Bismuth Bronze from Machu Picchu, Peru

Abstract. *The decorative bronze handle of a tumi excavated at the Inca city of Machu Picchu, Peru, contains 18 percent bismuth and appears to be the first known example of the use of bismuth with tin to make bronze. The alloy is not embrittled by the bismuth because the bismuth-rich constituent does not penetrate the grain boundaries of the matrix phase. The use of bismuth facilitates the duplex casting process by which the tumi was made and forms an alloy of unusual color.*

During an expedition to Peru in 1912, Bingham recovered about 150 bronze artifacts from Late Horizon times (A.D. 1476–1534) at the Inca city of Machu Picchu (*1*). Some of these artifacts were examined by Mathewson in 1915, and his paper on them is one of the first to demonstrate the use of metallography in the study of archeological materials (*2*). A small kinfe, or tumi, with a handle in the shape of a llama head is of particular interest; Mathewson found the blade and stem to be 3 percent tin bronze of high purity and discovered later that the handle is of different composition and had been cast onto the stem. He inferred from metallographic examination that the handle was made of a high-tin bronze.

The llama-head knife (number 17962 in the Peabody Museum of Natural History) was found in cave 54 at Machu Picchu; this cave also contained two skulls, some other bones, and a large bronze pin (*3*). A section through the upper part of the knife (Fig. 1) reveals coarse grains and dendritic structure in the handle with no evidence of deformation or of solder in the joint with the stem, which consists of recrystallized tin bronze. These observations confirm that the handle has been cast onto the stem. However, the microstructure of the handle (Fig. 2) does not contain the $\alpha + \delta$ structure expected in high-tin bronze (*4*). Instead of being hard, the white component has a diamond pyramid hardness of only 45 (measured with a 25*g* load), whereas the continuous matrix has a hardness of 95.

The compositions of the microstructural constituents shown in Fig. 2 were determined with an energy dispersive x-ray spectrometer attached to a scanning electron microscope and a Tracor Northern standardless semiquantitative analysis program. The average composition of the handle is 73 percent copper, 18 percent bismuth, and 9 percent tin. No other metals were detected. The white component in Fig. 2 is approximately 93 percent bismuth and 7 percent copper but is not homogeneous; heavy etching with $FeCl_3$ solution shows that fine particles of a second phase are occasionally present. The continuous constituent in the microstructure is on average 90 percent copper and 10 percent tin and also shows the presence of a small amount of precipitate in the form of thin plates. There are a few spherical, nonmetallic inclusions in the bismuth-rich component that are too small to analyze.

In nearly 1000 published analyses of bronzes from the Old World only one shows more than 1 percent bismuth; most have none or only a trace (*5–6*) as do most samples from South America, except for a few which contain up to 0.8 percent (*7*). We know of no previous reports of the use of bismuth as an alloying element in bronze. The introduction of bismuth in the bronze from Machu Picchu may have been a metallurgical accident, but we will argue that the alloy was used to facilitate the composite casting procedure by which the tumi was made.

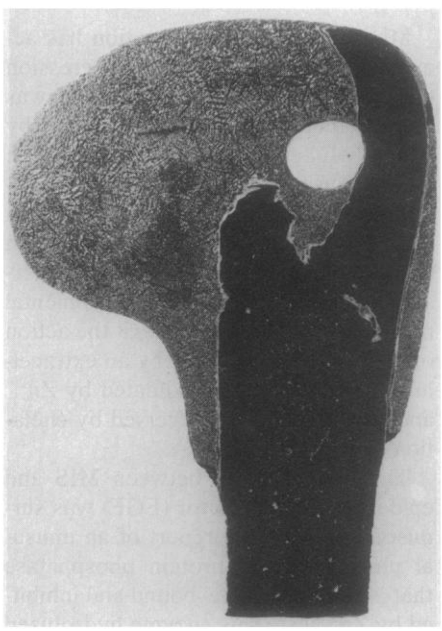
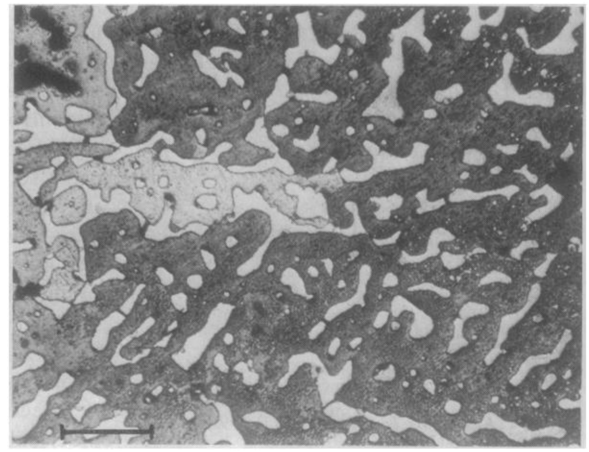


Fig. 1. Cross section of the figure of a llama head made of bismuth bronze cast on the stem of a knife made of low-tin bronze. The color of the head is whiter than that of high-tin bronze. The width of the head is 13 mm. [Photograph by W. Sacco]

In modern copper metallurgy care is taken to remove bismuth which, by penetrating the copper grain boundaries, causes brittleness. Bismuth is a less deleterious impurity in copper-base alloys such as brass, where the addition of zinc to the copper changes the relative interfacial energies so that grain boundary penetration does not occur (*8*). The bismuth-rich component in the microstructure in Fig. 2 forms blunt dihedral angles at the grain boundaries of the matrix, showing that addition of tin also inhibits embrittlement of copper by bismuth.

Bismuth occurs as native metal and as bismuthinite in many localities in Peru and in association with tin in Bolivia (*9*). We have next to decide whether the alloy used in the llama-head casting resulted from the accidental inclusion of bismuth metal or ore in the copper smelting procedure. In modern copper pyrometallury, bismuth is eliminated as vapor in both matte smelting and in the converter (*10*). We infer from the Ellingham diagram (*11*) that in a primitive smelting furnace the oxides Bi_2O_3 and Cu_2O would be reduced at about the same temperature and CO pressure and that the amount of bismuth impurity entering the copper metal would depend on how much of the bismuth impurity in the ore was converted to fume during reduction. Experiments carried out by Tylecote *et al.* showed almost complete elimination of bismuth in smelting of both

Fig. 2. Optical micrograph of a polished section of the llama-head casting etched with acidified $FeCl_3$. The white-colored constituent is 93 percent bismuth and 7 percent copper. It does not penetrate the grain boundaries of the dark-etching component (90 percent copper and 10 percent tin), which is continuous in the microstructure. Scale bar represents 0.1 mm.



oxide and sulfide copper ores (*12*). We think it unlikely that an Inca metalworker would confuse bismuth with tin or copper minerals and that, if there had been accidental admixture of minerals, most of the bismuth would have been eliminated during smelting. If the bismuth were derived from the copper ore, we expect that other impurities would be detected in the alloy, as in European bronzes in which bismuth is present (*5*). They are not found. Native bismuth was probably used to make the alloy. Could bismuth have been added to copper by mistake instead of metallic tin? Native bismuth has a color and surface texture quite different from tin and, in a society in which metals were relatively scarce, it is unlikely that they would have been handled carelessly. Furthermore, if it was intended to make tin bronze, too much alloy addition was used—most bronze from Machu Picchu contains about 5 percent tin (*2*). It is most likely that the alloy used for the llama-head casting was deliberately made by the addition of native bismuth to molten tin bronze, which could be done easily since the denser bismuth would sink to the bottom of the melt before much was lost by vaporization.

Use of bismuth bronze would facilitate making the composite knife in several ways. Addition of small amounts of bismuth to bronze helps make sounder castings (*13*). Better adhesion to the stem would be obtained because of reduced shrinkage during solidification, although the amount of bismuth used is less than that required to obtain expansion upon solidification in most alloys where this effect has been studied (*14*). The addition of bismuth may have produced better adhesion between the head and the stem because of more effective wetting at the interface. But it is possible that the Inca smith may have simply wanted the whiter color of the bismuth bronze. These results show a new dimension of metallurgical sophistication in Inca metalwork.

ROBERT B. GORDON
JOHN W. RUTLEDGE

Kline Geology Laboratory,
Yale University,
New Haven, Connecticut 06511

References and Notes

1. H. Bingham, *Machu Picchu, A Citadel of the Incas* (Yale Univ. Press, New Haven, 1930), chap. 7.
2. C. H. Mathewson, *Am. J. Sci.* **40**, 525 (1915).
3. E. C. Erdis, *Notes on Yale Peruvian Expedition*, entry for 6 September 1912, manuscript in Yale University Library.
4. A. Schimmel, *Metallographie der Technischer Kupferlegierungen* (Springer, Berlin, 1930), p. 18.
5. P. T. Craddock, *J. Archaeol. Sci.* **3**, 93 (1976); *ibid.* **4**, 103 (1977).
6. ———, *Br. Mus. Occas. Pap. 15* (1981), pp. 1–31.
7. E. Nordenskiold, *Copper and Bronze Ages in South America* (Elanders Baklryckeri Aktiebolag, Göteborg, 1921), p. 139.
8. C. S. Smith, *Trans. AIME* **175**, 15 (1948).
9. B. L. Miller and J. T. Singewald, *The Mineral Deposits of South America* (McGraw-Hill, New York, 1919).
10. A. K. Biswas and W. G. Davenport, *Extractive Metallurgy of Copper* (Pergamon, Oxford, ed. 2, 1980), pp. 97 and 190.
11. D. W. Hopkins, *Physical Chemistry and Metal Extraction* (Macmillan, New York, 1954), p. 113.
12. R. F. Tylecote, H. A. Ghaznani, P. J. Boydell, *J. Archaeol. Sci.* **4**, 305 (1977).
13. G. S. Ershov, Yu. D. Korogodov, I. V. Gavrilin, *Liteinoe Proizvod.* **6**, 11 (1979).
14. *Metals Handbook* (American Society for Metals, Novelty, Ohio, ed. 8, 1961), vol. 1, p. 1061.
15. We thank A. Pooley for assistance with the chemical analysis and P. T. Craddock for helpful comments.

27 October 1983; accepted 15 December 1983

Phosphorylation Events During Müllerian Duct Regression

Abstract. *Regression of the fetal rat Müllerian duct in vitro was stimulated by sodium fluoride in the absence of Müllerian inhibiting substance. The action of Müllerian inhibiting substance was inhibited by sodium vanadate, adenosine 5'-triphosphate, and several related nucleotides in the presence of manganese ions. Epidermal growth factor specifically inhibited the substance, but only with manganese ions present. Insulin, platelet-derived growth factor, and nerve growth factor had no effect. These results suggest that dephosphorylation of membrane proteins mediates the action of Müllerian inhibiting substance.*

Much descriptive information has accumulated on Müllerian duct regression (*1*); until recently, however, little was known about the molecular events by which Müllerian inhibiting substance (MIS) causes regression. Our observations (*2*) that EDTA imitated the action of MIS and that Zn^{2+} inhibited MIS in organ culture provided clues to understanding this complex developmental mechanism. We proposed that the action of MIS may be mediated by an extracellular enzyme that is modulated by Zn^{2+} and that this effect is reversed by chelation of Zn^{2+} with EDTA.

The potential link between MIS and epidermal growth factor (EGF) was surmised following the report of an unusual phosphotyrosyl protein phosphatase that is cell membrane–bound and inhibited by Zn^{2+} (*3*). This enzyme hydrolyzed phosphate tyrosine bonds in membrane proteins phosphorylated by an EGF-stimulated protein kinase independent of adenosine 3',5'-monophosphate (cyclic AMP) (*4*). Even more intriguing was the association of specific tyrosyl protein kinase and phosphatase activities in membrane vesicles from rat cells transformed by Rous sarcoma virus (*5*). Oncogenes of several RNA tumor viruses have also been found to be tyrosine-specific protein kinases (*6*) showing similarities to the EGF-stimulated kinase (*7*). Since MIS inhibits growth of human ovarian and endometrial carcinoma cell lines in vitro and in nude mice (*8*), it is possible that MIS might act through dephosphorylation of membrane proteins, thus opposing the action of EGF or even the process of transformation. Studies of the effects of various agents, including epidermal and other growth factors, on Müllerian duct regression in vitro now suggest that MIS causes regression by antagonizing the effect of an EGF-sensitive, tyrosine-specific protein kinase in the Müllerian duct.

Regression of the fetal rat Müllerian duct was detected by a graded organ-culture assay (*9*). The urogenital ridge of the female rat fetus was removed at 14½ days of gestation and placed in organ culture for 72 hours. Serial sections of the ridge were examined for regression of the Müllerian duct and graded on a scale of 0 to 5, with 0 representing no regression and 5 complete regression. MIS was partially purified from newborn calf testes (*10*) and portions, with or without various test solutions, were mixed 1:1 with the standard culture medium.

Sodium fluoride (> 1 mM), reported to weakly stimulate the same phosphotyrosyl-protein phosphatase that was inhibited by Zn^{2+} and stimulated by EDTA (*3*), induced almost complete Müllerian duct regression (Fig. 1A). With < 0.6 mM sodium fluoride the duct was intact and with intermediate concentrations it was only partially affected. This result is analogous to that seen with EDTA (*2*), except that the fluoride concentration causing complete regression was about twice that of EDTA. Sodium vanadate, an inhibitor of phosphotyrosyl protein phosphatase (*11*), progressively inhibited MIS-induced regression at concentrations > 5 μM (Fig. 1B). MIS activity was suppressed almost completely by 37.5 μM sodium vanadate.

Since the action of MIS could be mimicked by agents that activate a tyrosyl protein phosphatase, we surmised that agents which stimulate tyrosine phos-