Of forming, gilding and intentionality in Pre-Columbian goldwork: analytical characterisation of artefacts from the Museo del Oro, Bogotá

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The analytical study of ancient metalwork is a useful strategy to characterise past technologies, but in contrast with other American metalworking traditions this approach has been relatively limited in the context of pre-Columbian Colombia. As a contribution to this emerging research area, this paper presents the results of a compositional and technological study on seven gold alloy artefacts from the collections of Museo del Oro, Bogotá D.C., Colombia, focusing on alloy selection, forming technologies and surface treatments. The artefacts come from four different metalworking regions, and include personal adornments, a votive figure, and an unidentified sheet fragment. Surface imaging and microanalyses were carried out by scanning electron microscopy with energy dispersive spectrometry (SEM-EDS). X-ray mapping was undertaken to gain further insight into depth and nature of surface treatments and internal microstructures. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) data was also collected, enabling cross-analytical technique comparisons and the collection of trace element data. The results allow the identification of alloying technologies and forming methods, as well as the characterisation of corrosion products and gilding layers, and discussion of the intentionality of the latter where present. The case studies are discussed in relation to the existing pool of evidence and used to assess the potential for further analyses on the region's metalwork.

Keywords: gold; tumbaga; gilding; lost-wax casting; SEM-EDS; pre-Columbian

1. Introduction

The pre-Hispanic gold metallurgy of Colombia displays a wide range of manufacturing technologies, alloy types, styles and iconographies. Inferring patterns of temporal and regional change on the basis of extant artefacts has proven to be challenging, however, given the prevalent lack of contextual information but also by the lack of production debris found within the region (Lleras Pérez, 2015; Plazas, 1998; Scott, 1998). Traditionally, the task of archaeometallurgists working in the region has therefore been to group their assemblages largely according to the macroscopic examination of their stylistic, iconographic and technological features, enabling them to assign unprovenanced objects to regional cultures through comparisons with objects of known provenience (Falchetti, 1993; Lleras Pérez, 2015; Uribe Villegas, 1991). The area of present-day Colombia has been particularly well studied using this approach, enabling the identification of 12 metalworking zones (Figures 1, 2) (Plazas and Falchetti, 1978, 1985; Uribe Villegas, 1988).

Some added input was provided by early semi-quantitative or qualitative fire assay, touchstone, colorimetric or volumetric analyses (Pérez de Barradas, 1954, 1958, 1966; Rivet and Arsandaux, 1946). While valuable contributions, the results of these analyses are mostly approximative, and the microstructure of the metals was barely examined at the time. More recent microscopic and compositional studies have also started to contribute to the reconstruction of past metallurgical activities within the region, showing an array of alloys and manufacturing techniques (Bustamante Salazar et al., 2006; Davis-Kimball and Twilley, 1982; La Niece, 1998; Martinón-Torres and Uribe-Villegas, 2015a; Perea et al., 2016; Sáenz-Samper and Martinón-Torres, 2017; Scott, 2012; Uribe Villegas and Martinón-Torres, 2012a). Such applications, while limited in scope to-date, have shown that archaeometric data has significant potential in complementing, disproving, or supporting macroscopic lines of evidence; in the context of pre-Columbian metallurgy, technical examinations are thus likely to contribute to how the assemblages are grouped and analysed in the face of spatio-temporal uncertainty.

Each of the 12 metallurgical groups identified so far, and the temporal divisions within them, exhibit their unique sets of characteristics, although continuity of practice can also be observed. The use of ternary Au-Ag-Cu alloys or *tumbaga* (it is worth noting that for most of Colombia, the silver in the alloy originates from native argentiferous gold as opposed to being an intentional alloying element), lost-wax casting technology, as well as the importance of colour symbolism and gilding practices have traditionally received significant attention in the region's literature. At the same time, previous studies have also identified significant quantities of hammered objects, unalloyed gold and non-gilded tumbaga. In general, metallurgical cultures in the southwest (Figures 1, 2) are said to be characterised by the use of high-purity gold as well as the direct working of metals (Bray, 2000; Plazas and Falchetti, 1985) while the northern traditions are more leaned towards the use of copper-rich alloys as well as fabrication by lost-wax casting (Falchetti, 1993). For more detailed descriptions of individual metallurgical cultures, see references cited within this introduction.

Importantly, however, as seen in Figures 1 and 2, this classificatory framework is still based on broad regional generalisations over long time spans. Consequently, the understanding of the inception and movement of technologies remains limited, and while some studies do suggest the exchange of ideas and materials between specific metalworking zones (e.g. Falchetti, 1993), we argue that the assessment of these hypotheses would benefit from cross-regional archaeometric research paradigms. Overall, our current state of knowledge on the pre-Hispanic metallurgy of Colombia remains limited in comparison to, for instance, areas further south in the Andes, where metalwork is not only better contextualised, but where the analytical work undertaken on metallurgical assemblages has been more substantial.

As one of the first invasive analytical studies in the region, this article presents a pilot study that sought to assess the potential for further analyses on the metalwork of pre-Hispanic Colombia, comparing the results of invasive and non-invasive analytical techniques, and informing future research of optimum analytical protocols. This is achieved through case studies whereby technological information is extracted from microscopic and analytical data. Due to the limited scope and the opportunistic sampling strategy used, the case studies do not lend themselves to in-depth discussions of pre-Columbian craftsmanship on their own; when discussed in relation to other existing data, they can however be used to draw attention to technological features that are of interest for future studies on the region's metallurgy.

2. Materials and methods

2.1 Samples

All of the samples analysed here come from the collections at the Museo del Oro, Bogotá, and were exported to Europe with permission for invasive analyses in 2011. Notwithstanding curatorial constraints, we sought to cover geographic variability and to sample objects that, although fragmentary, could be assigned to recognisable typologies by reference to other artefacts. The cultural attribution, place of origin (department and municipality), function, and area of analysis (where applicable) of each artefact are reported in Table 1.

Archaeological context type is known for only one of the artefacts, O33811, which is reported to come from a votive offering deposited inside a ceramic vessel and found at Tenjo in the department of Cundinamarca, Colombia (Martinón-Torres and Uribe-Villegas, 2015a). For the rest of the artefacts, the municipality of origin is reported in the museum database for all of the samples except for the composite Calima artefact, O05639a. These recovery locations are represented on a map of Colombia in Figure 1.

Registration no.	**Cultural attribution**	**Department**	**Municipality**	**Function / area of analysis**
O21954a	Nariño	Nariño	Pupiales	Personal (nose) adornment?
O10062a	Quimbaya	Quindío	Circasia	Sheet fragment
O10062b	Quimbaya	Quindío	Circasia	Personal (ear?) adornment
O21154	Muisca	Boyacá	Pesca	Personal adornment (necklace bead?)
O33811	Muisca	Cundinamarca	Tenjo	Votive figure / wired detail on headdress
O05639a1	Calima	Unknown	Unknown	Personal adornment (dangler) / wire
O05639a2	Calima	Unknown	Unknown	Personal adornment (dangler) / sheet

Table 1: A summary of the cultural attribution, provenance, as well as function and area of analysis for each of the analysed artefacts.

2.2 Methods

The current analytical program consisted of the examination of the artefacts' surface topographies and internal microstructures by SEM imaging, EDS analysis of the artefacts' bulk and phase compositions, as well as X-ray mapping of representative areas in-cross-section, with the primary objective of investigating forming methods, surface treatments, alloying technologies and corrosion products. Three different SEMs were used because of changing availability throughout the course of this research. LA-ICP-MS analyses were also carried out, allowing a comparison of the two analytical techniques, as well as adding to the small corpus of trace element data on pre-Hispanic Colombian metallurgy.

The surface imaging was carried out without prior sample preparation, using two scanning electron microscopes, a JEOL JSM-6301F and a Hitachi S-3400, both operating under high vacuum at an accelerating voltage of 5 kV, using mainly the secondary electron (SE) mode. Additionally, the back-scattered electron (BSE) mode was used in the Hitachi S-3400, which has a radial backscattered detector that enables the creation of topographic detail slightly below the sample surface in BSE, and is often more successful in counteracting the effects of surface dirt or sample charging than conventional SE imaging. Subsequently, cross-sections of each sample were mounted in epoxy resin and polished to a grade of 1μm. Given the susceptibility of gold to scratching, we used wax instead of water for grinding, and alumina instead of diamond suspension for polishing. All polished blocks were carbon coated prior to analysis to prevent charging; this is because while gold, silver and copper are highly conductive, the samples exhibited variable degrees of corrosion and were not 100% metallic.

BSE imaging and compositional analysis of the cross-sections were then undertaken with the Hitachi S-3400 SEM with an Oxford Instruments EDS detector, using INCA software. The EDS analyses were conducted under high vacuum, at an accelerating voltage of 20 kV, and a working distance of 10 mm; instrument calibration was undertaken with a cobalt standard. In order to determine the bulk compositions of the samples, we used the scan mode to analyse small areas on the artefacts, as this provides a better approximation of the bulk metal than the analysis of single spots. An attempt was made to obtain three area scans of c. 100x50 µm, although limitations to do with the size and shape of the samples themselves, as well as the need to avoid porosity and corroded areas as far as possible, did not always permit for this. Point analyses were used for the other phases. The live acquisition time for each area and point analysis was 100s. Three certified reference materials commonly employed for archaeological goldwork (e.g. Blakelock [2016]) were analysed to test for accuracy and precision and are reported in Supplementary Material A. All sample preparation and the above analyses were conducted at the Wolfson Archaeological Science Laboratories at University College London, UK.

X-ray maps were collected at the Department of Earth Sciences, University of Cambridge, using a QUANTA-650F SEM with two EDS detectors, under high vacuum, an accelerating voltage of 20 kV, acquisition time of 1200s per area, and using ESPRIT software.

Lastly, LA-ICP-MS analyses were conducted on the surfaces and underneath surface layers, such as corroded and enriched surfaces, where accessible through cracks. This permitted the comparison of the results produced by this quasi-non-destructive method with the results obtained in cross-section by SEM-EDS, to assess the extent to which results from the two techniques can be pooled together. LA-ICP-MS also offers much lower detection limits for geochemical characterisation and was used for the collection of trace element data. This analysis was undertaken at the Curt-Engelhorn Centre for Archaeometry, under 'wet-plasma' conditions, with a Nd:YAG nano-second laser operating at 213 nm. Following pre-ablation to remove surface contamination, spot ablations (spot size 50µm) or line ablations (300µm long, 50 µm wide) were performed, depending on the artefact. A more detailed description of the analytical procedure can be found in Martinón-Torres and Uribe Villegas (2015a), for which the LA-ICP-MS data was collected in conjunction with the data presented here; instrument optimisation followed the procedure described in Kovacs et al. (2009).

All of the samples reported are alloys of gold with variable amounts of silver and copper. As common in the literature, we calculated the silver-in-gold ratio by neglecting the copper content in the alloy and re-normalising the results to 100%, using the following ratio: $Ag\ wt\%/(Ag\ wt\% + Au\ wt\%)$. This value is useful to estimate the silver levels of the original gold employed in cases where naturally argentiferous gold was alloyed with copper (Uribe Villegas and Martinón-Torres, 2012a).

3. Results and discussion

Since the analysed artefacts come from four different metallurgical cultures, each with different stylistic and technological repertoires, the results in this section are organised by region, while drawing attention to similar features of interest, in particular forming methods and presence/absence of surface treatments. For comparative purposes, the technological observations on each artefact are reported in Table 2.

3.1 Nariño sheet fragment (nose ornament?) (O21954a)

Our first sample comes from the metallurgical region of Nariño, located in the southwestern highlands of present-day Colombia (Figure 1). Sample O21954a is reported to belong to the Late Nariño Period (Figure 2), during which the majority of pre-Columbian metal production took place, and which, for the southwestern territory where the object was found in, is traditionally divided into two sub-traditions, the Capuli and the Piartal (Alba Goméz, 2015; Plazas de Nieto, 1977-78). The sample is a fragment of a once complete, flat object (possibly a nose ornament), and geometric shapes prevail in its design.

3.1.1 Analytical characterisation (O21954a)

The results of the compositional SEM-EDS analyses show that object is made from an Au-Ag-Cu alloy rich in copper (Table 3). BSE imaging in cross-section (Figure 3) shows that O21954a has a fibrous internal microstructure, and that the light-grey (copper oxide) and dark-grey (copper sulphide) inclusions appear deformed alongside the length of the metal. X-ray mapping revealed additional evidence of the metal's packed crystal structure (Figure 4A-C). Under higher-magnification mapping, inter-granular corrosion reveals remnants of a recrystallised structure (Figure 4D-F). A bright layer can be observed on both sides of the object in cross-section (Figure 3); this is also reflected in the X-ray maps in Figure 4. The thickness of the bright layer is less than 10μm (Figure 4D-F). On the surface, the gold content appears increased, and copper and silver proportionally reduced (Table 3).

When comparing the LA-ICP-MS analyses (Supplementary Material B) with SEM-EDS, analyses of the metal core showed absolute differences lower than 2wt%, while the analysis of the surface by LA-ICP-MS showed much higher copper and lower gold than SEM-EDS. The trace element data shows a comparatively elevated presence of platinum and other platinum group elements (PGE).

3.1.2 Discussion (O21954a)

Both the object's fibrous internal microstructure, typical of two-phased metals that have been cold-worked extensively, and the deformation of the copper oxide and sulphide inclusions alongside the direction of working suggest that O21954a was mechanically worked to shape. Preference for the mechanical working of metals over casting is typical of both the Nariño region (Alba Goméz, 2015; Scott, 2012) and of southwestern Colombia in general

Sample	Alloy	Forming method	Surface enrichment/treatments	Details/decoration	Other observations
O21954a (Nariño)	Tumbaga (Au-Ag-Cu)	Hammered and annealed	Surface enrichment	Geometric openwork	Pt & PGE group trace elements, Cu sulphides
O10062a (Quimbaya)	Argentiferous gold	Hammered and annealed	Polishing		
O10062b (Quimbaya)	Tumbaga (Au-Ag-Cu)	Hammered and annealed		Embossed around outer edge	
O21154 (Muisca)	Tumbaga (Au-Ag-Cu)	Lost-wax cast with matrix		Incisions in wax model and/or engravings on cast metal	
O33811 (Muisca)	Tumbaga (Au-Ag-Cu)	Lost-wax cast in pre-heated mold	(Unintentional) surface enrichment	Wired detail fashioned as part of original wax model	
O05639a1 (Calima)	Argentiferous gold	Hammered			
O05639a2 (Calima)	Argentiferous gold	Hammered		Embossed	

Table 2: Summary of technological observations on each artefact.

Sample (area of analysis)	O (wt%)	Si (wt%)	S (wt%)	Cl (wt%)	Fe (wt%)	Cu (wt%)	Ag (wt%)	Au (wt%)	Analytical total (wt%)	Ag / (Ag + Au)
O21954a (bulk)	≤0.5	bdl	bdl	bdl	bdl	70.7	4.3	24.5	105.4	14.9
O21954a (gilding)	1.2	bdl	bdl	bdl	bdl	15.0	7.5	76.3	111.6	n/a
O21954a (light-grey inclusions)	11.5	bdl	bdl	bdl	bdl	84.0	1.3	3.2	111.7	n/a
O21954a (dark-grey inclusions)	26.2	bdl	5.2	bdl	bdl	63.8	0.9	3.9	111.1	n/a
O10062a (bulk)	bdl	bdl	bdl	bdl	bdl	bdl	19.6	80.4	101.6	19.6
O10062b (bulk)	1.0	bdl	bdl	bdl	bdl	33.7	11.7	53.6	110.9	17.9
O10062b (corrosion)	1.7	bdl	bdl	bdl	bdl	3.4	2.4	92.5	98.3	n/a
O21154 (bulk)	0.4	bdl	bdl	bdl	bdl	59.6	6.3	33.7	111.6	15.8
O21154 (corrosion)	7.6	bdl	bdl	0.4	0.5	3.9	9.3	78.3	96.5	n/a
O33811 (bulk)	0.7	bdl	bdl	bdl	bdl	63.9	6.1	29.3	103.7	17.2
O33811 (surface layer)	2.7	≤0.5	bdl	≤0.2	bdl	20.1	12.0	64.5	100.4	n/a
O33811 (corrosion)	3.3	bdl	bdl	0.8	bdl	7.6	11.4	76.9	87.4	n/a
O05639a1 (bulk)	bdl	bdl	bdl	bdl	bdl	1.4	15.8	82.8	101.0	16.0
O05639a2 (bulk)	bdl	bdl	bdl	bdl	bdl	bdl	19.0	81.0	100.4	19.0

Table 3: Normalised SEM-EDS compositions of the samples analysed in the present study, including bulk and other phase compositions. The analytical total refers to the total prior to normalisation.

(Bray, 2000; Plazas and Falchetti, 1985). The recrystallised microstructure reveals that annealing was used to increase the ductility of the metal for working. However, this annealing was not sufficient to remove the fibrous microstructure of the metal.

One feature that separates the Nariño metalworking tradition from others in the Colombian southwest is the use of very copper-rich alloys. As discussed earlier, the southwest is generally characterised by the use of high-purity gold (Bray, 2000; Plazas and Falchetti, 1985), and while the Nariño did make use of it (as is associated with the Capuli style), they employed even larger amounts of heavily debased gold-silver-copper alloys, as associated with the Piartal style (Plazas de Nieto, 1977-78); suggesting that our sample composition (70.7wt% Cu) is more typical of Piartal metalwork.

Interestingly, the relative abundance of copper sulphide inclusions points to the possible use of a sulphidic copper ore. Further, the elevated presence of platinum and PGE elements is both typical of Nariño artefacts (Scott, 2012) and consistent with the known richness in platinum of the underlying geology, indicating a local source of gold.

In order to enrich the surfaces of the copper-rich alloys, the Nariño frequently employed both fusion and oxidative (depletion) gilding (Alba Goméz, 2015; Scott, 2012). The presence of a gold-enriched, bright layer depleted in gold and silver on both sides of the object suggests oxidative gilding; this is also reflected in the golden appearance of the sheet in Figure 1. Nonetheless, considering the thickness of the gilded layer (<10μm), and that subsequent cycles of annealing and hammering can result in the preferential oxidation and removal of copper (Lechtman, 1984), it is difficult to ascertain whether the gilding would have been intentional for this individual object. Whichever the case, the reduced depth of the gilding has permitted for higher structural stability than is normally the case with Nariño sheets with thicker gilding layers, where the core metal tends to appear much more corroded (Scott, 2012).

A second technological feature that is considered unique to the Nariño region is the use of gold alloys artificially high in silver; this is in contrast to the rest of Colombia, where the silver in the alloys originates from native argentiferous gold, as opposed to being an intentional alloying element. In this case, the silver-in-gold content of O21954a (14.9wt%) is comparable to those in other regions and could be consistent with the use of naturally argentiferous gold, as opposed to artificial silver alloying: geological Colombian gold has been found to contain between 5-37wt% Ag (Uribe Villegas and Martinón-Torres, 2012b).

Finally, it is of interest to note that geometric, flat shapes are considered typical of the Piartal sub-tradition of Late Nariño assemblages (Plazas de Nieto, 1977-78). Ultimately, then, if we are to accept the division of Late Nariño metalwork into two stylistically separate traditions, sheet O21954a tentatively shows more affinity with the Piartal than the Capuli style – it has been hammered into shape from a heavily copper-rich tumbaga alloy, with either intentional or unintentional gilding, and has a flat, geometric design.

LA-ICP-MS showed a good degree of correspondence with SEM-EDS for the major alloying constituents. On the other hand, the surface analyses are in stark contrast to one another; this is likely due to the depth of the ablation exceeding that of the gilded layer.

3.2 Quimbaya sheet fragments (O10062a & O10062b)

The next two samples come from further north in the mid-Cauca valley of Central Colombia, inhabited by the so-called Quimbaya people (Figures 1, 2) in pre-Hispanic times. They consist of two sheet fragments O10062a (unidentified function, Figure 1) and O10062b (earring, Figure 5), which has multiple round embossed decorations along the outer edge.

3.2.1 Analytical characterisation (O10062a & O10062b)

Surface imaging of O10062a reveals that intergranular stress and fracture lines, characteristic of a recrystallised microstructure, have formed alongside points of weakness in the metal; in addition, irregular microporosity and small minerals embedded in the matrix are observed (Figure 6A). Subparallel striations on the sample surface can be seen in the BSE surface imaging mode (Figure 6B). In BSE imaging in cross-section, only one phase is detected (Figure 6C); the X-ray mapping conforms to this (Figure 7). Compositional analysis (Table 3) confirms that the object is made of a single-phase AgAu alloy with Cu levels below the detection limit of the SEM-EDS (~0.1%).

Intergranular stress and fracture lines are also present on the surface of O10062b (Figure 8A). Mild corrosion has developed alongside grain boundaries, and porosity alignment alongside the length of the metal can be observed (Figure 8B). Chemical analyses (Table 3) show that the metal is a ternary Au-Ag-Cu alloy with moderately high copper levels. Corroded areas, appearing brighter under BSE imaging, are depleted in copper and silver. X-ray mapping (Figure 9) of the cross-section of O10062b reveals a fibrous two-phased microstructure.

The absolute differences between the SEM-EDS (Table 3) and LA-ICP-MS (Supplementary Material B) analyses were ~ 2wt% or lower for both objects.

3.2.2 Discussion (O10062a & O10062b)

Both O10062a and O10062b were worked to shape, as shown by the intergranular stress and fractures lines on their surfaces that are characteristic of a hammered and annealed microstructure. The mild corrosion and porosity alignment perpendicular to the direction of working in O10062b further point to mechanical working and annealing. The mechanical working of metals was practiced both during the Classic and Late Quimbaya periods (Figure 2). However, its importance is proportionally much higher in Late assemblages (Uribe Villegas, 1991), in comparison to Classic Quimbaya assemblages which are renowned for their skilfully crafted, technologically complex lost-wax castings (Perea et al., 2016; Plazas and Falchetti, 1985; Uribe Villegas, 2005).

The relatively high copper levels (33.7wt%) of the ternary Au-Ag-Cu alloy identified for O10062b are consistent with the reddish colour of the earring (Figure 5). Although native Colombian gold sources are considered more or less copper-free (Rovira, 1994), the Quimbaya did employ copper as an alloying constituent in the creation of a wide range of Au-Ag-Cu alloys, or tumbaga (Plazas and Falchetti, 1985). Considering the lack of evidence for gold-silver parting or extractive silver metallurgy within most of pre-Hispanic Colombia, sample O10062b then seems to have been manufactured by alloying copper with argentiferous gold. Since copper would have actually reduced the metal's ductility and malleability, the addition of copper is unlikely to have been motivated by a desire to adjust mechanical properties; the search of a particular colour, or other socio-cultural factors may be behind this choice.

The fibrous microstructure of O10062b in cross-section is broadly similar to that of the Nariño sample O21954a. However, no gilding was observed on the surface of the artefact. Thus, either annealing was not extensive enough to produce oxidative gilding, or any gilded layer formed as a by-product of the manufacturing process was removed by polishing, either during manufacture or later in the object's lifetime. It is interesting to note that previous research has shown that in some cases gilding appears to have been intentionally removed from the front surfaces of Classic Period Quimbaya artefacts, similarly to examples of Nahuange goldwork (AD 100-1000) from northern Colombia, and that this may reflect a desire to bring out reddish hues (Sáenz-Samper and Martinón-Torres, 2017).

The composition of O10062a, on the other hand, is consistent with unalloyed native gold. As such, despite the likely presence of annealing, no gilding would be expected and was not observed. Interestingly, the irregular microporosity and presence of small minerals on the sample surface are a potential indicator of the use of native nugget gold to fabricate the object, without melting; when native nugget gold is hammered without melting, porosity will tend to remain angular, preserving the texture of the original nugget (Martinón-Torres et al., 2012).

The correspondence of SEM-EDS and LA-ICP-MS analyses was good for both objects.

3.3 Muisca personal adornment (O21154) and votive figure (O33811)

From the Muisca metalworking zone of the Eastern Cordillera (Figure 1, Figure 2), two samples were analysed. O21154 is likely a zoomorphic pendant or bead similar to the ones it is shown alongside with in Figure 10. O33811 (Figure 1) is an anthropomorphic votive figure or *tunjo* and had previously been analysed non-invasively in Martinón-Torres and Uribe-Villegas (2015a).

3.3.1 Analytical characterisation (O21154 and O33811)

SEM-EDS analyses (Table 3) show that O21154 is a copper-rich Au-Ag-Cu alloy. The sample has a dendritic, unaltered microstructure that has undergone significant corrosion, seen as the loss of copper in areas around cracks and the corresponding enrichment in gold (Figure 11B-C, 12). In cross-section, a relatively sharp indentation for a line forming part of the pattern observed in Figure 10A is seen (Figure 11B); surface imaging shows lines that appear both sharp and less sharp (Figure 11A). The LA-ICP-MS (Supplementary Material B) and SEM-EDS (Table 3) analyses show absolute differences lower than 5wt%.

O33811 has a highly porous surface texture (Figure 13B). BSE imaging in cross-section shows this porous surface layer is brighter than the bulk of the metal (Figure 13C). The X-ray maps (Figure 14) show that O33811 has an as-cast dendritic microstructure. These dendrites are large enough to be visible on the object's outer surface under relatively low magnification (Figure 13A). Chemical analyses (Table 3) reveal that O33811 is made of a copper-rich Au-Ag-Cu alloy. The bright, porous surface layer is enriched in gold, highly depleted in copper, and slightly depleted in silver. The X-ray maps (Figure 14) also show the severe extent of corrosion in O33811, and the preferential survival of silver and copper on the surface. The results of the LA-ICP-MS analyses showed absolute differences of up to ~14wt%.

3.3.2 Discussion (O21154 and O33811)

Both O21154 and O33811 were cast, as suggested by their unaltered dendritic microstructures, conforming to the general pattern observed within the Muisca region; similarly to the Classic Quimbaya, Muisca metalsmiths also employed lost-wax casting more often than the mechanical working of metals. However, they tended to have a preference towards creating flat shapes that were highly unlike the solid and hollow three-dimensional Quimbaya castings (Falchetti, 1989; Plazas and Falchetti, 1985). As seen in Figure 1, both O21154 and O33811 fall within this category of flat, cast shapes.

Previous studies have suggested that zoomorphic pendants that resemble O21154 (Figure 10) were manufactured by utilising a stone matrix as part of the lost-wax casting process, whereby the same design could be replicated multiple times (Long et al., 1990). While post-casting alterations are typically not observed on the majority of Muisca votive offerings, they are often observed on ornaments (Lleras Pérez, 1999; Martinón-Torres and Uribe-Villegas, 2015b). It was then of interest to explore whether the lines on the surface of O21154 were produced by incisions on the wax model, or by post-casting engravings on the metal.

The profile of the lines being relatively sharp in cross-section would speak in favour of engravings, as more rounded indentations could be expected if they resulted from incisions in the original wax model, owing to the high surface tension of molten metal. On the other hand, some of the lines appearing less sharp on the surface could speak in favour of the opposite. It is also possible that the lines were incised onto the original wax model and in places sharpened post-casting by engraving.

The silver-in-gold ratio (15.7%) of O21154 is within the range found in Colombia's native gold deposits, and furthermore is typical of other analysed Muisca assemblages (Uribe Villegas and Martinón-Torres, 2012b). So is the bulk composition of the artefact (with 59.6wt% Cu, contributing to the reddish surface colour), for the Muisca are known to have worked with a wide range of artificial alloys made of copper and argentiferous gold, including heavily Cu-rich alloys. No surface enrichment could be observed on O21154. Contrary to the inevitable surface oxidation and copper depletion that may result from the hammering and annealing of tumbagas, casting on its own does not result in the preferential removal of copper from the surface; hence such enrichment would have required a further intentional step in the manufacturing sequence. The use of intentional gilding treatments in Muisca assemblages is very rare (Uribe Villegas and Martinón-Torres, 2012a).

The correspondence of these analyses with LA-ICP-MS was poorer than for the artefacts previously discussed – it is possible that the reduced copper and increased gold of the LA-ICP-MS analyses reflect areas with some corrosion present.

In comparison to repeated designs produced by stone matrices, Muisca votive figures or *tunjos* such as O33811 are always thought to be unique, with the wire-like details fashioned with wax coils as part of the original model. Accordingly, a previous study (Martinón-Torres and Uribe-Villegas, 2015a) suggested that this was the case also for O33811, noting the lack of soldered joins. The present study, which revealed that the analysed fragment of wire from the headdress was directly cast to shape, confirms this observation. Moreover, the visibility of dendrites under relatively low magnification suggests the use of pre-heated moulds, as only the slow cooling of the metal would permit the dendrites to grow this large. The casting of metals in a single pour into pre-heated moulds is considered characteristic of the region (Uribe Villegas and Martinón-Torres, 2012a).

The copper levels of O33811 (63.9wt%) would have facilitated fluidity during the casting process, although the known variability in the composition of tunjos demonstrates that metalworkers could cast tunjos of virtually any gold-copper alloy. The silver-in-gold ratio of the artefact (17.3%) is also within the range previously observed for the region (Uribe Villegas and Martinón-Torres, 2012b). It is interesting to note, however, that this composition differs significantly from the LA-ICP-MS analyses (with 50wt% Cu) and previous pXRF analyses (with Cu levels provided by two analyses as low as 30.5wt% and 36.4wt%) conducted on the same object, originally published in Martinón-Torres and Uribe-Villegas (2015a).

There are two possible explanations for this, which are not mutually exclusive. Firstly, sampling uncertainty is significantly higher in pXRF analyses in comparison to SEM-EDS, a serious issue considering that the analysed surfaces tend to be dirty, corroded, uneven and/or heterogenous. Sampling uncertainty may also affect LA-ICP-MS analyses, in particular considering the large phase segregation and the small area of the ablated spots (50μm, compared to several mm in pXRF). Another explanation for these compositional differences may be that a degree of macrosegregation occurred during the casting and solidification process. Since the *tunjo* would have been cast upside down (as indicated by the presence of excess metal at the figure's base in Figure 1), the wire analysed here would have been one of the first parts to fill and solidify within the mould.

Curiously, a gold-enriched layer was observed on the surface of O33811. This, together with the sample's porous surface texture, is indicative of gilding by oxidation. The 2015 study (Martinón-Torres and Uribe-Villegas, 2015a) of O33811 suggested that this surface enrichment is likely due to exposure to burning rather than intentional depletion gilding. This argument was backed by the presence of soot on the surface of the object, and the preferential depletion of copper in comparison to silver between the gilded layer and the bulk of the metal, an observation that is reiterated in the compositional analyses presented here.

The consistency of the technological and stylistic features of Muisca metalwork has previously been noted by other scholars (Falchetti, 1989; Scott, 1991). The two samples analysed here do not sway from this trend. Both items were lost-wax cast in a single pour using alloys of copper and argentiferous gold; where wire decoration is present on O33811, it is part of the original wax model rather than soldered on separately; and moreover, while the enriched surface of O33811 would be a significant exception amongst Muisca metalwork if intentional, it is likely to be the by-product of fire exposure.

3.4 Calima dangler O05639a (wire and sheet)

The last sample comes from the Calima region, located in the river valleys and highlands neighboring the Calima and Cauca Rivers (Figure 1). The zenith of metal production took place in this region during the Yotoco period, followed by a later phase that continued at least until the 15th century, known as the Sonso Period (Figure 2). The dangler analysed here, made of wire O05639a1 and sheet fragment O05639a2 with embossed decorations (Figure 15A-B), cannot be dated precisely on stylistic grounds, since danglers are frequently observed on Calima nose ornaments, diadems and breast plates – Figure 15C shows an example of a nose ornament of the Calima tradition (O04322), with danglers similar to the analysed sample.

3.4.1 Analytical characterisation (O05639a)

BSE imaging of O05639a1 shows a homogenous, single-phase metal that is quadrangular in cross-section and has an irregular outer surface (Figure 16A). Compositional analysis (Table

3) of the sample reveals a binary Au-Ag alloy with a minor concentration of copper. O05639a2 is also homogenous in composition (Figure 16B), with the results of the SEM-EDS analysis (Table 3) revealing an Au-Ag alloy slightly higher in silver, and with no copper detected. Porosity within O05639a2 appears to be concentrated towards the metal surface (Figure 16B).

Up to 3wt% absolute differences were found between LA-ICP-MS (Supplementary Material B) and SEM-EDS (Table 3).

3.4.2 Discussion (O05639a)

The irregular surface and quadrangularity of O05639a1 in cross-section indicates that the wire was directly hammered into shape or cut from a metal sheet, as opposed to strip-twisted, block-twisted, or cast – all documented techniques of making wire in pre-Hispanic Colombia (Scott, 1991). Porosity concentrated towards the surface of sheet O05639a2 is also indicative of it being shaped to form by hammering.

Both the wire and the sheet have been manufactured using high purity argentiferous gold, with copper detected in only one of the samples, O05639a2 (1.4wt% Cu), likely reflecting the presence of copper in the native gold deposit used (or potentially the recycling of gold-copper alloys). The levels of silver in O05639a1 and O05639a2 are 16.0wt% and 19.0wt% respectively. These concentrations, particularly for sample O05639a2, are on the higher end of the spectrum found in the analysed artefacts of the Calima area (Rovira, 1994; Scott, 2012), but still fall within the range attributable to argentiferous gold deposits.

Ultimately, the divergences in these compositions also reveal that the sheet and the wire have been made from metal with different compositions. This does not seem particularly surprising, considering that the two components of the dangler could have been directly hammered from two different lumps of native and/or recycled metal.

The correspondence between SEM-EDS (Table 3) and LA-ICP-MS (Supplementary Material B) was good.

4. Conclusions

The compositional and microstructural case studies presented in this paper have demonstrated how technological information may be extracted from pre-Columbian metal artefacts using SEM-EDS, whether it be in regard to their forming methods, compositions, or surface treatments. Moreover, as the extracted information was discussed in relation to the pre-existing evidence of the region's metallurgy, attention could be drawn to features considered either characteristic or uncharacteristic of the samples' respective metallurgical cultures. In some cases, the data even enabled discussing the attribution of the artefacts into more refined time periods and/or metallurgical traditions, albeit with a high level of reservation due to the small sample sizes concerned. Nevertheless, it is possible to see how such attributions could have been more plausible with larger sample sizes, particularly when considering archaeometric data in conjunction with object style and iconography.

The identification of gilding is of particular importance for the study of pre-Hispanic metallurgy, since much of it has focused on colour symbolism. The intentionality of surface enrichments can be difficult to establish owing to several processes that can lead to the unintentional oxidation and removal of copper, such as prolonged fire exposure or annealing aimed at increasing ductility for mechanical working. However, by combining different sources of information on gilding depth, forming method, cultural context of manufacture, and by observing surface residues such as the soot on O33811, it was still possible to make suggestions regarding intentionality behind gilding.

Moreover, these results show that larger-scale cross-regional archaeometric research paradigms could have significant potential in complementing, disproving, or supporting the macroscopic lines of evidence that are the backbone of the spatio-temporal framework in use today, through systematic comparisons of the identified technological traits in pre-Hispanic Colombian assemblages. This, in turn, should enhance our understanding of the continuity and variability in metallurgical practices and inform us of the intensity of material and/or information exchanges.

A comparison of analytical data obtained by SEM-EDS and LA-ICP-MS showed an acceptable degree of correspondence for major elements, in particular where homogenous samples were concerned. By allowing for the selection of specific areas for compositional analysis under the microscope, SEM-EDS was however more suited to analysing heterogenous archaeological samples and revealing technological traits. LA-ICP-MS, however, has the advantages of its quasi-non-destructive nature and lower detection limits.

It is worth noting that while we took advantage of the opportunity to sample a small number of fragmentary objects, much of the technological information presented here could also be extracted without invasive sampling – for instance, evidence for the forming method could frequently be detected by surface examination alone. Provided that the sampled objects are small enough to be placed in an SEM chamber as a whole, future studies could still make use of some of the powerful capabilities of SEM, in conjunction with a non-destructive or quasi-destructive analytical method for compositional analysis. With over 34,000 items stored in the collections of Museo del Oro alone, it is clear that much of the potential for archaeometric study within the region’s archaeometallurgy remains yet to be exploited. Hopefully, this paper has demonstrated the potential of applying similar research paradigms on a larger scale.

Acknowledgements

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Figures

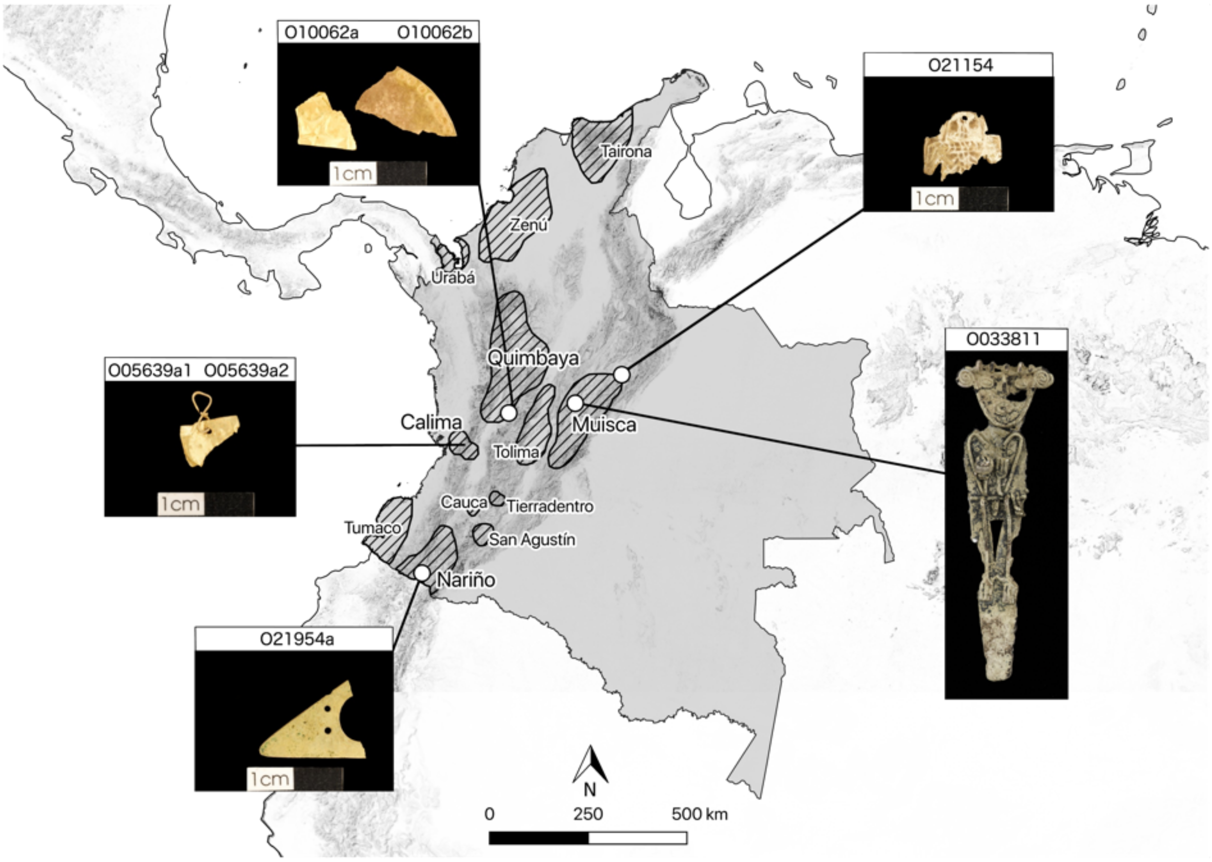

Figure 1: Map showing the spatial division of pre-Hispanic Colombia into 12 metalworking zones. Find locations of the seven analysed samples within their respective metallurgical tradition areas are also indicated on the map. Please note that the recovery location is unknown for the dangler O05639a, and the whole of the Calima region is referred to. The dimensions of O33811 are approximately 7 x 2.1 cm. Hill shade on map © OpenStreetMap contributors.

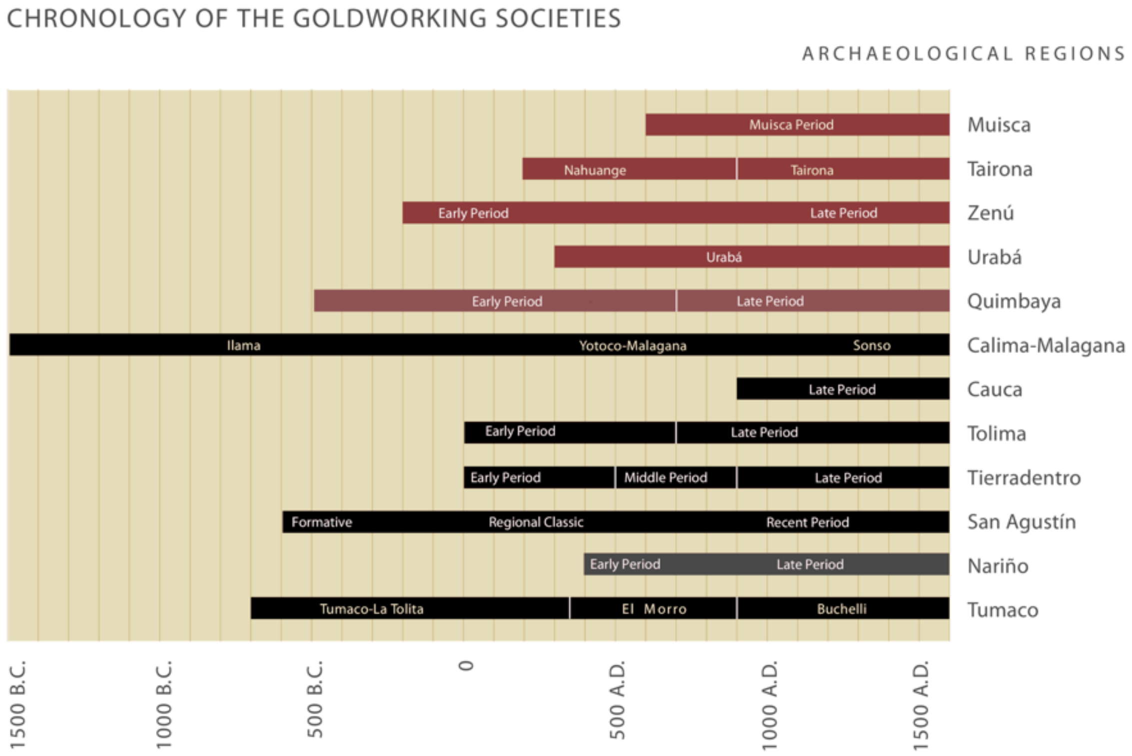

Figure 2: The chronology of 12 pre-Hispanic Colombian metalworking zones and temporal divisions thereof. The northern traditions are shown in red, with the southwestern traditions in black. Quimbaya and Nariño are sometimes considered peripheral to their broader northern/southwestern groups (Quimbaya showing similarities with both; Nariño assemblages presenting several unique characteristics not present elsewhere in Colombia). Adapted with permission © Museo del Oro, Banco de la República.

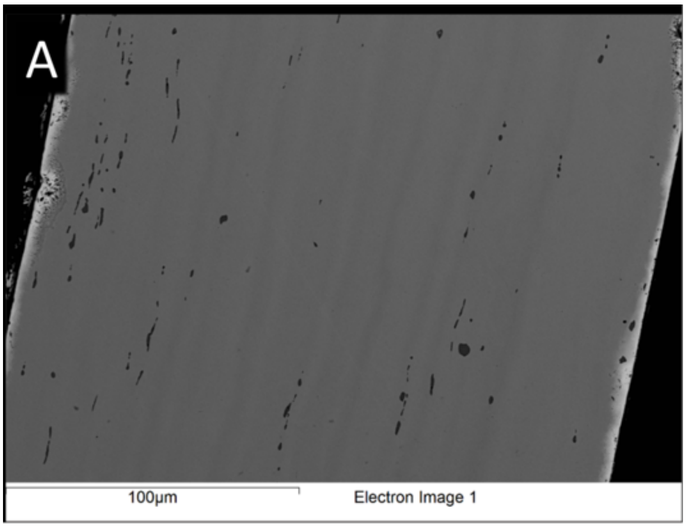

Figure 3: O21954a in cross-section; note the fibrous microstructure, the deformation of the oxide and sulphide inclusions, and the presence of surface enrichment (Hitachi S-3400, BSE).

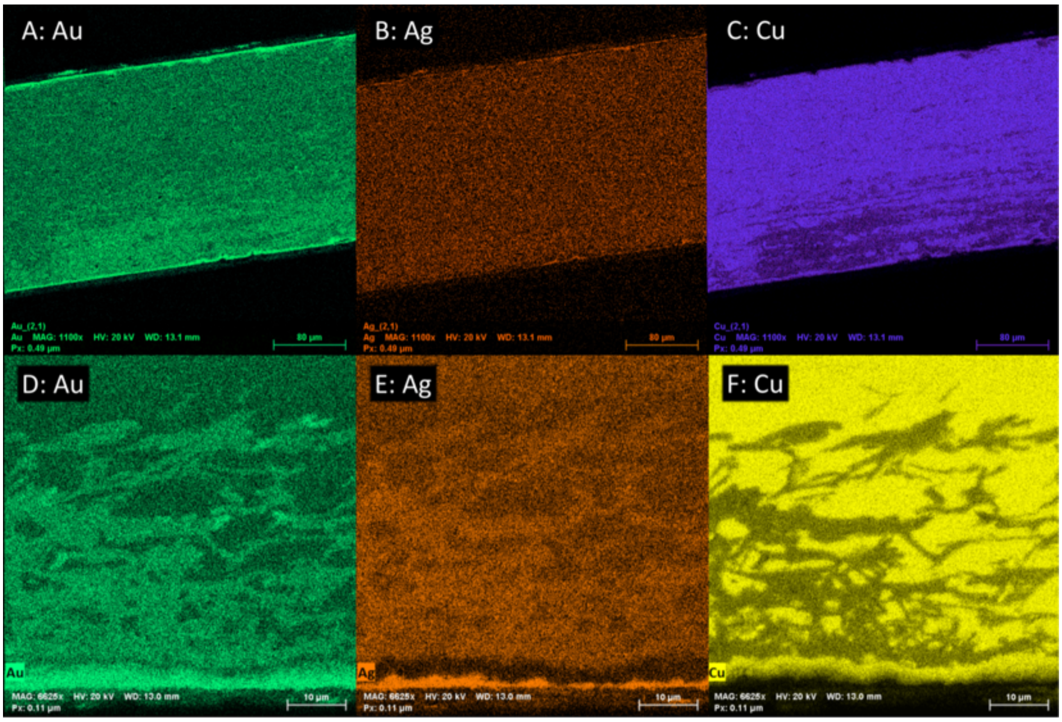

Figure 4: A-C) X-ray compositional maps of O21954a in cross-section; note surface enrichment and fibrous microstructure (QUANTA-650F). D-E) Higher magnification X-ray maps of O21954a; note thickness of gilded layer (<10mm). Corrosion alongside grain boundaries reveals recrystallised grains, indicative of a hammered and annealed microstructure (QUANTA-650F).

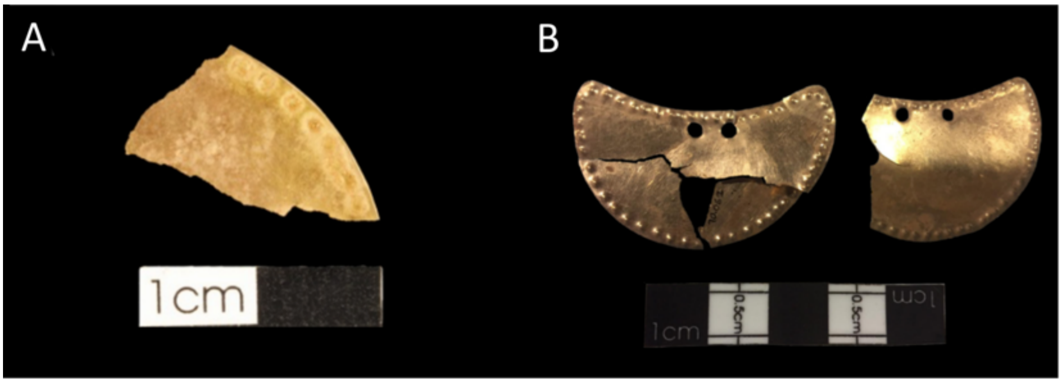

Figure 5: A) Sample O10062b. B) The sampled pair of earrings.

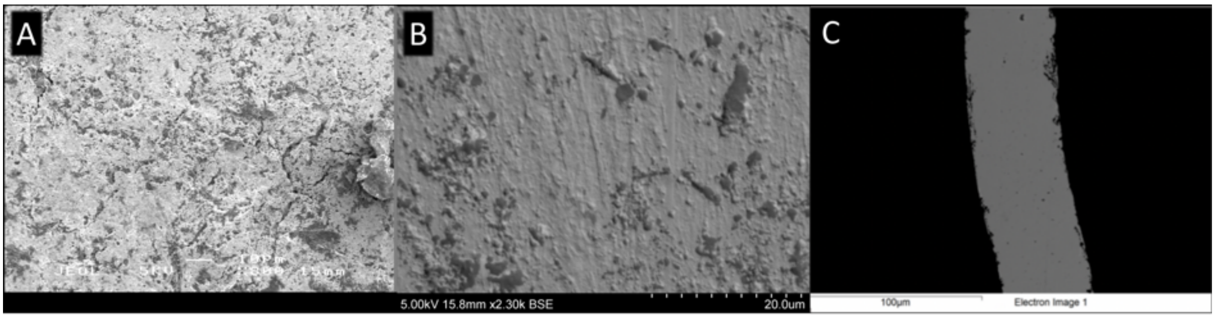

Figure 6: A) Surface of O10062a; note intergranular cracks that are probably indicative of a hammered and annealed grain structure (JEOL JSM- 6301F, SE). B) Surface of O10062a; note non-parallel striations (Hitachi S-3400, BSE). C) O10062a in cross-section; note microporosity (Hitachi S-3400, BSE).

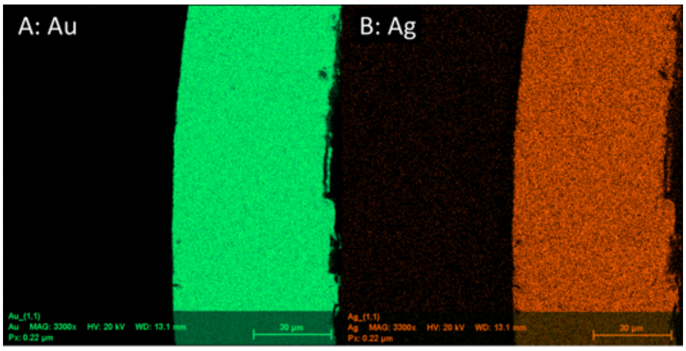

Figure 7: X-ray maps of sample O10062a in cross-section, showing the metal is a solid solution and the absence of surface treatment.

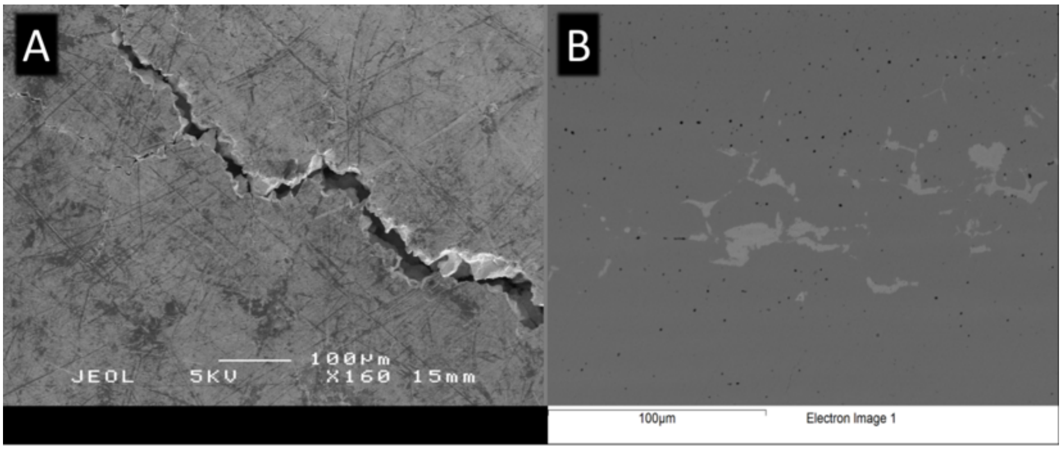

Figure 8: B) Surface of sample O10062b; note how the ragged shape of cracks and fractures that have formed alongside weak points in the metal are indicative of a recrystallised (hammered and annealed) grain structure (JEOL JSM-6301F, SE). B) O10062b in cross-section; note casting porosity orientated perpendicular to the direction of working, and corrosion alongside grain boundaries revealing recrystallised microstructures from annealing (Hitachi S-3400, BSE).

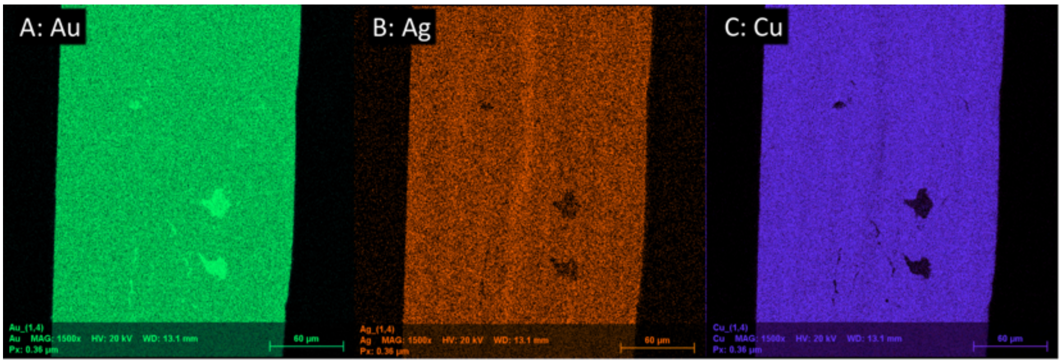

Figure 9: X-ray maps of sample O10062b in cross-section, with evidence of a packed microstructure resulting from hammering (QUANTA-650F).

Figure 10: A) Sample O21154. B) Sample O21154 alongside a frog pendant (O20068) from the collections of Museo del Oro. C) Sample O21154 alongside fish beads (O21152) from the collections of Museo del Oro.

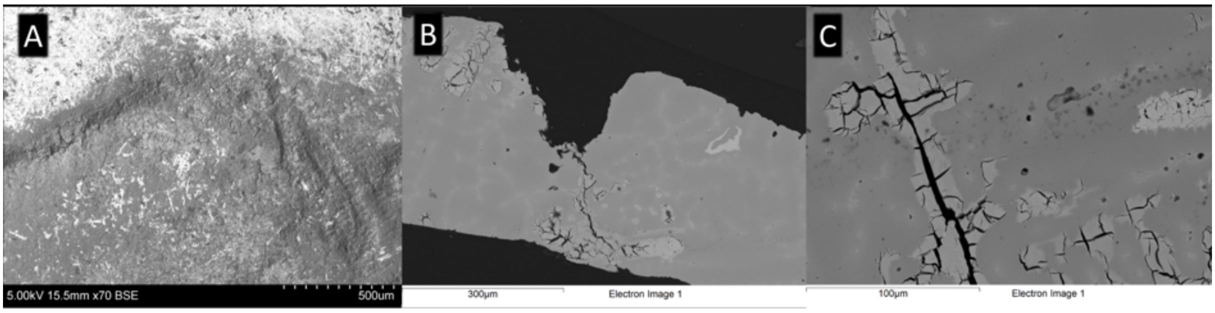

Figure 11: A) Lines on the surface of O21154; note their relative roundness on the left-hand side, and sharpness on the right-hand side (Hitachi S-3400, SE). B) O21154 in cross-section showing the unaltered dendritic microstructure of the metal (Hitachi S-3400, BSE). C) Higher magnification photomicrograph of O21154 in cross-section, showing corrosion alongside dendrites within the metal (Hitachi S-3400, BSE).

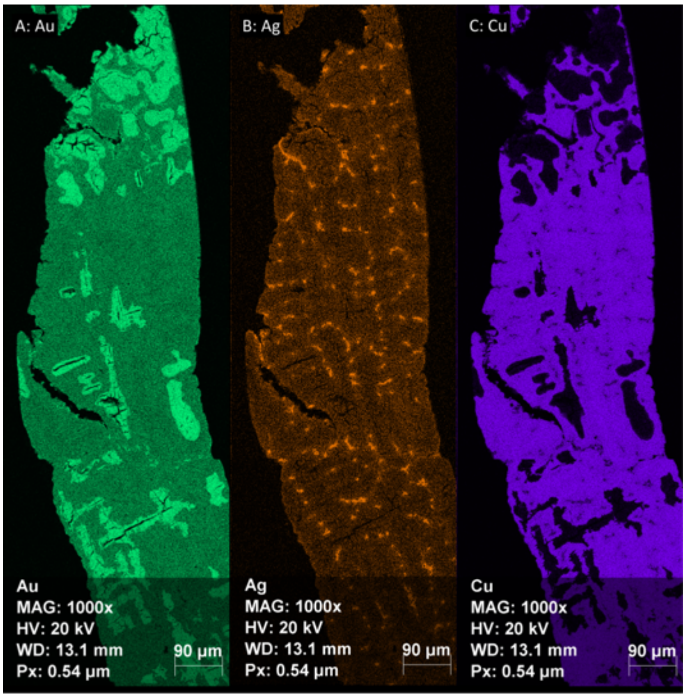

Figure 12: X-ray maps of sample O21154 in cross-section, with further evidence of unaltered dendritic microstructure and corrosion alongside dendrites (QUANTA-650F).

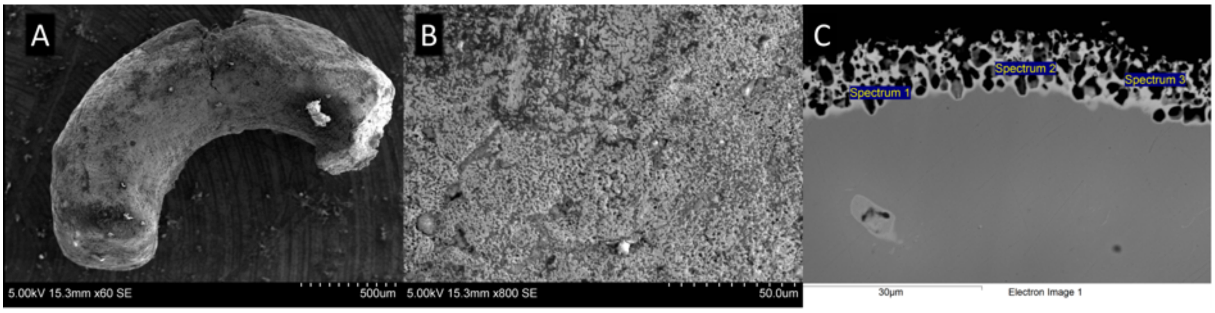

Figure 13: A) Photomicrograph of sample O33811 with visible dendrites at low magnification (Hitachi S-3400, SE). B) Surface of O33811 at higher magnification; note highly porous surface texture (Hitachi S-3400, SE). C) A close-up of the enriched surface of O33811 in cross-section (Hitachi S-3400, BSE).

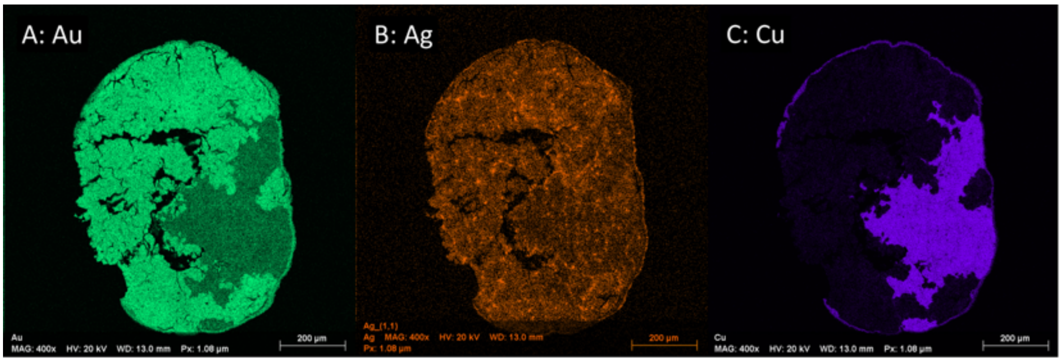

Figure 14: X-ray maps of sample O33811 in cross-section, with evidence of unaltered of dendritic microstructure and showing extensive corrosion with onion-like structure (QUANTA-650F).

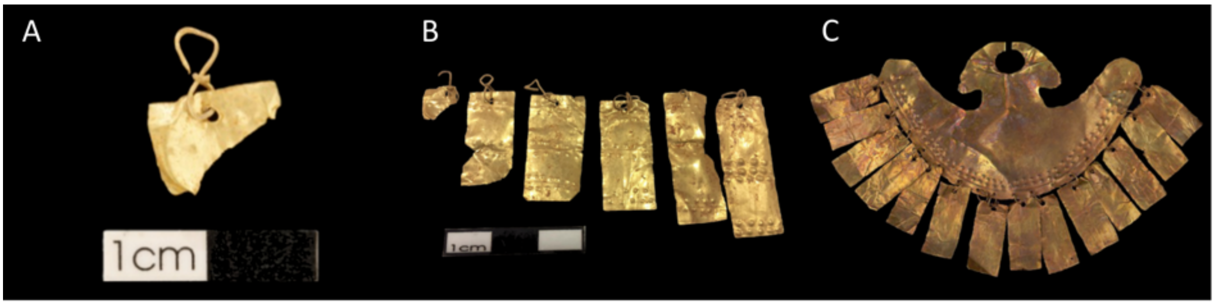

Figure 15: A) Calima dangler with wire O05639a1 and sheet O05639a2. B) Other danglers from the same design as O05639a. C) Calima nose ornament (O04322), a type of object that O05639a may have belonged to. Figure 15C reproduced with permission © Museo del Oro, Banco de la República.

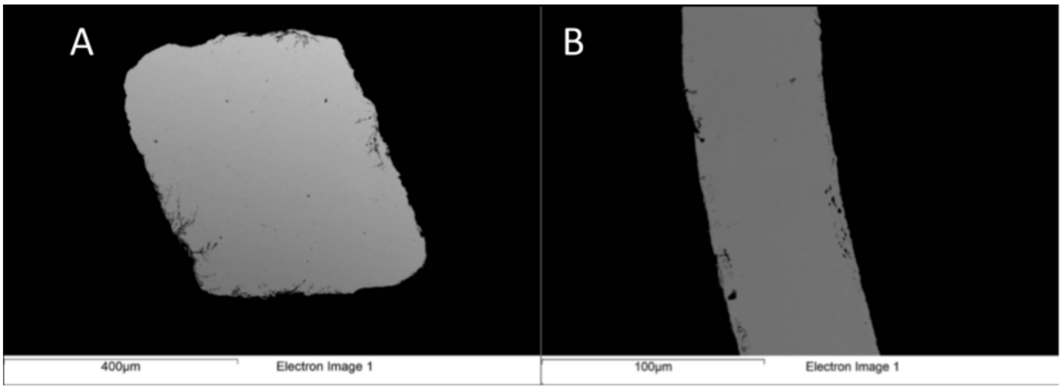

Figure 16: A) Sample O05639a1 showing the rectangularity of the wire in cross-section; note also irregularities on the surface (Hitachi S-3400, BSE). B) Sample O05639a2 in cross-section; note porosity concentrated towards the surface (Hitachi S-3400, BSE).