Meas. Sci. Technol. **14** (2003) 1527–1537 PII: S0957-0233(03)56722-4

Gold cultural heritage objects: a review of studies of provenance and manufacturing technologies

Maria Filomena Guerra and Thomas Calligaro

Centre de recherche et de restauration des musées de France, C2RMF-UMR 171 CNRS, Palais du Louvre-6, rue des Pyramides, 75041 Paris cedex 01, France

E-mail: maria.guerra@culture.gouv.fr and Thomas.calligaro@culture.gouv.fr

Received 27 November 2002, in final form 7 March 2003, accepted for publication 18 March 2003
Published 29 July 2003
Online at stacks.iop.org/MST/14/1527

Abstract
An overview of the use of the elemental composition of gold in the study of manufacturing technologies for objects as well as of the provenance of the metal is given. Depending on the objects, techniques based either on atomic physics or on nuclear physics and mass spectrometry are required to answer the questions surrounding the process of metalworking in the past. Several archaeological examples covering different periods of time and involving diverse analytical techniques are presented here. With those examples we illustrate the main research questions on precious objects and coins and show how far the elemental analysis of the objects can reveal the way they were made and provide information on the origin of the gold.

Keywords: gold, analysis, manufacture technologies, provenance, trace elements, jewels, coins, IBA techniques, ICPMS

1. Gold

Gold is one of the first metals used by humans. The most ancient gold objects known were found in a burial site at the Chalcolythic cemetery near Varna, Bulgaria, and date from the fifth millennium BC [1]. The ductility of gold and the fact that it can be found in its native form—in placers—allowed the production of gold artefacts by simple hammering before the development of heating metallurgy. For example, we should note that alluvial deposits, containing gold powder, pellets and nuggets, can be exploited by simple panning and washing.

Native gold is often called ‘natural electrum’ by authors; it is essentially an alloy of gold and silver. In this natural alloy silver may attain a concentration of up to 40%, copper up to 1% and iron up to 5% [2, 3]. Depending on the geological region of exploitation several elements can be found together with native gold: other alluvial metals such as tin and heavy elements accumulating with gold such as platinum [4]. We should note that primary gold, commonly present in quartz veins, was also exploited in antiquity. An example is the archaeological remains found in the Galish mines of Limousin, France, enabling the reconstitution of ore processing from that period [5, 6]. The other primary sources of gold are pyrites and arsenopyrites—the so-called invisible gold—and the telluride minerals of gold such as calaverite and petzite [7].

The first gold objects manufactured in ancient times were made with native gold. However, if we consider the Ur III texts which cite the loss of weight during melting of gold, refined gold was already being obtained in the second half of the second millennium BC [8, 9]. That loss of weight is clearly referred to in Egyptian texts from the nineteenth to twentieth dynasties (around the fourteenth century BC) for the different stages of refining.

In addition to the separation of base metals from gold, silver was also separated from gold as refining techniques evolved [10]. Cupellation separates gold and silver from the base metals, such as copper and iron, and is performed by the addition of lead. The separation of silver and gold is performed by parting, by the addition of acidic salts, in general chlorides and sulphates. Pure gold could already be obtained around the sixth century BC in Lydia as shown by the type and the composition of the different archaeological remains

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found in the excavations of the refinery of Sardis [11] and the composition of Lydian gold coins struck by Croesus (561–546 BC) [12].

In parallel with the evolution of refining and alloying technologies the increase in the skill of goldsmiths led to the development of several other techniques such as soldering and gilding. In order to study the development of gold working we must obtain appropriate information by analysing gold artefacts. Information can be obtained about both the manufacturing technologies used to make the objects and the provenance of the metal. We can perform metallurgical (microstructural) or elemental composition analysis to gain complementary information on gold working. Since ancient gold comes mainly from secondary ores, lead is almost absent and isotopic lead measurements cannot be performed.

In this paper we deal only with the elemental composition of gold and we illustrate the different possibilities and limitations of several non-destructive techniques.

2. The analytical techniques

Depending on the desired information, very different techniques can be used to analyse the composition of gold. In general, studies of manufacturing technologies need the measurement of major elements in selected regions such as solder (point analysis), but the distribution of major elements in a defined area (mapping) might also be useful. For these purposes, XRF (x-ray fluorescence), SEM (scanning electron microscopy) and IBA (ion beam analysis) techniques such as PIXE (particle induced x-ray emission), PIGE (particle induced γ-ray emission) and RBS (Rutherford backscattering spectrometry) are used. By changing the energy and the type of particle of the incident beam and by combining several techniques, IBA techniques provide surface and depth concentration profiles.

The provenance of a metal—fingerprinting—can be inferred by two methods: either by measuring the concentration of characteristic trace elements present in the gold or by determining the ratios of the different lead isotopes [13]. The latter, based on thermal ionization mass spectrometry (TIMS), is not considered in this paper since lead is absent for the most part in ancient gold objects. In order to determine the provenance of gold we need to measure trace elements with good limits of detection [14]. In the work discussed here we used proton activation analysis (PAA), inductively coupled plasma mass spectrometry (ICPMS) in liquid mode and with laser ablation, combined PIXE with PIGE analysis and PIXE induced x-ray fluorescence (PIXE-XRF) recently developed at C2RMF [15].

XRF and SEM rely on the x-rays emitted by the sample excited by x-ray tubes and radioactive sources or by electron beams respectively. The detection limits for these techniques are in the 500–1000 ppm range [16, 17]. These techniques also enable rapid point analysis for the study of details. While micro-XRF is a very portable technique allowing direct analysis in air, SEM yields high-magnification images and elemental maps.

The development of activation analysis for the study of gold coins using a beam of protons from a cyclotron was done in the 1960s by Meyers [18] and improved by Poirier in the 1980s [19]. For 12 MeV incident protons the production of only (p,n) nuclear reactions minimizes the interference and improves the detection limits. A 3 mm thick lead sheet positioned between the detector and the sample absorbs the γ-rays (inferior to 300 keV) emitted by the two isomers of mercury-197 produced by nuclear reaction on gold nuclei. Quantitative calculations use the flux monitoring technique and the Ricci and Hann mean σ method [20, 21]. The proton range in gold is about 240 μm and major, minor and some trace elements (Au, Ag, Cu, Pb, Sn, Sb, Pt, Pd, Te, ...) can be measured with detection limits down to 1 ppm [21].

For ICPMS the sample can be introduced as a liquid solution or by laser ablation (LA). LA-ICPMS was first used in 1994 by Kogan *et al* [23] for the determination of trace elements in gold in industrial samples and by Watling *et al* [24] in geological samples. However, in the archaeological sciences it is necessary to quantify the concentration of the elements present in the objects and also to consider sources of interference such as the $CuAr^+$ ion formed in the argon plasma with rhodium. Guerra *et al* [25] developed the quantification of trace elements in gold by using a shot frequency of 6 Hz for a UV laser and 60 s acquisition time in pick jumping mode after 10 s of pre-ablation, 10.24 ms dwell time, and a 3×3 raster scan pattern to produce 40 μm diameter and 130 μm depth craters (sample weight estimated to 1 μg). The limits of detection ranged from 10 ppb to 1 ppm on a high-purity NBS SRM685 gold standard using the $AuAr^+$ ion as an internal standard [26].

The difficulties observed in the quantitative determination of certain elements using laser ablation led to the development of ICPMS in liquid mode. In the case of liquid mode ICPMS Gondonneau *et al* [27] performed the acquisition in pick jumping mode, with a 10.24 ms dwell time and a 30 s acquisition time, using three repeat runs. For gold samples of about 2 mg and In as internal standard, the limits of detection ranged from 0.01 to 10 ppb.

However, we must still note the use of LA-ICPMS for the study of provenance using isotopic tracers. In the case of gold artefacts, the platinum group element inclusions are enriched in Os and *in situ* laser-ablation based isotopic analysis (LA-MC-ICPMS) can be performed. Measurements of the $^{187}Os/^{188}Os$ ratio were developed and applied by Junk [28] to provenance the gold sources used to produce Celtic gold coins.

PIXE uses a 3 MeV external proton beam of diameter 30 μm and two Si(Li) detectors to collect the x-rays emitted by the sample [29, 30]. One of the detectors has a 1 mm lead collimator and measures major elements while the other has a 75 μm copper filter to absorb the gold lines to enable measurement of trace elements. With a 20 nA current the limits of detection reach 13–90 ppm for elements of atomic number between 20 and 60 and 100–300 ppm for atomic numbers higher than 75 [15]. Being a near-surface technique (penetration less than 30 μm for gold), the possible elimination of copper from the surface by oxidation may influence the final result. To overcome this problem, γ-ray lines (produced deeper in the sample) are simultaneously measured by PIGE using a 30% efficient HPGe detector placed at 45° from the beam (see figure 1). PIXE and PIGE can produce simultaneous elemental maps [31] by mechanically moving the sample under the fixed beam. Together with RBS, PIXE and PIGE are able to perform non-destructive depth–concentration profiles [32, 33].

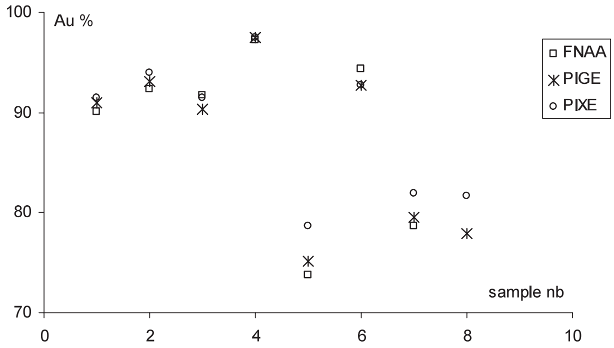

Figure 1. Comparison of the gold concentrations obtained in different archaeological samples by PIGE, PIXE and neutron activation analysis, the latter providing bulk analysis. We obtain the same concentrations by neutron activation and by PIGE.

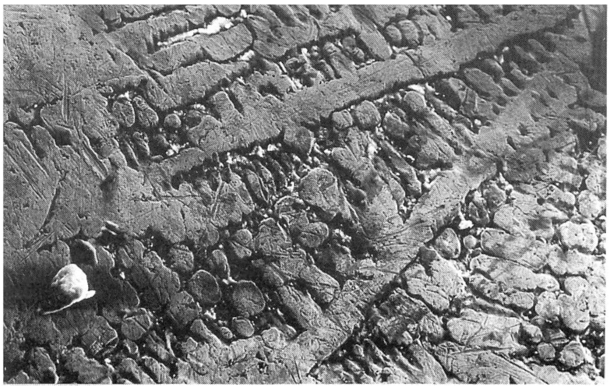

Figure 2. SEM image of a cast gold alloy obtained by Lehrberger and Raub [36].

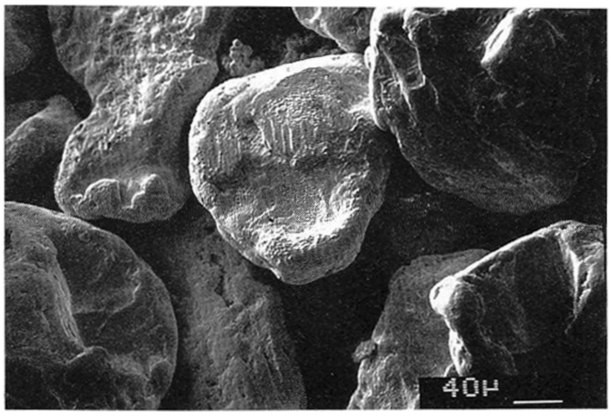

Figure 3. SEM image of a sintered gold alloy obtained by Raub [3].

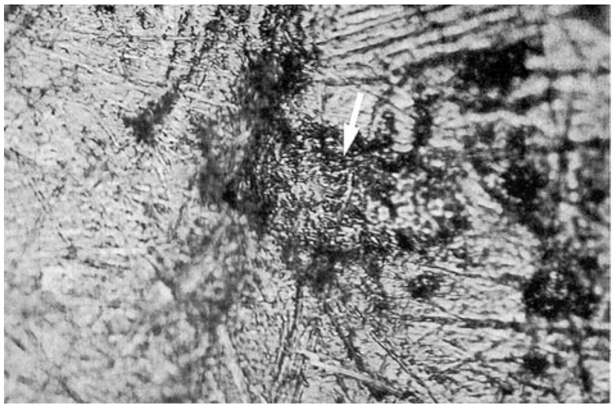

Figure 4. SEM image of an osmium–iridium inclusion in a gold alloy obtained by Lehrberger and Raub [36].

For the specific measurement of platinum in gold a PIXE-XRF set-up was developed by using the quasi-monochromatic x-ray radiation emitted by a primary target of arsenic under proton bombardment [15]. By exciting platinum lines without exciting gold lines, the limit of detection, which is ruled by the Raman and Rayleigh scattering [34], reaches about 80 ppm [35].

3. The manufacturing technologies

Alloying, soldering and gilding are some of the different manufacturing techniques used by goldsmiths to fabricate gold objects. These different aspects of gold working can be studied either by measuring the concentration of, in general, major elements or by simple observation of selected areas by optical and electron microscopy (hammering, torsion, decoration, etc).

Figures 2, 3 and 4 respectively show the characteristic dendrites of a cast alloy (gold melting point 1063 °C) on the surface of a Celtic gold coin from the Grossbissendorf hoard [36]; a sintered alloy (300 °C for 10 h) of alluvial powder gold from near Lugano [3]; and an osmium–iridium inclusion on the surface of a Celtic gold coin from the same Grossbissendorf hoard [36]. The platinum group inclusions, which are sometimes found in gold alloys (related to the refining technique), were analysed by Meeks and Tite in 1980 [37] and recently discussed by Zwicker [38] and Craddock [39]. Recently the measurement of the of osmium isotope ratios in those inclusions was used to determine the origin of the gold [28].

Using gold, silver and copper, the goldsmith could produce a large number of alloys with different mechanical properties (strength, hardness and ductility) as well as different colours, meaning that each alloy is tailored to a particular application. Hardness can be improved by alloying gold with copper and silver and by using annealing and quenching. The addition of copper (red) and silver (white) in different proportions to gold (yellow–orange) changes the colour of the final alloy. This colour can extend from green to red, pink, white, etc. These alloys also have different melting points and thus can be used as solders.

For the study of precious objects, the determination of the soldering technique, namely the technique used to join the different pieces, is very important. In ancient times almost every join was made by diffusion brazing and copper diffusion. These techniques use a filler of lower melting point than the pieces being joined and differ in their heating temperature. In the past the fillers could be either copper salts or natural alloys of gold and silver. These natural alloys need to have lower melting points than the pieces to be joined, for example an alloy of gold with about 20% copper melts at 200 °C less than pure gold.

Composite objects are produced by assemblage of different separate pieces; this can be revealed by radiography. Figure 5 shows a radiograph of the Vix gold torque (Burgundy, France, around 500 BC) by Eluère [40, 41]. It shows the different components of the torque. The base alloy was made of 2% silver and 1–2% copper, but analysis showed the presence of a brazing soldering between the lion's paw and the arc as well as between the horse's tail and the sphere with an alloy richer in silver (7–17%) and copper (4–9%) while the other elements were soldered by copper diffusion [41].

The surface mapping of major elements can be performed by SEM in the case of small objects or by PIXE with an external beam for objects of all sizes. This is illustrated by the study of a decorative gold foil from Susa, Iran, fabricated in the second millennium BC [42]. Figure 6 shows a SEM composition map of a section of a granulation of 0.5–0.7 mm diameter. The increase in copper concentration 60 μm from the soldering point is characteristic of the copper diffusion technique [40, 42].

(a)

(b)

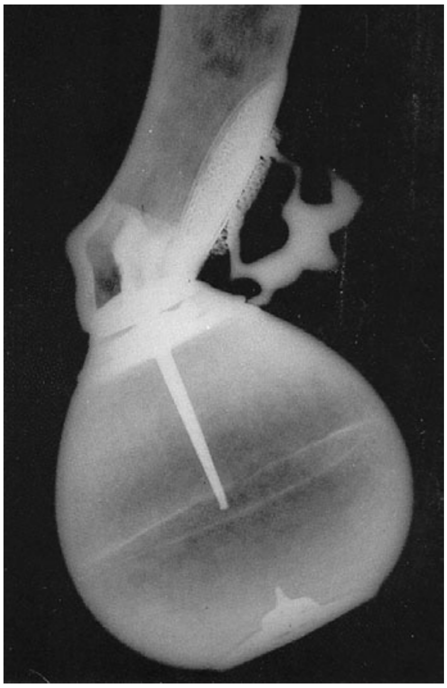

Figure 5. The Vix torque (Burgundy, France, around 500 BC) and the radiography of a detail obtained by Eluère *et al* [41] showing how the sphere and the lion's paw were assembled.

3.1. The Visigothic treasure of Guarrazar

The analysis of a large series of objects reveals not only the gold-working techniques used to produce these objects but also the previous restorations performed on the objects. This is illustrated by the recent analysis of the Guarrazar jewels, the most important Visigothic treasure of the Iberian Peninsula. The treasure of Guarrazar was found in the nineteenth century near the Visigothic capital, Toledo, and was certainly hidden at the beginning of the eighth century during the Arab invasion. The treasure consists of different crowns, crosses and chains offered by nobles and bishops to a church in Toledo. Among the objects we can find the crown and cross of king Recceswinth (653–672) [43]. At present the remaining objects are kept in the National Archaeological Museum of Madrid, in the Royal Palace of Madrid and in the National Museum of the Middle Ages in Paris.

All the objects were analysed by PIXE in order to determine the concentrations of major elements [44]. The Spanish treasures were sampled and analysed at LARN (Namur, Belgium) while the French objects were non-destructively analysed at C2RMF (Paris, France) as illustrated in figure 7. The results showed that gold ranges from 98 to 62%, silver from 1.5 to 35.5% and copper from 0.3 to 7.5% in these pieces. Several alloys were used to fabricate different pieces of the same object, except in the case of the crown and cross of Recceswinth, which are of better quality.

The increase in copper and silver content in the region of the joins was observed for the objects kept in Paris but also the use of other alloys was identified in these pieces. Brass (copper and zinc alloy with a golden colour) rings and soft soldering (lead, tin and bismuth) were found. They correspond to a nineteenth-century restoration. The different compositions seem to reveal successive restorations at the same point. The weakness of certain solders can be explained by the use of alloys similar to those of the parts to be joined.

Some pieces of the Guarrazar treasure were made with quite debased gold alloys, produced by increasing the silver content. Gold debasement is usually achieved by an increase in the amount of silver, of copper or of both these metals in different proportions. However, these techniques are hard to differentiate through analysis, except in one case. In antiquity the most important silver sources were the lead ores: cerusite, anglesite and galena. When silver is separated from lead by cupellation a small quantity of the metal remains in the silver. A correlation between silver and lead content is found for gold debased with lead–silver, since native gold has in general a lead content of less than 50–100 ppm [45, 46]. When the concentration of silver increases but the concentration of lead remains constant we can suggest the use of low-processed native gold–silver alloys (electrum).

For the Guarrazar treasure the lead concentrations are on average below 250 ppm while the contemporary Visigothic coins have lead contents that may attain 1500 ppm [47]. In figure 8 we can observe the lead and silver concentrations measured by PAA on a group of coins struck by the Visigothic kings from 621 to 709. This seems to correspond to a debasement by addition of silver extracted from a lead ore. If we consider in the same figure the gold coins struck between 936 and 1017 by the Arabs in the Iberian mints, the low lead

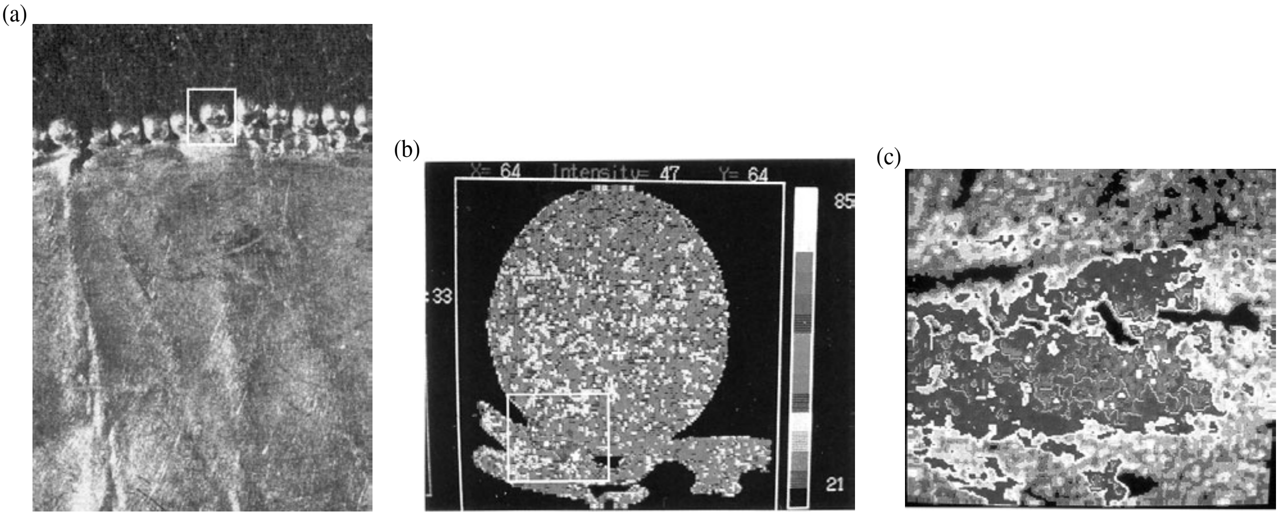

Figure 6. Detail of a decorative gold foil fabricated in Susa, Iran, in the second millennium BC. The SEM mapping for copper on a granulation obtained by Duval *et al* [42] shows the use of a copper diffusion joining technique.

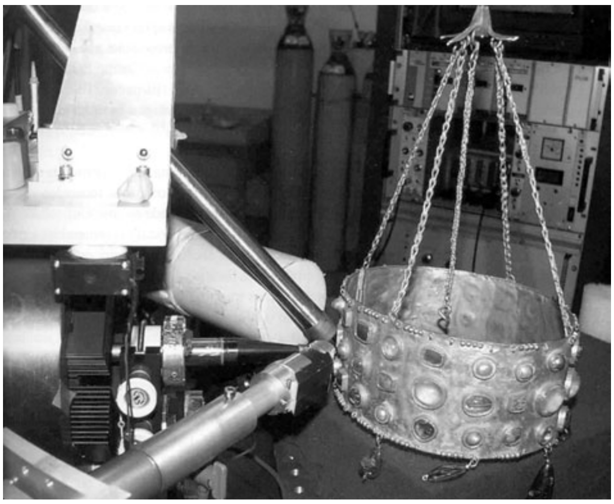

Figure 7. One of the Visigothic crowns from the collection of the National Museum of the Middle Ages in Paris is non-destructively analysed by PIXE at the AGLAE accelerator at C2RMF installed in the Louvre Museum (Paris, France).

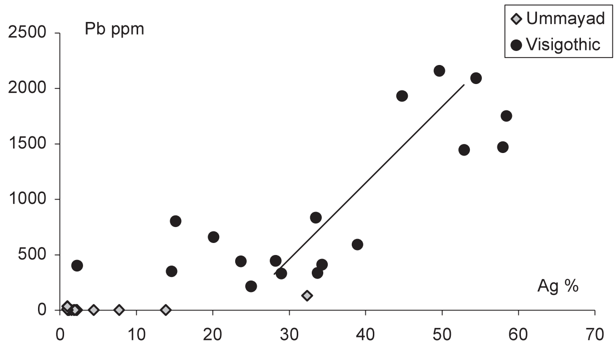

Figure 8. The concentration of lead (in parts per million) and silver (in per cent) measured for a group of Visigothic and Ummayad gold coins struck in the Iberian Peninsula. The diagram shows two different debasement techniques.

and high silver concentrations are evidence of a debasement certainly achieved by the non-refining of native gold [48].

3.2. Gilding

The application of a gold coating to the surface of a lower-quality alloy to make an object look like cast gold is commonly used and is called gilding. There are different types of gilding: water gilding, fire (or mercury) gilding, depletion gilding and electroplating (used nowadays). Water gilding uses gold leaf of high quality applied to the surface of an object by means of an adhesive (animal glue). Mercury gilding uses the amalgamation phenomenon of gold with mercury: either a paste of mercury and gold or a gold leaf on a layer of mercury are applied on the surface of an object before heating to boil off the mercury. Depletion gilding uses the removal of base metals from the surface of the object, leaving a surface enriched in gold.

The identification of gilding requires not only an analysis of the surface of the object but also an analysis of the substrate. This means that the concentration of major elements must be measured at different depths. The combination of the IBA techniques RBS, PIXE and PIGE at different energies allows depth profiling for gold layers from about 2 to 12 μm, as well as the determination of the composition of the substrate and evaluation of the thickness of the gold layer.

Fire gilding was much employed by goldsmiths in antiquity. Beck [32] showed how IBA techniques give information on that type of manufacturing technology. This is illustrated by the PIXE, PIGE and RBS depth profiling for gold, silver and copper as well as the mercury determination by PIXE for the fifth to seventh century gilded or partially gilded Merovingian brooches from the north-east of France. PIXE analysis showed a mercury content of 15–20% for one of the partially gilded fibulae and the use of a silver, copper, zinc base alloy. Depth profiling identified a 70% gold gilding layer of thickness 5.9 μm, as shown in figure 9 [32]. Mercury gilding was used to produce a golden region opposed to the non gilded zones having a white silvery aspect.

Another example of depletion gilding is tumbaga, a low-quality gold–copper alloy popular among South American

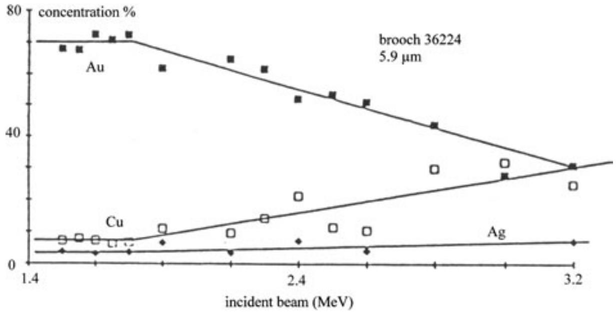

Figure 9. Gold, silver and copper depth profiles of a Merovingian fibula partially gilded obtained by PIXE. The profiles show on one hand a 5.9 μm gilding layer containing 70% of gold and on another hand a substrate with a high content of copper and a constant silver concentration.

goldsmiths before the arrival of the Spanish. This gilding is obtained by removal of the copper oxide formed by heating on the surface and is described by several authors, Lechtman [49] for instance. Several researchers have analysed this type of object (for example [50, 51]); the use of differential PIXE and RBS-PIXE to obtain concentration profiles by Ruvalcaba [52] is specifically noted.

4. The circulation of raw material

When the concentration of the characteristic trace elements of gold alloys changes, this indicates a change in the metal supply (according to the elements this might also indicate a change in the refining techniques [10] or of the type of gold deposit exploited [53]). The identification of those changes, and if possible of the origin of the gold, gives information about the circulation of gold in the past. However, when we consider the manufacture of precious objects, we must also consider all the other materials such as glass, gems and stones. The analysis of all the elements of an object allows a determination of the circulation of the raw materials employed by the goldsmith in the past.

When performing analysis of trace elements in gold, we must be aware of several problems:

(1) the loss of certain elements by oxidation and evaporation or absorption by the cupel during gold processing;
(2) the loss of information due to mixing during recycling of gold alloys from different origins [11]; and
(3) the interpretation of the results considering our lack of information on the geochemistry of ancient gold mines.

Recent mines exploited during the gold rushes which occurred after the sixteenth century are known, and their ores have been analysed in the past by geologists who reported their main characteristic trace elements. For example, in the nineteenth century De Launay indicates that eighteenth-century Brazilian gold is characterized by high concentrations of palladium [54] (other geologists have studied the platinum and palladium content in Brazilian gold, Jedwab and Cassedane [55] for example). The analysis of the Brazilian ingots fabricated in the Brazilian mints of the eighteenth to nineteenth centuries with the gold powder and nuggets found by the gold prospectors showed the expected high content of

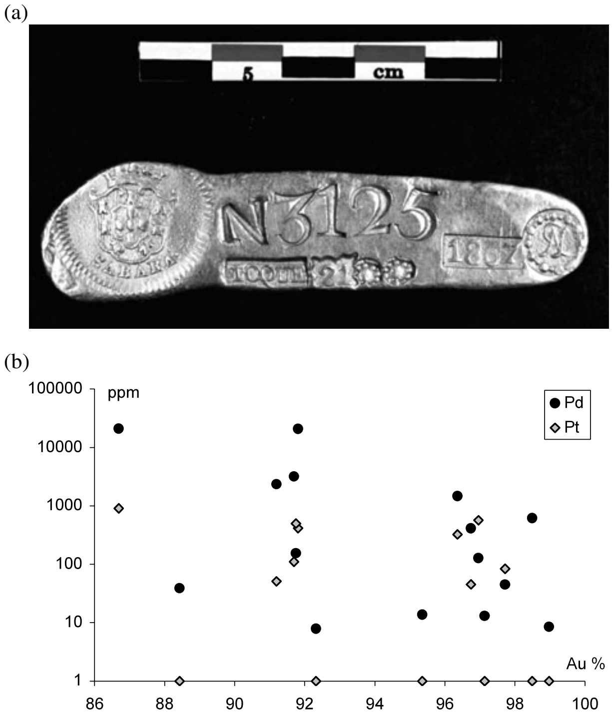

Figure 10. (a) One of the Brazilian ingots fabricated in Sabará in 1897 with the gold powder and nuggets found by the gold prospectors (photograph M F Guerra); (b) the ratios of palladium and platinum concentrations (in parts per million) to gold content (in per cent) measured by PAA for the Brazilian ingots fabricated between the eighteenth and nineteenth centuries.

palladium. Figure 10(b) shows that this element is present at concentrations that are from 10 to 100 times greater than the platinum content [56, 57].

Contemporary objects matching a chemical group formed by the Brazilian ingots would be said to be manufactured with Brazilian gold. However, the geochemistry of very ancient mines, and sometimes even their situation, is unknown. In most cases the identification of a gold used in the fabrication of objects is made by a comparison of the composition of the object with that of a group of well documented objects used to define the possible chemical groups. When both groups of objects chemically match they are said to be manufactured from the same gold.

Nevertheless we must be aware of periods of scarcity, as objects might be fabricated with mixed recycled gold. The use of trace elements for finding the provenance of gold is particularly convenient for periods of gold rushes. For important sources of gold exploited in the past, no mixture of gold from different origins is (statistically) observed. In order to approach the provenance of gold, techniques, preferably non-destructive, with good detection limits for trace elements are necessary.

The following examples illustrate the information obtained through the analysis of archaeological objects depending on the historical records.

4.1. *The Xiongnu gold*

The excavations of the necropolis of Gol Mod in the Arhangay led by the French Archaeological Mission in Mongolia revealed a large number of Xiongnu tombs (third century BC to the first century AD). Among the tombs, one was assumed to be imperial. In this tomb a profusion of objects of very high quality was found. The wood coffin was covered with gold stripes and quatrefoils of 30–60 μm thickness, characteristic of Chinese artwork.

In order to determine if the gold foils were imported or made *in situ* a set of about 50 gold foils from the two main tombs labelled 1 and 79 and two Chinese plaques from the Guimet Museum (Paris, France) were analysed using a combination of PIXE, PIGE and PIXE-XRF in external beam mode [15].

The average concentrations measured by PIGE on the different analysed foils are for tomb 1, Au $= 96.1 \pm 1.8\%$, Ag $= 3.5 \pm 1.6\%$, Cu $= 0.21 \pm 0.16\%$; for tomb 79, Au $= 89.7 \pm 0.6\%$, Ag $= 9.6 \pm 0.4\%$, Cu $= 0.21 \pm 0.04\%$; and for the two Chinese objects, Au $= 92.0 \pm 0.5\%$, Ag $= 7.3 \pm 0.6\%$, Cu $= 0.8 \pm 0.04\%$. The imperial tomb (number 1) has a higher quality decoration than tomb 79 which is closer in quality to the Chinese plaques. For all the objects copper content is very low, at levels expected for native gold.

All the Xiongnu foils showed a high content of iron and tin. The highest quantities were obtained for tomb 79. These results seem to indicate the use of an alluvial gold. In fact, iron and tin are metals which can be panned together with alluvial gold. SEM analysis revealed one inclusion of cassiterite, an alluvial tin oxide. Since tin melts at about 232 °C and cassiterite requires about 1200 °C to be smelt to metal, the native gold might not have been cast but just hammered to fabricate the foils. Further analysis will clarify this hypothesis.

If we consider the palladium content in the gold foils, the assumption of the use of different golds or the exploitation of distinct panning regions to manufacture the foils from tomb 1 and tomb 79 seems to be reinforced. In fact we observe an average concentration of 34 ± 16 ppm for tomb 1 and 68 ± 17 ppm for tomb 79.

The two Chinese gold plaques show a lower iron and tin content than in the Xiongnu foils, while palladium shows an average composition of 48 ± 12 ppm. This seems to denote a different method of gold processing. This would support the hypothesis of different origins for the Chinese and the Xiongnu gold. A small number of analyses performed by PIXE-XRF to measure the platinum content of both the Xiongnu and the Chinese objects [35] seem to corroborate the hypothesis based on the previous analyses. The average content is 150 ppm for tomb 79, under the detection limits for the Chinese plaques, and between 80 and 1000 ppm for tomb 1.

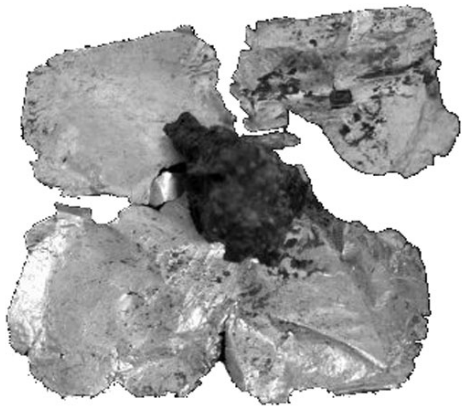

Figure 11. One of the Xiongnu quatrefoils from the imperial tomb labelled 1 (photograph Bagault).

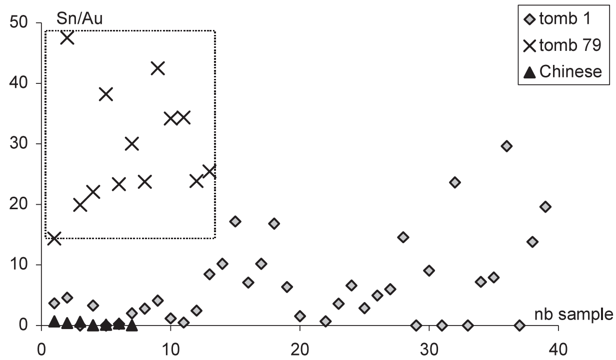

Figure 12. The ratio of tin concentration (in parts per million) to gold content (in per cent) measured for the Xiongnu foils and the Chinese objects by PIXE.

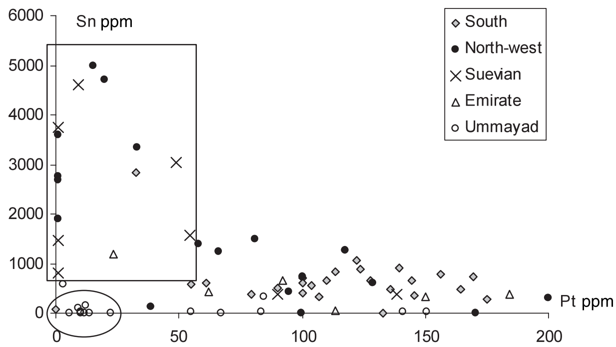

Figure 13. The concentrations of tin and platinum in parts per million show two different gold supplies for the Visigothic and Suevian coins struck in the Iberian Peninsula.

4.2. *Visigothic and Arabian gold in the Iberian Peninsula*

A large number of findings concerning the Visigothic treasure found in Guarrazar, already referred in section 3, were published in a book edited by Perea [43]. However, the study of trace elements was not considered for gold. In order to identify the type of gold used to manufacture the objects, about 20 samples from those kept in Spain were analysed by PIXE and PIGE association [58]. The results were compared with those obtained for a group of Visigothic coins analysed by PAA [47, 48].

The concentrations of tin, platinum, palladium and zinc allowed the differentiation of two types of gold supply used to strike the Visigothic coins in the Iberian Peninsula: one minted in the north-eastern regions and another minted in the central-southern part. The existence of a north-eastern gold is confirmed by the results obtained for ten Suevian coins as illustrated in figure 13. We recall that the Suevian kingdom was established before the arrival of the Visigoths in Galicia and to the south of the Douro river in north-eastern Iberia. This seems to prove that no external gold supplies arrived in the Iberian Peninsula under the Suevians and the Visigoths.

As the analyses were performed on 50–200 μm diameter samples included in a resin, platinum could not be measured by PIXE-XRF since this technique requires a larger object

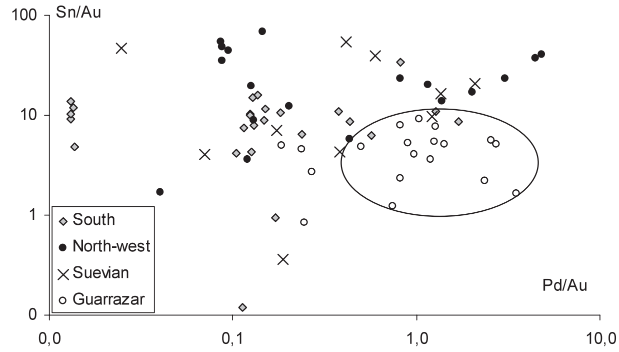

Figure 14. The ratios of tin and palladium concentrations (in parts per million) to the gold content (in per cent) for the Visigothic coins and the jewels from the treasure of Guarrazar.

(the calculation of the concentration of platinum is made by subtraction of the Raman peak obtained by the analysis of a pure gold standard at the same geometry). In order to check if the Visigothic crowns and crosses from the Guarrazar treasure were manufactured with Iberian gold, we compared the ratios of palladium and tin concentrations to the gold content in figure 14 for both coins and jewels. As the Guarrazar objects match the chemical group of the coins, we can assume that they were made with a local gold similar to that struck by the Visigoths [58].

The gemstones mounted on the objects of the Guarrazar treasure bring additional information about the provenance of materials. The large variety of gems used for the crowns and crosses has been characterized by means of non-destructive techniques: a combination of PIXE and PIGE for the determination of major constituents and trace elements and Raman spectrometry for the identification of inclusions. The gems were identified as mother of pearl, amethysts, sapphires, garnets and emeralds together with glass beads [59]. By comparing the chemical composition of these ancient gems and the various inclusions present with the values obtained on gems from known deposits, it was possible to infer their provenance. The pale blue sapphire was shown to originate from Ceylon (Sri Lanka), the pyrope-type garnets extracted from the Bohemia mountains (Czech republic) [60] and the emeralds mined in the Alps (Habachtal, Austria) [61] (see figure 15). These results constitute the evidence of a trade route for gems during the Dark Ages.

Under the Visigoths no ‘foreign’ gold seems to enter the Iberian Peninsula. After the Islamic invasion in 711 the first gold coins were produced by recycling of previous monetary gold from the Arabian empire. However, after 750 the gold supplies changed [62]. Figure 16 shows that in the Iberian Peninsula the first Arabian coins were obtained by recycling of the Visigothic coins, while under the Ummayad Caliphate a new gold supply was exploited in order to fabricate the Islamic coins.

Identification of the origin of the new gold supply under the Arabian dynasties of Iberia was made by the analysis of North African coins. Documents cite the importance of West African gold in the Arabian empire. They also indicate the most important sites on the routes of the gold caravans, such as Sijilmasa, the most important mint situated on the major North African caravan route.

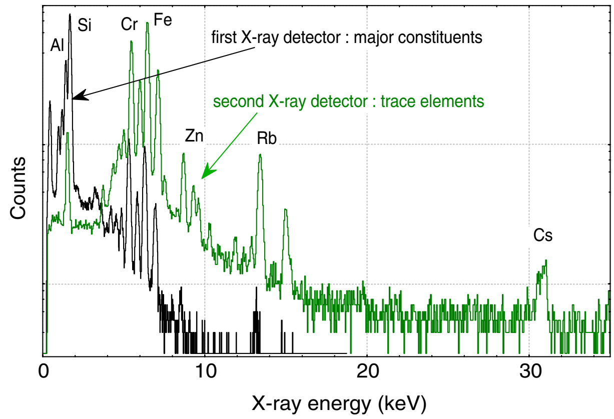

Figure 15. PIXE spectrum of an emerald from the Guarrazar treasure. Trace elements determined that the emeralds were imported from Habachtal, Austria.

(This figure is in colour only in the electronic version)

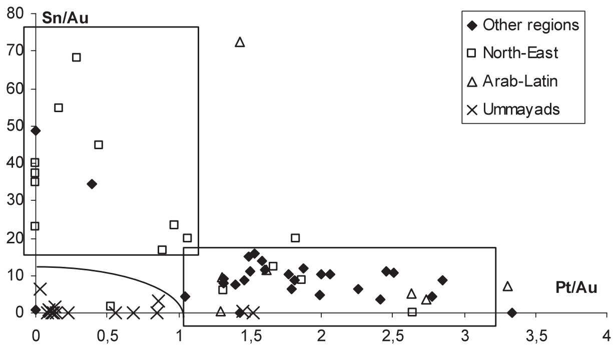

Figure 16. Under the Ummayads the gold supplies in the Iberian mints change around 750. This new supply corresponds to a new chemical group defined by the ratios of tin and platinum concentrations (in parts per million) to the gold content (in per cent).

Table 1. Average trace element contents for a group of Almoravid dinars analysed by PAA and a group of 18 gold West African nuggets analysed by ICPMS.

Element (ppm)	Coins	Nugget
Sb	1	5
Pt	1	0.5
Pd	1	0.3
Zn	57	13
Te	1	0.6

Analysis of the gold struck in the African mints and in Spain by the Almoravids showed a similar composition for all the coins [62, 63]. As the Almoravids controlled Africa, Spain and the West African gold commerce, we can suppose that West African gold circulated in the Iberian Peninsula.

To check the composition of West African gold, a set of 18 modern small nuggets (a few milligrams) from the Ivory Coast, Ghana and Mali were analysed by ICPMS in liquid mode [64]. The dissolutions were performed by Michael Cowell of the research laboratory of the British Museum. The trace element content in the nuggets and in the Almoravid coins struck in Sijilmasa (table 1) reinforce the assumption that the coins were struck with West African gold.

5. Conclusion

Very different aspects of gold analysis have been considered. The choice of analytical technique depends on the issue under investigation and on the type of object. Micro-XRF is applied to the measurement of base alloys and to the concentration of major elements in details when a non-destructive *in situ* analysis has to be performed. However, to study manufacturing technologies the most interesting techniques are SEM and IBA. The first SEM technique permits major element point analysis and produces high magnification images and elemental mappings for small objects while IBA implemented in an external microbeam arrangement is applied for surface profile and depth point analysis for objects of any size and shape. Filtered PIXE measures, in addition to major elements, a certain number of characteristic trace elements in gold. Filtered PIXE is among the few techniques providing non-destructive trace element profiles.

The study of the changes of metal supplies and the identification of the origin of gold requires techniques with good detection limits. For this purpose filtered PIXE, PAA and ICPMS can be used. PIXE and PAA are non-destructive, ICPMS needs a 2 mg sample when in liquid mode and about 3 μg when coupled to laser ablation. However, if ICPMS is quantitative, LA-ICPMS is, in most cases (depending on the laser), rather qualitative.

PAA was developed to analyse coins and other small objects. In addition to the restrictions due to radioactive conditions, very big, very small and very thin objects are difficult to analyse. With a range of about 240 μm, protons will, for the referred analytical conditions, lose all their energy in the gold matrix.

Simultaneous PIXE and PIGE are not constrained by the size and thickness of the object and can be coupled to PIXE-XRF to measure one or two elements for each primary target with very good detection limits. However, in the case of gold, these techniques present poor detection limits for lead.

If the expertise of the goldsmith can be evaluated by classical techniques, the provenance of the raw material is still difficult to infer. The interpretation of the analytical results depends on historical documents and so on the period. We could obtain only very few (but important from the point of view of manufacturing technology) conclusions for the gold used by the rather unknown Xiongnu nomadic people, but profuse information was obtained from an analysis of the objects made by the rather well known Visigoths and Arabs. The study of an object as a whole sheds some light on the commercial routes used in the past by goldsmiths. This statement is illustrated by a study of the gold and gems of the Guarrazar treasure.

Acknowledgments

The authors are very grateful to Michael Cowell from the British Museum, Francisco A Magro and Carlos Costa from the Associação Numismática de Portugal, Alexandra Gondonneau and Corrine Roux whose PhD concerned the Arabian gold coinages, Christophe Moulhérat from the Louvre Museum, Jean-Paul Desroches from the Guimet Museum, Christiane Eluère from C2RMF, our colleagues of AGLAE at C2RMF, Christopher Deeb for his suggestions, the Cabinet des Médailles of the Bibliothèque Nationale de France, the Pierre-Süe laboratory (CEA-CNRS), the French Archaeological Mission in Mongolia, the CERI and IRAMAT CNRS laboratories.

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