Evolution of Pre-Columbian Metallurgy from the North of Peru Studied with a Portable Non-invasive Equipment Using Energy-Dispersive X-Ray Fluorescence

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Abstract: On the north coast of present-day Peru, between the Andes and the Pacific Ocean, prospered approximately between 1000 BC and 1375 AD, several relevant cultures: Chavín (1000-200 BC), Vicús and Frías (200 BC - 300 AD), Moche (400 BC-700 AD), Sicán (700-1375 AD). These cultures are interconnected and characterized by a high metallurgical ability, demonstrated by the presence of beautiful artifacts on gold, silver and copper alloys. More than hundred metal artefacts from these cultures were analyzed with a portable equipment which uses the non-destructive and non-invasive technique of energy-dispersive X-ray fluorescence (EDXRF). Following objects were analyzed: (1) gold, silver and copper objects from the Chavín culture (Museo Municipal of Piura and and Museo Enrico Poli in Lima); (2) gold and silver objects from the Vicús and Frías cultures (Museo Municipal of Piura); (3) gold, silver and copper objects from the Moche culture ("Museo Tumbas Reales de Sipán", "Museo de Sitio de Huaca Rajada" in Lambayeque and Museo Enrico Poli in Lima); (4) gold, silver and copper objects from the Sicán culture (Museum of Sicán, Ferrañafe). Portable equipments were employed, mainly composed of a small size X-ray tube and a thermoelectrically cooled, small size, Si-PIN or Si-drift X-ray detectors. The main characteristics of the EDXRF-technique is of being non destructive and multi-elemental. Standard samples of gold and silver alloys were employed for calibration and quantitative analysis. The aims of this campaign of analysis were: (1) to analyze a large number of objects; (2) to differentiate gold, gilded copper and tumbaga (this last being a poor gold alloy enriched at the surface by depletion gilding); (3) to correlate, when possible, composition of analyzed alloys to the specific culture; (4) to determine a possible evolution of metallurgy; (5) to better determine characteristics and beginning time of tumbaga production. It was determined that the analyzed artefacts are composed of gold, silver and copper alloys, of gilded copper or silver and tumbaga, the last being a poor gold-alloy rich on copper and enriched at the surface by depletion gilding, i.e. by removing copper from the surface. About 120 alloys were analyzed. In the case of gold, silver and copper alloys, their composition was determined by EDXRF-analysis by employing standard alloys. In the case of gilded copper (or gilded silver) and of copper based tumbaga, the ratios $Cu(K_\alpha/K_\beta)$ and

Au(L_α/L_β) were determined from the X-ray spectra, first to clearly differentiate gold, gilded metal and tumbaga, and then to determine the gilding thickness. Concerning the correlation composition-culture, it seems that the Chavín did not use to mix copper in the gold alloy. This element, with a mean concentration of 1.5%, is only present in Au-alloys as in nature. Further, silver was measured in all cultures of the north of Peru at relatively high levels of purity, but by the Chavín was associated to Cu and Pb, by the Moche to Cu and Au, by the Sicán to Cu, Au, Pb and Br. Also copper was measured in all cultures of the north of Peru at high levels of purity. However, this element seems to contain small quantities of Zn by the Chavín, is almost pure by the Moche, and contains as by the Sicán. With reference to copper based tumbaga, it is not clear when it was "produced" for the first time in the north of Peru, may be by the Vicús; in any the largest number of tumbaga was produced by the Moche, and are characterized by a mean "equivalent" Au-thickness of ~2.5 μm.

Key words: Pre-hispanic gold, tumbaga, X-ray fluorescence, portable equipment.

1. Introduction

On the north coast of present-day Peru (Fig. 1) flourished between 1000 BC and 1375 AD approximately, various relevant civilizations. Among them the most important were:

(1) Chavín: the Chavín is a civilization developed in the northern Andean highlands of Peru from about 1000 BC to 200 BC. The most well-known archaeological sites of the Chavín era are Chavín de Huántar, located in the Andean highlands north of Lima, and Kuntur Wasi, located in the Northern Mountain Range of Peru, close to Cajamarca. Chavín de Huántar is now a UNESCO world heritage site. It is believed to have been built around 900 BC and it was the religious center of the Chavín people. Kuntur Wasi, first discovered by Julio Tello in 1945, is thought to have been constructed around 1000-700 BC [1-4]. The early stage (ca. 1000-800 BC) antedated the use of metal, and was characterized by painted clay idols. In the second phase (ca. 800-500 BC) dubbed the Kuntur Wasi period, is associated to graves containing beautiful gold objects, such as the "14-Face crown" and "5-jaguar crown". The third period (ca. 500-250 BC), called the Copa period from the name of the mountain showed improvements in flattering, cutting and shaping the gold, silver and copper like the necklace of jaguar masks. In the final, or Sotera period, the entire complex was overthrown and the site abandoned; that happened sometime before 50 BC;

(2) Vicús: the Vicús culture (200 BC – 400 AD) occupied the territory of Peru's northern coastal desert from the upper Piura (from Tambi Grande to Salitral) as far as the Macarà river and perhaps as far as the highlands of present day Ecuador. The centre of the Vicús culture has been identified as Cerro Vicús (50 km east of the city of Piura) and includes the complexes of Yécala, Loma Negra and Tamarindo. The Vicús culture is characterized by its pottery with white designs on a red background. Vicús metalworking was characterized by large objects such as plumes, crowns, rattles and necklaces, fashioned using the technique of gilding, plating and hammering [5, 6]. These settlers in the Piura region were known for their work in ceramics and gold. Recently, a mysterious pyramid complex was discovered in the province of Piura;

(3) Moche: the Moche civilization flourished in areas south of the Vicús, in the Moche and Chicama valleys, where its great ceremonial centres have been discovered from around 200 BC to 700 AD, producing painted pottery, monuments and gold ornaments. The Vicús and Moche cultures thrived within a relatively short distance of each other. The Moche (or Mochica) was a highly developed culture and the Moche were known as sophisticated metal-smiths, both in terms of their technological sophistication, and the beauty of their jewels. The Moche metalworking ability was impressively demonstrated when Walter Alva and co-workers discovered in 1987 the "Tumbas Reales de Sipán" [7, 8]. Spectacular gold, silver and copper funerary ornaments were excavated, and are now exposed in the namesake Museum, in Lambayeque. The tombs are composed of a sequence of graves. The

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Fig. 1   Ancient North Peru civilizations positioned around the present-day Chiclayo, Trujillo and the Andes, and between the Andes and the Pacific. After Ref. [12], with permission.

oldest is "la tumba del Viejo Señor" dating back to about 50 AD; the richest is "la tumba del Señor de Sipán. Of lower interest are "la tumba del Sacerdote", which is approximately contemporary to the tomb of the Señor de Sipán, and "la tumba del Guerrero". More recently, other tombs were discovered, and other objects analyzed, such as those from Huaca Rajada;

(4) Sicán: Sicán culture is the name archaeologist Izumi Shimada gave to a culture that predated the Inca in what is now the north coast of Peru between about 750-1375 BC [9]. Sicán means "temple of the moon" and this culture is also referred to as Lambayeque culture, after the name of the region in Peru. The Sicán culture, which capital was situated in the present day Pomac Forest Historical Sanctuary, extended as far as present day Piura in the north and Trujillo in the south, and its cultural influence was felt as far away as Ecuador and Pachamac on Peru's central coast. The Sicán culture was strongly influenced by the Moche culture, specifically in its metallurgical development. The Sicán not only worked in gold, but also employed silver, copper, gilded copper and arsenical bronze, as well as tumbaga, following the Moche tradition.

Not much is known about the early period of the Sicán culture (750-900 AD) due to a lack of artefacts, but it seems that the Sicán were probably descendants of the Moche. The Middle Sicán period lasted from about 900 to 1100 AD. This is the period of the cultural florescence, including art and technology. Metallurgy is one of the Sican's greatest legacies and the precious

metal objects found in Middle Sicán sites reveal the unprecedented scale of their production and use.

With reference to metallurgy metalworking from the North of Peru in the period between Chavín and Sicán cultures (from about 1000 BC to about 1000 AD) [10-27] and more specifically to analysis of gold, silver and copper alloys, following may be observed concerning previous analysis:

(1) Only a very few Chavín objects were analyzed: a crown, composed of Au and traces of Pt (no Ag and Cu were detected; the shaft of a pin, composed of 74% Ag and 26% Au [26, 27], a Cu metal-foil from Mina Perdida [28];

(2) A gilded copper serpent of Vicús style appliqué, of unknown provenance, was analyzed from British Museum scientists: the body metal of the serpent was found by EDX-analysis to be copper with 0.7% gold and 1.2% silver. The gilding thickness is 2 μm thick.

Only a limited number of fragments from Moche objects and more specifically from Sipán alloys could be analyzed by using various destructive techniques [29-39]; however, several important information could be deduced from all these measurements and from ancient reports of Spanish conquerors:

(1) Moche metalworking was based primarily upon objects made of hammered sheet metal; besides native gold and native gold-silver alloys (with copper), gold and silver were already intentionally alloyed at that time;

(2) The Moche developed very low carat gold or silver alloys appearing from outside as silver or gold by depleting the surface from copper; this alloy is called tumbaga; the low carat alloy was burned and/or treated with acids extracted from plant juices, which produced a copper oxide which could be removed mechanically, leaving the surface covered with a thin film of almost pure gold. The object was then placed in an oxidizing solution containing, it is believed, salt, and ferric sulfate. This process removed through oxidation the silver from the surface of the object leaving only gold.

Depletion gilding is a known technique which was used in many cultures worldwide, and as early as the 3rd millennium BC in Mesopotamia [40].

Only objects made of gold (gold + silver + copper alloy), or tumbagas, containing a high concentration of gold at the surface, preserved their gold aspects during the 1,500 years burial in the adobe pyramids. Other objects, made of copper, or silver-copper alloy, or gilded copper, were found covered with green patinas containing copper corrosion products.

From the analytical point of view, a relevant number of fragments on gold and silver (and also on silvered gold) of Moche artefacts from Loma Negra, Peru, were accurately studied and analyzed by D. Schorsch by employing EDXRF attached to a scanning electron microscope and wave dispersive X-ray Spectrometry [32]. The gold objects from Loma Negra showed following approximate composition: Au ~ 80%, Ag = 10%-20%, Cu = 5%-15%. The analyzed silver objects showed a high Ag-content, of about 97%− 99%. Copper covers the difference from 100%, and no gold was registered. Interesting and unusual, is the case of silvered gold, where the silver sheet was measured to have a thickness of about 4-6 μm.

Fragments from 17 Moche objects on copper, silver alloys and gold alloys from the "Museo Tumbas Reales de Sipán" have been analyzed by G. Hörz and M. Kallfass [29, 30], using optical emission spectrometry with inductively coupled high frequency plasma (ICP-OES), wavelength-dispersive spectrometry (WDS) and structural analysis. These authors were able to distinguish various techniques of manufacture (working, casting, gilding, depletion silvering, embossing, depletion gilding). More specifically the authors were able to identify:

• Gilded copper objects: A series of objects found in the tomb of the "Señor de Sipán" was identified as made of gilded copper (platelets, human male figures, rattle cones), characterized by a thin gold film (2-6 μm). The coatings consist of a gold-copper alloy containing some silver;

• Copper-silver alloys: Fragments from several

human head shapes beads have been analyzed, made of a sheet composed of 79% Cu, 20% Ag, 1% Au approximately; several peanut beads belonging to a necklace were also analyzed, showing a silver content of about 80%;

• Copper-gold-silver alloys (tumbaga): Fragments were analyzed from a headdress, a chin ornament, an ornamental disc and ornamental beads; the average composition of the headdress was calculated to be 60% Cu, 34% Au and 6% Ag; the average composition of the chin ornament is 40% Cu, 50% Au, 10% Ag; the average composition of the ornamental disc is 30% Cu, 60% Au, 10% Ag; the average composition of the ornamental bead is 20% Cu, 65% Au, 15% Ag. The alloy composition is strongly depending on the distance from the surface.

It is evident from all measurements carried out on fragments from the "Tumbas Reales de Sipán", and from the variety of object composition, that the analytical problems are extremely complicated, because of the variety of alloys and manufacture techniques, of the long time burial, and of not homogeneous composition of the alloy.

The Sicán culture used, in the same manner as the Moche, tumbaga. The east tomb of Huaca Loro contained over a ton of diverse grave goods, over two-thirds of which were objects of arsenical bronze, silver and copper alloys, and high-carat gold alloys [41, 42].

To analyze and to differentiate Sipán and Sicán alloys, portable EDXRF-equipments were transferred to the Museum "Tumbas reales de Sipán" and to the Museum of Sicán, to systematically analyze the most important objects. Then, also some selected Au-alloys from the "Museo de la Nacion" in Lima, were analyzed. Successively, Vicús gold objects were analyzed from the "Museo Municipal" of Piura, and Chavin objects from the Museum Enrico Poli in Lima and one object from the Museum of Piura.

For a systematic analysis of many areas of the same object, and for the analysis of a large number of gold,

silver and copper pre-Hispanic alloys, only non-invasive techniques may be proposed and applied, and among them, energy-dispersive X-ray fluorescence (EDXRF) - analysis is the most suited, because it is not only absolutely non-destructive, but also multi elemental, reliable and rapid. Further, EDXRF - analysis may be carried out "in situ" with a small size and small weight portable equipment [43].

2. Experiment

2.1 EDXRF- Characteristics and Experimental Set-up

EDXRF-analysis is able to quantify the composition of a gold, silver or copper alloy by using standard samples of the same alloys (see Sections 3.3-3.7).

EDXRF is a surface analysis, in the sense that the thickness of the alloy involved in the analysis is of the order of microns to a maximum of tens of microns; the results are therefore related to this feature and are generally valid in absence of surface enrichment phenomena (patina, ions migration processes and etc.). In the case of ancient alloys, EDXRF-analysis gives reliable results on the concentration of a gold alloys when they contain a reduced quantity of copper. Also in the case of a copper or silver alloy not containing relevant quantities of other elements, EDXRF-analysis should give sufficiently reliable results.

Being EDXRF a surface analysis, it can be able to distinguish a gold alloy from gilded copper or tumbaga, and a silver alloy from a gilded silver, by using the internal ratio of Cu and Ag-lines, as will be described in Section 3.2. EDXRF-analysis should also give the gold thickness value in the case of gilded copper or tumbaga (the surface-behaviour of these two examples is similar).

On the contrary, in the case of tumbaga, in the case of copper-rich gold alloys, in the case of gilded copper and in the case of copper-rich silver alloys, the results of EDXRF-analysis are incomplete and/or affected by large uncertainties. The EDXRF-measurements give in fact average values related to a given alloy thickness, mainly defined by the energy of secondary radiation

emitted by the object.

In general, a laboratory energy-dispersive X-ray fluorescence (EDXRF)-equipment is mainly composed of an X-ray tube (characterized by the anode material, maximum voltage and current), an X-ray detector (generally a Si (Li) or HpGe, characterized by its energy resolution and efficiency) and a pulse height analyzer [44]. A portable EDXRF-equipment differs because the X-ray source must be of small size and, therefore, low power, and the detector can only be a thermoelectrically cooled, small size detector, Si-PIN or Si-drift.

For the first measurements (Museums of Sipán and Sicán, the portable equipment was composed of an X-ray tube (Eclipse II by AMPTEK-Oxford [39], which has a weight of 300 g, length of 17 cm (including the collimator) and diameter of 3.7 cm), which is characterized by a Ag-anode, and works at 30 kV and 100 µA maximum voltage and current, and a Si-PIN detector (Fig. 2); In some cases a second EDXRF-equipment was employed, composed of a W-anode X-ray tube, working at 40 kV and 1 mA maximum voltage and current, and a Si-PIN detector [39].

For the last measurements (Museum Enrico Poli and Municipal Museum of Piura) the portable equipment was composed of a mini X-ray tube by AMPTEK, which is characterized by a Ag-anode, and works at 40 kV and 100 µA maximum voltage and current, and a 123-Si-drift detector. Bias supply and Electronics of both X-ray tube and detector and located in the case of tube and detector respectively; in such a manner the equipment is extremely compact (Fig. 3).

These portable EDXRF-equipments irradiate and analyze areas of about 5 mm diameter, when the object is at a distance of a few cm; when analysis of smaller areas is required, then a conic capillary collimator (CCC) can be put as a cap at the detector entrance. In such a manner, only photons from an area of about 0.2 mm diameter are collected by the CCC and processed by the detector.

Fig. 2 Experimental set-up, showing, on the left, the Eclipse II X-ray tube (collimated with a brass cylinder), with Ag-anode and working at 30 kV, 100 µA maximum voltage and current, and the Si-PIN detector (also collimated with a brass cylinder), during measurements on the golden mask, in the Museum "Tumbas Reales de Sipán". A typical measurement takes 50-200 s, depending on the geometry and object composition.
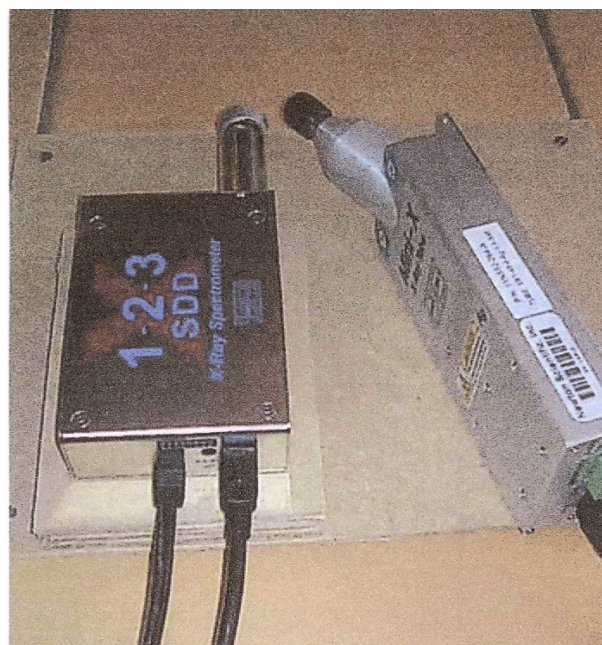

Fig. 3 EDXRF-portable equipment, composed of a Si-drift detector (~450 µm thickness, 7 mm^2 area and 140 eV energy-resolution at 5.9 keV) and a X-Ray tube (40 kV, 100 µA maximum voltage and current, and Ag-anode). Electronics, including bias supply and MCA are in the case of tube and detector.

Apart from this last case, the X-ray beam intensity, with the described not collimated and not filtered X-ray tubes is largely in excess for analysis of alloys, according to the fact that the Si-PIN detector is able to process only a few thousands of photons/s without loss of energy resolution. For this reason the X-ray beam is collimated with a brass cylinder 2 cm long and with an internal hole of 2 mm diameter, covered with a tin-foil. Further, to excite in a more efficient manner silver, which is a common element in a gold-alloy, the X-ray tube output is also filtered with about 0.1 mm Ti, to better "form", and to partially monochromatize the X-ray beam. The radiation protection problem will be therefore negligible, and the low energy tail of the X-ray spectrum, which is not suited to excite for example silver, is strongly reduced, while excitation of low atomic number elements is reduced. A partial monochromatization is also preferable for a quantitative evaluation of an X-ray spectrum (see Section 3). The X-ray spectrum of the AMPTEK-X ray tube, collimated and filtered as above described, is shown in Ref. [42].

However, the low-energy part of the X-ray spectrum (from 1.5 to 6 keV approximately) can contain useful analytical information (presence of Au-M lines, of Ag-L lines, of Sn-L lines). It is therefore useful to carry out a measurement with the Ti-filter (typically working at 30 kV, 50 µA approximately) and one without the filter (typically working at 15-20 kV and 5-10 µA).

The specifics of employed X-ray detectors are following:

(1) Si-PIN: It is a thermoelectrically cooled detector, with about 250 µm and 7 mm^2 thickness and area of the Si-crystal, and a thin Be-window (typically 10-20 µm) with about 180 eV energy resolution at 5.9 keV [45]). This detector has an efficiency of 87%, 46%, 24%, 12% and 8% at 10, 15, 20, 25 and 30 keV, respectively. It has a weight of 150 g, a length of 14 cm and a width of 4.5 cm. It is also collimated with a brass cylinder 3 cm long and with an internal hole of 2 mm diameter to

limit background and scattered photons;

(2) Si-drift: It is a thermoelectrically cooled detector, with a 450 µm, 7 mm^2 thickness and area of the Si-crystal, a thin Be-window (typically 10-20 µm), and with about 140 eV energy resolution at 5.9 keV [45]. This detector has an efficiency of 97%, 67%, 39%, 23% and 14% at 10, 15, 20, 25 and 30 keV respectively. It has a weight of 300 g, a length of 18 cm and a width of 5.5 cm.

The geometrical arrangements are shown in Figs. 2 and 3; X-ray tube and detector are positioned at a reciprocal angle of about 50°- 55°, and the detector is put normally to the object surface, to improve the analyzed thickness of the object. The possibility to vary the angles was not considered, but could be useful in the future to obtain information from different alloy depth.

The object to be analyzed is positioned at 1.5-3 cm distance from both X-ray tube and detector. Larger distances should be avoided. The measuring time ranges from about 50 s to about 200 s, mainly according to the sample composition and size. The dead time of the equipment, including electronic chain and pulse height analyzer was of a few percent. Larger dead times should be avoided, because of the increase of energy resolution.

Standard gold alloys, containing known concentration of gold, silver and copper were employed for calibration and for quantitative determination of alloy composition (Table 1). Also standard silver alloys were employed for calibration, which contain known concentration of silver and copper (Table 1). The ratios Cu/Au and Ag/Au were employed for calibration (Section 3.2).

To measure gilding thickness of gilded gold or silver, the Cu(K_α/K_β)-ratio or Ag(K_α/K_β)-ratio and the (Au-L_α/Cu-K_α) or (Au-L_α/Ag-K_α)-ratios were employed (see Sections 3.3-3.7). To simulate the experimental situations of Sipán alloys, commercial gold leaves (each Au-foil 0.125 µm thick) to simulate gilded copper or tumbaga, and silver foils, were

Table 1   Standard gold alloys (Au-Cu-Ag) and silver alloys (Ag-Cu) employed for the analysis of alloys from the "Tumbas Reales de Sipán".

Sample N.	Au (%)	Ag (%)	Cu (%)
1	100	0	0
2	90	50	50
3	90	70	30
4	75	25	0
5	90	0	10
6	90	10	0
7	75	15	10
8	65	35	0
9	58	27	15
10	37.7	40.7	20.8
11-		100	-
12-		99	1
13-		95	5
14-		90	10

employed (each Ag-foil 0.28 μm thick) to simulate the "silvered copper" or "Ag-tumbaga". Thick sheets of pure copper and silver were also employed to this aim.

It is worthwhile to observe that the distance covered by secondary Au-L_α, Au-L_β, Cu-K and Ag-K X-rays in a gold alloy is not the same. The analytical information arrives therefore from different depths of the alloy. In fact the incident radiation (assumed to have a mean energy value of about 23 keV) halves after 7 μm Au, while Au-L_α, Au-L_β, Ag-K_α and Cu-K_α rays halve in 3 μm, 4.5 μm, 2 μm and 1 μm respectively. EDXRF-analysis is, therefore, a fully surface method.

2.2 SEM-EDS, OM and XRD Set-Up

In order to further investigate the nature of the thin gold and silver coatings, also some micro-fragments were carefully sampled from the artefacts found during the archaeological excavation of the "Tumbas reales de Sipán" before the preventive conservation and restoration procedures and analyzed by means of optical microscopy (OM), field emission scanning electron microscopy (FE-SEM), scanning electron microscopy (SEM) with backscattered and secondary electron imaging and energy dispersive spectrometry (EDS).

The surface morphology of the samples was observed by using a Leica MZ FLIII and a multi-focus Leica optical microscope equipped with a digital camera.

In order to prepare cross-section of the samples, the micro-fragments were embedded in epoxy resin for 24 h and sectioned by using a diamond saw in order to preserve the corrosion products and the thin gold or silver coating. The sections were polished with silicon carbide papers until 1,200 grit and the final polishing was performed with diamond pastes up to 0.25 μm in order to have mirror like surfaces. OM investigation of cross-sectioned samples was carried out by using a Leica MEF 4 microscope equipped with a digital camera.

Both FE-SEM-EDS and SEM-EDS characterisations were carried out by a Cambridge 360 scanning electron microscope (SEM), equipped with a LaB_6 filament, and a high brilliance LEO 1530 field emission scanning electron microscope (FE-SEM) apparatus, equipped with an energy dispersive X-ray spectrometer (EDS) INCA 250 and INCA 450, respectively, and a four sectors backscattered electron detector (BSD).

SEM images were recorded both in the secondary electron image (SEI) and backscattered image (BSD) mode at an acceleration voltage of 20 kV. FE-SEM images were recorded both in SEI and BSD mode at different acceleration voltage ranging from 3 kV to 20 kV.

The micro-samples were coated with a thin layer of carbon or chromium in order to avoid charging effects. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K250 carbon coating attachment and a carbon cord at a pressure of 1×10^{-2} mbar in order to produce a carbon film with a constant thickness of about 3.0 nm. The chromium coating was deposited by using a Bal-Tech SCD 500 equipped with turbo pumping for ultra clean preparations at a pressure of 5×10^{-3} mbar in order to produce a chromium film with a constant thickness of about 0.5 nm.

3. Theoretical Background

3.1 X-Ray Spectrum of a Gold-Alloy

The final result of EDXRF – analysis of a sample is a X-ray spectrum containing a set of X-lines for each detectable element present in the analyzed object.

Theoretically, when K-shells are excited, four characteristic lines are emitted by each element: $K_{\alpha1}$, $K_{\alpha2}$, $K_{\beta1}$, $K_{\beta2}$ [46, 47]. When L-shells are excited, nine characteristic lines are emitted by each element, i.e., $L_{\alpha1}$, $L_{\alpha2}$, $L_{\beta1}$, $L_{\beta2}$, $L_{\beta3}$, $L_{\gamma1}$, $L_{\gamma3}$, L_l and L_η [46, 47]. When M-shells are excited, four lines are emitted, i.e. $M_{\alpha1}$, $M_{\alpha2}$, M_β, M_γ. When more external shells are excited, emitted lines are not detected with EDXRF-equipments because of the too low energy.

From a practical point of view, and because of the finite energy-resolution of thermoelectrically or N_2 cooled semiconductor detectors, the lines combinations $K_{\alpha1}$ - $K_{\alpha2}$, coincide in a unique peak, and the same happens for the lines pairs $K_{\beta1}$ - $K_{\beta2,}$ $L_{\alpha1}$ - $L_{\alpha2}$ - $L\beta_1$ - $L\beta_5$ and, at least for elements with atomic number up to about Z = 50. K-lines are therefore identified by two lines K_α and K_β, and L-lines by six lines L_α, L_β, $L_{\gamma1}$, $L_{\gamma3}$, L_l and L_η, of which only the first two of high intensity. $M_{\alpha1}$, $M_{\alpha2}$, M_β, M_γ always coincide in a unique peak, and M-lines detected as a single line, are in any case only "visible" for heavy elements.

Apart from K, L and M lines of "visible" elements present in the analyzed object, spurious peaks are often present, due to "escape" or "sum" effect in the detector [46].

The first effect is due to photoelectric effect of photons of energy E_0 in the detector, and escape of the Si-X rays; this happens more often at the borders of the detector. The second effect is due to the fact that two E_0 photons are processed within the resolving time of the electronic chain. Using a Si-detector, a peak of energy E_0 may originate in the Si-detector a second peak at energy E_0 -1.74 keV (escape peak, where 1.74 keV represents the Si-K shell excitation energy) and 2 E_0 (sum of two contemporary E_0 photons in the detector) respectively.

For example, in the case of a Au-Cu alloy, secondary X-ray peaks may be expected at 6.26 keV (escape due to Cu-K_α-lines),16 keV (sum of 2 Cu-K_α-lines),8 keV (escape due to Au-L_α lines), 9.7 keV (escape due to Au-L_β lines), 19.4 (sum of 2 Au-L_α-lines), 22.9 keV (sum of 2 Au-L_β-lines), 21.1 keV (sum of Au-L_α and Au-L_β-lines). Escape or sum peaks are not always visible, depending on the energy of E_0 line, detector characteristics and intensity of the primary peaks. The ratio of "escape peak" to E_0 peak in a Si-detector is about (0.5-1)%, while the sum effect is one order of magnitude lower, and is, therefore, generally not visible in the X-ray spectrum. The escape effect can be reduced by strongly collimating the detector with respect to the detector size; this reduces the detector border effects. The sum effect can be practically eliminated by reducing the secondary photon flux.

Further, Ar-X rays from the air are generally present in the X-ray spectrum (at 2.96 keV), a peak of the anode element, and a continuous background reflecting the scattering of the X-ray spectrum by the sample. Also X-rays from elements of the collimators are often visible. To reduce this last effect, collimators should be employed on pure and not disturbing elements (for example Al), both for the X-ray tube and the detector.

3.2 Quantitative Analysis of an Homogeneous Gold Alloy, Composed of Gold, Silver and Copper

Artefacts of very different size, composition and surface form were analyzed. Therefore, it is very difficult to reproduce a fixed geometrical arrangement and, in particular, to have always the same distances X-ray tube-object-detector. For these reasons, an absolute determination of the alloy components on the basis of the fundamental parameters method is difficult. An approach should be preferred in this case, of using, instead of the intensity of secondary photons emitted by a single element, the intensity ratio of two components (for example Cu/Au and Ag/Au), which is not depending on the geometry.

Standard gold-silver-copper alloys have been employed for calibration and for the determination of alloy composition (Table 1). The ratios (Cu-K_α/Au-L_α) = h and (Ag-K_α/Au-L_α) = k versus Cu or Ag-concentration are shown in Figs. 4 and 5. Assuming that Au (%) + Cu (%) + Ag (%) = 100, the Au-concentration is calculated from difference to 100%, i.e., Au (%) = 100/ (1 + h + k). In a similar manner is calculated the concentration of Ag and Cu. When other elements are present, their concentrations can be determined by using fundamental parameters, through attenuation coefficients, fluorescence yields and detector efficiency. These concentration values should be then used to re-calculate the Au, Ag and Cu concentrations. Also Au sheets of given thickness were employed, i.e., commercial sheets of 0.125 μm and specially prepared 2 μm and 4 μm sheets.

In a similar manner, silver-copper standard alloys were employed for calibration and quantitative determination of these elements in silver alloys (Table 1). There is a linear correlation between silver counts and concentration, at least in the silver concentration range 80%-100%. Gold, which was always present, and other possible elements present in Sipán silver, were determined by using fundamental parameters [48].

3.3. (K_α/K_β) and (L_α/L_β)-Ratios Alteration Due to Self-Attenuation

The K_α/K_β and L_α/L_β -ratios, can be calculated theoretically, and are tabulated [46-50]. For example, K_α/K_β are for the elements copper and silver 6.9 and 5.1 respectively and for the element gold, L_α/L_β = 0.96.

Both experimental and theoretical values are subject to relatively large fluctuations. It should be observed that these values are valid for an infinitely thin sample, i.e. when secondary interactions in the sample are negligible. This corresponds, for example, to a thickness less than 1 μm, 0.5 μm and 0.2 μm for copper, silver and gold respectively. For a sample of any thickness, self attenuation effects must be considered [50].
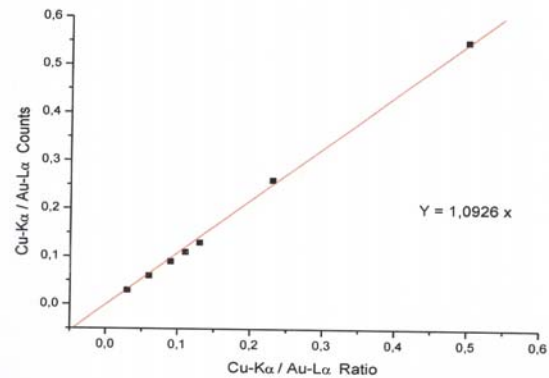

Fig. 4 (Cu/Au)-counts versus (Cu/Au)-ratio, by using the standard Au-Ag-Cu alloys of Table 1, showing a linear relationship. A relative error of about 5% may be assumed.

Further, when measurements are carried out, besides self attenuation, also the detector efficiency should be considered, which is different for α β and X-rays. Following Equations may then be calculated:

$$(K_\alpha/K_\beta)= (K_\alpha/K_\beta)_0 \{\varepsilon(K_\alpha)/\varepsilon(K_\beta)\} \{(\mu_0+\mu_2)/(\mu_0+\mu_1)\}$$
$$[(1-\exp-\{\mu_0+\mu_1\}d)/(1-\exp-\{\mu_0+\mu_2\}d)] \quad (1)$$
$$(L_\alpha/L_\beta)=(L_\alpha/L_\beta)_0\{\varepsilon(L_\alpha)/\varepsilon(L_\beta)\}\{(\mu_0+\mu'_2)/(\mu_0+\mu'_1)\}$$
$$[(1-\exp-\{\mu_0+\mu'_1\}d)/(1-\exp-\{\mu_0+\mu'_2\}d)] \quad (2)$$

where $(K_\alpha/K_\beta)_0$ and $(L_\alpha/L_\beta)_0$ represent K_α/K_β and L_α/L_β–tabulated (and/or experimental) ratios for infinitely thin samples, ε represent the efficiency of the detector, μ_0 is the linear attenuation coefficient (in cm^{-1}) of the element under study at incident energy E_0 (or mean incident energy E_0); it should be observed that this energy value is not easy to determine when using a X-ray tube, depending on its characteristics, on the X-ray beam filtering and on the beam hardening in the sample. For all these reasons, μ_0 and the consequent related Eqs. are modulated according to the experimental results carried out on standard samples; attenuation coefficients are tabulated [51]; μ_1 and μ'_1 are the linear attenuation coefficient (in cm^{-1}) of the element under study, at the energy of its K_α or L_α energy; μ_{12}, $\mu_1'_2$ and are the linear attenuation coefficients (in cm^{-1}) of the element under study, at the energy of its K_β and L_β radiation respectively; d represents the thickness (in cm) of the element under study.

For "infinitely thin" and "infinitely thick" samples, Eqs. (1-3) may be written as:

$$(K_\alpha/K_\beta)_{thin} = (K_\alpha/K_\beta)_0 \{\varepsilon(K_\alpha)/\varepsilon(K_\beta)\} \quad (1a)$$

$$(L_\alpha/L_\beta)_{thin} = (L_\alpha/L_\beta)_0 \{\varepsilon(L_\alpha)/\varepsilon(L_\beta)\} \quad (2a)$$

and

$$(K_\alpha/K_\beta)_{thick} = (K_\alpha/K_\beta)_0 \{\varepsilon(K_\alpha)/\varepsilon(K_\beta)\}$$
$$\{(\mu_0+\mu_2)/(\mu_0+\mu_1)\} \quad (1b)$$

$$(L_\alpha/L_\beta)_{thick} = (L_\alpha/L_\beta)_0 \{\varepsilon(L_\alpha)/\varepsilon(L_\beta)\}$$
$$\{(\mu_0+\mu'_2)/(\mu_0+\mu'_1)\} \quad (2b)$$

respectively.

Because of the terms $\varepsilon(E)$ and $\mu_0(E_0)$, Eqs. (1) and (2) depend on the incident energy (or mean incident energy) and detector.

For example in the case of Cu, Ag and Au samples:

(1) when assuming $E_0 \approx 18$ keV (X-ray tube working at 30 kV and filtered with about 0.1 mm Al), and measuring with a Si-PIN detector of about 250 μm Si-thickness, Eqs. (1) and (2) may be written as:

$$Cu(K_\alpha/K_\beta)=6.15\{[1-\exp(-850d_{Cu})]$$
$$/[(1-\exp(-730d_{Cu})]\} \quad (3a)$$

$$Ag(K_\alpha/K_\beta)=6.65\{[1-\exp(-610d_{Ag})]$$
$$/[(1-\exp(-565d_{Ag})]\} \quad (3b)$$

$$Au(L_\alpha/L_\beta)=0.98\{[1-\exp(-4295d_{Au})]$$
$$/[(1-\exp(-3455d_{Au})]\} \quad (3c)$$

(2) when assuming $E_0 \approx 25$ keV (X-ray tube working at 35 kV and filtered), and measuring with a Si-drift detector, having a Si-thickness of about 450 μm, Eqs. (1) and (2) may be written as:

$$Cu(K_\alpha/K_\beta) = 5.6\{[1-\exp(-1280d_{Cu})]$$
$$/[(1-\exp(-1045d_{Cu})]\} \quad (4a)$$

$$Ag(K_\alpha/K_\beta) = 6.4\{[1-\exp(-610d_{Ag})]$$
$$/[(1-\exp(-565d_{Ag})]\} \quad (4b)$$

$$Au(L_\alpha/L_\beta) = 0.76\{[1-\exp(-3185d_{Au})]$$
$$/[(1-\exp(-2345d_{Au})]\} \quad (4c)$$

For infinitely thin samples:

$$Cu(K_\alpha/K_\beta) = 7.15, Ag(K_\alpha/K_\beta) = 7.15 \text{ and Au } (L_\alpha/L_\beta)$$
$$= 1.22 \text{ with Si-PIN}$$

$$Cu(K_\alpha/K\beta)_\infty = 6.85, Ag(K_\alpha/K_\beta)_\infty = 6.9 \text{ and } Au(L_\alpha/L_\beta)_\infty$$
$$= 1.03 \text{ with Si-drift.}$$

For infinitely thick samples:

$$Cu(K_\alpha/K_\beta)_\infty = 6.15, Ag(K_\alpha/K_\beta)_\infty = 6.65$$

and

$$Au(L_\alpha/L_\beta)_\infty = 0.98 \text{ with Si-PIN}$$

$$Cu(K_\alpha/K_\beta)_\infty = 5.6, Ag(K_\alpha/K_\beta)_\infty = 6.4$$

and

$$Au(L_\alpha/L_\beta)_\infty = 0.76 \text{ with Si-drift}$$

As an example, in Fig. 6 are reported the values of $Cu(K_\alpha/K_\beta)$ versus Cu-thickness due to self-attenuation, following Eq. (4a).

The ratio $Au(L_\alpha/L_\beta)$ (Fig. 7) is particularly important, because it is one of the elements allowing to distinguish gold from gildings or tumbagas.

It is worthwhile to observe that, if the surface layer (gilding or silvering) is not mono-elemental, but an alloy, then the attenuation coefficients of Eqs. (1) and (2) should refer to the alloy composition, and Eq. (4) should be written differently.

It is important to remind that, following Eqs. (1) and (2), $[K_\alpha/K_\beta]$ and $[L_\alpha/L_\beta]$-ratios also depend on the incident energy and when bremsstrahlung radiation is employed, on a mean energy value.

3.4 (K_α/K_β) and (L_α/L_β)-Ratios Altered Due to Differential Attenuation

When a sheet of metal a, of infinite thickness, is covered by a sheet of another metal b, then the ratio (K_α/K_β) or (L_α/L_β) is further altered in the following manner because of the attenuation of the covering sheet:

$$(K_\alpha/K_\beta) = (K_\alpha/K_\beta)_{s.a.}\exp-[\mu_1-\mu_2] d \quad (5)$$

where

$(K_\alpha/K_\beta)_{s.a.}$ is the ratio R of the metal a, after calculation of self-attenuation;

μ_1 is the linear attenuation coefficient of the sheet of element b at the energy of K_α radiation of the element of the internal sheet;

μ_2 is the linear attenuation coefficient of the sheet of element b at the energy of K_β radiation of the element of the internal sheet;

 d is the thickness (in cm) of the sheet of element b.

An Equation similar to Eq. (5) may be deduced for L_α/L_β – ratio.

From Eq. (5) following equations may be calculated, for thick metal a and Si-PIN or Si-drift detectors

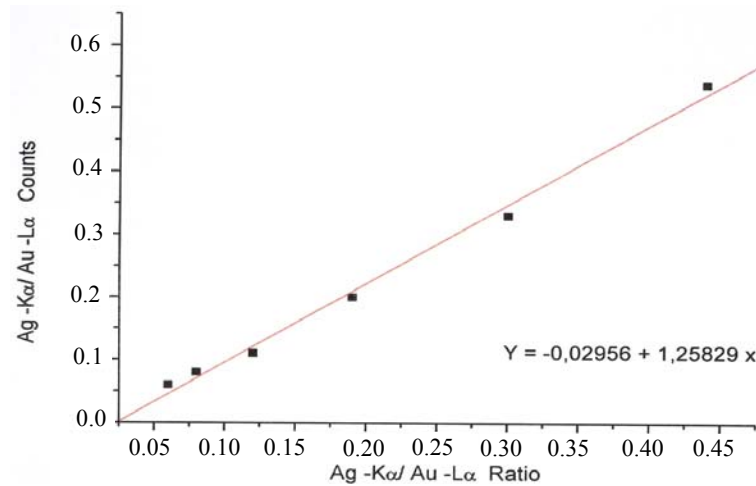**Fig. 5** **(Ag/Cu)-ratio versus (Ag/Au)-ratio, by using the standard Au-Ag-Cu alloys of Table 1, showing a linear relationship. A relative error of about 10% may be assumed at high Ag-concentration.**
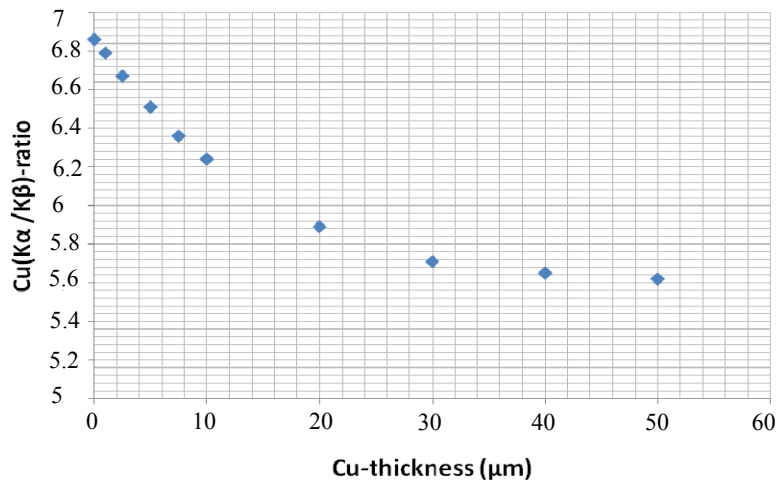
$Y = -0,02956 + 1,25829 \, x$

Fig. 6 **Self-attenuation of copper (K_α/K_β)-lines versus Cu-thickness, in the case of a Si-drift detector of 450 μm thickness, according to Eq. 4a.**
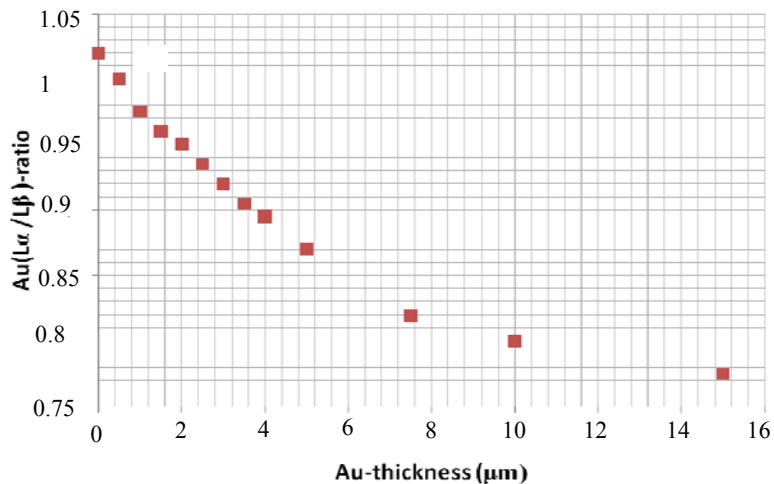

Fig. 7 **Self-attenuation of gold (L_α/L_β)-ratio versus Au-thickness, according to Eq. (4c). From this ratio gold can be differentiated from gilded copper or tumbaga. Following typical values were measured with a Si-drift detector: Au 100% = 0.75 ± 0.3; Chavin crown = 0.79 ± 0.3; Chavin collar = 0.75 ± 0.3; set of six Chavin heads = 0.98 ± 0.4; Chavin vessel = 1.00 ± 0.05.**
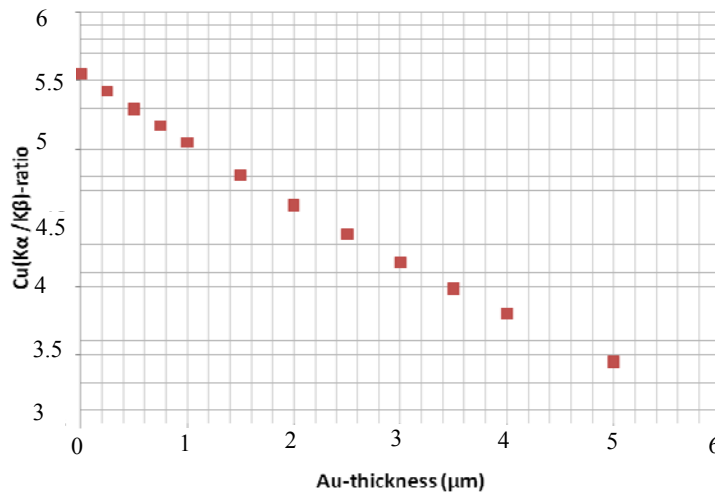
Fig. 8   Cu(K_α/K_β)-ratio versus gold leaf thickness, for Si-drift detectors, according to Eqs. (6a). Following typical values were measured with Si-drift detectors: Sipan, family (Museo Poli, on gilded copper copper)= 5.4 ± 0.2 → 0.2 ± 0.2 µm Vicus, feline head, lower part of the lips (Museo Piura, on tumbaga) = 5.15 ± 0.3 → 0.8 ± 0.3 µm.

$$Cu(K_\alpha/K_\beta) = 6.15 \exp{-}(950 d_{Au}) \text{ for Si-PIN} \qquad (6a)$$
$$Cu(K_\alpha/K_\beta) = 5.6 \exp{-}(950 d_{Au}) \text{ for Si-drift} \qquad (6b)$$
$$Ag(K_\alpha/K_\beta) = 6.3 \exp{-}(320 d_{Au} \text{ for Si-PIN} \qquad (6c)$$
$$Ag(K_\alpha/K_\beta) = 6.1 \exp{-}(320 d_{Au}) \text{ for Si-drift} \qquad (6d)$$

which corresponds to:

Cu-Au (gilded copper);

Ag-Au (gilded silver).

As an Example, Fig. 8 shows the behaviour of Eq.(6b).

3.5 (Au-L_α/Cu-K_α) – Ratio versus Au Thickness, and (Au-L_α/Ag-K_α)–Ratio versus Ag-Thickness

Another way to experimentally determine, from the X-ray spectrum, the thickness of the second element b (for example gilding) assuming that the first element a (for example copper) has an infinite thickness is the use of the X-ray ratio of the two elements, i.e., the ratio (Au-L_α/Cu-K_α). This ratio for two generic elements a and b (a at infinite, b at variable thickness respectively), at fixed incident energy and geometrical arrangement, is given by following equation [52-54]:

$$N_b/N_a = P\,(\mu_{a0}+\mu_{aa})/(\mu_{b0}+\mu_{bb})[1{-}\exp{-}\{\mu_{b0}+\mu_{bb}\}\rho_b d_b]$$
$$\exp\{\mu_{b0}+\mu_{ba}\}\rho_b d_b \qquad (7)$$

where the term P indicates the detection probability of the line and element of interest, which includes the emission probability of a given line, the fluorescence yield of the element and the detector efficiency at the energy of the line; μ_{a0} or μ_{b0} (in cm^2/g) are the total mass attenuation coefficient of elements a and b at incident energy; μ_{ab} (in cm^2/g), and similar symbols indicates the mass attenuation coefficient of element a at energy of the involved line of element b; ρ_b (in g/cm^3) is the density of element b.

90° angles is assumed (incident and secondary beam orthogonal to sample surface). Otherwise, the attenuation coefficients may be divided by the sinus of the involved angles.

For the ratio (Au-L_α/Cu-K_α), and modulating Eq.(8) to experimental measurements with standard samples, Eq. (8) may be written as:

$$(N_{Au}/N_{Cu}) = 0.31\,(1{-}e^{\,-4500\,d})\,e^{\,6000\,d} \qquad (7a)$$

for the Si-PIN, and

$$(N_{Au}/N_{Cu}) = 0.53\,(1{-}e^{\,-3170\,d})\,e^{\,4700\,d} \qquad (7b)$$

for the Si-drift detector.

It should also be observed that a mean incident energy value was assumed in the above Equations (18 keV for the Si-PIN and 25 keV for the Si-drift), due to the fact that bremsstrahlung (and not monoenergetic) radiation was employed. However the experimental conditions (see Section 3) are not too far from that of a monochromatic incident radiation.

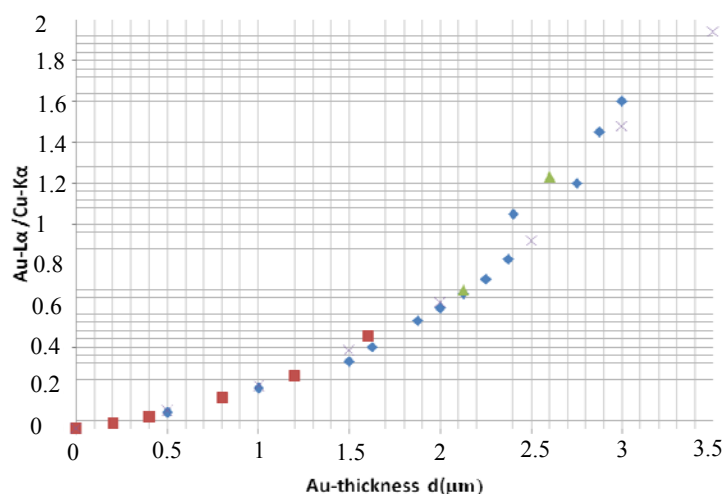Fig. 9 represents theoretical values (from Eq. (7a)) and experimental measurements values for

Fig. 9   Theoretical values (from Eqs.7a) and experimental measurements (red and green points) for (Au-L$_\alpha$/Cu-K$_\alpha$)-ratio versus Au thickness, assuming Cu of infinite thickness (gilded copper), in the case of Si-PIN and Si-drift detectors. Following typical values were measured with both detectors: ear ring on gilded Cu from Huaca Rajada = 0.06 → 0.4 μm Au; right eye protector on tumbaga from Museo Tumbas Reales = 2.3 → 3.7 μm Au; The mean value for all Sipán tumbaga objects is (Au-L$_\alpha$/Cu-K$_\alpha$) = 1.25 ± 0.5 corresponding to 2.8 ± 0.7 μm.

(Au-L$_\alpha$/Cu-K$_\alpha$) and (Au-L$_\alpha$/Ag-K$_\alpha$)–ratios respectively, versus Au or Ag thickness, assuming Cu and Ag of infinite thickness. These cases correspond to gilded copper and gilded silver respectively.

Eq. (7) and curves depend on the shape of X-ray spectrum, i.e., on the high-voltage of the X-ray tube and on the output photon filtering, on the geometrical arrangement and on the detector efficiency.

It should be observed that an "anomalous" value for K$_\alpha$/K$_\beta$ − ratio (lower than that without absorber) is a certain indication of the presence of an absorbing material, while from Eq. (8) and Fig. 9 alone, a reliable indication of the presence of an absorber is not possible. However, Fig. 9 can be employed to calculate with a higher precision the thickness of an absorber, after the "anomalous" K$_\alpha$/K$_\beta$–ratio has been certainly determined.

3.6 XRF-Measurements at Various Angles

In the case of gilded copper or Cu-tumbaga, the ratio (Cu-K$_\alpha$/Au-L$_\alpha$) strongly depends on the angle between the normal to the sample surface and the detector. At the contrary, the same ratio is constant versus angle for a homogeneous Au-Cu alloy. From angular

measurements following additional information may be deduced on the sample nature and composition:

- If the sample is an homogeneous alloy, or a gilded copper;
- If the copper peak belongs to the gilding or the bulk metal;
- If the sample is a gilded copper or a tumbaga;
- The gilding thickness.

3.7 Errors and Uncertainties

All methods described in Section 3 to differentiate gold, gilded copper and Cu-tumbaga (and in the same manner silver, gilded silver and Ag-tumbaga) require an accurate evaluation of the net area of the involved X-ray peaks (Cu-K$_\alpha$, Cu-K$_\beta$, Au-L$_\alpha$, Au-L$_\beta$, Ag-K$_\alpha$ and Ag-K$_\beta$), and their ratio.

An accurate evaluation of an X-ray peaks means:

- An adequate statistics of the peak;
- A correct background subtraction;
- A good separation of the peak of interest from contiguous, disturbing peaks.

An adequate statistics is related to higher counting times, while a good separation of peaks is related to the energy resolution of the detector. For portable systems

a Si-drift detector is, therefore, better than a Si-PIN.

To give an example, Cu-K_α (at 8 keV) corresponds to a peak generally free from complications, but Cu-K_β (at 8.9 keV) corresponds to a peak which can suffer from interference with the Au-L_η peak at 8.5 keV, and with the possible presence of a Zn-K_α peak at 8.6 keV. Finally, Cu-K_β peak can be statistically weak, being approximately six times less intense than the Cu-K_α peak. A total relative error ranging from 3% to 6% was assumed, corresponding to Au-thickness error from 0.35 to 0.7 μm. For these reasons very low gilding thickness, of the order of 0.1-0.4 μm are difficult to be determined.

To give another example, let consider Au(L_α/L_β)-ratio versus Au-thickness, due to self-attenuation. The evaluation of Au-L peaks is complicated by the presence of multiple peaks composing the Au-L_β, of the disturbing Au-L_η peak, and of the relatively high background under the Au-L_α peak, due to some interference from the Cu-K_β peak; an overall relative error of (2-5)% may be expected, corresponding to a Au-thickness error of 0.5−1 μm.

For all these reasons, it is also mandatory to carry out measurements always in the same experimental conditions.

Finally, it should be observed that a non-flat surface of the object to be analyzed further increases the related errors.

4. Results

4.1 Alloys from the Chavin Culture

Gold, silver and copper alloys from the Chavín culture (1000 BC−200 BC) were analyzed, located in the Museo Enrico Poli in Lima [55], and in the Municipal Museum of Piura [56].

4.1.1 Gold Objects

Following objects were analyzed in the Museum Enrico Poli in Lima:

• a crown with 5 sheets, three of them symbolizing the masculine nature, and two symbolizing the feminine nature (Fig. 10);

• a necklace with six pendants representing figures of fishes;

• a sheet.

Further, a plate supposed Chavín was analyzed in the "Museo Municipal" of Piura.

Results are summarized in Table 2.

4.1.2 Silver-Tumbaga Object

A vessel of the Chavín period, with the aspect of gold, was analyzed, from the Museum Enrico Poli, Lima. The X-ray spectrum showed the presence of copper, gold, lead (traces) and silver-lines. The internal ratio calculation of Ag and Cu gave following results:

Ag(K_α/K_β)-ratio = 5.8 ±0.2 →(1.0 ± 0.5 μm)

Cu(K_α/K_β)-ratio = 4.5 ±0.5 →(2.0 ± 1 μm)

Au(L_α/L_β)-ratio = 0.97 ± 0.02 →(1 ± 0.5 μm)

showing that the vessel is composed of silver-tumbaga (or, less probable, of gilded silver), and that copper is not connected to the gilding, but to silver. From the Ag-ratio it turns out that the gilding thickness is ~0.6 μm.

The silver alloy has following mean composition:

Ag = 98%, Cu ≤1.5%, Pb = 0.4%.

4.1.3 Copper-Tumbaga Object

A complex of six heads was analyzed (Fig. 11). The X-ray spectra (similar for the six heads) showed the presence of high quantity of copper, zinc, gold and silver (traces). The anomalous ratio:

Cu(K_α/K_β) = 4.6 ± 0.3

demonstrates that the heads are composed of copper-tumbaga (or, less probable, gilded copper), and that the gilding thickness is 1.5 μm approximately. The copper seems to be quite pure, because the traces of silver belong to the gilding or to the Ag-anode X-ray tube.

4.2 Alloys from Vicus and Frias Cultures ("Museo Municipal" of Piura)

Vicús gold artifacts from the "Museo Provincial" of Piura [54] were analyzed: the famous Lady of Frías (Fig. 12), a masculine figure on gold and silver (Fig. 13), five half-moon shaped gold tweezers, one of them with zoomorphic figures (Fig. 14), a gold feline head with sequins, teeth and a tongue, an ornament representing a bird with a pendant in its beak, a vessels,

two bowls and a pendant.

It was measured that the Lady of Frías is composed of laminated and relatively homogeneous gold, with a mean composition of Au = 86.5%, Cu = 7%, Ag = 6.5% (Table 3), corresponding to a "normal" gold alloy. The other objects have following composition:

• Vessel: Au = 90.3%, Ag = 7.4%, Cu = 2.3%;

• Pendant: Au = 89.5%, Ag = 5%, Cu = 5.5%;

• Bowl n.1: Au = 61%, Ag = 6%, Cu = 33%;

• Bowl n. 1: base; Au = 58%, Ag = 8%, Cu = 34%;

• Bowl n.2: Au = 70%, Ag = 11%, Cu = 19%;

• Bowl n. 2, base: Au = 65%, Ag = 4%, Cu = 31%;

• Big tweezers with antropomorphic figures: Au = 88.5%, Ag = 9%, Cu = 2.5%;

• Small tweezers: these three tweezers have same composition: Au = 84%, Ag = 12%, Cu = 4%;

• Feline head: Au = 83%, Ag = 12%, Cu = 5% (except areas 1 and 2).

The masculine figure (Fig. 13) has a composition shown in Table 4.

4.3 Alloys from the Moche Culture (Museo Tumbas Reales de Sipan and Museo de Sitio Huaca Rajada)

A relevant number of objects from the "Tumbas Reales de Sipán" were analyzed, on gold, gilded copper, tumbaga, silver and copper alloys. The majority of them originates from the tomb of the "Señor de Sipán" (code S/T1); several are from the tomb of the "Sacerdote" (code S/T2); some come from the tomb of the "Viejo Señor" (S/T3), "Guerrero" and other tombs.

4.3.1 Gold Objects Composition

Several objects from the "Tumbas Reales de Sipán" are on gold, i.e. characterized, as usually, by Au, Cu and Ag as main components. In some samples traces of Fe, Zn and Br are visible.

The results of EDXRF analysis on gold objects are shown in Table 5.

Of particular interest is a gold mask (Fig. 2), which complete analytical details are following:
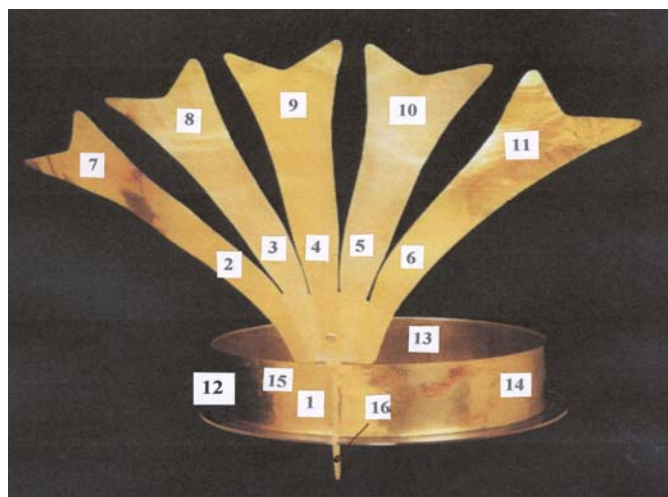

Fig. 10 Crown with plumes from the Chavin culture (Museo E. Poli, Lima). Plumes 1, 3, 5 are supposed to represent the masculine aspect, plumes 2 and 4 the feminine aspect (this hypothesis was suggested by E. Poli). Analyzed areas are shown.

Table 2 EDXRF-analysis of gold objects from the Chavin culture.

Object and analyzed areas	Au (%)	Ag (%)	Cu (%)
Crown (areas 1,12,13,14,15)	78±2	21±2	1±0.5
Crown (masculine plumes areas 2,4,6,7,9,11	81.5±1.5	15±3	3.3±0.4
Crown (feminine plumes areas 3,5,8,10	56.5±2.5	40.5±3	3.3±0.5
Collar with six fish-pendants	86	14	0.2
Sheet	67.5±1	30±1	2.5±0.5
Plate (Museum of Piura)	92.5±1	7.5±0.5	0.1±0.05

Fig. 11   Complex of six small heads of Chavin culture (Museo Poli, Lima), possibly on tumbaga. Following was determined: $Cu(K_\alpha/K_\beta)$= 4.5 ± 0.2, corresponding to an equivalent gold thickness of 2 μm. The composition of the internal copper was determined to be: Cu = 98.5%, Zn = 1.5%, Fe = traces. X-Ray tube (top left) and Si-drift X-ray detector (top right) are also visible.

Fig. 12   The Lady of Frias, on gold (Au=86.5%, Cu = 7%, Ag = 6.5%). The height of the statue is 15.3 cm, and the weight 60 g.

Fig. 13   Masculine figure on gold (Au = 78.8%, Cu = 3.4%, Ag = 17.8%). The eyes, left hand, the disk in the right hand, the belt and the tip of the penis are on silver. Analyzed areas are shown.
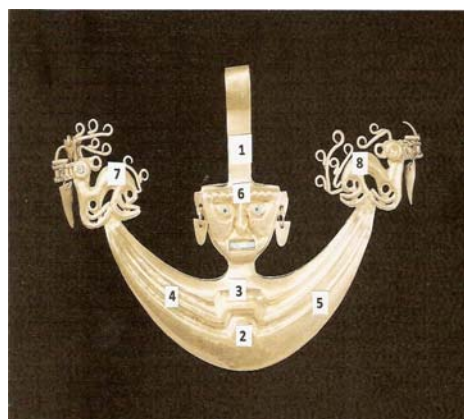

Fig. 14   half-moon shaped gold tweezers with two zoomorphic figures at the edges and an anthropomorphic figure in the centre. The gold composition is following: Au = 88.5%, Ag = 9%, Cu = 2.5%. Analyzed areas are shown.

Table 3   Analysis of the Lady of Frias (Fig. 12).

Analyzed area	Au (%)	Ag (%)	Cu (%)
Right leg	85	9	6
Left arm	85	6	9
Right arm	86.5	7	6.5
Head posterior	85.5	6	8.5
Head posterior	87	7	6
Left eye	85.5	5	8.5
Right eye	84	8	8
Head post. 2	87	6	7
Forehead	89.5	6	4.5
Stomach	87.5	6	6.5
Mean value	86.5±1.5	6.5±1	7.0±1.5

Table 4   Analysis of the masculine figure (Fig. 13).

Analyzed area	Au (%)	Ag (%)	Cu (%)
Head anterior	71	27	2
Head posterior	78	19	3
Right arm	81	18	1.5
Left arm	80	17	3
Mean value without head anterior	78.8	17.8	3.4

(1) Front side: Au = (74.5 ± 1)%; Ag = (23 ± 1)%; Cu = (2.5 ± 1.5)%;

(2) Back side: Au = (64.5 ± 3)%; Ag = (20 ± 2)%; Cu = (15.5 ± 2)%;

(3) Left eye: Silver plus Copper and Gold; Gold plus some copper could depend on the Au-support (see front side composition); Copper can be part of a Ag-Cu alloy. From the altered $Au(L_\alpha/L_\beta)$-ratio = 0.91, a Ag thickness of about 4 μm was deduced. A similar result was obtained from the $Au(L_\alpha/L_\gamma)$-ratio;

Table 5   Composition of gold objects. The code and the name of the objects are given. Trace elements are also indicated.

Object description and code	Au (%)	Cu (%)	Ag (%)	Minor elements
Earring with a warrior S/T1-O:2 (external spheres)	78.5	5	16.5	Zn
Earring with a warrior S/T1-O:2 (command stick)	70.5	9.5	20	
Earring with a warrior S/T1-O:2 (nose decoration)	66.5	15.5	18	
Earring with a warrior S/T1-O:2 (leg protection)	79.5	7	13.5	
Earring with gosling S/T1-O:3 (all golden areas)	69.5 ± 3	6.5 ± 2	24 ± 4	Zn ~(0.7-1)%
Command stick S/T1-O:15(Figure 16)	72 ± 5	4 ± 1	24 ± 4	Br
Command stick S/T1-O:15(Figure 16-area 67)	63	12	25	
Ceremonial knife S/T1-O:19	73 ± 10 *	8 ± 2	19 ± 8	Zn
Necklace with disks S/T1-O:20	62 ± 5	11.5 ± 3	26.5 ± 4	
Earring with a head in the centre S/T2-O:1 (internal ring)	80 ± 3	6 ± 1	14 ± 2	Zn
Earring with a head in the centre S/T2-O:1 (head)	67.5 ± 3	9.5 ± 1	23 ± 3	Zn
Cylindrical support for earring S/T2-O:1A	78 ± 3	7 ± 1	15 ± 2	Br, Zn
Earring with a head in the centre S/T2-O:2 (internal ring)	80,5 ± 3	6,5 ± 1	13 ± 2	Zn
Earring with a head in the centre S/T2-O:2 (head)	67.5 ± 3	9.5 ± 1	23 ± 3	Zn
Cylindrical support for earring S/T2-O:2	78 ± 3	7 ± 1	15 ± 2	Br, Zn
Nose protector S/T2-O:3	69.5 ± 2	1.5 ± 0.5	29 ± 2	-
Nose decoration S/T2-S:1	65 ± 4	10 ± 3	25 ± 3	-
Nose ornament S/T3-O:6	56.5 ± 1.5	12 ± 1.5	31.5 ± 2	
Cylindrical support for earring S/T6-O:1A	64 ± 4	12 ± 3	24 ± 3	-
Cylindrical support for earring S/T6-O:1B	74 ± 3	13 ± 2	13 ± 2	-
Cylindrical support for earring S/T6-O:4A	61 ± 4	16 ± 2	23 ± 3	or tumbaga ?
Earring S/T6-O:4A (external decoration)	80 ± 3	6 ± 1	14 ± 2	-
Cylindrical support for earring S/T6-O:4B	76 ± 3	7 ± 1	17 ± 2	-
Earring S/T6-O:4B (external decoration))	84 ± 2	10 ± 1	6 ± 1	-
Mask MB-09398 (Figure 2) (front side)	74.5 ± 1	2.5 ± 1.5	23 ± 1	-
Mask MB-09398 (rear side)	61 ± 1	16 ± 2	23 ± 2	Zn
Small peanut MB-9403	54 ± 2	16 ± 1	30 ± 2	-
2nd small peanut MB-9404	58 ± 2	16 ± 1	26 ± 2	-
Mean value	**70 ± 7**	**9.5v5**	**20.5 ± 4**	**-**

* The large error associated to analysis of Ag is due to bad statistics, due the fact that a capillary collimator was employed, which reduces the intensity of the secondary high-energy part of the X-ray spectrum.

(4) Right eye: Copper plus gold and silver; Gold could depend on the Au-support; Silver is possibly related to Cu as a Cu-Ag alloy. From the altered Au(L_α/L_β)-ratio = 0.85, a Cu-thickness of about 10 μm wascalculated.

An quite similar mask was analyzed at the "Museo Poli" (Fig. 15). Following results were obtained:

• Front side: Au = (75 ± 2)%; Ag = (22 ± 2)%; Cu = (2.5 ± 1)%;

• Rear side: Au = (63 ± 3)%; Ag = (26 ± 3)%; Cu = (11 ± 2)%;

• Left eye: Ag + small quantities of Au and Cu; Right eye: Ag + small quantities of Au and Cu.

It appears sufficiently clear that the composition of the two heads is, within the experimental errors, quite similar. The only difference lies in the composition of the eyes: the right one, from the Sipán Museum, is mainly composed of Cu, the other one, from the Poli Museum, is on Ag. Possibly, the first eye is not original.

4.3.2 Gilded Copper: Analysis and Thickness Measurement of Gilding

Only a few analyzed objects from the "Tumbas reales de Sipán" are surely on gilded copper. They were identified by the presence of copper alone, in some analyzed areas, and by the deteriorated surface. In

many cases it was also possible to clearly determine the Au-leaf thickness from both Cu (K_α/K_β) and (N_{Au-L}/N_{Cu-K})-ratios. On gilded copper are the earrings S/T1: O: 1 and O: 2, where only the internal rings and the central heads are on gold, while the external sides are on gilded copper show the X-ray spectra. From one of the earring it could be deduced that the gilding thickness is (1.5 ± 0.5) µm.

A beautiful mask clearly on gilded copper is shown in Fig. 17. The gilding composition of this object is: Au~97.5%, Ag~2.5% (Cu, if present in the gilding, can not be determined, because it is presented at high concentration below the gilding). The gilding thickness was measured to be ~ 0.5 µm.

The thigh protector S/T3-Cu: 71, with "iguanas" is also possibly on gilded copper. The X-ray spectrum shows a very high content of copper, and traces of gold. No silver is present. The object could be on copper, with traces of gold; however, this hypothesis seems to be unlikely. If the object would be on gilded copper, then the gold thickness would be 0.1-0.2 µm.

Then several sheets and fragments of sheets on gilded copper were analyzed. They are characterized by a Cu (K_α/K_β) = 6.1 ± 0.1, corresponding to a gilding thickness of (1.2 ± 0.5) µm. From the ($Au-L_\alpha/Cu-K_\alpha$) = 0.1 ratio it turns out, however, a value (0.5 ± 0.1) µm.

Also object code S/T1-O: 6 (earring with the figure of a deer, has the external ring and the eye of the fox on gilded copper. Following average values were obtained:

Gilding thickness of the external ring: (2.5 ± 0.5) µm; Au = (90 ± 2)%; Ag = (10 ± 2)%; Cu-concentration in gold is assumed to be Cu = 0.

The eye has a similar composition as the ring, with a gilding thickness of (2.2 ± 1) µm.

It is not easy to give mean values of the gilding thickness; an approximate value of (1.5 ± 0.9) can be finally calculated. The gilding is possibly made with high carat gold.

Fig. 15   Golden mask from the Museum E. Poli; this mask is quite similar to the Sipan mask shown in Fig. 2.
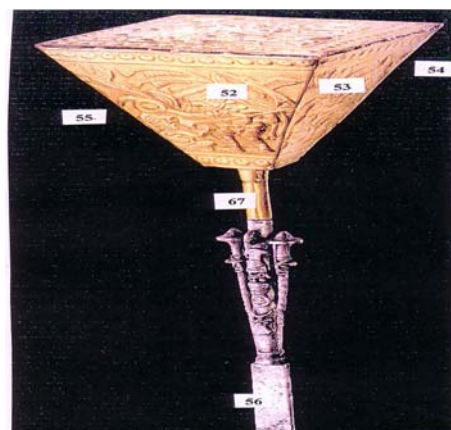

Fig. 16   Command stick of the "Señor de Sipán, on gold, with a support on silver Code S/T1-O: 15). After Ref. [7], with permission. The average composition of gold is: Au = 72%, Ag = 25%, Cu = 3%. Analyzed areas are shown.

Fig. 17   Mask made of gilded copper from the tomb n. 3 of "tumbas reales de Sipán" Areas relatively free from Cu-compounds have been analyzed. A gilding thickness of ~ 0.6 µm was determined.

In order to precisely measure the typical thickness of the gold layer and its chemical nature, some micro-fragments were taken from some artefacts found during the archaeological excavation of the "Tumbas reales de Sipán" and studied by means of SEM-EDS and OM. The results are shown in Figs. 18 and 19.
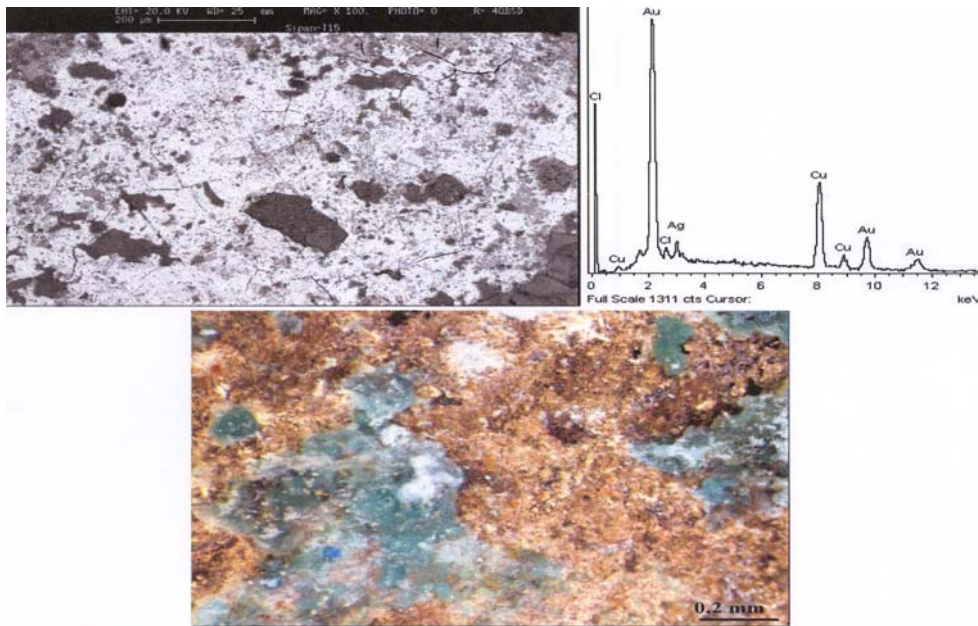

Fig. 18   SEM image, ED spectrum and optical micro-graph of the surface of a gilded object from the "Tumbas Reales de Sipan". The thin coating is composed by gold (95%) and silver (5%). The presence of copper comes from the substrate, and corrosion products are also shown.
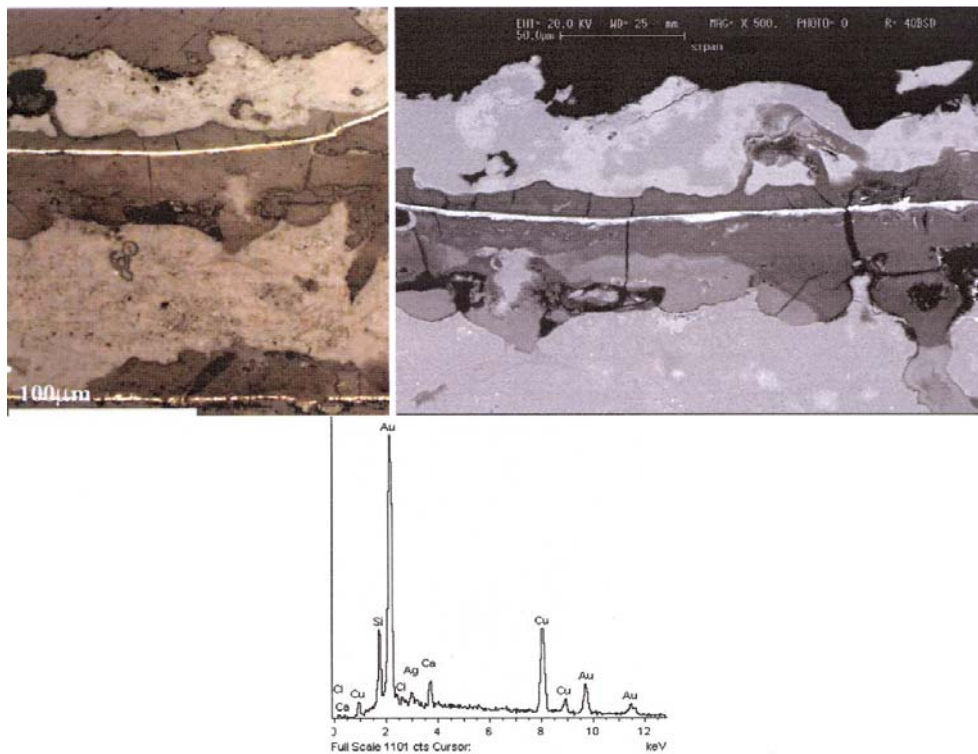

Fig. 19   SEM-image, ED spectrum and optical micro graph of a cross section of a gilded object from the "Tumbas Reales de Sipan". The thickness of coating is about 2 μm and the gilding is composed of gold (95%) and silver (5%). Copper comes from the substrate, and corrosion products and elements from the soil are also visible.

The SEM image, ED spectrum and optical micro-graph of figure 18 shows the surface morphology and the chemical nature of the gold layer present on an object from the "Tumbas reales de Sipán". The thin coating is composed by gold (95 wt%) and silver (5 wt%). The presence of copper from the substrate and of corrosion products is also disclosed by the SEM-EDS data.

The SEM image, ED spectrum and optical micro-graph of the cross section of a gilded object from the "Tumbas reales de Sipán" are shown in Fig. 19. The thickness of coating is about 2 microns and it is composed by gold (95 wt%) and silver (5 wt%). The presence of copper from the substrate and of corrosion

products including elements from the soil is also disclosed.

4.3.3 Tumbaga Average Composition and Gold Thickness Measurement

The majority of the gold alloys from the "Tumbas reales de Sipán" are on tumbaga, which behaves in a similar manner as gilded-Cu for EDXRF-analysis. As explained in Section 3, from the X-ray spectra the "gold-equivalent" surface thickness can be determined from Cu-K_α/K_β and from (N_{Au-L}/N_{Cu-K})-ratios. Table 6 shows the Au-thickness. Concerning the composition of a tumbaga, it is very difficult to give reliable values, because, as explained above, the concentration of Au decreases going inside from the surface up to about

Table 6 Tumbaga gold objects, and "Au-equivalent" thickness, derived from various methods (see Section 3).

Object description and code	(N_{Au-L}/N_{Cu-K})-ratio	Au-thickness (0.1/0.2)(μm)	$(Cu$-$K_\alpha/K_\beta)$	Au-thickness (0.4/0.6)(μm)
Earring with a warrior S/T1-O:2 *(external ring, internal circle)	2.1 ± 0.5	3.6	-	-
Earring with a deer S/T1-O:6*(eye of the deer, external spheres))	1.4 ±1	2.9	-	-
Chin protector S/T1-0:7	1.5 ± 0.5	3	5.4	1.4
Nose decoration S/T1-0:8	0.86 ± 0.05	2.4	5.2	1.8
Nose decoration S/T1-0:9	1.24 ± 0.1	2.7	4.8	2.6
Brain container S/T1-O:11	1.2 ± 0.2	2.7	5.2	1.8
Right eye protector S/T1-0:12	1.04 ± 0.05	2.5	-	-
Nose protection S/T1-0:13	1.1 ± 0.05	2.6	-	-
Convex nose protector S/T1-0:14	2.6 ± 0.3	4.4	-	-
Necklace with peanuts S/T1-O:17* (areas 86,88)	2.0 ± 0.6	3.5	5.4	1.4
Left eye protector S/T1-0:18	0.65 ± 0.05	1.7	5.5	1.2
Tooth protection S/T1-0:23	1.01 ± 0.05	2.5	-	-
Small rattle with a figure of bat S/T1-O:26	0.6 ± 0.1	2.0	5.3	1.6
Crown in the form of half moon S/T1-O:28	1.1 0.2	3	5.3	1.6
Necklace with 72 spheres S/T1-0:29	1.76 ± 0.2	3.3	-	-
Thigh protector S/T1-O:	1.1 ± 0.2	2.6	4.8	2.6
Thigh protector on Au and Ag S/T2-O:5 *	0.76 ± 0.05	2.7	4.9	2.4
Small rattle with figure of a bat S/T3-O:8	2.6	3.8	-	-
Small rattle with a figure of bat S/T3-O:9 *	2.6 ± 0.6	3.8	5.2	1.8
Big rattle with figure of a bat S/T3-O:10 (Fig. 20)	0.85 ± 0.3	2.4	5.5	1.2
Earring with figure of animal S/T6-O:1A (golden areas)	1.4	2.7	-	-
Earring with figure of animal S/T6-O:1A (eye in form of a star)	-	-	$Au(K_\alpha/K_\beta) = 0.98$	6 ± 2.5
Earring with figure of animal S/T6-O:1B (golden areas)	1.6	3.2	-	-
Earring with figure S/T6-O:4A (except external decoration)	1.5	3.0	-	-
Cylindrical support for earring S/T6-O:4A	2.0	3.5	-	-
Earring with figure S/T6-O:4B *(external decorations)	1.6 ± 0.9	3.1	-	-
Earring with figure of animal S/T6-O:6	1.4	2.7	-	-
Total mean value	**1.4 ± 0.6**	**2.9 ± 0.6 μm**	**5.2 ± 0.4**	**1.8 ± 0.5 μm**

* Presence of traces of zinc.

5-10 μm, while Cu-concentration increases in a parallel manner [28]. Apart from these difficulties, objects on tumbaga analyzed in many different areas showed a high level of homogeneity.

Finally, it may be observed that all these tumbaga objects contain relatively high concentration of Ag, not less than 10%. Considering that about 50% of Cu counts comes from the "gold" layer, a mean composition of the tumbagas reported in Table 6, i.e., Au = 70 ± 9, Ag = 13 ± 4 and Cu = 17 ± 8 may be calculated.

4.3.4 Silver Objects

EDXRF-analysis of silver objects from the Royal Tombs of Sipán is shown in Table 7. From these results it may be observed that the silver content is relatively high, and that this silver systematically contains gold.

4.3.5 Copper Objects

Only parts of a few objects from the royal tombs of Sipan are on copper. All are composed of about 99% Cu, and traces of Fe and/or Ni. At the contrary, several objects on copper were analyzed, from the same culture, from the Brüning Museum in Lambayeque [57]. Their composition is shown in Table 8.

4.3.6 Turquoise

Many of the gold objects include turquoise, which is a hydrated phosphate of aluminium and copper, i.e., $CuAl_6 (PO_4)_4(OH)_8 \, 4(H_2O)$. According to this formula, it comprises of three primary ingredients copper, aluminium and phosphor. Turquoise has got occasional presence of zinc, iron and chromium as impurities, resulting in deviation from the blue colour; iron presence leads to a green colour, while zinc changes the colour to yellowish [58].

Results on Sipán turquoise analysis are shown in Table 9. There is a systematic presence of Fe and Zn, at an average concentration of 10% and 8.5% respectively.

4.3.7 Weldings

Welding areas are often visible in the analyzed Moche artefacts. Welding areas were analyzed by

Table 7 Composition of silver objects. Also the presence of minor elements is indicated. Remarkable is the presence of Br in object n. 24.

Object n. and measurement n.	Ag (%)	Cu (%)	Au (%)	Minor elements
Command stick S/T1-O:12 (Ag-stick)	88	6.5	5.5	-
Necklace S/T1-O:14	96	3.5	0.5	-
Necklace with peanuts (Fig. 21) S/T1-O:17	92	4	4	In 1 point relevant Zn
Silver knife S/T1-O:19 (area 32)	88	10.4	1.6	Zn
Silver knife S/T1-O:19 (area 33)	95	4	1	Zn
Silver knife S/T1-O:19 (area 34)	93	5	2	Zn
Convex earring S/T1-M:12 (area 36)	96	3	1	Zn
Convex earring S/T1-M:12 (area 37)	99	5	1	Zn
Convex earring S/T1-M:12 (area 38)	98	1.7	0.3	Zn
Thigh protector on Au-Ag S/T2-O:5 (area 127)	84	10	2	Zn, Br (4%)
Eye of mask MB-09398 (Figure 2)	93	5	1.7	Br
Mean value	**93 ± 5**	**5 ± 2.5**	**2 ± 1.5**	

Table 8 EDXRF-analysis of copper objects from the Brüning Museum [57].

Object	Cu (%)	As (%)	Other metals
Knife	98	2	
Trapezoidal object	98.5	1.5	
Object in form of a wheel	100	-	-
Object in form of a wheel 2	100	-	Ni(traces)
Large object	100	-	-
Plate with textile	100	-	-

collimating the X-ray beam on the object. However, in some cases larger areas were excited, and also "disturbing" elements were detected.

In the thigh protector on gold and silver alloys, the two parts are soldered with copper; in the mask of Fig. 2 the front and rear side of the head were welded with a copper-silver alloy; in the case of the small peanut the soldering is made with silver; in the case of the second

Fig. 20 Big hand rattle on tumbaga (Code S/T3-O:10). After Ref. [7], with permission. The average composition is: Au-56%, Cu=35%, Ag=9%. The ratio N_{Au}/N_{Cu} = 0.85 corresponds to a Au-thickness of 2.7 μm A fragment of this object was analyzed with RBS analysis by Saettone et al. (33).
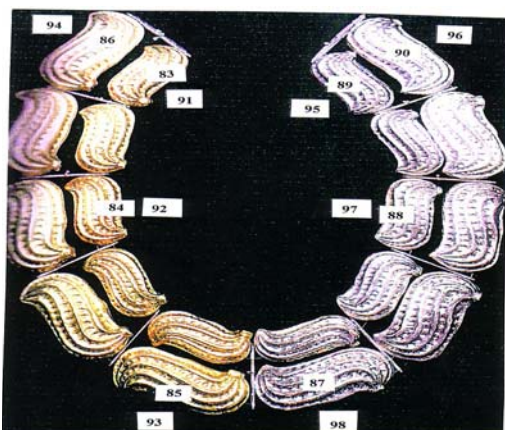

Fig. 21 Necklace with peanuts beads on gold and silver (S/T1-O:17). After Ref. 7, with permission, the average composition of the silver beads is: Ag = 92%, Cu = 4%, Au = 4%. The peanuts on the left are on tumbaga, with a mean thickness of about 2.5 μm.

small peanut the soldering is made with copper.

4.3. 8 Complex Objects

Many objects from the "Tumbas Reales de Sipán" are very interesting also for the variety of composition. By observing for example the beautiful with the figure of a warrior (Fig. 22), it is composed of various parts on gold, tumbaga and turquoise. The different composition of the various parts of the object is shown in Table 10.

4.3.9 Gilded Copper

Following objects were analyzed and identified as composed of gilded copper:

(1) Ear ring: This object is very damaged, and was analyzed in five different areas where the gold is still visible. The X-ray spectrum shows a high content on copper, and low quantities of Au. No Ag is present. This ear ring is therefore on gilded copper, with almost pure copper covered with a sheet of almost pure gold with a thickness, deduced from the Au-L/Cu-K ratio of about 0.4 μm;

(2) Nose decoration, apparently on gold: This object was analyzed in seven different areas, and showed the typical X-ray spectrum of tumbaga, i.e. high quantities of Cu and Au, with a Au-L/Cu-K of about 2.3, corresponding to an equivalent gold thickness of about 3.5 μm;

Table 9 Metal concentration in turquoises present in various Sipán objects, with the condition Cu+Fe+Zn=100. Object description, measurement area and object code are also given.

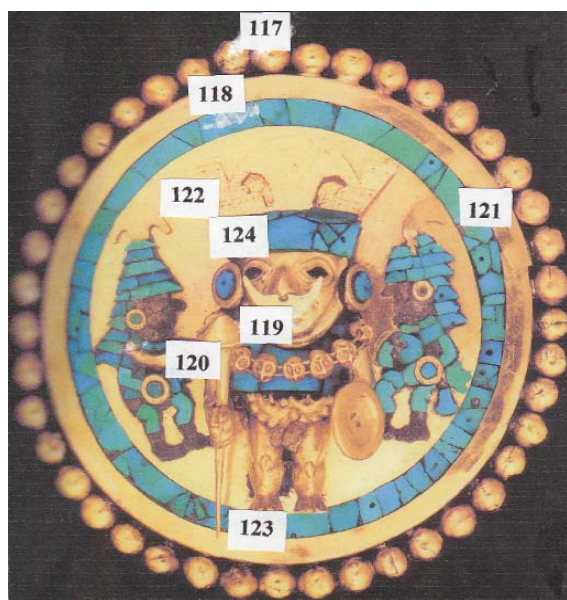| Object n., meas. n., code and name	Cu (%)	Fe (%)	Zn (%)	Trace elements
Earring with warrior (area124) S/T1-O:2	75	10	15	Sr
Earring with gosling (area105) S/T1-O:3	77	17	6	-
Earring with deer (area112) S/T1-O:6	91	3	6	-
Knife (area28) S/T1-O:19	79	12	9	-
Earring with Au-heads (area144) S/T2-O:1	73	17	10	-
Nose decoration (area138) S/T2-S:1	87	7	6	Sr
Nose decoration (area139)	79	11	10	-
Nose decoration (area149)	76	16	8	-
Earring with warrior (area154) S/T6-O:1	82	7	11	-
Earring with warrior (area156)	91	5	4	Sr
Earring with fox (area160) S/T6-O:4	76	8	16	Sr
Earring with fox (area163)	80	14	6	-
Earring with warrior (area171) S/T6-O:1B	80	7	13	-
Earring with warrior (area173)	90	3	7	-
Earring with fox (area179) S/T6-O:4B	85	9	6	-
Earring with fox (area182)	83	11	6	-
Earring with deer (area198) S/T6-O:6	85	9	6	-
Mean value	**81.5 ± 6**	**10 ± 4**	**8.5 ± 3.5**	

Fig. 22   Earring with the figure of a warrior (S/T1-O:2), composed of gold, tumbaga and turquoise. After Ref. [7], with permission.

Table 10   Composition of the various parts of the earring shown in Fig. 22.

Analyzed area	Au (%)	Cu (%)	Ag (%)
117-gold	78.5	5	16.5
118 and 121–tumbaga	Au-thickness=3.6 μm		
119 – gold	66.5	15.5	18
120- gold	70.5	9.5	20
122 – tumbaga	Au-thickness=3.6 μm		
123 – gold	79.5	7	13.5
124 – turquoise			

(3) Feline head: This object was analyzed in five different areas, and the X-ray spectra show the presence of high concentrations of Cu, and traces of Au (in three areas). Where Au is present, an approximate gilding thickness of 0.15 μm.

(4) Owl crown: This object was analyzed in four different areas, where the gold is still visible. The X-ray spectrum shows a high content of Cu, and low quantities of Au, with a mean ratio Au-L/Cu-K = 0.05, corresponding to about 0.35 μm gilding thickness. Silver is absent.

4.3.10 Silvered Copper

Nose decoration: This object was analyzed in four different areas. The X-ray spectra showed the presence of high quantity of Cu and Ag, and traces of Fe, Au and Br.

4.3.11 Bronzes and Copper Alloys from Huaca Rajada [59]

(1) Men-priest with owl aspect: The X-ray spectrum shows the presence of high quantities of Cu, and low quantities of As. This last varies in concentration between 0.4% and 2%, with a mean value of 1%;

(2) Lance: This lance was analyzed in three different areas, showing an X-ray spectrum composed of copper only. This object is therefore composed of almost pure copper;

(3) Knife: This object was analyzed in four different areas. It showed to be composed of Cu with relatively high quantities of as (from 2.5% to 8%, with a mean value of 6%);

(4) Sea-shell: This object is composed of pure Cu.

4.4 Alloys from the Museum of Sican

About 20 objects from the Museum of Sicán were analyzed, the majority of which on gilded copper; others are on gold, tumbaga, silver and copper alloys.

4.4.1 Objects Made of Gold

• Ornamental object MMS 51: Au = 62%, Cu = 7%, Ag = 31%;

• Tweezers in form of a "tumi": Au = 58%, Cu = 7%, Ag = 35%;

• Tweezers in form of a bird: Au = 65%, Cu = 3.7%, Ag = 30%, Fe = 1.3%.

Following mean values were calculated:

Au = (62 ± 4)%; Ag = (32 ± 3)%; Cu = (6 ± 2)%

4.4.2 Objects Made of Gilded Copper

• Object in form of a fan composed of various sheets: The concentration of the gilding is: Au = 79%, Ag = 19.5%; the gilding thickness is of about 5.5 μm. Several corrosion areas are present, showing a composition of about Cu = 98%, Fe = 2%;

• Disk composed of many sheets: The concentration of the gilding is: Au = 62.5%, Ag = 37.5%; the gilding thickness is of about 5 μm. Several corrosion areas are present, showing a mean composition of Cu = 99.5%, As = 0.5%;

• Other disk composed of many sheets (MNS-149): The concentration of the gilding is: Au = 61.5%, Ag = 38.5%; the gilding thickness is of about 4.5 μm;

• Mask "las ventanas": The concentration of the gilding is: Au = 67.5%, Ag = 32.5%; the gilding thickness is of about 2 μm. Several areas are corroded, with following mean composition: Cu = 96%, As = 4%.

• Vase "las ventanas": The concentration of the gilding is: Au = 71%, Ag = 29%; the gilding thickness is of about 2 μm. Area n.102 is highly corroded, showing the prevailing presence of Cu, and ratios $Au(L_\alpha/L_\beta) \sim 0.45$ and $Au(L_\alpha/L_\gamma) \sim 2$, corresponding to a silver thickness of about 20 μm (however, a restoration process with Ag may not be excluded). Areas n. 103 and 104 show the presence of Cu with traces of Br and As;

• Fragments composing a highly corroded disk: The concentration of the gilding is: Au = 62%, Ag = 38%; the gilding thickness is of about 2 μm;

• Sheet in form of a L, highly corroded: The gilding thickness is of about 2 μm;

• 2nd sheet in form of a disk, highly corroded: The gilding thickness is of about 1.5 μm.

4.4.3 Objects Made of Tumbaga

Several objects from the Museum of Sicán are of uncertain composition; they could be on gilded copper or on tumbaga. In fact, the gilded copper objects are identified because of the altered $Cu(K_\alpha/K_\beta)$-ratio, and because of the presence of highly corroded areas almost on pure copper (Section 4.2.2.). In other cases the ratio $Cu(K_\alpha/K_\beta)$ is altered, but no corroded areas were detected. These objects are possibly composed of tumbaga. Among them:

• Vase: The concentration of the gilding is: Au = 66%, Ag = 34%; the gilding thickness is of about 6 μm. Anomalous is the area 34, which seems to be on silvered gold, or restored;

• Vase twin of the previous one: The concentration of the gilding is: Au = 66%, Ag = 34%; the gilding thickness is of about 6 μm;

• Plumes composed of various vertical sheets (MNS-158): The concentration of the gilding is: Au =

65%, Ag = 35%; the gilding thickness is of about (4.5-5) μm;

• Sicán golden mask (Fig. 23), which is the most important object possibly on tumbaga.

More specifically, concerning the analysis of this mask, following was deduced [60] (Table 11):

(1) The Sheet and Almost all Pendants (areas 5-26, excluding areas 16, 17 and 22) are on tumbaga and have similar composition and "equivalent" surface gold thickness; the mean value of this last, determined on the basis of Cu (K_α/K_β), $(Au-L_\alpha/Cu-K_\alpha)$ and $Au(L_\alpha/L_\beta)$-ratios is: $d_{Au} = 3.1 \pm 0.4$ μm, 3.0 ±0.5 μm and 4.5±0.8 μm respectively. A mean value of 3.4 ± 0.4 μm may be calculated, in the hypothesis of a pure gold gilding.

The Ag (K_α/K_β)-ratio was measured in areas 5−30 and is Ag $(K_\alpha/K_\beta) = 6.9 \pm 0.5$, and in area 20 (long time measurement) is Ag$(K_\alpha/K_\beta) = 7.4 \pm 0.4$, which is compatible with a tumbaga alloy;

(2) The nose (areas 3 and 4) has a different equivalent X-ray spectrum and, therefore, different gold thickness and composition. It was perhaps superimposed to the mask; the gold thickness determined on the basis of $(Au-L_\alpha/Cu-K_\alpha)$ and Cu(K_α/K_β)-ratios is: $d_{Au} = 4.0 \pm 0.5$ and 6.1 ± 2 μm. A mean value of $d_{Au} = 4.4 \pm 0.7$ μm can be accepted;

(3) Pendant (area n. 17) appears different from the other pendants, i.e., thickness $d_{Au} = 2.5$ μm and following composition in the first 4-5 μm: Au = 26%, Ag = 6%, Cu = 68%;

(4) Clamps (areas n. 16, 28 and 29) are on silvered copper; Equations similar to Eqs. (1), (2) and (3) may be deduced. A mean silver thickness was determined as: $d_{Ag} = 3.8 \pm 0.4$ μm (4.5 ± 1.5 μm from the ratio Cu(K_α/K_β) and 3.4 ± 0.3 from the ratio Ag-K_α/Cu-K_α); the EDXRF spectrum of the clamp n. 28 is shown in Fig. 4; Au-traces are also visible;

(5) Clamps (areas n. 22 and 27) are on gilded copper, with a mean Au-thickness value of $d_{Au} = 1.9$ μm (2.0 μm from the ratio Cu(K_α/K_β) and 1.9 μm from the mean value of the ratio Au-L_α/Cu-K_α);
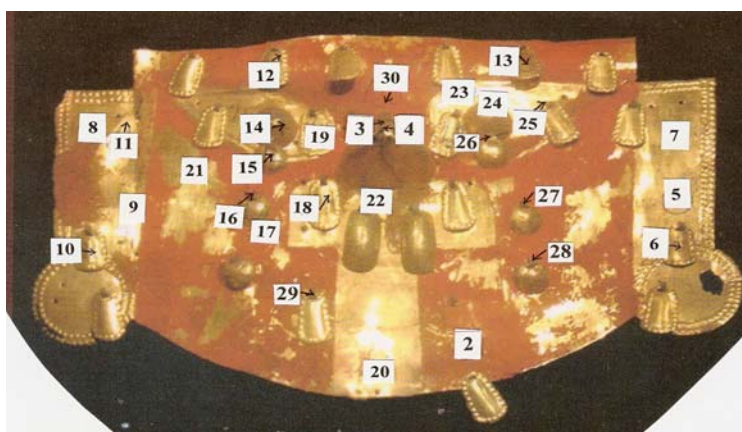
Fig. 23 Mask made of tumbaga (with lower probability of gilded copper) from the Museum of Sicán, showing the analyzed areas. The mask has following approximate size: maximum width = 35 cm; maximum height = 22 cm; the back side has the same aspect as the front side, but no areas have been analyzed, because of access difficulties for the equipment.

Table 11   Results of the EDXRF-analysis on the gold mask shown in Fig. 23 (*).

Measurement N. (Fig. 21)	Au (%)	Cu (%)	Ag (%)	Au-thickness via Cu-Kα/Kβ-ratio	Au-thickness via Au-Lα/Cu- Kα-ratio
2 (area covered with cinnabar)	−	−	−	PS	−
3 (nose)	49	39	10	3.8 ± 0.5	2.8 ± 0.3
4 (nose)	53	36	9	4.3 ± 0.5	3.4 ± 0.3
Nose mean value (3−4)	*51*	*37.5*	*9.5*	*4.0 ± 0.3→3.8 ±1 µm*	*3.1 ± 0.2→5.9 ± 1 µm*
5 (clean area)	31	59	8	4.8 ± 0.5	1.15 ± 0.3
6 (pendant)	37	53	8	5.0 ± 0.5	1.6 ± 0.3
7 (clean area)	31	60	7	5.0 ± 0.5	1.2 ± 0.3
8 (clean area)	33	58	7	4.9 ± 0.5	1.4 ± 0.3
9 (clean area)	32	58	8	4.8 ± 0.5	1.3 ± 0.3
10 (pendant)	32	59	7	5.4 ± 0.5	1.3 ± 0.3
11 (clean area)	34	56	8	4.9 ± 0.5	1.5 ± 0.3
12 (pendant)	35	55	8	5.3 ± 0.5	1.6 ± 0.3
13 (pendant)	33	59	6	5.1 ± 0.5	1.3 ± 0.3
14 (pendant)	37	54	8	5.2 ± 0.5	1.7 ± 0.3
15 (pendant)	29	62	7	5.1 ± 0.5	1.1 ± 0.3
16 (area with cinnabar)	−	−	−	5.2 ± 0.5	~0.16
17 (clean area)	25	67	6	5.7 ± 0.5	0.85 ± 0.3
18 (pendant)	35	55	8	5.5 ± 0.5	1.45 ± 0.3
19 (pendant)	35	54	9	4.8 ± 0.5	1.5 ± 0.3
20 (clean area)	35	55	8	5.1 ± 0.5	1.4 ± 0.3
21 (clean area)	33	57	8	5.7 ± 0.5	1.3 ± 0.3
23 (pendant)	36	55	7	4.9 ± 0.5	1.5 ± 0.3
24 (pendant)	34	57	7	4.8 ± 0.5	1.4 ± 0.3
25 (pendant)	34	57	7	PS	1.4 ± 0.3
26 (clamp?)	PS	PS	PS	PS	3.8 ± 0.5
Mean value (no areas 3, 4, 16, 17,26)	*34 ± 3*	*57 ± 5*	*7 ± 1.5*	*5.1 ± 0.3→1.8 ± 0.9 µm*	*1.35 ± 0.2→2.9 ±0.7 µm*
22 (clamp) on gilded Cu?	29	47	22	6.0 ± 0.5→0.2µm	0.38 ± 0.04→0.8µm
27 (clamp as 22)	−	−	−	6.2 ± 0.5 →0	0.4 ± 0.05→0.8µm
28 (clamp on silvered Cu)	−	−	Ag/Cu = 0.11	5.3 ± 0.5→4µm	0.04
29 (clamp as 28)	−	−	−	6.1 ± 0.5→2.2µm	0.035

(*) The value of Au(%)+Cu(%)+Ag(%) = 98, because in all areas there is also As ~ 1.7% and Fe < ~ 0.5%.

(6) Clamp (area 30) is covered by cinnabar (HgS_2), and gold thickness and composition could not be determined;

(7) Arsenic is present in almost all areas (with the exception of lamina of area 9) and it is clearly related to copper; As(%) ~ (0.03 ± 0.01) Cu(%) corresponding to a concentration of As = 1.7 ± 0.5%); the "internal" alloy is, therefore, arsenical copper;

(8) Iron is present in many areas; at very low levels in the main sheet, in the pendants and in the nose (<0.5%), at higher concentration values in clamps n. 16, 25, 26, 27 and 28 (relative concentration with respect to Cu = 6, 7, 10, 8 and 5, respectively);

(9) The red pigment partially covering the mask is cinnabar.

4.4.4 Objects Made of Silver

Only one object is made of silver: brooch in form of a monkey, with following composition:
Ag = 94%, Cu = 3.7%, Au = 0.5%, Pb = 0.8%, Br = 1%.

4.4.5. Gilded Silver or Tumbaga-Silver

There are no gilded silver objects (or tumbaga-silver) among those from the Museum of Sipán but there are several in the Museum of Sicán and in a small object in form of a ring from the National Museum of Lima. This last case, which is very significant, is characterized by a low value of Ag(K_α/K_β) = 5.45 ± 0.3, corresponding

to a gilding thickness of (6.5 ± 1.5) µm and Au(L_α/L_β) = 0.95 ± 0.3.

4.4.6. Silvered Gold

In spite of the strangeness, there is almost one example of silvered gold among the alloys from the Museum of Sicán, which is clearly visible because of the extremely altered Au(L_α/L_β) –ratio = 0.48, and Au(L_α/L_γ)–ratio = 3.15.

A similar behaviour was observed in several areas of another vase from the Museum of Sicán, called "las ventanas".

4.4.7 Objects Made of Copper

A few objects or part of objects are on copper; the results are summarized in Table 12. Sicán copper alloys are characterized by the systematic presence of arsenic and iron; possibly, arsenopyrite was also employed.

5. Discussion

5.1 Gold Alloy Artefacts

Native gold contains a moderate proportion of silver (up to about 30%) and a low proportion of copper (up to about 5%). Gold alloys of moderate to high fineness do not corrode, and therefore the problem of their analysis is not complicated by the presence of corrosion products. Very poor gold alloys, especially

Table 12   Copper composition.

Object and area	Cu (%)	Fe (%)	As (%)
Sheet MMS-216	96.7	2.4	0.9
Corrosion area of the object in form of a fan	97	3	-
Other corrosion area of the object in form of a fan	84.6	15	0.4
Corrosion area of the object in form of a disk	98.9	1	0.1
Other corrosion area of the object in form of a disk	98.7	1	0.3
Corrosion area of disk MMS-149	98.5	1	0.5
Other corrosion area of disk MMS-149	98.2	1.4	0.4
Corrosion area of mask "las ventanas"	96.6	1.4	2
Other corrosion area of mask "las ventanas"	97.4	0.6	2
Corrosion area of the sheet in form of L	97.3	1.5	1.2
Other corrosion area of the sheet in form of L	97.4	0.6	2
Corrosion area of the sheet in form of a disk	98.7	1	0.3
Other corrosion area of the sheet in form of a disk	98.5	0.5	1
Mean value	**98±1**	**1.2±0.5**	**0.8±0.5**

when the alloying metal is copper, may corrode under natural conditions [61].

A large number of gold artefacts were analyzed, in the form of laminated gold, from the Chavin culture (objects from the Museum Poli in Lima and Museo Municipal in Piura) from the Vicús and Frias culture (Museo Municipal of Piura), from the Moche culture (Museo Tumbas Reales de Sipán) and Sicán culture (Museum of Sicán). Following considerations may be deduced:

(1) Chavín: 4 objects from the Chavín culture were analyzed; they are characterized by a variable Au and Ag concentration (Au from 60% to 90%, Ag from 10% to 40% approximately) and a very low Cu-concentration (from 0.1% to 3.3%) demonstrating that Cu was not added intentionally;

(2) Vicús and Frias: 13 objects were analyzed; concentration of all components is very variable:
- Au from 60% to 90%;
- Ag from 5% to 25%;
- Cu from 2% to 33%;

(3) Moche: about 20 objects were analyzed; concentration of all components is variable, but a mean value can be calculated:
- Au = (70 ± 7)%;
- Ag = (20 ± 4)%;
- Cu = (10 ± 5)%.

Objects from different tombs (tumba N.1 del Señor de Sipán, N.2 del Sacerdote, N. 6 other tombs) show the following:
- Tomb n. 1: Au = 68.6%, Cu = 8%, Ag = 23%;
- Tomb n. 2: Au = 69%, Cu = 8%, Ag = 23%;
- Tomb n. 6: Au = 75%, Cu = 10.5%, Ag = 14.5%.

Tombs 1 and 2 show a quite similar gold composition, while gold from tomb n. 6 seems to have a different composition.

The average concentration of all objects is: Au = 69.5 ± 7, Cu = 9.5 ± 5, Ag = 21 ± 7, corresponding to about 17 carats.

(4) Sicán: Gold from the Sicán culture showed following mean composition: Au = (62±4)%, Cu = (6 ± 2)%, Ag = (32 ± 3)%.

5.2 Copper-gold Tumbaga

(1) Vicús and Frias: From the X-ray spectra, only a limited area of the feline head, the sheet over the teeth, seems to be made on tumbaga;

(2) Moche: (a) Museo "Tumbas Reales de Sipán": Twenty objects were analyzed, which show a tumbaga like behaviour. Tumbaga gold was differentiated from poor gold from the altered $Cu(K_\alpha/K_\beta)$-ratio. In the case of tumbaga, the composition averaged over many points could be measured, and an equivalent "gold thickness". It should be observed that there is a great homogeneity of gold thickness measurements, resulting in the value d = 2.75 ± 0.4 μm. The average composition of the 21 objects concerning the first 4-5 μm involved in EDXRF-analysis is: Au = 57.5 ± 6, Cu = 30 ± 8, Ag = 12.5 ± 4. The number of these gold objects belonging to tombs 2, 3 and 6 is too limited to make any deduction. (b) Site Museum Huaca Rajada: Following object from the Museum "Huaca Rajada" was analyzed and identified as composed of gilded copper:

Nose decoration, apparently on gold: This object was analyzed in seven different areas,and showed the typical X-ray spectrum of tumbaga, i.e., high quantities of Cu and Au, with a Au-L/Cu-K of about 2.3, corresponding to an equivalent gold thickness of about 3.5 μm.

(3) Sicán: vase: The concentration of the gilding is: Au = 66%, Ag = 34%; the gilding thickness is about 7 μm:
- Vase twin of the previous one; the concentration of the gilding is: Au = 66%, Ag = 34%; the gilding thickness is of about 7 μm;
- Object in form of a fan composed of various sheets: The concentration of the gilding is: Au = 79%, Ag = 19.5%; the gilding thickness is of about 5.5 μm. Several corrosion areas are present, showing a composition of about Cu = 98%, Fe = 2%;
- Disk composed of many sheets: The concentration of the gilding is: Au = 62.5%, Ag =

37.5%; the gilding thickness is of about 5 μm. Several corrosion areas are present, showing a mean composition of Cu = 99.5%, As = 0.5%;

• Other disk composed of many sheets (MNS-149): The concentration of the gilding is: Au = 61.5%, Ag=38.5%; the gilding thickness is of about 4.5 μm;

• Mask "las ventanas"; the concentration of the gilding is: Au = 67.5%, Ag = 32.5%: The gilding thickness is of about 2 μm. Several areas are corroded, with following mean composition: Cu=96%, As=4%;

• Vase "las ventanas"; the concentration of the gilding is: Au = 71%, Ag = 29%; the gilding thickness is of about 2 μm. Area n.102 is highly corroded, showing the prevailing presence of Cu;

• Fragments composing a highly corroded disk: The concentration of the gilding is: Au = 62%, Ag = 38% ; the gilding thickness is of about 2 μm;

• Sheet in form of a L, highly corroded;

• Plumes composed of various vertical sheets (MNS–158): The concentration of the gilding is: Au = 65%, Ag = 35%; the gilding thickness is of about 6 μm.

5.3 Gilded Copper

Among the many analyzed objects not many are surely on gilded copper. The reason for that is the corrosion process that tends to destroy the gilding. For the same reason gilded copper objects are generally well visible, because of the many areas without any residual gold.

(1) Chavín: A complex of six heads were analyzed, which showed a very similar X-ray fluorescence spectrum, and an anomalous Cu (K_α/K_β) -ratio = 4.6 ± 0.3, corresponding to a Au-thickness of about 1.5 μm. This is confirmed by the Au(L_α/L_β)-ratio = 0.98, which corresponds to a Au-thickness of about 1 μm. However this situation could correspond to gilded Cu, but also to tumbaga. No damage was visible in the six heads.

(2) Vicús and Frias: No object was analyzed on gilded copper; only the area above the lips of the feline head shows a strange XRF-spectrum with a high Cu-content. The Cu (K_α/K_β)-ratio = 5.15 ± 0.5, and the

(AuL_α/CuK_α)-ratio = 0.33 demonstrate that this part of the feline head could be on gilded-Cu or on tumbaga, with a Au-thickness of 0.8-1.4 μm.

(3) Moche:

(a) Museum "Tumbas Reales de Sipan"

On gilded copper are the earrings N. 27, where only the internal rings and the central heads are on gold, while the external sides are on gilded copper. From the earring on the right, it could be deduced that the gilding thickness is (1.5±0.5) μm.

A beautiful mask clearly on gilded copper is shown in Figure 17. The gilding composition of this object is: Au~97.5%, Ag~2.5% (Cu, if present in the gilding, cannot be determined, because present at high concentration below the gilding). The gilding thickness was measured to be ~ 0.5 μm.

The thigh protector S/T3-Cu: 71, with "iguanas" is also possibly on gilded copper. The X-ray spectrum shows a very high content of copper, and traces of gold. No silver is present. The object could be on copper, with traces of gold; however, this hypothesis seems to be unlikely. If the object would be on gilded copper, the gold thickness would be 0.1-0.2 μm.

Then several sheets on gilded copper were analyzed. They are characterized by a Cu (K_α/K_β) = 6.1±0.1, corresponding to a gilding thickness of (1.2 ± 0.5) μm. From the $(Au-L_\alpha/Cu-K_\alpha)$ = 0.1 ratio it turns out, however, a value (0.5 ± 0.1) μm.

Also object N. 33 (earring with the figure of a deer) has the external ring and the eye of the fox on gilded copper. Following average values were obtained:

Gilding thickness of the external ring: (2.5 ± 0.5) μm

(b) Museum Huaca Rajada

Following objects from the Museum "Huaca Rajada" were analyzed and identified as composed of gilded copper:

• Ear ring: This object is very damaged, and was analyzed in five different areas where the gold is still visible. The X-ray spectrum shows a high content on copper, and low quantities of Au. No Ag is present. This ear ring is on gilded copper, with almost pure

copper covered with a sheet of almost pure gold with a thickness, deduced from the Au-L/Cu-K ratio of about 0.4 μm;

• Feline head: This object was analyzed in four areas; it is made of copper with traces of Au is some areas; the Au-thickness was measured as 0.15 μm;

• Crown with the figure of a monkey: This object was analyzed in four different areas, where the gold is still visible. The X-ray spectrum shows a high content of Cu, and low quantities of Au, with a mean ratio Au-L/Cu-K = 0.05, corresponding to about 0.35 μm gilding thickness. Silver is absent.

(4) Sicán: vase: The concentration of the gilding is: Au=66%, Ag=34%; the gilding thickness is about 7 μm:

• Vase twin of the previous one; the concentration of the gilding is: Au = 66%, Ag = 34%; the gilding thickness is of about 7 μm;

• Object in form of a fan composed of various sheets: The concentration of the gilding is: Au = 79%, Ag = 19.5%; the gilding thickness is of about 5.5 μm. Several corrosion areas are present, showing a composition of about Cu = 98%, Fe = 2%;

• Disk composed of many sheets: The concentration of the gilding is: Au = 62.5%, Ag = 37.5%; the gilding thickness is of about 5 μm. Several corrosion areas are present, showing a mean composition of Cu = 99.5%, As = 0.5%;

• Other disk composed of many sheets (MNS-149): The concentration of the gilding is: Au = 61.5%, Ag = 38.5%; the gilding thickness is of about 4.5 μm;

• Mask "las ventanas": The concentration of the gilding is: Au = 67.5%, Ag = 32.5%; the gilding thickness is of about 2 μm. Several areas are corroded, with following mean composition: Cu = 96%, As = 4%;

• Vase "las ventanas": The concentration of the gilding is: Au = 71%, Ag = 29%; the gilding thickness is of about 2 μm. Area n.102 is highly corroded, showing the prevailing presence of Cu;

• Fragments composing a highly corroded disk: The concentration of the gilding is: Au = 62%, Ag = 38%; the gilding thickness is of about 2 μm;

• Lamina in form of a L, highly corroded;

• Plumes composed of various vertical sheets (MNS–158): The concentration of the gilding is: Au = 65%, Ag = 35%; the gilding thickness is of about 6 μm.

5.4 Silver Alloy Artefacts

Silver objects from early civilizations are scarce, apparently because they were always made from the scarce native metal. At first, the nearly pure metal was used without the addition of any alloying metal. Later, its alloys with copper were used to a greater extent. Impurities of Fe, Pb, Sn, Ni, Au are often present [61].

Concerning the Chavín civilization, only one object was analyzed, which is made of gilded silver; the Ag composition is: Ag=98.1%, Cu ≤ 1.5%, Pb = 0.4%.

No object on Ag was analyzed from the Vicús and Frias cultures.

Five silver objects or part of objects from the Moche culture were analyzed, giving the following average concentration values: Ag = 92±4, Cu = 5±2.5, Au = 3 ± 1.5. Remarkable is the systematic, and relatively constant presence of gold in silver: Au/Ag = 0.31 ± 0.015.

Ag-objects from the Sicán culture showed following composition: Ag = 94%, Cu = 3.7%, Pb = 0.8%, Br = 1%.

5.5 Silver Based Tumbaga

Also in this case the Ag ($K_α/K_β$) and the Au($L_α/L_β$)-ratios may be evaluated. The use of silver-tumbaga in the pre-Columbian cultures of the north of Peru is not common. Following examples can be given:

Vessel from the Chavin culture (Museo E. Poli) is in very good conditions with the appearance of a gold vessel. Following ratios were determined from the X-ray spectra, with the Si-drift detector:

Ag($K_α/K_β$)-ratio = 5.8 ±0.2 →(1.0 ± 0.5 μm)

Cu($K_α/K_β$)-ratio = 4.5 ±0.5 →(2.0 ± 1 μm)

Au($L_α/L_β$)-ratio = 0.97 ± 0.02 →(1 ± 0.5 μm)

5.6 Copper Alloy Artefacts

The earliest useful metal objects in any region are nearly always of copper. Sometimes this is native copper of high purity. Often it is crude copper produced by smelting. Frequently the crude copper in use in early periods contained sufficient arsenic to harden the metal and make it more suitable for tools and weapons [61]. Also in the case of copper alloys, EDXRF-analysis is generally not reliable because of the almost invariable presence of corrosion products. However in the case of all analyzed artefacts, the copper is almost pure, and therefore the analysis should be considered reliable.

An object from the Chavín culture was analyzed, composed of six small heads on gilded copper. The Cu-composition is: Cu = 98.5%, Zn = 1.5%, Fe (traces), Pb (traces). No Cu objects were analyzed from the Vicús-Frias cultures.

Cu-objects from the Moche culture showed following composition: Cu ≥ 99%, traces of Fe and Ni. The Moche probably knew how to produce pure copper; the four analyzed copper samples show only the presence of nickel in two cases, at a concentration of about 1%, and traces of iron in two cases; no arsenic is present, which, at the contrary, was detected in all Sicán copper objects. Sicán Cu-objects showed following mean composition: Cu = 98%, Fe = 1.2%, As = 0.8%.

5.7 Artefacts Containing Turquoise

Turquoise is a copper based mineral. Among all analyzed objects, only in the "tumbas reales de Sipan" many gold or tumbaga objects contain turquoise. In this case turquoise was probably imported from Chile, because not present in the peruvian-region, all samples also contain relevant quantities of iron and zinc. Average composition of the Sipán turquoises is: Cu = (81.5 ± 6)%, Fe = (10 ± 4)%, Zn = (8.5 ± 3.5)%.

5.8 Artefacts Including Welding Areas

Welding of Sipán gold alloys is made of copper and of a copper-silver alloy.

5.9 Trace Elements [62]

With regard to detection of trace elements, it should be observed that no trace element can be detected, for elements with atomic number Z<20. Then it is difficult to detect trace elements, when their X-rays are close to X-rays of major elements. Concerning the analyzed pre-Columbian alloys, following trace elements were systematically (or sometimes) detected:

(1) Iron: This element is often present in the pre-Columbian alloys. However, Fe is always present at trace levels in the X-ray spectra, due to many reasons (X-ray tube body and window, collimators, filters and so on. Then, there is a partial overlap between Fe-Kα peak (6.4 keV) and Cu-Kα escape peak (6.26 keV). Finally, Fe is present in the soil, and its presence in the X-ray spectrum could derive from the interramento of the object;

(2) Nickel: This element is sometimes present in Sipán alloys; however, it is also a typical background element for Si-PIN detector. For this reason it was generally neglected;

(3) Zinc: This element was detected in the "complex of six heads" of Chavin culture (mean concentration = 1.7%), and it is also often detected in Sipán alloys; relatively high content of Zn were detected in the silver knife (S/T1-O: 19), in the silver convex earring (S/T1-O: 14) and in one point of the necklace with peanuts (S/T1-O: 17). At lower levels Zn was also detected in the earring with warrior (S/T1-O: 6), in some parts of the earring with gosling (S/T1-O: 3), in some parts of the earring with deer (S/T1-O9), and in some areas of object S/T1-O: 25;

(4) Arsenic: This element was never detected before the period of the Moche culture. It was detected in several Cu-objects from the Brüning Museum (concentration between 1.5% and 2%) and from the "Museo de Sitio de Huana Rajada" (concentration between 1% and 6%). It was also systematically analyzed in Sicán copper alloys. This element was never detected in Sipán alloys;

(5) Bromine: This element was detected at relatively high concentration in a few silver objects; in the thigh protector (S/T2-O: 5) (Br~4%) and in the silver eye of the mask (MB-09398) "human head" (Br~2%). At level of traces it is probably present in several other objects. It was also detected in the small Ag-heads from the Museum E. Poli, and in several Ag-objects from the Museum of Sicán;

(6) Strontium: This element is not a component of the alloy, and it was detected in a few turquoise samples;

(7) Mercury: Mercury, in form of cinnabar, is clearly visible and detected in several Sicán objects, and specifically in the mask. It was employed as cinnabar powder to give to these objects a red colour. Very high quantities of mercury were also detected in the alloy of a Huanuco mask analyzed in the "Museo Poli". No Hg was detected in all other samples at more than trace levels [63];

(8) Lead: Lead was not detected in any analyzed gold and copper object. This element was detected, at levels < 0.5% in a Chavin silver vessel and in several other objects of unknown origin from the Museum E. Poli (a knife and a brooch, both on silver);

(9) Platinum: There are indications of the presence of this element as impurity in several Sipán gold objects. However this element is difficult to detect and identify because its L-lines are close to those of Au. Only an enlargement of Au-Lβ may be expected for Pt-concentrations lower than 5% approximately, and this enlargement was observed in several cases.

6. Conclusions on the Evolution of Pre-Columbian Metallurgy Versus Time

It seems that the Chavin did not use to mix copper in the Au-alloy. Gold is only present in Au-alloys as in nature, associated to Au. Successively, all types of Au-Ag-Cu alloys were used by the populations of the north of Peru.

Silver is present in all cultures of the north of Peru at relatively high levels of purity: ~98% by the Chavin (associated to Cu and Pb); ~93% by the Moche

(associated to Cu and Au); ~94% by the Sican (associated to Cu, Au, Pb and Br).

Copper is present in all cultures of the north of Peru at high levels of purity: 98% by the Chavin (associated to Zn); >99% by the Moche (with traces of Fe and Ni); 98% by the Sican (with 1.2% Fe and 0.8% as).

There is no evidence of the use of gilded copper by the Chavin and by the Vicus-Frias; a few objects on gilded Cu from the Moche culture survived, having a very thin Cu-layer (<1 μm). At the contrary several objects from the Sican Museum are on gilded copper, with the characteristics that the Cu-layer is relatively thick (~5 μm).

It is not clear when tumbaga was employed for the first time; the complex of six small heads (attributed by E. Poli to the Chavin culture) could be on tumbaga, with an equivalent Au thickness of ~2 μm. Among the analyzed objects of the Vicus-Frias culture no-one is on tumbaga; only the layer over the teeth of the feline head (see Section 4.2.1) could be on tumbaga.

The Moche, at the contrary, made a very large use of tumbaga (see Section 4.3.3); many beautiful objects were on tumbaga, with a mean equivalent Au-thickness of ~2.5 μm.

Also the Sican knew how to make tumbaga; however their metallurgical ability was not at the level of the Moche; the mean equivalent Au-thickness is ~3-6 μm.

A vessel of the Chavin period, from the Museum Poli (see Section 4.1.2, seems to be on gilded silver (or silver-tumbaga), with an Au-thickness of about 1 μm.

Only one object, the nose decoration from "Huaca Rajada" (see Section 4.3.11) i.e., of Moche culture is on silvered copper; the silver thickness could not be determined.

Acknowledgments

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