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SOLDER CHARACTERIZATION ON ANCIENT GOLD ARTIFACTS
WITH THE ELECTRON MICROPROBE

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Abstract

The Laboratoire de Recherche des Musées de France has tested the applicability of the scanning electron microscope with X-ray analysis facilities in the study of ancient gold artifacts and particularly the joining processes. Three types of joining methods are known to have been used in Ancient Times : sintering, brazing with Au-Ag-Cu alloys and copper-salt binding. X-ray distribution maps of selected elements on very small areas show clearly the different processes used in the manufacture of Oriental and Iron-Age artifacts.

Introduction

For one year, the Laboratoire de Recherche des Musées de France has been carrying out a study of more than one hundred gold objects from the Louvre collections (Egyptian, Greek and Roman, and Oriental Departments). This extensive investigation contributes new knowledge to our understanding of antique goldwork. Several analytical techniques available in the Laboratory have been used : X-ray fluorescence analysis to determine the amounts of the major components of gold alloys (i.e., silver and copper). Minor and trace elements were identified by U.V. emission spectrography. One of the most interesting problems concerns the explanation of joining techniques and especially solders. To this purpose, metallographic and X-ray examinations have been fruitfully associated with Scanning electron microscopy (SEM) observation. Initial success encouraged us to enlarge this study to include Iron Age gold artifacts from France.

Here we present some of the results describing the different joining processes used in gold jewelry during different periods.

Experimental device and analytical possibilities

We used a JEOL JSM 840 scanning electron microscope with energy dispersive spectrometer (ORTEC System 5000). The instrument enabled us to study the elemental composition of very small areas. Quantitative analyses of samples were obtained with a standardless program using ZAF corrections. The energy resolution of the Si - Li detector was 150 eV at 5.89 keV. Furthermore, the system provided X-ray colored maps showing the distribution of selected elements and their concentration gradients.

KEY WORDS : Scanning electron microscope, energy dispersive spectrometry, gold alloy, joining processes

Ancient joining techniques

Three different types of joining processes have to be distinguished in the manufacture of ancient jewelry [5] :

- sintering : where both parts are joined without any additional alloying element by heating the surfaces to be joined to the melting point. The bulk melting point must not be reached. Because

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the two parts are welded by narrowly localized rearrangement, no important change occurs in the composition of the contact area. (We may observe a rather slight selective elimination of less noble metals during the heating process).

- brazing with Au-Ag-Cu alloys : a thin foil of alloy is placed between the parts to be joined. It melts when heated and fills the contact area. Both surfaces are enriched in copper and/or silver. The melting point of the foil must be lower than that of the gold alloy jewel.

- copper-salt binding : a copper-salt, such as malachite, azurite is mixed with carbon and glue and spread on the surfaces to be joined. When heated the copper-salt is reduced by carbon to metallic copper, which subsequently diffuses into the gold alloy. However the copper enrichment is low and the diffusion zone very narrow, therefore, identifying this technique is rather difficult.

These processes involve fusion temperatures between 850° C and 1000° C according to the alloy composition [2]. Therefore, goldsmiths may use several joining processes to make complex gold artifacts. In this case the highest temperature process was used first, and the lowest last.

Analytical results

We have selected for our study only those objects which could be securely placed within their archeological contexts and which have been kept unrestored in various museums since their recovery.

- Pendant from Susa (fig. 1).

This little dog-shaped pendant was found in Susa (Iran) in 1939 and is dated to 3200 B.C. [3]. It belongs to the Department of Oriental Antiquities of the Louvre (SB 5692).

In the late 4th millennium B.C., Susa was a big city dominating the Iranian plateau due to its great economic power. During this period, gold, silver, copper and also lead metallurgy developed in a decisive way [1].

This pendant is hollow and has been cast by the lost wax technique. A hanging ring is soldered to the back of the animal (fig. 2). The silver concentration in the ring and the pendant are very similar (9 - 10 %, by weight), as are those of copper (1 - 2 %). The concentrations are higher in the joining area, as is shown by the X-ray distribution maps of silver and copper (fig. 3). In this area the gold alloy contains 15 - 20 % silver and 5 - 6 % copper. With this pendant, we may have identified one of the oldest examples of Au-Ag-Cu alloy soldering.

- Ornamental sheet fragment from Susa (XIIIth century B.C.).

This piece of ornament is decorated with a row of granules soldered onto its edge (fig. 4). We were particularly interested in discovering how the granules were held in place. The amounts of silver (20 %) and of copper (2%) in the gold sheet are different from the average composition of the granules (31 % silver, 2 % copper). Non-destructive analysis with the electron microprobe seems to show a rather slight copper enrich-

ment in the contact area. With the agreement of the Louvre department, a granule was sampled in order to examine a cross-section where the gold sheet, the granule and the joining area are visible. The copper X-ray map demonstrates slight enrichment of this element in the joining area (fig. 5 a), where the concentration is between 3 and 4 %. The silver X-ray map shows different concentrations in the granule and the sheet, as was already mentioned (fig. 5b).

It therefore appears that copper-salt binding was used to fashion this object. This technique characterizes Etruscan jewellery (VIIIth - IIInd century B.C.). Therefore, these results show that this process has been in use long before that time in Ancient Iran.

- Ornamental gold cylinder from Susa (IIInd millennium B.C.).

This object was probably a sceptre or an ornamental weapon. It is decorated with granulations and filigree (fig. 6). The gold contains on the average 22 % silver and 2 % copper. No significant difference was detected between the composition of the granules and the joining areas. Copper and silver X-ray maps of the cross-section of a granule confirm these results.

No soldering alloy was used. The decorations, therefore were joined by sintering.

- Bead collar from Brittany (~ 500 B.C.).

This collar (fig. 7), containing 13 hammered beads, was found in an Iron Age underground gallery in Brittany (Western France) [4].

These beads are made of two soldered half-shells, which vary considerably in their silver content (33 to 40 %). Their copper content is about 1.5 %. An X-ray distribution map of the joining area shows a rather slight copper enrichment (fig. 8). The diffusion area is 20 to 40 µm wide and has a copper content of 2.5 %. It can be concluded that the copper-salt process was used to bind the half-shells.

- Fragment of collar (Eastern France, VIth century B.C.).

This Iron Age fragment of a collar is made of three gold alloy soldered sheets.

After polishing the fragment edge, we obtained an X-ray map (fig. 9). A copper enrichment corresponding to 3 - 4 % was observed; the sheet contained 0.5 % copper, 12 - 13 % silver. The copper diffusion zone is 200 µm wide.

In this case too, the copper-salt process was used.

Conclusions

These few examples show the possibilities of electron microprobe (EMP) with X-ray distribution map attachment in the field of archeological research. As EMP can be used to analyze tiny samples, in many instances nondestructively, it is suitable for gold artifact investigations. In this study, we have been able to identify different types of joining processes: sintering, soldering with Au-Ag-Cu alloys, and copper-salt binding. The small increase in the copper content and the narrow diffusion area make it difficult to differentiate copper-salt from sintering.

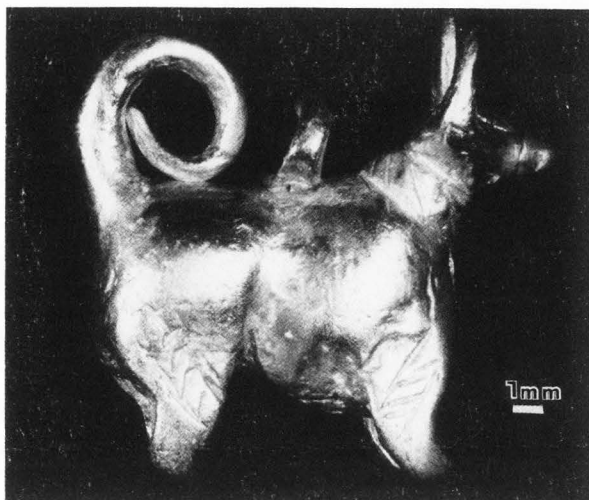


Fig. 1 : Gold pendant - 4th millennium B.C. (Louvre SB 5692).

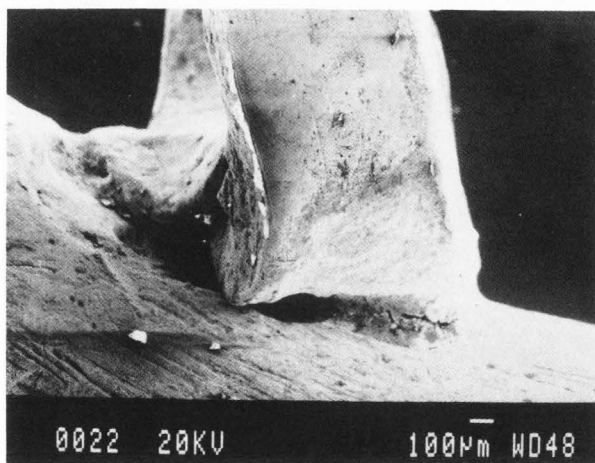


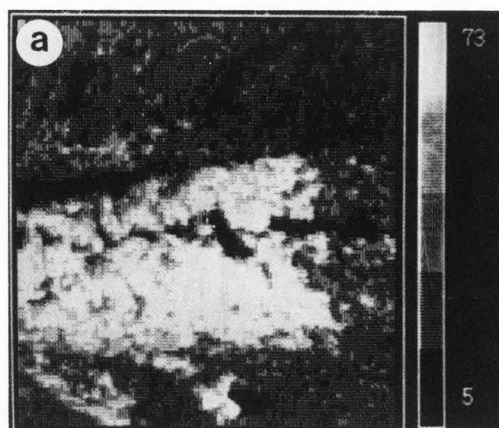
Fig. 2 : Gold pendant. Photography with the SEM of the joining area between ring and pendant.

Copper-salt joining is characteristic of Etruscan jewellery and does not seem to appear in Gaul before the IXth century B.C. However, this process must have been known long before in Iran, since it appears in first millennium artifacts from Susa.

Consequently, this investigation has advanced our knowledge of the abilities of ancient goldsmiths.

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100 µm

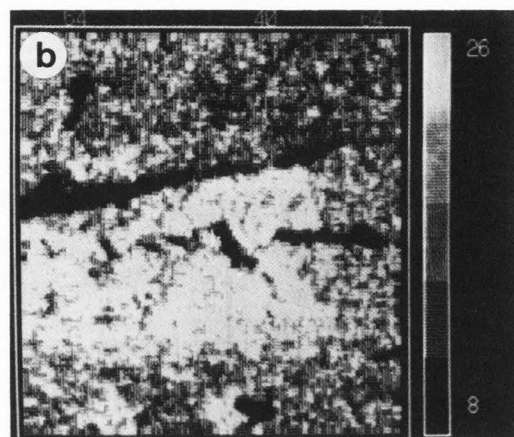


Fig. 3 : X-ray maps of copper (a) and silver (b) on the joining area, showing the local enrichment of these elements.

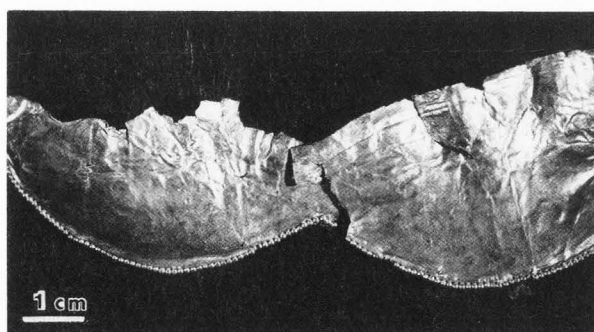


Fig. 4 : Gold sheet decorated with a row of granulations - 13th century B.C. (Louvre Sb 575)

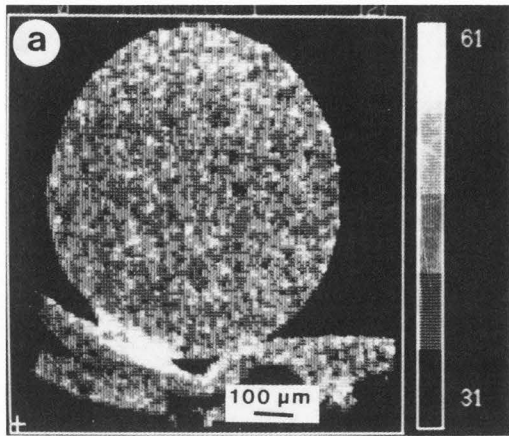


Fig. 5a : X-ray map of copper on the cross section of a granule identify copper-salt soldering.

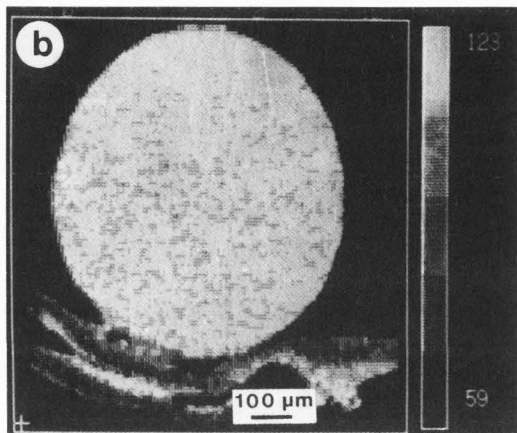


Fig. 5b : The silver content is higher in the granule than in the sheet.

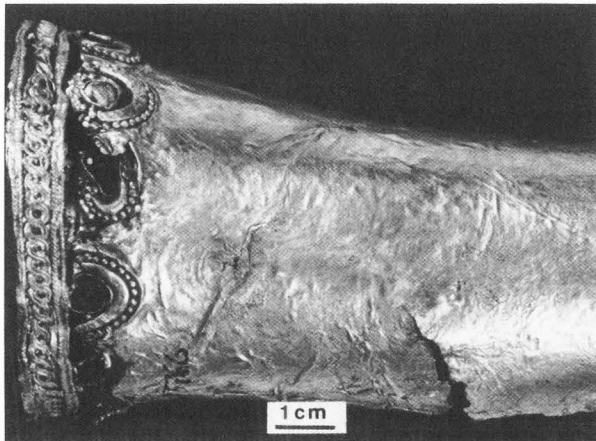


Fig. 6 : Ornamental gold cylinder from Susa IIInd millennium B.C. (Louvre SB 5766).

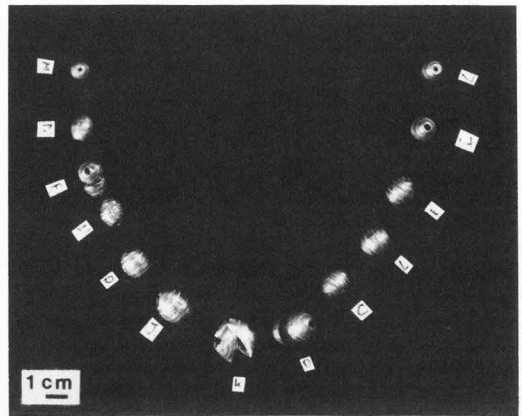


Fig. 7 : Gold beads from Brittany - Iron-Age ~500 B.C. (Musée de Quimper)

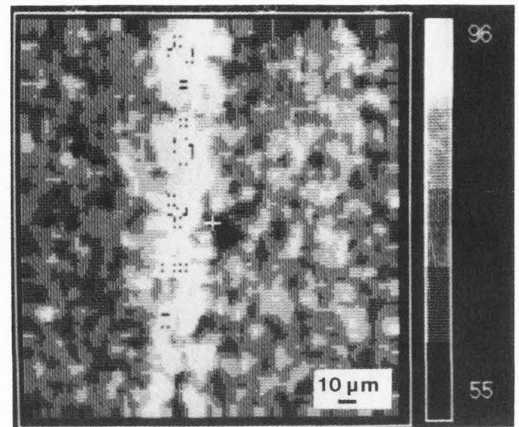


Fig. 8 : Copper X-ray map showing copper-salt soldering used to join both halfshells of the bead.

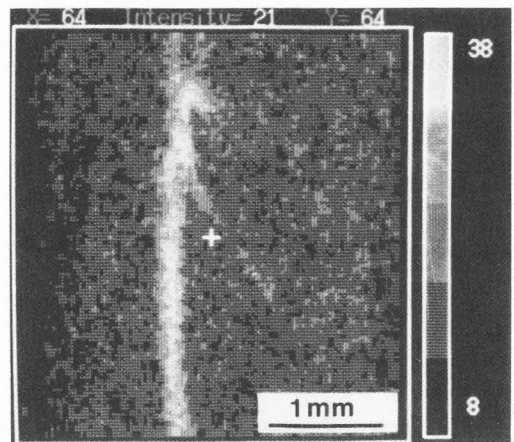


Fig. 9 : Copper X-ray map showing the copper diffusion binding. Iron-Age collar fragment (Musée des Antiquités National 25478).

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Discussion with Reviewers

G.W. Carriveau : How do the authors know that the small number of objects tested are of the age stated and that they have not tested more modern repairs ?

Authors : Age is given by the archeological context. We are also sure that no modern repairs have been made on the objects presented here. Nowadays, joining process like copper-salt binding is no more used by goldsmiths.

G.W. Carriveau : The authors should discuss the statistical significance of their measurements in so much as they are drawing conclusions from small differences in concentrations.

Authors : Copper-salt binding is characterized by a very slight copper enrichment. It is not possible to be sure of the use of this process if analyses are made directly on the objects. Therefore we have to take a sample. Analyses of very flat and polished surfaces can reveal differences in concentrations as small as 1 - 2 % of copper in gold.

V. Thien : Are there comparable works of other investigators in this field (Literature also)?

Authors : Many investigators analyze gold objects (jewels, coins) by different methods : X-ray fluorescence, neutronic and protonic activation, proton induced X-ray emission (PIXE), etc... But solder characterization needs specific methods. With electron microprobe, analyses can be made on the object but more often on a sample. Therefore the number of tested solders is limited. We know only one paper (reference 5). With PIXE, G. Demortier in Namur analyzed many gold artifacts and solders. He used a proton microbeam of a few microns in diameter.

