# The Huastec Region: A Second Locus for the Production of Bronze Alloys in Ancient Mesoamerica

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Chemical analyses of 51 metal artifacts, one ingot, and two pieces of intermediate processed material from two Late Post Classic archeological sites in the Huastec area of Eastern Mesoamerica point to a second production locus for copper-arsenic-tin alloys, copper-arsenic-tin artifacts, and probably copper-tin and copper-arsenic bronze artifacts. Earlier evidence had indicated that these bronze alloys were produced exclusively in West Mexico. West Mexico was the region where metallurgy first developed in Mesoamerica, although major elements of that technology had been introduced from the metallurgies of Central and South America. The bronze working component of Huastec metallurgy was transmitted from the metalworking regions of West Mexico, most likely through market systems that distributed Aztec goods.

Archeological and technical investigations have produced new evidence for the production of bronze alloys in ancient Mesoamerica in the late Post Classic period (1350 to 1550 A.D.). Earlier studies had indicated that the two binary bronze alloys, Cu-As and Cu-Sn, and the ternary Cu-As-Sn bronze (1) were produced exclusively in West Mexico (2, 3) (Fig. 1), a major metalworking zone and the region where metallurgy first developed in ancient Mesoamerica. In West Mexico artifacts made from these alloys first appear about 1200 A.D. Material found in the Huastec region of Eastern Mesoamerica (Fig. 2) is later, dating to the century before the Spanish invasion in 1518. West Mexican Sn- and As-bronze artifacts sometimes were exported to other regions of Mesoamerica (4), and some artifacts in the Huastec assemblages may represent such exports. In this article, however, we present chemical analyses of 51 metal artifacts, one ingot, and two pieces of intermediate processed material from two Late Post Classic sites that point to a second production center of bronze alloys in the Huastec region. The data demonstrate that peoples in western and eastern Mesoamerica were in contact during this time, and further, that the contact was sufficient to result in the introduction of a complex metalworking technology.

### West Mexican and Other New World Metallurgies

Metallurgy initially appeared in Mesoamerica at approximately 650 A.D., when it was introduced to West Mexico from the south (5). Laboratory studies have shown that West Mexican metallurgy had its roots in the two major metalworking traditions of the ancient Americas: the casting technology of lower Central America and Colombia and the sheet metal tradition of the Central Andean area of Ecuador, Peru, and Bolivia (3, 4) (Fig. 1). Both regional traditions contributed information and technical know-how to the metallurgy that took shape in West Mexico through contacts that spanned many hundreds of years.

West Mexican metallurgy developed through two chronological periods. During Period 1 (650 to 1200 or 1300 A.D.), metalsmiths worked most extensively with native copper and Cu ores. They crafted objects both by casting and by working, techniques introduced from lower Central



Fig. 1. Locations of ancient American metalproducing zones referred to in text.

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America and Colombia and the Central Andean area, respectively. During Period 2 (1200 or 1300 A.D. to 1521), new elements of these more southerly metalworking traditions were integrated into the basic repertoire, and West Mexican smiths began to work with Cu alloys, especially the binaries of Cu-As, Cu-Sn, and Cu-Ag (3, 4). However, the laboratory and archeological data indicate that during neither of these two periods was metal as such imported to West Mexico. The number of objects that reached West Mexico was relatively small (3). What was disseminated to West Mexico was technical information, which sparked the development of a regional West Mexican metalworking tradition. West Mexican metallurgy contained elements of these two external metallurgies but reconfigured them in keeping with the interests of groups controlling production and local precepts concerning the nature of the material (3, 4).

The earliest evidence for metallurgy in the New World appears in the Central Andean region, at about 1500 B.C. in highland Peru (6) (Fig. 1). By the time metallurgy emerged in western Mexico, the Central Andean tradition was diverse and technically sophisticated. Smiths used copper, silver, gold, and their alloys and had begun to experiment with Cu-As and Cu-Sn alloys. Objects made from Cu-As alloys were generally restricted to northern Peru and southern Ecuador, where both arsenopyrite and coppersulfarsenide ores are found. Copper-tin bronze alloys were developed by metalworkers in the cassiterite-rich southern Andean highlands of Bolivia, Peru, and northwest Argentina. Both bronze alloys were in use by about 850 A.D.

Metalworkers in the Central Andes treated metal as a solid, plastically deforming it to fashion elite ritual and status objects: masks, nose rings, earrings, drinking vessels, and others. Shaping metal by hammering was such a pronounced preference that Andean smiths usually rendered three-dimensional forms by joining pieces of sheet metal rather than by casting solid or hollow shapes. In cold hammering and annealing Cu-Au, Cu-Ag, and Cu-Ag-Au alloys into sheet, the surfaces gradually became enriched in the noble alloy metals, Ag and Au. The complex surface enrichment techniques (7) Andean smiths in-

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vented to produce such golden and silvery surfaces on Cu-alloy objects are a hallmark of this tradition. Central Andean metalworkers also used metal extensively for tools such as tweezers, needles, axes, and awls, crafting them from both Cu-As and Cu-Sn bronze. When the Europeans invaded the Inca empire in 1532, Cu-Sn bronze was widely disseminated among the peoples of the southern and Central Andean zone, and these gilding and silvering procedures had been in place for a millennium.

In lower Central America and Colombia metallurgy arose somewhat later, around or slightly before 200 B.C. That tradition is distinguished by the nearly exclusive use of gold and Cu-Au alloys (tumbaga) to cast both hollow and solid forms by the lost-wax technique. Metalworkers in this region of the Americas treated metal as a liquid, in contrast to their counterparts to the south. This approach resulted in technically ingenious developments in lost-wax casting that often produced metal objects as thin as metal sheet. Most served ritual and status functions: masks, containers, diadems, bells, and small zoomorphic and anthropomorphic figurines. These artisans also occasionally crafted tools from tumbaga. Lower Central American and Colombian peoples as well as people in the Central Andes shared a deep interest in golden, silvery, and coppery colors in metal, whether cast or hammered to shape.

We do not yet know whether these two metalworking traditions developed independently or arose from a common source. However, the evidence is strong that components of both metallurgies were intermittently transmitted to West Mexico after 650 A.D. by a system of Pacific maritime trade (8). A maritime exchange network was centered in coastal Ecuador during this period and probably was managed by the Manteño, a powerful regional chiefdom. These coastal dwellers possessed complex watercraft technology, including large seagoing balsa wood rafts with sails. We know from ethnohistoric and other sources that these sailors navigated as far north as the modern border of Ecuador and Colombia. Specialists who have considered both the raft design and the pattern of Pacific ocean currents estimate that these craft were fully capable of making the voyage to Mexico (9), either nonstop on the open sea or through coastal expeditions. The archeological record and documentary sources suggest that the single most important item sought by these merchants was the seashell Spondylus (10). Spondylus inhabits the warm tropical waters of the Pacific Ocean in discontinuous pockets from the Gulf of Guayaguil (Ecuador) to the Gulf of California (Mexico). Francisco Pizarro's chief pilot captured one of these sail-propelled rafts as

it traveled northward along the Ecuadorian coast. It carried numerous metal objects including bells, bands, tweezers, tiaras, and crowns. This cargo, the pilot explained, was to exchange for seashells (11), most likely Spondylus. Spondylus was considered sacred, the preferred food of the gods among the Andean peoples, and was acquired and processed in large quantities (12).

Whether or not it was Spondylus that these merchants were seeking along the coast of West Mexico (13), the discontinuous distribution of specific metallurgical materials (metal and alloy types), techniques, and artifact types (appearing in lower Central America and Colombia and the Central America and Colombia and the Central Andes, then in West Mexico) provides strong evidence for a maritime introduction of metallurgy to Mexico. These elements were virtually unknown in the intervening region during the time periods in question.

These traders then introduced technical information and some artifacts from both traditions to West Mexico. The artifacts bells, tweezers, needles, open rings, axes, and awls—served as prototypes for objects that were subsequently fashioned locally from local materials. During Period 1, West Mexican smiths fashioned large numbers of small, untuned (3) lost-wax-cast bells from copper. They also sometimes crafted implements from Ecuadorian prototypes such as

sewing needles, depilatory tweezers, fishhooks and other items, by cold working the metal from an initial cast blank. During Period 2, metalworkers in highland Michoacan, northwestern Guerrero, the Infiernillo area on the Balsas river, and the Lake Chapala region of Jalisco (Fig. 2) first used the two bronze alloys, Cu-As and Cu-Sn. Copper-arsenic alloys were introduced from southern Ecuador and northern Peru, whereas Cu-Sn alloys were introduced from southern and central coastal Peru and the adjacent highlands. All were brought by the system of maritime exchange that had operated during Period 1 (3). West Mexican smiths used these alloys, and a ternary Cu-As-Sn alloy developed locally, to produce the same object types made previously in copper. They took advantage of the increased fluidity, strength, toughness, and color properties to create finer, harder tools and thinner, more intricate lost-wax castings. They incorporated the alloying elements in low concentrations for tools and, in status objects, in high concentrations for color. High-tin Cu-Sn alloys were used to cast bells with a golden color and high-As Cu-As alloys (to 23% As by weight) for bells with a silvery hue (3). This Period 2 bronze metallurgy in West Mexico sparked the subsequent developments in the Huastec region that we describe.



Fig. 2. Mesoamerican sites and regions cited in text.

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### ARTICLES

### The Huastec Evidence

The two Huastec sites from which the artifacts were recovered, Platanito and Vista Hermosa (Fig. 2), were excavated between 1965 and 1968 (14). The sites are found in an area that had been occupied by sedentary Huastec peoples for hundreds of years before the Spanish invasion (15). Platanito was located in a province that was conquered by the Aztecs in the mid-15th century, during the period of imperial expansion outward from the basin of Mexico. The peoples of Platanito probably paid tribute to Tenochtitlan (Fig. 2), the Aztec capital in the basin of Mexico. The Huastec place-name for Platanito has not been identified, so we do not know whether the settlement appears on Aztec tribute lists. The site was probably abandoned after the great epidemics during the 16th century when Spanish authorities resettled surviving populations. Vista Hermosa, to the north, may have come under Aztec control in the century before the Spanish conquest, although direct evidence is unavailable. Following the conquest, the Spanish administered Vista Hermosa for some 50 years, then the settlement was abandoned by local inhabitants following raids by seminomadic Chichimec peoples.



Fig. 3. Ingot excavated at Vista Hermosa. Dimensions: vertical, 1.6 cm; horizontal, 2.2 cm.

Vista Hermosa, where 43 metal objects were recovered, currently consists of some 120 platform mounds and a well-defined ball court. The French archeological mission located approximately 100 burials at Vista Hermosa, some 10% of which had been looted. A few others were disturbed in prehispanic times. Most metal artifacts were found in burials; a small number came from test pits. Excavations yielded three pieces of intermediate processed metallurgical material (16) [one ingot (Fig. 3) and two small semimetallic masses] and 40 metal artifacts.

Twenty-four of these objects are bells. They represent three different subtypes (types 1, 3, and 4 illustrated in Fig. 4), all three of which were also fashioned in West Mexico (17). Others could not be classified. Eight bell clappers, two needles, three axes, several metal fragments, and a piece of Cu-Ag-Au alloy sheet metal (18) were also recovered.

Archeologists identified 150 mounds at Platanito, many of which contained multiple burials. Unfortunately all but one had been looted when the site was initially surveyed. In all, the French mission obtained 78 metal objects from Platanito: 77 bells and 1 axe. Nine bells came from excavated contexts (Fig. 4, subtype 5); all others were purchased from local people who had participated in informal excavations carried out before the systematic site survey. The Platanito bell assemblage is more diverse than that of Vista Hermosa. It includes the three bell subtypes found at Vista Hermosa as well as two others (Fig. 4, subtypes 2 and 5). Subtype 5 is unknown elsewhere in Mesoamerica; bells similar but not identical to subtype 2 appear in West Mexico.

Tamtok (Fig. 2), a large late Post Classic Huastec center to the southeast of Platanito, was also excavated, but archeologists encountered only one metal artifact (19, 20). However, Tamtok did provide an important radiocarbon date of 1470  $\pm$  35 A.D. (21) associated with a ceramic assem-

> **Fig. 4.** Vista Hermosa and Platanito bell subtypes. Subtypes 1, 3, and 4 appear at Vista Hermosa; subtypes 1 to 5 at Platanito.

blage that included two Post Classic Huastec ceramic types (Huastec black and white and Huastec polychrome) and several unusual ceramic forms. This same assemblage also appears at Vista Hermosa and Platanito (22) and, together with the radiocarbon date, permits approximate dating of the three sites to the late Post Classic period.

Metal artifacts from Vista Hermosa and Platanito were analyzed by atomic absorption spectrometry (Table 1). Twenty artifacts were selected from Vista Hermosa: three axes, the metal fragment, a bell clapper, and 15 bells representing all three subtypes. Thirty-one artifacts were analyzed from Platanito: one axe, 26 bells selected from among the four major subtypes, one from subtype 5, and three bells which either belong to other subtypes (designated by "0" in Table 1) or were damaged or fragmentary.

Nearly all the artifacts analyzed from Vista Hermosa and Platanito fall into one of four compositional groups (Table 2). All objects contained Cu as the major element. One group consists of objects made essentially of unalloyed Cu with As usually present in trace or minor concentrations (<0.19% by weight). Most artifacts in this group are smooth-walled bells: subtype 1 from Vista Hermosa and subtypes 1 and 2 from Platanito. The second group consists of objects made from Cu-Sn alloys with Sn concentrations ranging from 1.1 to 5.28%; As is present in some artifacts in trace or minor concentrations (to 0.21%). Most are subtype 3 wirework bells from Platanito; the single subtype 5 bell also belongs to this group. The third compositional group comprises Cu-As alloy objects with As present from 0.52 to 2.14%; the majority of these objects are subtype 4 wirework bells. The fourth group consists of ternary alloys of Cu, As, and Sn, with As concentration at about 0.50% and Sn ranging from 1.78 to 9.31% by weight. Objects in the final group (other) contain Sn in concentrations of about 0.75%, which probably represents metal obtained from remelted artifacts (23-25).

**Table 1.** Number of Vista Hermosa and Platanito bells by subtype and number analyzed by subtype. No., number; *n*, number of artifacts analyzed.

Sub-	Vis Herm		Platanito		
type	No.	n	No.	n	
1	18	9	8	3	
2	0	0	18	7	
3	1	1	23	7	
4	1	1	9	9	
5	0	0	9	1	
0 (other)	4	4	9	3	



The intermediate processed material and the ingot from Vista Hermosa were analyzed with an electron microbeam probe (Table 3). Average compositions determined from transects across the matrix metal (intermediate 1, 37 points; intermediate 2, 15 points; ingot, 36 points) show that these are Cu-As-Sn alloys with 1% Sn in the two pieces of intermediate material and approximately 5.0% in the ingot (26). Because intermediate 2 turned out to be highly metallic, we analyzed another part of the material by atomic absorption spectrometry (see Table 3). Both analytical methods gave comparable results. Metalworkers were working with a Cu-Sn bronze alloy containing As in concentrations varying from about 0.20% to approximately 0.67%. As a result of segregation some areas of the matrix metal in intermediate 1 contain As concentrations as low as 0.07% by weight. In the matrix metal of intermediate 2, As concentrations reach 1.27%; Sn concentrations are as high as 2.14%.

#### Production at Vista Hermosa and Platanito

The compositions of the Vista Hermosa ingot and pieces of intermediate material indicate that local metalsmiths were manufacturing Cu-As-Sn allovs from smelted ores. Ore minerals of Cu, As, and Sn, while not extremely common, are present within the region (27). Moreover, the compositions of some Vista Hermosa artifacts including one axe (ID nos. 35, 38, 39, 46, and 50, Table 2) are close enough to those of the ingot and or the intermediate material to have been made from similar alloys. These objects are fashioned from Cu-Sn and Cu-As-Sn alloys with As present from trace to significant concentrations, but always lower than that of Sn. The compositional data presented in Table 2 also show, however, that other Vista Hermosa objects, particularly those subtype 1 bells made from Cu, were not fashioned from the alloys just described. Nonetheless, macroscopic evidence suggests that some also were crafted locally. For example, subtype 1 Cu bells, which are small (<1 cm in height) and fragile, are sometimes miscast. Macroscopic observations also show that at least one of the Cu-As alloy bells (no. 41) was cast locally. Dirt and charcoal, perhaps remains of a mold, enclosed the bell, and the resonator chamber contains similar material that may be residue from a core used in lost-wax casting. The bronze bell clappers present in the Vista Hermosa assemblage further substantiate the idea that alloy bells were assembled in situ.

Thus, at Vista Hermosa we have established local production of (i) tiny Cu bells, (ii) Cu-As-Sn alloy metal, and (iii) a Cuatomic absorption. ID, identification number. Numbers following bell indicate subtype. Elements with no numerical value were not detected.

Table 2. Chemical compositions in weight percent of Vista Hermosa and Platanito artifacts by

Metal or alloy	Туре	ID	Ag	As	Au	Fe	In	Pb	Ni	Sb	Sn
Cu	Bell-1 Bell-1 Bell-1 Bell-1 Bell-1 Bell-1 Bell-1	32 33 34 47 48 49 51	0.001 0.002 0.002	0.10 0.06 0.07 0.07 0.14 0.07 0.06	Vista He	rmosa 0.016 0.012 0.016 0.024 0.017 0.022 0.022					
	Bell-0 Bell-1 Bell-1	52 53 58	0.003 0.05	0.08 0.14 0.08 0.12		0.022 0.033 0.012 0.016		0.02		0.014	0.071
Cu-Sn	Axe Clapper Bell-0	38 46 50	0.001 0.001	0.05 0.05 0.09		0.006 0.006 0.02	0.166 0.104	0.007 0.023	0.008	0.013 0.056	5.28 3.90 1.57
Cu-As	Bell-4 Bell-0 Fragment	36 41 54	0.002	1.25 1.22 2.14		0.009 0.034 0.02		0.01	0.008	0.055	0.038
Cu-As-Sn	Axe Bell-0 Bell-3	40 35 39	0.002 0.001	0.47 0.67 0.52		0.01 0.042	0.364 0.08 0.09	0.016 0.47 0.008	0.012 0.025 0.007	0.18 0.058 0.01	9.07 1.78 4.69
Other	Axe	37	0.064	0.15	Platar	.,	0.008	0.027	0.10	0.47	0.72
Cu	Bell-0 Bell-1 Bell-1 Bell-4 Bell-2 Bell-2 Bell-2 Bell-2 Bell-2 Bell-2 Bell-2 Bell-2 Bell-2 Bell-2	5 7 9 10 28 27 28 55 56 57 59	0.004 0.001 0.003 0.002 0.003 0.049	0.17 0.06 0.12 0.18 0.04 0.14 0.02 0.16 0.17 0.11 0.15	, ieitei	0.008 0.024 0.008 0.008 0.014 0.007 0.012 0.025 0.007 0.012 0.012 0.012		0.016	0.035	0.019	0.038
Cu-Sn	Bell-3 Bell-3 Bell-3 Bell-3 Bell-3 Bell-3 Bell-4 Bell-5	11 12 14 15 16 17 20 31	0.002 0.001 0.002 0.002	0.04 0.01 0.21		0.037 0.03 0.024 0.052 0.025 0.033 0.01 0.17	0.114 0.171 0.101 0.181 0.22 0.18 0.088 0.44	0.011	0.005 0.005 0.006	0.087	1.63 1.98 1.11 2.67 3.28 3.57 2.47 2.83
Cu-As	Bell-0 Bell-4 Bell-4 Bell-4 Bell-4 Bell-4 Bell-4 Bell-4 Bell-0	6 8 19 21 22 23 24 25 29	0.014 0.002 0.014 0.006 0.005 0.002 0.002	1.47 1.62 2.20 1.02 1.58 1.23 0.54 0.85 0.52	0.004 0.004 0.004 0.004 0.006	0.024	0.007	0.13 0.022 0.011 0.009 0.011 0.009 0.006 0.012	0.041 0.051 0.032 0.02 0.024 0.041 0.048 0.035	0.33 0.43 0.24 0.18 0.21 0.10 0.077 0.17 0.085	0.02 0.041 0.041 0.049 0.02 0.033 0.02
Cu-As-Sn	Axe	30	0.05	0.41			0.84	0.013	0.005	0.11	9.31
Other	Bell-3	13	0.001			0.024	0.048				0.84

Table 3. Composition of ingot and intermediate material from Vista Hermosa, in weight percent.

Artifact	Ag	As	Au	Fe	In	Ni	Pb	Sb	Sn
			Electro	on microa	nalysis				
Intermediate 1	0.063	0.248	0.005	0.005	0.006	0.004	0.018	0.003	0.97
Intermediate 2	0.278	0.671	0.039	0.018	0.010	0.015	0.073	0.023	1.35
Ingot	0.065	0.423	0.0	0.008	0.028	0.002	0.062	0.0	5.15
			Aton	nic absor	otion				
Intermediate 2	0.01	0.21	0.007	0.02	0.09	0.004	0.014	0.04	2.48

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As alloy bell (no. 41) whose type could not be determined. Local production also is likely of a subtype 3 wirework bell (no. 39), bell clappers, and an axe (no. 38). The compositions of these latter objects are similar to those of the intermediate material and the ingot. However, artifacts of these types and compositions do occur in West Mexico and could have been imported.

At Platanito, bells were made from Cu, from Cu-Sn and Cu-As alloys, and from Cu-Sn alloy metal containing As in trace concentrations. Some Platanito Cu bells (subtype 2), like their subtype 1 counterparts from Vista Hermosa, were miscast or retain parts of the casting sprue, features which strongly suggest local production. Several subtype 3 bells (nos. 11 and 12) and a subtype 5 bell (no. 31) are made from metal resembling the Vista Hermosa intermediate material in composition and could have been cast locally from similar stock materials.

Local production at Platanito is established for the miscast Cu bells. Among the alloy objects, local production is most likely for the subtype 5 bell which is unique to the region and made from Cu-Sn alloy metal with traces like that smelted at Vista Hermosa. Local production is possible but less likely for subtype 3 and subtype 4 Cu-Sn alloy bells and subtype 4 Cu-As alloy bells. The two bell subtypes also appear in West Mexico. Among these possibilities, Huastec production of subtype 4 Cu-As bronze bells is the most probable given the miscast Cu-As alloy bell from Vista Hermosa.

In summary, the evidence strongly supports Huastec production of small Cu bells, Cu-As-Sn alloy metal, and subtype 5 Cu-Sn bells which also contain As. Production was likely of Cu-Sn bronze bell clappers and subtype 3 wirework bells made from Cu-As-Sn alloys. However, we do not know whether some of the other bronze objects, especially the Sn- and As-bronze subtype 3 and subtype 4 wirework bells, which are common in the West Mexican state of Guerrero (28), and the axes, which are stylistically nondiagnostic, were manufactured locally or could have been imported from West Mexico. We have no chemical analyses of examples of these bells or axes from Guerrero for purposes of comparison.

Therefore we lack the evidence to determine whether the peoples in regions of Eastern Mesoamerica copied certain standard bell designs (subtypes 3 and 4) using whatever materials were available that possessed the necessary properties or if these subtypes were made in West Mexico and then exported. As Table 2 indicates, Platanito bell subtype 3 contains bells belonging to at least two distinct compositional groups, one made from Cu-Sn alloys and the other from Cu-Sn alloys, which also

contain low concentrations of As and in some cases Sb. The differences in artifact chemistries among these subtype 3 bells suggest either that a variety of materials was on hand at certain production localesingots of Cu-Sn, Cu-As-Sn, or Cu-Asand metalworkers used any that would work, or that there were multiple manufacturing locales each of which focused on certain materials but for the production of similar designs.

One of the most intriguing characteristics of these Huastec metal assemblages is that here, like in West Mexico, metalsmiths became so interested in bells. Ethnographic studies show that Huastec people still wear metal bells in traditional dances. They fasten tiny, high-pitched bells around the calf that sound when the dancer stamps on the ground. Larger, lower-pitched bells are fastened at the lower part of the back, and the dancer rings them with a lateral motion of the hips. Until recently local people sometimes collected these bells from archeological sites (29). Although Huastec emphasis on the use of metal for sound appears to have been as important as in West Mexico in the prehispanic era, metalworkers did not add Sn and As to Cu in high enough concentrations to alter bell color, nor did they import such golden and silvery bells. In the bells we studied, Sn concentrations never exceed 4%.

#### Transmission of the Technology

We do not know how metallurgy was introduced to the Huastec region from West Mexico. The most likely possibility is that the technology was transmitted through the market systems and merchants responsible for distributing Aztec trade goods (30) rather than through direct contact with the primary Period 2 metal-producing areas of West Mexico such as highland Michoacan (Fig. 2). The archeological evidence suggests that during this period contact between the Huastec region and these West Mexican zones was limited. Most of the intervening area was occupied by seminomadic Chichimec groups (31). However, we do know that relations existed between peoples in the Huastec region and the Aztec in the Basin of Mexico. Huastec potterý has been reported at Aztec sites there (30), as well as to the south in the neighboring state of Morelos (32). We also know (33) that parts of the Huastec region where Platanito and Tamtok were located was a tributary province of the Aztec. Furthermore, Cu-Sn bronze bells were one tribute item to Tenochtitlan, the Aztec capital from Guerrero (3) after the Aztec imperial expansion in 1440, and some of those bells were likely fashioned in Guerrero. Given that two of the primary Huas-

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tec bell designs (subtypes 3 and 4) are subtypes also found in Guerrero, we must investigate the possibility that Huastec metallurgy was introduced from Guerrero through the same trade and communication networks that distributed Aztec goods. Yet the interactions were qualitatively different because the nature of the activity, the transfer of a complex technology, demands long-term face-to-face contacts.

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- 16. Intermediate processed metallurgical material refers to pieces of metal that appear to have been partially or wholly smelted from ore but which have not been refined. They contain extraneous non-metallic inclusions and probably remains of partially smelted ore minerals.
- D. Hosler, unpublished data. 17.
- 18. Electron microprobe analyses were carried out at Massachusetts Institute of Technology on one piece of sheet metal. The object is made from a . Cu-Ag-Au alloy: (Au = 47.9%, Ag = 15.4%, and Cu = 36.2%).
- 19. G. Stresser-Pean, in preparation
- 20. Chemical analyses show that the bell is a Cu-As-Pb alloy.
- 21. Dating was carried out at the Laboratorio de Radiocarbono del Departamento de Prehistoria del Instituto Nacional de Antropología e Historia (INAH), Mexico City, Mexico. Date is uncalibrated. Calibrated date is 1390 to 1435 A.D. Calibration was performed using radiocarbon calibration tables in J. Klein, J. C. Lerman, P. E. Damon, E. K. Ralph, Radiocarbon 24, 103 (1982).

22. G. Stresser-Pean, unpublished data.

- 23. Sn can be present to 0.4% by weight in disseminated form in chalcopyrite, a Cu-Fe sulfide and the most common source of copper metal in Mexico.
- 24. We consider an artifact to be made from an alloy when the concentration of the alloying element is sufficient to alter the working properties of the metal. In the case of As, that is  $\geq 0.5\%$ ; for Sn, it is  $\geq 1\%$ .
- The bells made from Cu tend to be smooth walled (Fig. 4; nos. 1 and 2); the bronze bells (Cu-As and Cu-Sn) are wirework types. This particular relation between metal or alloy and design attributes also holds for West Mexican bells and has been shown to result from the mechanical requirements of these designs: The increased fluidity and strength that the alloys provide optimize the design of the thin, intricate, wirework forms.
  Intermediate 1 and intermediate 2 were studied
- 26. Intermediate 1 and intermediate 2 were studied previously by D. M. K. de Grinberg, R. E. Rubinovich, and A. A. Gasca [Metalurgia de America Precolombina (Banco de La República, Bogotá, Columbia, 1986), pp. 37–65] also using an electron microbeam microanalyzer. The results differ in that we detected As and Fe in both samples; Grinberg et al.'s results show both to be absent in intermediate 1. The difference could possibly reflect segregation in the material or the number of points that were analyzed in the section; we analyzed 37 points in the matrix metal; Grinberg et al. analyzed five.
- 27. See geológical maps for Cu and Sn deposits produced by the Instituto de Geología, Universidad Nacional Autónoma de México (UNAM). Two Sn deposits are shown in the State of San Luis Potosi; Cu deposits occur in the states of Tamaulipas and San Luis Potosi. Arsenopyrite

occurs in San Luis Potosí at the deposits of Catorce and Guadalcázar (W. Panczner, *Minerals of Mexico* (Van Nostrand Reinhold, New York, 1987).

- C. L. Diaz Oyarzabal, Colección de Objetos de Piedra, Obsidiana, Concha Metales y Textiles de Estado de Guerrero (Col. Catálogo de Museos INAH, Mexico City, Mexico, 1990); D. Hosler, unpublished data.
- 29. G. Stresser-Pean, unpublished data.
- See M. Smith [*Anc. Mesoam.* 1, 153 (1990)] for an extended discussion of late Post Classic longdistance trade of Aztec goods, particularly of ceramic and obsidian.
- D. Michelet, *Rio Verde San Luis Potosí (Mexique)* (CEMCA, Mexico, 1984); W. Jimenez Moreno, *El Norte de México y el sur de Estados Unidos* (Tercera Reunión de Mesa Redonda, Sociedad Mexicana de Antropología, Mexico, 1943).
- 32. M. Smith, personal communication.
- 33. The Aztec tribute province of Oxitipa appears in the Codex Mendoza [F. Berdan and P. Anawalt, The Codex Mendoza (Univ. of California–Berkeley, 1992)], but the codex does not mention the villages included in the province.
- 34. The study and sampling were carried out under a permit granted by the Instituto Nacional de Antropología e Historia in Mexico City. The authors gratefully acknowledge INAH's support. The French Archaeological Mission carried out the excavations, directed by G. Stresser-Pean. D. Hosler performed the laboratory analytic studies at the Massachusetts Institute of Technology. F. Leipziger performed the atomic absorption studies. We also thank L. Compton and the Undergraduate Research Opportunities Program (UROP) at MIT for funding her work.

# Protein Oxidation and Aging

## Earl R. Stadtman

A number of systems that generate oxygen free radicals catalyze the oxidative modification of proteins. Such modifications mark enzymes for degradation by cytosolic neutral alkaline proteases. Protein oxidation contributes to the pool of damaged enzymes, which increases in size during aging and in various pathological states. The age-related increase in amounts of oxidized protein may reflect the age-dependent accumulation of unrepaired DNA damage that, in a random manner, affects the concentrations or activities of numerous factors that govern the rates of protein oxidation and the degradation of oxidized protein.

 ${f T}$ hirty-six years ago, Harmon (1) suggested that free radicals are likely involved in the aging process. In the meantime, the free radical theory of aging has become widely accepted and is the basis of numerous hypotheses to explain how free radicals might be involved. Nevertheless, the relevance of free radicals in aging is clouded by diverse opinions as to what aging really is. Some hold that aging is a programmed phase of cellular differentiation and normal development that culminates in death. Others believe that aging is the manifestation of progressive losses in physical and mental acuity caused by the impairment of fundamental physiological processes by illdefined factors. So far as the radical theory is concerned, distinction between these

concepts is blurred by a growing body of evidence that free radical damage to cellular function is associated with a number of age-related diseases-namely, atherosclerosis, arthritis, muscular dystrophy, cataractogenesis, pulmonary dysfunction, various neurological disorders, and very likely cancer (2). This notwithstanding, few would question the importance of free radical damage to nucleic acids and lipids in agerelated disease processes. From measurements of the in vivo production of modified purine and pyrimidine bases, presumed to arise from the excision and repair of damaged nucleic acid, Ames et al. (3) have reasoned that oxygen free radicals are responsible for 10,000 or so DNA base modifications per cell per day. It requires little persuasion to accept the argument that a finite fraction of such a massive amount of damage would escape repair by even the

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most sophisticated mechanisms and that the accumulation of unrepaired damage could account for the age-related loss of physiological function. There is little reluctance to accept the view that oxygen free radical-mediated lipid peroxidation could lead to the loss of membrane integrity and hence compromise cellular function. Accordingly, much attention has been given to the potential roles of free radical damage to nucleic acids and lipids in aging. Curiously, until recently, the possibility that free radical damage to proteins might also contribute to aging has received less attention. This lack of interest may be a result in part of a failure to demonstrate age-related defects in the protein synthetic machinery or in the in vivo production of oxidatively damaged protein (4). In addition, it seemed reasonable that damaged protein would not accumulate because cellular proteins are constantly turning over and that abnormally formed or damaged proteins turn over more rapidly than normal proteins.

It was, in fact, an effort to understand how cells regulate the turnover of individual enzymes that led to the work summarized here, which shows that metal catalyzed oxidation (MCO) of enzymes is a marking step in protein turnover and that the accumulation of oxidized protein is likely implicated in aging.

# Two-Step Mechanism of Enzyme Degradation

The rates of synthesis and degradation of some enzymes are dependent on nutritional factors. In Escherichia coli and Klebsiella aerogenes, glutamine synthetase (GS) and several other enzymes are rapidly degraded under conditions of nitrogen starvation (5-7). Subsequently, it was determined that the degradation of GS involves two steps (6). In the first step, the enzyme is oxidized to a catalytically inactive form, which in the second step is rapidly degraded by intracellular proteases. The first step involves the oxidation of amino acid residues of the enzyme by the combined action of  $H_2O_2$  and  $Fe^{2+}$  (Fig. 1). In the case of some amino acids, this leads to the formation of carbonyl derivatives.

The production of  $H_2O_2$  and  $Fe^{2+}$  is catalyzed by any one of several different enzyme systems that are variously referred to as mixedfunction oxidation systems (8) or MCO systems (9). These systems include a large class of flavoproteins, reduced forms of nicotinamide adenine dinucleotide phosphate [NAD(P)H] oxidases, the reduced form of nicotinamide adenine dinucleotide quinone reductase, dehydrogenases, and cytochrome P-450 reductases, which in intermediary metabolism normally serve as electron carriers between various metabolic reactions. However, under conditions of oxidative stress or in

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