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Gold and Silver joining technologies in the Moche Tombs "Señor de Sipán" and "Señora de Cao" jewellery

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ABSTRACT
About 200 gold and silver funerary ornaments from the Moche tombs "Señor de Sipán" and "Señora de Cao" were analyzed to determine their metallurgic characteristics. Of particular interest was the question about the gold-silver joining process. To this aim, following methods were employed, all based on the use of X-rays:
- energy dispersive X-ray fluorescence;
- transmission of monoenergetic fluorescent X-rays;
- radiography.
At least three joining methods were possibly identified:
- of gluing gold and silver sheets;
- of brazing using a proper solder;
- of using a mercury amalgam.

Section: RESEARCH PAPER

Keywords: EDXRF; radiography; soldering; welding; pre-Moche

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1. INTRODUCTION

On the north coast of present-day Peru developed between 1200 BC and 1375 AD approximately, various relevant civilizations. Among them the most important, from the point of view of metallurgical ability, was the **Moche** civilization (also called Mochica).

The Moche civilization flourished mainly in the Moche and Chicama valley (Figure 1), where its great ceremonial centres have been discovered, from around 100 BC to 600 A.D., producing painted pottery, gold-silver ornaments and beautiful tissues.

The Moche were known as sophisticated metal smiths, both in terms of their technology, and of 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" [1 , 2] and, more recently, when Regulo Franco Jordan discovered in 2005 the tomb of the "Lady of Cao" (Figure1) [3-6].

Figure 1. Map of the Moche territory, covering an area of about 50000 km^2, showing the Moche sites Loma Negra, Sipán and El brujo. The tomb of the lady of Cao is located in the “complejo el brujo”. (Courtesy of Fundacion Wiese).

In the late 1960, tombs rich of metals, attributed to the Moche, were discovered and located in a site that came to be known as Loma Negra, district of La Arena, Piura Province.

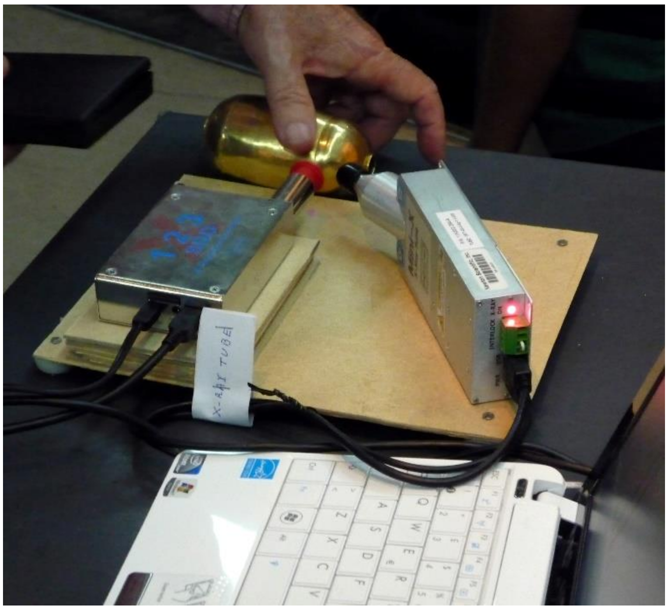

Figure 2. Energy-dispersive X-ray fluorescence portable equipment, composed of a Si-drift detector (on the right; 123 SDD: 450 µm thickness, 7 mm^2 area, and 125 eV energy-resolution at 5.9 keV) and an Ag-anode X-ray tube (40 kV, 100 µA maximum voltage and current) [10]. Electronics including bias supply and Multi-Channel Analyzer (MCA) are in the case of the detector; X-ray tube bias supply is in the case of the X-ray tube. A typical measurement takes 50–100 s.

Hundreds of objects attributed to Loma Negra were sold to US-collectors and finally partially transferred to the Metropolitan Museum of New York [7,8]. The site of Loma Negra was approximately dated about 2nd-3th Century A.D., possibly before the tombs of the lady of Cao (~300 A.D.) and of the lord of Sipán (~350 A.D.).

As explained in previous papers [9,10], the manufacturing technology of the Moche was very various and partially unknown, and, also after six campaigns of analysis, many questions remain open:

- why the Moche used to put relatively high quantities of Gold in the Silver sheets (tomb of Cao)?
- why the Gold artifacts from the tomb of Cao have approximately the same composition, differently from the Gold from the tomb of Sipán?
- How are joint together Gold and Silver sheets?

We can only make hypothesis on the first two questions; to answer to the last question a sub-millimetric EDXRF portable equipment was developed to carry out detailed millimetric measurements on the Au/Ag interface; further radiographs were carried out with special attention to the interfaces.

2. EXPERIMENTAL SET-UP

2.1. Energy dispersive X-ray fluorescence: characteristics and experimental set-up

Energy dispersive X-ray fluorescence analysis is able to quantify the composition of a gold, silver, or copper alloy by using, for example, standard samples of the same alloys (Section Quantitative analysis of gold and silver alloys). EDXRF-analysis is also able to detect, and qualitatively determine trace elements, when approximately present a level of 0.1 % or more. 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 depth and are generally valid in absence of surface enrichment phenomena (patina and ions migration processes).

For the measurements carried out in the Museum of Cao, the portable equipment was composed of a mini X-ray tube by AMPTEK (Bedford, MA, USA), which is characterized by a Ag anode and works at 40 kV and 200 µA maximum voltage and current, and a 123-Si-drift detector [11]. Bias supply and electronics of both X-ray tube and detector are located in the case of tube and detector, respectively; in such a manner, the equipment is extremely compact (Figure 2).

The Si-drift is a thermoelectrically cooled detector, with 450 µm thickness and 7 mm^2 area of the Si-crystal respectively, and a thin Be-window, of typically 12.5 µm thickness (0.5 mil) with about 125 eV energy resolution at 6.4 keV [11]. This detector has an efficiency of 97 %, 39 %, and 14 % at 10, 20, and 30 keV, respectively. The irradiated and analyzed area is of about 20 mm^2, when the object is at a distance of a few centimeters.

The X-ray beam intensity with a not collimated and not filtered X-ray tube is largely in excess for analysis of alloys. For this reason, the X-ray beam is collimated and filtered, also to better its ‘form’, and to partially monochromatize the X-ray beam. The object to be analyzed is positioned at 1.5–3.0 cm distance from both X-ray tube and detector. The measuring time ranges from about 50 s to about 200 s, mainly according to the sample composition and size.

Standard gold and silver alloys were employed for calibration and for quantitative determination of alloy composition.

To measure gilding thickness of gilded copper 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. Further, commercial gold leaves were employed (each Au-foil 0.125 µm thick) to simulate gilded copper or tumbaga, and silver foils (each Ag-foil 0.25 µm thick) to simulate the 'silvered copper' or 'Ag-tumbaga'. Also, calibrated Au-leaves were employed, and several gilded-copper samples with calibrated gilding thickness. Thick sheets of pure copper and silver were also employed.

2.1.1. X-ray spectrum of gold alloys

The final result of EDXRF – analysis of a sample is an X-ray spectrum containing a set of X-lines for each detectable element present in the analyzed object [12,13].
When K-shells are excited, four characteristic lines are emitted by each element: $K_{\alpha1}$, $K_{\alpha2}$, $K_{\beta1}$, and $K_{\beta2}$.

From a practical point of view, and because of the finite energy resolution of semiconductor detectors, the line combinations $K_{\alpha1} - K_{\alpha2}$, coincide in a unique peak, and the same happens for the lines pairs or triplets $K_{\beta1} - K_{\beta2}$, $L_{\alpha1} - L_{\alpha2}$, and $L_{\beta1} - L_{\beta2} - L_{\beta3}$. K-lines are therefore identified by two X-rays K_α and K_β, and L-lines by six X-rays L_η, L_α, L_l, L_β, $L_{\gamma1}$ and $L_{\gamma3}$ of which only L_α and L_β are of high intensity.

By analyzing a gold alloy, containing Au-Ag-Cu, and using a proper filter at the X-ray tube output to attenuate the low-energy part of the spectrum, a typical X-ray spectrum is obtained, as shown in Figure 3.

2.1.2. Quantitative analysis of gold and silver alloys

In the case of gold or silver alloys, composed by Au-Ag-Cu and Ag-Cu-Au respectively, and assuming that Au(%)+Cu(%) +Ag(%)=100 % (both for Au and Ag-alloys), by plotting the ratios (Cu-K_α/Au-L_α)-counts versus (Cu-K_α/Au-L_α)-concentration, (Ag-K_α/Au-L_α)-counts versus (Ag-K_α/Au-L_α)-concentration and the same for Ag-alloys, it turns out that there is approximately a linear relationship, at least for Ag-concentrations in Au up to about 30%, Cu-concentrations in Au up to 20%, for Au- concentrations in Ag up to 30%, and Cu-concentrations in Ag up to 20%.

When other elements are present as trace elements, their concentrations can be determined by using the method of fundamental parameters.

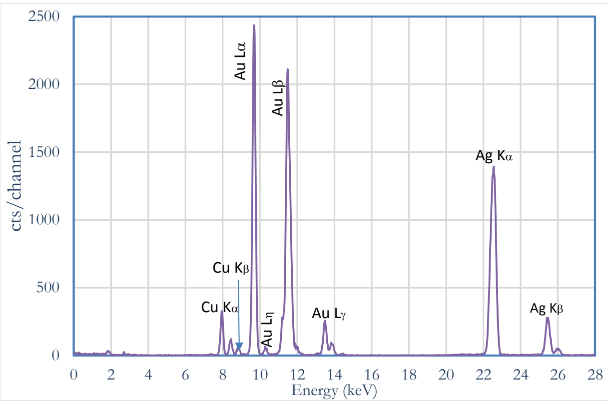

Figure 3. X-ray spectrum of an Au-Ag-Cu alloy, obtained with the equipment shown in Figure 2; the X-ray tube was working at 35 kV and 30 µA. The X-ray peaks are, from left: Cu-K_α line (8 keV), Au-L_l (8.5 keV), Cu-K_β (8.9 keV), Au-L_α (9.7 kev), Au-L_η (10.3 keV), Au-L_β (11. keV), Au-L_γ (13. keV), Ag-K_α (22 keV), and Ag-K_β (25 keV). Au X rays.

Figure 4. Front side of the nose decoration PACEB-F4-0002 from the tomb of the lady of Cao. It is composed of a body on a gold-alloy sheet with, superimposed, two shields on silver and, partially superimposed, two huts on silver. Silver huts and shields, these last only present in the front side, were probably glued to the gold body with an organic resin.

2.2. Radiography

X-ray radiography is an imaging method that uses X-rays to reveal the structure of an object based on the different densities of its constituent materials. In the case of the objects from the tomb of the Lady of Cao, we should consider the fact that the large majority of the objects are sheets, basically on gold or silver alloys, and the approximate thickness was measured to be about 100 µm for Au-layers and 200–300 µm for Ag-layers.

Radiographs were carried out with the following portable equipment:

- a portable mini X-ray tube by AMPTEK, working at 50 kV and
- 100 µA maximum voltage and current;
- a flat panel detector by Schick Technologies; and
- Image analysis software ISEE.

To image the Moche jewels under study the equipment worked at 25, 35, 45 and 50 kV. The first value appeared to be ideal to visualize the Ag-areas, while the last values (45 and 50 kV) were able to image the gold areas.

3. RESULTS

By analyzing the Gold-Silver interfaces of many of the forty nose ornaments with the internal X-ray method [14], at least four typical situations were identified, and an additional fifth hypothesis was considered:

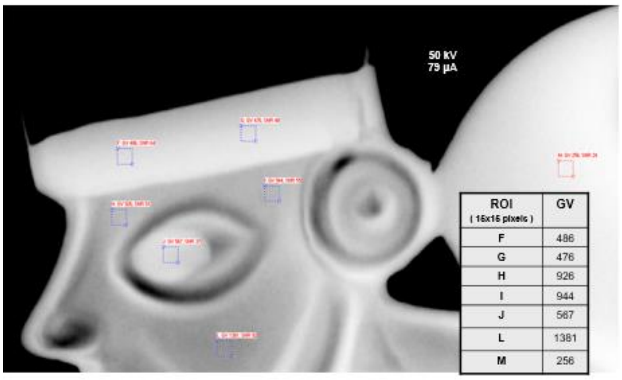

Figure 5. Radiography of nose-ornament shown in Figure 4, and behaviour of grey numbers in the interface Au/Ag. The grey number shows a sharp discontinuity between the Ag hut and the area where Ag is glued to Au. Then there is a discontinuity between this area and the Au area.

1. Silver sheets glued to Gold sheets; this is the case of nose decoration PACEB-F4-00002 (see Figures 4 and 5), where the Silver huts and disk are glued to the Gold body; this is not a common case and was also observed only in nose decoration PACEB-F4-00006.
2. Silver and Gold sheets brazed together; this is the case of nose decoration PACEB-F4-00106 (Figures 6 and 7) and peanut MB-8404 from the tombs of Sipán (see Figure 8), where the presence of additional Silver in the Au/Ag interface was identified in the X-ray spectrum, and also can be hypothesized from several radiographic measurements; this is a common case, and was observed in many other nose ornaments.
3. Silver and Gold sheets joint together by using mercury amalgam; this is the case of nose decoration PACEB-F4-00011 (Figure 9), where the systematic presence of Mercury, identified in the X-ray spectra of the Au/Ag interface, and only there, indicates the use of mercury for soldering together gold and silver. A test carried out by joining a gold to a silver foil by using mercury confirms this hypothesis.
4. It cannot be completely excluded that in a few cases a unique sheet on silver or on gold could have been employed, and a process of depletion gilding or silvering applied to the desired area. This possibility was considered in the case of nose decoration PACEB-F4-00018, where attenuation of X-rays by silver and gold areas, determined by radiographic measurements, are similar.

4. CONCLUSIONS

From all measurements, following may be deduced on the forty nose ornaments:

- the Moche artisans employed different techniques to join gold and silver: by gluing, by using an Ag brazing alloy and by using a mercury amalgam; a simultaneous process of heating can never be excluded.

Figure 6. Front and rear side of the nose decoration PACEB-F4-00106 from the tomb of the lady of Cao. It is composed of a body on a gold-alloy sheet, soldered on five heads on Silver, which are further soldered to a half-moon sheet on Gold. The soldering between the head in the middle and the upper gold shows a gap, which was covered in the rear side by a tape.

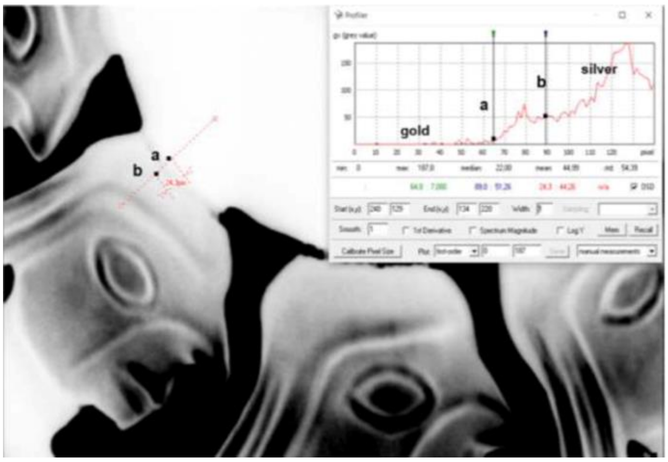

Figure 7. Radiography of nose decoration PACEB-F4-100106 (second Ag-head from the left and interface gold-silver, see Figure 4). The region between a and b corresponds to the soldering region, possibly carried out **with** an Ag-alloy.

Figure 8**.** Two peanuts on Gold, from the royal tombs of Sipán, code MB-9404 and MB-9405. Each peanut is composed of two parts soldered with a Ag-alloy containing Cu and Br. The same method was employed by the Moche for soldering front and rear side of the famous mask MB-09398.

Figure 9**.** Front side of nose ornament PACEB-F4-00011, composed of two sheets on Ag and Au, joined together by using a mercury amalgam; along the red line in the upper Figure, it was observed the systematic presence of mercury.

- the gold sheets of the forty nose ornaments from the tomb of the lady of Cao have a quite similar composition;
- the silver sheets of these forty nose ornaments have a completely erratic composition, with large differences also inside the same object. Also thickness differences were observed;

Obvious deductions from above points are:

- the forty-two nose decorations were produced in different periods and by different artisans; this is not surprising, because it is likely that the Lady of Cao may have inherited several of the nose decorations, and that the others may have been made in different times;
- the Moche possibly knew how to reproduce gold-alloys with the same composition. This consideration also derives from the previous point;
- the Moche were possibly trying to yield silver alloys with special characteristics of visual aspect and/or resistance to oxidation, by putting relatively high concentrations of gold; the presence of gold in silver is almost constant, while its concentration is highly variable. This could indicate a continuous investigation to produce an ideal Silver-alloy;

The **extraordinary metallurgic ability of the Moche**, at least in the period characterized by the tombs of Span and Cao must be finally pointed out.

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