Early Central Andean Metalworking from Mina Perdida, Peru

Richard L. Burger and Robert B. Gordon

Copper and gold artifacts in contexts dated to $\sim$3120 to 3020 carbon-14 years before the present ($\sim$1410 to 1090 calendar years B.C.) recovered in excavations at Mina Perdida, Lurín Valley, Peru, show that artisans hammered native metals into thin foils, in some cases with intermediate anneals. They gilded copper artifacts by attaching gold foil. The artifacts show that fundamental elements of the Andean metallurgical tradition were developed before the Chavín horizon, and that on the Peruvian coast the working of native copper preceded the production of smelted copper objects.

The peoples of the Andes created the oldest and most elaborate tradition of metallurgy in the Pre-Columbian Americas (*1*). By the mid-Early Horizon ($\sim$600 to 200 cal yr B.C.) artisans of the Chavín and Cupisnique cultures were making elaborate metal artifacts for use in religious ceremonies and in the costume of elites (*2*). The origins of their techniques have been obscure. With the exception of the isolated find of hammered gold foil at Waywaka in the south central highlands of Peru in 1970, no reliable evidence has been available for Andean metallurgy in Peru before the Chavín horizon (*3*). Here we describe copper and gold artifacts recovered in excavations at the Initial Period center of Mina Perdida in the Lurín Valley on the central coast of Peru (Fig. 1) that date from 3120 to 3020 ^{14}C yr B.P. ($\sim$1410 to 1090 cal yr B.C.) (*4*). These artifacts reveal a previously unknown stage of Andean metalworking.

Mina Perdida is the largest of six civic-ceremonial centers erected in the lower Lurín Valley during the Initial Period ($\sim$2000 to 900 cal yr B.C.) (*5*). Located 25 km south of Lima on a natural terrace above the alluvial floodplain of the coastal valley, this site covers $\sim$30 ha and lies 8 km inland from the Pacific coast. It is dominated by a flat-topped terraced pyramid 22 m high and two long, lower lateral platform mounds. Household refuse and the traces of dwellings surrounding the monumental architecture were coeval with the final building episodes of the pyramid complex ($\sim$1400 to 1000 cal yr B.C.).

Elaborate supernatural iconography on the walls of the buildings, the presence of altars, and the recovery of ceremonial paraphernalia at Mina Perdida and other similar sites show that the monumental U-shaped centers were used for religious rituals and other community activities. Eighteen ^{14}C measurements from Mina Perdida range from 2870 ± 90 to 3520 ± 100 ^{14}C yr B.P. ($\sim$900 to 2000 cal yr B.C.). These dates along with ceramic materials demonstrate that Mina Perdida was occupied for at least eight centuries during the second millennium B.C. It was abandoned before the Chavín horizon, and evidence of subsequent reoccupation is slight.

The Initial Period society that built Mina Perdida relied on a mixed subsistence system that included irrigation agriculture, the collection of wild plant foods, fishing, shellfish collection, and hunting. Despite the impressive scale of the public constructions, there is little suggestion of sharp economic inequalities or a strongly stratified society. While there is evidence of close social and cultural links among the villages and centers in Lurín's lower and middle valley during the Initial Period, the settlements do not appear to have been subsumed within a single political unit (*6*).

Copper foil was first found at Mina Perdida during the 1991 excavation of the 280 m by 75 m low platform mound (Sector IA) running along the northwestern edge of the central plaza (Fig. 1). Our excavations revealed a complex series of construction episodes during which the stone-faced platform was increased in height and made wider in small increments. During its final widening coarse stone walls were built at short intervals perpendicular to the older platform wall; these walls usually supported sterile fills, but one section was covered with redeposited cultural materials including ceramics and textiles typical of the late Initial Period. Small fragments of copper foil were found in three layers within this fill, including in one lens resting on the floor of the older structure. These artifact-bearing strata were sealed by a layer of stone fill. A sample from the fiber bags holding the fill that covered the copper-containing lenses yielded a ^{14}C date of 2870 ± 90 ^{14}C yr B.P. ($\sim$1210 to 920 cal yr B.C.) (I-16, 762). The copper artifacts must have been produced before this time, and carbon associated with the copper foil yielded a measurement of 3050 ± 90 ^{14}C yr B.P. ($\sim$1430 to 1160 cal yr B.C.) (I-16, 833). The containment wall, built before the deposition of these layers of fill, was dated to 2960 ± 90 ^{14}C yr B.P. ($\sim$1320 to 1040 cal yr B.C.) (I-15, 577), but the copper foil and the associated carbon and cultural materials could have been removed from older archaeological deposits.

Excavations in 1993 and 1994 unearthed fragments of copper foil (Figs. 2 to 4) on the summit and terracing of the main pyramid (Sector IIIA). These were nearly identical to those found in Sector IA. The eastern side of the pyramid summit contained six superimposed floors in the upper 2 m of stratigraphy. Carbon samples taken from the upper floors yielded dates ranging from 3120 ± 130 to 3020 ± 100 ^{14}C yr B.P. ($\sim$1500 to 1100 cal yr B.C.). Three fragments of copper foil were recovered, with other small artifacts on floor surfaces. Additional pieces of foil were encountered in a disturbed summit context that combined materials from the upper four floors; the admixture included a fragment of gold foil that had been attached to a piece of copper (Fig. 3).

Four other copper artifacts, including one with traces of gold, were recovered from refuse deposited on an upper terrace immediately to the east of the pyramid's rear staircase. The terrace on which these pieces were found is located 17 m to the south of the masonry summit platform. The top of the pyramid was a focus of public activities, and the terrace refuse appears to be derived from the summit activities. An accelerator mass spectrometry ^{14}C date taken from a sacred effigy recovered on the same terrace is 3030 ± 50 B.P. ^{14}C yr ($\sim$1390 to 1160 cal yr B.C.) (Beta 100302). This age reinforces the conclusion that the terrace refuse (including the metal artifacts) dates to the late Initial

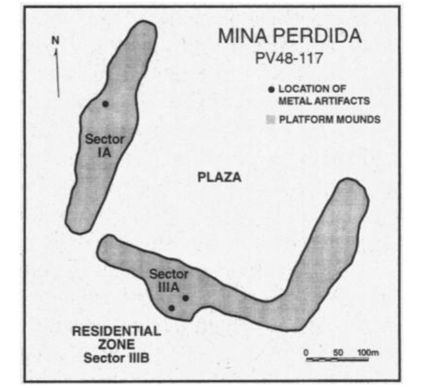

Fig. 1. Map of Mina Perdida showing the locations where the metal artifacts were excavated.

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Period and is contemporary with the materials from the final summit floors (*5*). The dates from the summit and the back terrace are more than a century older than from Sector IA where the metal artifacts were initially encountered. This difference may reflect the secondary deposition in Sector IA of older cultural materials taken from the pyramid summit. Metal artifacts were not recovered from the domestic refuse in the flatland immediately to the southeast of the pyramid (Sector IIIB), and this absence underscores the inference that the Mina Perdida metal artifacts were used in activities on the pyramid summit.

None of the artifacts had been intentionally shaped into a recognizable form, nor were any perforated or shaped into three-dimensional objects. We analyzed six samples of copper foil (Table 1), including samples from both Sector IIIA and Sector IA and one sample of gold foil from Sector IIIA (*7*). Although corrosion had reduced the thicknesses of all the copper foils and occasionally penetrated through them, the volume of verdigris suggests that at least half, and usually more, of the original metal survived. Several of the copper foils had been folded over on themselves at their corners. Two of the specimens consisted of more than one foil.

Microprobe analyses showed all the copper artifacts to be highly pure (Table 1) and free of other phases and nonmetallic inclusions. Each foil has greatly elongated, generally parallel grains 5 to 10 μm thick with lengths more than 10 times their thicknesses. Specimens 3294 and 3354 also contain grains from 4 to >40 μm thick; the large grains are as long as 4 mm (Fig. 5). In these specimens, single grains were observed covering up to 15 mm^2 of the foil surface. The elongated grains in the foils show that artisans thinned the copper by hammering it cold.

Although artisans can sometimes hammer bulk copper into foil without annealing the metal (*8*), an intermediate anneal facilitates their work. Were this done, remnants of annealing twins could be retained in the microstructures despite the distortion of the grains by subsequent hammering. Although no twins were found in three of the specimens (3294, 3354, and 3357A), we saw traces of deformed twins in foils 3293, 3365 (Fig. 6), and one of the foils in 3356. The makers left all the foils in the cold-worked condition, however, perhaps to give them sufficient stiffness to retain the shape of a finished product.

Foils 3294, 3354, and 3356 have corners and edges bent over on themselves (Fig. 2). The gradual bends and the absence of evidence of localized failure show that, although heavily cold-worked and not subsequently annealed, the metal in the foils retained sufficient ductility to be bent back on itself without breaking (*8*).

The fragment of gold attached to specimen 3357A ranges from 5 to 10 μm thick and contains 7.3% silver by weight (Fig. 4). Another fragment of gold found adhering to the copper foils in specimen 3365 was identified by its color. Artisans at Mina Perdida made gilded objects by hammering native gold into foil, and attaching it to copper foil with adhesive. Formation of verdigris on the artifacts eventually displaced the gold from its substrate.

Because some examples of native copper contain more iron, arsenic, and silver than smelted copper (*9*), the high purity of the

Table 1. Descriptions and microprobe analyses of metal foils from Mina Perdida.

Specimen number	Item	Size (mm)	Thickness (mm)	Fe (%)	As (%)	Sn (%)	Ag (%)	Sb (%)	Au (%)	Cu (%)
3293	Cu foil	9 by 12	0.12	0.00	0.03	0.01	0.04	0.02	–	99.9
3294	Cu foil	9 by 17	0.12	0.00	0.06	0.00	0.04	0.01	–	98.9
3354	Cu foil	10 by 13	0.14	0.00	0.04	0.00	0.15	0.01	–	98.0
3356-1	Cu foil	15 by 15	0.064	0.00	0.04	0.00	0.04	0.00	–	99.92
-2	Cu foil	15 by 15	0.099	0.00	0.05	0.00	0.02	0.01	–	99.2
-3	Cu foil	15 by 15	0.050	0.01	0.02	0.01	0.04	0.00	–	99.2
-4	Cu foil	15 by 15	0.045	0.00	0.04	0.01	0.04	0.02	–	98.9
3357A	Cu foil	4 by 6	0.70	0.00	0.24	0.00	0.05	0.01	–	97.0
	Au foil	0.55 by 0.15	0.010	–	–	–	7.3	–	92.7	–
3357B	Au foil	5 by 5	0.050	–	–	–	4.2	–	95.8	–
3365	Cu foil	4 by 4	0.070	0.01	0.04	0.00	0.08	0.01	–	98.6

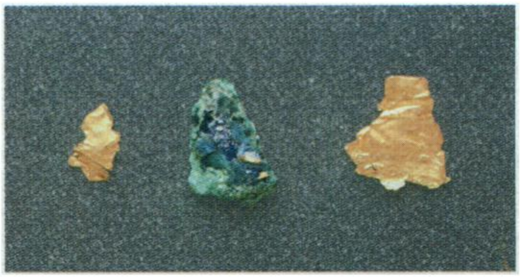

Fig. 2 (above left). Copper foil (specimen 3294) with corrosion products. The foil has been bent at the corners. Size: 9 mm by 17 mm. [Photograph by W. Sacco] **Fig. 3 (above right).** Gold foils and copper foil with traces of gilding (specimen 3357). Size: 2 mm by 3 mm (left), 4 mm by 6 mm (middle), and 5 mm by 5 mm (right). [Photograph by W. Sacco] **Fig. 4 (below).** Enlargement of specimen 3357A illustrating fragment of gold foil attached to copper foil. [Photograph by W. Sacco]

Mina Perdida foils (>99.5%) (Table 1) does not necessarily prove that they were made of native metal (*10*). The iron content of early smelted coppers is often small because of the use of high-grade ore but remains higher than in most native coppers. The earliest Egyptian copper contains from 0.03 to 0.33% iron (*11*). Copper prills smelted at the Batan Grande site in Peru range in purity from 91.1 to 99.0% (*12*). Copper smelted at the Ramaditas site in the Atacama about 250 B.C. contained from 0.05 to 0.06% iron (*13*). Had we analyzed the Batan Grande samples, we would have detected arsenic in excess of 0.5% and silver in excess of 0.1% in all the prills, and iron in all but one. Analyses of copper prills from an early smelting site in Jordan showed iron in excess of 0.01% in all 48 specimens (*14*).

The antimony contents of the foils are higher than those found in most native coppers. However, native copper is now rare in South America, so few analyses are available for comparison (*15*). Except for the arsenic in 3357A and tin, which exceeded the detection level in only 2 of 37 analyses, the variability of each element within each specimen was as large as the average concentration of that element. Composition variations in native copper due to changes in the compositions of the depositing solutions are as large as those caused by segregation during solidification of melted copper (*16*).

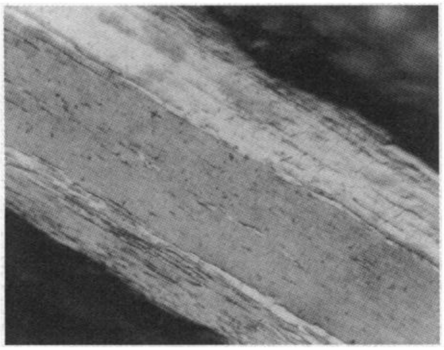

Fig. 5. Cross section of foil 3354; bichromate etch. The microstructure consists of several large, greatly elongated grains. There is no evidence that the copper was annealed during the foil-making process. The large grains must have been present in the starting material and are commonly found in native copper. The thickness of the section shown is 0.14 mm.

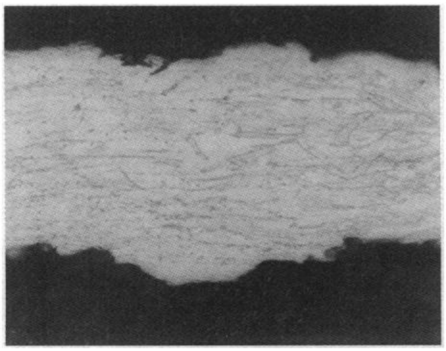

Fig. 6. Cross section of foil 3365; peroxide etch. The uniformly small grain size and traces of twins, now heavily distorted by subsequent cold working, suggest that this metal was annealed in the course of hammering it into foil. The greatest thickness of the section shown is 0.086 mm. The gold foil formerly attached to the copper has been displaced by verdigris and is out of the field of view.

Because of the presence of arsenic and silver, which are commonly found in native copper, the absence of iron, which is present at higher concentrations in smelted coppers than in our specimens (*17*), and the very large grains found in some of the microstructures (*18*), we conclude that the artisans at Mina Perdida worked native copper. They made foils with thicknesses between 0.1 and 0.05 mm during the late Initial Period, over a millennium before ore was smelted in this area. The sources of their native metals were probably local, because small veins of both copper and gold crop out along the central coast. The straight edges on the artifacts were probably made by cutting the foil rather than by repeated bending and breaking. The uniformity of thickness, small number of defects in the foils, and their microstructures indicate that the Initial Period metalworkers understood copper's natural ductility, the strengthening of the finished product by work hardening, and, probably, the use of annealing to restore ductility during working.

The artifacts from Mina Perdida suggest an early stage of metallurgical activity in the Central Andes and that, as in the Old World, there may have been a lengthy period of experimentation with naturally occurring metals (*19*). There is some indication from other sites that the working of native copper may have continued throughout the first millennium B.C. in Peru (*20*).

These early examples of Andean metalworking from Mina Perdida show three patterns that were to characterize the Central Andean metalworking tradition for the next three millennia: (i) an unusual concern with the production of thin metal foils, (ii) the gilding of copper, and (iii) the close association of metalworking with religious ritual and the supernatural realm. The origin of these technological developments in the Central Andes occurred in a sociopolitical context preceding the emergence of strong social stratification and state organization.

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7. The specimens were polished successively with diamond paste, 1 μm cerium oxide, and 0.05 μm alumina. After examination of the polished surfaces, potassium bichromate etch was used to develop the microstructures. Some of specimens were repolished and etched with a solution of ammonia in hydrogen peroxide to reveal fine details of their microstructures. Chemical analyses were performed on the metallographic specimens with a JOEL JXA-8600 electron microprobe. The specimens were carbon-coated. Initially, qualitative analyses were made to detect the range of elements that might be present and the homogeneity of the specimens. Quantitative analyses with a sensitivity of 0.01 weight % were made for iron (often found in smelted copper), arsenic and tin (common alloying elements), silver (usually present in native copper), and antimony (usually absent in native copper) with the use of wavelength-dispersive, x-ray spectrometry, pure metal standards, and ZAF matrix correction procedures. Here no analyses were made for copper; instead, its concentration was fixed at 99.5 weight %. Averages of analyses made at four places on each specimen are shown in Table 1.
8. C. S. Smith has demonstrated that native copper free of nonmetallic inclusions can be hammered into foil without annealing provided the artisan stops to cut off any tears that form at the edges during the process [C. S. Smith, *Search for Structure* (MIT Press, Cambridge, MA, 1981), p. 78.
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15. G. Petersen, quoted by H. Lechtman in (*1*), p. 287. Copper is exploited commercially in Lurín and neighboring Chilca, and any native copper present was probably mined out long ago [U. Petersen, personal communication; ——— and C. E. Vidal, *Magmatic and Tectonic Controls on the Nature and Distribution of Copper Deposits in Peru* (Society of Economic Geologists, Denver, 1996); F. Camus, R. M. Sillitoe, R. Petersen, Eds., *Andean Copper Deposits: New Discoveries, Mineralization, Styles and Metallogeny, Special Publication Number 5* (Society of Economic Geologists, Denver, CO, 1996), pp. 1–18.
16. D. Rye, personal communication.
17. The solubility of iron in copper at room temperature is below our detection limit. The iron concentration at the freezing-in temperature associated with cooling rates used in ordinary metallurgical practice

would be detected, however. We found no evidence of precipitation of iron in the microstructures of our specimens, and believe we would have detected iron had it been present.

18. Grains up to 1 mm in diameter are found in native copper [M. Wayman, *CIM Bull.* **78** (no. 880) 67 (1985); *ibid.* **78** (no. 881), p. 75].
19. R. F. Tylecote, in *A History of Metallurgy* (Institute of Metals, London, 1992), pp. 1–11; P. T. Craddock, *Early Metal Mining and Production* (Smithsonian Institution, Washington, DC, 1995), pp. 94–95.
20. Two copper disks were recovered by the University of Tokyo Expedition from Tomb 5 at Kuntur Wasi, Jequetepeque Valley, in the northern highlands of Peru; the contents of this tomb were dated to the Kuntur Wasi phase (700 to 450 B.C.) [Y. Onuki, Ed., *Kuntur Wasi y Cerro Blanco: Dos Sitios del Formativo en el Norte del Perú* (Hakusen-Sha, Tokyo, 1995), pp. 210–213]. Analysis by Y. Hirao [in (*2*), p. 30], Table 1, and Fig. 5 identify the metal used as native copper. A copper artifact has also been reported from the Cupisnique cemetery of Puémepe in the lower Jequetepeque Valley, but no technical analysis is available [I. Shimada, in (*1*), p. 43]. A single sample of copper wire from the terminal Early Horizon cemetery on the Tablada de Lurín was analyzed by R. Gordon and proved to be made of melted native copper.

21. We thank L. Salazar-Burger, J. Pinilla, B. Ojeda, and members of the Proyecto Arqueológico Lurín for support in the field; Peru's Instituto Nacional de Cultura for permission to export the metal samples for analysis at Yale; the Selz Foundation, Heinz Charitable Trust, and the Joseph Fisher Foundation for funding the excavations at Mina Perdida; and Yale's Provostial Research Fund for supporting the laboratory analysis.

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Nanoengineering of Inorganic and Hybrid Hollow Spheres by Colloidal Templating

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Hollow silica and silica-polymer spheres with diameters between 720 and 1000 nanometers were fabricated by consecutively assembling silica nanoparticles and polymer onto colloids and subsequently removing the templated colloid either by calcination or decomposition upon exposure to solvents. Scanning and transmission electron microscopy images demonstrate that the wall thickness of the hollow spheres can be readily controlled by varying the number of nanoparticle-polymer deposition cycles, and the size and shape are determined by the morphology of the templating colloid. The hollow spheres produced are envisioned to have applications in areas ranging from medicine to pharmaceutics to materials science.

In recent years, there has been intense interest surrounding the fabrication of composite micro- and nanoparticles that consist of either organic or inorganic cores coated with shells of different chemical composition (*1–8*). These core-shell particles often exhibit properties that are substantially different from those of the templated core (for example, different surface chemical composition, increased stability, higher surface area, and different magnetic and optical properties), thus making them attractive from both a scientific and a technological viewpoint. Applications for such particles are diverse, including capsule agents for drug delivery, catalysis, coatings, composite materials, and protecting sensitive agents such as enzymes and proteins. Previous investigations have demonstrated that polymeric microparticles and inorganic cores can be coated with layers of various materials, including silica, yttrium basic carbonate, and zirconium hydrous oxide, either by controlled surface precipitation reactions on the core particles or by direct surface reactions (*1–8*).

A recently introduced method that allows the construction of composite multilayer assemblies is that of layer-by-layer (LbL) adsorption (*9*). The basis of the LbL technique is the electrostatic attraction between the charged species deposited (*9*). Composite multilayers comprising biological macromolecules, multivalent dyes, silicate sheets, or nanoparticles and polymer have been constructed using the LbL approach (*9, 10*). The buildup of such multilayers has, however, almost exclusively been performed on macroscopically flat substrates (for example, quartz or gold). Recently, the formation of pure polymer multilayers on colloids with the LbL method has been demonstrated (*11*). The fabrication of composite, regular inorganic-polymer multilayers on colloidal particles has also been achieved (*12*), opening the way to the production of novel core-shell materials of given size, topology, and composition. An important extension of core-shell particles is the subsequent removal of the core by either dissolution to produce hollow particles (*1–4*) or decomposition to give hollow polymer shells (*11*).

Here we report on the fabrication of hollow inorganic silica and inorganic-hybrid spheres through the colloid templated electrostatic LbL self-assembly of silica nanoparticle (SiO_2)–polymer multilayers, followed by removal of the templated core and, optionally, the polymer (Fig. 1). Polystyrene (PS) latex particles 640 nm in diameter were used as templates, and SiO_2 particles approximately 25 nm in diameter were used as the coating nanoparticles. These nanoparticles electrostatically self-assemble onto the linear cationic polymer poly(diallyldimethylammonium chloride) (PDADMAC) (*13*). The versatility of the process in forming composite multilayers is demonstrated by the control that can be exerted over the number of deposition cycles, allowing regular uniform multilayers to be formed. Submicrometer-sized hollow spheres, with wall thicknesses ranging from tens to hundreds of nanometers, have been produced. The wall thickness of the hollow spheres and ultimately their shape and stability are dependent on the number of SiO_2-PDADMAC layer deposition cycles (Fig. 1, steps 2 and 3).

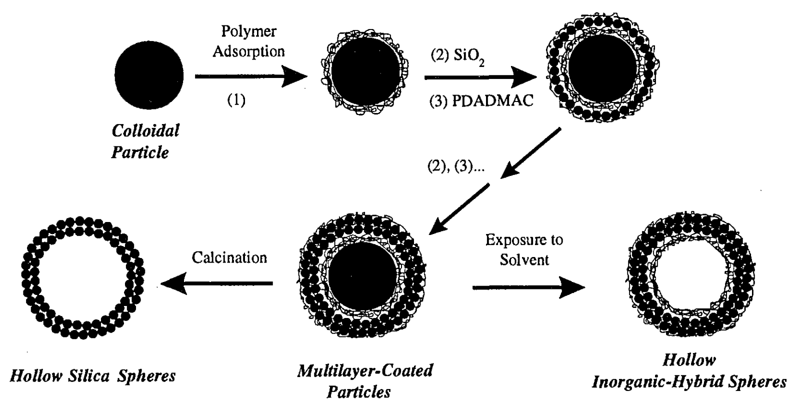

Fig. 1. Illustration of procedures for preparing inorganic and hybrid hollow spheres. The scheme is shown for PS latex particles.

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