this general type have characteristic spiral seam lines, so to speak, along the wire, the number and spacing of which largely depend on the ratio of width to thickness of the original strip. The resulting wires have been classified under various names, including “strip twisted” and “block twisted,” but I prefer to use the generic term *strip twisted* for all such wires. The various ancient technologies for making such twisted wires and their chronology have been dealt with at length by several authorities and will not be discussed here (Oddy 1977; Ogden 1991). Suffice it to say that the majority of wires in gold jewelry made prior to early medieval times show the characteristic spiral seam lines resulting from their twisted construction.

In wiredrawing, a rod or metal strip is pulled through consecutively smaller holes in an iron or steel drawplate; thus, it is literally drawn out in longer and thinner wires. Simple hand drawing, with strong forceps or tongs and a drawplate mounted on a sturdy piece of wood, is seldom practical for wires over about 2 mm in diameter. More complex drawing machines—termed *draw benches*—provided greater leverage and strength and allowed long lengths of wire to be made in a great variety of diameters.

The use of drawing for the production of Roman and pre-Roman gold wires has not been demonstrated despite the microscopic examination of thousands of ancient ornaments. On the basis of current knowledge, it is possible to conclude that gold wiredrawing probably first appeared in the Western world in about the seventh or eighth century C.E. Pre-seventh-century examples of drawn gold wire from Europe or the Mediterranean world have not yet been identified with certainty (Ogden 1991). The use of certain drawn wire on Korean gold earrings of the fifth to seventh centuries C.E. might suggest that the origins of wiredrawing lie in the East (Ogden 1991).

Duczko's study of Viking filigree work has demonstrated the general adoption of wiredrawing by the ninth century C.E. (1985). More recently Whitfield (1990) studied the various surviving drawplates and examined many examples of northern European filigree work. She concludes that wiredrawing was used in Northern Europe by around 800 C.E. According to Craddock (Youngs 1989), Celtic gold wires of the sixth to ninth centuries were made by twisting. Duczko's work on Viking jewelry has not found drawn wire dating from before the ninth century. On the other hand, it would be surprising to find that the braided silver wires on the eighth-century Derrynaflan paten were not drawn. The braided Trichinopoly work (named after the town in India where this type of braided chain was a traditional craft) of the ninth-century Trewhiddle silver scourge is certainly drawn (Fig. 2).

A well-known lunate earring type that straddles the Byzantine and early Islamic world, and which can be dated fairly accurately to the tenth century C.E., sometimes



FIGURE 2. Detail of drawn silver wire from the scourge in the Trewiddle hoard. Anglo-Saxon, 870 C.E. British Museum, MLA 80.4-10.4.



FIGURE 3. A gold lunette earring exemplifying a well-known Byzanto-Islamic earring type dating from the tenth century C.E. This earring incorporates drawn round wire and spiral-beaded wire. The loops originally bore pearls.

includes drawn wire (Fig. 3). Drawn and strip-twisted gold wires have both been noted in Fatamid Islamic work of the eleventh century (Ogden 1987). Current research in progress by the author suggests that drawn wire was the most common type used for Fatamid work and that examples of this work presumed to be strip-twisted should perhaps be reexamined.

The earliest description of wiredrawing might lie in a Greek compilation of goldsmiths' recipes. The surviving manuscript dates from 1478 but is almost certainly, for the most part, a copy of far earlier sources (Berthelot [1888] suggests possibly the eleventh century and earlier). This provides a good, but sadly ambiguous early account of drawing silver wire: "Take fine silver, hammer it and cut it into strips and twist [?] it with a rounding [?] iron [?]. Then put it in the drawplate and draw once" (Berthelot 1888:doc. no 33). The part about the "rounding iron" (perhaps roller) is unclear; the original Greek is **και γυσε το εις σιδερον στρογγυλον**. The Greek word used for drawplate is **συρτεν**.

The earliest datable description of wiredrawing is by Theophilus in the twelfth century. His book 3, chapter 8 describes the manufacture of the iron plates through which wires are drawn. Once into the thirteenth century, many documentary references to drawn wire may be found; for example, *filum auri tractum* (Lehmann-Brockhaus 1960:nos 2741, 2743, 2745). Thirteenth- and fourteenth-century English literary texts often refer to gold wire. Although these are almost invariably poetic descriptions of a heroine's hair, the allusion would better suit fine-drawn gold wire than shorter lengths of strip-twist wires. From the second half of the thirteenth century, details of iron and brass wiredrawers in Paris (Boileau 1837:61–63) and a reference to what may be a corporation of gold wiremakers may be found in a document dealing with "Des Batteurs d'or et d'argent à filer." It has been assumed that these were gold wire drawers, and certainly they are distinct from the beaters of gold foil, which are described separately (Boileau 1837:74–78). Unfortunately, the word "filer" could apply to gold threads as well as wires; and the mention of striking with a hammer in the text perhaps makes gold threadmakers more likely than wire-drawers.

Wiredrawing and some quite complex wiredrawing machinery are described at some length by Biringuccio in the early sixteenth century. He notes that wire "can be made in any thinness and length that the craftsman wishes, especially that which is made of gold and silver" (Smith and Gnudi 1943).

The earliest surviving representation of wiredrawing is probably in a manuscript of 1389 C.E. called the "Mendel Brothers Hausbuch," now in Nüremberg. This depiction, illustrated by Oddy (1977), shows a monk drawing wire. The drawplate is held on a heavy wood block or tree stump. The monk, holding the wire with a large pair of tongs, is seated on a swing to allow full leverage by pushing on the ground or wood with his feet. From the sixteenth century onward, representations of jewelry workshops typically show the use of draw benches. Theophilus states that round wires of relatively large diameters for conversion into beaded wires were made by hammering. This might mean that during the twelfth century only thin gold wires were being drawn. If this is so, it would place the invention of the draw

bench and other more powerful drawing equipment into the thirteenth to fifteenth centuries—after Theophilus but before Biringuccio and his contemporaries. On the other hand, some Fatamid Islamic goldwork dating from the eleventh century includes drawn wires of more than 2 mm in diameter.

Old processes can be continued for generations, particularly in small family workshops where tools and skills are handed down from generation to generation. Wiredrawing also suggests the preparation of some stock of raw materials. The fourteenth century monk on the swing, mentioned above, is shown with several coils of wire he had made. A goldsmith would hardly draw just a couple of centimeters of gold wire needed to decorate a single ring bezel.

Biringuccio makes a very perceptive remark when he notes that “goldsmiths also draw gold wire to make the ornamentation of their work easy and more attractive” (Smith and Gnudi 1943). The introduction of wiredrawing clearly facilitated certain decorative and functional ideas. Several types of filigree work only came into their own, in fact, when wiredrawing permitted the easy manufacture of long, thin lengths of gold wire, while such components as suspension loops and hinges made from springlike coils of wire tended to replace the sheet-gold equivalents.

#### DECORATIVE WIRE

A major change in gold filigree decoration during the course of the medieval period was the change from beaded wires to twisted wire ropes. A rope, in jeweler’s terminology, is a tight twist of two thin wires. With wiredrawing, it was easier to draw thin wires and twist these into ropes than to hammer or draw a thicker wire and convert this to a beaded wire. Ropes became more and more common during the course of the medieval period and, in the Renaissance, almost totally superseded beaded and other decorative wires in gold jewelry.

Beaded wires had been popular in jewelry from about the seventh century B.C.E. onward. They were originally made by rolling a round section wire under a single or double edge, which would leave one or two grooves around the wire. By rolling the wire and moving the tool sequentially along its length, a series of grooves could be made that would produce a beaded effect. Theophilus describes the use of a double-edged tool for making beaded wires and this ancient process is illustrated schematically in Figure 4. By the late Roman period, some beaded wires were also being produced by swaging; that is, the wire would be stamped between two metal plates, each bearing a line of hemispherical hollows. If the wire were rotated and moved through the swage blocks, a very regular beaded effect could be produced. Swaged, beaded wire typically has very spherical beads, because hemispheres are the easiest depressions to cut in the swage blocks. The heavy beaded wires on the fourth-century Huntress plaque in the British Museum has lateral tool marks that would point to the use of a swage (Ogden and Schmidt 1990). Swaged, beaded wires certainly became usual in early Byzantine and Dark Age times. Theophilus describes the swage for making beaded wires, a tool he terms an *organarium*, literally “little organ,” a term found in no other medieval writings.

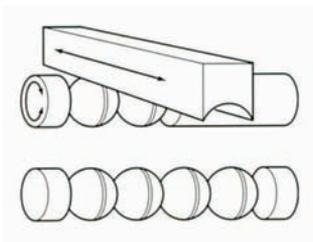


FIGURE 4. Diagram of the two-edged implement for making beaded wire as described by Theophilus in the twelfth century and used in Roman times, if not earlier.

Beaded wire is very common in European jewelry well into the medieval period and is found in Northern European goldwork up to the twelfth century, but it is far rarer after that and practically absent in Renaissance goldwork. Duczko points out that beaded wire almost totally disappears in Slavonic jewelry after the early tenth century (1985). There is also an almost total lack of beaded wires in early medieval Islamic jewelry (Ogden 1987).

An alternative type of decorative beaded wire has a groove running around the wire rather like a screw thread (Fig. 5). This type of wire was produced by rolling a round wire under a single edge held at a slightly oblique angle. The process was ideal for thin-gauge wires where true beading was more difficult to produce. This type of wire, which may be called *spiral-beaded* wire, is found from around the middle of the first millennium B.C.E. and, apart from an apparent break during the Roman period, continues well into the Middle Ages. Spiral-beaded wire is characteristic of Viking jewelry (Fig. 6). It is neither mentioned by Theophilus, nor is it found on his book cover in Trier, though it is found on the work of some of his contemporaries, and the technique may have survived into the thirteenth century. Further east we see spiral-beaded wire on some of the Byzanto-Islamic lunate earrings of the tenth century but not in Fatamid or other medieval Islamic goldwork from the mid-eleventh century onward. Just how widespread the technique was remains to be studied, but we can note the presence of some spiral-beaded wires (made from strip-twisted round wires) in Javanese gold jewelry of about tenth to twelfth centuries (Fig. 7).

In Northern European medieval jewelry of the tenth to twelfth centuries one often finds a combination of beaded and spiral-beaded wires, the spiral-beaded wires



FIGURE 5. Diagram of spiral-beaded wire. A plain round wire is rolled under a single edge at an oblique angle to produce a groove similar to that of a screw thread.

FIGURE 6. An example of spiral-beaded wire and granulation on a Viking silver pendant from Birka, Sweden, ninth century C.E. (Duczko 1985, no. Bj 943).

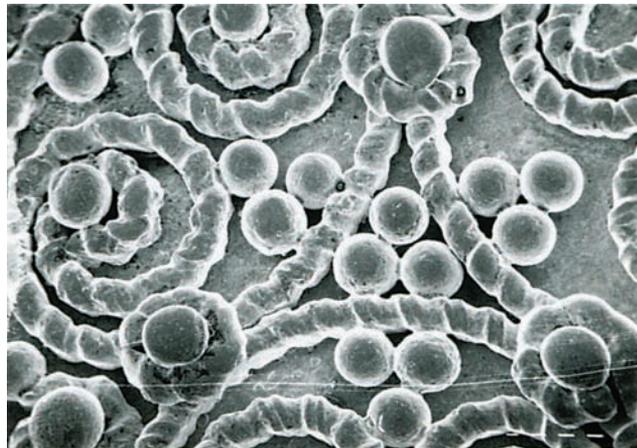


FIGURE 7. Detail of the wire collar on an ear decoration from Central Java. The wire was made by a strip-twist technique and then rolled under a single edge to form a spiral-beaded wire, tenth century C.E.



being of finer gauge. We can see this on the Dowgate Hill brooch found in London and dated to the early eleventh century (Figs. 8, 9). This brooch was traditionally seen as a German product, but the flat, nonarchitectural style of the object has led to a recent reassessment of the object as Anglo-Saxon (Westermann-Angerhausen 1983–84). The Townley brooch (Figs. 10–13), of about the same date and said to have been found in Scotland, also incorporates both beaded and spiral-beaded wires, but its more architectural structure points to an Ottonian German origin. It is of interest that neither of these brooches, among all their copious filigree, incorporate any plain, round-section wire.

The use of hollow-beaded wires—in effect, beaded tubes—in Byzantine gold-work has been examined (Ogden and Schmidt 1990). This is another decorative technique that found occasional use well into medieval times. Examples include the famous Konrad crown in Vienna (along the lower edge of the panels and also for the hinges) and a Viking silver ornament from Enggarda (Stenberger 1947:no. 435).

Another type of decorative wire-work that is visually very similar to beaded wire consists of a compact, springlike coil (Fig. 14). This type of coil work, another product of the wiredrawing revolution, is rare prior to medieval times (there are some Etruscan precedents) and seems not to have been widespread. One example is the

FIGURE 8. A cloisonné enamel and gold filigree brooch found in London at Dowgate Hill, late tenth to eleventh centuries C.E. British Museum, MLA 56.7-1.1461.



FIGURE 9. Detail of the Dowgate Hill brooch in Figure 8, showing the filigree.



FIGURE 10. Ornament of cloisonné enamel and applied filigree, the so-called Townley brooch, probably Ottonian German, early eleventh century C.E. British Museum, MLA Townley collection.



FIGURE 11. Detail of the back of the Townley brooch in Figure 10, showing the flattened beaded wire forming the framework.



FIGURE 12. Detail of the side of the Townley brooch, near right, showing open scrollwork of flattened spiral-beaded wire.

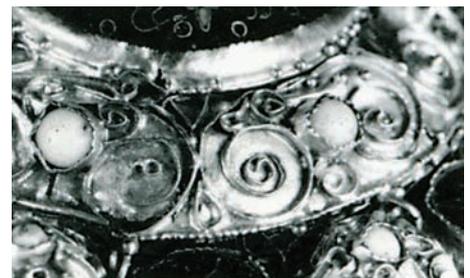


FIGURE 13. Detail of the upper surface of the Townley brooch, far right, showing applied filigree scrollwork of flattened spiral-beaded wire.



FIGURE 14. Diagram of helical spiral wire.

border of the stone setting on the fifteenth-century Middleham jewel (Fig. 1). This technique might be seen as a late medieval and Renaissance characteristic. A more open springlike coil is also found in medieval goldwork; and a squashed version, providing a series of flat loops, forms a border to stone settings, rims, and other features from about the tenth century onward.

Both beaded and spiral-beaded wires (and occasionally ropes) were flattened for use in filigree work (Fig. 15). In the twelfth century Theophilus describes the process in his book 3, chapter 52, titled *The Art of the Metalworker*, as follows: “Pick up the fine [beaded] wires and hammer them lightly on an anvil so that they become



FIGURE 15. Diagram of flattened beaded wire.

somewhat flat and thin, but without the top and bottom of the beads losing their shape” (Dodwell 1986). The wires were shaped into the required forms and soldered to their background. By flattening the filigree wires in this way and then attaching them on edge to the background, the goldsmith could produce precise, fine detail with good depth and, thus, definition. The book cover by Roger of Helmishausen (Theophilus) in the Domschatz at Trier shows just this type of flattened beaded-wire-filigree scrollwork with the occasional granule highlight. These flattened wires were often termed *serrated* in older works when their mode of manufacture from wire was not understood.

Flattened beaded wire and, in particular, flattened spiral-beaded wire, is often found in ancient Iberian and late Hellenistic work. After the end of the Hellenistic period the technique apparently almost disappears until the Dark Age and Viking periods. An early post-Classical example of flattened beaded-wire filigree is on the Hunterstone brooch of about 700 C.E. (Stevenson 1974:pls. 12b, 13b, etc.). There is also flattened beaded wire on the eighth-century Derrynaflan chalice and on the silver trefoil brooch from Kirkoswald, which dates to the mid-ninth century or slightly earlier. Flattened beaded and spiral-beaded wires are common in Viking jewelry of the ninth and tenth centuries (Duczko 1985:210), and one occasionally also finds flattened ropes from this same period, such as on a silver ornament from Eastern Europe (Benda 1967:pl 74). Both flattened beaded and spiral-beaded wires are common on European decorative precious metalwork of the tenth to twelfth centuries, but not much after this. Both the Dowgate Hill and Townley brooches include flattened filigree. The Dowgate Hill brooch has an unusual openwork filigree composed of doubled, flattened spiral-beaded wires highlighted with some granulation. This is reminiscent of the Fatamid openwork with its double wires surmounted with granules (Fig. 9). The entire back framework of the Townley brooch is made up of flattened beaded wire (Fig. 11), while the serpentine openwork scrolls on the side and the scroll filigree on the upper surfaces are made from flattened spiral-beaded wire (Figs. 12, 13).

The gold brooch set with an earlier cameo, shown in Figure 16, is usually seen as an Ottonian product of about the same date as the Townley brooch, but the whole approach to the filigree is different. The cameo brooch employs no beaded or spiral-beaded wire, or flattened wires. Instead, the decoration includes fine twisted-wire ropes, plain (drawn) round-section wires, and perfect lines of regular granules (Fig. 17). The major technical distinctions between the filigree work on the Townley and cameo brooches also serve to separate other supposed Ottonian gold objects. Further research is needed to confirm the origins and relative chronologies of these pieces.

The choice of wires for filigree depended on both practical reasons and personal whim. For example, a gem-set gold cover for a cup in the Fitzwilliam Museum, Cambridge, probably from the late thirteenth to fourteenth century (Fig. 18), employs true beaded wire for the main decoration around the central setting but spiral-beaded wire for the finer gauge decorative wire around the individual stone settings. Here, as in comparable ancient and medieval objects, the choice might well have been practical: The thinner wires were easier to make this way. In other cases, personal choice must have played a part, and perhaps further study will allow more



FIGURE 16. *Granulated and filigree brooch, above, set with an earlier cameo. The goldwork is Ottonian German, tenth century C.E.; the cameo is of late Roman date. British Museum, MLA AF352.*



FIGURE 17. *Detail of the side of the brooch shown in Figure 16, revealing granulation and twisted-wire ropes as opposed to beaded and spiral-beaded wires.*



FIGURE 18. *Detail showing the use of beaded and spiral-beaded wire on a gold cover. Probably German, twelfth century C.E. Fitzwilliam Museum, inv. M/P.1.1921*

characterization of the workshops in which they were produced. For example, Theophilus's book cover in Trier uses flattened beaded wire. A contemporaneous book cover in the same collection (Ronig 1984:no. 68) uses flattened spiral-beaded wire. The well-known tenth-century portable altar, known as the Egbert shrine, also in Trier (Ronig 1984:no. 23) has flattened beaded-wire filigree but no granulation. The nail reliquary of the same date and supposedly from the same workshop (Ronig 1984:no. 24) has filigree of ordinary beaded wire, not flattened, but including some granulation.

One type of decorative wire work that disappears totally in medieval times is wavy ribbon, which is last seen in Dark Age work of the seventh century C.E. Wavy ribbon was made by coiling a narrow gold strip into a tube, flattening it and then unfolding it. The strip has a series of regular diagonal creases, creating an attractive, wavy appearance. It might not be coincidental that a type of decorative strip made by twisting died out just at the time that round wire made from strip twisting was superseded by wire-drawing. A type of undulating strip that might be seen as a successor to wavy ribbon, again with precedents in Etruscan work, became popular in medieval jewelry right across Europe during the medieval period. An early post-Roman example is seen on a series of gold pendants from Cyprus that probably dates from the seventh century and that also includes what is possibly the earliest drawn-gold wire that has been identified thus far from the ancient Old World (Whitfield 1990). This undulating strip is common in medieval jewelry. For example, it is seen on the Townley, Dowgate Hill, and cameo brooches discussed earlier, and on examples of the lunate type of earring from the eastern fringes of Europe. The gold strip used to form this undulating decoration is often of shallow D-section, which in at least some cases appears to have been produced with a one-sided swage. The serpentine-scroll type of openwork, as seen on the side of the Townley brooch (Fig. 12), is also common in about the eleventh century throughout Europe and in the Islamic world. Sometimes the serpentine scroll is composed of narrow strips of gold sheet. In other cases, as on the Townley brooch, it is formed from flattened spiral-beaded wire.

Cellini notes that skilled exponents of filigree could work without a preliminary drawing, but the best work resulted from careful designing first (Ashbee 1967). Biringuccio also noted that a goldsmith should be a good designer. Guidelines for filigree were sometimes lightly scored on the gold or silver surface. The author has seen lightly incised lines laying out the position of filigree on Anglo-Saxon goldwork. The positions for the settings on the Cambridge gold cover were also marked out by scoring fine lines—perhaps by tracing around the stone, since the settings were clearly designed to receive existing cut gems. Fuller jewelry designs sketched out on other materials, such as paper or vellum, are rare prior to Renaissance times; early examples include flat stones from Ireland with the scratched designs for brooches (Youngs 1989:nos. 154, 155)

## Chains

In the ancient world, precious-metal chains were characteristically of the loop-in-loop type. Simple or plain chains—the form most common today—were seldom used, and when they were they were often reserved for particular decorative purposes. During the Byzantine period the ratio of loop-in-loop chains to simple chains changed, but loop-in-loop chain was still typical of much Dark Age and Viking jewelry. After about the tenth-century loop-in-loop chains were rare in goldwork, and the early Renaissance saw their almost total demise. One late example is the chain in the mid- to late-fifteenth-century Fishpool hoard from London (Fig. 19). Yvonne Hackenbroch's corpus of almost one thousand jewels dating between about 1500 and 1600 only includes a single example with any loop-in-loop chain (Hackenbroch 1979:no. 633), and even here the chain might not be original to the piece. Loop-in-loop chain is also surprisingly rare in medieval Islamic jewelry (Ogden 1987).



FIGURE 19. Detail of two gold chains from the Fishpool hoard, found in London. One chain is of loop-in-loop type, the other of conjoined figure of eight links (the links joining the figures of eight are left unsoldered to avoid possible fusing during the final assembly of the chain). British Museum, MLA 67.12-8.1-9.

The demise of gold loop-in-loop chains was probably a result of changing taste. The Renaissance chains on the flamboyant figural jewels are attempts at looking mechanical and structural; they bind a monster or constrain a vessel. Loop-in-loop chains are a fairly extravagant use of gold wire, but their massive and elaborate Renaissance successors hardly represented a savings in metal. Loop-in-loop chains continued to be used for silver and base-metal jewelry, particularly the so-called European peasant jewelry. Gold loop-in-loop chains reappeared with late eighteenth-century Neoclassical goldwork and then became popular with the archaeological jewelry styles of the nineteenth century.

The multiple loop-in-loop chain, which has a tightly linked cylindrical form with an almost plaited appearance (often erroneously termed *plaited*), might have inspired the wire-mesh tubes made from a continuous length of wire, like the so-called French or spool knitting with wool produced by generations of children. This type of braided chain, sometimes called Trichinopoly, first appears in Europe in about the eighth century. It is seen on the Tara brooch and a long length forms the principal part of the Trehwiddle scourge. The curious herringbone-braided wire decorations on the Derrynaflan paten and the Ardagh chalice are closely related, if not of identical construction. It has been suggested that Theophilus describes the manufacture of Trichinopoly work in his book 3, chapter 62, when he writes: “First draw

thin or thicker wires of copper or silver and intertwine them, using an awl, in three braids, or in four, five or six, depending on the thickness you want.” This braided wire was then drawn through a series of circular holes of diminishing size in a wood block to produce an even, round length. Trichinopoly, made possible by wire-drawing, does not appear to have been produced much after the tenth century in Europe. But similar work in drawn-gold wire can be seen in jewelry from medieval Southeast Asia, and the technique has been used there ever since.

## Solder

Several medieval solder recipes have survived ranging from those in the “Mappae Clavicula,” and by Eraclius and Theophilus in the West to al-Hamdani and Kashani in the Islamic world. Typically, the solders were binary or ternary alloys of gold, silver, and copper. The choice of proportions depended on the color and melting temperature of the alloy being worked and the inherent or perceived benefits of particular alloy combinations. Solders would generally have been made up as required, usually by alloying a little silver and/or copper to the gold being worked—a procedure recommended in jewelry text books up to recent times. Kashani, writing in the fourteenth century, gives a solder alloy specifically for red gold of the popular Islamic and European type. This solder was composed of two-thirds gold alloyed with one-sixth part each of silver and copper. This would assume that Islamic red gold contained less than 17% copper—which would suit the coinage alloys with up to 15% copper mentioned earlier. Silver solders were typically silver-copper alloys; Biringuccio recommends 75% silver, 25% copper, while a seventeenth-century English silversmith says that silver solder was 67% silver and 33% copper (Jackson 1905).

Solders could be produced as alloys or as copper-salt mixtures. The former could be used as fillings or as cut platelets, the latter called *paillons* today. A medieval Greek recipe for “royal solder,” which is 75% gold and 25% silver, explains that filings would be used for thin gold, *paillons* for thicker gold (Berthelot 1888:doc. no. 9.) The subsequent recipe says the same about silver solder. Biringuccio also writes of solder cut into small pieces.

Copper-salt solders are assumed to have been used for at least some of the fine granulation work in antiquity and must relate to Pliny’s discussion of *chrysocolla* (literally “gold solder” and certainly some type of copper mineral or compound) for soldering gold. The “Mappae Clavicula” and Theophilus describe solders based on a copper salt, probably copper oxide. In one case this was mixed with olive-oil soap, in another, alum. Cellini used a verdigris mixture, which he noted was really not soldering at all because the parts really just fuse together without any solder alloy (Ashbee 1967). A similar technique of soldering without solder is described by Biringuccio. We can note that the granulation and filigree work on medieval goldwork tends to be more flooded than its earlier counterparts.

The “Mappae Clavicula” also contains recipes for gold-mercury solders. The use of mercury amalgam solders for early goldwork is certainly a possibility, but examples have not been detected on extant goldwork. Taruashvili of the Georgian National Museum of Fine Arts suggests that the gold cell walls of the finest *cloisonné*

FIGURE 20. Detail of the interior of the brooch in Figure 16, showing two types of join in the sheet metal (indicated by arrows).

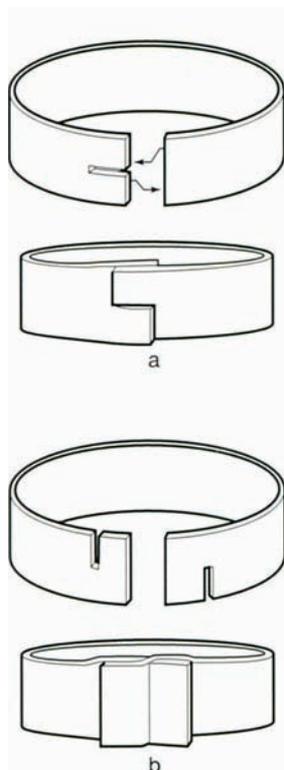


FIGURE 21a, b. Diagram of the joins in Figure 20.



FIGURE 22. Detail of the side of a stone setting on the gold cover in Figure 18, showing sheet metal join.

enamel work was produced with an amalgam solder. Taruashvili produced successful replicas in this way, but seemingly no analysis work on the ancient enamels was undertaken (Amiranashvili n.d.:18). However, a silver-mercury solder has been identified on a silver spoon from the late Roman Mildenhall Treasure (Lang and Hughes 1984) and examples in gold might well be forthcoming.

By the early Renaissance, borax as a flux for solder was in general use. Borax was noted by the Islamic writer Ibn Hawqal in the late tenth century, and Theophilus in the twelfth century described its use as a flux for niello. According to Biringuccio, the components of filigree work were attached to the substrate with quince-seed paste or gum arabic and then soldered with borax and a gold or silver alloy solder in a little furnace. Bran or dry elder twigs provided the heat. In earlier times chaff or straw were usual sources of heat for goldsmiths.

A variety of medieval work, ranging from some sections of the Konrad crown to the little lunate earring shown in Figure 3, made use of small clippings of wire to fill gaps between components during soldering. The small section of beaded wire so used on the Konrad crown has been fairly well placed to minimize disfigurement. This is not so true of the earrings.

One type of soldered join seen on some medieval goldwork is worth noting. The sheet gold setting borders on the Ottonian cameo brooch in Figure 16 are formed from strips of sheet gold that are slit and overlapped in a manner more frequently seen in sheet-copper and brass work. The cameo brooch shows two type of join (Fig. 20). One is a simple opposed-slit type, the other a more complex interslotting. Both of these assemblies are shown in Figure 21a, b. It is hard to see how the additional strength of such a join would be needed in goldwork, but the technique is not unique; the simple opposed-slit join is also seen on the settings of the Cambridge gold cover (Fig. 22), also supposedly of German origin, and many other examples presumably await discovery. The technique was not universal; it is not seen on the Townley brooch for example, which has the more usual overlap join.

#### GRANULATION

Granulation work is just one subsection of soldering. The persistent belief that granulation died out during the Dark Ages in Europe and was only rediscovered by the diligence of nineteenth- and twentieth-century goldsmiths is a product of European

chauvinism. Granulation is found to fine effect well into the medieval period, and some ninth- and tenth-century work is of remarkable quality. In England the Alfred jewel is a fine example, and there are some superb Viking and Eastern European examples from the ninth and tenth centuries. Some eleventh-century Fatimid Islamic granulation work, including the lines of granules soldered on double-wire frameworks, is of exceptional quality.

Later in the medieval period, granulation work became less prominent, perhaps largely displaced by drawn wire filigree; but it was not forgotten, and it often forms highlights on filigree work. We see such granulation on Theophilus's book cover in Trier. Theophilus does not explain the technique of granulation, but he does describe small tweezers for manipulating the individual grains (Dodwell [1961]1986: book 3, ch. 7). A mid-thirteenth-century description of the treasures in St. Paul's Cathedral, London, describes goldwork as "cum margatiti et grani auri," which might be a reference to granulation; small gold beads seem less likely (Lehmann-Brockhaus 1960:no. 2748). The Dowgate Hill, Townley, and cameo brooches (Figs. 8–9, 10–13, 16–17) all have granulation work. In Renaissance goldwork, granulation is relegated to the odd grain and is seldom part of the main decorative scheme.

## Casting

As in antiquity, casting was very seldom employed by goldsmiths apart from the initial production of the ingot or blank. Solid and often quite massive gold ornaments that manufacturers would find natural to cast today were generally fabricated from wrought gold. Casting was potentially wasteful of metal and provided little advantage in days when workmanship was relatively inexpensive. Neckham (1867) does tell us that the goldsmith should be skilled "in the work of casting," but no medieval gold jewelry is unequivocally known to have been made by casting. Possibly some of the solid rings were cast, but many undoubtedly were not.

Theophilus describes the manufacture of ingots and blanks by casting—the usual starting point for vessels or other objects—but the only mention of cast gold is for decorative handles and mounts such, as "a cast lion's head very elegantly carved" that could grace the end of the handle of a "gold or silver strainer" (Hawthorne and Smith 1979:ch. 57). Cellini talks about casting silver seals and decorative mounts for silver vessels and also mentions lost-wax casting for gold and silver, but he does not give examples of the type of objects cast (Ashbee 1967).

Cellini also describes the use of cast lead ornaments that would then be worked on by the master and then used as models for the casting of precious metal (Ashbee 1967). Base-metal ornaments were often cast and numerous molds have survived, including those for the ubiquitous lead Pilgrim badges.

## Engraving

The medieval use of true engraving, in which a sliver of metal is gouged from the metal surface, contrasts with the methods of earlier periods. The depth and sharpness of engraving on medieval signet rings is noteworthy; the precision possible can



FIGURE 23. Medieval gold ring brooch with engraved inscription. (The other side says “I am here in place of a friend.”)

be seen in the fine Middleham pendant in Figure 1. The use of engraving in antiquity was probably more common than generally assumed (examples include Mycenaean, Phoenician, and Hellenistic gold rings), but it was not widespread.

Theophilus describes the manufacture of engraving tools with sharp, oblique cutting edges that are nearly indistinguishable from their modern counterparts. An English statute of 1300 underlines the potentially wasteful nature of engraving in its ruling that “gravers, cutters of stone and of seals shall give each [i.e., return to the patron] their weight of gold and silver as near they can” (Jackson 1905:7).

Engraving could be used for functions other than just decorative designs or inscriptions. For example, on the Cambridge gold cover of around 1300, the goldsmith scored a fine line to mark the position of the settings and then used an engraving tool to push up small curls of gold to act as guides to hold the settings in place during soldering.

The texts engraved on medieval jewelry are not always readily readable. In some cases this is due to current lack of understanding of ancient conventions or convolutions. For example, the side of the ring brooch in Figure 23 is not immediately readable and at one stage was assumed to be of magical significance. In fact, the letters are probably the alternating letters of the names Robert and Marger [?]. In some cases, the literacy of the engravers must legitimately be doubted. From 1487 we hear of problems when an apprentice engraver noted for his expertise in engraving “all manner of letter” was found to be unable to read or write (Prideaux 1896–97:28).

Another form of engraving, the *pointillé* (dot) engraving that became common toward the end of this period, had a long history and can be traced back to dotted inscriptions on Classical vessels.

## Enamel and Niello

In medieval work, three main types of enamel may be distinguished. These are *champlevé*, in which the enamel is applied in hollows in the metal; *cloisonné*, in which the enamel is held in cells bounded by thin walls of metal strip; and enamel *en ronde boss*, in which there is an overall coating of a three-dimensional figure, usually with white enamel. Cloisonné enamel, employing thin, soldered strips of metal, was best suited to gold, while *champlevé* enamel, using engraved depressions, required thicker metal and was thus most common with copper alloys. These manufacturing differences can often obscure the stylistic similarities of the final work. The Dowgate Hill and Townley brooches (Figs. 8–9, 10–13) both have fine cloisonné enamel centers.

Medieval European texts often describe enameled precious-metal objects in the most glowing terms, describing it as of the finest work and of robust beauty (Lehmann-Brockhaus 1938:2838, 2842). References are made to Anglo-Saxon enameled regalia and to enameled objects from Constantinople (Lehmann-Brockhaus 1938:2972, 2857). We can assume that most of this enamel was of the cloisonné type which can be seen on Dark Age goldwork and which was fairly widespread through medieval times from Britain to the Byzantine and Islamic worlds. Early medieval English examples include the late ninth-century Alfred jewel. Fine cloi-

sonné enamel in late ninth- to early tenth-century contexts in Eastern Europe includes recently excavated gold lunate earrings with circular cloisonné enamel motifs (Vazarova 1980:pl. 7).

Westermann-Angerhausen (1983–84) argues for a native Anglo-Saxon origin and an early eleventh century date for the Dowgate Hill brooch. The even more recent study and publication of a group of English cloisonné enamel copper alloy brooches of late tenth to early eleventh-centuries leads Buckton to state (1986:16):

This would establish the existence of a previously unsuspected centre of *cloisonné* enamelling in England at a time when *cloisonné* enamel in Europe, particularly in the German and Lotharingian centres of the Rhineland, Regensburg and Trier, was at its peak.

Champlevé enamel was an old European tradition dating back into the Iron Age. In medieval times champlevé work on copper alloys was associated with the town of Limoges, and documentary references to *opere Levovitico, labore Limogiae, opere Lemovicensi*, and so on, occur from the mid-twelfth century onward (Gay [1887]1928:s.vv. *email* and *Limoges*). Champlevé enamel was used on medieval goldwork and possibly can be seen as largely taking over niello on goldwork. Examples of champlevé work on gold include the Middleham jewel (Fig. 1), although only traces of the blue enamel filling the engraved lines now remain. Champlevé enamel is also found in silver and copper-alloy rings of medieval Islamic origin (Ogden 1987). A regulation of Edward II dated 1370 notes that “cutters of seals and enamellers shall return to each his weight of gold and silver as near as they can save it” (Prideaux 1896–97:doc. no 440). This certainly implies champlevé enamel, where the precious metal would need to be cut out with engraving tools.

The mention of enameled silver is interesting since it is almost entirely absent in ancient work. We can assume that this was due to problems relating to adhesion and relative coefficients of expansion. Something of the sort is suggested by Biringuccio who states, “each kind of gold, silver or copper requires enamel harmonious to its nature else it does not respond.” In Paris in the early fourteenth century, enamellers agreed to enamel only on silver and gold of high standard and not to use lead glass, which was suitable only for silver of fraudulent alloy (Lightbown 1978:83). The continued use of niello on silver, compared to black champlevé enamels on gold, must relate to the difficulties in enameling silver.

The final coating of a three-dimensional gold object with a layer of enamel (enamel *en ronde boss*) was known in Hellenistic Italy but became popular in the second half of the fourteenth century. This type of enamel is particularly ubiquitous in Renaissance jewelry, where the general delicate and piecemeal construction of the underlying goldwork can usually be contrasted with the cast and often coarse work of much of its nineteenth-century imitators.

Filigree enamel, in which filigree wires form the boundaries of the enamel, was typical of Hellenistic work, but is very rare in medieval jewelry and only reappears in the Renaissance when it was supposedly introduced into Italy from the Balkans by the Venetians (Hackenbroch 1979). A text of about 1400 seems to refer to a type of

mastic inlay used to imitate enamel (Gay [1887]1928:s.v. mastic); this might relate to the use of bitumen as an imitation of niello in some medieval Islamic jewelry.

Niello is a black sulphide of silver or a mixed sulphide including silver and lead. This material was fused into designs engraved on a gold or silver surface and polished. In some case a form of niello was used to paint designs straight onto a metal surface. This attractive technique is described in the “Mappae Clavicula” and can be seen quite frequently on medieval Islamic gold jewelry. Niello appears in late Roman gold jewelry and continued to be popular through the Dark Ages and into the medieval period. A fine mid-ninth-century English example is a ring with the name of King Ethelwulf (British Museum, MLA 29.11-14.1). This miter-shaped ring is made from heavy hammered gold sheet with an overlap join at the back. The design is deeply engraved to hold the niello.

The addition of lead to the niello makes it far more fluid and improves the bond with the surrounding metal. As far as analyses show, the use of leaded niello in Europe was a development of the medieval period and perhaps does not predate the tenth century (Oddy et al. 1983). Both the “Mappae Clavicula” and Eraclius provide niello recipes that include lead (Smith and Hawthorne 1974:chs. 56, 58, 195, 196; Merrifield 1849:ch. 48).

Both silver and gold with niello decoration are mentioned in late thirteenth- and fourteenth-century documents; one account of 1396 tells how a French goldsmith had to reniello a goblet when he repaired it (Lightbown 1978:75). Cellini notes in the introduction to his book that the art of niello had fallen into disuse by the early sixteenth century, although the process was still discussed by a few old men (Ashbee 1967).

## T H E D A W N O F T H E R E N A I S S A N C E

In many ways the goldsmiths of the early Renaissance continued the same traditions of their forebears, which in turn harked back to the Hellenistic and earlier times. Goldwork was usually assembled from sheet gold and decorated with filigree. However, there were considerable stylistic changes and changing fashions in decorative processes.

The Renaissance signaled the rebirth of an affection for the ancient Classical world; Renaissance jewelers looked back on classical goldwork with awe and admiration. The highest praise, quoted by the ever-vain Cellini, was Michelangelo’s statement that one of Cellini’s jewels was “so beautiful that I do not think any goldsmith of the ancient world ever fashioned anything to match it” (Ashbee 1967). In view of this, one must ask why those perennials of Hellenistic and Etruscan work—loop-in-loop chain, beaded wire, and granulation—were almost totally banished from the Renaissance jeweler’s repertoire.

## A C K N O W L E D G M E N T S

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