

# Gold coated copper artifacts from the Royal Tombs of Sipán (Huaca Rajada, Perú): manufacturing techniques and corrosion phenomena

Gabriel M. Ingo · Angel D. Bustamante · Walter Alva · Emma Angelini · Roberto Cesareo · Giovanni E. Gigante · Sandra Del Pilar A. Zambrano · Cristina Riccucci · Gabriella Di Carlo · Erica I. Parisi · Federica Faraldi · Luis Chero · Julio S. Fabian

Received: 12 April 2013 / Accepted: 13 April 2013 / Published online: 27 April 2013  
© Springer-Verlag Berlin Heidelberg 2013

**Abstract** Twenty five years ago, close to the northern Peruvian town of Lambayeque (Huaca Rajada) beneath two large and eroded pyramids, built of adobe mud bricks, Professor Alva discovered the world-famous unlooted pre-Columbian burial chambers of the Royal Tombs of Sipan. The tombs contained a large amount of objects of exceptional artistic and historical value including the greatest intact number of gold and silver artefacts in the Americas to be considered one of the most important archaeological discoveries of the last century. Some copper based objects coated with thin layers of gold have been studied by means of

the combined use of analytical techniques such as optical microscopy (OM), scanning electron microscopy coupled with energy dispersive X-ray micro-analysis (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) in order to identify the chemical composition and the manufacturing processes of the gold layer as well as the corrosion products formed during the long-term burial. The micro-chemical and structural results give useful information about the manufacturing techniques used by the Moche metalsmiths to modify the surface chemical composition of the coated artefacts likely based on the depletion gilding process carried out by oxidising the surface copper containing the noble metal and etching away the copper oxides. Furthermore, the results reveal that the main degradation agent is the ubiquitous chlorine and that copper has been almost completely transformed during the burial into mineral species giving rise to the formation of stratified structures constituted by different mineral phases such as cuprous oxide ( $\text{Cu}_2\text{O}$ ) and copper carbonates [azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) and malachite ( $\text{CuCO}_3\text{Cu}(\text{OH})_2$ )] as well as dangerous chlorine-based compounds such as nanokite ( $\text{CuCl}$ ) and atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) polymorphs. These information evidence the strict interaction of the alloying elements with the soil components as well as the occurrence of the copper cyclic corrosion as post-burial degradation phenomenon. The present study confirms that the combined use of micro-chemical and micro-structural investigation techniques such as SEM-EDS, XPS, XRD, and OM can be successfully used to investigate the technological manufacturing processes of the ancient coated artefacts and to achieve information about degradation agents and mechanisms useful to define tailored conservation strategies possibly including new, more reliable, and safer materials.

---

G.M. Ingo (✉) · C. Riccucci · G. Di Carlo · E.I. Parisi  
Area Ricerca RM1-Montelibretti, Istituto per lo Studio dei  
Materiali Nanostrutturati-CNR, via Salaria km 29.5,  
00015 Monterotondo Stazione, Rome, Italy  
e-mail: [gabriel.ingo@ismn.cnr.it](mailto:gabriel.ingo@ismn.cnr.it)  
Fax: +39-06-90672714

A.D. Bustamante · S.D.P.A. Zambrano · J.S. Fabian  
Facultad de Ciencias Físicas, Universidad Nacional Mayor  
de San Marcos, Ap. Postal 14-0149, Lima,  
Peru

W. Alva · L. Chero  
Museo “Tumbas Reales de Sipán”, Lambayeque, Peru

E. Angelini · F. Faraldi  
Dipartimento Scienza dei Materiali e Ingegneria Chimica,  
Politecnico di Torino, Corso Duca degli Abruzzi 24, Turin,  
Italy

R. Cesareo  
Dipartimento di Matematica e Fisica, Università di Sassari,  
Sassari, Italy

G.E. Gigante  
Dipartimento di Energetica, Università di Roma “La Sapienza”,  
Rome, Italy

## 1 Introduction

Before the Inca Empire (1430 AD), the following civilisations flourished and fell in the Central Andean region, roughly corresponding to today's Peru: Chavín, Moche, Sicán, and Chimù [1–4]. One of the most important among them was the Moche culture (100–700 AD), which was agriculturally based with a significant production of elaborated painted ceramics, metal works, constructions, and irrigation systems and evolved in the oasis river valleys located on the arid north coast between the Andes and the Pacific Ocean [1–4].

The Moche society was stratified and organised with high degree of specialisation of labour and was governed by an aristocracy including priests, warriors, and legal authorities. They were sophisticated metalsmiths whose skill has been extraordinarily demonstrated by the amazing artefacts found in the Royal Tombs of Sipán [5–8]. Indeed, 25 years ago, in the northern Peruvian town of Lambayeque (Huaca Rajada) beneath two large and eroded pyramids, built of adobe mud bricks, Professor Alva discovered the world-famous pre-Columbian burial unlooted chambers of the Lords of Sipán [5–9].

The tombs contained a large amount of ceremonial and ornamental objects of exceptional artistic and historical value including the greatest intact number of gold artefacts in the Americas to be considered one of the most important archaeological discoveries of the last century. The excavations yielded many metal objects of utmost relevance such as a copper sceptre, gilded jewels such as a pectoral, necklaces, nose rings, ear rings, helmets, falconry, bracelets, and a collar of gold owl heads and many other ornamental objects as well as hundreds of decorated ceramic vessels [5–9].

This discovery revolutionised the Moche studies offering the opportunity to investigate a wide panorama of objects of the highest quality and value produced by using the most sophisticated skill of the Moche civilisation [1–9] that have invested a large effort in metal working, thus demonstrating that these objects must have a strong relevance and value for them [9].

In order to identify chemical composition, metallurgical features, manufacturing processes and corrosion products formed during the long-term burial of some relevant copper based objects coated with thin layers of gold, the artefacts have been first studied in situ by X-ray fluorescence (XRF) analysis [10, 11] at the Museum of the Royal Tombs of Sipán, located in Lambayeque Chiclayo (Perù), and then the objects have been sampled to be studied by means of the combined use of analytical laboratory techniques such as optical microscopy (OM), scanning electron microscopy coupled with energy dispersive X-ray micro-analysis (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) [12–14]. The aim of the scientific activities was also to achieve information useful to ascertain the

actual conservation state of the artefacts, after the long term burial, and to provide recommendations for the selection of tailored and reliable conservation methods and materials [15–19].

## 2 Experimental methods

Small fragments were carefully sampled from some selected artefacts at the Museum of the Royal Tombs of Sipán, located in Lambayeque Chiclayo, and submitted to different treatments according to the specific requirements of the following analytical techniques: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), optical microscopy (OM), scanning electron microscopy (SEM), and field emission scanning electron microscopy (FE-SEM) equipped with backscattered (BSE) and secondary electron (SED) detectors and an energy dispersive spectrometer (EDS) sensitive to elements from carbon to uranium [20–24].

In order to prepare cross-section of materials, representative fragments were embedded in epoxy resin for 24 hours and sectioned by using a diamond saw in order to preserve the micro-chemical structure and the surface features. The sections were polished with silicon carbide papers until 1200 grit and the final polishing was performed with diamond pastes up to 1.4  $\mu\text{m}$  [20, 21, 23].

Both SEM-EDS and FE-SEM-EDS characterisations were carried out by a Cambridge 360 scanning electron microscope equipped with a LaB<sub>6</sub> filament and a high brilliance LEO 1530 field emission scanning electron microscope apparatus equipped with an energy dispersive X-ray spectrometer (EDS) INCA 250 and INCA 450, respectively, and a four sectors backscattered electron detector (BSE). Samples were coated with a thin layer of carbon or chromium in order to avoid charging effects. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K 250 carbon coating attachment and a carbon cord at a pressure of  $1 \times 10^{-2}$  mbar in order to produce a carbon film with a constant thickness of about 3.0 nm. The Cr coating was deposited by using a Bal-Tech SCD 500 equipped with turbo pumping for ultra clean preparations at a pressure of  $5 \times 10^{-3}$  mbar in order to produce a chromium film with a constant thickness of about 0.5 nm [20, 21, 23].

The structural identification of crystalline phases was determined by a Siemens 5000 X-ray powder diffractometer using a Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Angular values in the range between  $10^\circ$  and  $80^\circ$  in additive mode, a step size of  $0.05^\circ$  and a sampling time of 2 s were the experimental parameters used for data acquisition. In order to identify the crystalline species, X-ray diffraction patterns analysis was carried out by using electronic databases.

XPS investigations were carried out using an ESCALAB MkII (Thermo-VG Scientific Ltd., UK) spectrometer

equipped with a standard non-monochromatised Al K $\alpha$  excitation source and a 5-channeltron detection system [22–24].

### 3 Results and discussion

Moche artisans used different copper alloys with silver and/or gold in a wide range of composition to produce the objects whose surface chemical and structural nature was in some cases modified by depositing a thin layer of precious metal [25–30]. The Moche metalsmiths adopted various methods including depletion gilding based on the copper removal [25, 26] or the electrochemical formation of a noble metal film onto a copper surface as proposed by Lechtman and co-workers [27–29]. The aim of these surface treatments could be cultural, political, religious, or ideological due also to the symbolic meaning of the colour of the metal surface [11, 25, 26].

The attention of the Italian–Peruvian team has been focused on the objects consisting of hammered copper sheet metal coated with a thin layer of gold that are typical artefacts made by Moche that were the most sophisticated metalsmiths of the Central Andean region at that time.

The studied objects have been selected from those found in different tombs including that of the Lord of Sipán (grave T-03) that is considered to be one of the richest, relevant and untouched by the thieves burial tomb of the pre-Inca period. Due to the relevance of the artefacts found at Sipán and their unique and outstanding value nature, particular attention has been paid to select the fragments for the analysis without causing damage to the artefacts.

The selected objects are characterised by a high copper content and are almost completely covered by a green *patina* constituted by copper corrosion products that only in few and small areas allows to observe the presence of a thin layer of gold in the near-surface.

In Fig. 1, the optical images (OM) show some examples of the typical aspect of the samples used in this investigation constituted by small fragments of broken high status objects found in the funeral outfits of the Warrior Priest and Young Warrior tombs, T-14 and T-15, respectively that represented the social and political rank of the deceased during his life and for the afterlife [5–8].

The images reveal that the artifacts were structurally composed by a Cu-based substrate whose chemical composition cannot be determined because the matrix has been completely mineralised during the long-term burial [12–19]. The optical images disclose also the presence of a thin gold layer under the thick *patina* composed by copper corrosion products and soil residues and encrustations.

Figures 2, 3, 4, and 5 show some selected optical micrographs (OM), back scattered scanning electron microscopy

(BSE SEM) images and EDS spectra of a cross-sectioned fragment from the dress of the Warrior Priest (T-14) and of the owl-crown of the Young Warrior (T-15) that reveal a surface continuous metallic thin layer and rare localised enrichments in the form of halos.

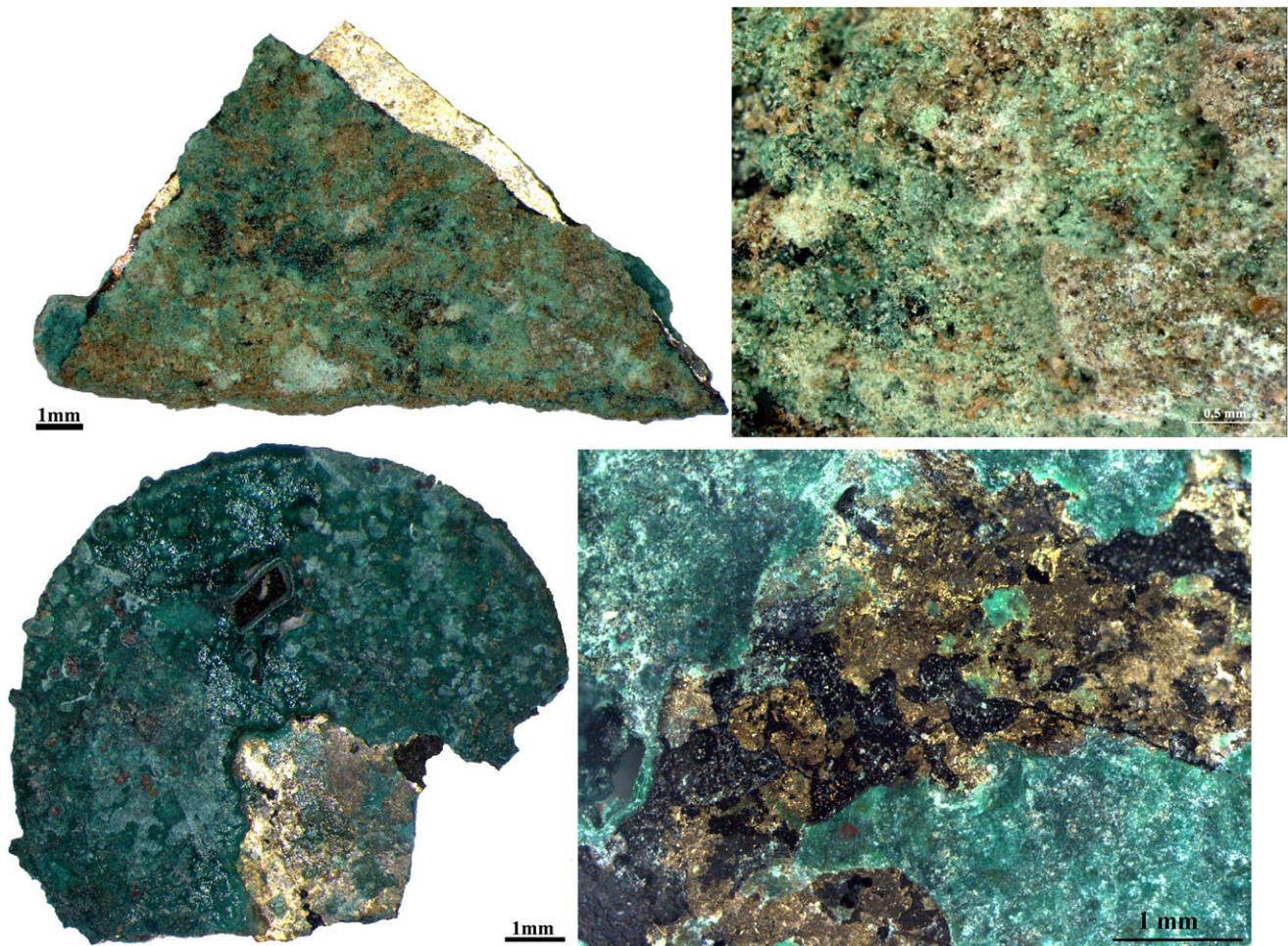
The OM images shown in Figs. 2 and 4 reveal the complete mineralisation of the artefact with the formation of different copper corrosion products such as cuprous oxide (brownish–red, Cu<sub>2</sub>O), blue–greenish copper carbonates [i.e. azurite (Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> and malachite (CuCO<sub>3</sub>Cu(OH)<sub>2</sub>)] and dangerous chlorine-based compounds such as nantokite (yellow–orange, CuCl) and atacamite (greenish, Cu<sub>2</sub>(OH)<sub>3</sub>Cl) polymorphs [12–14, 31, 32]. It is worth mentioning that all the examined fragments were heavy deteriorated and almost completely transformed into corrosion products and do not exhibit large areas of residual metallic core.

Other information can be achieved from the high resolution BSE SEM image shown in Fig. 3 that discloses the presence of a thin gold layer produced likely via depletion gilding carried out in ancient times by Moche metalsmiths. Indeed, the presence of Au and Ag enriched areas in the bulk of the copper sheet shown in Fig. 3 could demonstrate the use of a depletion gilding process to produce a thin gold layer on the surface of the artifact. Indeed, the EDS spectrum E of the metallic relic areas located in the central zone of the copper alloy sheet shows the presence of few percents of Au and Ag suggesting the use of depletion gilding. The EDS spectrum F confirms this hypothesis revealing the presence of Au and Ag local enrichments formed by the selective copper corrosion that has concentrated the noble metals [25–30].

The gold layer marks the original surface of the object and the BSE SEM image reveals also the presence of a gold gradient increasing from the inside to the outside of the artefact suggesting the use of a Cu/Au alloy with a low amount of silver purposely produced to be submitted to the surface depletion gilding technique. Furthermore, the high resolution BSE SEM image of the area under the gold layer and the EDS spectra shown in Fig. 5 reveal the presence of nano-particles of gold dispersed in copper–chloride species formed by the complete corrosion of the Cu–Au alloy used by Moche metalsmiths to carry out the depletion gilding process and to induce the surface gold enrichment by selective removal of copper from the near-surface regions of the object.

By comparing these BSE SEM image and EDS spectra with those shown in Fig. 6 that shows OM and BSE SEM images and EDS spectra of a cross-sectioned fragment of a copper based artefact from the tomb of the Lord of Sipán (T-03), it is possible to observe the different chemical composition of the gold thin layers. Indeed, this latter object is characterised by a noticeable content of silver thus indicating





**Fig. 1** Some examples of the fragments sampled from the funeral outfits of the Warrior Priest and Young Warrior tombs: a dress fragment (first row) and an owl-crown (second row). The optical images dis-

close the presence of the original surface of the thin gold layer under the thick *patina* constituted by greenish copper corrosion products

the use of copper alloys characterised by different amounts of Au and Ag with respect to the dress and owl-crown found in tombs T-14 and T-15.

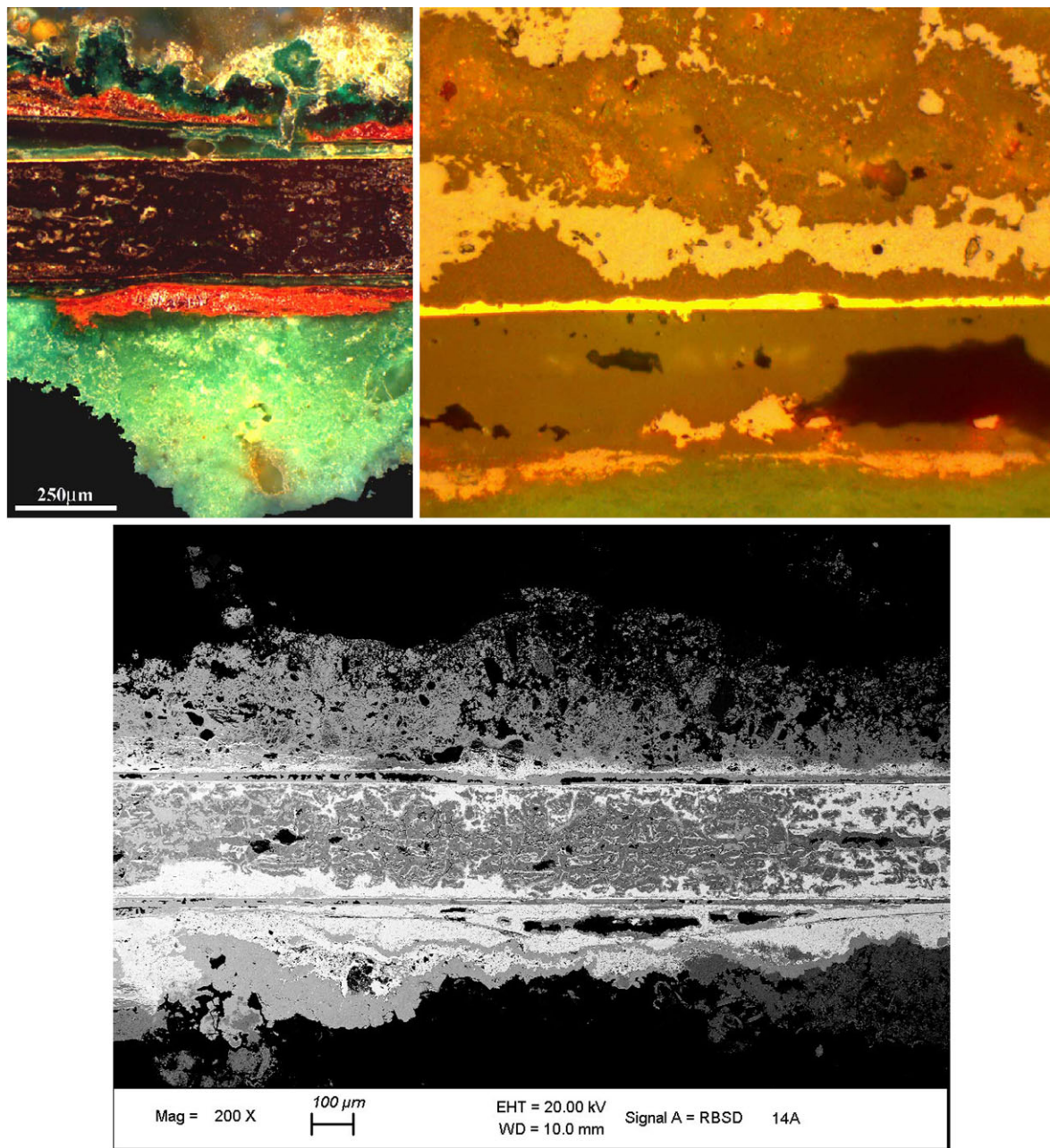
These results could reflect the skill of the metallurgists to produce alloys in a wide range of chemical compositions [33–36]. Moreover, the results achieved from the study of uncoated copper objects that are composed by pure Cu without the presence of noble metals allow to rule out that gold and silver were casually accessory elements and, therefore, it is possible to suggest an intentional addition of Au and Ag.

These data demonstrate clearly that on the base of their sophisticate and high grade, even though empirical, skill the Moche metallurgists without having any knowledge regarding the chemical-physical processes involved and the metallurgy of the Cu-based alloys were capable of systematically manipulating these alloys even at a micro- and nano-scale dimension for the tailored production of artefacts with defined esthetical and symbolical features.

Finally, the above described results could support the hypothesis that depletion gilding was the technique used by Moche metallurgists to produce the coated artefacts and that a copper alloy with gold (low carat) and a lower amount of silver was submitted to several cycles of beating and heating to form in air a layer of oxides (cuprite,  $\text{Cu}_2\text{O}$ , or tenorite,  $\text{CuO}$ ). The removal of these superficial products, with acids extracted from plant juices, allowed the progressive formation of a gold and silver enriched surface so that the artefacts seemed to be completely made of pure gold.

For what concerns, the copper corrosion products formed during the long-term burial, the presence of the above mentioned different compounds has been observed via OM and confirmed by XRD investigation whose results are shown in Fig. 7. These latter results clearly show the presence of cuprous oxide ( $\text{Cu}_2\text{O}$ ), copper carbonates [i.e. azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$  and malachite ( $\text{CuCO}_3\text{Cu}(\text{OH})_2$ )] and dangerous chlorine-based compounds such as nantokite





**Fig. 2** Optical micrographs (OM, dark and bright field observation) and back scattered scanning electron microscopy (BSE SEM) image of a cross-sectioned fragment from the dress of the Warrior Priest (T 14-B) that reveal on the external region of a continuous metallic thin metallic layer embedded in the copper corrosion products. The OM images reveal the complete mineralisation of the artefact with the

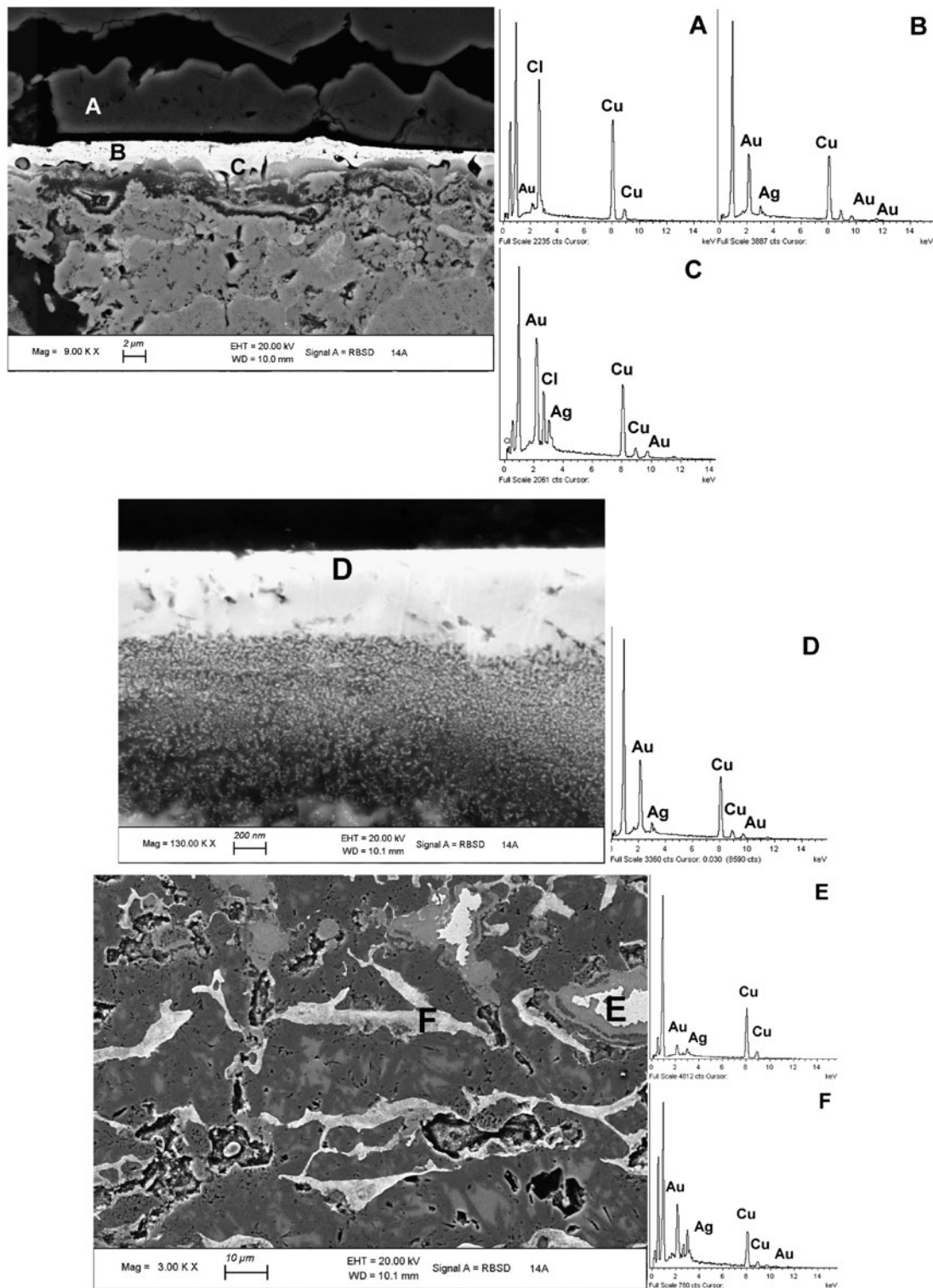
formation of different copper corrosion products such as cuprous oxide (brownish-red,  $\text{Cu}_2\text{O}$ ) and dangerous chlorine-based compounds such as nantokite (orange-yellow,  $\text{CuCl}$ ) and atacamite (greenish,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) polymorphs. Only the thin gold layer withstood the corrosion phenomena thus marking the original surface of the object

( $\text{CuCl}$ ) and atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) polymorphs [12–14, 31, 32].

Furthermore, the assignment of the surface chemical state of the corrosion products have been also achieved via XPS characterisation that have excluded the presence of tin species [37, 38] or of other elements such as As, Sb, and Pb and, therefore, have ruled out the use of a Cu-Sn alloy

[31, 32, 37, 38] or the use of an impure Cu-based alloy [33–35].

XPS has been used to achieve other chemical information about the *patina* surface nature and has confirmed the hygroscopic nature of the archaeological corrosion products. The lineshape analysis of the O 1s photoemission peaks (not shown) evidences both the presence of anhydrous and

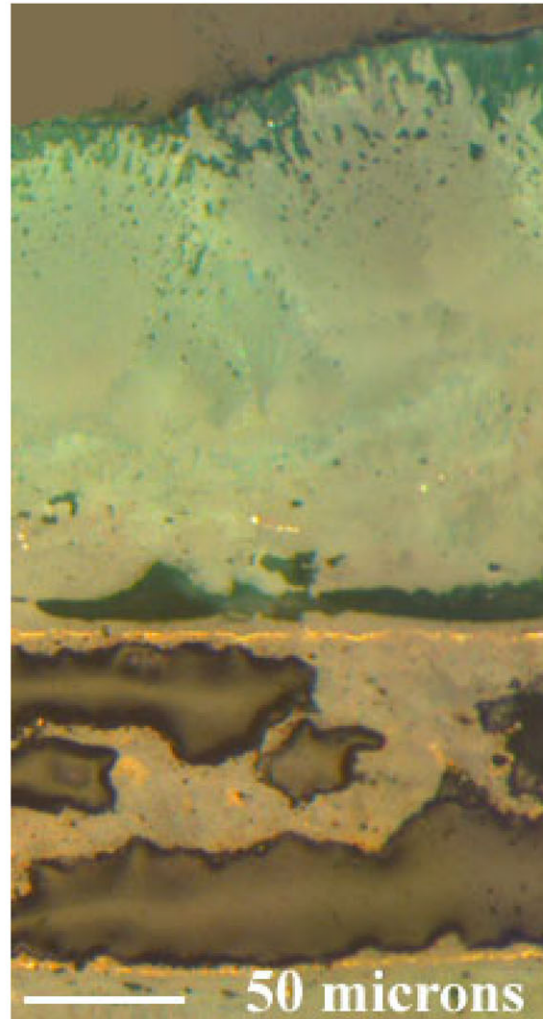
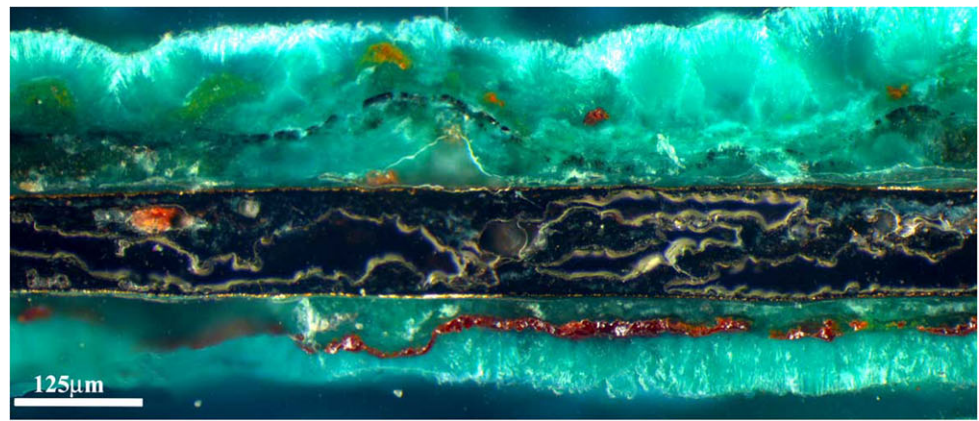


**Fig. 3** Back scattered scanning electron microscopy (BSE SEM) images and energy dispersive spectra (EDS) of a cross-sectioned fragment from the dress of the Warrior Priest (T 14-B) that disclose the presence of a surface gold thin layer with a low amount of silver. The high resolution image reveal the progressive gold enrichment on the external surface of the object due to the deposition process carried out in ancient times by Moche metalsmiths. The EDS spectrum E of the

metallic relic areas located in the central zone of the copper alloy sheet shows the presence of Au and Ag and could demonstrate the use of a depletion gilding process to produce a thin gold layer on the surface of the artefact. The EDS spectrum F confirms this hypothesis revealing the presence of Au and Ag local enrichments formed by the selective copper corrosion that has concentrated the noble metals



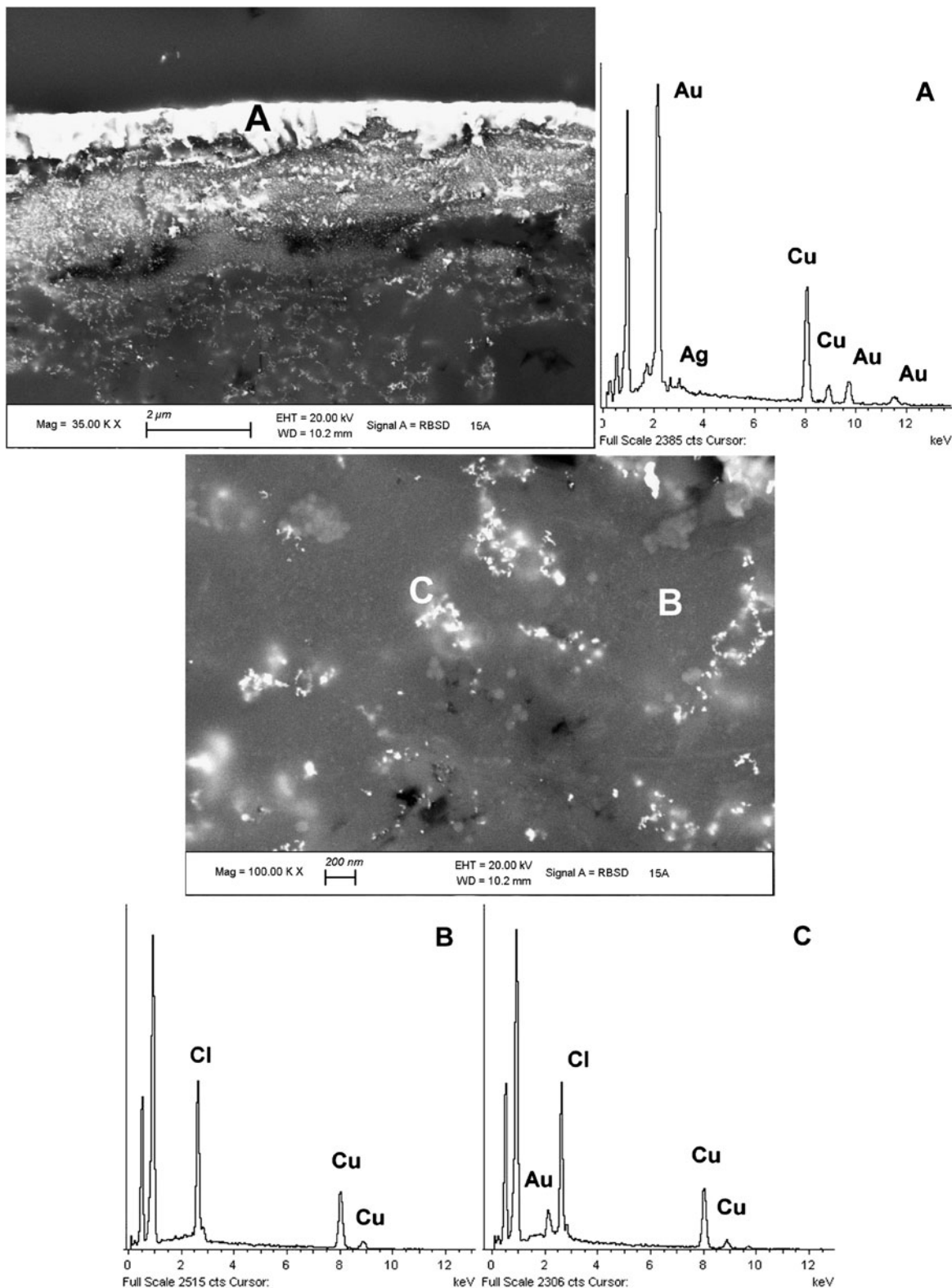
**Fig. 4** OM (dark and bright field observation) image of a cross-sectioned fragment from the crown of the Young Warrior (T 15-B) that reveal a surface metallic thin layer. The OM images reveal the complete mineralisation of the artefact with the formation of different copper corrosion products such as cuprous oxide ( $\text{Cu}_2\text{O}$ ), copper carbonates (i.e. azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$  and malachite ( $\text{CuCO}_3\text{Cu}(\text{OH})_2$ )] and dangerous chlorine-based compounds such as nantokite ( $\text{CuCl}$ ) and atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) polymorphs



hydrated metallic oxides at the surface, their co-existence being disclosed by the two-component of the O 1s band peaked at about 531.1 eV and  $532.2 \pm 0.3$  eV, typical of O–Met and O–H or  $\text{H}_2\text{O}$  chemical bonding, respectively [31, 37, 38].

The XPS spectral features for copper (not shown) such as binding energy (BE) and lineshape of the Cu  $2p_{3/2}$  signal and its shake-up satellite, the kinetic energy of the Cu

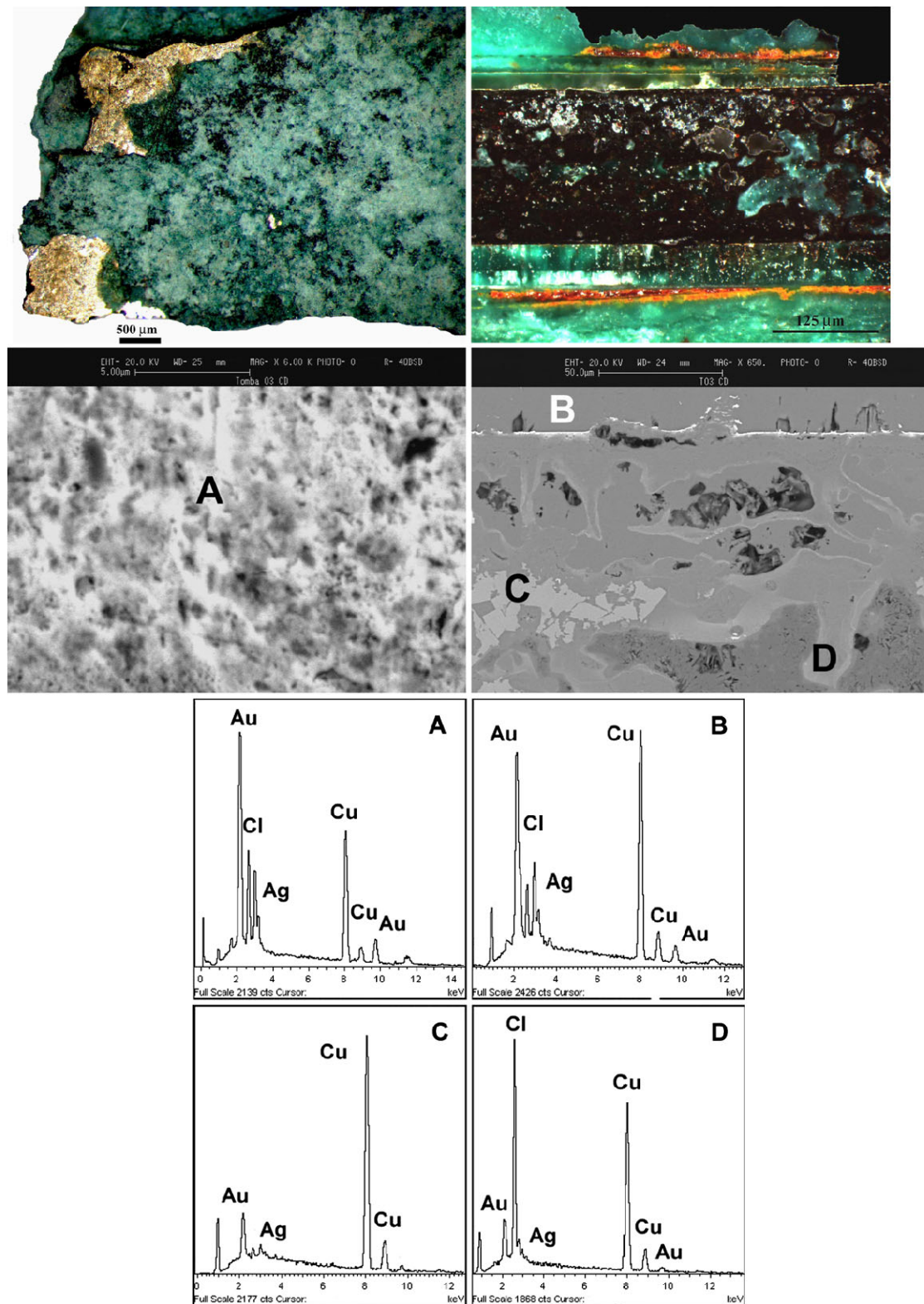
LMM signal and the  $\alpha'$  Auger parameters of the *patinas* reveal the presence of Cu (II) corrosion products such as copper oxychlorides and carbonates, moreover, the Cu 2p signal is characterised by the typical intense shake-up satellites [39–42] confirming the assignment to Cu (II) species. Furthermore, the modified  $\alpha'$  Auger parameters for silicon and aluminium are  $1713.3 \pm 0.1$  eV and 1461.5 eV, respectively. As expected, these results are quite similar to those for illite



**Fig. 5** Back scattered scanning electron microscopy (BSE SEM) images and energy dispersive spectra (EDS) of a cross-sectioned fragment from the owl-crown of the Young Warrior (T 15-B) that disclose the presence of a surface gold thin layer with a low amount of silver. The high resolution image of the area under the gold layer reveals the pres-

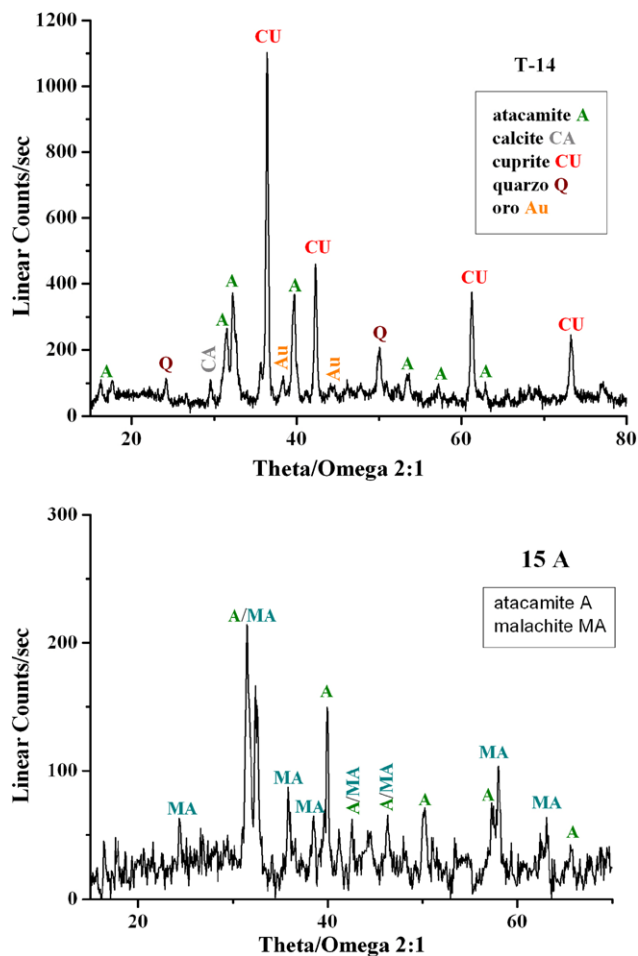
ence of copper-chloride species which are dispersed nano-particles of gold coming from the complete corrosion of the Cu–Au alloy used by Moche metalsmiths to induce the surface gold enrichment likely via depletion gilding process





**Fig. 6** OM images (*first row*, surface, and dark field observation) of a fragment of a copper based artefact from the tomb of the Lord of Sipán (T-03) that disclose the presence of the thin gold layer under the thick *patina* constituted by copper corrosion products. The images show that the artefact has been completely mineralised with the formation of different copper corrosion products. BSE images and EDS spectra

(*second and third row*) of the cross-sectioned fragment reveal a gold thin layer with a noticeable content of silver that could indicate the use of copper alloys with different amounts of Au and Ag and reflects the skill of the metallurgists to produce alloys in a wide range of chemical compositions



**Fig. 7** XRD patterns of the surface of the dress of the Warrior Priest (T-14) and of the owl-crown of the Young Warrior, the patterns show the presence of different copper corrosion products and a weak signal of gold

(layered forms of micaceous clay minerals) that is a typical soil constituent [43, 44].

The above described results show that different copper corrosion products have grown during the long term archaeological burial due to the intense and selective dissolution of copper that, in many cases, induce the formation of a stratified structure, whose internal zone is mainly composed of cuprous oxide and copper chlorides [12, 32, 45].

The external patina is formed by the interaction between soil constituents (Cl, S, Si, Ca, Fe, P, Al, K, CO<sub>2</sub>) and copper corrosion products. The presence of these elements demonstrate a strict interaction between soil constituents and artefacts corrosion products that could be enhanced by the effect of a long-term burial in a chlorine-enriched soil and the use of fertilisers used for the sugar plantations surrounding the archaeological site. These latter chemical compounds are dangerous for chemical-physical stability of the metallic archaeological artefacts, both for their high solubility and for the high ionic conductivity of their solutions as well as for

the role played by the reactive cuprous chloride (CuCl) that induces the dangerous cyclic copper corrosion phenomenon, the so-called “bronze disease” [13–19, 32, 45].

The degradation phenomena are further enhanced by the contact between different metals, such as the gold superficial coating and the copper-based alloy of the bulk. This galvanic coupling of different metals, speeded up the copper corrosion process.

As a consequence of the joining between Au or Ag and Cu-based alloy, the behaviour and the rate of corrosion of copper is remarkably influenced by the intimate contact between metals with different electrochemical potential and electrically connected by an electrolyte. This contact induces the less noble metal (Cu) to become anodic and the current will flow from the more noble cathodic metal (Au) to Cu, thus inducing its preferential corrosion. The amount of current which flows and the extent of corrosion depend on many variables, such as chemical-physical parameters of the burial context, the presence and the nature of the electrolyte and the micro-chemical structure of the alloy [12, 45].

#### 4 Conclusions

Some copper-based objects coated with a thin layer of gold found during the archaeological excavation of the Royal Tombs of Sipan have been studied by means of the combined use of analytical techniques such as optical microscopy (OM), scanning electron microscopy coupled with energy dispersive X-ray micro-analysis (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

The aim of the studies was to identify the chemical composition and manufacturing processes of the gold layer as well as the corrosion products formed during the long-term burial.

The micro-chemical and structural results give useful information to identify the manufacturing techniques used by the Moche metalsmiths to modify the surface chemical composition of the coated artefacts based likely based on the depletion gilding process carried out by oxidising the surface copper containing the noble metal and etching away the copper oxides.

Furthermore, the results reveal that the main degradation agent is the ubiquitous chlorine and that copper has been almost completely transformed during the burial into mineral species giving rise to the formation of stratified structures constituted by different mineral phases such as cuprous oxide (Cu<sub>2</sub>O) and copper carbonates [azurite (Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> and malachite (CuCO<sub>3</sub>Cu(OH)<sub>2</sub>)] as well as dangerous chlorine-based compounds such as nanokite (CuCl) and atacamite (Cu<sub>2</sub>(OH)<sub>3</sub>Cl) polymorphs that induce the cyclic corrosion reaction of copper (“bronze

disease”). Furthermore, an electrochemical corrosion phenomenon induced by the intimate contact of different metals, was proposed.

From a conservation point of view, the results suggest that these artefacts must be kept under a well-controlled atmosphere and its conservation state must be continuously monitored and further, to maintain the integrity of the objects, mechanical stresses and vibrations must be avoided, as well as their transportation.

**Acknowledgements** The activities have been carried out in the framework of the bilateral Italian–Peruvian project between CNR and CONCYTECH (2009–2011 and 2012–2014).

## References

1. R.F. Townsend (ed.), *The Ancient Americas. Art from Sacred Landscapes* (The Art Institute of Chicago, Chicago, 1992)
2. C.C. Morris, A. von Hagen, *The Inca Empire and Its Andean Origins* (American Museum of Natural History, Abbeville Press Publishers, New York, 1993)
3. M.E. Mosely, *The Incas and Their Ancestors. The Archaeology of Peru* (Thames and Hudson, London, 1992)
4. R. Stone-Miller, *Art of the Andes from Chavín to Inca* (Thames and Hudson, London, 1995)
5. W. Alva, in *Sipán, Descubrimiento e Investigación*, ed. by W. Alva (Quebecor World Perú S.A., Lima, 2004)
6. W. Alva, C.B. Donnan, *The Royal Tomb of Sipán* (Los Angeles Fowler Museum of Cultural history; University of California at Los Angeles, Los Angeles, 1993)
7. W. Alva, Discovering the New World’s richest tomb. *Natl. Geogr.* **174**, 510–548 (1988)
8. W. Alva, New tomb of royal splendour. *Natl. Geogr.* **177**, 2–215 (1990)
9. I. Shimada, J.A. Griffin, *Sci. Am.* **April**, 82–89 (1994)
10. R. Cesareo, C. Calza, M. Dos Anjos, R.T. Lopes, D.A. Bustamante, S.J. Fabian, W. Alva, L.Z. Chero, Pre-Columbian alloys from the royal tombs of Sipán; energy dispersive X-ray fluorescence analysis with a portable equipment. *Appl. Radiat. Isot.* **68**, 525–528 (2010)
11. R. Cesareo, D.A. Bustamante, S.J. Fabian, A.S. Zambrano, W. Alva, L. Chero, Z.M.C. Del Carmen Espinoza, R. Rodriguez, R.M. Seclen, F.V. Guitierrez, E.B. Levano, J.A. Gonzalez, M.A. Rizzutto, E. Poli, C. Calza, M. Dos Anjos, R.T. Lopes, G. Gigante, G.M. Ingo, C. Riccucci, C. Elera, I. Shimada, V. Curay, M.G. Castillo, F. Lopes, Evolution of pre-Columbian metallurgy from the north coast of Peru studied with a portable non-invasive equipment using energy-dispersive X-ray fluorescence. *Mater. Sci. Eng. B* **1**, 48–81 (2011)
12. G.M. Ingo, E. Angelini, T. de Caro, G. Bultrini, *Appl. Phys. A, Mater. Sci. Process.* **79**, 171–179 (2004)
13. D.A. Scott, *Metallography and Microstructure of Ancient and Historic Metals* (Paul Getty Conservation Institute, Malibou, 1991), p. 25
14. D.A. Scott, *Copper and Bronze in Art, Corrosion, Colorants, Conservation* (Paul Getty Conservation Institute, Malibou, 2002)
15. L. Robbiola, J.-M. Blengino, C. Fiaud, *Corros. Sci.* **40**, 2083 (1998)
16. D.A. Scott, *Stud. Conserv.* **30**, 49 (1985)
17. D.A. Scott, *J. Am. Inst. Conserv.* **29**, 193 (1990)
18. C.G. Fink, in *The Corrosion Handbook*, ed. by H.H. Uhlig (ed.) (Wiley, New York, 1948)
19. F. Schweitzer, in *Proceedings of the Symposium Organised by the Paul Getty Museum*, ed. by D.A. Scott, J. Podany, B.B. Considine (Paul Getty Museum, Malibou, 1994), pp. 1–20
20. G. Padeletti, G.M. Ingo, A. Bouquillon, S. Pages-Camagna, M. Aucoeurier, S. Rohers, P. Fermo, *Appl. Phys. A, Mater. Sci. Process.* **83**, 475–483 (2006)
21. G.M. Ingo, S. Kaciulis, A. Mezzi, T. Valente, F. Casadei, G. Gusmano, *Electrochim. Acta* **50**, 4531–4537 (2005)
22. G. Cossu, G.M. Ingo, G. Mattogno, G. Padeletti, G.M. Proietti, *Appl. Surf. Sci.* **56–58**, 81–88 (1992)
23. G. Fierro, G.M. Ingo, F. Mancina, *Corrosion* **45**, 814–823 (1989)
24. G.M. Ingo, G. Marletta, *Nucl. Instrum. Methods Phys. Res., Sect. B, Beam Interact. Mater. Atoms* **116**, 440–446 (1996)
25. G. Horz, M. Kallfass, *Mater. Charact.* **45**, 391–420 (2000)
26. G. Horz, M. Kallfass, *J. Met.* **December**, 8–16 (1998)
27. H. Lechtman, A. Erlij, E.J. Barry Jr., *Am. Antiq.* **47**, 3–30 (1982)
28. H. Lechtman, *Invest. Cienc.* **95**, 20–28 (1984)
29. H. Lechtman, Ancient methods of gilding silver, examples from the Old and New Worlds, in *Science and Archaeology*, ed. by R.H. Brill (MIT Press, Cambridge, 1971)
30. J.F. Merkel, A.I. Seruya, D. Griffiths, I. Shimada, Materials issues in art and archaeology IV. *Mater. Res. Soc. Symp. Proc.* **352**, 105–125 (1995)
31. G.M. Ingo, E. Angelini, T. de Caro, G. Bultrini, I. Calliari, *Appl. Phys. A, Mater. Sci. Process.* **79**, 199–203 (2004)
32. G.M. Ingo, T. de Caro, C. Riccucci, S. Khosroff, *Appl. Phys. A, Mater. Sci. Process.* **83**, 581 (2006)
33. P.T. Craddock, *J. Archaeol. Sci.* **3**, 93 (1976)
34. P.T. Craddock, *J. Archaeol. Sci.* **4**, 103 (1977)
35. P.T. Craddock, *J. Archaeol. Sci.* **5**, 1 (1978)
36. A. Butts, *Copper, the Science and Technology of the Metal. Its Alloys and Compounds*, Am. Chem. Soc. Monogr. Ser., vol. 12 (Reinhold, New York, 1954)
37. G.M. Ingo, L. Giorgi, N. Zacchetti, N. Azzetti, *Corros. Sci.* **33**, 361–377 (1992)
38. E. Papparazzo, G. Fierro, G.M. Ingo, N. Zacchetti, *Surf. Interface Anal.* **12**, 438–439 (1988)
39. R. Schlesinger, H. Klewe-Nebenius, M. Bruns, *Surf. Interface Anal.* **30**, 135 (2000)
40. V. Hayez, A. Franquet, A. Hubin, H. Terry, *Surf. Interface Anal.* **36**, 876 (2004)
41. D. Chadwick, T. Hasemi, *J. Electron Spectrosc. Relat. Phenom.* **10**, 79 (1997)
42. R.F. Roberts, *J. Electron Spectrosc. Relat. Phenom.* **4**, 273 (1974)
43. C.D. Wagner, A. Joshi, *J. Electron Spectrosc. Relat. Phenom.* **47**, 283 (1988)
44. C.D. Wagner, Appendix 4 “Auger chemical shifts and the Auger parameter”, in *Practical Surface Analysis by Auger and XPS*, ed. by D. Briggs, M.P. Seah (eds.), 2nd edn. (Wiley, New York, 1990)
45. P. Lucey, *Br. Corros. J.* **7**, 36 (1972)