Technical examination of ancient South American metals: Some examples from Colombia, Peru and Argentina

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Left : La Aguada style bronze cast plaque, 84mm x 51 mm, dated to about 650 AD - 850AD, from Argentina or Bolivia. Cast in a copper-tin-antimony alloy. Probably cast by the lost-wax process.

Acknowledgements

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Abstract *This paper presents some metallurgical and technical studies of ancient South American metal objects from Colombia, Peru and Argentina. They are presented as fascinating representatives of disparate cultural traditions and different metalworking practices from the pre-Hispanic era. The first material which will be discussed is a collection of copper and copper-rich tumbaga alloy fragments from Colombia, representing several different cultural areas, such as Nariño, Sinu, and Muisca. Later in the paper some very different, but technically important objects, in gold, platinum, and silver will be examined from the Recuay and Huari cultural areas of Peru, and finally a bronze plaque, possibly from the La Aguada culture, Argentina or Bolivia.*

Resumen: *Este artículo presenta algunos estudios metalúrgicos y técnicos de objetos procedentes de Colombia, Perú y Argentina. Estos artefactos son representantes fascinantes de tradiciones culturales dispares y de diferentes prácticas metalúrgicas de la época prehispánica. El primer grupo de objetos que se discuten incluye fragmentos de artefactos de cobre y de tumbaga de Colombia, procedentes de varias regiones como Nariño, Sinú y Muisca. Luego se analizan algunos objetos tecnológicamente importantes aunque muy diferentes, de oro, platino y plata de las áreas culturales peruanas Recuay y Huari. Finalmente se presenta el estudio de una placa de bronce de la cultura La Aguada de Argentina o Bolivia.*

Some Colombian Copper

Ancient Colombia is well-known as contributing some of the most exquisite lost-wax castings to the corpus of art from the Ancient World (Plazas and Falchetti 1978; Bray 1978). Some of these objects are made in tumbaga alloys, alloys of copper and gold in varying proportions whose composition was directed by the choices of the metalsmiths regarding colour and symbolism, casting properties and the possible alteration of the surface colour by depletion gilding or fusion gilding (Scott 1982,1986a) to name only two possible approaches in the Colombian sphere to methods of surface treatment. Many of these castings require the deliberate alloying of copper and gold to create a whole range of colours and alloy types, from those with 90% - 80% copper content, which may characterize much Nariño Piartal period metalwork, for example (Plazas 1979; Scott 1982), to those of the Sinu and Quimbaya region where many cast tumbaga alloys may have only 10% - 30% copper.

The question naturally arises as to where the Indians procured the copper used to make these numerous tumbaga alloys, and whether the copper used was obtained in the native state, or smelted from oxide or sulphide ores of copper. The problem is particularly acute for ancient Colombia, for unlike Peru or Ecuador where there is plenty of evidence for the use of arsenical copper and tin bronze, these two alloys are largely absent from the pre-Hispanic Colombian cultures, and no smelting slags of copper or primitive bowl furnaces have yet been found in the ancient Colombian region. The problem is exacerbated by the fact that it can be very difficult, if not impossible to distinguish between copper which has been smelted from malachite, or copper melted from pieces of the native metal. Work on questions of this kind for Old World alloys began in earnest with the Sumerian copper research project in England, reported in Man, the Journal of the Royal Anthropological Institute, which began to illuminate the problems of differentiation with a series of emission spectrographic analyses of native copper and smelted products (Voce 1948). Whilst the work was useful in a chemical sense, it began to raise doubts about the possibility of relating particular objects to specific copper sources, or even being able to distinguish between native copper utilization and the smelting of copper from oxide or carbonate ores. This situation has changed during the 1990's: in some cases it is now possible, with a combination of metallographic and compositional studies to differentiate between native copper and smelted copper, particularly if the native copper has been shaped into an object without being molten in a crucible. The recent work of Rapp et al (1990), Wayman et al (1985), Hancock (1991) and Maddin et al. (1980), has shown that some progress is possible on this difficult question that the earlier investigators tackled with an optimism that was ill-conceived. In part, these advances are due to the application of sophisticated modern methods of analyses such as thermal neutron activation analysis, and, in this study, inductively coupled plasma-mass spectrometry (ICP-MS). Pavlish et al. (1994), for example, reported on a detailed analytical study, attempting to distinguish between natural and processed copper-based metals within North America. They found that a clear separation could be made between copper materials used by the native North American Indians, before European contact and those imported after contact. The results showed that the North American copper could be several orders of magnitude purer in terms of key trace elements such as gold. Following from this premise, the antimony to gold ratios were found to be very diagnostic between the two groups of copper. There are greater difficulties than that with the Colombian copper objects examined here however:

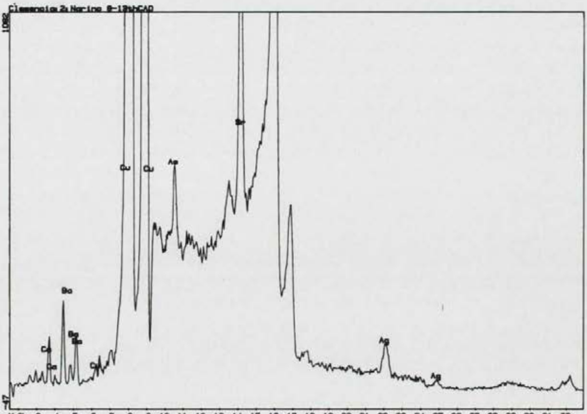

Figure 1 : Colombia sample C2. X-ray fluorescence spectra for this Nariño bell reveals clear indications for the presence of arsenic. The alloy is otherwise relatively pure copper with a trace of silver.

we are not trying to distinguish between European smelted copper and native copper, but between indigenous smelted copper and native copper, which is much more problematic.

Previous studies (Wayman 1985) have shown that some of the most important elements to distinguish native copper from smelted copper are: arsenic, nickel, selenium, antimony, gold and sometimes silver. The concentration of elements such as cobalt, zinc, tin, mercury and iron have not been found to be generally diagnostic. In the case of native copper, the levels of arsenic, nickel, selenium and antimony may be in the low parts per million region or below detection limits, whereas smelted copper may contain several hundred parts per million of arsenic, a few hundred ppm of nickel, 10 - 100 ppm of selenium and 10 -400 ppm of antimony.

Fifteen samples from different archaeological regions of Colombia were studied during the investigation. These fragments had been selected by Clemencia Plazas, Director of the Museo del Oro, Bogota, as representative of the copper or copper-rich end of the tumbaga spectrum. The samples, with relevant information, are tabulated in Table 1. A preliminary analysis of each piece was carried out non-destructively with x-ray fluorescence analysis in order to ascertain if the object was, in fact, primarily fabricated from copper, the abbreviated results of which are also given in Table 1. The analysis with x-ray fluorescence spectrometry was carried out using a Kevex 0750A Spectrometer in air with a barium-strontium secondary target and accelerating voltage of 55KV, 3,3mA, with an acquisition time of 240 seconds.

The results of a typical XRF scan are shown in Figure 1, where the spectrum for sample C2 is reproduced. The results show that this bell, from the Department of Nariño, 8th-13th century AD, is made in a relatively pure copper containing some arsenic. The discovery of arsenical copper alloys from the Nariño area is not so surprising, since the Department of Nariño is contiguous with the Ecuadorian border, representing the Southerly limit of the smelting of copper from arsenical ores, as we understand the data today. Nonetheless, it is interesting that arsenical copper should be found from the Nariño area and suggests the possibility that the bell is an import into the region from the Ecuadorian territory. The archaeological area of Nariño, in any case, extends into the Ecuadorian highlands. which makes the possibility for trade that much more possible. Tin bronze beads from

TABLE 1

SAMPLE	FIGURE	OBJECT	CULTURE	DATE	XRF ANALYSIS
C1	2	Fragment of bell	Nariño	800 AD- 1300 AD	Copper, little gold, silver
C2	3	Fragment of bell	Nariño	800 AD- 1300 AD	Copper, arsenic alloy
C3	4	Broken tunjo	Muisca	800 AD- 1600 AD	Copper, little gold, silver
C4	5	Broken tunjo	Muisca	800 AD- 1600 AD	Copper, iron, some lead
C5	6	Ear ornament	Sinu	1000 AD-1500 AD	Copper little gold, silver
C6	7	Darien pectoral	Sinu	1000 AD- 1500 AD	Copper little gold, silver
C7	8	Nose ornament	unassigned	after 1000 AD	Copper little gold, silver
C8	9	Nose ornament	Sinu	100 AD - 1000 AD	Copper little gold, silver
C9	10	'U' shaped ornament	unassigned	after 1000 AD	Copper little gold, silver
C10	11	Nose ornament	Sinu and Tairona	after 1000 AD	Copper, trace gold, silver
C11	12	Bell	Sinu	1000 AD-1500 AD	nearly pure copper
C12	13	Necklace piece	Tairona	1000 AD-1500 AD	Copper, little gold, silver
C15	14	Gold ornament	Tairona	1000 AD-1500AD	Gold-rich tumbaga alloy

the Nariño area have also been reported (Scott 1980) and as more detailed analyses become available, it is very likely that further examples of either arsenical copper or tin bronze will be reported from the Nariño area.

X-ray fluorescence analysis is extremely useful, since the objects can be examined totally non-destructively, but it is inadequate for reporting on the range of trace elements needed to characterize copper objects in order to decide whether they represent smelted copper or not. If major alloying elements such as arsenic, antimony, or tin are absent, what evidence is required of elemental composition in order to make an informed judgement? In the present study, the ICP-MS technique was employed to examine elemental composition over a range of 65 elements which can be conveniently measured by ICP-MS to the low parts per million simultaneously. Special analytical techniques were applied additionally, to estimate low levels of arsenic, and some elements have been quantitatively determined where they are of especial significance, such as: antimony, arsenic, cobalt, iron, nickel, silver, tin and zinc. The ICP-MS instrumentation has made very significant progress over the last ten years in terms of resolution, interferences, and detection limits for samples of 10mg - 30mg in weight. For the analyses, about 15mg of clean metal drillings were removed with a high speed tungsten steel twist drill.

It has become increasingly necessary to specify the full range of elements which were sought in such a detailed analysis, since, in future years, we may yet discover new patterns in the data and new significance to the presence or absence of a particular element: this is why the results presented here are shown for all 65 elements sought in the study: it is particularly relevant to the problem of distinguishing between native and smelted copper in ancient Colombia, since very few objects made in ancient Colombia do not contain gold and silver, even if present only in the parts per million, since contamination with gold on melting and casting would be highly probable; gold being a universal commodity in Colombia as far as the metalsmiths are concerned. The occurrence of elevated trace amounts of gold and silver in the copper alloys hinders any possible inferences concerning copper sources based on these two elements. It is also common for native gold in Colombia to be contaminated with small amounts of copper from melting without the alloy necessarily being a deliberate tumbaga alloy, although this kind of alloy is also difficult to characterize since native gold, besides silver may also contain copper, although this is usually less than 1%.

The ICP-MS analysis for sample CI, illustrated in Figure 2 and data shown in Table 2, revealed the presence of 18 detectable elements of which the most significant discoveries are the presence of small amounts of gold, iridium, palladium, platinum, rhodium, ruthenium, tellurium and silver. It is also significant that there is an absence of both antimony and arsenic showing that the copper was not obtained from copper arsenic ores. There is a higher percentage of silver present than gold which may indicate that some of the silver content originates from the copper itself rather than from

Figure 2 : Colombia sample C1. Fragment of a bell from the Nariño cultural area dated to between 800AD - 1300AD.

TABLE 2 — Sample : Colombia C1

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
Aluminum	5	2	Mercury	ND<8	8
Antimony	ND<6	6	Molybdenum	2.6	0.5
Arsenic	ND<40	40	Neodymium	ND<0.1	0.1
Barium	0.4	0.1	Nickel	13	2
Beryllium	ND<1	1	Niobium	ND<0.1	0.1
Bismuth	ND<0.3	0.3	Osmium	ND<0.1	0.1
Boron	ND<10	10	Palladium	1.2	0.1
Bromine	ND<30	30	Platinum	36.2	0.1
Cadmium	ND<0.5	0.5	Praseodymium	ND<0.1	0.1
Calcium	ND<800	800	Rhenium	ND<0.1	0.1
Cerium	ND<0.3	0.3	Rhodium	2.4	0.1
Cesium	ND<0.1	0.1	Rubidium	ND<0.1	0.1
Chromium	ND<20	20	Ruthenium	0.2	0.1
Cobalt	0.3	0.3	Samarium	ND<0.1	0.1
Copper	MATRIX		Selenium	ND<20	20
Dysprosium	0.4	0.1	Silver	2440	0.3
Erbium	ND<0.1	0.1	Sodium	ND<200	200
Europium	ND<0.1	0.1	Strontium	ND<0.1	0.1
Gadolinium	ND<0.1	0.1	Tantalum	ND<0.1	0.1
Gallium	ND<0.7	0.7	Tellurium	1.3	0.2
Germanium	ND<0.3	0.3	Thallium	ND<0.1	0.1
Gold	1590	10	Thorium	ND<0.1	0.1
Hafnium	ND<0.1	0.1	Thulium	ND<0.1	0.1
Holmium	ND<0.1	0.1	Tin	17	2
Iodine	ND<1	1	Titanium	ND<60	60
Iridium	0.8	0.1	Tungsten	2.5	0.1
Iron	ND<200	200	Uranium	ND<0.1	0.1
Lanthanum	ND<0.1	0.1	Vanadium	ND<100	100
Lead	7.4	0.3	Ytterbium	ND<0.1	0.1
Lithium	ND<2	2	Yttrium	ND<0.1	0.1
Lutetium	ND<0.9	0.9	Zinc	ND<2	2
Magnesium	ND<5	5	Zirconium	ND<0.1	0.1
Manganese	ND<1	1			

Date Analyzed : 1-2-95
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element

Fragment of a bell from the Nariño cultural area dated to between 800 AD-1300 AD.

Figure 3 : Colombia sample C2. Fragment of a bell from the Nariño cultural area dated to between 800AD - 1300AD.

TABLE 3 Sample : Colombia C2

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
Aluminum	23	2	Mercury	ND<8	8
Antimony	43	6	Molybdenum	ND<0.5	0.5
Arsenic	2570	30	Neodymium	0.2	0.1
Barium	121	0.1	Nickel	90	2
Beryllium	ND<1	1	Niobium	ND<0.1	0.1
Bismuth	1.6	0.3	Osmium	ND<0.1	0.1
Boron	ND<10	10	Palladium	0.8	0.1
Bromine	ND<30	30	Platinum	ND<0.1	0.1
Cadmium	ND<0.4	0.4	Praseodymium	ND<0.1	0.1
Calcium	ND<800	800	Rhenium	ND<0.1	0.1
Cerium	ND<0.2	0.2	Rhodium	2.2	0.1
Cesium	ND<0.1	0.1	Rubidium	ND<0.1	0.1
Chromium	ND<20	20	Ruthenium	ND<0.1	0.1
Cobalt	3	0.1	Samarium	ND<0.1	0.1
Copper	MATRIX		Selenium	291	20
Dysprosium	0.3	0.1	Silver	3130	0.3
Erbium	ND<0.1	0.1	Sodium	ND<100	100
Europium	ND<0.1	0.1	Strontium	11.6	0.1
Gadolinium	ND<0.1	0.1	Tantalum	ND<0.1	0.1
Gallium	ND<0.7	0.7	Tellurium	9.6	0.2
Germanium	0.4	0.3	Thallium	ND<0.1	0.1
Gold	718	80	Thorium	ND<0.1	0.1
Hafnium	ND<0.1	0.1	Thulium	ND<0.1	0.1
Holmium	ND<0.1	0.1	Tin	ND<2	2
Iodine	ND<1	1	Titanium	ND<60	60
Iridium	ND<0.1	0.1	Tungsten	0.6	0.1
Iron	ND<200	200	Uranium	ND<0.1	0.1
Lanthanum	0.4	0.1	Vanadium	ND<40	40
Lead	7.3	0.3	Ytterbium	ND<0.1	0.1
Lithium	ND<2	2	Yttrium	0.3	0.1
Lutetium	ND<0.9	0.9	Zinc	3	2
Magnesium	10	5	Zirconium	ND<0.1	0.1
Manganese	ND<1	1			

Date Analyzed : 1-2-95
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element

Fragment of a bell from the Nariño cultural area dated to between 800 AD-1300 AD.

Figure 4 : Colombia sample C3. Fragment from a broken Tunjo. Muisca cultural area, dated to between 800AD-1600AD.

contamination with gold alloys since extracted silver was not used in the ancient Colombian region. This normally implies that a small amount of gold impurity would be accompanied by an even smaller amount of silver. It is interesting to note the presence of small amounts of the platinum group elements in this analysis which are probably derived from the gold traces that show up in this study. In an earlier study (Scott 1982) it was noticed that many Nariño gold and tumbaga objects show significant trace impurities of the platinum group elements.

Sample C2, also a bell fragment from the Nariño area, Figure 3, Table 3, showed the presence of 24 different elements, including significant amounts of antimony, arsenic, gold, nickel, selenium and silver. On the basis of the criteria discussed above, it can be seen that this object from Colombia contains significant levels of impurities such as arsenic, selenium and silver, showing quite conclusively that smelted copper was employed to make this object.

Sample C4, the lower part of a Muisca tunjo, Figure 5, Table 4, produced 14 detectable elements which revealed very low amounts of antimony, arsenic, selenium and silver. A surprisingly high trace of lead was found in this analysis at 190ppm. This level of lead is not usually associated with native copper utilization, and suggests that the copper may have been obtained from relatively pure copper ores containing some minor lead impurity. The lead content is noticeably higher than any of the other objects examined in this study.

Figure 5 : Colombia sample C4. Fragment of a tunjo figure from the Muisca cultural area, dated to between 800AD-1600AD.

TABLE 4 — Sample : Colombia C4

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
*Aluminum	290	10	*Mercury	ND	1
*Antimony	3	0.7	*Molybdenum	5	0.7
*Arsenic	11	0.3	Neodymium	ND	0.7
*Barium	28	3	*Nickel	ND	2
*Beryllium	ND	0.7	Niobium	ND	0.7
*Bismuth	ND	0.7	Osmium	ND	0.7
*Boron	ND	9	Palladium	ND	0.7
Bromine	ND	800	Platinum	ND	0.7
*Cadmium	ND	0.7	Praseodymium	ND	0.7
*Calcium	ND	900	Rhenium	ND	0.7
Cerium	ND	0.7	Rhodium	18	0.7
Cesium	ND	0.7	Rubidium	ND	0.7
*Chromium	ND	50	Ruthenium	ND	0.7
*Cobalt	ND	0.7	Samarium	ND	0.7
Copper	MATRIX		*Selenium	ND	20
Dysprosium	ND	0.7	*Silver	26	0.8
Erbium	ND	0.7	*Sodium	ND	600
Europium	ND	0.7	*Strontium	18	8
Gadolinium	ND	0.7	Tantalum	ND	0.7
Gallium	ND	7	Tellurium	ND	0.7
Germanium	ND	0.7	*Thallium	ND	0.7
*Gold	20	1	Thorium	ND	0.7
Hafnium	ND	0.7	Thulium	ND	0.7
Holmium	ND	0.7	*Tin	2	1
Iodine	ND	100	*Titanium	ND	30
Iridium	ND	0.7	Tungsten	0.6	0.1
*Iron	ND	200	Uranium	ND<0.1	0.1
Lanthanum	ND	0.7	*Vanadium	ND	500
*Lead	190	0.7	Ytterbium	ND	0.7
*Lithium	ND	0.7	Yttrium	ND	0.7
Lutetium	ND<0.9	0.9	*Zinc	ND	30
*Magnesium	160	60	Zirconium	ND	0.7
*Manganese	13	2			

Date Analyzed : 3-7-97and 3-13-97
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element
* = Quantitative results

Fragment of a bell from the Nariño cultural area dated to between 800 AD-1300 AD.

Figure 6 : Colombia sample C5. Fragment of a gold alloy filigree ear ornament from the Sinú cultural region dated to the period from 1000AD - 1,500 AD, possibly originating from the area of Serranía de San Jacinto.

TABLE 5 — Sample : Colombia C5

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
Aluminum	ND<40	40	Mercury	ND<40	40
Antimony	ND<100	100	Molybdenum	ND<10	10
Arsenic	ND<600	600	Neodymium	ND<2	2
Barium	ND<2	2	Nickel	ND<9	9
Beryllium	ND<20	20	Niobium	ND<2	2
Bismuth	ND<2	2	Osmium	ND<2	2
Boron	ND<70	70	Palladium	ND<3	3
Bromine	ND<2000	2000	Platinum	5	2
Cadmium	ND<2	2	Praseodymium	ND<2	2
Calcium	ND<5000	5000	Rhenium	ND<2	2
Cerium	ND<2	2	Rhodium	4	2
Cesium	ND<2	2	Rubidium	ND<2	2
Chromium	ND<200	200	Ruthenium	ND<2	2
Cobalt	ND<2	2	Samarium	ND<2	2
Copper	MATRIX	100	Selenium	ND<100	100
Dysprosium	ND<2	2	Silver	4550	20
Erbium	ND<2	2	Sodium	ND<9000	9000
Europium	ND<2	2	Strontium	ND<2	2
Gadolinium	ND<2	2	Tantalum	ND<0.1	0.1
Gallium	ND<8	8	Tellurium	ND<2	2
Germanium	ND<5	5	Thallium	ND<2	2
Gold	15000	1000	Thorium	ND<2	2
Hafnium	ND<2	2	Thulium	ND<2	2
Holmium	ND<2	2	Tin	ND<20	20
Iodine	ND<400	400	Titanium	ND<1000	1000
Iridium	ND<2	2	Tungsten	ND<2	2
Iron	ND<2000	2000	Uranium	ND<2	2
Lanthanum	ND<2	2	Vanadium	ND<4000	4000
Lead	ND<30	30	Ytterbium	ND<2	2
Lithium	ND<100	100	Yttrium	ND<2	2
Lutetium	ND<10	10	Zinc	16	20
Magnesium	70	70	Zirconium	ND<2	2
Manganese	ND<10	10			

Date Analyzed : 3-21-95
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element

Fragment of gold alloy filigree ear ornament from the Sinú cultural region dated to the period from 1000 AD - 1500 AD possibly originating from the area of Serranía de San Jacinto.

Figure 7 : Colombia sample C6. Fragment from the lower part of a stylized anthropomorphic pectoral, in the style of Darién, probably originating from the Sinú cultural area. Dated to between 1000AD - 1,500 AD. The object was discovered in tombs in the area of Serranía de San Jacinto.

TABLE 6 — Sample : Colombia C6

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
*Aluminum	420	20	*Mercury	ND	1
*Antimony	ND	0.7	*Molybdenum	20	0.7
*Arsenic	121	0.3	Neodymium	ND	0.7
*Barium	83	3	*Nickel	7	2
*Beryllium	ND	0.7	Niobium	ND	0.7
*Bismuth	ND	0.7	Osmium	ND	0.7
*Boron	18	9	Palladium	ND	0.7
Bromine	ND	800	Platinum	5	0.7
*Cadmium	ND	0.8	Praseodymium	ND	0.7
*Calcium	2300	900	Rhenium	ND	0.7
Cerium	2	0.7	Rhodium	15	0.7
Cesium	ND	0.7	Rubidium	ND	0.7
*Chromium	ND	50	Ruthenium	ND	0.7
*Cobalt	3	0.7	Samarium	ND	0.7
Copper	MATRIX		*Selenium	ND	20
Dysprosium	ND	0.7	*Silver	5800	0.8
Erbium	ND	0.7	*Sodium	ND	600
Europium	ND	0.7	*Strontium	55	8
Gadolinium	ND	0.7	Tantalum	ND	0.7
Gallium	ND	8	Tellurium	ND	0.7
Germanium	ND	0.7	*Thallium	ND	0.7
*Gold	21100	2	Thorium	ND	0.7
Hafnium	ND	0.7	Thulium	ND	0.7
Holmium	ND	0.7	*Tin	6	1
Iodine	ND	100	*Titanium	ND	30
Iridium	ND	0.7	Tungsten	16	0.1
*Iron	2600	200	Uranium	10	0.1
Lanthanum	ND	0.7	*Vanadium	ND	500
*Lead	5	0.7	Ytterbium	ND	0.7
*Lithium	ND	0.7	Yttrium	ND	0.7
Lutetium	ND	10	*Zinc	130	30
*Magnesium	370	60	Zirconium	ND	0.7
*Manganese	18	2			

Date Analyzed : 3-7-97 and 3-13-97
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element
* = Quantitative results

Fragment from the lower part of a stylized anthropomorphic pectoral, in the style of Darién, probably originating from the Sinú cultural area. Dated to between 1000 and 1500 AD. The object was discovered in tombs in the area of Serranía de San Jacinto.

Figure 8 : Colombia sample C7. Nose ring of a form which is common in ancient Colombia, and which could be assigned to many different cultural areas within Colombia, probably relatively late.

TABLE 7 Sample : Colombia C7

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
Aluminum	20	2	Mercury	ND<8	8
Antimony	ND<6	6	Molybdenum	0.5	0.5
Arsenic	ND<30	30	Neodymium	ND<0.1	0.1
Barium	0.8	0.1	Nickel	6	2
Beryllium	ND<1	1	Niobium	ND<0.1	0.1
Bismuth	ND<0.3	0.3	Osmium	ND<0.1	0.1
Boron	ND<10	10	Palladium	1.4	0.1
Bromine	ND<30	30	Platinum	26.9	0.1
Cadmium	ND<0.5	0.5	Praseodymium	ND<0.1	0.1
Calcium	ND<800	800	Rhenium	ND<0.1	0.1
Cerium	ND<0.3	0.3	Rhodium	2.1	0.1
Cesium	ND<0.1	0.1	Rubidium	ND<0.1	0.1
Chromium	ND<20	20	Ruthenium	ND<0.1	0.1
Cobalt	ND<0.2	0.2	Samarium	ND<0.1	0.1
Copper	MATRIX		Selenium	20	20
Dysprosium	0.3	0.1	Silver	3850	0.3
Erbium	ND<0.1	0.1	Sodium	ND<200	200
Europium	ND<0.1	0.1	Strontium	0.2	0.1
Gadolinium	ND<0.1	0.1	Tantalum	ND<0.1	0.1
Gallium	ND<0.7	0.7	Tellurium	0.3	0.2
Germanium	ND<0.3	0.3	Thallium	ND<0.1	0.1
Gold	8030	80	Thorium	ND<0.1	0.1
Hafnium	ND<0.1	0.1	Thulium	ND<0.1	0.1
Holmium	ND<0.1	0.1	Tin	8	2
Iodine	ND<1	1	Titanium	ND<60	60
Iridium	0.3	0.1	Tungsten	1.3	0.1
Iron	ND<200	200	Uranium	ND<0.1	0.1
Lanthanum	ND<0.1	0.1	Vanadium	ND<30	30
Lead	2.9	0.3	Ytterbium	ND<0.1	0.1
Lithium	ND<2	2	Yttrium	ND<0.1	0.1
Lutetium	ND<0.9	0.9	Zinc	8	2
Magnesium	5	5	Zirconium	ND<0.1	0.1
Manganese	ND<1	1			

Date Analyzed : 1-25-95
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element

Nose ring of a form which is common in ancient Colombia, and which could be assigned to many different cultural areas within Colombia, probably relatively late.

Figure 9 : Colombia sample C8. Fragment of a nose ornament of elongated horizontal style from the Sinú cultural area dated to between 100AD-1000AD.

In sample C5, Figure 6, Table 5, a fragment of a cast filigree ear-ornament from the Sinu area, only six elements could be detected: the only major impurities discovered are significant amounts of gold and silver with tiny traces of platinum and rhodium. Significantly, arsenic, selenium, nickel and antimony are below the detection limits for this particular analysis, which varies with the amount of solid supplied for the analytical determination. It is possible, then, that the copper used to make this object was either obtained from the smelting of very pure oxide or carbonate ores, or from the use of native copper. By the criteria outlined above, the possibility of the use of native copper is strong, although not possible to prove conclusively. This copper was alloyed or contaminated with a small amount of gold containing some silver during melting and casting operations.

Sample C6, Figure 7, Table 6, a fragment of a Darien style pectoral from tombs in the area of Serrania de San Jacinto, showed the presence of twenty-two elements, which includes an odd assortment of elements from uranium and strontium to barium and boron.

The amount of gold present, at 21100ppm, and silver at 5800ppm show that the metal was mixed with a small amount of a native gold alloy, probably from the melting of the alloy to cast to the Darien pectoral. The matrix of the metal is rather heavily corroded and the range of elements determined in the study may be influenced by the degree of corrosion. It is probably difficult to draw any very firm conclusion from the data, apart from the

Figure 10 : Colombia sample C9. Fragment of a penannular nose ornament of a common U shape with terminals which could be from quite a few different cultural areas in the pre-Hispanic Colombian region.

TABLE 8

Sample : Colombia C9

Semi-Quantitative Report
Inductively Coupled Plasma - Mass Spectrometry

	ppm	Detection limit		ppm	Detection limit
Aluminum	166	30	Mercury	ND<30	30
Antimony	ND<90	90	Molybdenum	ND<9	9
Arsenic	ND<500	500	Neodymium	ND<1	1
Barium	18	1	Nickel	ND<8	8
Beryllium	ND<20	20	Niobium	ND<1	1
Bismuth	ND<1	1	Osmium	ND<1	1
Boron	ND<50	50	Palladium	2	2
Bromine	ND<2000	2000	Platinum	15	1
Cadmium	ND<1	1	Praseodymium	ND<1	1
Calcium	ND<4000	4000	Rhenium	ND<1	1
Cerium	ND<2	2	Rhodium	3	1
Cesium	ND<1	1	Rubidium	ND<1	1
Chromium	ND<100	100	Ruthenium	ND<1	1
Cobalt	ND<1	1	Samarium	ND<1	1
Copper	MATRIX	100	Selenium	ND<100	100
Dysprosium	ND<1	1	Silver	11800	10
Erbium	ND<1	1	Sodium	ND<8000	8000
Europium	ND<1	1	Strontium	ND<1	1
Gadolinium	ND<1	1	Tantalum	ND<1	1
Gallium	ND<6	6	Tellurium	ND<1	1
Germanium	ND<4	4	Thallium	ND<1	1
Gold	75000	1000	Thorium	ND<1	1
Hafnium	ND<1	1	Thulium	ND<1	1
Holmium	ND<1	1	Tin	ND<20	20
Iodine	ND<300	300	Titanium	ND<1000	1000
Iridium	ND<1	1	Tungsten	ND<1	1
Iron	ND<2000	2000	Uranium	ND<1	1
Lanthanum	ND<1	1	Vanadium	ND<3000	3000
Lead	ND<20	20	Ytterbium	ND<1	1
Lithium	ND<80	80	Yttrium	ND<1	1
Lutetium	ND<10	10	Zinc	38	10
Magnesium	ND<60	60	Zirconium	ND<1	1
Manganese	ND<10	10			

Date Analyzed :3-21-95
Elements not analyzed : All Gasses, C, P, S, K, Si, Sc, In, Tb
MATRIX - major element

Fragment of a pennanular nose ornament of a common U shape with terminals which could be from quite a few different cultural areas in the pre-Hispanic Colombian region.

Figure 11 : Colombia sample C10. Fragment of a nose ornament with elongated ornamental terminals probably from the Sinú or Tairona cultural areas, possibly of a relatively late date.

fact that the arsenic content is very low, showing that the object was not made from copper with an arsenic impurity.

For sample C7, Figure 8, Table 7, a pennanular style nose ornament, 19 elements were detected as well as notable absences; such as the absence of antimony and arsenic. Traces of gold and silver were detected together with small amounts of the platinum group elements, iridium, palladium, platinum and rhodium. The low levels of selenium, nickel, antimony and arsenic indicate that the primary copper or smelted malachite, is characterized by very low levels of these impurities, which are suggestive of native copper, but could also possibly be from the smelting of very pure oxide or carbonate minerals.

The analysis for sample C9, Figure 10, Table 8, a common 'U' shaped nose ornament with button-like terminals, saw nine elements being detected, including significant amounts of gold and silver with small amounts of the platinum group elements. Once again the nickel, selenium, antimony and arsenic contents are very low, suggesting the possibility that the copper used was native or obtained from very pure oxide or carbonate deposits of copper.

The results of this study tend to confirm the fact that, in the absence of metallurgical debris from smelting, such as tuyeres, furnaces, slag, copper prills, or ore, it is very difficult with Colombian copper alloy objects to work backwards from finished product to the possibilities of smelted copper utilization. Nonetheless, it is clear that only in the Nariño area are objects to be found with significant amounts of tin or arsenic. The Colombian copper objects are characterized by very low or undetectable amounts of arsenic which

Figure 12 : Colombia sample C11. Fragment of a bell of typically Sinú style decorated with attached spiral ornamentation, dated to between 1000AD - 1500AD, from tombs in the area of Serranía de San Jacinto.

Figure 13 (left): Colombi sample C12. Fragment of a anthropomorphic necklac collar element from th Tairona cultural area date to between 1000AD 1500AD.

Figure 14 (right): Colombi sample C15. Small curve rectangular gold ornamen for attachment on a texti backing, Tairona cultura area dated to 1000AD 1500AD.

shows that oxidized copper ores were used in their manufacture, such as cuprite and malachite. Because of low-level alloying or contamination with small quantities of gold on casting the objects by the lost-wax process, it is not possible to use the trace amounts of gold and silver present in the artifacts as a reliable guide to possible ore sources, which is a handicap compared with studies where gold is not present other than as an impurity element in the copper. The relatively high trace amount of lead found in the Muisca tunjo fragment, sample C4, argues for the probable smelting of copper from oxidized ores, although the sweep of the impurities found in this analysis are also surprisingly low, with very little silver, antimony, arsenic or gold, and with nickel and selenium undetected.

Figure 15 : Recuay fo attached to gold crown wit cut-out anthropomorphi design. 1st century AD - 5 century AD. Crown 5.5 c in height. Serrated teet made in gold-platinum allo

A Recuay Fox

From the determination of trace amounts of platinum in tumbaga alloys, we turn to the discovery of major amounts of platinum as a component in a Recuay Fox and Crown, dated from approximately the 1st century AD to the 5th century AD, shown in Figures 15, 16, 17, and 18.

This piece is an impressive example of ancient South American goldworking and can be ascribed to the Recuay cultural area, located in the area of Callejon de Huaylas and the headwaters of the Rio Santa. The Recuay style is characterized by vibrant artistic designs, and is known primarily from collections of fine ceramics vessels generally made in a white kaolinite paste. It is reminiscent of the Moche style in technical mastery and iconography. Serpents, felines and condors are common motifs. Very little metalwork is known from the Recuay cultural area and few pieces have been adequately published.

The Recuay crown examined here is a very fine example of ancient goldworking. The crown itself consists of a band of gold alloy about 5.5 cm high and about 0.2mm thick. The band is made in hammered sheet which has been ornamented with a cut-out design showing small human faces in a repeating pattern, with the eyes, nose and mouth of the face shown by cut-out areas. From microscopic examination it can be seen that this design has been cut using a chisel. The pattern is repeated so that the small faces appear upside down on the top of the band, in a design executed with great skill. Pairs of small holes at the top and bottom of this crown probably indicate where attachments of small dangles were affixed. The design on the crown is rather similar to textile patterns from the Paracas-Nazca cultural regions. The method of construction is essentially the same as the techniques used to construct Moche metalwork, with most of the joins between pieces of metal being made mechanically. The crown itself is made in a native gold alloy, with no platinum content that could be detected by x-ray fluorescence analysis. This band has an unusual matte appearance with some staining which is difficult to characterize, possibly due to some oxidation of the silver content, but this is hard to prove without destructive sampling, which was not undertaken on the band.

The head, which has a serpent-like quality, is of a fox and has been attached to the band with four tabs passing through slots cut into the crown. The head of the fox is made of two pieces of gold which are joined together by a technique which is distinctively pre-Hispanic: the two rounded gold strips are cut with tabs and the tabs are then overlapped and hammer welded to join the strips together, thus reinforcing the join between the two pieces and making good use of the hammer welding potentialities of gold alloys.

The head has two raised elliptical rims for the inset eyes, which appear to be of turquoise. The ears are carefully made with a subtle rim of gold on the edge of the ears, hammered back to thicken the edge and make a smooth line to the shape of the ear. The mouth of the animal head is fixed to the head with four staples, three on one sheet of gold on the top of the mouth and one underneath. This mouth is made in a number of components: the two major pieces are shaped into a curve for the upper and lower parts and these are closed at the top and bottom inside of the mouth to form two solid shapes. A strip of gold sheet has been attached to the corner of the mouth at each side to complete the jaw.

Figure 16 : Partial view of Recuay fox. The anthropomorphic design of part of the headband or crown can just be seen with the animal head attached showing part of the upper view of the figure. Small staples that attach the jaw to the head through the gold sheet of the jaw can be clearly seen.

Copper alloy whiskers have been applied to the top mouth part by pushing small holes through the gold sheet and attaching small round hammered copper wires, most of which are now very heavily corroded and lost. The mouth itself is completed with four gold alloy parts representing teeth on the top and bottom jaw, held in place with three small tabs which slot into the sheets forming the floor and roof of the mouth. Two copper alloy fangs are attached to the jaws at the front and a serpent-like gold tongue protrudes between the fangs. All of these components appear to be original to the piece and there is no evidence for the recent attachment of any foreign elements.

An analysis of the object was carried out using x-ray fluorescence analysis. A major and unexpected surprise was the discovery that the serrated teeth are made in a gold-platinum with minor components of silver and copper. These serrated teeth components are silvery in colour and without analysis would be mistaken for a silver or silver-copper alloy. In order to investigate the composition and structure of these serrated teeth, a tiny sample was taken from a folded over edge and mounted for metallographic examination. The resulting polished section is shown in Figure 18, after etching in aqua regia to reveal the platinum grains. The microstructure reveals a heavily worked matrix in which extensive dissolution of the platinum laths has occurred, resulting in a very well dispersed scatter of platinum particles. The successful dispersion of the remnant platinum grains, and the dissolution of some of the platinum into the gold matrix, is responsible for the silvery colour of the resulting al-

loy: not all gold-platinum composites will produce a silvery colour: there is a whole range of possibilities from dull golden to silver-gold and silver-coloured, often with a grey-silver aspect or steel-grey patination. This is because of the iron content of the native platinum grains of South America, which usually contain between 1% - 4% of iron, giving rise to possible interference colours on tarnishing or thin films of iron oxide from oxidation.

There is a strong resemblance between the microstructure of this gold-platinum alloy sheet and those from the La Tolita-Tumaco cultural area, crossing the Ecuadorian-Colombian border. Platinum could not be molten by the pre-Columbian Indians, and was sintered with gold, producing the World's first powder metallurgy. The principal site, La Tolita, is thought to have been largely abandoned after 800AD, so the date of this Recuay object, from the 1st - 5th century AD does represent a period when platinum metallurgy was well-developed in these areas of Ecuador and Colombia, although there is a lack of evidence from Peru as to the extent to which platinum was utilized. For an account of Colombian sources the geological literature can be referred to (Scott and Bray 1994; Monroy 1978; Mertie 1969; McDonald 1959).

These gold-platinum alloy components represent the most Southerly extension of the use of platinum in ancient South American goldwork so far recorded. Although the Recuay cultural group is at least towards the Northern part of Peru, it is still a long way from La Tolita, and the Esmeraldas-Tumaco zone in which platinum alloys are frequently encountered. Further research on the discovery of platinum in this Peruvian object is obviously necessary.

The gold alloy used to make the head and the fang, on the other hand do not contain any platinum and these are made in a gold alloy with some silver and a little copper. The copper alloy teeth were shown by x-ray fluorescence analysis to be made in a copper-gold-silver alloy with mercury being detected in the study as well. Around some of the teeth and fangs are the remains of red pigment which were shown in this study to be made from cinnabar, the natural mineral, mercuric sulphide. Cinnabar has often been reported as a pigment from the ancient cultures of Peru and x-ray analysis was supplemented with polarized light examination which showed that the pigment had every characteristic associated with natural mineral cinnabar, ground, and used as a pigment, originally applied to the copper fangs to make them appear red. This is also an interesting discovery: the cinnabar was used to paint the copper alloy fangs to make them appear red, as if dipped in blood, and the colour contrast used in this part of the design is impressive: with the golden head, silvery teeth, golden tongue, red fangs, blue-green eyes, coppery whiskers and golden crown, the original appearance must have been even more striking than the present surfaces suggest. The surface corrosion on the crown is very unusual and suggests that some cleaning of this component may already have taken place: further metallurgical studies are needed in order to clarify this question: one unusual finding was the discovery by x-ray fluorescence analysis that the

Figure 17 (Left): Another view of Recuay animal head showing some of the detail of the jaw with protruding gold alloy strip for the tongue, platinum gold alloy inset teeth, represented by the serrated components in the upper and lower jaw. The copper alloy fangs in the mouth can be seen an the slight reddish hue under the corrosion reveals parts of the cinnabar painted surface as confirmed by powder X-ray diffraction.

Figure 18 : Recuay animal head : sample from silver colored serrated teeth. The microstructure reveals a heavily worked and annealed gold-platinum alloy matrix incorporating undissolved platinum particles, finely dispersed through the gold. The extensive and very fine scatter of the remnant undissolved platinum particles shows that a considerable attempt has been made to homogenize and disperse the platinum through the gold matrix, resulting in a very silvery colored surface to the composite material. Magnification x490, etched in aqua regia.

band is made from a gold-silver-copper alloy which contains a little platinum. Platinum will lighten the colour of the gold a little and may contribute to the unusual appearance of the slightly tarnished areas of the crown which have not been cleaned.

A Huari Spoon

This Peruvian object is an unusual Huari spoon, inlaid with gold on both sides, weight 28.40 grams, dated to about 550AD - 800AD, (shown in Figure 19).

A detailed examination of this interesting and rare figurine was carried out in order to ascertain its probable cultural identity and metallurgical composition. The object is a figurine, made in silver, with a spoon at the lower end and a fanged head at the top. This head, made in silver, is hollow and has a rattle in the interior. The thickness of the silver sheet from which the figurine has been made is 0.43mm. The thickness of the flange surrounding the head is 0.83mm, confirming the visual impression that there is a double thickness of silver sheet present. The hollow, rattle head has therefore been made by joining the repoussed fanged face onto the flat backing of the spoon and body by welding or soldering the two silver components together around the perimeter of the flange.

One of the most interesting aspects of this figurine, is the very detailed inlay in gold which has been accomplished on both sides of the object. Examination of the front decorative panels reveals rather stubby hands and feet and a central design broken into a number of triangular panels. The type of design and repeated elements in these triangular panels is very suggestive of Huari designs in textile. Immediately below the line across the

Figure 19 : Huari ritual silver alloy spoon, inlaid with gold foil on both sides. Weight 28.40 grams, length 14.8 cm, 0.43 mm thick silver. The gold design is laid into incised lines in the silver spoon and joined metallurgically with a diffusion bond to the silver substrate.

mid-point of the body, there are four design panels which show a symmetry also rather characteristic of Huari design. There may be an additional face depicted immediately above the spoon, where two large round gold circles are enclosed in a border which suggests the shape of the eye.

This same motif is repeated in an identical design, inlaid on the back of the spoon. Indeed, the entire design on the front is repeated on the back, except that the head is rendered in a series of vertical gold stripes with rows of chevrons joining them together. This chevron design is another feature which is strongly suggestive of Huari influence and is a pattern often found running around the lip of Huari pottery (Dr. Alana Cordy-Collins: personal communication: January 1996).

The face of the figurine is a fanged animal, with prominent 'N' shaped fangs which are another typical Huari feature. Sometimes these fangs occur in a backwards 'N' shape. The stylistic examination therefore strongly suggests that this unusual silver figurine is Huari, from the Highlands of Peru, and dated from about 550AD- 800AD.

A non-destructive x-ray fluorescence analysis was carried out using a Kevex 0750A spectrometer, using a Ba/Sr target. The results of this study were of interest, since the silver base of the figurine was shown to contain copper, gold, lead, bromine and silver. The bromine content arises from the affinity of silver for bromine in the burial environment, leading to the formation of silver bromides and silver chlorobromides. The presence of a small amount of lead in the silver is of some interest, since lead may be associated with the refining or extraction of silver, either by cupellation of lead ores, or by using lead as an additive in the extraction of the silver from the ores. The occurrence of significant amounts of lead, from about 0.1% - 1.5%, in ancient Peruvian silver alloys has been observed previously by Howe et al (1994) and by Scott (1996). Howe showed that some silver alloys of the Wanka culture, located in the upper Mantaro valley, were smelted from silver-lead ores which were subsequently refined by cupellation. Wanka I through III date from about 1000AD - 1500AD, with most of the silver showing evidence of lead, occurring in the later phases. The remnants of small amounts of lead are strongly indicative that similar processes may have been used in the Huari cultural area. The data is suggestive of this possibility, but more detailed and thorough studies of a range of Huari silver pieces would have to be undertaken to really present a convincing corpus of data.

A tiny cross-section of the silver Huari spoon was mounted and prepared for metallographic examination in the usual way (Scott 1991). The polished cross-section was examined and then etched in acidified potassium dichromate solution, diluted 1:9. The grain boundaries of the silver crystals were clearly evident after etching and reveal a discontinuous precipitation which is quite typical for ancient silver, and which, in fact, proves that the object in question is ancient, for this kind of discontinuous precipitation is never seen in modern silver-copper alloys: it is an event which can only happen slowly at ambient temperatures. The microstructures are shown in Figures 20a and 20b.

The silver figurine has been gilded by the application of hammered gold foil to grooved or incised regions of the surface and the foil has been attached to the silver by diffusion bonding, which is revealed in the microstructure as a region of dark etching below the gold surface. The use of diffusion bonding of gold foil in the Huari period has not previously been reported, partly, of course, for the reason that very few Huari objects have been examined scientifically, in fact, there is not much published information relating to the use of foil gilding in ancient South America at all. Enough work has been done to show that foil gilding was used from Peru to Costa Rica: use was made of a complete gold cladding in one sheet, and of small squares of individual gold sheet which could be partially overlapped. Macroscopic evidence for foil gilding in Ecuador has been mentioned by Bushnell (1951), Christensen (1954), Saville (1907-1910), Ubelaker (1981), and Scott (1986b), while foil-gilded pins with elaborate heads are known from Pashash, Peru, dating to the early centuries AD (Grieder 1978), although it is not certain that Grieder is correct in this matter: the pins concerned may have been gilded by other techniques and the identification of foil gilding requires metallographic study which was not published in this case.

Foil gilding over copper was occasionally used in Colombia, sometimes for small nose-ornaments and penannular nose-rings in Panama and Costa Rica are found, often made in carved stone, with gold foil coverings (Bray 1993). Foil gilding does not appear to be restricted in a geographical or temporal sense; why this should be, when other gilding techniques were also in use, remains unknown. From the very limited work which has been carried out it is presently impossible to link material choices within cultural areas to the use of foil gilding.

A bronze anthropomorphic plaque from Argentina or Bolivia

This interesting plaque, weight 87.80 grams, measures 84 mm x 51mm, and including the height of the human figures, is 84mm x 76.5mm. It is shown in Figure 21. The plaque is about 2mm thick and dates from the period around 650 AD- 850 AD, probably from the La Aguada cultural region. Gonzalez (1975) states that these types of bronze plaques are rare. A surface examination of the plaque was carried out using the binocular microscope at a magnification of x40 . The surfaces of the plaque are corroded and covered in a well developed patina which has all the appearance of a natural corrosion crust. Within the crevices of the line ornamentation which form the long bodies of the two human figures, there is a complex assemblage of mineral material associated with the burial environment. The plaque has been cast by the lost-wax process: none of the surfaces show any sign of working of the metal, instead the plaque is skillfully modeled in wax and then cast in bronze.

A non-destructive x-ray fluorescence analysis was carried out on this plaque on the reverse. The elements detected were iron, copper, arsenic, tin and antimony. This is of considerable interest because antimony is not commonly mentioned in pre-Hispanic materials but the ores of the Bolivia-Argentina area are complex and high nickel or arsenic or antimony concentrations accompanying the extraction of the copper before alloying with tin would certainly not be unexpected.

The composition of the plaque was estimated quantitatively to be:
88% copper, 0.8% arsenic, 8% tin, 2.7% antimony and a trace of iron.

In fact, this surmise is borne out by some previous analyses from Argentina: for example Alberto Rex Gonzalez (1975) mentions a semicircular copper fragment , number 5550, from Grave 11 of the Corral Blanco cemetery, Laguna Blanca, Belen which was analyzed by Fester (1962) and had composition of: copper 92.33%, arsenic 3.40%, zinc 1.22% tin 2.05% and antimony 0.42%., from the Condorhuasi cultural period.

A flat axe with socket, number 11549 associated with the Cienaga cultural area also contained antimony. An analysis by Fester (1962) showed 85.07% copper, 4.36% lead, 5.59% zinc, 3.54% tin, 0.96% antimony, 0.45% iron and 0.16% nickel. These examples confirm the presence of antimony in copper alloys from the region. Antimony, for example, is never found in ancient bronzes from Ecuador above 0.1-0.2% which is why the percentage is so startling here, and why it is understandable in the Argentine context. Ore survey work by Lechtman (1996) indicates that mixed copper-arsenic ores such as enargite, Cu_3AsS_4 , and tetrahedrite, $Cu_{12}(As,Sb)_4S_{13}$ were available from southern Ecuador through to northern Bolivia, with substantial deposits of these minerals being available to pre-Hispanic miners in northwest Argentina and central Chile. Smelting of such ores could easily

Figure 20a : Unetched cross-sectional view of part of the silver sheet of the spoon with a gold inlay over part of the surface. As polished; magnification x80.

Figure 20b : Etched microstructure showing the diffusion interface at the surface between the gold foil inlay and the silver substrate. The junction appears double because corrosion has only attacked the underlying alloy to a certain depth below the surface, diffusion of gold into the topmost silver layer has resulted in enhanced resistance to corrosion. The silver grains clearly show discontinuous precipitation of copper at the grain boundaries. Etched in acidified potassium dichromate, magnification x320.

produce an antimonial copper alloy. Tin could then be added to the smelted metal to produce a ternary alloy of copper, tin and antimony. Both arsenic and antimony are useful additions to cast bronze, helping to either lower the melting point, increasing fluidity, or mitigating the effects of oxygen absorption on casting, depending on the particular features of the casting process involved.

The imagery of the plaque is of interest, since these anthropomorphic figures are reminiscent of Bolivian rock art imagery, and it would be of interest to study the iconography of these figures to examine in greater detail their possible relationship to other examples of Bolivian or Argentinean art.

Conclusions

The variety of metallurgical studies afforded by pre-Columbian metal objects shows how rewarding the detailed examination of these objects can be from the technological perspective. There may be very little temporal distance between the areas of La Aguada and Muisca, but there is a startling difference in terms of metallurgy and the smelting of metals. Research on the origins of Colombian copper needs to be undertaken in a systematic manner together with detailed information on Colombian ore sources, although what is really needed is archaeological finds of metalworking in copper, with furnaces and blowpipes and slag.

The unexpected discovery of platinum so far South in a Recuay fox, clearly raises the possibility that there must be more platinum alloys used in ancient Peru than previously thought. Further work is needed on Peruvian silver-looking alloys to examine if they are really made of silver, silver- copper, or gold-platinum alloys.

Some information is available for ancient Peruvian metalwork, especially Moche metalwork, but very little published information can be accessed for Huari or Recuay metalwork. The discovery of traces of lead in the silver used to make the Huari spoon suggests the possible smelting of mixed silver-lead ores followed by cupellation in the Huari cultural area. Further detailed studies are needed to address this issue.

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