Pre-Columbian Alloy Objects from Guerrero, Mexico

Abstract. Fifteen metal artifacts from coastal Guerrero were analyzed. Gold-, silver-, and copper-base alloys were found, and a deliberate manufacture of bronze is indicated. Metallographic studies show a high degree of sophistication in the art of cold-working metal.

A spectroscopic examination of 15 metal objects and two pieces of slag from the Barnard Site near Zihuatanejo, Mexico, has been made. A celt (Fig. 1, sample No. 7), purchased from a small boy at Palos Blancos, was also analyzed. Palos Blancos is about 20 miles to the southwest, along the coast, from the Barnard Site, and sherd similarities indicate that the two sites are within a common ceramic area. In addition, metallographic and hardness studies of four specimens have been completed (*1*).

The late Don Carlos Barnard of Acapulco brought the site to the attention of my wife and me after purchasing a large number of metal artifacts from some treasure-hunting farmers. The collection contained a number of beautifully worked obsidian lip plugs inlaid with thin gold, together with gold bells, fragments of gold sheet, ear plugs, and crumpled artifacts seemingly of silver, as well as many open rings, bells, needles, awls, fishhooks, and plaques of a green metal. This material appears to be generally similar to the specimens from Tzintzuntzan illustrated by Borbolla (*2*). The quantity of gold and silver objects in the Barnard collection led us to believe that the grave of some important personage had been plundered. Don Carlos kindly allowed us to take five specimens for analysis.

As part of a survey of coastal Guerrero, made under the auspices of the Institute of Andean Research, we visited the Barnard Site and made small test excavations, under a permit from the Instituto Nacional de Antropologia e Historia of Mexico.

The shallowness of the cultural deposit points to a relatively short period of occupation. Unfortunately, no absolute dates are available, but ceramics indicate the site to be pre-Hispanic and to fall within the Post-Classic era, the period of occupation presumably falling between A.D. 1200 and 1500.

In our limited excavations we uncovered 26 artifacts, all apparently of the same kind of metal. Of this group, eight specimens were tested spectrographically (see Table 1): seven proved to be bronze and one copper. This is by far the highest percentage of bronze yet reported for a group of excavated artifacts (*3*). As all these samples were found in association with domestic refuse, it appears that bronze was in common use.

Although bronze is not particularly rare in preconquest Mexico, there has always been some question as to whether this alloy was produced accidentally or intentionally (*3*). Highly pertinent to this question are the results for indium for samples 8, 9, and 10. Caley and Easby (*4*) recently found this metal in two essentially pure tin artifacts from Teloloapan in Guerrero and suggested the possibility that it may be a characteristic impurity in cassiterite from that region. As indium is rare, these three samples from the Barnard Site were retested. It seems highly probable that the ore that produced the tin for Caley and Easby's specimens and the ore that supplied tin for the three indium-bearing bronze samples came from the same locality. A strong case for the smelting of tin during preconquest times in Guerrero has been made by Caley and Easby (*4*). Essentially pure copper is not rare in Mexico, and one artifact of this metal (sample No. 15) was uncovered at the Barnard Site. As both tin and copper were known, and as there is no technological reason why they could not have been combined to form bronze, the existence of indium in Guerrero tin and in Guerrero bronze points to a deliberate manufacture of bronze.

The 30-percent tin content of the bell (sample No. 10) is unusual and far higher than tin contents generally published for pre-Columbian bronze artifacts from either Mexico or South America. The only reported object of copper-tin alloy having a higher percentage of tin—a bead of half tin and half copper—is also from Guerrero (*4*). The bronze of the bell differs markedly from the other bronzes of the group analyzed in the high percentage of tin present, and it may be significant that the tin content of some bell metals approaches this high value. As indium is present as a trace element in the

Table 1. Data from analyses of samples from coastal Guerrero. The laboratory states that synthetic standards were prepared, from oxides of the metals present in the samples, for the range of estimated content. The metal samples were then weighed and arced against equivalent weights of these standards. Where a range is given, the figures indicate maximum and minimum limits. In the other cases a possible error of ±15 percent of the value given is to be expected for all values over 1 percent; for smaller values the range of possible error is larger. The sensitivity of the method used varies for each element. Consequently, trace (+) indicates an amount less than the smallest value given for any particular element. As no standards were available for arsenic, antimony, and bismuth, the figures for these elements are not quantitative and may not be used as a basis for quantitative comparison. The values for arsenic, antimony, and bismuth provide a basis for comparing the content of these three elements in the samples tested. For example, sample No. 9 contains 5 times as much bismuth as sample No. 1, and these two samples contain equal amounts of arsenic, but no statement may be made as to the relative proportions of bismuth and arsenic. Sample No. 7, the first tested, was analyzed by an emission spectrographic procedure that involves the use of a dried solution on a rotating electrode, and the results were compared with synthetic copper standards. The sulfur content was determined by wet-chemical methods. The 5-percent tin content reported here could be in error by ±1 percent. Because of the difference in methods, no comparative figure for arsenic can be given. (+) Trace; (−) not detected; (MAJ) major constituent; (blank), not tested.

Sample		Content (%)											Content (relative)		
No.	Object	Cu	Sn	Au	Ag	Pb	Ni	Al	Fe	In	S	Si	As	Sb	Bi
						Copper									
15	Wire	MAJ	+	−	0.1	+	0.01	+	+	−			3	3	30
						Bronze									
7	Celt	MAJ	5	−	+	0.15	0.025	+	−0.05	−	0.04		+	−	−
11	Wire	MAJ	10	+	0.2	+	0.01	+	+	−			2.5	1	10
12	Wire	MAJ	10	+	0.1	+	0.01	+	+	−			−	1.5	1
1	Ring	MAJ	10–12	+	0.05	0.1	+	−	−0.1	−			2.5	3.5	20
8	Needle	MAJ	10–15	−	0.2	+	+	+	+	+			2	1.5	10
9	Bracelet	MAJ	10–15	−	0.3	0.2	+	+	+	+			2.5	4.5	100
10	Bell	MAJ	30	−	0.3	0.3	+	+	+	+			1	4	30
16	Ring	MAJ	+			(Qualitative analysis)							+	+	+
17	Ring	MAJ	+			(Qualitative analysis)							+	+	+
						Silver base alloys									
5	Sheet	3	+	1.5	MAJ	0.25	−	+	−0.1	−			−	−	−
3	Sheet	4	+	30	MAJ	0.01	−	+	−0.1	−			−	−	2
4	Sheet	3	−	45	MAJ	0.01	−	+	−0.1	−			−	−	−
6	Sheet	20	−	+	MAJ	0.01	−	+	−0.1	−			−	−	4
						Gold base alloy									
2	Sheet	10–15	0.05	65–70	15–20	0.01	−	+	−0.1	−			−	−	1
						Slag									
13	Slag	0.02	+	−	+	−	+	7–10	2	−		35	−	−	−
14	Slag	0.1	0.001	−	0.01	−	−	10	5	−		40–50	−	−	−

excavated bell and in two other excavated bronze artifacts, a common ore source for the tin in these metals is probable. The different values for tin for these three bronze specimens indicates a deliberate alloying process.

Several chunks of slag were uncovered with the bronze artifacts during excavation. X-ray diffraction techniques were tried, but the globules were too small to be identifiable. However, their silver color indicates that they are not a copper-base material. We agree with the laboratory that there is a very high probability that these slags are a product of some metal smelting operation.

During excavation, two open rings (samples Nos. 16 and 17), one of round and one of square cross section, were found linked together. Qualitative analysis reveals the presence of both copper and tin, and metallographic examination shows them to be bronze. Presumably, quantitative results will be similar to those for the open ring (sample No. 1) already studied. Undoubtedly these rings were shaped by hammering thin strips of metal, as both appear to have been cold-worked to a moderate extent and subsequently annealed. Cross section hardness (Rockwell *b* scale) of each ring was 52; longitudinal hardness was 72 for the round ring and 64 for the square one (*5*).

Microscopic examination of six beads from the bracelet (sample No. 9) failed to reveal any point of fracture because of a heavy deposit of corrosion products. Metallographic examination of one sectioned bead revealed that these beads were not cast but were formed of rolled sheet metal, cold-worked and subsequently annealed. No positive evidence as to whether or not this bead was ever soldered could be obtained because of corrosion products at the point of juncture. The greater recrystallization makes it appear that more heat was applied at that point, but the amount of heat needed to produce the recrystallization would have been far greater than that needed for solder. The average of three measurements (Rockwell *b* scale) for hardness at the juncture point was 74, and the average of three readings 180 degrees away was 79 (*5*).

The 5-percent tin content of the bronze of the celt (sample No. 7) would be ideal for a wrought, heavy-duty tool. The reading for hardness (Rockwell *b* scale) at the back, non-cutting edge, where cold-working the tool would seem to be of little advantage, is 53 (*5*). This reading contrasts with one of 97 at the cutting edge. Readings for successive increments of approximately one-eighth inch in from this edge are as follows: 95, 89, 81, 78, 72, and 70. These figures show that cold-working was primarily limited to the cutting portion of the celt, and the extreme hardness of the edge demonstrates a high degree of sophistication in this art.

Samples 2 through 6 are of interest, as deliberately produced alloys are uncommon in Mexico and silver is rare. The high purity of the silver in sample No. 5 contrasts with the silver-base alloys of samples No. 3, 4, and 6 and points to a deliberate synthesis of these metals. The gold, copper, silver alloy of sample No. 2 is known as *tumbaga*. The thin sheet from which the specimen was taken must have been formed by cold-working and annealing the material.

There is always a possibility that some or all of the artifacts analyzed were introduced into the area through trade, perhaps from as far away as South America, where both bronze and silver are more common than they are in Mexico. However, in the case of bronze, the existence of indium as a trace element in other Guerrero artifacts (*4*), the presence of a pear-shaped bronze bell (sample No. 10) of undoubted Mexican origin (*6*), and the common use of bronze and the good possibility that smelting was carried on at the Barnard Site make it probable that the bronze was of local manufacture.

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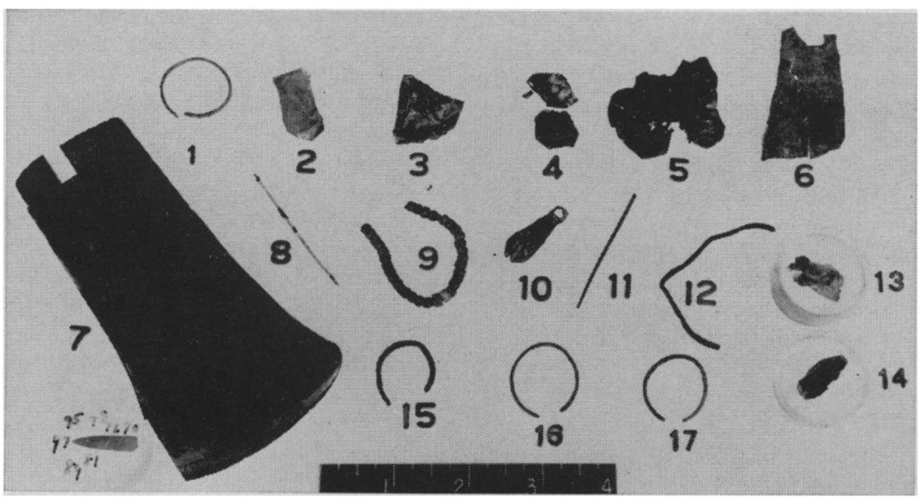

Fig. 1. Samples for which data are given in Table 1. Samples 1 through 5 are from the Barnard collection. Sample 6 was taken from the back dirt of the pot-hunters' excavation. Sample 7 was purchased. Samples 8 through 17 were recovered during excavation. Sample 15 appears similar to the open rings (samples 1, 16, and 17) in the photograph, but it has a compound curve and thus is quite different. There are large numbers of open rings in the Barnard collection, and nine were recovered during excavation. They often occur connected together in complex jumbles, and they generally range in diameter from 1/2 to 1-1/4 inches. The rings shown here were photographed after analysis; the size of the opening had been increased by removal of a section for testing. An illustration of a similar ring, in gold, is given by Borbolla (*2*). Such rings appear to fit into the Pendergast classification (*7*) under wire loop type V11B and seem to be limited in distribution to west Mexico. Sample 1 had a square cross section and was not measured. Sample 16 had a round cross section of 0.048 inch; the patina or oxide extended to a maximum depth of 0.0197 inch. Sample 17 had a square cross section measuring 0.043 inch along the square, and a maximum oxidation depth of 0.0118 inch. Hardness, on the Rockwell *c* scale, of the patina layer was 24. Sample 7 was sectioned for metallographic and hardness studies; the mounted section from which cutting-edge hardnesses were determined is shown. This celt fits into the Pendergast classification under type 1VB and seems to be distributed throughout Mexico. The stringing material of the bracelet (sample 9) has been preserved by copper salts. A sample bead had a length of 0.108 inch, an outside diameter of 0.162 inch, and a maximum oxidation depth of 0.020 inch. The metal was 0.0189 inch thick near the juncture point and 0.0118 inch thick 180 degrees from that point. The bell (sample 10) fits into the Lothrop classification under type D-1 (*6*) and into the Pendergast classification under type 1D2a. Sample 5 is badly crumpled but recognizable as an ear spool; it probably would fall under type 111A1 of the Pendergast classification. Samples 3 and 4 were taken from badly crumpled artifacts that resembled crushed toothpaste tubes. Possibly they were staff coverings. Sample 6 has a woven cotton fabric, preserved by copper salts, adhering to it. Sample 2 is from an irregularly shaped sheet of metal having a maximum length of about 8 inches. Samples 13 and 14 were sectioned and mounted for study. In the photograph sample 13 is shown sectioned-side down; sample 14, sectioned-side up.

References and Notes

1. I am indebted to the Brush Beryllium Company for the contribution of their facilities; to Leonard F. Bunck, supervisor of the company's spectrographic and x-ray laboratory at Elmore, Ohio, who developed the methods and made the analyses; to Keith Wikle, manager of the metallurgy division, and William N. Ling, who undertook the metallographic studies and made the hardness and size measurements; and to Tom Davidson for the photograph.
2. D. F. Rubin de la Borbolla, *Cuadernos Am.* **3**, No. 3 (1944).
3. W. C. Root, in S. K. Lothrop, "Metals from the Cenote of Sacrifice Chichen Itza, Yucatan," *Mem. Peabody Museum Archaeol. Ethnol., Harvard* **10**, No. 2 (1952).
4. E. R. Caley and D. T. Easby, Jr., "New evidence of tin smelting and the use of metallic tin in pre-conquest Mexico," paper presented at the 35th International Congress of Americanists in Mexico City, 20 Aug. 1962.
5. For samples 7, 16, and 17, micro-hardness results were obtained with a diamond pyramid indenter and a 500-g load; for sample 9 a 100-g load was used.
6. S. K. Lothrop, "Metals from the Cenote of Sacrifice Chichen Itza, Yucatan," *Mem. Peabody Museum Archaeol. Ethnol., Harvard*, **10**, No. 2 (1952).
7. D. M. Pendergast, *Am. Antiquity* **27**, No. 4 (1962).

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Spontaneous Electrical Activity of Dionaea muscipula

Abstract. Instillation of four to six drops of 3-percent saline in the leaf trap of *Dionaea muscipula* Ellis causes the appearance of a series of spontaneous action potentials. Mechanical stimulation of the sensitive leaf hair elicits only a single response. Immersion in 3-percent, but not in 1-percent, saline effects a loss of weight in *Dionaea* but not in the leaves of gardenia or geranium.

Dionaea muscipula Ellis, the Venus flytrap, contracts upon stimulation by mechanical, electrical, or chemical means (*1*). The action potential elicited is believed essential for the occurrence of this phenomenon and has been studied in detail (*2–4*). The mechanism of closure has been linked to a loss of turgor in the leaf trap upon stimulation of the sensitive hairs or stimulation of nearby areas (*2*) and linked more specifically to a sudden reduction in the hydrostatic pressure of the cells of the inner epidermis through depolarization (*5*). The study reported here concerned the discovery that saline solution in relatively low concentrations causes spontaneous electrical activity and leaf closure. An attempt was made to relate these findings to permeability changes in the leaf.

Table 1. Induction of spontaneous action potentials in *Dionaea muscipula* by instillation of saline. Since great variability of spontaneous activity was observed, an arbitrary system of grading was used to assign a value to the response, as follows: 0, No electrical activity elicited; 1, a single large action potential or a series of at least three action potentials; 2, a series of more than three action potentials of the magnitude of those represented in Fig. 1.

Leaves (*N*)	Mean activity	S.D.	S.E.	*p*
		Distilled water		
16	0.31	±0.58	±0.14	
		Saline, 1 percent		
45	.48	±.80	±.12	>.5
		Saline, 3 percent		
49	1.45	±1.11	±.16	<.01

The action potential was recorded by a technique previously reported (*4*). In brief, brush electrodes are applied to the outer surface of the leaf blades, and a direct-current amplifier and oscilloscope, with oscillograph, complete the circuit. Fresh adult leaves maintained in a terrarium under 24-hour fluorescent lighting were used. No spontaneous activity was observed in the resting leaves. Instillation of four drops (0.26 ml) of distilled water or of 1-percent saline into the trap effected an occasional response. Instillation of 3-percent saline in the same amount caused most of the leaves to demonstrate electrical activity and to close tightly. The electrical activity consisted of a series of action potentials, as previously described for activity elicited by mechanical touching of the sensitive leaf hair (*4*).

A typical record is shown in Fig. 1. The amplitude was 20 to 30 mvolt of 2- to 4-second duration. There was great variability in frequency and duration. Generally, the pulse frequency of spontaneous potentials was 2 to 4 pulses per minute, and the total duration was from 1 minute to several hours. There was a distinct tendency for the frequency to slow with time. Table 1 gives the system for grading the responses, together with data for a large number of leaves. The *p* values indicate that the effect of 1-percent saline was not very different from that of distilled water but that 3-percent saline was decidedly stimulatory.

In another experiment 1-percent and 3-percent saline were demonstrated to have opposite effects on leaf weight. Fresh *Dionaea* leaves were weighed and immediately immersed in saline solution for periods of time varying from 1 to 60 minutes. After exposure the leaves were carefully blotted and reweighed. As may be seen in Fig. 2, the *Dionaea* leaf immersed in the 1-percent saline always gained weight, unless exposure was very long; on the other hand, the leaf immersed in 3-percent saline always lost weight. Different results were obtained in two varieties of common leaves, *Gardenia jasminodes* and *Pelargonium* (geranium), chosen because of their contrasting textures. Both of these leaves gained weight on exposure to 3-percent saline for periods up to 10 minutes. After 15 minutes, geranium leaves showed a loss in weight.

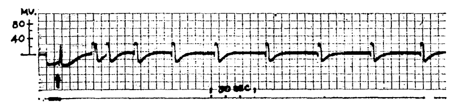

Fig. 1. Spontaneous activity induced in the leaf of *Dionaea muscipula* by the instillation of four to six drops of 3-percent saline.

The significance of the spontaneous electrical activity induced by exposure to 3-percent saline may be deduced from previous observations of the *Dionaea* leaf closure. In hundreds of experiments, no leaf ever closed without electrical activity. The more times the sensitive leaf hair is mechanically stimulated, the tighter the leaf closes. If no insect is in the trap, the leaf opens in 5 to 10 hours. By contrast, if there is an insect or a bit of meat in the trap, closure lasts for 10 or more days. When an insect is first caught, its struggles to escape produce mechanical stimulation of the sensitive hairs, but the tightening closure of the leaf soon causes the insect to die. Some mechanism must exist to keep the leaf closed beyond this initial period. It is suggested that the juices of the insect, which either are expressed by the compression of the leaf or exude during the struggle, have an action similar to that of 3-

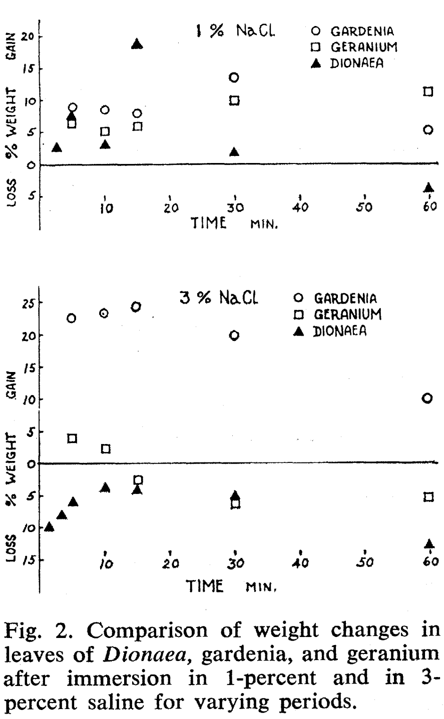

Fig. 2. Comparison of weight changes in leaves of *Dionaea*, gardenia, and geranium after immersion in 1-percent and in 3-percent saline for varying periods.