

**ORIGINAL ARTICLE**

# Interdisciplinary methodology for the characterisation of archaeological metal grave goods from the Museum of Patagonia by PIXE, DRX, and SEM/EDS

Josefina M. Schweickardt<sup>1,2</sup>  | Pablo D. Pérez<sup>2,3</sup>  |Mauricio Morán<sup>1,2</sup> | Marcia Bianchi Villelli<sup>2,4</sup> | Florencia Cantargi<sup>1</sup>

<sup>1</sup>Laboratorio Argentino de Haces de Neutrones (LAHN), Comisión Nacional de Energía Atómica (CNEA), Bariloche, Argentina

<sup>2</sup>Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Bariloche, Argentina

<sup>3</sup>Centro Atómico Bariloche (CAB), Comisión Nacional de Energía Atómica (CNEA), Bariloche, Argentina

<sup>4</sup>Instituto de Investigaciones en Diversidad Cultural y Procesos de Cambio (IIDyPCa), Universidad Nacional de Río Negro (UNRN), Bariloche, Argentina

**Correspondence**

Josefina Schweickardt, Laboratorio Argentino de Haces de Neutrones (LAHN), Comisión Nacional de Energía Atómica (CNEA), Bariloche, Argentina.  
Email: [josefinamsch@gmail.com](mailto:josefinamsch@gmail.com)

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**Abstract**

We present a study of a selection of metal ornaments belonging to archaeological funerary goods from Patagonic Indigenous groups. They are part of the 'Andrés Gai' Collection, under the guard of the Museum of Patagonia (Nahuel Huapi National Park [PNNH]; National Parks Administration [APN]), Argentina. The absence of contextual information and its current conservation status motivated the design of an interdisciplinary methodology to develop an Integral Conservation Plan that considered the selection of analytical techniques. Here, we implemented complementary nondestructive characterisation techniques such as particle induced X-ray emission (PIXE), X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS). We developed a methodology enabling us to characterise each piece with respect to its metallic composition and degradation products, and in certain cases, their manufacturing process. These findings have contributed with essential information for the tailored conservation treatment proposal. Moreover, they provided key information in regard to the reconstruction of contextual data for each piece. In addition, the methodology proposed for the Integral Conservation Plan takes into account an optimisation of the techniques to be used in order to minimise unnecessary handling of goods whilst ensuring an appropriate use of technological and economic resources whilst minimising time on potentially inconclusive measurements and results.

**KEYWORDS**

analytical investigation of deterioration, cultural contact period, integral conservation approach, ion beam analysis, materials characterisation techniques, metal body ornaments, Patagonian archaeology, PIXE, SEM/EDS, XRD

**INTRODUCTION**

The ‘Andrés Gaii’ Collection is under the guard of the Museum of Patagonia (PNNH-APN). This institution was created in 1940 in San Carlos de Bariloche City, Río Negro, Argentina, to organise and preserve the cultural heritage of the past and history of the Patagonian Region. Currently it is the main repository of archaeological collections in the region. The Gaii Collection was named after the explorer who, commissioned by the Museum in 1943, extracted several Indigenous funerary artefacts from different sites along the north limit of Lanin National Park, in the west-centre of the present-day Neuquén Province, Argentina, as shown in Figure 1. The archives of the Gaii Collection lacked fields or excavation records due to the absence of methodological strategies and adherence to scientific standards during the gathering and compilation of the objects at the excavation site (Bianchi Villelli et al., 2023). It comprises a diverse array of artefacts proceeding from several burials. The pieces associated with the human remains are ceramic wares, pipes, and various metallic body ornaments, such as earrings, rings, headbands, and fragments of pectoral adornments. This archaeological complex is related to the colonial period onwards. It reflects a period characterised by interethnic relations, conflictive encounters, and exchanges, matters of significant relevance for its study. Upon consideration of the typological, stylistic, and general characteristics of this collection, we a priori estimated a chronology indicative of a later period. Specifically, the presence of European manufactured goods places this collection between the beginning of 16th and the 19th centuries. As highlighted before, the Gaii Collection comes from different archaeological sites and its temporal and background homogeneity is yet to be assessed.

This work focuses on the analysis of the metallic items from The Collection because of their natural chemical instability (Watkinson, 2013) and their severe conservation problems. These items are copper-based and silver-based alloys, judging by the appearance of their corrosion products, and some of them are combined with glass beads and animal tendon threads. In terms of its origin, there are locally manufactured objects—as flat pendants, tubes or cones—and others produced in Europe—jingle bells, thimbles, and glass beads. The provenance of raw material for the locally manufactured goods remains a subject of discussion given the possibility of local production utilising both European and indigenous raw materials. Some evidence of European raw materials reused by locals include brass sheets and silver objects from the 16th century onward and during the late 19th century, there are records of coin smelting to forge *mapuche* adornments (Campbell, 2015; Inostroza et al., 1986; Nuñez-Regueiro & Guerra, 2015).

The general conservation status of the metallic items was reviewed. Overall, the artefacts presented several corrosion products and crusts, as well as a high degree of structural fragility. Some were inappropriately treated in the past, leaving cleaning residues and heterogeneous distribution of the degradation products on the surface, exposing parts of the noncorroded metallic surface (Schweickardt, 2024).

The conservation-restoration field aims to maintain both the physical and symbolic properties of cultural objects (Calvo, 1998) whilst focusing on the stability of the supporting material and preventing its degradation processes through deliberate treatments. Thus, studying the degradation and its subsequent products is mandatory, considering past, present, and future



**FIGURE 1** Exploration region map. Argentina, west-centre of the actual Neuquén Province. In the upper left corner is shown South America, and the Patagonian region marked in yellow. In the upper right corner is shown a close-up of the region of interest. Below, in the boxed dashed region, red lines represent the actual boundary of Lanin National Park with Neuquén Province. The limits between Argentina and Chile are the yellow lines. Google Maps (2023). South America and Patagonia region maps.

interactions within their environments (Cronyn, 2003; Pasies et al., 2011; Piqué, 2007). Hence, the types of raw material, their specific composition, the manufacturing techniques, the particularities of the burial context, and the records of past interventions are all essential information to develop sustainable conservation treatments (Baca et al., 2019; Costa, 2001). This is also the reason why the archaeological and historiographical background are the primary sources that provide precise information about the biography of the objects and their characteristics. In addition, this information attends to the conservation of their symbolic aspects. For all these reasons, the two main objectives of this study are to address the recovery of contextual information of the locally manufactured metal pieces and evaluate their conservation problems.

This led us to consider the implementation of analytical techniques as necessary tools to evaluate the complexity and multidimensionality of the two objectives. This implies, from the outset, the need to address this problem through interdisciplinary research as the only approach capable

of yielding meaningful answers and solutions (Coria & Porta Massuco, 2022; Joint ICTP-IAEA Workshop, 2019). Therefore, we developed an integral conservation plan with two main goals: first, to establish scientifically informed conservation treatments, and second, to develop a systematic workflow with a diagnosis stage and analytical techniques as the only way to guarantee the sustainability of the interventions (Barrio, 2002). We know that the selected techniques in this work have been widely used for heritage studies (Gutiérrez Neira, 2009; Marchand et al., 2014; Piccardo et al., 2007, among many others). Here, we propose an approach that does not only evaluate the pertinence and invasiveness of each technique but also their complementarity, sensitivity, sampling design, and tailored conservation treatments (Angelini et al., 2014).

## Integral Conservation Plan

The above-mentioned Integral Conservation Plan was developed in two main stages, (1) the conservation status diagnosis itself and (2) the subsequent proposal of treatments in the short, medium, and long terms. This work focuses on developing an interdisciplinary methodology for the conservation diagnostic stage (Baca et al., 2019). As a result, Stage (1) has a complex and interdisciplinary character, involving two programmes: (1.a) a prior technical examination and (1.b) an analytical deterioration research. Although this methodology was developed for the analysis of the metallic ornaments of the Gai Collection, the selected variables were designed to encompass a diverse array of heritage objects. As such, this methodology could be applied to ceramic, glass beads, and lithic instruments, broadening the scope of materials.

The programme (1.a) involves a comprehensive and general review of material and contextual aspects, including historical and archaeological backgrounds. It also comprises a precise and exhaustive macroscopic evaluation of each object and its degradation products as typically addressed in conservation studies (Schweickardt, 2024). This information is combined with the theoretical foundation on degradation mechanisms to assess specific deterioration patterns. Finally, the detected problems are posed as guidance questions, mainly about the inner characteristics of the artefacts, their history and context, and the stability of the degradation products.

Programme (1.b) determines the relationship between the degradation pattern observed, technically identified in the previous step, and its causes. First, experimental hypotheses about materials and their physical and chemical interactions—past, present, and future—are proposed based on the guiding questions. Each interaction can manifest itself at atomic, isotopic, ionic, molecular, microstructural, and microtopographic levels. The hypotheses should establish specific chemical and morphological fingerprints, and within, indicators based on these levels of interactions. These fingerprints involve the patterns of materials, corrosion, and degradation products. They will indicate the analysis technique needed and the appropriate sampling design to analyse their related indicators. For example, one of the typical green degradation products in copper alloys is atacamite and its polymorphs, represented by its chemical fingerprint  $\text{Cu}_2\text{Cl}(\text{OH})_3$ . Hence, the detection of chlorine in specific proportions together with copper will be indicators of the presence of atacamite compound. Thus, we can apply analytical techniques with prior knowledge of the type of indicator that requires detection. The detected indicators establish a link between the observable phenomenon and their patterns. Nevertheless, the analytical results must be interpreted with an interdisciplinary approach in order to link them unequivocally with the corresponding pattern. For example, the detection of chlorine does not unambiguously determine the presence of atacamite. Usually, fingerprint indicators need to be detected and interpreted combining more than one technique (ICTP Trieste-Workshop IAEA, 2019).

In this study, we focus on the diagnosis Stage (1) applied to a set of locally manufactured metallic body adornments—copper and silver-based alloys. The results obtained allowed the initial discussions for stage (2), regarding conservation treatments for these artefacts, see section ‘[Recommendations for conservation](#)’.



## MATERIALS AND METHODS

In order to obtain compositional and structural results for the raw materials and degradation products, we worked with particle induced X-ray emission (PIXE), X-ray diffraction (XRD), and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) techniques. In this section, we will expose the methodological steps taken prior to the implementation of these techniques.

### Sample selection criteria

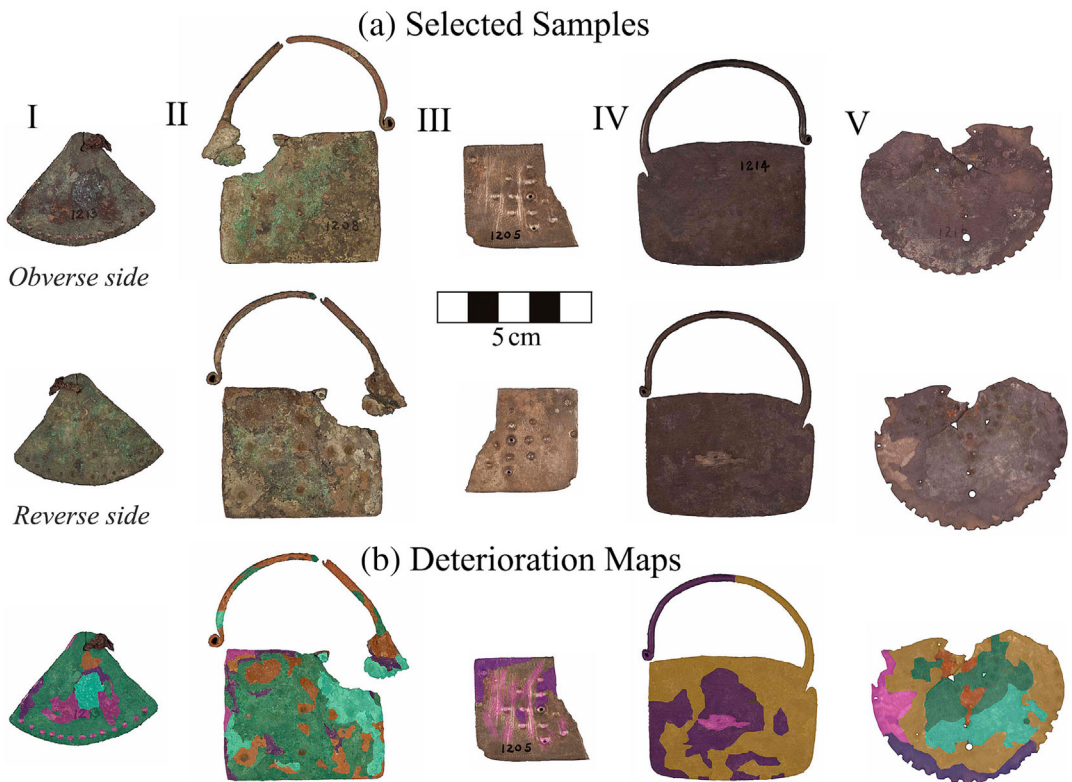
The first selection criterion addressed was to ensure typological representativeness, including both alloy types—copper and silver-based. Second, the selected samples chosen according to geometric and dimensional features as dictated by the used analytical technique. Third, those objects with an exposed noncorroded metal surface, caused by abrasions from previous cleanings, were prioritised to improve access to the metallic surface of the samples. This allowed us to perform measurements without the interference of corrosion products and or soil residues without any sample modification nor preparation as requested by the museum. The selected samples are shown in Figure 2a.

### Sample characteristics

Samples I to IV are pendants, whilst sample V is the discoidal head of a pinch. The five samples are flat and 1 mm thick approximately. The minimum dimensions and weight in the set are  $3.7 \times 4.1 \text{ cm}^2$  and 3.75 g for the earring (III); the maximum dimensions and weight are  $7.3 \times 6.2 \text{ cm}^2$  and 19.24 g for the earring IV. Four of them have decorations made by hammer punching, except for the earring IV, which has a smooth surface. There is no evidence of other types of surface treatments. Figure 2b shows deterioration maps of the samples made through visual inspection and optical microscope imaging. They are presented with the aim of demonstrating different deterioration features and their superficial distribution through colour codes, independent of the base alloy: (1) metallic surface exposed due to abrasion damage, (2) and (3) zones associated with typical copper corrosion products, (4) and (5) zones linked with typical silver corrosion products, and (6) zones of white crusting.

### Temporal context attribution of the samples

The estimated chronological frame for this collection covers 300 years approximately, implying a complex history that left clear imprints on the local technological and stylistic features, such as the different types of raw materials utilised and in the diversity of manufacturing techniques, decorations, sizes, and typologies (Campbell, 2004, 2015; Campbell et al., 2018; Campbell & Quiroz, 2015; González Caniulef, 2019; Nuñez-Regueiro & Guerra, 2015; Vasallo et al., 1996). These specific technological features are key to a more specific temporal ascription for The Collection. Our research relied mainly on the work of Roberto Campbell about the South-Andean metallurgical record. In his work, an exhaustive cadastral survey of the metallic archaeological pieces was carried out, incorporating all the recorded pieces from Argentina and Chile (Campbell, 2004, 2015; Campbell et al., 2018; Campbell & Quiroz, 2015). Regrettably, the Gaii Collection was omitted because its existence was unknown until we initiated our research in year 2017.

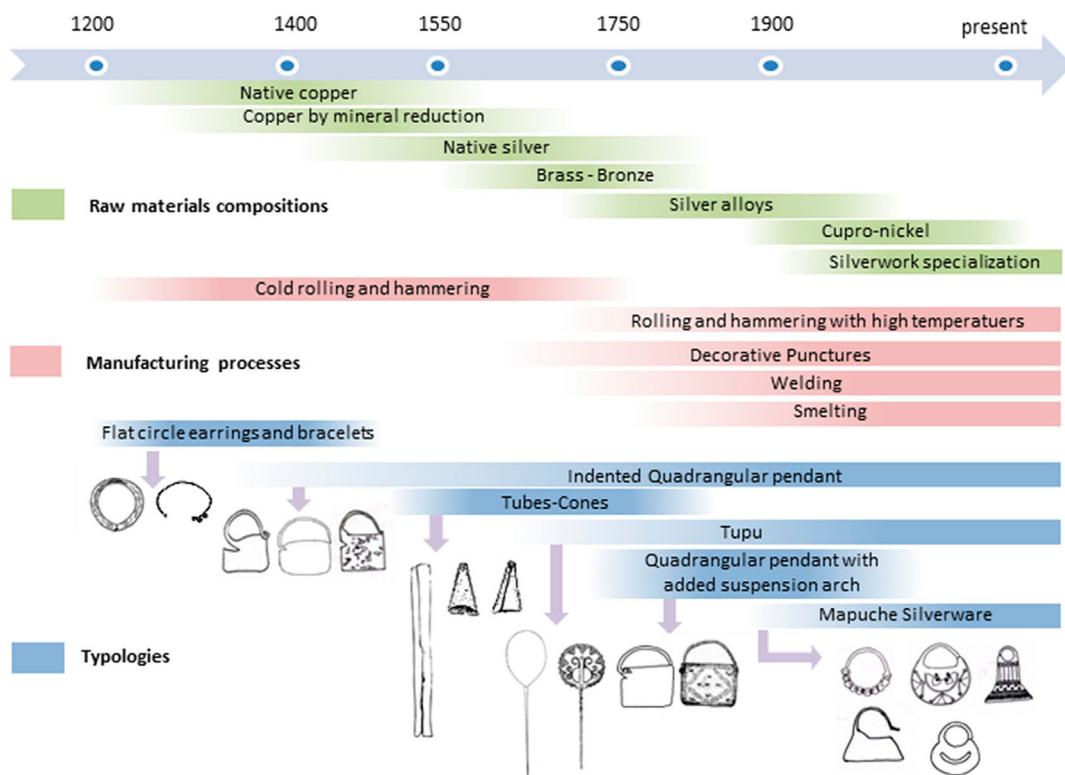


**FIGURE 2** (a) Selected samples: I. Triangle earring, *Chaguay*, copper alloy; II. Quadrangular earring *Chaguay Chapel*, copper alloy; III. Quadrangular earring, *Chaguay Chapel*; silver alloy; IV. Indented quadrangular earring, *Chaguay Chapel*, silver alloy; V. *Tupu*, disc head, silver alloy. (b) Deterioration maps, colour references: superficial abrasion—clean metal surface exposed; reddish corrosion products; greenish corrosion products; grey lavender corrosion products; black darkening; whitish depositions.

The studies made by Campbell include as elements of comparison the stylistic precisions of the objects, their associations with specific compositions of raw materials, and their connection with manufacturing processes as well as technical modifications. All these elements together make up a ‘technological behaviour’ associable with a specific sociocultural event (Campbell, 2004:25). Other authors who study these processes from the beginning of metallurgic production in the area, including the *Mapuche* silversmithing of the 19th century, to the present times, were also considered (De Rosa & Tapia, 2014; González Caniulef, 2019; Inostroza et al., 1986; Mera et al., 2015; Morris von Bennowitz, 1997; Nuñez-Regueiro & Guerra, 2015; Vasallo et al., 1996).

Based on their research, we formulated a trajectory of metallurgy for these regions with the aim of contextualising their sociocultural processes. Figure 3 highlights the representative historical milestones and their influence on metallurgy, mainly focused on the compositions of raw materials according to a given period. It is important to note that this chronology is a reconstruction based on archaeological and museological information systematically collected for decades, predominantly in Chile.

According to these studies, we established a first approximation of the temporal frame, guided only by the typological and stylistic characteristics of the selected set. The composition of raw materials and the implemented manufacturing process must be addressed to obtain a more precise association with a specific period. Hence, in this work, we intended to associate



**FIGURE 3** Timeframe. Technological behaviours across time are based on the mentioned authors. Raw materials composition, in weight percent (% wt), for each type of alloy are: native copper (Cu 99%); copper by mineral reduction: sulphur mineral reduction (Cu 90%, Ag 2%, S  $5 \pm 2\%$ ), arsenical copper (As 10%, Cu 89.8%, Se 0.07%, Ag 0.07%); native silver (Ag 99.9%, Cu < 2.7%); brass (Cu 70% Zn 25  $\pm$  5%, Pb 2%); bronze (Cu 88%, Sn 12%). Silver alloys (Ag 90  $\pm$  3%, Cu 6  $\pm$  3%); Cupro-nickel (Cu 70%, Zn 10%, Ni 20% - Cu 75%, Ni 25%). Colour bars from each type of alloy, manufacturing process, and typologies show smooth transitions over time.

the technological behaviours of the selected set with specific sociocultural events of the region. The chemical and structural characterisation of these materials might add critical information to define their time frames with greater precision, to assess diversity within the collection, and to further understand the specificity of each context.

In this section, we report a summary of programme (1.a) from which we detect four main problems regarding the lack of information on the samples that should be resolved by implementing analytical techniques. The guidance questions for these detected problems are about (A) the type of composition for the raw materials of each object; (B) its temporal contexts; (C) each object manufacturing process; and (D) the type of degradation products, mainly corrosion products, of each object.

## Procedures for the selection of analytical techniques

The selection of analytical techniques first involves proposing hypotheses to answer the guiding questions as a means to establish indicators to be analytically validated. Subsequently, the analytical deterioration programme (1.b) is implemented to address the guidance questions by implementing analytical techniques.

## Hypothesis

Firstly, regarding (A) the type of alloy and (B) temporalities for each type of object, we established compositional hypotheses based on the compositional framework in Figure 3. Regarding copper objects, their typologies and decoration styles led us to favour postcontact alloys, thus:

**Hypothesis 1.** We expect the detection of certain elements in combination with copper, such as zinc or tin, in specific proportions, serving as indicators for brass and/or bronze copper alloys. (See specific composition in Figure 3.)

For the silver objects, we do not rule out the presence of native silver for pendant IV because its typology and decoration style have been registered from precontact periods and transcend several historical milestones. Our search for indicators also includes nickel, as these objects may have belonged to temporal early casting stages with cupro-nickel coins (Nuñez-Regueiro & Guerra, 2015). Therefore

**Hypothesis 2.** We expect to detect certain elements in combination with silver, such as copper or nickel, in specific proportions as indicators of the type of silver alloy, including native silver (see specific compositions in Figure 3).

Second, considering that some technological procedures span over specific temporal ranges, to evaluate (C) the manufacturing process, we addressed the microstructural characteristics of this selection, that is, the preferential orientation of grains in the material. Thus, based on technical examination (1.a) and Figure 3:

**Hypothesis 3.** We consider that the probable manufacturing processes involved hammering or rolling at low temperatures.

Third, we addressed the analysis of the degradation products (D). Their determination is a complex matter because they are strongly related to the composition of the alloy and the manufacturing process, which might initiate various physical degradation products. In addition, both alloys in buried contexts can be affected by different degradation mechanisms and various products can be generated, such as stable patinas or unstable greenish, bluish, or reddish, from copper corrosion and darkening and ‘grey lavender’ colouration for silver alloys (Angelini et al., 2012; Scott, 2002). There are many types of corrosion and degradation products with a unique chemical fingerprint, and each one may have a similar colour. Table S1 shows the most common relative corrosion products of each alloy. Thus, we cannot be sure by visual inspection, which is the specific degradation product, nor what type of corrosion product it is (Abu-Baker & Khalil, 2022). Other degradation mechanisms are characteristic of these contexts, such as macro and microstructural cracking due to possible metal defects and/or underground mechanical forces; microsegregation of sedimentary compounds leads to the formation of insoluble crusts, among others.

Considering this complexity, we define our hypothesis to discard or verify the presence of the most unstable—therefore dangerous—corrosions and degradation products, typically known for these types of metals in burial contexts and museum environments. Hence:

**Hypothesis 4.** For copper-based alloys in a buried context, we expect to detect or discard indicators for cuprite ( $\text{Cu}_2\text{O}$ ), atacamite and its polymorphs ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) and chrysocolla ( $(\text{Cu}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ); among others.



**Hypothesis 5.** For silver-based alloys in a buried context, we expect to detect chlorargyrite ( $\text{AgCl}$ ), bromargyrite ( $\text{AgBr}$ ) and, regarding museum environmental context, silver sulphide ( $\text{Ag}_2\text{S}$ ).

According to the deterioration maps areas in Figure 2b, the informing questions, the development of hypotheses and their analytical requirements, as well as the chemical and morphological indicators, we selected the following techniques to evaluate the posed hypothesis.

## EXPERIMENTAL: SELECTED TECHNIQUES

Based on the hypotheses (H1–H5), we determined that the identification of chemical and morphological indicators would require quantitative multi-element information of detection limits of the order of ppm and microstructural information. These measurement conditions and the indicators were considered for the selection of the techniques.

Thus, we employed PIXE to elucidate compositional characteristics, due to its high sensitivity for quantification. Second, we implemented SEM/EDS to test the compositional homogeneity throughout both sides of the sample. Finally, XRD was implemented to obtain information about the metallic matrix and its preferred crystallographic orientation and to identify patterns of specific degradation or corrosion products. All measurements were conducted at the Bariloche Atomic Center, National Commission of Atomic Energy -CAB/CNEA-, Argentina.

### PIXE

PIXE was the first applied technique in order to obtain the composition of metal alloy, degradation products, and trace elements. It provides a multi-elemental analysis of materials with detection limits of the order of parts per million (ppm). To establish the composition at levels that allows, for example, the differentiation of instability factors in the formulation of the alloys, which may contribute to the existence of selective corrosion phenomena.

PIXE measurements were made using a 1.7 MV Tandem Ion Accelerator and a Sirius SD X-ray detector (Limandri et al., 2014). The irradiations were carried out with 3 MeV protons in a high vacuum chamber. The beam current was 1 nA or lower for the purpose of avoiding sample damage. The beam spot diameter was varied from 2 to 0.5 mm, according to the size of the zone of interest. The spectra were analysed using the GUPIX software (Campbell et al., 2010).

Due to the small size of the prevacuum chamber, the largest samples had to be introduced directly in the measurement chamber. This unconventional procedure limited the repetition of the measurements. Therefore, only the most representative side was selected for each case, see Figure 2b. Because of these restrictions, we complemented these analyses with SEM/EDS.

### Scanning electron microscope with energy dispersive spectrometer (SEM/EDS)

SEM/EDS was also implemented to determine the composition of metal alloys and the problems caused by degradation products. In this case, the analyses were focused on rapid measurements on both sides of the earrings with the aim of verifying the compositional homogeneity and representativeness of the areas measured by PIXE. Moreover, SEM/EDS is a fast technique of multi-elemental analysis with the advantage of researching multiple areas within a few  $\mu\text{m}^2$ . However, it allows detection and quantification with higher limits of detection than those of PIXE.

SEM measurements were carried out using a SEM FEI Inspect S50 with a thermionic emission gun (W) operated between 1 and 30 kV associated with an EDAX Octane Pro energy dispersive spectrometer (EDS) and a backscattered electron detector. These irradiations were made using 100  $\mu$ A beam currents and a 50 s collection time. The multi-elemental quantification was performed using EDAX Genesis software. The compositional homogeneity was checked on both sides of the samples.

The PIXE and SEM/EDS techniques determine the elemental composition; that is, they do not provide information about the compounds present in the sample. In some cases, it is possible to infer this information from the ratio between the elements that compose the molecule. Other techniques were considered for this purpose, such as the implemented RAMAN technique. However, due to the fluorescence emission of the samples it was not possible to detect any compounds in the spectrum. The time-of-flight secondary ion mass spectrometry (ToF-SIMS) technique was also considered, but it was not implemented, given it is a destructive technique. Hence, XRD was chosen to obtain information of the compounds using the crystalline structure of the sample.

## XRD

Finally, we used XRD to identify present crystalline phases in the objects. Once the crystalline phases are identified on the metallic base, pole figure maps can be made to obtain the preferential crystallographic orientation of the grains. These maps could enable us to infer the employed manufacturing processes.

The XRD measurements were carried out employing a PANalytical Empyrean diffractometer using Cu K $\alpha$  radiation and equipped with a PIXcel2D detector. The diffractometer also mounts an Eulerian cradle that can orient the samples by movements in the Z direction and by two rotating axes ( $\chi$  and  $\phi$ ). Twenty scans were obtained in the 20–120° range onto uncorroded and corroded areas of the samples. Crystallographic measurements were made by obtaining texture pole figures using the Schulz (1949) reflection method with  $0^\circ < \chi < 60^\circ$  and  $0^\circ < \phi < 360^\circ$  in 5° steps for both angles. The background and defocusing corrections and orientation distribution function (ODF) calculations were performed using the MTEX Toolkit on MATLAB (Hielscher & Schaeben, 2008).

## RESULTS AND DISCUSSION

The proposed hypotheses will be addressed in alignment to the four identified issues detected regarding the guidance questions. After the analytical results were interdisciplinary discussed, we obtained data that will be important for both their conservation and archaeological matters.

### (A) and (B) Raw materials specific composition and temporalities

The quantitative information obtained by PIXE allowed us to infer the type of alloy for each pendant. Due to the fact that the metal surfaces did not receive any sample treatment prior to the measurements, chemical elements ordinarily associated with burial context, e.g. Si, S, P, Cl, and Ca (Mera et al., 2015), and contaminants were detected. Thus, in order to obtain the compositions for these metal alloys, a renormalisation of the concentrations was carried out considering only the main metallic components. The calculated compositions for each sample are exposed in Table 1.

**TABLE 1** Alloy compositions, in weight percent (% wt), of each object determined by particle induced X-ray emission (PIXE). For copper-based objects, the relative uncertainty values for major components (Cu, Zn) were less than 2%, whilst for Pb, it was less than 9%. For silver objects, Samples IV, and V presented relative uncertainties of 10% for Ag, and 7% for Cu. Sample III presented lower relative uncertainties. For Ag it was 1%, and for Cu 2%, probably because its surface was in better conditions (clean and flat surface).

	Samples	Elements			
		Ag	Cu	Zn	Pb
Copper based alloys	I	-	80.7		2.1
	II	-	72.6	25.1	2.3
Silver based alloys	III	93	5.5	-	-
	IV	90	5.4	-	-
	V	90	4.4	-	-

For copper-based earrings, the concentrations obtained for copper ( $81 \pm 2\%$ ), zinc ( $21 \pm 4\%$ ), and lead ( $2.0 \pm 0.2\%$ ) were associated with leaded brass alloy (Korenberg & Baldwin, 2006). On the other hand, for the three silver-based objects, the concentrations obtained for silver were between 90% and 93%, and for copper was ( $4 \pm 2\%$ ). Those values were associated with a typical ‘high-purity silver alloy’ (Angelini et al., 2012). The presence of copper in these three cases will be discussed later on item D.

Regarding Hypotheses (1) and (2), the compositions for these samples were compared and linked with those of Figure 3 in order to place them in a temporal frame.

The characterisation of brass for copper-based pendants is an indicator of the postcontact period because this type of alloy was unknown in the region before the arrival of the Europeans (Campbell, 2004; De Rosa & Tapia, 2014). At the same time, decorations crafted by punching and incising are associated with items manufactured during late contact periods.

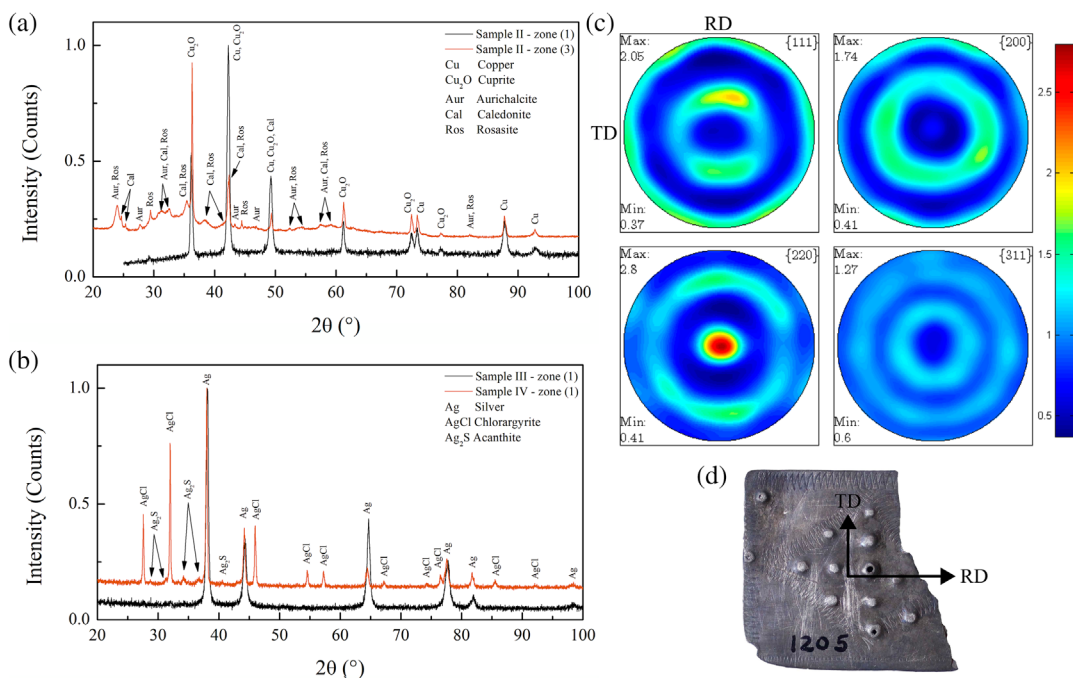
The composition characterisation for silver-based objects made it possible to limit the time periods, starting in postcontact periods because only native silver was used before that time-frame. This range ended at the beginning of the 19th century, as thereafter the source for silver raw materials shifted to coin melting with added nickel (Nuñez-Regueiro & Guerra, 2015), a component not detected in silver-based objects.

### (C) Manufacturing processes

The XRD results show that the copper alloy earrings have a face-centred cubic (FCC) phase with a lattice parameter close to pure copper. In the case of the silver pendants, the silver phase is also FCC with a lattice parameter similar to pure silver. Figure 4a,b shows representative XRD patterns for copper and silver, respectively.

Upon obtaining the diffraction patterns of the metals, it was possible to characterise the crystallographic texture for two silver objects (III and IV). Texture measurements on copper-based pendants and for silver object V have partially failed due to the prevalence of corrosion products and crust on these samples and the absence of a sufficiently large and clean metallic surface. Metallography techniques could potentially solve this question, however, the museum does not allow for the application of these techniques at initial stages of the research. The implementation of these destructive measurements will be recommended in future research focused on this collection.

Figure 4c shows recalculated pole figures of Pendant III, which are similar and representative to Pendant IV, obtained for the (111), (200), (220) and (311) reflections. The (220) pole figure shows a centred and intense maximum of 2.8 multiples of random distribution (m.r.d),



**FIGURE 4** (a) Shows a diffraction pattern representative of both brass samples. Besides the detection of FCC copper, it is possible to see the detection of cuprite ( $\text{Cu}_2\text{O}$ ). The red pattern is representative of the measured green zones, Zone (3), where aurichalcite, rosasite, and caledonite were identified; (b) shows diffraction patterns. Red pattern is representative of Samples IV and V, whilst black is the result for sample III. As this last sample was cleaner than the others, chemical compounds for the silver degradation process could not be identified; (c) shows the pole figures for Sample III; (d) indicates the rolling direction (RD) and transverse direction (TD) relative to the sample position.

which represents the (220) planes being mostly pointing parallel to the pendant surface normal. In addition, the (111) and (200) pole figures present features represented by the orientation of  $\{110\} \langle 100 \rangle$  to  $\{110\} \langle 211 \rangle$ .

As a whole, these exposed results are consistent with cold rolled deformed silver, with no evidence of recrystallisation texture components (Liu et al., 1998). This finding enabled us to validate Hypothesis (3). Along with its postcontact alloy composition, a cold-rolled process is compatible with a timeframe spanning the 16th to the 18th century. Furthermore, decorations created through punching and incising are associated with artefacts crafted during late contact periods, and this discovery helped us to narrow down its temporality to the second half of the 17th century.

## (D) Type and distribution of degradation products

After obtaining the compositions of the alloys, it was possible to delimit some chemical degradation mechanisms for each specific material and also to discard some specific chemical fingerprints. For example, degradation products of non-brass copper alloys, such as those containing tin, were discarded.

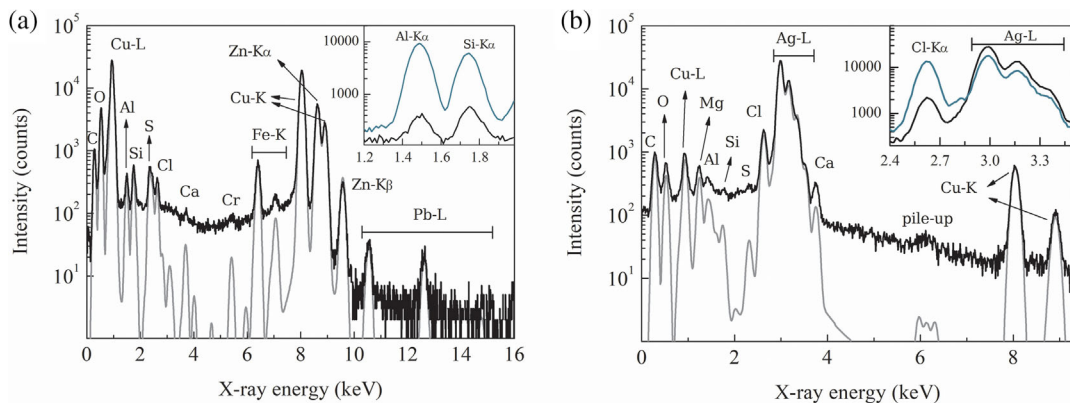
As a way of finding indicators for compounds present in the corrosion and degradation products, first, the compositional variation between corroded zones and the elements present in the abraded metallic Zones (1) were considered. It aimed to identify the increase or appearance of indicator elements regarding the compounds from Hypotheses (4) and (5).



Brass pendants present a heterogeneous distribution of the identified degradation products and white crusts, especially in Sample II. The reddish corrosion product, Zone (2), identified for this pendant was mainly detected in the stratum closer to the metal surface. In addition, through XRD, we detected reflections indexed as cuprite ( $\text{Cu}_2\text{O}$ ); this oxide typically forms first and serves as a substrate for other corrosion products. This compound was detected and reported in Figure 4a.

Additionally, the quantitative analysis given by PIXE on the greenish Zone (3) allowed us to verify a significant increase of silicon and aluminium for both brass objects. This variation led us to consider a relationship between these indicators (Si, Al) and the presence of copper silicates, known as chrysocolla— $(\text{Cu}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ —shown in Figure 5a. Also, given that chlorine was not detected, we were able to eliminate the presence of unstable and more dangerous copper corrosion products, such as copper chlorides (atacamite or paratacamite). Here we also identify other brass corrosion indicators related to zinc and lead migration from the matrix to the surface. An increase in zinc was detected and associated with copper-zinc carbonates, such as rosasite— $(\text{Cu}, \text{Zn})_2\text{CO}_3(\text{OH})_2$ , and aurichalcite— $(\text{Cu}, \text{Zn})_5(\text{CO}_3)_2(\text{OH})_6$  (Abu-Baker & Khalil, 2022; Gharib, 2014). Likewise, an increase in lead was detected and associated with a copper-lead-sulphide named caledonite— $\text{Cu}_2\text{Pb}_5(\text{SO}_4)_3\text{CO}_3(\text{OH})_6$ . Their presence is consistent with XRD patterns where the three compounds were identified, as shown in Figure 4a.

In the case of silver objects, degradation products consisted predominantly of a ‘grey lavender’ corrosion product, indicated in Zone (4), even though other degradation products, such as severe abrasions and darkening are observed on pendant III. Degradation products from Zone (4) and (5) could be related to the presence of chlorargyrite and bromargyrite because a considerable increment of the elements Cl and Br, especially chlorine, compared to the cleaned metal surface were observed. This increment is shown in Figure 5b. In addition, XRD results showed peaks belonging to chlorargyrite ( $\text{AgCl}$ ), as can be seen in Figure 4b. This compound does not appear homogeneous on the surface, and a more porous and voluminous phase can be seen in Zone (4). It is associated with a more significant amount of chlorine, which may indicate a more advanced stage of corrosion in those sectors. In addition, Zone (5) results also demonstrate an increase in sulphur. In this zone, the previously mentioned cleanings seem to have rid the possible degradation products from the metal surface, which could have allowed postexcavation



**FIGURE 5** Plots for X-ray spectra by PIXE. A representative spectrum of Zone (1) for (a) brass pendant and (b) silver pendant. In the upper right corner of both spectra, the increase of the indicator elements for each case is shown with green lines. Zoom (a) shows the increase in silicon and aluminium, measured in areas with greenish corrosion products, Zone (3), whilst zoom (b) shows the increase in chlorine, measured in areas mainly of ‘grey lavender’ products in Zones (4) and (5).

environmental reactions with silver. These reactions may lead to the formation of silver sulphide, a topic that will be discussed later. Thus, we were able to verify the presence of chlorargyrite for samples IV and V in Zones (4) and (5), but in the case of the Zone (5) for sample IV, it is mixed with silver sulphides. Silver chlorides do not create a protective film; thus, the metal can be completely transformed into silver chloride over time (Costa, 2001; Marchand et al., 2014: 5). After detecting this compound, direct and clear lines of action for the conservation treatments can be established.

The presence of pronounced abrasion marks on silver Pendant III is attributed to cleaning process undertaken. Its surface appearance does not show any signs of chlorargyrite formation. Chlorine was not evident in SEM/EDS measurements nor detected at trace levels with PIXE; therefore, we can infer that this product was not formed in this object. For this pendant, surface darkening, Zone (5), were predominant. The quantitative PIXE analysis shows an increase in sulphur, thus the darkening zones were also related to silver sulphide (which was identified on silver pendant IV). The formation of this compound usually occurs by atmospheric contamination- and not in a burial context (Cronyn, 2003). Hence, its presence for both silver pendants III and IV could indicate that the formation of this compound is influenced by its museum environment, either during its time on an exhibition or within the storage system.

Finally, a greenish corrosion product in Zone (3) was identified on the surface of the silver object V, and copper was detected by PIXE as the main compound in this zone. SEM/EDS microanalysis demonstrated the decrease and disappearance of copper in areas of the metal surface adjacent to these products. This could indicate the migration of this element from the matrix itself to allow for the formation of the copper corrosion product. Thus, its presence in a silver object allowed us to infer that a selective corrosion process has occurred. The percentage of copper detected in these alloys (see Table 1) falls within the range where this type of corrosion is possible (Costa, 2001; Cronyn, 2003).

## Recommendations for conservation

Regarding the recovery of the contextual information and the biography of the objects, we highlight the importance of a technical record system predefined both in the diagnosis and the conservation treatment stages. The proposition of controlled terminologies and the inclusion of essential variables is designed to standardise the approach, making it less dependent on the perspective of the observer.

We also define two levels of treatments regarding materiality-related conservation problems: preventive and direct interventions. For copper alloys, because the presence of unstable compounds in the substrate was ruled out, we recommend only a passive stabilisation until more analytical studies and cleaning procedures are defined. It requires ensuring a relative humidity atmosphere of less than 40%, free from contaminants such as chlorides, sulphides, or airborne particles (Abu-Baker & Khalil, 2022).

To achieve the stabilisation of silver objects, containing evidence of selective corrosion of copper within the matrix, we propose the atmospheric conditions described above. These environmental conditions prevent the proliferation of the detected chlorargyrite compound until its cleaning procedures are defined. Moreover, the detection of sulphides led us to consider the presence of a contaminated atmosphere in the museum, and therefore, we recommend reconditioning the environment for exhibition and storage, appropriately to ensure the absence of contaminants. Finally, due to the detected selective corrosion process, especially in Object V, we recommend using benzotriazole chemical for cleaning and stabilisation of copper compounds (Costa, 2001; Cronyn, 2003). Given that silver is a relatively soft metal, chemical cleaning is preferred over mechanical methods.

The complete removal of corrosion products from archaeological objects is not a standard practice, and the decision to pursue this treatment should be subject to specific discussions for each object. However, it is considered in cases where degradation products cannot be stabilised through atmospheric control or when they create electrochemical potentials that facilitate reactions. Total cleaning treatments are also taken into account when degradation products disrupt the aesthetic appreciation of the object. Thus, for the case of these objects, we recommend prioritising the treatment of the environment in order to preserve these objects facilitating their accessibility for future studies. Nevertheless, if further total cleanings are to be considered, we suggest the implementation of laser cleanings instead of chemical or mechanical interventions (Bertasa & Korenberg, 2022).

## CONCLUSIONS

The combined techniques implemented in this work allowed comprehensive assessment of the main issues detected within the Gaii Collection. The outcomes contribute significantly to the fulfilment of the objectives of this work, addressing both the conservation and contextual problems. Regarding the characterisation of the materials conforming to each ornament, we determined that both copper-based earrings were crafted from brass, whilst the three silver earrings were composed of alloys with a high percentage of silver and copper. These results represent several key implications for research.

First, we connect the five earrings with the postcontact periods, spanning the 17th to the 18th century. This chronology is also reinforced by the cold-rolled manufacturing process observed in both silver objects and the association with specific typological designs. Second, the compositional characterisation of the alloys contributed significantly to proposing specific degradation processes and products, enabling us to identify specific zinc and lead compounds for brass degradation products, and to identify selective corrosion processes for silver samples III and V.

Third, the integrated results of this work allowed us to establish the first recommendations to attend to their integral conservation, including historical aspects. Based on the degradation product identification, we were able to propose some first short-term treatments, especially regarding the environmental conditions and their monitoring. In addition, the reconstructed contextual and historiographical information is now a valuable part of the history of these objects and the collection, contributing to the narrative of their biography. Its treatment proposals are oriented toward the systematisation of the obtained data. In addition, this new information contributes to expand and enhance the research of the historical and archaeological backgrounds of the Gaii Collection.

Finally, the development and implementation of the Integral Conservation Plan enabled us to guide an optimal selection of analytical techniques. We highlight the importance of the methodological instances in providing the necessary guidance for this selection. We also remark that complex issues such as those exposed in this study are undoubtedly opportunities to develop highly synergistic interdisciplinary relationships that guarantee sustainable solutions for the integral conservation of archaeological heritage.

## DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article.

## PEER REVIEW

The peer review history for this article is available at <https://www.webofscience.com/api/gateway/wos/peer-review/10.1111/arcm.12966>.

## ORCID

Josefina M. Schweickardt  <https://orcid.org/0000-0003-1033-9182>

Pablo D. Pérez  <https://orcid.org/0000-0002-9388-1569>

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