Chapter 1

Ancient Methods of Gilding Silver: Examples from the Old and the New Worlds

Heather N. Lechtman
Massachusetts Institute of Technology

Introduction

To illustrate a representative selection of ancient techniques for the gilding of silver, I have chosen material from two distinct geographical regions, the Near East—more specifically Turkey and Iran—on the one hand, and South America—very precisely, the northern coast of Peru—on the other. The objects from the Near East all cluster about the third through the sixth centuries A.D., from the Sasanian empire in Iran and from one of the most splendid periods of the early Byzantine empire with its capital at Constantinople. It is difficult to date the particular Peruvian objects discussed in this paper with the same accuracy as the Old World artifacts. They span a much broader period of time, ranging from the classic Vicus period (ca. 400 B.C.–A.D. 100) through that of the Chimu culture, which was prominent in Peru roughly from A.D. 1000 until the time of the Inca conquest in 1470. But the rigors of precise dating of artifactual material need not be of concern here, for the purpose of this investigation is to demonstrate the ways in which craftsmen, at various points and places in history, have used virtually the same materials but have arrived at totally different yet completely effective solutions to a specific problem, the gilding of silver.

True Gilding and Depletion Gilding

In any discussion of gilding metal, the distinction is usually made between true gilding and processes that may be subsumed under the term depletion gilding, often referred to as gold coloring.[1] True gilding techniques involve the external application of gold to the surface of some other metal. Upon its application the two metals may, in certain instances, undergo interalloying and complete metallic bonding. Processes of depletion gilding, on the other hand, always begin with the gold already alloyed with some other metal. In such cases, the object is to remove enough of the alloying element so that the surfaces become enriched in gold and eventually appear golden. Depletion gilding techniques are thus based upon chemical reactions that occur only at the surfaces of alloys.[2] They include processes that rely on solid-state diffusion reactions at a moderately high temperature, that is, all *mise-en-couleur* and cementation techniques such as removal of copper from tumbaga, of silver from gold-silver alloys, and of both copper and silver from silver-copper-gold alloys. Electrochemical processes, for example superficial parting, are also included in the term.

The distinction between gilding and coloring is not meaningful from the aesthetic point of view. Both types of process lead to results that, at least under the usual conditions of viewing and handling an object, are similar. But the distinction does have significance from the standpoint of technology, for the metallurgical principles and operations involved are quite different and stem from two approaches to the use of materials that are, in a sense, philosophically distinct. The objects I shall discuss from the Near East are all examples of true gilding, while those from northern Peru may prove to illustrate a unique variety of gold-coloring technique.

Methods of Applying an External Layer of Gold

Aside from the modern processes of electrolytic plating, electrochemical plating, sputtering, and other methods of depositing a thin gold film from solution or from the vapor phase, there have been relatively few techniques for the external application of gold. These have utilized gold in the solid state, in the molten state, and in the form of an amalgam whose properties lie somewhere between those of the other two. Solid gold has been applied most often in the form of thin sheets of foil or leaf, although finely powdered gold has also been used.[3] To differentiate between gold foil and gold leaf, I shall arbitrarily define foil as sheet metal that is greater than about one micron in thickness ($1\mu = 10^{-3}$ mm), while leaf constitutes thicknesses smaller than this value. This definition is not altogether peremptory, since there is a marked difference in the way in which sheet gold handles when it becomes much thicker than about a micron. The metal is as malleable when thick as it is thin, but it cannot follow

[1] Paul Bergsøe's plea for and definition of this clarification of terms is classic. In discussing the process of *mise-en-couleur* he remarks: "However, when this process is described as 'gilding,' a protest must be lodged in the name of metallurgy. By gilding we understand a process by means of which an overlay of gold is applied to the object *externally*. If the gilding proceeds from the gold *in the object itself*, it can at most be called coloration. This, however, is only a question of terminology and has no actual bearing upon the subject, but I call attention to it, as it seems to me a pity that anthropologists and metallurgists make use of a different terminology when speaking of metal." (Reference 2, pp. 35–36.) Rather than use Bergsøe's term "coloration," which has also been used to describe coloring methods that do not utilize metallic gold (see next note), I prefer *depletion gilding* and define it as the enrichment of a surface in gold by removal of other alloying elements already present.

[2] No discussion will be made here of the many recipes for creating golden surfaces on metal without the use of any metallic gold. These abound in the early literature. Some are alchemical in nature, and others involve simple coloring substitutes, but none is a metallurgical process in the strict sense.

[3] I am referring not to the use of gold powder as a pigment in an organic binder which is then painted onto a metallic surface but rather to the rubbing of very finely divided gold onto a clean metallic surface to which it bonds mechanically.

sharp changes of contour easily, tends to buckle perceptibly and to retain the wrinkling upon burnishing, and to become very springy when burnished cold. The mechanical application of thick foil to metal surfaces of widely varying topography is therefore quite difficult, whereas it is easily accomplished with the thinner leaf. Discussion of the first two objects from the Near East shows this difference quite clearly.

Regardless of whether foil or leaf was used, some auxiliary means of attaching the gold to the substrate metal had to be found. The most direct method was that of simple mechanical bonding. Either the surfaces of the substrate were deliberately roughened to accept the applied and subsequently burnished-on gold or the topography of those surfaces, which included all their decorative features, was varied enough to constitute an adequately toothed stratum onto which the gold could be burnished and held mechanically. Once the gold was in place, the entire object might have been heated to cause sufficient solid-state diffusion of the two metals across their common interface so that a zone of interalloyed metal, albeit very thin, might then form an additional and very strong bond to hold the two together. Thin sheet gold has also been applied to metal surfaces with organic binders of various types, a not uncommon practice in ancient Egypt,[4] and, finally, mercury has frequently been used as the agent to facilitate the bonding of leaf to substrate metal.[5]

The application of gold in the molten form to a metallic surface is much rarer chiefly because it is a much more difficult technique, it is more wasteful of gold, and it does not lend itself easily to parcel gilding, that is, to the gilding of only certain areas of a metallic surface for the decorative contrasts produced between gilded and nongilded metal. The technique, akin to tinning of iron or steel, is often referred to as fusion or wash gilding and almost always involves an alloy of gold with copper, which melts at a considerably lower temperature than pure gold itself.[6] The molten metal tends to run over the heated surface of the substrate, and the bond in such cases is usually a fusion bond caused by the melting together of the metals at their interface. An interesting account of such a technique is given by Paul Bergsøe and is based upon his studies of the gilding practices of the pre-Columbian peoples of Esmeraldas in Ecuador. He concluded that the Indians gilded very small cast copper objects by flushing on the gold-copper alloy of lowest melting point. (Reference 2) It would be well to reexamine this material, both metallographically and with the electron microbeam probe, to reassess Bergsøe's interpretation.

Finally, the peculiar properties of the amalgam of gold have made it an ideal material for gilding metals, one that has been used extensively since at least the first century A.D. and probably even earlier. Gold and mercury, when gently heated, together form an alloy that, on cooling, is of a pasty consistency. As long as the metal to be gilded will also amalgamate with mercury, this pasty alloy can conveniently be spread over those areas of a surface to be gilded. If desired, other areas may be left untreated. When the object is heated to a temperature above the boiling point of free mercury (356°C), the mercury in the amalgam volatilizes leaving the gold behind. The gold is thus held in place as the result of solid-state diffusion between it and the substrate metal, often with the formation of intermediate compounds. Several of the Near Eastern objects illustrated here were gilded by the amalgam process, and the details of the technique are given with the descriptive and analytic material.

Depletion Gilding: A Contribution of Pre-Columbian Metallurgy

The Indians of pre-Columbian Central and South America were master goldsmiths. It is not extraordinary, therefore, to find that, when it came to gilding metals, they employed a wide variety of techniques ranging from the use of gold foils through the fusion gilding procedure described earlier to methods based on coloring procedures. It is in this last category that the peoples of Central America and of northern South America made a unique and important contribution to the development of early metallurgy in the New World. This was the invention, perhaps by the peoples of Colombia, of the gold-copper alloy commonly referred to as tumbaga and the extensive utilization of this alloy by the Indians of Panama, Costa Rica, and eventually Mexico. A wide variety of objects was cast from tumbaga, and the castings were subsequently treated in one of two ways in order to remove the surface copper, leaving the gold behind. When completed, the objects were completely covered with a thin layer of gold and indeed looked golden. The coloring methods involved (1) the formation of copper oxide on the surface of the casting by heating the object in air, followed by chemical solution and removal of the copper oxide, or (2) the slow removal of metallic copper

[4] Lucas describes the plating of copper by attaching gold leaf to this metal with a gum or glue adhesive. He claims that the large marguerites sewn to the linen pall from the tomb of Tutankhamūn were gilded in this manner (Reference 9, p. 232).

[5] One of the earliest references to the gilding of copper with gold leaf applied with the aid of mercury is found in Pliny's *Natural History* (Reference 11).

[6] The maximum depression of the melting point occurs at an alloy composition of approximately 80 percent Au, 20 percent Cu, by weight. This alloy melts at about 900°C, 163 degrees below the melting point of pure gold (1063°C).

from the surface of the casting by allowing the object to remain immersed in a corrosive bath for extended periods of time. The dark, spongy layer of gold formed was later consolidated by burnishing.[7] There is no doubt that similar alloys (coinage alloys, for example) were made in the Old World and that surfaces of most gold alloys were given an improved color in a similar manner, but the technique was never developed and perfected anywhere in the world to the extent that it was in the Americas.

Although the pre-Columbian objects I shall discuss are from Peru, where tumbaga was rarely used, and are examples of gilding alloys that are primarily silver-based, I shall endeavor to show that the gilding methods used by at least some of the North Peruvian peoples were actually coloring methods and that they are analogous to those employed in the more traditional treatment of the copper-based tumbaga alloys.

Objects from the Near East

The Near Eastern material illustrates many, though not all, of the techniques for applying an external layer of gold to a silver surface. The object reproduced in Figure 1.1 is a silver rhyton, in the form of a horse, in the Cleveland Museum of Art (Reference 19). It is from Sasanian Iran, dating to the third century A.D., and is made of several pieces of thin sheet silver carefully fitted together. All the decorated areas, including the trappings, the mane and tail, and the two round phalerae on either side of the chest, were produced by the repoussé technique followed by final chasing with a variety of tracing tools. Many of these traced areas were originally gilded, but most of the gilding has been lost and is now immediately visible only on the muzzle, the straps that secure the saddlecloth, and the hair of the mane. On the other hand, examination under the microscope reveals that the entire saddlecloth was probably originally gilded, although only small fragments of gold remain clinging to some of the rosettes. Similarly, bits of gold can be found on the frames of the phalerae and in other areas within these medallions.

As Dorothy Shepherd has pointed out, the extensive loss of gilding is undoubtedly due to inadequacies in the method of applying the gold. A heavy gold foil, between 8 and 14μ in thickness, was burnished onto the decorated areas of the metal depending mainly on the contours of the traced details to supply the necessary "tooth" to hold it in place. The straight, cut edges of the foil are quite evident in certain areas where they overlap from the heavily traced portions of the metal onto the undecorated, smooth surfaces of the silver. Careful inspection of Figure 1.1 reveals such an overlap of foil running from the closely hatched, vertical muzzle strap behind the animal's eye onto the ungilded metal just below its ear. The gold is visible here as a highly reflecting, geometrically defined area on a matte silver ground. Figure 1.2, a detail of a similar area of the muzzle, shows a portion of the traced leather strap, which is gilded, and of the ungilt silver below it. The arrow indicates the edge of the thick foil that still covers most of the decoration where that edge has overlapped onto the undecorated smooth silver surface.

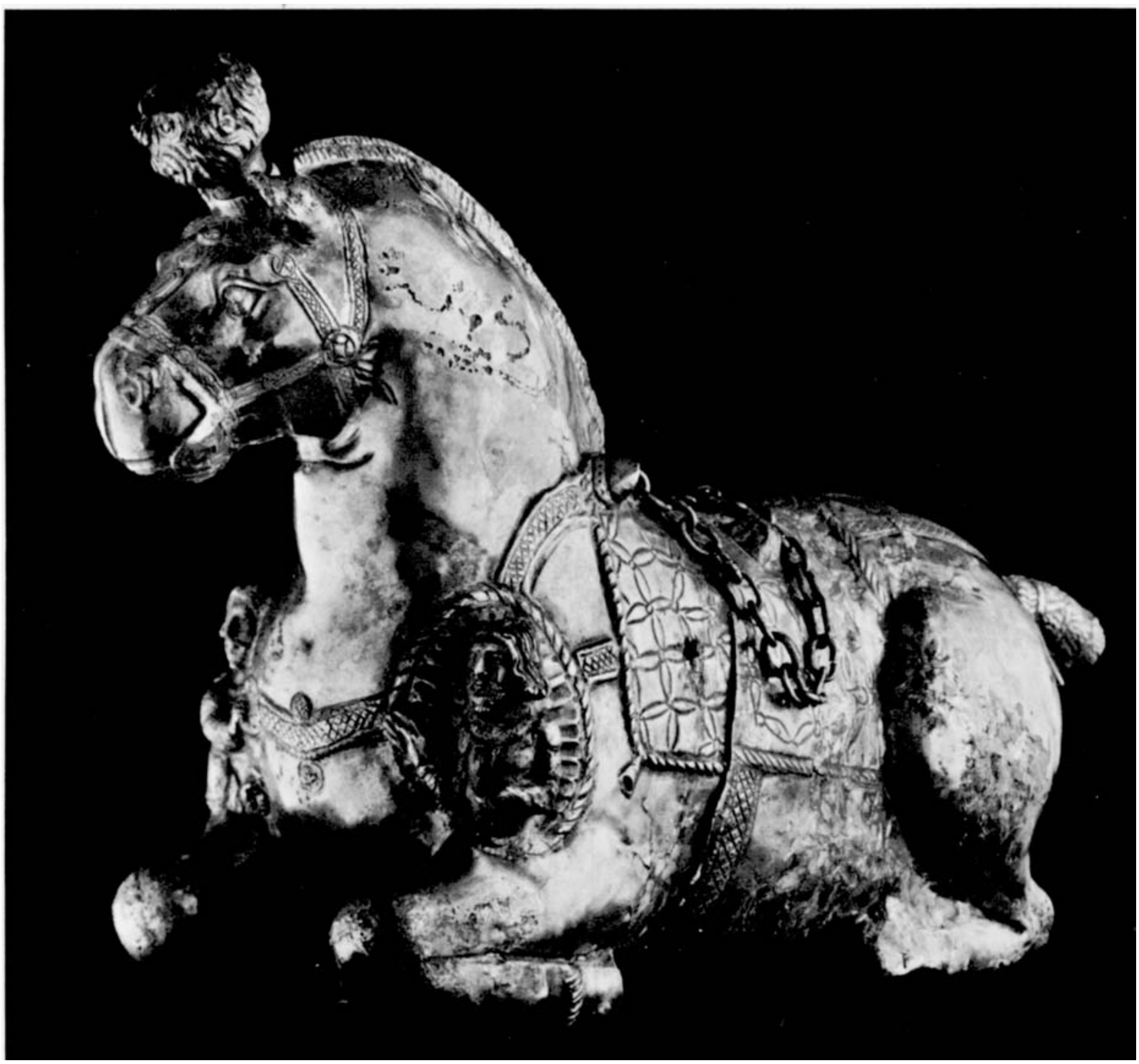
Figures 1.3 and 1.4, details of the straps of the harness, reveal quite clearly the extent to which the foil has stretched, cracked, and is peeling away from the underlying silver, demonstrating the inadequacy of even these quite irregular surfaces to hold foil of this thickness in place. Both photographs also illustrate the way in which the gold has buckled badly in the depressions of the traced lines. It never adhered well to the silver even in these declivities. From these observations, it is quite easy to understand why the gold has been lost so extensively within the borders of the saddlecloth where only the traced rosettes offer some interruption to the otherwise broad, smooth surfaces of silver. Moreover, inadequate cleanliness of either metal, inadequate heating, and inadequate mechanical pressure in applying the gold would have resulted in poor bonding regardless of the presence or absence of gross surface "tooth."

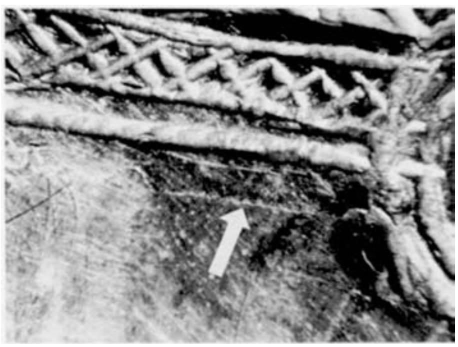
Because it was impossible to obtain a sample of some of the silver that still retains its gilding without impairing the integrity of the object, no studies were made which might have shown whether or not the object was heated after application of the gold in order to effect a diffusion bond.[8] The fact that some fragments of gold cling tenaciously even to very smooth areas of silver implies that the silver may have been heated while the gold was being applied and that, in a few places, the heating was sufficient to form such a diffusion bond. This would almost certainly have been necessary to maintain the ductility of the thick foil while it was

[7] Bergsøe used both methods successfully to reproduce the gold coloring of experimentally cast tumbaga alloys (Reference 2, pp. 35–37). See also Reference 14.

[8] Several tiny pieces of the peeling foil were removed and examined, however. Qualitative spectrographic analysis of the gold indicated the presence of between 0.1 and 1.0 percent mercury, by weight. It is likely that the concentration of mercury is near the lower limit of this range, for the electron microbeam probe analyzer found no point within the foil at which counts above background were measured for mercury. The silver concentration within the gold did not show a Au-Ag diffusion zone, but the gold appeared to be contaminated with silver, probably in the form of corrosion products, on both its surfaces. Until it is possible to examine a cross section of the gilded silver, it will be difficult to ascertain whether or not mercury was used in applying the foil. Its level of concentration in the gold raises some doubts as to its presence there as a simple contaminant. (See Appendix.)

1.1
Silver rhyton in the form of a horse 34 cm long x 22 cm high. Iran, Sasanian period, ca. third century A.D. The Cleveland Museum of Art, Purchase, John L. Severance Fund [CMA 64.41].





1.2
Horse rhyton. Arrow indicates edge of thick gold foil applied over decorated muzzle strap. Photo by Katharine C. Ruhl.

1.3
Horse rhyton. Wrinkled gold foil is peeling away from traced silver surface. Photo by Katharine C. Ruhl.

1.4
Horse rhyton. The "toothed" surface has failed to bond the foil to the silver. Photo by Katharine C. Ruhl.

being worked and pushed into the traced recesses of the silver. (See the Appendix at the end of this chapter.)

A much more effective use of gold leaf for the parcel gilding of repoussé sheet silver is illustrated by the sixth-century gilt silver book cover shown in Figure 1.5. This book cover, one of a pair now at Dumbarton Oaks, was found in Turkey and may be from a workshop in Constantinople in approximately A.D. 570. (Reference 5) Almost all of the raised design elements are gilded, namely the meander border, the shell niche, the capitals and other portions of the columns, the central cross, and its flanking palm branches. The flat silver field has been left ungilded, producing a brilliant interplay between the silver and the gold motifs.

Simple macroscopic examination of this object affords several clues to the method employed to gild it.[9] As with the horse rhyton, there are a few areas where the cut edge of a piece of leaf has overlapped from a raised, gilded motif onto the flat silver field. Figure 1.6, a detail of one of the palm branches, shows the V-shaped intersection of two gilded, raised areas of metal and the spanning of that intersection by a sheet of leaf that has fallen over onto the silver field. The horizontal edge of the leaf is quite evident in the photograph. Second, peeling away of the leaf from the silver occurs in many areas on this object, especially in the recesses, as can be seen at the extreme lower left corner of Figure 1.6.[10] On the whole, however, the leaf follows the contours of the silver very closely and is well bonded to it. Finally, one of the properties of thin leaf with which the craftsman must always contend is its tendency to tear. If it tears upon application to a metal surface, more leaf must be applied above the tear to hide the underlying metal and to produce an uninterrupted, smooth gold surface upon final burnishing. Occasionally a tear in a sheet of leaf can be found, however, and is incontrovertible evidence that the gold was applied in the form of thin leaf. Figure 1.7 is a detail of a torn piece of leaf noted on the mate to the book cover in question. The light silver metal shows through from below. The fact that this horizontal, irregular band is a tear and not a scratch in the leaf is obvious from the matching contours of its two edges.

The microscopic evidence for the existence on this object of several layers of leaf, each approximately one micron in thickness, is quite clear. Figure 1.8, a cross section of a gilded fragment of silver, illustrates one part of the surface where at least four separate pieces of leaf are superimposed. The silver is heavily corroded here, which accounts for the peeling away of the leaf. Figure 1.9, another section, reveals other characteristics of the thin leaf, notably its ability to be pushed into broad, shallow depressions on the silver surface, following closely the surface topography (note the way in which three layers of leaf hang down into a surface irregularity, at the left of the photograph, the lowest layer clinging closely to the surfaces of this pit) and the tendency of the leaf to wrinkle upon application. The uppermost layer of gold at the extreme right of the micrograph travels along the surface, folds under itself, travels a little further, folds again, and continues along to the right. This too is a diagnostic feature for the presence of thin sheet metal. Still another photomicrograph, Figure 1.10, illustrates a characteristic of this gilding that was explained only after laboratory experiments were performed to try to reproduce the technique. Once again, the material beneath the gilding is completely mineralized, and the gold now rests on a thick bed of silver corrosion product. Although the micrographs in Figures 1.8 to 1.10 were all taken at the same magnification (1110X), the gold layer in Figure 1.10 appears considerably thicker than in either of the other two illustrations. Furthermore, there appears to be only one continuous layer of gold present, and this thick layer has managed to enter a deep and narrow surface cavity, to line that cavity, and to reemerge onto the surface without breaking. Is this reasonable behavior for a gold sheet of only one micron thickness?

To answer this question, a cross section of a fragment of gilded silver from the book cover was analyzed with an electron microbeam probe.[11] The probe traces for gold, silver, and mercury at the gilded surface and well into the substrate silver are shown in the plot of Figure 1.11. The probe operated at 30 kV, specimen current of approximately 0.007μA, and with a take-off angle of 52.5°. The gold spectra were obtained with a quartz crystal spectrometer, the silver with ADP (ammonium dihydrogen phosphate), and mercury with LiF. The beam size averaged about 2–3μ in diameter.

It is quite evident from this analysis that

[9] A description of the techniques employed to gild this object was first given at the May 1968 annual meeting of the American Group of the International Institute for Conservation of Historic and Artistic Works, Washington, D.C.

[10] The peeling and eventual loss of gold on this object was most often caused by the formation of silver corrosion products beneath the gilding which tended to push it away from the substrate silver. It was rarely caused by poor initial bonding of the leaf to the metal beneath.

[11] All the electron microbeam probe analyses of the Near Eastern material were performed on an Applied Research Laboratories instrument operated by the X-ray and Electron Optics Group in the Department of Metallurgy and Materials Science at M.I.T.

The probe data for the Peruvian objects were taken on a Materials Analysis Co. instrument at the Ledgemont Laboratory of Kennecott Copper Corp.

the gold leaf was applied to the silver with the aid of mercury. Most probably those areas of the silver to be gilded were amalgamated, the leaf was superimposed, and the entire object was then heated to drive off the excess mercury. The probe traces show that there is a considerable zone of diffusion, approximately 16μ broad, between the gold and the silver and that it is within this zone that the mercury is concentrated. The position of highest mercury concentration occurs several microns inside of the gold peak and falls off slowly through the diffusion zone, finally reaching zero concentration within the silver.[12] The broadness of the interalloyed band of gold and silver indicates that either the metals were heated several times, consistent with multiple applications of leaf, or the object was given a final, prolonged heat treatment to drive off the mercury and perhaps to lighten the color of the gold.[13]

With this much information, reproduction of the leaf gilding was attempted. A piece of thin silver sheet was repeatedly bent until fissures of appreciable depth began to form on one surface. This surface was then amalgamated with pure mercury, and a piece of gold leaf 1.3μ thick was laid on the silver. When the leaf appeared white with mercury, the sample was placed in a small muffle furnace at 540°C for one minute. This sequence was repeated three times, a total of three layers of approximately one-micron-thick leaf having been applied to the silver.[14] A cross section of the unburnished metal is shown in Figure 1.12 at a magnification of 200. Several observations may be made about the structures at or near the surface: (1) It is nowhere apparent that three individual layers of leaf had been applied to the silver; (2) the total thickness of the gilding is considerably greater than 3.9μ; (3) the gold has been drawn down into the deep, narrow surface fissures and has lined these cavities in a continuous fashion just as it did on the book cover itself (illustrated in Figure 1.10). There are two ways in which gold might enter and line these cavities. One is by simple capillarity, for if gold leaf is applied to surfaces coated with a limited amount of liquid mercury, surface tension will draw the gold into close contact with the silver, though it is unlikely that the leaf would penetrate very narrow or deep cavities by this means. The second possibility involves the solution of gold in mercury and its diffusion through the liquid and deposition upon the silver surface as a layer of gold-silver-mercury alloy having lower solubility than gold. This layer would thicken as the mercury in the alloy is evaporated, which might also produce a skin upon the surface of the silver. In both cases the gold, though in the form of thin sheets, has been entirely reformed as an alloy and modified by the continuous diffusion into the silver base and subsequently by evaporation of the mercury.

Interdiffusion of gold and silver in the solid state accounts at least in part for the thickened appearance of the gold leaf and for the disappearance of visible junctions between the successive layers of leaf in successfully gilded areas. Two gold surfaces, both joined by mercury, would maintain their metallic continuity even after the mercury had been removed to produce an apparently single layer of coating.[15] Interdiffusion requires good contact between the gold and the silver, and its extent depends upon the temperature and time of heating. Thus, the single thick layer of gold in Figure 1.10 was formed in an area where the layers of leaf were in close contact with one another when heated and in equally good contact with the underlying silver. On the other hand, these conditions were not met in areas such as that shown in Figure 1.8, where, despite the fact that the metal was subjected to the same heating conditions, little or no interdiffusion has taken place, and the layers of leaf remain separate. The apparent thickening of the gold leaf as a result of interdiffusion is shown schematically in Figure 1.13.

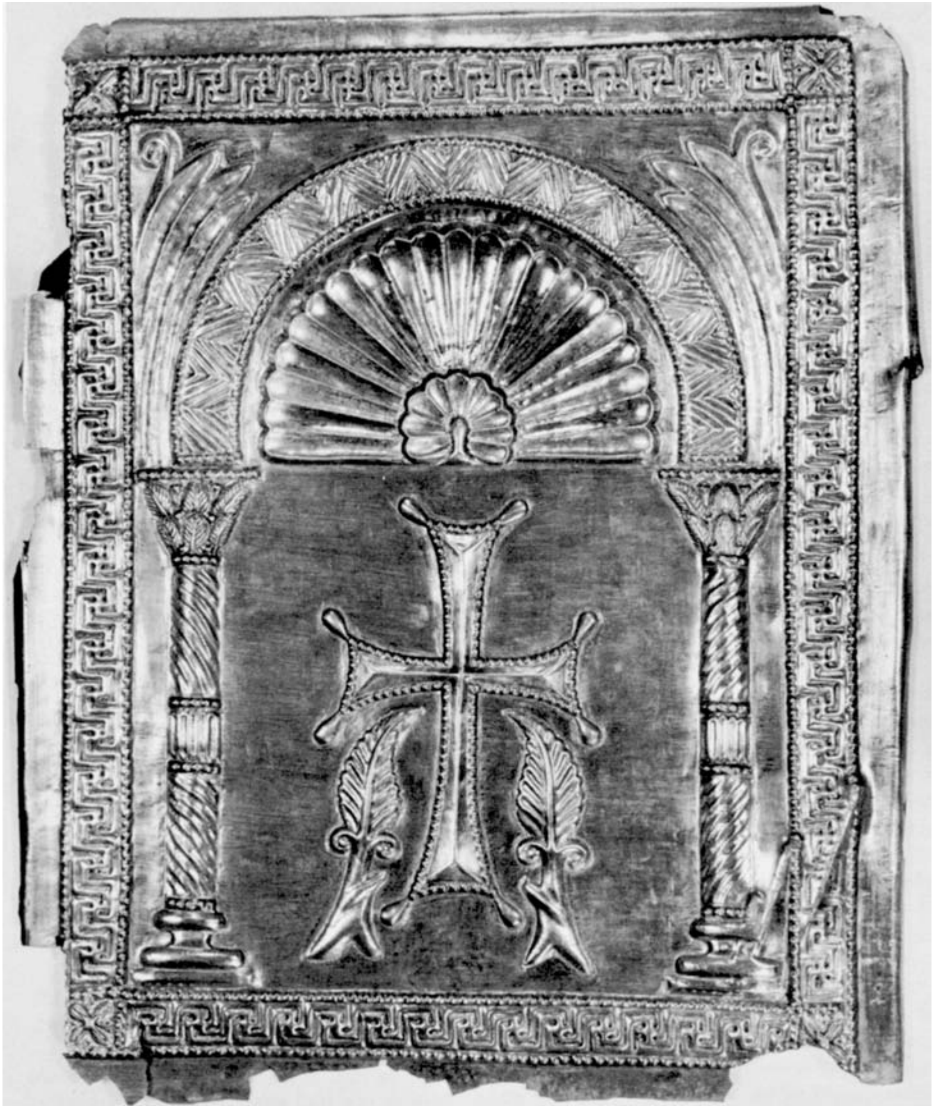
[12] Several 2θ scans taken with the probe of the spectra of all elements within the silver failed to reveal the presence of mercury in the metal itself.

[13] Theophilus, in describing the amalgam gilding of a silver chalice, directs that, once the metal has been thoroughly gilded, it must be heated to dryness, that is, until all of the excess mercury has evaporated. Once dry, the metal should be heated" . . . again until it begins to turn pale." The pale color of the gold is caused by the rapid diffusion of silver into the gold layer forming a Au-Ag alloy which is paler than pure gold. Of course, the formation of this diffusion zone also increases the strength of the bond between the gold and the silver (Reference 6, p. 114).

[14] The silver was later given a long anneal of 16.5 hours at 340°C, which undoubtedly accounts for the thickness of the gold and the extent of Au-Ag diffusion at these metal interfaces. (See next footnote.)

[15] The apparent thickening of one metal in a diffusion couple upon heating is known as the Kirkendall effect. (See Reference 20.) It is illustrated for a Au-Ag diffusion couple by the diagram in our Figure 1.13. A series of fixed, inert markers has been placed at the interface between a thin gold film and a much thicker silver sheet. When the two metals are heated, some of the gold diffuses into the silver and some of the silver into the gold. Because the rate of diffusion of silver into gold is greater than the reverse reaction, as indicated by the relative lengths of the arrows in the diagram, after a given period of time there will have been a net transfer of matter in the direction of the gold. This shift of the center of gravity of the system or apparent shift in the position of the inert markers can be interpreted instead as a thickening of the gold layer above the position of the markers. This is why the gilding in Figures 1.10 and 1.12 appears as thick as it does. When measuring the thickness of gold leaf in a cross section, it is important to choose an area where Kirkendall thickening of the leaf has not occurred.

1.5
Silver parcel-gilt book cover. 37 x 30 cm. Byzantine Turkey, ca. A.D. 570. Dumbarton Oaks, Washington, D.C. [D.O. 63.36.9].

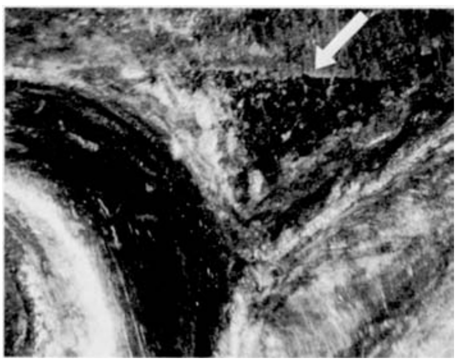


1.8 (to right)
Book cover. Cross section through four layers of gold leaf lying above corroded silver surface. Magnification 1050X, etched by 5% KCN + 5% $(NH_4)_2S_2O_8$.

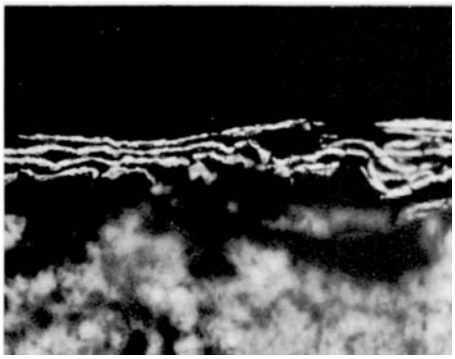
1.9
Book cover. Cross section. Leaf-gilded silver surface shows layers of leaf within surface pit (left) and wrinkled leaf (right). Magnification 1050X, etched by 5% KCN + 5% $(NH_4)_2S_2O_8$.

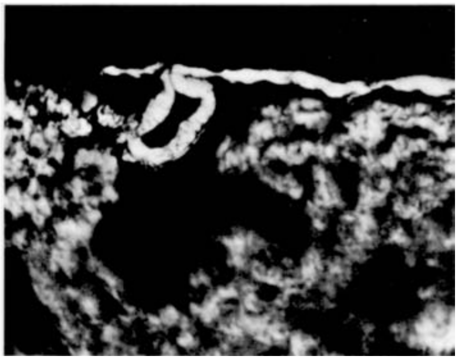
1.10
Book cover. Cross section of leaf-gilded surface. Thickened gold layer has entered and coated the surfaces of a narrow fissure. Magnification 1050X, etched by 5% KCN + 5% $(NH_4)_2S_2O_8$.

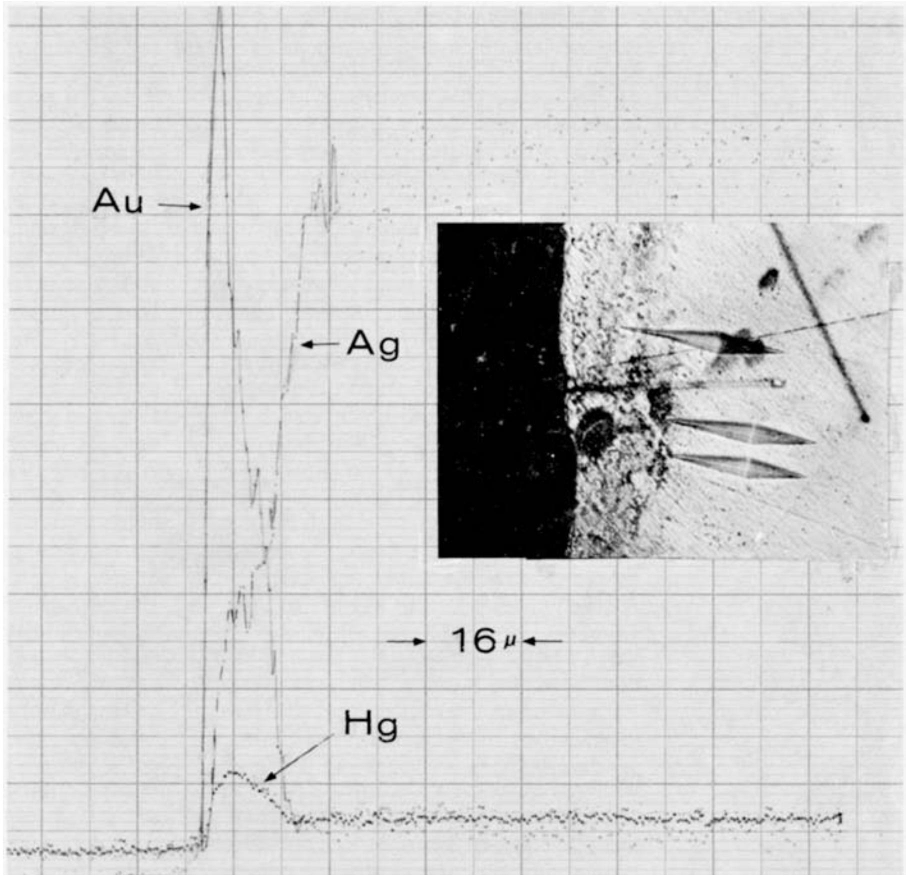
1.6
Book cover. Arrow indicates edge of gold leaf overlapping onto smooth silver ground.



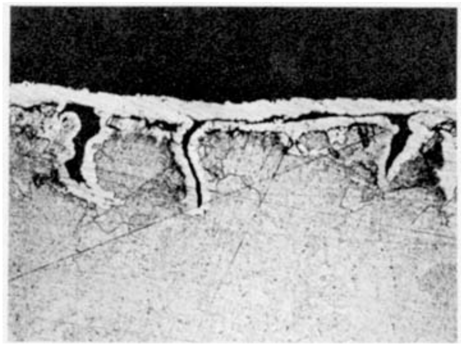
1.7
Book cover. Arrow points to silver showing through tear in gold leaf.



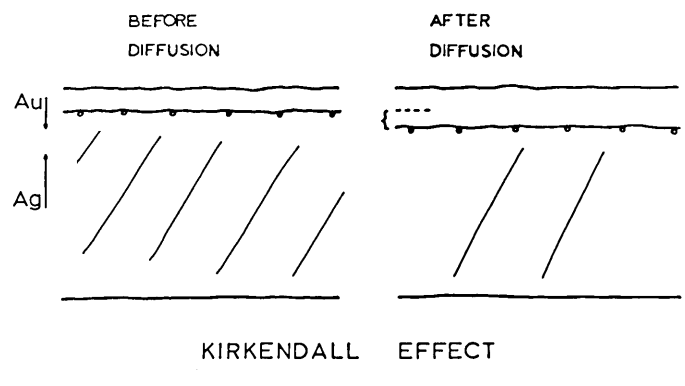




1.11
Book cover. Electron microbeam probe traces of Au, Ag, and Hg across a section of leaf-gilded silver. Photomicrograph (315X) indicates beam path across the gilt surface.



1.12
Photomicrograph of silver sheet gilded in the laboratory with gold leaf and mercury. Section shows penetration of gold into surface fissures and Kirkendall thickening of gilded layer. Magnification: 150X etched by 0.2% H_2CrO_4 + 0.2% H_2SO_4.



1.13
Schematic diagram of the Kirkendall effect in an Au-Ag diffusion couple. The distance through which the inert markers have apparently moved or by which the gold layer has apparently thickened is indicated by the bracket and is known as the Kirkendall shift.

All the phenomena observed in the photomicrographs of the gilded silver of the book cover can, therefore, be explained on the basis of the interactions of gold, silver, and mercury during periods of heating when solid-state diffusion processes and mass transfer in liquid occur.

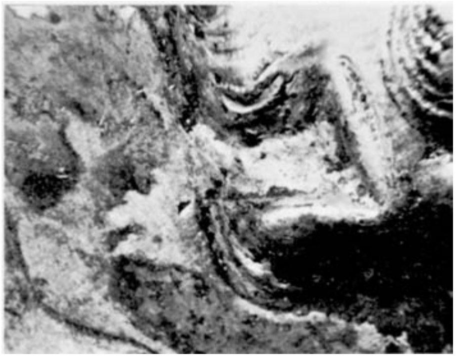
The next three silver objects were all parcel-gilded by the amalgam method and have been chosen because they illustrate properties of that technique. The silver plate depicting a royal hunting scene, shown in Figure 1.14, is from Sasanian Iran and presumably was made during the reign of King Hormizd II, A.D. 302–309. It is in the Cleveland Museum of Art (Reference 18). Many of the areas of highest relief on this plate, such as the head and torso of the king and portions of both lions and of the horse's body, are actually individual pieces of silver fabricated separately and later set into place on the body of the plate. All the gilding was carried out after these pieces were inserted. The bodies of both lions, the horse's body, and most of the apparel of the king are gilded. The irregularity of the edges of the untarnished gilded motifs, especially in comparison with the precise outlines of the gilding on the book cover, is striking. The gold appears to have spilled over onto the silver background along most of these edges, notably along the proper left side of the king's chest, along his bent right arm, and along the tail of the felled lion. Particular note should be made, however, of places where the amalgam has spilled onto the silver background to such an extent that it traverses the surface of the silver, connecting one gilded area with another. Three prominent spills visible in Figure 1.14 occur between the tip of the king's scabbard and the mane of the slain lion, between the proper right side of the king's torso and the horse's mane, and between the open mouth and the right paw of the attacking lion. A detail of the latter spill is given in Figure 1.15.

Such areas are characteristic of amalgam gilding.[16] Typically, the silver area to be gilded is first amalgamated with mercury, although this is not a necessary step. The mercury diffuses rapidly along the surface of the silver and cannot readily be confined within any prescribed region unless some stopping-out material is used to protect the portions that are to remain free of gold. The pasty gold-mercury amalgam is then spread over the designated area. Some of this amalgam will naturally spill over onto any surfaces where mercury has already alloyed with the silver. It will be difficult to confine even when the preparatory mercury coating is absent. When the object is subsequently heated to drive off the mercury, the gold remains in place. If the gilt edges are particularly rough because of irregular spillage, the excess gold is removed by gently scraping the surface until relatively pure silver is once again obtained. Quite often, however, the gold will have diffused deeply enough into the silver, alloying with it, so that the areas of spilled amalgam always appear slightly pale and shiny owing to the presence of this alloy. Even if not visibly yellow, such areas corrode less severely than pure silver, and with time they stand out by virtue of the contrast between their preserved surfaces and that of the tarnished or otherwise corroded silver. This phenomenon is rarely encountered with leaf, which tends to remain where it is placed even if the mercury may have spread around it.

The gilt silver rhyton of Figure 1.16 with its four representations of the goddess Anahita is also from the early fourth century of Sasanian Iran. It too is among the collections of the Cleveland Museum of Art (Reference 18). Unlike either of the other two amalgam-gilt objects, here it is the background that is golden and the relief design elements that remain silver. In order to accentuate the outlines of these raised areas of metal, a pronounced, deeply traced line defines their contours. When the thick amalgam was spread over the silver background, it tended to accumulate within these deep depressions. Later, after the mercury was volatilized away, the gold was carefully burnished. But burnishing tools are rarely small enough to enter the depressions caused by engraving or tracing tools; thus, the contour lines have remained full of unburnished gold with the characteristic spongy, open, "bubbly" look of accumulated, dried amalgam. Figure 1.17 is a detail of the proper right hand of the goddess shown in the preceding illustration. The deep, traced contour groove outlining the edge of the little finger and the beginning of the palm is filled with this spongy gold. It is in striking contrast to the smooth, polished gold of the background alongside it. The bubbly effect occurs primarily in the regions where the amalgam is able to accumulate in relatively thick layers. In such regions the bubble structure forms in the solidifying metal by virtue of the escaping mercury vapor. The sponginess may be typical of even thinner layers of amalgam, however, resulting simply from crystallization of the gold during solidification. This is rarely seen except in surface depressions because it can be burnished smooth elsewhere.

The porous, spongy quality of an amalgamated gold surface is not surprising when one looks at cross sections of silver that have been amalgamated with mercury alone, then dried but left unburnished. Figure 1.18 is just such a section of a

[16] Microbeam probe data of a cross section of gilded silver from this plate indicate the presence of mercury in association with the gold and silver at the surface of the section. The analyses were performed at Case–Western Reserve University under the direction of Prof. Donald F. Gibbons and Mrs. Katharine C. Ruhl. Personal communication, June 1968.



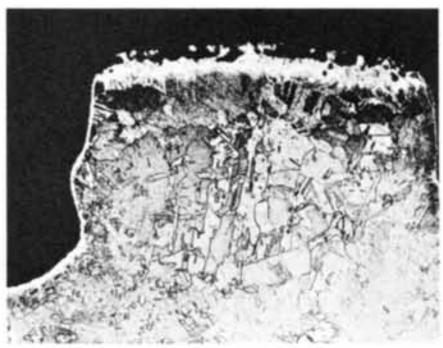
1.14
Silver plate with royal hunting scene. Iran, Sasanian, ca. A.D. 302–309, approximately 20.5 cm diameter. The Cleveland Museum of Art, Purchase, John L. Severance Fund. [CMA 62.150].

1.15
Silver plate. Detail of the amalgam spill between the jaws and paw of the attacking lion. Photo by Katharine C. Ruhl.

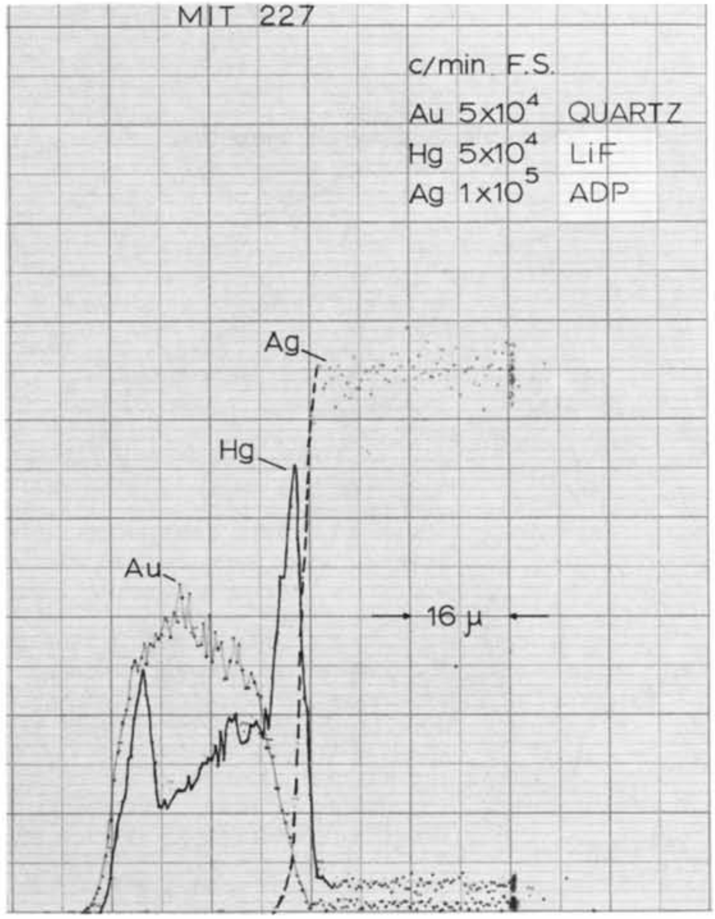
1.16
Silver rhyton with figures of the goddess Anahita, 18 cm high x 11 cm maximum diameter. Iran, Sasanian period, early fourth century A.D. The Cleveland Museum of Art, Gift of Katharine Holden Thayer [CMA 62.294].

1.17
Silver Anahita rhyton. Detail of the spongy, porous gold accumulated within the traced groove outlining the hand. Photo by Katharine C. Ruhl.

1.18
A section of worked silver sheet amalgamated with mercury in the laboratory. Magnification 150X, etched by 0.2% H_2CrO_4 + 0.2% H_2SO_4.



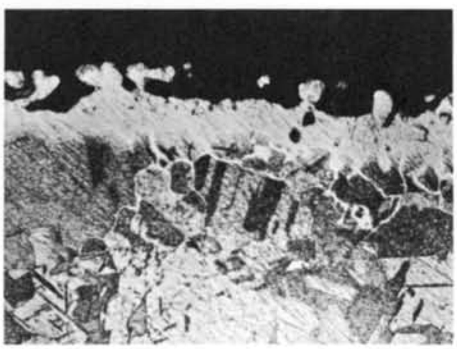
1.19
More highly magnified detail of section shown in Figure 1.18. Note entry of mercury into grain boundaries. Magnification 370X.

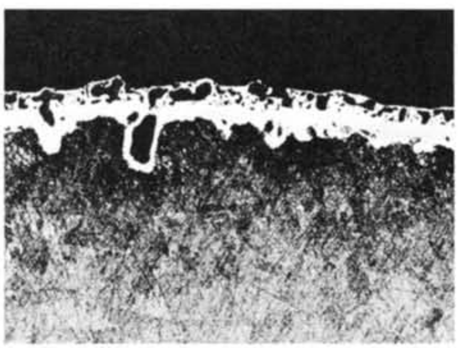


1.20
A section of worked silver sheet gilded in the laboratory with Au-Hg amalgam. Magnification 75X, etched by 0.2% H_2CrO_4 + 0.2% H_2SO_4.

1.21
Silver Anahita rhyton, cross section showing the thick, surface layer of gilding. Magnification 375X etched by $K_2Cr_2O_7$ + NaCl + H_2SO_4 diluted 1:9.

1.22
Silver Anahita rhyton. Electron microbeam probe traces of Ag, Au, and Hg across the gilded surface shown in Figure 1.21.





piece of sheet silver that was cold worked until both tiny surface fissures and deeper fatigue cracks were produced. The surface was then amalgamated with mercury and the sample heated in a muffle furnace at 540°C for one minute. The amalgamation and heating were repeated three times. The specimen was then annealed at 340°C for 16.5 hours. The photomicrograph shows, in the first place, how uniformly the mercury has amalgamated with the silver in the deepest surface pits and, second, how open and granular the upper surface of the silver remains. Figure 1.19, a more highly magnified detail of this same specimen, illustrates the extent to which the mercury has cracked the worked metal along grain boundaries and shows even more clearly the spongy nature of the silver.

A similar piece of metal, also worked to produce cracking, was amalgamated with mercury and placed in a furnace at 570°C for half a minute. Afterward it was coated with a layer of Au-Hg amalgam and heated again for one minute at the same temperature. Two further applications of amalgam followed by two identical heat treatments ensued. Figure 1.20 is a photomicrograph of a cross section of this gilded, but unburnished, silver. The porosity of the gold layer is quite apparent here as is the obvious penetration of the mercury and, therefore, of the gold into the surface irregularities.

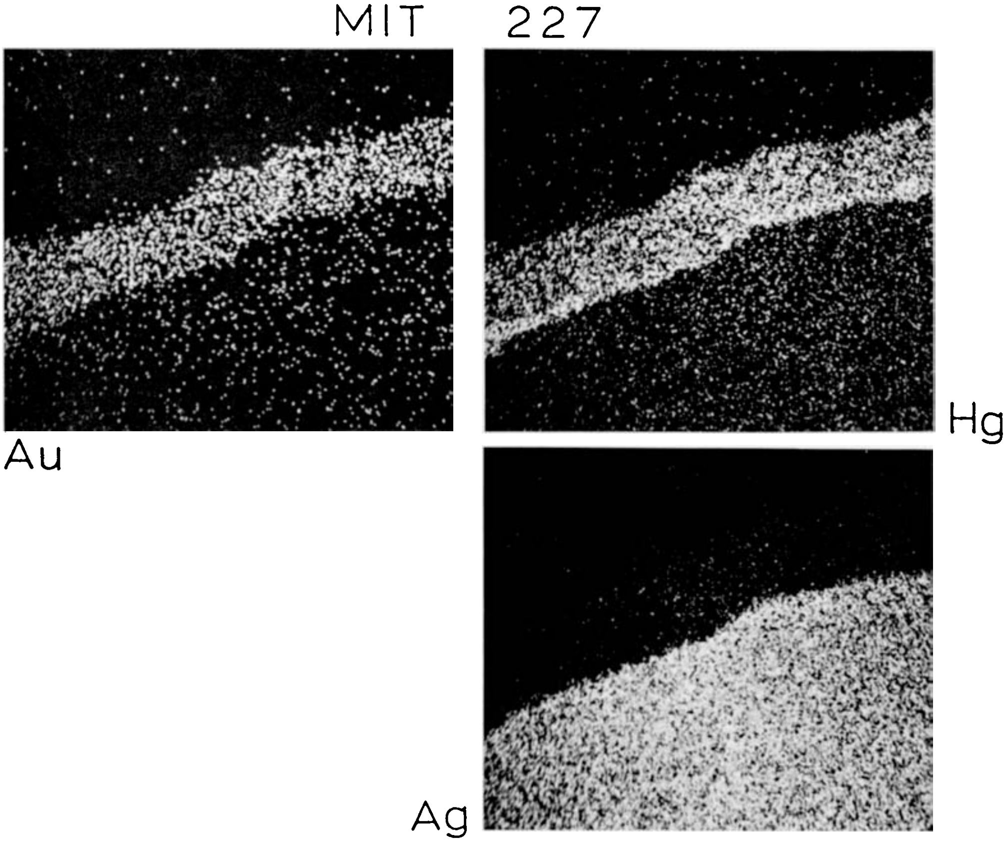
A cross section was made of a tiny gilded fragment removed from a broken edge of the figured rhyton. A photomicrograph of the gilded surface is given in Figure 1.21. The gold layer superimposed above the worked silver substrate is extremely smooth, indicating extensive final burnishing.[17] It is also extremely broad, measuring approximately 26μ in thickness. Although it is possible that a single layer of amalgam could have resulted in such a thick deposit of gold, it is more likely that a series of applications was made and the final layer burnished and possibly scraped to make it uniform and compact.

Electron microbeam probe traces through this same section are shown graphically in Figure 1.22. It is quite clear that very little diffusion has occurred between the silver and the gold and that the mercury is associated primarily with the gold. A characteristic feature of the mercury traces in all the amalgam-gilded samples studied thus far has been the very high concentration of this element at the interface zone between the gold and the silver. An intermediate compound of mercury-gold-silver must form in this region where the gold concentration is quite low but where the concentration of silver has begun to rise. The peak mercury concentration in this case is approximately 24 percent, while the average concentration of mercury within the gold is approximately 7 percent. The distribution of the three elements in this cross section is nicely given in the set of probe scanning display photographs of Figure 1.23. The high concentration of mercury at the Au-Ag interface is particularly clear in the mercury scan. As a comparison, probe traces were also taken of the experimental sample shown in Figure 1.20; these appear in Figure 1.24. In this case, too, very little diffusion has occurred between the gold and the silver, whereas the mercury has diffused quite deeply into the silver as well as being retained within the gold. The characteristic interface mercury peak, here definitely more closely associated with the silver than in the case of the rhyton sample, is quite apparent. The concentration of mercury at the peak position is approximately 75 percent, while its highest concentration within the gold is about 37 percent.

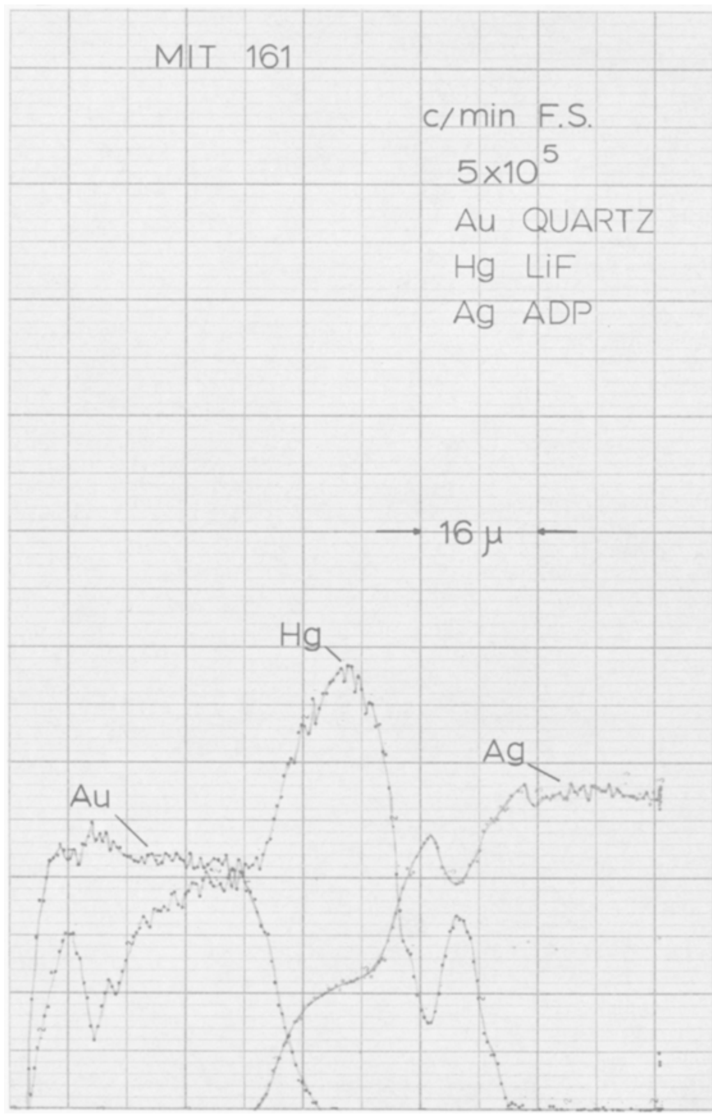
[17] The crack in the gilding occurred when the rhyton was damaged. It is not a characteristic feature of an amalgam-gilt surface.

The third object gilded by the amalgam method is the small (approximately 7 × 4 cm) silver torso shown in Figure 1.25 which is almost identical with that of the king depicted on the hunting scene plate in Figure 1.14 and can safely be said to be from Iran sometime within the fourth to sixth centuries A.D. This torso is one of the separately fabricated pieces of relief decoration described earlier, which was made for insertion onto a silver plate previously prepared to receive it. It is presently in a private collection in Cleveland.

The surface decorative tooling, both traced and engraved, was completed before the gilding was applied. The gilt areas include the sleeve cuff, the shoulder and chest straps, the "bib" between the shoulder straps, and the waistband. A small metal sample was removed from the lower proper left corner of the waistband and included the three small, punched tool marks visible there in Figure 1.25. The photomicrograph in Figure 1.26 is a cross section through part of one of these punched depressions. The smooth, burnished layer of gilding on the flat surface of the waistband is located in the upper right portion of the photograph. The average thickness of this layer is approximately 10μ. The unburnished gold within the depression, however, has accumulated in large, spongy clumps, and only that portion immediately adjacent to the underlying, heavily worked silver is closely bonded to it. A set of electron microbeam probe traces taken through the burnished portion of the gilding (Figure 1.27) is comparable with those of Figures 1.22 and 1.24 and is particularly close in profile to the traces through the Anahita rhyton. Here the mercury concentration at the peak position is approximately 15 percent, whereas the average mercury concentration within the gold itself is about 6

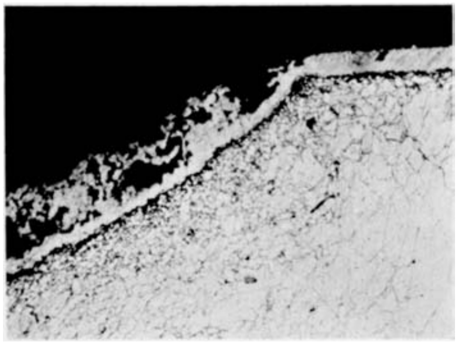


1.23
Silver Anahita rhyton. Electron probe scanning display photographs showing the distributions of Au, Hg, and Ag in the section of Figure 1.21.

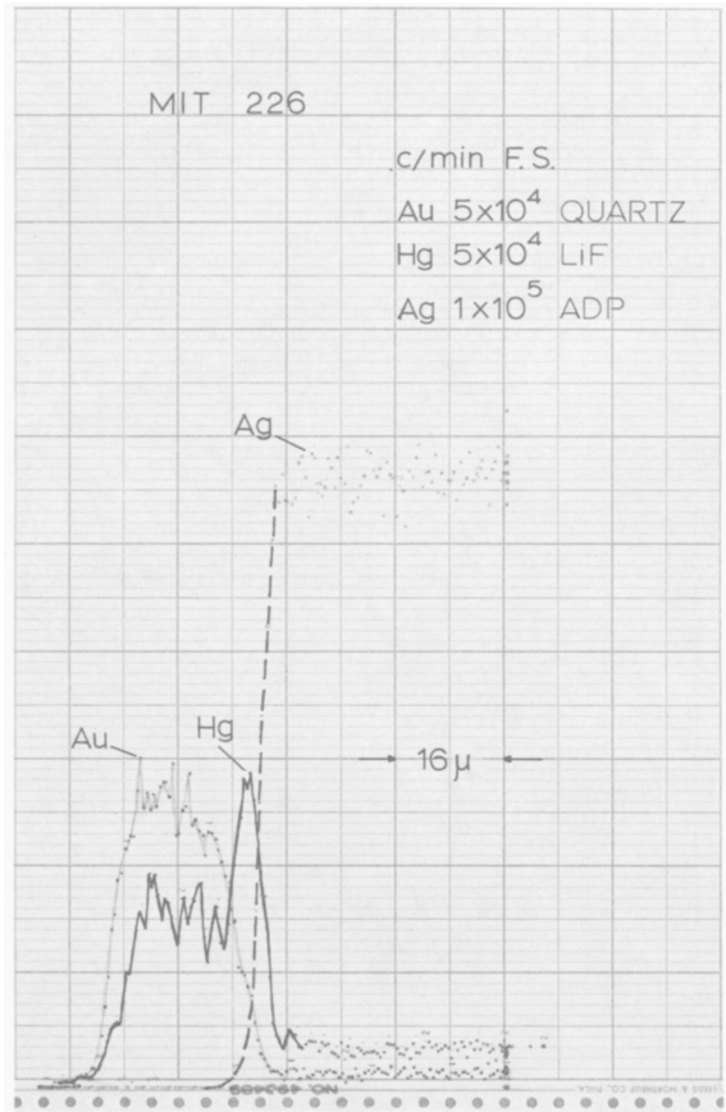


1.24
Electron microbeam probe traces of Ag, Au, and Hg across the experimental sample shown in Figure 1.20.

1.25
Silver torso insert from a plate. Iran, Sasanian period, fourth to sixth century A.D. Private collection, Cleveland. Photo by Katharine C. Ruhl.



1.26
Torso insert, section through a decorative punched hole. Accumulation of spongy gold is seen within depression. Magnification 300X, etched by $K_2Cr_2O_7$ + NaCl + H_2SO_4, diluted 1:9.



1.27
Torso insert. Electron microbeam probe traces of Ag, Au, and Hg across the burnished portion of the gilt surface in Figure 1.26.

1.28
Disk thought to come from Vicus in northern Peru. Lent for study by Mr. and Mrs. Dudley T. Easby, Jr.

1.29
"Vicus disk," detail of a traced motif on the obverse surface.

percent. The fact that the probe traces from the amalgam-gilded objects and from the experimental sample exhibit such little diffusion between the silver and the gold evidently suggests that the heating that took place after each application of amalgam was both brief and at a relatively low temperature. In the case of the experimental sample, heating the object for a total of three minutes at 570°C was insufficient to allow much Au-Ag diffusion to take place, whereas diffusion and retention of mercury under these conditions proved more than adequate to produce excellent alloying and bonding.

Summary

The gilding techniques exhibited by these five objects from the Near East have certain features in common that may serve, in part, to characterize them.

1. All the objects are parcel gilt, that is, they were gilded only in certain areas in order to take advantage of the highly decorative effect of the juxtaposition of silver and gold.

2. The gold was applied after the surface chasing—by tracing or engraving—was completed. In the case of the horse rhyton, it was the decorative tooling itself that was to hold the gold in place. Gold tended to accumulate in these tooled areas in both the leaf-gilded book cover and the amalgam-gilded objects.

3. The gold layer, regardless of its method of application, is of considerable thickness. Even the leaf-gilded object had several layers of leaf applied to it, creating a gilded coating of about 4μ. Generally the gilding is between 10 and 30μ thick.

4. In four of the five examples, the gold was applied with the aid of mercury. The possible employment of mercury in the gilding of the fifth example has been discussed. See also the Appendix.

Objects from Peru

Analysis of the gilded material from the Near East proved fairly straightforward. Often clues to the gilding techniques employed became evident on a thorough macroscopic examination of the objects, and these were later substantiated by metallographic evidence. The two objects from Peru that have been chosen for discussion were selected precisely because surface examination offered few insights, and they remained puzzling even after metallographic studies were undertaken. Note has been made in the introductory section of the fact that a host of gilding techniques was undoubtedly used in Peru and in South America generally, but a particular type of gilded object which defies simple analysis appears to be characteristic of the development of metallurgy along the north coast of Peru. It is these artifacts that will be treated in this section. These particular investigations are in an early stage, and my comments will, therefore, be more in the nature of suggestions as to the gilding techniques employed and indications of the direction that the investigations should take rather than solutions to the posed problem.

The gilded disk that appears in Figure 1.28 is said to be from Vicus, a burial site in the upper Piura Valley very close to the Ecuadorian border. The metal artifacts from this site are extremely difficult to date and to relate to the associated ceramic sequences. Generally speaking, the artifacts tend to group themselves into an early or classic Vicus style, (ca. 400 B.C.–A.D. 100) and a later style, the negative Vicus style (ca. A.D. 100–700), which takes its name from the negative-decorated pottery that characterizes it.[18] Therefore, the disk may fall anywhere within this broad time period. It was kindly lent for study by Mr. and Mrs. Dudley T. Easby, Jr.[19]

The disk is fabricated of thin sheet metal, ostensibly silver, hammered to its present shape with a high central boss and a series of traced motifs that decorate both the front and the back of the object. The gilding covers all its surfaces, and only where the gold has been lost through wear or corrosion of the underlying metal can the silver be seen beneath it. The lighter, pock-marked areas evident in Figure 1.28 are patches of silver that have lost their gilded covering. The gold is extremely smooth and appears to be very thin as well. It is as uniformly deposited within the rather narrow and shallow grooves left by the tracing tool as it is on the smooth, flat surfaces. A detail of one of the decorative motifs is shown in Figure 1.29. The smooth, uninterrupted quality of the gold is apparent except in those areas, such as the eye of the figure, where corrosion has pitted the metal. The surfaces give no indication of the way in which the gilding was accomplished. The only feature of note is that there is no accumulation of gold within the declivities. A uniform, continuous layer appears to cover the entire object. In fact, one has the impression that the gilding was completed before the final decorative tooling was carried out.

[18] The styles and chronological periods followed here are those outlined recently by Alan R. Sawyer, Reference 17.

[19] The disk illustrated in Figure 1.28 may not be from Vicus, however. Two disks, virtually identical with it, have more recently been lent for study by Junius B. Bird. He describes these as having come from a tomb with a relatively dry environment, whereas objects from Vicus are subject to moist soil conditions. He believes, therefore, that these disks are from a site south of Vicus and that their style places them in the Chimu period. (Personal communication, December 1968).

Table 1.1
Analysis of the "Vicus" and Chimu Disks

	Wet Chemical*			Spectrographic (Qualitative)							
				Percent, by weight							
	Ag	Cu	Au	Bi	Fe	Hg	Mg	Mn	Ni	Pb	Si
"Vicus" Disk (MIT 217)	29.2	60.8	10.1	0.01–0.1	N.D.†	N.D.	0.0001–0.001	N.D.	0.001–0.01	0.1–1.0	N.D.
Chimu Disk (MIT 218)	43.4	33.5	6.4	0.01–0.1	0.0001–0.001	N.D.	0.0001–0.001	0.0001–0.01	N.D.	0.1–1.0	0.001–0.01

* The maximum relative experimental error in the determination of Au and Cu is ±0.5%; for Ag it is ±2%. The gold was determined gravimetrically as a residue; the silver was determined as silver chloride by gravimetric analysis; the copper was determined colorimetrically by iodometric titration. See Earle R. Caley, *Analysis of Ancient Metals*, Oxford, 1964, pp. 51–53 and 67–74; Charles M. Dozinel, *Modern Methods of Analysis of Copper and Its Alloys*, Amsterdam, 1963, pp. 87–92

† Not detected

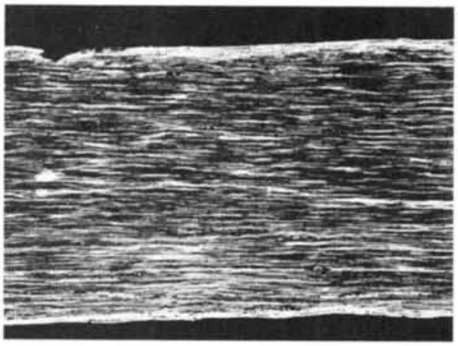
The photomicrographs illustrated in Figures 1.30 to 1.32 show, in cross section, the microstructure of a small fragment of metal removed from the edge of the "Vicus" disk. It is immediately apparent from the two-phase structure that the metal from which this object is made is not pure silver. The analysis in Table 1.1 indicates that it is essentially an alloy of silver and copper. Several other features are notable in these photomicrographs. The heavily worked metal has been severely deformed, and the silver-rich (light etching) and copper-rich (dark etching) phases have become narrow, interlayered bands elongated in the direction of working of the metal. Figure 1.30, which shows the entire cross section from front to back, also exhibits most clearly the rather thick silver-enriched zones on both surfaces of the metal. A detail of one of the surfaces, given in Figure 1.31, shows this thick, almost copper-free surface zone more clearly. It is almost impossible at this magnification (380X) to discern any gold whatever. It is only in the more highly magnified (750X) detail in Figure 1.32 that the thin gold coating can be seen (see arrow). It is approximately one micron in thickness.

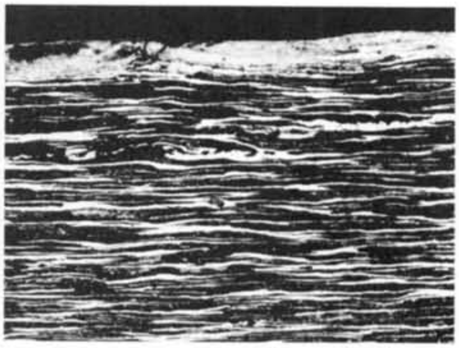
When certain Ag-Cu alloys are made into sheet metal, it is almost inevitable that the final sheet will appear as if it is of pure silver because of the depletion of copper from the surfaces by oxidation during annealing.[20] A reconstruction of the sequence of metallurgical events taking place is given in Figures 1.33–1.35. An alloy resembling that of the metal in the disk, namely a 60/40 Cu-Ag alloy, was cast and allowed to air-cool in a crucible. It is shown in the as-cast condition in the photomicrograph of Figure 1.33. The structure reveals large cored dendrites (dark etching) of the copper-rich, beta solid solution of silver in copper surrounded by the eutectic (light etching) structure of the alpha (silver-rich) and beta phases. The eutectic structure varies from areas where it is quite fine to others where it is reasonably coarse. The cast alloy was put through a series of 15 courses of hammering, flame annealing, and pickling in order to reduce it from a slab 0.44 cm in thickness to a thin sheet 0.07 cm in thickness, a reduction of 84 percent. A cross section of the resulting sheet is shown in Figure 1.34. The structure is not unlike that of the disk, though it is considerably coarser. In the photomicrograph of Figure 1.35, one can still see vestiges of the original thick dendrites now much reduced and elongated by deformation. The beta phase of the eutectic has tended to ball up as a result of annealing but would, on further hammering, become thin stringers similar to those present in the disk metal. The origin of the banded structure of the disk metal can be explained, therefore, in terms both of the original two-phase microstructure of the cast alloy and of the deformation of those phases through cold or hot working. Figure 1.35 also gives a more detailed picture of the enriched silver surface of the experimental sample. In fabricating the experimental sheet, it was necessary to anneal it repeatedly to soften it. During the course of each annealing operation, the copper within the alloy diffused rapidly onto the surface where it was oxidized. This dark scale of copper oxide was dissolved by pickling the metal in dilute sulfuric acid or in ammonia, and hammering was recommenced.[21] After only about three such sequences, enough copper had been removed from the surface so that it appeared silver.[22] The thinner the metal became, the more often annealing and pickling were necessary and the thicker the enriched silver layer grew. It is quite

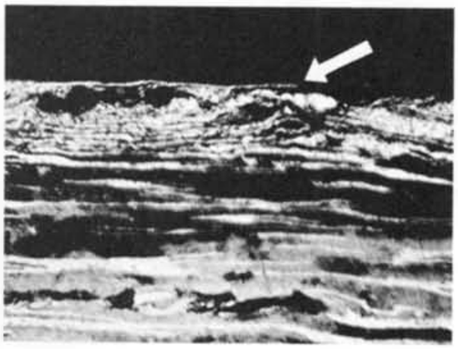
[20] See Reference 12 for a description of the phenomena involved in this process.

[21] There are many naturally occurring acids such as oxalic or acetic acid which could be used to remove the copper oxide scale. Similarly, urine might have been used by the pre-Columbian Indians for this purpose, ammonia being one of its decomposition products.

[22] The Peruvian Indians utilized this effect in the manufacture of many objects that were meant to look like silver. Copper-silver alloys were often used on the south coast of Peru from the late Ica period onward, and it was a common alloy of the Chimu culture as well. See Reference 13 and also the two Chimu wall plaques from the north coast of Peru, made of silver-copper alloy, illustrated in Reference 3, Figure 45.



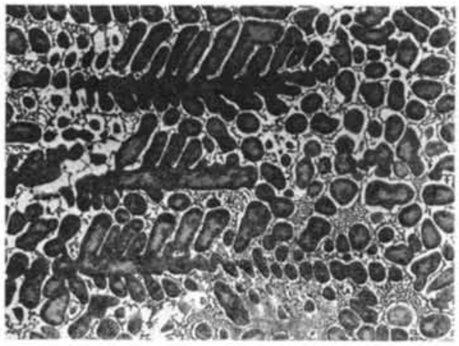




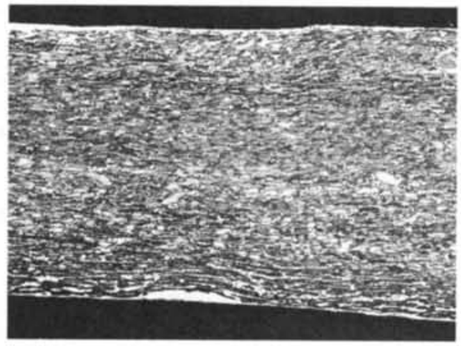
1.30
"Vicus" disk, photomicrograph of an entire section through the metal. Magnification 120X, etched by $K_2Cr_2O_7 + H_2SO_4 + HCl$.

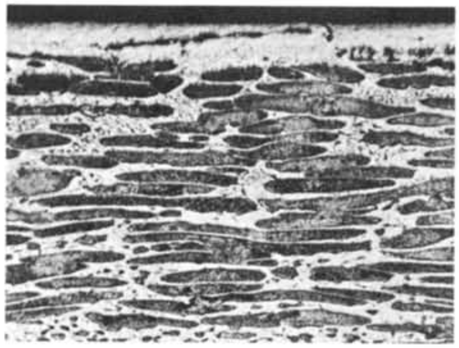
1.31
"Vicus" disk. Detail of Figure 1.30 showing the enriched surface layer of silver. Note the tiny, white precipitates of silver within the copper-rich areas. Magnification 380X.

1.32
"Vicus" disk. Section through the surface; arrow indicates thin gold layer above silver. Magnification 750X. As polished.



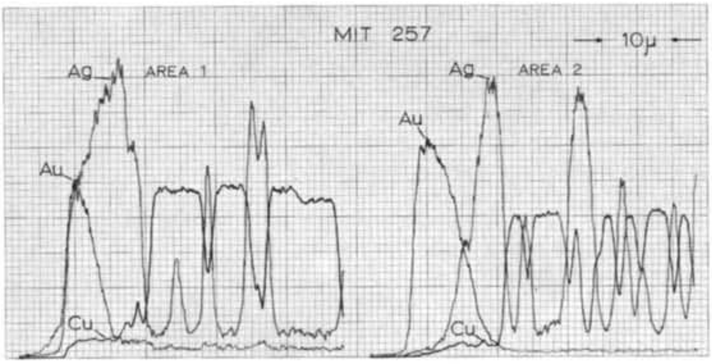
1.33
A section of 60/40 Cu-Ag alloy in cast condition. Magnification 120X, etched by $FeCl_3$.



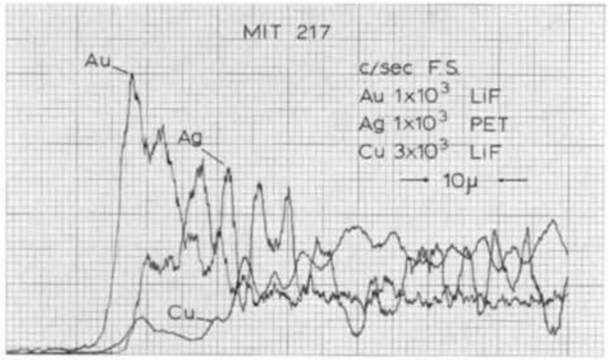


1.34
A section through sheet metal hammered from the casting shown in Figure 1.33. Magnification 60X, etched by $K_2Cr_2O_7 + H_2SO_4 + HCl$.

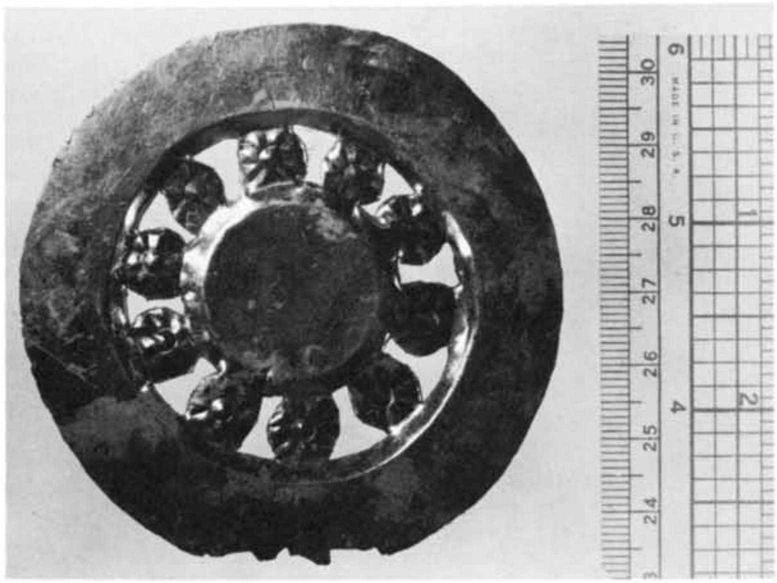
1.35
Detail of Figure 1.34 showing enriched silver surface layer. Magnification 275X.



1.36
Electron microbeam probe traces of Au, Ag, and Cu across two areas of a leaf-gilded silver sheet. Area 1, single leaf layer: Ag-PET-1K; Cu-PET-10K; Au-LiF-1K. Area 2, double leaf layer: Ag-PET-1K; Cu-Lif-10K; Au-LiF-3K.



1.37
"Vicus" disk. Electron microbeam probe traces of Au, Ag, and Cu across the gilded surface of a cross section of the metal.



1.38
Chimu disk. Vicinity of Trujillo, ca. A.D. 1000–1470. American Museum of Natural History [AMNH 41.2/5876].

evident that a good deal of the silver metal observable on the disk in areas where the gilding has been lost is simply the silver of these enriched surface zones.

The question still remains as to the manner in which the gilding was formed on the silver surface of the disk. It is entirely possible that the gold was applied in the form of thin leaf of approximately one micron thickness or that it was rubbed onto the surfaces as a finely divided powder. In either case the gold would have had to be applied at or very near the completion of the object. Otherwise the continued heating necessary to anneal the metal would cause such extensive diffusion between the gold and the silver that the gold would become pale and lose its covering power. In order to illustrate this effect, some gold leaf of approximately one micron thickness was burnished onto the silver-enriched surface of a piece of the experimentally prepared Cu-Ag sheet metal. In some areas only a single layer of leaf was applied; in others two layers were attached. The metal was then put through four additional courses of hammering, annealing, and pickling. The leaf work hardened rapidly upon both burnishing and hammering, and it became quite clear that even had it been applied after the object was completed, some annealing operations would have been carried out to soften the metal and to facilitate bonding between the silver and the gold.

A cross section of the gilded sample was analyzed with an electron microbeam probe, and the probe traces for silver, copper, and gold are shown in Figure 1.36. The probe had a 35° take-off angle, was operated at 20 kV and at a specimen current of $0.01 \mu A$. The gold spectra were taken with a LiF crystal, the silver with PET (pentaerythritol), and copper with either LiF or PET. The beam size was about $1-2\mu$.

Area 1 is a surface onto which a single layer of gold was applied. Two layers of gold were burnished onto Area 2. Diffusion between the silver and gold is extensive in both areas. In the case of Area 1, however, the gold and silver have completely alloyed, and there is no place where the gold does not contain large amounts of silver. In fact, this is an area where the gold became so pale that one could no longer see that any gold was present. On the other hand, the double layer of gold in Area 2 was thick enough so that about two microns of gold remain that contain virtually no silver. This area appeared very golden at the end of the hammering-annealing sequences.

A similar set of microbeam probe traces was made through the cross section of the disk metal. These appear in Figure 1.37. The profile of these traces is not dissimilar to that of Area 2 of the experimental sample. There is a fairly broad region at the surface containing virtually no silver as well as a deeper zone in which the gold and the silver are alloyed. The most important information carried by these traces, however, is the fact that there is an appreciable amount of gold within the body of the metal itself (compare the Au trace in the body metal of the experimental Ag-Cu alloy with the trace in the body metal of the disk). The analysis indicates that there is approximately 10 percent of gold, by weight, in the disk metal, and it is evident from the probe traces that this gold is *not* confined to the surface gilding layers but that it is a constituent of the alloy. The disk is a ternary alloy of silver, copper, and gold. The relatively high concentration of the gold indicates that it is probably a purposeful additive. It is certainly present in excess of what one would expect of silver with a high gold impurity level.

The disk illustrated in Figure 1.38 is the second object from Peru. It shares many characteristics with the disk assumed to come from Vicus. It is made of even thinner sheet metal, with pierced, openwork design and with gilding on all surfaces. This object, which is presently in the collection of the American Museum of Natural History, is probably of Chimu origin (ca. A.D. 1000–1470) and is said to come from the coastal region near the modern city of Trujillo. The surfaces of the disk are extremely smooth, although many areas are covered with copper corrosion products that give it the patchy appearance evident in Figure 1.38. The gilded layer appears incredibly thin and also has a pale, greenish hue characteristic of gold alloyed with silver. The traced motifs on the "rosettes" are shallow, and in a number of places the tracing shows strong evidence of having been accomplished after the gold was already in place. Nowhere is there any accumulation of gold within these depressions. As with the "Vicus" disk, there are no observable indications on the surfaces of this object as to the gilding method employed.

The composition of the metal is given in Table 1.1. As is evident from the microstructure of a cross section of the metal (Figure 1.39), the copper has corroded extensively and exists mainly in the form of cuprous oxide within the body of the object. This undoubtedly explains why the sum total of the major metallic constituents of the metal is only about 83 percent by weight. Normalizing this to 100 percent, the uncorroded metal contained approximately 51 percent Ag, 39 percent Cu, 7.5 percent Au. The microstructure of the unetched section is virtually identical with that of the "Vicus disk." Here, however, it is the corroded copper-rich phase that provides the contrast to the lighter silver-rich areas. The broad, enriched silver surfaces are also quite evident. Examination of the section with the optical microscope at a magnification of 1000X did not reveal any distinct layer of gold above the silver.

The electron microbeam probe traces taken across this section are shown in Figure 1.40. The gold trace reveals the extremely thin surface gilding, indicates quite clearly that this layer is entirely associated with the silver-enriched surface zone, and explains why it does not appear as a discrete layer in the cross section. The gold and silver are interalloyed, which accounts for the pale greenish color of the disk itself. The probe profile of this disk is similar to that of Area 1 in Figure 1.36, and the same arguments that might account for the "Vicus" gilding in terms of an extremely thin, externally applied gold layer—in this case completely diffused into the silver—could be equally valid for the Chimu object. Once again, however, it should be noted that the gold is present throughout the body of the metal, the gold trace indicating quite clearly that this metal is a ternary Ag-Cu-Au alloy.

There is at least one other method by which both these disks might have been gilded, however, a method that would explain the macroscopic characteristics of the gold surfaces and that would satisfy the data provided by the probe traces. Such a method involves depletion gilding, that is, surface enrichment of the gold already present in the alloy by selective removal of the silver. We may conservatively assume that the pre-Columbian Indians did not have available to them a reagent, such as nitric acid, which has been used in Europe since the twelfth or thirteenth century for parting silver and gold. The removal of silver from the alloy by simple acid dissolution is highly unlikely.[23] On the other hand, it is perfectly plausible that the Indians may have used some operation akin to cementation to remove some of the surface silver. Cementation has traditionally been used for the purpose of purifying gold containing impurities such as copper and silver. It is undoubtedly a process of great antiquity, but literary evidence for its use in Europe and the Near East before the early Middle Ages is scant. Descriptions which seem to relate to it are to be found in both Strabo and Pliny, but the details are hard to follow. By the twelfth century, in the treatise of Theophilus, we have a detailed account of the method, and its use thereafter is documented in many sources. See References 1, 6, 7, 10, 21, 22, and 23.

In all cementation recipes, the gold is packed in a reactive powder (the cement), which, when heated, combines chemically with the impurities on the surface of the gold and eventually, by diffusion, with the impurities throughout the entire body of the metal. The cement, which invariably contains salt, reacts to form chlorides of silver and other impurity metals, leaving the gold unattacked. Both the reagent and the reaction products are absorbed in the largely inert matrix of brick dust or some similar material. Additional ingredients may be ammonium chloride, potassium nitrate, copper sulfate, iron sulfate, vinegar, or urine. The most direct method is simply to place the salt-clay mixture in an earthenware crucible, add a layer of gold in some form with a high surface area such as granules or thin sheet, then another layer of cement, and alternate layers until the crucible is filled. It is then luted and placed in a furnace at a temperature well below the melting point of the alloy, generally for from 12 to 24 hours. The copper and silver in the gold are attacked by the chlorine generated and react to form copper and silver chlorides. Depending upon the furnace temperature, these salts either will melt and be taken up by the clay matrix or by the walls of the crucible itself or will remain solid and can be dissolved later from the surface of the gold. The process may be repeated as many times as necessary and is a drastic and thorough procedure for the removal of all the impurities.

To my knowledge, there is no evidence that cementation has ever been used for purposes of gilding by surface enrichment of gold in an alloy of low gold content. A somewhat similar technique has been used, on the other hand, to improve the surfaces of alloys that are rich in gold but contain some silver as well. Gowland describes such a coloring procedure that has been used in Japan since the sixteenth century. At that time it was employed to color the surfaces of gold coins, minted by the government, containing approximately 25 percent of silver. The mixture used in the reaction contained iron and copper sulfates, potassium nitrate, calcined sodium chloride, and resin rather than powdered brick dust. These were mixed with water to make a paste that was painted onto the pale-colored coins. The coins were "heated to redness" on a grate over an open charcoal fire, later immersed in a strong solution of salt to remove the reaction products that had formed on the surfaces, and dried. The surfaces were pure gold at the end of this treatment.[24]

Furthermore, we also know that by the time of the Spanish conquest of Mexico in the sixteenth century the Aztec goldsmiths were well aware of the effect of

[23] One should keep in mind, however, the possibility that certain acid solutions such as aqueous ferric sulfate or ferric sulfate and salt might have been used. Their effectiveness in both removing the silver and in creating a coherent gold layer on alloys of low gold content will have to be tested in the laboratory.

[24] See Reference 4. I am grateful to Professor Cyril Stanley Smith for having called my attention to this practice.

clay and salt as an agent for enrichment of the surface color of an object cast in gold or in tumbaga. Fray Bernardino de Sahagún, a Spanish priest living among the Aztecs of preconquest Mexico, compiled a manuscript between the years 1558 and 1569 entitled "Historia general de las cosas de la Nueva España." In it are recorded detailed accounts of the mode of life of the Indians, as related by the Indians themselves, including a section devoted to metalworking. In a passage describing the finishing operations used to smooth and clean the surfaces of a cast gold object, the Indian craftsman recounts burnishing it, treating it with alum, and heating it over a fire. Subsequently, ". . . when it came forth, once more, for the second time, it was at once washed, rubbed, with what was called 'gold medicine.' It was just like yellow earth mixed with a little salt; with this the gold was perfected; with this it became very yellow."[25] Although we have no way of knowing how early such coloring techniques were used in South and Central America, the notion that some form of cementation was practiced and had become a traditional operation by the sixteenth century is not an unreasonable one.

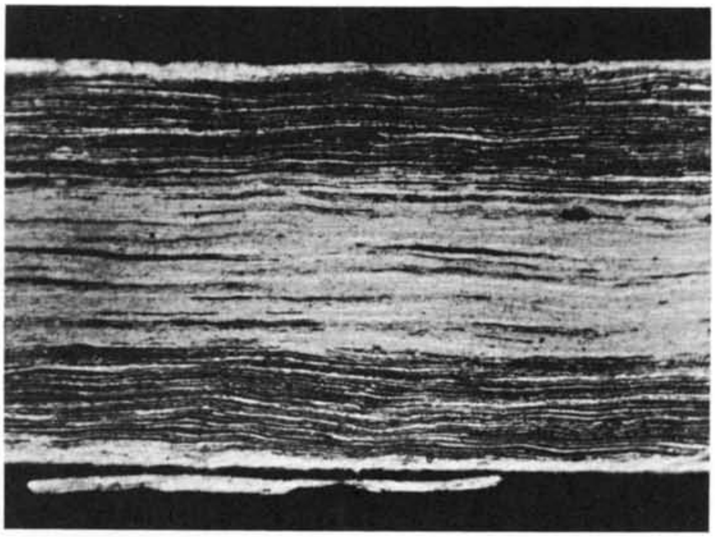
Obviously if the Peruvian alloys were gilded by cementation, the cementing mixture must have been mild and the action relatively slow so that it could be controlled easily. Only the outermost surface silver in these objects had to be removed in order for a uniform gold layer to form. That layer, as we have seen, need be no thicker than about one micron for the metal to appear golden. A delicate balance had to be achieved between the rate at which the chloride reacted with the metal and the rate at which the silver diffused to the surface. If the action was too drastic, too large a proportion of silver and copper would be removed, the gold formed would be powdery and noncohesive, and the surface would appear severely pitted and irregular.

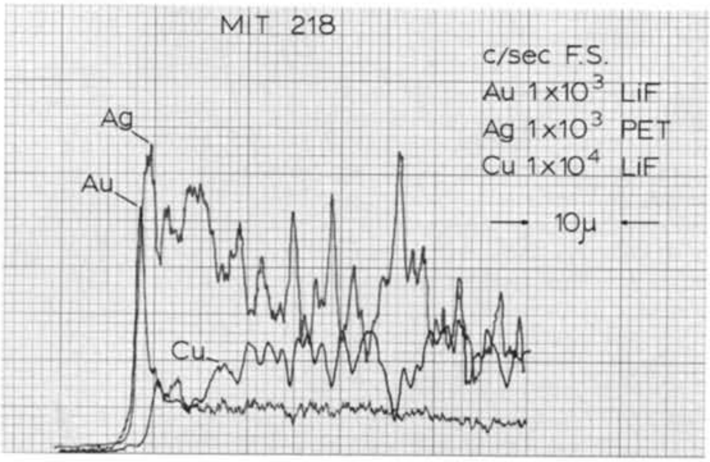
Laboratory experiments indicate that the process is indeed feasible and not difficult to perform. An alloy containing 60 percent Cu, 30 percent Ag, 10 percent Au was cast and subsequently hammered into a thin sheet in the manner previously described. The formation of enriched silver surfaces occurred after only a few annealing and pickling sequences. The microstructure of a cross section of the resulting sheet is shown in Figure 1.41. It should be compared with that of the disk presumed to come from Vicus, Figure 1.31, as well as with that of the experimental Ag-Cu alloy in Figure 1.35. The deformed, copper-rich dendrites in both gold-containing alloys are filled with fine white specks that represent tiny precipitates of silver formed within the beta solid solution during some stage of the annealing operations and suggest that the solubility of gold in the copper-rich phase varies considerably with temperature. By contrast, the binary alloy contains none of this precipitate.

Pieces of the sheet metal were placed in fireclay crucibles, surrounded by a cementing mixture. The cement comprised two parts of ground (approximately 50 mesh) common brick dust and one part of similarly ground rock salt. It was very slightly dampened with either water or urine immediately before use in the crucibles. The crucibles were luted and placed in a furnace at 350°C. After ten minutes, those pieces of metal exposed to the salt-clay-urine cement had formed a continuous, compact, and smooth layer of surface gold, while it took twice that length of time to develop a similarly cohesive layer on the pieces surrounded with cement dampened with water. When the metal was allowed to remain in the furnace for longer than these brief periods, the gold layer became associated with the corrosion products of the copper and silver, which in turn adhered firmly to the siliceous matrix of the cement. The reactions had gone too far, and the gold layer pulled away from the underlying metal, remaining in association with the metallic salts and the matrix. Undoubtedly the cementing mixtures were too strong, and the action was too rapid. Further experiments will have to be designed to determine the optimum conditions under which cementation can be carried out. Nevertheless, reasonably successful results were obtained with the cement and heating conditions described, and the color photograph in Plate I shows a gold-covered, cemented piece of metal alongside an uncemented piece with enriched silver surfaces. The gold layer is obviously very thin, and there are a few areas where the silver shows through. The color of the gold is not dissimilar to that of the Chimu disk, but it is nowhere near as rich and deeply golden as the surface of the disk from "Vicus," which has a much thicker layer of gold. Before cementation, several decorative marks were made on the metal with a tracing tool. The gold layer has formed quite evenly over the surfaces of these depressions. Obviously these same tool marks could have been made after the gold layer had been formed. As long as the metal was simply displaced and not cut by the tool (the usual distinction between tracing and engraving), the gold surface would be retained within the depressions formed.

Electron microbeam probe traces were taken across sections of several pieces of gold-colored metal. One such trace is

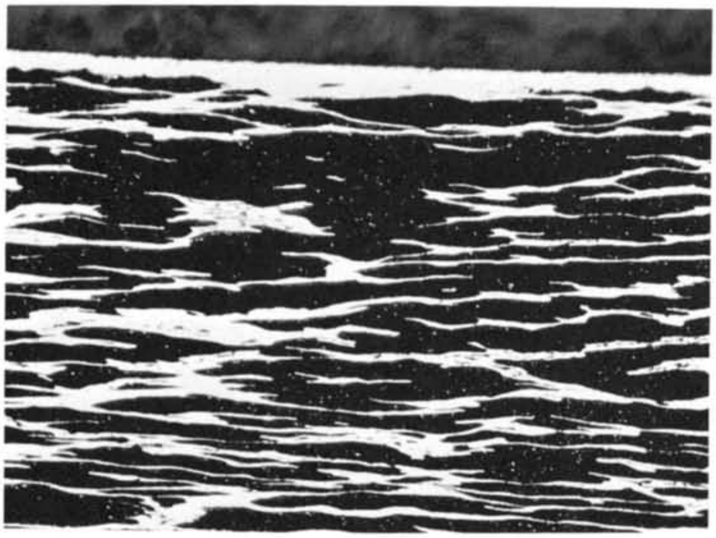
[25] This manuscript is known as the *Florentine Codex* and was written originally by Sahagún in his transcription of Náhuatl, the language of the Aztec. It has recently been translated into English by Dibble and Anderson (Reference 16).

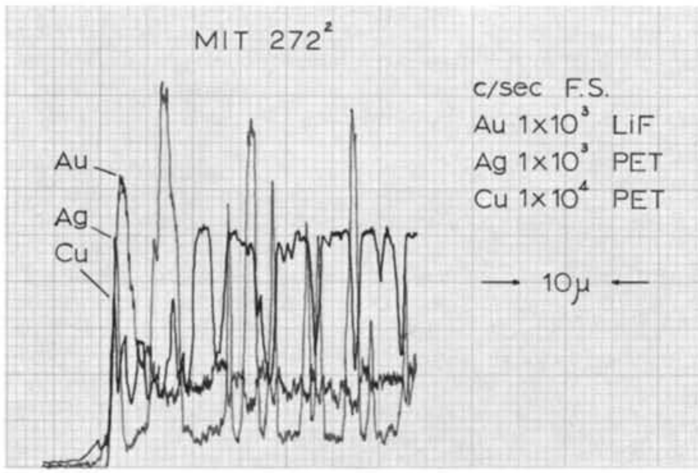




1.39
Chimu disk. Photomicrograph of an entire cross section through the metal. Magnification 495X. As polished.

1.40
Chimu disk. Electron microbeam probe traces of Au, Ag, and Cu through the gilded surface of the section shown in Figure 1.39.





1.41
A section through sheet metal hammered from a 60/30/10 Cu-Ag-Au alloy. Compare with microstructure of "Vicus" disk in Figure 1.31. Magnification 570X, etched by $K_2Cr_2O_7$ + NaCl + H_2SO_4 diluted 1:9.

1.42
Electron microbeam probe traces of Au, Ag, and Cu across the surface of a section of cemented sheet metal (60/30/10 Cu-Ag-Au alloy).

shown in Figure 1.42. Its profile is similar to the traces of both the "Vicus" and the Chimu disks. There is a high, narrow gold peak at the surface containing virtually no silver or copper. (The very narrow silver and copper peaks at the extreme surface of the gold are undoubtedly due to the presence of bits of silver and copper corrosion products adherent to the metal.) Although the gold is only 1–2μ thick, once optimum conditions are established for the formation of this layer, it should be possible to produce much thicker surface coatings.

Summary

The characteristics of the gilding on these Peruvian objects will be treated in the same order as were those of the earlier Near Eastern material in order to facilitate direct comparison between the two.

1. The gilding covers all surfaces of the objects in a smooth, uniform, and continuous layer as if the craftsman clearly intended to have the objects look golden.

2. It is difficult to ascertain whether the gilding was completed before or after the decorative tooling. The gold in the tooled depressions is as thin and as smooth as it is elsewhere on these objects, which suggests that depletion gilding rather than leaf gilding was the method employed.

3. The gilding is very thin, only about 2μ thick in the case of the Chimu disk and 4μ on the "Vicus" artifact.

4. Mercury was not used to facilitate the gilding of these objects. In fact, no analyses of gilded metals from pre-Columbian America have ever demonstrated the presence of mercury.

Conclusion

The intent of these investigations has been not only to document as closely as possible the ways in which an individual craftsman confronted the materials and tools of his craft in the manufacture of particular objects but to try to demonstrate the variety of technical solutions that can arise in response to a given objective. There has not been time to discuss the traditions of metalworking in the two geographic areas treated here, but certainly the heritage of technical style is very important in the sense that it conditions the way in which an individual meets the range of alternatives open to him. The materials he has available will also, obviously, color the breadth of technical diversity of which he is capable. But we ought not to see a given technical solution as governed solely by the state of the technology itself. It is evident that the Peruvians and the Iranians were after two very different effects when they gilded metal and that the techniques they devised were as much a part of the economics, the aesthetics, the religion, the utilitarian objectives of their respective milieus as they were part of their technical capability or point of view. For example, one cannot explain the differences merely on the basis of the presence of mercury in one setting and its absence in another.

The two most outstanding features of the gilt silver objects from the Near East are, it seems to me, on the one hand the purely aesthetic presence of the gold in juxtaposition to the silver, and on the other the purely technical expedient of applying the gold with the aid of mercury. The use of mercury for gilding metal, once it was introduced into this region, was rapidly adopted, widespread, and longstanding. It was a particularly simple and economic way of using gold and of obtaining its glitter in just those areas on a metal surface where it was desired. Certainly in the case of Byzantine art gold was used in mosaics, in icons, on metal objects not only as a representation of an imperial or a sacred color but for the effect it had in generating different atmospheres of light—light creating the space surrounding figures in a mosaic, light emanating from an icon, or light glittering from the surface of a golden cross on the cover of a holy book. Being able to control with relative ease the placement of gold on the surface of a silver object was important, because it was precisely the interplay between the gold and the silver that was to produce the desired life of that surface.

On the other hand, one ought to raise the question of whether or not methods other than mercury gilding were used by silversmiths in the Near East at this time, and if so when and why they were used. All the objects I have illustrated, both Byzantine and Sasanian, were either ecclesiastical or, if not imperial, at least elegant possessions of persons or institutions of some significance. Most of them were probably made in imperial workshops. Were other, less prestigious objects or objects made in provincial workshops fabricated in the same way? It would be instructive, for example, to examine gilt silver jewelry, although little remains, or other small, occasional objects that may have had greater circulation and may have been more generally available. Imperial jewelry and jewelry of the wealthy in Byzantium was made of gold. But silver and gilt silver were used for the more popular varieties and gilded bronze for the really inexpensive kinds. Apparently the affluent often wore gilt bronze jewelry in the streets rather than their valuable possessions that might have been attractive to thieves! (Reference 15) Was gilding with mercury the technique used on such minor objects, or were other available methods employed? Although it was available to the more privileged artisan, was it a common material supplied to the average workshop?

The kinds of economic considerations that must have governed the use and distribution of gold in the Near East were not those of Peru. Native gold was found there in great quantity and was plentiful also in the neighboring states of Ecuador, Colombia, and Bolivia. From the variety of surviving artifactual material made of gold it seems apparent that the metal was widely available. Although there are a good many bimetallic objects that take advantage of the decorative juxtaposition of gold and silver as well as some silver objects that are parcel-gilt, for the most part the uninterrupted expanse of a gold surface was the quality most desired. This predilection reached its peak at the time of the Chimu kingdom and later during the Inca empire when the walls of palaces and of the sun temples were covered with plaques or sheets of gold. It is not surprising, therefore, to find that when an object was gilded—by whatever process—its entire surface was covered with gold. The use of gold foil for this purpose is one of the most efficient methods in the sense that it utilizes the least amount of gold and wastes little. On the other hand, we have seen that the Chimu disk contains about 7 percent of gold and that from "Vicus" approximately 10 percent. Regardless of whether these disks were gilded by leaf or by cementation, the presence of these amounts of gold in the alloys indicates some lack of concern with efficient use of this metal. By A.D. 1000 when the era of the big city began, the quantity of gold being mined and distributed must have been enormous, and economizing on the metal could not have been a vital consideration. One of the more intriguing aspects of the proposed cementation process is precisely that it is suitable to gilding large expanses of metal easily and quickly.[26] Even a vessel already shaped so that access to its hollow interior is difficult can readily be gilded in this manner. Once we are able to date the metal artifacts from Vicus more securely, we may find that the gilding of large areas of metal, especially metal in the form of thin sheet, is considerably earlier than we now consider it.

Another observation that warrants consideration is the fact that, thus far, the examples of gilded sheet-metal objects of silver-copper-gold alloys have all come from the north of Peru. If these artifacts were indeed gilded by the cementation coloring method proposed, I believe we are justified in regarding the philosophy behind this technique as very similar to that behind the manufacture of tumbaga, discussed in the introductory section. We know that tumbaga was rarely used in Peru. It has been argued that on the northern coast of Peru copper was plentiful and gold scarce, that objects of pure copper and later of bronze were covered with gold leaf when they were gilded, and that, therefore, there was probably little or no trade between Colombia and Peru. (Reference 14) While this may be true in the sense of the movement of metals, it seems not at all unreasonable to suppose that there was a strong metallurgical tradition in the north of South America, common to Peru and Colombia and, to a lesser extent, Ecuador, which resulted in the application of a characteristic set of metallurgical principles and attitudes to the particular problems at hand. The concept of removing silver from the surface of a hammered sheet of Ag-Cu-Au alloy is not really very different from the concept of removing copper from the surface of a cast Cu-Au alloy. The methods are different both because of the alloys involved and the fact that some are worked while others are cast. Tumbaga was used primarily for castings, whereas the ternary alloy appears to have been more suitable for sheet metal. But the rationale behind the methods is really quite similar. If, after further experimental work and examination of more objects of this kind, it becomes apparent that depletion gilding was the process employed, we may wish to address ourselves more seriously to a consideration of the extent to which the northwest corner of South America was a region of shared metallurgical principles and procedures. The movement of metalworkers rather than of metals may have been the substance of any such common tradition.

[26] If cementation was used for gilding, it supposedly was also used for the purification of gold in bulk. Bergsøe argued for the likelihood of the Indians' acquaintance with cementation in Reference 2. He points out that in Samuel K. Lothrop's description of the metal artifacts from Coclé, Panama, there is mention of 16 items made of Au-Cu alloys that are free from silver. (See Reference 8.) Bergsøe argues that it is entirely possible these alloys were made with gold from which the silver had been extracted by cementation. His own successful experimental attempts to cement powdered gold with clay and salt are described.

Acknowledgments

This paper is dedicated to William C. Root, whose death in June 1969 has meant the loss, to those of us engaged in the study of pre-Columbian metallurgy, of one of the field's most active and enthusiastic scholars. It was he who gave me the first bits of gilt metal from South America with which to begin my research into early gilding techniques, and in his suggestions and criticisms he gave me as well the benefit of his many years of experience in studying the technologies of these cultures. He was a pioneer in a field still largely unexplored. The kindest tribute to him will be to pursue that exploration with the rigor and the excitement that were the substance and the motivation of his work.

I should like to thank, first, those individuals whose scholarly interest and delight in the objects I have studied made it possible for me to pursue my own enthusiasm for the technology of this material. They are: Junius B. Bird, Elizabeth H. Bland, Mr. and Mrs. Dudley T. Easby, Jr., Dorothy G. Shepherd, and John S. Thacher. I am especially grateful to Dorothy Shepherd for her kind cooperation and generosity during the course of this study.

The assistance I have had in the analytical examination of the objects was no less valuable. None of the electron microbeam probe data in connection with the Peruvian material could have been assembled without the assistance, advice, and patient skill of Stephen L. Bender and John K. Hill of the Ledgemont Laboratory, Kennecott Copper Corporation. At M.I.T., I would especially like to thank Donald L. Guernsey, Stephen M. Nagy, and Walter W. Correia, who were responsible for the wet chemical and spectrographic analyses of the Peruvian objects; Joseph A. Adario, who ran all of the microbeam probe traces of the Near Eastern artifacts; and Richard A. Berry for his assistance in casting the alloys used to reproduce the pre-Columbian techniques. I am particularly grateful to Katharine C. Ruhl of the Cleveland Museum of Art for having taken all the color slides of the Sasanian objects that I showed at the conference as well as the details of the Iranian objects which illustrate this paper.

Finally, my warm thanks to Cyril Stanley Smith for sharing with me his wealth of knowledge of metallurgy, materials, and man—but especially for his encouragement during all those hours when ancient technology seemed to defy modern resolve.

Table A.1
Composition of Metal Samples Removed from Surface of Horse Rhyton*

Sample Type	No. and Site of Sample	Composition† (weight percent) Au	Ag	Cu	Hg
1	8 Loose fragment of gold foil	90.5	6.8	1.0	1.7
1	1 Gilding: chest harness, proper right side	57.4	40.0	0.5	2.1
1	4 Gilding: nose harness	65.9	32.0	0.5	1.6
2	6 Gilt area, gilding lost: medallion strap on proper right chest	8.4	89.2	1.6	0.8
2	2 Probable gilt area, gilding lost: top right strand of mane	1.2	97.6	0.9	0.3
2	7 Possible gilt area, gilding lost: roping on saddle, proper right front edge	0.6	97.9	1.2	0.3
3	3 Ungilt silver: body, near hoof of proper right leg	0.8	98.2	1.0	<0.02
3	5 Ungilt silver: proper right hock	0.7	98.5	0.8	<0.02

* A tiny fragment of gold foil (Sample #8), similar to that analyzed by emission spectrography, was the only "bulk" sample studied. All the other samples were taken by Sayre, who used an essentially nondestructive technique he has developed for removing minute quantities of metal from a surface by stroking the surface lightly with a small quartz plate or cylinder. (See E. V. Sayre, "The Nuclear Age and the Fine Arts," *Proceedings of the 1967 Youth Congress on the Atom*, Chicago, 1967.)

† Approximate composition calculated upon the assumption that the elements determined are the only components in significant concentrations.

Appendix

Since this paper was written, further studies of the gilding on the Cleveland Museum horse rhyton have been most generously undertaken, at the request of the author, by Edward V. Sayre and Pieter Meyers at the Chemistry Department of Brookhaven National Laboratory. Three types of sample were removed from the rhyton: (1) metal from gilded areas; (2) metal from areas that appear to have been gilded but have lost their gold foil; (3) metal from areas presumed never to have been gilded. The composition of these samples was determined by neutron activation analysis, and the results are given in Table A.1.

The analyses show that mercury was used in applying the gold foil to the silver surfaces. Furthermore, the concentration of mercury in the silver presumed to have been gilded is at least ten times as great as the trace amount in the ungilded silver, demonstrating that the sampled areas must have been either covered with gold at one time or preamalgamated with mercury. The loose fragment of foil contains very little silver in comparison with the silver concentration in the gilding still in situ. This may indicate that the flake never adhered to the surface and little or no Au-Ag diffusion occurred when the metal was heated to drive off the mercury. By contrast, the high concentration of silver in Samples 1 and 4 and the tenacity of this gold to the surface of the rhyton may indicate extensive interdiffusion resulting in effective bonding. The inability of the thick gold foil to make close contact with the irregular contours of the rhyton surface still remains the primary reason for poor bonding in spite of the presence of mercury.

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