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Pre-hispanic goldwork technology. The Quimbaya Treasure, Colombia

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ABSTRACT

One of the most important pre-Columbian gold assemblages made up of more than one hundred objects from two tombs in the Cauca river valley, Colombia, was studied to obtain archaeometric information. Although several attempts have been made to arrange gold production in time and space from the stylistic point of view, no firm conclusions were possible due to the lack of archaeological contexts. This paper presents first results of a new, fully instrumental approach, in which different analytical techniques, including OM, SEM-EDS, XRF, PIXE, RBS, AMS and X-ray imaging, were applied in order to determine a technological, metallurgical and chronological frame of the so-called Quimbaya Treasure.

The Quimbaya Treasure is the most important pre-Columbian gold assemblage kept since 1941 at the Museo de América in Madrid. We have accomplished an interdisciplinary study of these 135 (museum inventory numbers) gold objects with a twofold purpose, firstly the technological and metallurgical characterization of the assemblage, and furthermore an attempt for dating it. Due to the restricted extension of this paper we present an overview. A detailed archaeometric study will be published in the near future.

This well-known treasure has embodied sensitive social concerns, appropriating ideological meanings that were never at its origin. For this reason we prefer to introduce our work within the frame of current Colombian archaeology.

1. Background

We can distinguish three main issues that have conditioned Colombian archaeology, the first one stems from the construction of the Colombian state after the independence from Spanish rule in 1819, and it is related to the search for a national identity. The need to integrate the different social groups that made up the new

* Corresponding author. Tel.: +34 91 602 24 88. E-mail address: alicia.perea@cchs.csic.es (A. Perea). society was soon made evident. These groups, created by Spanish colonial segregation, included the indigenous people. The identitarian discourse arose from anthropology with the aim of solving a dichotomy: on the one hand to redeem native communities and convert them to civilization, and on the other hand to rationalize pre-hispanic society as the cornerstone of national identity. As Gnecco (2008) states archaeology was built upon anthropological premises and contributed only to perpetuate internal colonialism.

The second issue concerning research in past societies refers to the theoretical premises at its base. During the first half of the XX century foreign researchers undertook major archaeological and anthropological enterprises, not only in Colombia but all over Latin America. Meanwhile, Colombian archaeologists went abroad to be prepared as scientists. For example the National Ethnological Institute was founded by the French anthropologist Paul Rivet in 1941; the Spaniard José Pérez de Barradas and the Austrian Gerardo Reichel-Dolmatoff laid out the bases for pre-Columbian goldworking chronology and interpretation. In this case, while anthropology overcame the old fashioned nationalistic discourse, vindicating the indigenous legacy, archaeology "kept strengthening nationalism by incorporating native societies into a common history" (Gnecco, 2008: 1108). In the opinion of G. G. Politis (2003) the culturehistorical paradigm for the reconstruction of the past remains



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strong in Colombia. Present-day researchers have adopted modern scientific techniques and discourse, but in general, ethnographic analogy and current extrapolation are long standing traditions used to explain the archaeological record. One of the reasons of this state of affairs is the primary concern for accumulating descriptive data of the archaeological record due to lack of excavations and the existence of poorly known vast regions (Politis, 2003: 130).

The systematic looting of archaeological sites in search for valuable objects is a common activity known as guaquerismo (or huaquerismo) and widespread throughout Latin America. Guaquerism is not only a normal activity, but a way of earning a living (Gamboa Hinestrosa, 2002). The result is large archaeological collections, mainly of gold but also pottery and textiles, without a context and even without a place of origin. This practice already occurred during the 16th century, when Royal documents attest that the Spanish conquistadors plundered many sites searching for gold in the Cauca river valley. The second large plundering wave in this same region occurred during the second half of the 19th century when this activity became one of the factors for capital accumulation (Valencia Llano, 1989). Since 1826 the mining activity of the Colombian Mining Society was another factor behind the indirect spoiling of archaeological sites. The Museo del Oro in Bogotá, founded in 1939, has played an important role in recovering pre-Columbian gold objects from the Antiquaries market, collecting some 34,000 gold items at present.

The absence of archaeological contexts has prevented the construction of a safe chronological frame where to place the archaeological record. As a result archaeology turned firstly to stylistic analysis, and secondly to ethnology in search for symbolic and functional explanations.

As far as analytical data is concerned, there is only a small amount of studies about pre-Columbian gold-work except for some generalities regarding the Cu–Au–Ag alloy known as *tumbaga* (Ruvalcaba Sil and Demortier, 1997).

In the last decade field archaeology programmes have been developed, building up regional chronologies with an emphasis on social change and organization. For example the *Valle de la Plata* project (Drennan, 2000, 2008) or more recently the *Proyecto Arqueológico Tierradentro*, funded by the Instituto Colombiano de Antropología e Historia ICANH (Langebaeck and Dever, 2009). Still, the wheels of field-archaeology/pottery based chronologies and stylistic/gold periodizations are not definitely assembled.

2. Materials & methods

2.1. The Quimbaya Treasure

The so-called Quimbaya Treasure was looted in 1890 from two tombs in the site of La Soledad, near the Municipality of Filandia (Ouindío Department, Colombia), amidst the Central Cauca Valley. They say it was made up of more than 200 gold objects, but only 123 objects were acquired in 1891 by the President of the Republic, Carlos Holguín, with three purposes in mind. Firstly, to present the treasure at the 1892 exhibition in Madrid commemorating the 4th Centennial of the discovery of America. Secondly, to display the treasure at the International Exhibition of Chicago dedicated to Columbus. And finally to give it as a present to the Regent Queen of Spain, Doña María Cristina de Absburgo Lorena, in appreciation for her mediation in a frontier conflict with Venezuela. The treasure was kept at the National Archaeological Museum in Madrid, until the opening of the Museo de América in 1965 where it continues to be in permanent exhibition (Plazas, 1978; Cuesta Domingo and Rovira Llorens, 1982; Rovira Llorens, 1992; Gamboa Hinestrosa, 2002).

Ernesto Restrepo (1892a, 1892b, 1929) was the first to publish this assemblage associating it with the Quimbaya ethnic group that the

Spanish chronicles mentioned when describing the region in the 16th century. From then on all the gold findings in the area were attributed to the historic Quimbaya group. Not until the middle of the 20th century was a more elaborate classification for pre-Columbian gold production. José Pérez de Barradas (de Carrera Hontana and Martín Flores, 2008), had worked in Colombia between 1936 and 1938 in the archaeological area of San Agustín and Tierradentro. In 1946 he was charged by Luís Ángel Arango, manager of the Banco de la República, with the classification of the gold collection at the Museo del Oro which had 7000 gold objects at the moment. His method was based on the concept of style as defined by Meyer Schapiro who put an emphasis in its communicative function. Without archaeological contexts he warned about the real implications of this classification, stating its use only as a spatial manifestation of recurrent iconographic features. He was very conscious of the feeble connection between the names of the historical people described in the Spanish chronicles and the archaeological people who really produced that goldwork. With all these drawbacks in mind he defined eight stylistic groups: Calima, Quimbaya, Darién, Sinú, Tairona, Muisca, Tolima and Invasionist (Aceituno, 2008). His classification lacked chronological references and archaeological connections, resulting in long periods which spanned for over a millennium.

The groups stated by Pérez de Barradas are still in use, although their importance and meaning have slightly changed in favour of a more general division for metal production in two metallurgical provinces (Plazas and Falchetti, 1986), the North province and the Southwest.

In the meantime Gerardo Reichel-Dolmatoff carried out his research with the aim of establishing an evolutionary sequence of the human occupation in the country. In his book *Colombia* (Reichel-Dolmatoff, 1965) description was left out in favour of social change processes from a diffusionist point of view, developing important concepts like the Intermediate Area that covers from Centroamérica to the central Andean region or the idea of "tradition" or "horizon". He played an important role in the academic life of the country, and he was the first professor in charge of a Department of Anthropology at the Universidad de los Andes in 1963. He began to be more interested in ideology and ethnography due to his reading of Lévy-Strauss with an idea in his mind: the past could be explained through contemporary native communities (Langebaeck, 2005). One of his most influential works refers to the interpretation of pre-hispanic goldwork in terms of shamanism (Reichel-Dolmatoff, 1988).

Research in pre-Columbian gold at the inception of the 21st century entails a double task. On the one hand one must accomplish the enormous classification of the archaeological record, filling gaps in connection with the ever increasing data from scientific field archaeology (McEwan, 2000). On the other, it is necessary to pose questions that call for new methods under an autochthonous and independent discourse, negotiating the relation between research, the academy and the active social and political movements (Rodriguez, 2002).

2.2. Experimental

Today the Quimbaya gold production includes the old Quimbaya and Invasionist groups from Pérez de Barradas. According to M.A. Uribe (1991, 2004) there are two periods, Classic/Early Quimbaya between 500 BC and 600 AD, associated to the so called *marrón inciso* pottery, and Late Quimbaya that extends until the Spanish conquest and should be better named *Sonsoide* considering its association to this particular archaeological group. The connections between both periods are not at all explained, but from the typological and technological points of view both productions are very different (Rodriguez, 2002). The Quimbaya Treasure belongs to the first of these periods, which it helped to define. After Pérez de Barradas there has been a limited attempt to study this important assemblage (Cuesta Domingo and Rovira Llorens, 1982; Rovira Llorens, 1994).

Aware of the limitations and risks of dealing with politically sensitive and, ideologically meaningful, archaeological materials we undertook its study persuaded that only an archaeometricallyoriented analysis could help to shed some light on this long shadowed assemblage.

To cope with the complex technology of these archaeological materials it is necessary to combine different analytical procedures to allow the physical characterization of the samples (Contreras et al., 2007; Ruvalcaba Sil et al., 2004). After a first characterization by optical microscopy (OM), all the objects were analysed using XRF with portable equipment. The use of Scanning Electron Microscopy (SEM) was ruled out due to the size of the objects (Perea and García-Vuelta, 2012), and only the gold micro-beads were examined. The high cost of moving the assemblage obligated the selection of 63 objects for the elemental characterization using PIXE-RBS. In the third phase the inside of the funerary urns were explored for any organic remains which could be dated using AMS. Finally, X-ray pictures were taken of the more complex objects, helping us to understand the technical features.

2.3. Samples

We had unrestricted access to all types of objects from the treasure. These comprise anthropomorphic and phytomorphic vessels; headed pins for mixing coca leaves with lime; helmets; a crown; a whistle and possibly a second wind instrument; nose rings, earrings and rattle earrings; bells; bracelets; quite a variety of beads, micro-beads and zoomorphic and anthropomorphic pendants. All are described as made up of *tumbaga* alloy with an enriched surface in the literature. Traditionally the characteristic of these objects that attracted more attention was the very detailed representations of men and women in ecstatic attitudes although we lack an iconographic study of this assemblage.

3. Results and discussion

3.1. OM

Optical microscopy is a simple, efficient method for identifying tool marks, technical processes, usage, wear damage and deterioration in burial/museum conditions (Armbruster et al., 2003; Perea, 2010). Quimbaya technological processes as documented in the Madrid assemblage include lost wax castings in four variants:

- open cast,

- with one interior core,
- with two interior cores, as in the rattle earrings (Fig. 1),
- casting on for unions and repairs (Fig. 2).

Apart from the latter we could identify post-casting retouching with punches and chasing tools, cutting, inlaying of materials other than gold (Fig. 3), plastic deformation by hammering and burnishing, coloured surface finishings by depletion gilding, multicoloured surfaces – red, yellow, white – and mechanical twisting interlockings for added elements (Fig. 4). A useful index for the complexity and excellence of these processes is the size span of the castings that varies from 53.0 cm long of the biggest object to 0.16 cm diameter of the smallest one. We observed some casting defaults like voids or porosity but in general the quality standard is very high. Wear or usage marks were not visible, this circumstance together with the fact that some of the inner cores were not removed after casting, lead us to think that at least some of the objects were manufactured just before their interment.



Fig. 1. Rattle earring lost wax casted with two interior cores, one for the ring body and the second for the inner metal sphere (photo: Archivo Au, F. Cuesta).

Smooth shiny surfaces (Fig. 5) show colour stains due to burial conditions but also to repeated cleaning with abrasive products during modern times to the point of eliminating the enriched surface almost completely in some objects.

3.2. SEM-EDS

The Madrid assemblage includes 18 gold anthropomorphic and phytomorphic vessels known as *poporos* and *totumas*. They were used to keep the lime necessary to mix with coca leaves for its consumption, but also they served as funerary urns to keep a portion of the ashes after the cremation of the corpse, and in some cases they introduced a handful of gold micro-beads at the same time. The variable pressure Hitachi 3400N Scanning Electron Microscope, equipped with a Bruker Quantax 4010 energy dispersive X-ray spectrometer, was used for the topographic and analytical study of these remains at the MicroLab of the CCHS-CSIC.

Nearly one hundred of tiny gold beads of different shapes were recovered. Some of them show very fresh cutting traces from a lost wax hollow rod of about 1.6 mm in diameter (Fig. 6). Others were made shaping a small piece of gold sheet. Elemental analysis shows



Fig. 2. Casting on repair on of a void in the abdomen of a female anthropomorphic vessel. The same repair is noticeable in the X-ray image of Fig. 13 (photo: Archivo Au, CCHS-CSIC).



Fig. 3. Anthropomorphic vessel in the form of a man's head with openwork to inlay other material than gold. Museo de América, Madrid (photo: Archivo Au, CCHS, CSIC).

a variety of Cu contents (from not detected to 17%) on the contrary Ag remains around 15%, the mean value.

The ashes were identified as burned bone and sent for radiocarbon dating (see below, 3.5).

3.3. XRF

Quantitative elemental analysis using XRF were done *in situ* with a portable Innov X tube-based Alpha Series analyzer. The primary photon beam was produced with a silver anode X-ray tube. The source is equipped with a 2 mm Al filter in order to remove interfering components of the tube radiation and to improve the signal-to-noise ratio. The X-ray source provides a maximum power of 8 W and it was operated in normal conditions of voltage (35 kV) and current (2 μ A). The characteristic X-rays emitted by the samples were measured by a Peltier-cooled Si-PiN diode detector (230 eV FWHM). The circular beam port cross section of 15 mm² permitted global analyses on each analysed area. Data results are automatically processed by the instrument with the Data Analysis



Fig. 4. Helmet number 17428 decorated with two female figures whose heads are removable. Museo de América, Madrid (photo: Archivo Au, CCHS, CSIC).



Fig. 5. Anthropomorphic vessel, representing a seated man, in front of the detector at the CMAM accelerator while taking measures. Museo de América, Madrid (photo: Archivo Au, CCHS, CSIC).

Software in Alloy Analytical Mode, which utilizes a fundamental parameters algorithm to determine the elemental chemistry. Statistical errors associated to the measure are below 5% for Cu, 1% for Ag and 1% for Au.

In total, 287 XRF spectra were recollected from all Quimbaya items. Various spectra in different areas from the same object were taken in order to assess the homogeneity of the alloy, as it



Fig. 6. Micrography of one of the micro-beads showing fresh cutting traces. Museo de América, Madrid (photo: Archivo Au_MicroLab, CCHS, CSIC).

was the case, although the beam size of our instrument restricts a proper study. Nevertheless we observed noticeable differences in composition between reverse and obverse on circular pendants.

Major elements found were Au, Ag and Cu (Fig. 7a), together with low levels of iron, normally less than 1%, though in some areas of a sample it reached 4%. Samples are clearly positioned in the zone of the ternary diagram that comprises copper contents lower than 50% and silver levels between 12 and 25%. A small group of objects (beads, anthropomorphic vessels, helmets, ornamented pin heads, a Darien pendant, earrings and a nose ring) stand out for their high gold content (no copper was detected, LOQ for Cu: 3%). Absence of other elements confirms that there were no modern materials added to the samples, this is an important fact considering the difficult biography of the treasure.

3.4. PIXE-RBS

PIXE is widely used in the analysis of gold pieces as a totally nondestructive elemental analysis technique (Demortier and Ruvalcaba-Sil, 2005; Guerra and Calligaro, 2004). RBS technique is employed to determine thickness of thin layers and depth concentration profile. In particular the use of an external micro-beam allows the study of samples of different size and shape. RBS and PIXE were applied simultaneously on 63 Quimbaya objects in order to obtain detailed information about the elemental composition and its distribution in depth.

PIXE-RBS measurements were carried out in the external microbeam line at the CMAM facility with a proton beam of 3 MeV. Also, a proton beam of 5 MeV was used in order to increase the analysed depth. The proton beam crosses an exit Si_3N_4 window (100 nm thick) and 3 mm in atmosphere of helium (to minimize absorption of the incident beam and emitted X-rays) until it reaches the sample.

Emitted X-rays were collected by two Si(Li) detectors located at 43 and 50° with respect to the sample normal. The first one, with a resolution of 130 eV and an active area of 10 mm² was used for the detection of low energy X-rays, while the second detector with 150 eV FWHM, active area of 80 mm² and filtered by a 1000 or 500 μ m Mylar absorber (utilized to suppress the K alpha lines of copper) was employed for high energy X-ray detection. In general, several spots on each sample were chosen for analysis.

Quantification of PIXE spectra was done with the GUPIX software (Maxwell et al., 1995) assuming thick samples, i.e. constant concentration in depth and thickness larger than the particle range. Reproducibility of PIXE measurements has been checked by repeatedly analysing a 17 carats gold ring whose results were always consistent one to another within the experimental errors.

Backscattered ions were collected using a solid state Si diode with an active area of 50 mm² placed at backward angle of 140° under an atmosphere of helium. Data analysis of RBS spectra was performed with the computer code for simulation of elastic scattering spectra SIMNRA (Mayer, 1997).

3.4.1. PIXE results

The range of 3 MeV and 5 MeV protons in Au is 26.78 and 58.19 microns respectively (SRIM code, Ziegler et al., 2008). Taking into account that in XRF 95% of the Ag X-ray from the tube cathode is converted in 24 microns of Au and 95% of the 35 keV X-rays (maximum energy delivered by the tube) is converted in 70 microns, we may say that the thickness explored by the probe is comparable in the two cases. Furthermore we have proven (Zucchiatti, 2012; Ahlberg, 1977) that, when we use for the calculation of elemental concentrations the X-ray lines of maximum energy (L-lines for Au, K-lines for Cu and Ag), which suffer the lowest attenuation by the sample itself in their path to the detector, the PIXE and XRF compositions are very similar and refer to the sample bulk. The great advantage of PIXE is the spatial resolution: in the external beam of the CMAM was of the order of 50-80 microns, which allowed the examination of particular structures in the objects surface.

For all the 63 Quimbaya objects analysed at CMAM were taken 242 data points. PIXE spectra showed the presence of only a few elements: major elements Au, Ag and Cu (Fig. 7b) and in some of cases minor or trace elements Fe and Zn, probably due to inclusions of dust not uniformly distributed over the porous surface or to modern cleaning products. In the majority of cases multiple PIXE measurements on the same sample show that the bulk composition is essentially homogeneous (Fig. 8a) as it was known from the XRF measurements. In other cases it is possible to appreciate, thanks to the high spatial resolution of PIXE, composition differences that might or not have a trivial explanation.

In Fig. 8b we plot the results of different measurements on six objects identified by their catalogue number. For example, the object with catalogue number 17400 is a circular pendant in which one of the points (351 obverse) appeared less guilded than the other two (349-reverse, 350-obverse). Indeed the Cu content in point 351 is higher. The same occurs with objet 17401, another circular pendant, where measurements on the front (352,353) and back (354,355) are different; the back being richer in Cu. Objet 17413 is a bracelet where one of the measurements (261) was taken close to the joint and the other (262) in a dark spot. In the phytomorphic vessel 17440 (442–446), the lid is particularly rich in gold.



Fig. 7. Ternary diagrams showing Au–Cu–Ag compositions for all measures, where three main groups of objects are identified: a. XRF results (287 data points from all 135 Quimbaya items). b. PIXE results (242 data points from 63 Quimbaya items).



Fig. 8. a. Elemental composition of five objects showing internal homogeneity and inter object variability. b. Elemental composition of six objects taken in different points, showing internal variability.

As we said above, considering that PIXE measurements give substantially the bulk composition it is possible to distinguish at least three groups of objects: one is characterised by a low Ag content (<6%); the second one by a high Ag content (>27%) (Fig. 7b); and the third and largest group features a broadly distributed composition with an intermediate roughly constant Ag content, as it is the case for the XRF measurements (Fig. 7a). As a matter of fact only three objects (17426, 17429, 17432) are fully separated from the main group and two (17408, 17440) have only one point showing an outlier composition. For object 17408 this is a measurement taken on a recess and for object 17440 it is a measurement taken on a yellowish area.

The multi-technique examination of the objects has indicated on one side that depletion gilding was applied to surfaces but also that heavy surface cleaning, performed at some stage of the objects conservation may have removed most of the enriched surface. PIXE quantification of layered objects with the program GUPIX is not possible when Au, Ag and Cu are present, as it is our case, in various layers at different concentrations. However PIXE can give a qualitative indication of the presence of an enriched micrometric layer by looking at the intensity ratio between the K α and K β lines of Cu. The branching ratio of these two X-ray lines gives $K\alpha/K\beta = 7.1$. This will be the yield ratio observed measuring an ultra-thin copper sample that does not absorb either line. For any other sample the absorption of the K α (at 8.048 keV) will be higher than that of the K β (at 8.906) and the yield ratio will be lower than 7.1 depending on the matrix, the sample finite thickness and the angle of detection of the PIXE spectrum. We have calculated the yield ratio in an infinite sample (that in which protons loose all their energy) for a normal proton incidence and the detection at 45° (as in our PIXE set up) for various binary bulk compositions going from 100% Au to 100% Cu. To note that, as regards the Cu X-rays absorption Au and Ag are practically equivalent because their mass absorption coefficients for the K α line (Au 48.80 μ g/cm², Ag 48.35 μ g/cm²) and the K β line (Au 63.66 μ g/cm², Ag 63.67 μ g/cm²) are practically identical. Therefore a binary Au-Cu sample is equivalent to a ternary Au-Ag-Cu ternary sample. Then we have calculated the variation of the ratio due to a surface Au layer with thickness going from 0 to 5 microns. The results are shown in Fig. 9.

The calculated yield ratio, obtained at 45° for a bulk Au–Cu alloy, goes from 5.8 to 6.5 and then drops down with the increase of the absorbing surface gold layer. The distribution of experimental values has extremes at 6.5 and 4.0 and two maxima at 5.80 and 5.26. The majority of the measurements (peak at 5.80)

is compatible with no surface layer and a Cu rich bulk (40-50%) but the lowest experimental values can only be explained starting from a gold rich bulk (60-80%) followed by a 1-4 microns of gold on the surface. Guilding is therefore observed but only qualitatively being a quantification possible only through a specific technique like the RBS.

3.4.2. RBS results

A general inspection of the spectra allowed to distinguish between layered objects and those with homogeneous composition in depth although only for a few we could extract layer thicknesses. Elemental composition obtained with PIXE was used to provide starting values in the fitting of gold enriched samples and they represent the composition on the bulk alloy.

Only some anthropomorphic vessels, helmets, the crown, the whistle and one phytomorphic vessel exhibit a clear gold enriched surface; other samples may have lost the enriched surface as a consequence of abrasive cleaning. Different analysed spots of these same items show irregular gold surfaces layers regarding thickness and composition.

RBS fitted spectrum from the obverse of an anthropomorphic vessel (Fig. 10) show firstly a pure gold layer of about 0.6 μ m



Fig. 9. Variation of the Cu K $\alpha/K\beta$ ratio due to the alloy bulk composition and a surface Au layer with thickness going from 0 to 5 microns.



Fig. 10. RBS spectrum of an anthropomorphic vessel. Experimental data are shown in red line (top) and the simulated spectrum in blue. Contribution of Au, Ag and Cu elements, and He and air coming from the environmental are marked on the graphic. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

followed by an intermediate layer of 0.15 μm thickness with 90% gold and 10% silver, and finally the bulk alloy of 81% Au, 17% Ag and 2%Cu.

3.5. AMS dating

Although we use the term "assemblage" to name this group of objects found in the two looted tombs, we have no idea of the time span the necropolis was in use, or how many interment episodes occurred. To tackle the chronological problem we had the fortune that two of the anthropomorphic vessels still contained uncontaminated ashes which were used for radiocarbon dating. In addition, more samples were obtained from the inner cores (sediment) of an ear spool and a whistle (Table 1):

Some years ago the Museo del Oro (Bogotá, Colombia) undertook a dating programme for pre-hispanic metallurgy. There are six dates directly associated with Quimbaya goldwork all from the inner cores of gold objects except one that dates the charcoal (without specifying its origin) of a tomb. One of these dates (MA17424) corresponds to a pendant of the Madrid Quimbaya assemblage. The only data available was published by Plazas (1998) and Uribe (2005) as in Table 2.

The chronology of Classic Quimbaya period is nowadays based on these recent radiocarbon dates although it is surprising the date of 400 BC for a complex lost wax casting *poporo* according to Uribe (2005: 66). We must also take into account that the typology of the other dated items, zoomorphic pendants and a nose ring, are not

Table 1

Radiocarbon dates (Beta Analytic laboratory) from burned bone and inner cores contained in some objects of the Quimbaya Treasure (Museo de América, Madrid).

Lab. N°	Mus. N°	Material	BP	2 σ	Cal. date	Object
B-320629	MA17436	Sediment	1650 ± 30	340-430 AD	410 AD	Whistle
B-315972	MA17456	Burned bone	1620 ± 30	390-540 AD	420 AD	Poporo
B-315970	MA17422-5	Sediment	1600 ± 30	400-540 AD	430 AD	Ear spool
B-290934	MA17447	Burned bone	1480 ± 30	540-640 AD	590 AD	Poporo

B-: Beta Analytic laboratory.

Table 2

Radiocarbon dates as published by Plazas (1998) and Uribe (2005) obtained from Quimbaya gold objects in the Museo del Oro, Bogotá.

Lab. N°	Mus. N°	Material	BP (Plazas) ^a	Cal. date (Uribe)	Object
B-144489	MO00382	Sediment	_	$400\pm40\text{ BC}$	Poporo
B-97373	MO02023	Sediment	$2190\pm40\text{ BP}$	$240\pm40\text{ BC}$	Pendant
B-107961	MO00275	Sediment	$1900\pm50~BP$	$50\pm50~\text{AD}$	Nose ring
B-108843	MO06039	Sediment	$1760\pm40\text{ BP}$	$190\pm40~\text{AD}$	Pendant
B-190947		Charcoal	_	$250\pm50~\text{AD}$	Tomb
B-175663	MA17424	Sediment	_	$260\pm40~\text{AD}$	Pendant

^a Data available as published by Plazas (1998): conventional radiocarbon age is missing in some of the samples.

diagnostic of the Quimbaya production but common to a very wide area of the river Cauca valley and in use for a long period (Plazas, 1998).

The time span of our dates, obtained from ashes and inner cores (sediment), 410–590 AD, is a reasonable period for a necropolis to be in use and explains variability in terms of technological and analytical features of gold production.

3.6. Radiography

X-ray imaging techniques were applied at the Museo de América using a Yxlon International portable equipment. The



Fig. 11. X-ray image of a phytomorphic vessel showing the perfect modelling of the wax, and fine and homogeneous porosity (darker spots). Museo de América, Madrid (photo: Archivo Gabaldón-Antelo, IPCE).

X-ray beam, generated with a constant potential of 160 kV, crossed an exit window before reaching the object. Radiographic images were achieved in order to confirm technological features of the bulk metal which are not evident with an OM examination and to check actual state of conservation. We used this technique in technological complex items, like vessels, and only in those samples we could ascertain they did not contain more organic residues.

All the images show skilled modelling of the inner core of the wax casting and the control of very homogeneous and, in some cases extremely thin, wax layers (Fig. 11). The pegs for holding the inner cores in place leave perfectly circular holes filled in by burnishing gold rivets that are difficult to see with nude eyes, furthermore, they are situated in strict symmetry (Fig. 12). Some of these rivets have disappeared. In one case there were two gold micro-beads still left stuck to the inner wall of a vessel (Fig. 13).

The main problem the artisan had to cope with during the casting process was the evacuation of gases produced by the filling of the mould and subsequent solidification of the alloy. This produced microporosity and small voids in many of the items. Only in one case have we observed a big metal gap due to low temperature or excessive density of the alloy that could not fill the mould completely before cooling. All these small flaws were repaired by casting on.

Two of the items presented small fissures, probably developed from porous areas that ended in fatigue failure and finally fracture.



Fig. 12. X-ray image of a phytomorphic vessel showing porosity areas (darker) and the symmetrical position of the perfectly circular holes (brighter) of the inner core sustaining pegs. Museo de América, Madrid (photo: Archivo Gabaldón-Antelo, IPCE).



Fig. 13. X-ray image of an anthropomorphic vessel representing a seated woman. Some repaired voids can be seen on the abdomen (brighter spots) and a gold microbead stuck to the inner part of the left arm (square shaped and brighter). Museo de América, Madrid (photo: Archivo Gabaldón-Antelo, IPCE).

4. Conclusions

According to analytical results the Quimbaya assemblage shows variable bulk elemental compositions, comprising three main groups according to silver content. The largest group corresponds to silver levels of around 15%. A small number of objects stands out for being manufactured in a very high gold content alloy. Relating to objects themselves, they generally exhibit high bulk homogeneity. Finally, the existence of an enriched surface layer was proved by RBS, in those cases that this gilded surface was preserved from modern abrasive cleaning.

The Quimbaya Treasure is important not only for the quality and large number of items but for its common archaeological funerary context. It is in this sense that we have used the term assemblage. Considering the big items only, such as vessels, helmets, crowns and pins, we can ascertain a common craftmanship origin or technological tradition that could have developed only within a restricted period of time. It is very improbable that these technological traditions and processes could persist over a millennium. Even if we take tradition and continuity in pre-Columbian communities as the main feature in gold production, it is hard to accept the persistence of particular technical behaviours and iconographic characteristics without any change all throughout the Classical Quimbaya period 500 BC–600 AD. We suggest that this assemblage should be considered as characterising a specific phase in the long goldwork production period of the area. The new radiocarbon dates, 410–590 AD, would mark the time span of this phase.

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References

- Aceituno, F.J., 2008. El segundo viaje de José Pérez de Barradas a Colombia: la orfebrería prehispánica. In: de Carrera Hontana, E., Martín Flores, A. (Eds.), Arqueología, América, Antropología. José Pérez de Barradas 1897–1981. Museo de los Orígenes, Madrid, pp. 287–301.
- Ahlberg, M.S., 1977. Comparison of yield versus depth for particle induced and photon induced X-ray emission analysis. Nuclear Instruments and Methods 146, 465–467.
- Armbruster, B., Comendador, B., Montero, I., Perea, A., Pernot, M., 2003. Tools and tool marks. Gold and bronze metallurgy in Western Europe during the Bronze and Early Iron ages. In: Archaeometallurgy in Europe. Proceedings, Milano (2003), Associazzione Italiana di Metallurgia, vol. I, pp. 255–266.
- de Carrera Hontana, E., Martín Flores, A. (Eds.), 2008. Arqueología, América, Antropología. José Pérez de Barradas 1897–1981. Museo de los Orígenes, Madrid.
- Contreras, J., Ruvalcaba Sil, J.L., Arenas Alatorre, J., 2007. Non destructive study of gilded copper artifacts from the Chichén-Itza cenote. In: Proceedings of the XI International Conference on PIXE and Its Analytical Applications, Puebla (2007) Mexico.
- Cuesta Domingo, M., Rovira Llorens, S., 1982. Los Trabajos en Metal en el Área Andina. Museo de América, Ministerio de Cultura, Madrid.
- Demortier, G., Ruvalcaba-Sil, J.L., 2005. Quantitative ion beam analysis of complex gold-based artefacts. Nuclear Instruments and Methods in Physics Research B 239, 1–15.
- Drennan, R.D., 2000. Las Sociedades Prehispánicas del Alto Magdalena. ICANH, Bogotá.
- Drennan, R.D., 2008. Chiefdoms of Southwestern Colombia. In: Silverman, H., William, H.I. (Eds.), Handbook of South American Archaeology. Springer, New York, pp. 381–403.
- Gamboa Ĥinestrosa, P., 2002. El Tesoro de los Quimbayas. Historia, Identidad y Patrimonio. Planeta, Bogotá.
- Gnecco, C., 2008. Modernity and politics in Colombian archaeology. In: Silverman, H., William, H.I. (Eds.), Handbook of South American Archaeology. Springer, New York, pp. 1103–1113.
- Guerra, M.F., Calligaro, T., 2004. Gold traces to trace gold. Journal of Archaeological Science 31, 1199–1208.
- Langebaeck, C.H., Dever, A., 2009. Arqueología regional en Tierradentro, Cauca, Colombia. Revista Colombiana de Antropología 45 (2), 323–367.

- Langebaeck, C.H., 2005. De los Alpes a las selvas y montañas de Colombia: el legado de Gerardo Reichel-Dolmatoff. Antípoda 1, 139–171.
- Mayer, M., 1997. SIMNRA User's Guide. Technical Report IPP 9/113, Max-Planck-Institut für Plasmaphysik, Garching, Germany.
- Maxwell, J.A., Teesdale, W.J., Campbell, J.L., 1995. The Guelph PIXE software package II. Nuclear Instruments and Methods in Physics Research B 95, 407–421.
- McEwan, C. (Ed.), 2000. Precolumbian Gold. Technology, Style and Iconography. British Museum Press, Singapore.
- Perea, A., García-Vuelta, O., 2012. Gold usage. Wear marks and/or deterioration in site conditions. In: Meeks, N., Cartwright, C., Meek, A., Mongiatti, A. (Eds.), Historical Technology, Materials and Conservation: SEM and Microanalysis. Archetype, London, pp. 86–92.
- Perea, A., 2010. Wands in the hand! Or Potter's powers. In: Guerra, M.F., Rehren, T. (Eds.), Authentication and Analysis of Gold Work. ArcheoSciences, vol. 33, pp. 21–28.
- Plazas, C., Falchetti, A.M., 1986. Patrones culturales en la orfebrería prehispánica de colombia. In: Plazas, C. (Ed.), Metalurgia de América Precolombina. Banco de la República, Bogotá, pp. 201–227.
- Plazas, C., 1978. Tesoro de los Quimbayas y piezas de orfebrería relacionadas. Boletín del Museo del Oro 2, 3–10.
- Plazas, C., 1998. Cronología de la metalurgia colombiana. Boletin del Museo del Oro 44-45 (Virtual Edition).
- Politis, G.G., 2003. The theoretical landscape and the methodological development of archaeology in Latin America. Latin American Antiquity 14 (2), 115–142.
- Reichel-Dolmatoff, G., 1965. Colombia: Ancient Peoples and Places. Thames and Hudson, London.
- Reichel-Dolmatoff, G., 1988. Orfebrería y Chamanismo. Un estudio iconográfico del Museo del Oro. Editorial Colina, Medellín.
- Restrepo Tirado, E., 1892a. Ensayo Etnográfico y Arqueológico de la Provincia de los Quimbayas en el Nuevo Reino de Granada. Bogotá.
- Restrepo Tirado, E., 1892b. Orfebrería de las tribus Quimbaya y Chibcha. Revista El Centenario tomo III, 341–345.
- Restrepo Tirado, E., 1929. Ensayo Etnográfico y Arqueológico de la Provincia de los Quimbayas en el Nuevo Reino de Granada. Sevilla.
- Rodriguez, C.A., 2002. El Valle del Cauca Prehispánico. Departamento de Historia, Facultad de Humanidades, Universidad del Valle, Santiago de Cali.
- Rovira Llorens, S., 1992. El oro de los Quimbayas. The gold of Quimbaya. In: El Oro de América. Exposición Universal de Sevilla, Sevilla, pp. 104–109.
- Rovira Llorens, S., 1994. Pre-Hispanic goldwork from the Museo de América, Madrid. In: Archaeometry of Pre-Columbian Sites and Artifacts. Proceedings of a Symposium, UCLA Institute of Archaeology (1992). The Getty Conservation Institute, Los Angeles, pp. 323–351.
- Ruvalcaba Sil, J.L., Demortier, G., 1997. Scanning RBS-PIXE study of ancient artifacts from South America using microbeam. Nuclear Instruments and Methods in Physics Research B 130, 297–302.
- Ruvalcaba Sil, J.L., Torres, L., Franco, F., Ortíz Díaz, E., 2004. Artifact rich gold surfaces: depletion gilding or natural surface corrosion? Study of corrosion and oxidation of gold alloys. In: Perea, A., Montero, I., García-Vuelta, O. (Eds.), Ancient Gold Technology: America and Europe. CSIC, Madrid, pp. 41–47.
- Uribe, M.A., 1991. La orfebrería Quimbaya tardía. Una investigación en la colección del Museo del Oro. Boletín del Museo del Oro 31, 31–124.
- Uribe, M.A., 2004. Desde la mirada del arqueólogo-curador. La construcción de los guiones de la región del Cauca Medio y el vuelo chamánico para el Museo del Oro 2004. Boletín del Museo del Oro 52, 31–55.
- Uribe, M.A., 2005. Mujeres, calabazos, brillo y tumbaga. Símbolos de vida y transformación en la orfebrería Quimbaya temprana. Boletín de Antropología 19 (36), 61–93.
- Valencia Llano, A., 1989. La guaquería en el viejo Caldas. Boletín del Museo del Oro 23, 60-75.
- Ziegler, J.F., Biersack, J.P., Ziegler, M.D., 2008. SRIM the Stopping and Range of Ions in Matter. SRIM Co., ISBN 0-9654207-1-X.
- Zucchiatti, A., 2012. Multidisciplinary Applications of Nuclear Physics with Ion Beams – Legnaro (Padova), June 6–8, AIP Conference Proceedings.