COMPOSITION OF ANCIENT PERUVIAN COPPER[1]

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ABSTRACT

Complete quantitative analyses were made of samples of metal taken from fifteen Peruvian copper objects that came from various sites and ranged in date from the fourth to the fifteenth century A.D. Twelve of the samples were found to be composed of arsenical copper containing a wide variety of impurities. One was native copper and one other was apparently native copper modified by heat treatment. Only one sample contained enough tin to warrant classification as bronze. Some tentative general conclusions are advanced.

INTRODUCTION

The existence of an extensive copper industry in Peru before the Conquest is known from the many ancient copper and bronze objects that have been discovered throughout this country and surrounding territory. Much descriptive information about these objects is available, but their exact chemical composition has not been determined even though nearly 500 chemical analyses of such objects from Peru and neighboring regions in Bolivia have been published. About half of these analyses are only qualitative, and most of the others are partial quantitative analyses in which only one or two components were determined. Listed in Table 1 are the only published analyses of copper objects from Peru with

TABLE 1

Previous analyses of copper objects from Peru

No.	Locality	Object	Cu %	Ag %	Sn %	As %	Sb %	Fe %	Other %	Total %
1	Pacasmayo	Adze	98.41	—	—	1.55	—	0.03	—	99.99
2	Trujillo	Implement	95.95	—	—	4.03	—	0.05	—	100.03
3	Lima	Adze	95.22	—	—	4.43	—	0.21	—	99.86
4	Chepen	Knife	99.62	—	0.02	—	—	—	S = 0.27	99.91
5	Chancay	Hoe Blade	95.62	none	none	4.27	0.08	—	Pb = none	99.97
6	Mochica	Ingot	99.57	trace	0.20	—	—	—	Au = 0.20	99.97
7	Mochica	Ingot	98.90	0.42	—	0.10	—	—	—	99.42

Sources of data: Nos. 1-3. Baessler, 1906.
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No. 4. Mead, 1915.
No. 5. Nordenskiöld, 1921, p. 168-169.
Nos. 6-7. Kroeber, 1954.

numerical results for three components of the metal, and in Table 2 the only published analyses of bronze objects with numerical results for four or more components. In spite of their generally high totals, most of these analyses also seem to be incomplete, for in analyses of ancient copper and bronze objects from other parts of the world, at least five components in addition to copper have usually been found.

Apart from lack of completeness, there are other defects in the previous analyses. In general, no information is given about sampling, so that doubt exists as to whether the samples analyzed were truly representative of the composition of the metal of the objects. Since very little is said about the methods of analysis

TABLE 2

Previous analyses of bronze objects from Peru

No.	Locality	Object	Cu %	Ag %	Sn %	Fe %	S %	Other %	Total %
1	Eastern Peru	Axe	93.94	0.65	5.58	none	0.08	Pb=trace	100.25
2	Machu Picchu	Axe	95.63	0.37	3.99	—	0.40	—	100.39
3	" "	Knife	94.26	—	4.82	0.32	0.23	—	99.63
4	" "	Chisel	93.90	—	5.53	0.06	0.15	—	99.64
5	" "	Axe	93.70	—	5.01	0.87	0.44	—	100.02
6	" "	Knife	90.09	0.68	8.99	—	0.13	—	99.89
7	Uncertain	Axe	93.25	0.88	5.10	—	—	Au=0.15	99.98
								Sb=0.60	

Sources of data: No. 1. Foote and Buell, 1912.
  Nos. 2-6. Mathewson, 1915.
  No. 7. Kroeber, 1954.

employed, their validity is uncertain.   In addition to these analytical defects, many of the published analyses are of little significance from the standpoint of archaeology, because they were made on samples of metal taken from objects of uncertain or unknown provenance.

The main purpose of the investigation here reported was to make complete analyses of properly selected samples of metal taken from Peruvian copper objects of known provenance.   Ideally, samples from hundreds of objects representing all the important sites and all time periods should have been analyzed, but the great obstacle to realizing such a comprehensive project is the natural reluctance of museums and other owners of valuable archaeological objects to allow them to be damaged by taking samples for analysis.   The fifteen objects that could be sampled came from thirteen widely scattered sites and covered a range of about fourteen centuries.   In a limited sense they may be considered representative.

OBJECTS, SAMPLES, AND ANALYTICAL METHODS

The objects analyzed in this study are listed in Table 3, along with the sites from which they came and the probable periods of their manufacture.   These

TABLE 3

List of objects analyzed

No.	Description	Site	Approximate Time Period Centuries, A.D.
1	Barbed spear	Vicús, Piura	IV–VIII
2	Ornament	San Pablo, Cajamarca	"
3	Needle or punch	Lambayeque	"
4	Tumi	Tantamayo	"
5	Rectangular sheet	Batán Grande, Lambayeque	"
6	Lance head (?)	Batán Grande, Lambayeque	VIII–XII
7	Rattle	Batán Grande, Lambayeque	"
8	Flat fragment	Chimbote	"
9	Fragment (fused?)	Chimbote	"
10	Bell without clapper	Litoral Norte (Chanchán?)	"
11	Axe	Gotush, Chavín	X–XII
12	Tumi	Jauja	"
13	Tupo	Tablada de Lurín	"
14	Club head	Pargo, Ayacucho	XII–XV
15	Axe	Cuzco	"

approximate periods are based solely on archaeological evidence. Unfortunately, no method for the closer dating of objects of this sort is available at present. All these objects are in the collections of the National Museum of Anthropology and Archaeology at Lima, Peru. We are greatly indebted to Sr. Jorge O. Muelle, Director, and to Sr. Toribio Majía Xesspe, Assistant Director, of this museum for their willingness to allow destructive sampling of the objects for analysis. We are also greatly indebted to Sr. Arturi Alcalde Mongrut, a chemist of Lima, for making all the necessary arrangements for obtaining the samples and sending them to us.

Four of the samples, Nos. 2, 11, 14, and 15, were in the form of drillings taken from the interior of objects. The remainder were in the form of severed sections. All external corrosion products were removed from these sections by filing, and pieces of suitable weight for analysis were cut from the cleaned metal. The metal of a third of the samples (Nos. 4, 6, 7, 11, and 14) was observed to contain dark specks or striae. Since these appeared to be composed of metal oxidized during the normal course of fabrication, no attempt was made to remove them.

Some of the components of the samples were determined by gravimetric analysis, some by spectrographic analysis, and some by both methods. The gravimetric determinations were made by the senior author and the spectrographic ones by the junior author. Details of the analytical procedures have been published elsewhere (Caley, 1964). Copper, silver, and sulfur were determined solely by gravimetric methods, antimony and bismuth solely by spectrographic methods, and the other components by both methods. In general the percentage figures obtained by the two methods agreed well and were averaged. However, there were a few exceptions. Because the spectrograph did not yield consistent and reliable results for the unusually high proportions of nickel in two of the samples, only the gravimetric results were taken as correct. In averaging the results for arsenic in some of the samples, greater weight was given to the spectrographic data, because of the suspected incomplete separation of this element in the gravimetric procedure, and the lack of sufficient sample to repeat this procedure. Although oxygen was evidently present as oxide in some of the samples, no direct oxygen determinations could be made because all samples were consumed in determining the other elements. However, since all other elements were determined, the difference between 100% and the sums of their percentages is an indirect approximate measure of the percentages of oxygen. It can be only approximate because these sums include the accumulated errors of all the individual determinations.

RESULTS

Listed in Table 4 are the results of the analyzes. The minus signs indicate that negative results were obtained by the procedures used. There is no heading for zinc, because none was found in any of the samples by either method of analysis. The low totals for Nos. 4, 6, 7, 11, and 14 are indicative of the presence of oxygen; the differences between such totals and 100% are approximate measures of the percentages of this element. The difference between the percentage of copper and the total for each sample is a measure of the total percentage of all impurities except oxygen.

In general there are wide ranges in the number, individual proportion, and total proportion of impurities in the samples of the series. Two samples, Nos. 1 and 13, not only contained the smallest number but by far the smallest total proportion of impurities. No. 15 is also exceptional because it is the only one that contained sufficient tin to warrant classifying the metal as bronze. The other twelve samples contained arsenic as the principal impurity, with other impurities ranging in number from three to eight, not counting the oxygen present in some. Shown in Table 5 are the frequency of occurrence, highest proportion, and average

TABLE 4

Results of analyses

No.	Cu %	Ag %	Au %	Sn %	Pb %	As %	Sb %	Bi %	Fe %	Ni %	Co %	S %	Total %
1	99.86	0.04	0.01	——	——	——	——	——	0.04	——	——	——	99.95
2	98.17	0.09	0.04	——	0.07	1.18	——	0.06	0.04	0.03	——	——	99.68
3	99.54	——	——	——	0.02	0.21	——	0.06	0.05	——	0.15		100.03
4	96.75	0.62	0.03	0.19	——	1.21	0.30	0.18	0.02	0.03	——	0.08	99.41
5	96.36	——	——	0.01	0.07	2.91	0.05	0.18	0.06	0.16	0.01	——	99.81
6	94.35	0.03	——	——	——	2.67	——	0.15	0.02	0.02	——	——	97.24
7	92.75	0.07	0.02	——	0.06	3.07	0.26	0.25	0.04	2.68	0.01	——	99.21
8	98.19	0.02	——	——	0.06	0.77	0.24	0.13	0.02	0.62	——	——	100.04
9	98.25	0.83	0.01	——	0.01	0.53	——	0.17	0.01	0.02	——	——	99.83
10	97.23	0.01	——	0.05	0.29	1.67	0.23	0.14	0.01	0.07	——	0.04	99.74
11	97.25	0.05	1.21	——	0.18	0.48	——	0.09	0.01	0.02	——	0.02	99.31
12	98.35	——	——	1.26	——	0.45	——	——	0.07	——	——	0.04	100.17
13	99.73	——	0.01	——	——	——	——	——	0.03	——	——	——	99.77
14	97.57	0.05	——	——	0.07	1.35	——	0.03	0.08	0.05	0.01	——	99.21
15	95.45	0.04	——	3.64	——	——	——	——	0.09	——	——	0.48	99.70

proportion of the individual impurities in these samples. In computing the average proportions, negative results as well as positive results were counted. The adjusted average proportions for certain elements shown in the last column were obtained by not including obviously atypical high results in the computation. For example, the result 1.26% for the gold in one sample was not included because the next highest result was only 0.04%. These adjusted averages are more representative of the usual proportions than would be the corresponding gross averages obtained by including all values.

TABLE 5

Frequency of occurrence and proportions of impurities found in samples of smelted coppers

Element	Frequency of occurrence %	Highest proportion %	Average proportion %	Adjusted average proportion %
As	100	3.07	1.38	
Fe	100	0.08	0.04	
Ni	92	2.68	0.31	0.10
Bi	83	0.25	0.12	
Ag	75	0.83	0.15	0.03
Pb	75	0.29	0.07	
Sb	42	0.30	0.09	
Au	42	1.21	0.11	0.01
S	42	0.15	0.03	
Sn	33	1.26	0.13	0.02
Co	25	0.01	0.003	

DISCUSSION OF RESULTS

The few characteristic impurities present in very low proportions indicate that the metal of No. 1 is native copper. The high total of the analysis indicates absence of oxygen such as would have been introduced by the fusion or hot working of such copper. It therefore seems very probable that the object from which this sample was taken was formed by the cold working of native copper.

The few impurities present in very low proportions in No. 13 also indicate

native copper, but the lower total of the analysis and the apparent absence of silver raise some doubts. The lower total may be ascribed to analytical error, the presence of oxygen, or both. That oxygen was present in the form of cuprous oxide was indicated by the pronounced reddish hue of filings of metal taken from this sample. Although silver is normally present in native copper, it is sometimes present in very low proportion and may have escaped detection in the analysis of this sample. On the whole it seems probable that the metal of No. 13 was native copper modified by slight oxidation such as could have been produced by the fusion or hot working of the metal.

The twelve samples that contained arsenic as the predominant impurity varied widely in composition. The arsenic content ranged from a low of 0.21% to a high of 3.07%. In five of the previous analyses (listed in Table 1), the range is from 0.10% to 4.43%. However, all these quantitative differences are less important than is the fact that in all but one of the seventeen analyses asenic was found to be the principal impurity in the metal. Such metal is properly termed arsenical copper. That the metal of these samples was produced by smelting is shown not only by their arsenic content but by the presence of numerous other impurities.

Of the other impurities in the twelve samples, iron was the only one present in all, as might be expected since this element is almost invariably present as an accidental impurity in ancient copper generally. In these samples its proportions varied over only a small range. That it is not listed in four of the previous analyses of Table 1 is probably due to faulty analysis.

Nickel was present in all but one of the twelve samples. In two, its proportions were much higher than in the others. These high proportions may have been the result of the accidental inclusion of some nickel mineral in the ore mixtures that were smelted. The present analyses indicate that nickel is a very common impurity in Peruvian smelted copper, as it is in much ancient smelted copper from other regions. The presence of this element has not been reported in previous analyses of copper from Peru, apparently because the analysts failed to examine their samples for this impurity.

Bismuth is the next most common impurity. Its proportion did not vary widely in these samples. It also has not been reported in previous analyses of copper from Peru. Lead and silver are the only other metallic impurities found to be present in over half the samples. As with bismuth, the proportions of lead did not vary widely. Lead is not listed in the previous analyses of Table 1, except for the one analysis in which its absence is indicated. In two of the samples, the proportions of silver are much higher than in the rest. This is not surprising, since some copper ore deposits in Peru also contain silver ores (Weed, 1908). Silver has been reported previously in some analyses (Table 1).

The occurrence of antimony in less than half the samples is somewhat unexpected, in view of the more frequent occurrence of arsenic and bismuth, with which it is so often associated in complex copper ores. Its proportion in the five samples did not vary widely. Antimony is not reported in previous analyses of copper objects from Peru (Table 1), but is reported in one analysis of Peruvian bronze (Table 2).

Since gold is often associated with copper and silver, its presence in five of the samples is not remarkable, though its proportion in No. 11 is unusually high for ancient copper. Such a high proportion might conceivably be the result of the accidental inclusion of some very rich gold ore in the mixture that was smelted. However, a more likely explanation is the inclusion of some gilded copper scrap or some copper-gold alloy, particularly the base alloy called *tumbaga* by archaeologists, which is well known to have been much used in ancient Central and South America. The presence of gold is reported in one previous analysis of a copper object (Table 1), and in one previous analysis of a bronze object (Table 2).

Five of the samples contained sulfur in small proportions. In analyses of Peruvian bronzes (Table 2 and Sample 15), generally higher proportions of sulfur have been found. However, in none does the proportion reach 0.50%. The presence of sulfur, even in such small proportions, is significant, because it indicates that sufiide ores or partly oxidized sulfide ores were present in the mixtures that were smelted. Additional evidence for the smelting of such ores for the production of copper in ancient Peru has been presented elsewhere (Caley and Easby, 1959).

Tin was present in only four of the samples, which was to be expected because most copper ores do not contain tin. The proportion of tin in No. 12 is not high enough to classify the metal as bronze, for a tin content of 2% is commonly considered to be the lower limit of this alloy. However, as an accidental impurity in ancient copper, this proportion of tin is usually high. The tin was probably introduced by the smelting of some unusual copper ore containing it. That some copper ores in northwest Argentina contain appreciable proportions of tin is indicated by some analyses of ancient copper objects from that region (Fester, 1962). In eight such objects, the following percentages of tin were found: 0.00, 0.00, 0.00, 0.91, 1.02, 1.56, 1.57, and 2.05, the average being 1.01. Tin in small proportions is reported in two previous analyses of copper objects from Peru (Table 1).

Cobalt was found in only three samples, and in the same small proportion in all three. Since nickel was present in all but one sample, and since cobalt is so often associated with nickel, it might be expected that cobalt would have been found in more of the samples. It may have been present in others, but in proportions too small to be determined by the methods of analysis employed. Cobalt is not reported in the analyses listed in Tables 1 and 2.

TENTATIVE CONCLUSIONS

The best previous analyses and these new analyses of samples taken from Peruvian copper objects indicate that the metal of a very large proportion of such objects is an arsenical copper containing a variety of impurities, and that only a very small proportion of them are composed of nearly pure natural copper. This conclusion should be regarded as merely tentative, since it is based on only 21 analyses. Many more are needed to test its validity.

The results of these new analyses are a clue to the type and general source of the ores used to produce the arsenical copper. Metal containing arsenic, antimony, bismuth, lead, nickel, cobalt, and sulfur must have come from complex sulfide ores or their immediate oxidation products. Complex ores containing tetrahedrite and other sulfide minerals occur at various places in the Peruvian Andes (Weed, 1908). Moreover, since the fully oxidized ores of the coastal region did not contain arsenic (Weed, 1908), it must have been those of the Andean region that were used to produce this arsenical copper.

It is not surprising that the single sample found to be a bronze came from an object assigned to the latest period. All available evidence shows that bronze manufacture was a very late metallurgical development in Peru, possibly as late as the fifteenth century (Fester, 1962). Therefore, it is probable that this object not only belongs in the latter part of this time, but that it is the latest object of the series.

The absence of arsenic from this one bronze and the fact that this element is not reported in previous analyses of Peruvian bronzes seems significant. Although it is possible that arsenic was not sought in previous analyses, the totals of the analyses of Table 2 certainly leave no room for any significant proportions of this element. Furthermore, there are distinct differences between the proportions of other elements, notably sulfur, in the smelted coppers and the bronzes. This general difference in composition indicates that the metallurgy of the copper

that was used to make the bronzes differed from that used to produce the earlier copper. However, this tentative conclusion is based on only a few satisfactory analyses. Its validity needs to be tested by many more analyses of Peruvian bronzes.

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