



**HAL**  
open science

## Ion beam analysis of silver leaves in gilt leather wall coverings

Marie Radepont, Laurianne Robinet, Céline Bonnot-Diconne, Claire Pacheco, Laurent Pichon, Quentin Lemasson, Brice Moignard

► **To cite this version:**

Marie Radepont, Laurianne Robinet, Céline Bonnot-Diconne, Claire Pacheco, Laurent Pichon, et al.. Ion beam analysis of silver leaves in gilt leather wall coverings. *Talanta*, 2020, 206, pp.120191. 10.1016/j.talanta.2019.120191 . hal-02551238

**HAL Id: hal-02551238**

**<https://hal.science/hal-02551238v1>**

Submitted on 18 May 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# Ion beam analysis of silver leaves in gilt leather wall coverings

Marie Radepont<sup>1,2</sup>, Laurianne Robinet<sup>1</sup>, Céline Bonnot-Diconne<sup>3</sup>, Claire Pacheco<sup>2,4</sup>, Laurent Pichon<sup>2,4</sup>, Quentin Lemasson<sup>2,4</sup>, Brice Moignard<sup>2,4</sup>

<sup>1</sup> Centre de Recherche sur la Conservation (CRC), Muséum national d'Histoire naturelle, Ministère de la Culture, CNRS, 36 rue Geoffroy Saint-Hilaire, 75005 Paris, France. [marie.radepont@mnhn.fr](mailto:marie.radepont@mnhn.fr)

<sup>2</sup> Centre de Recherche et de Restauration des Musées de France (C2RMF), Ministère de la Culture, Palais du Louvre, 14 quai F. Mitterrand, 75001 Paris, France.

<sup>3</sup> Centre de Conservation et de Restauration du Cuir (2CRC), 235 rue de Corporat 38430 Moirans, France.

<sup>4</sup> Fédération de Recherche NewAGLAE, FR3506 CNRS, Ministère de la Culture, Chimie ParisTech, Palais du Louvre, 75001 Paris, France.

*Abstract* – An analytical methodology involving Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectroscopy (RBS) was implemented to respectively characterize the composition and the thickness of silver leaves on gilt leather decors. These objects, ancestors of our wallpapers, are nowadays still difficult to date and their provenance is generally determined from stylistic studies. The initial aim of this study was to identify markers that could be correlated with the object provenance to help distinguishing the different gilt leathers workshops in Europe. The analytical methodology was validated on modern samples and applied to a corpus of 58 ancient gilt leathers from four countries. This study provided an assessment of the sensitivity of the ion beam techniques used, and highlighted the complexity of such analyses on thin silver leaves due to the different factors affecting them, and the composite nature of the object. Thus, the thicknesses calculated from the RBS analyses presented a great variability that seems to be related to the leaf characteristics, the manufacturing process and/or the life of the decor. Nevertheless, observations suggest that silver leaves coming from the Netherlands are thicker than the ones from Spain, Italy or France. Concerning the elemental composition, the results discarded previous hypotheses and the focus was made on gold and mercury trace elements, thus it was shown that leaves in Italian decors seem to have generally a low content of these two elements. Despite the large number of decor analyzed, the corpus should be expanded over to confirm the hypotheses raised by this research. Nevertheless the results gained from this work bring new light on the factors affecting thin metal leaves in general, which will be beneficial to all fields dealing with their analysis.

## 1. Introduction

Gilt leathers, ancestors of our wallpapers, are luxurious decorations used all over Europe between the 16<sup>th</sup> and the 18<sup>th</sup> century [1,2]. The manufacturing of these objects started in Spain and spread in Europe progressively, mainly in Italy, France and the Netherlands. Despite their name, gold is not present in the composition of these artifacts. Indeed, these decors were made by applying to the leather a silver leaf that is burnished with a stone, and then covered with a yellow varnish made essentially of linseed oil and pine resin to obtain a gold-like appearance [3]. For aesthetic effects, “gilt” and “silvered” areas can be combined (Figure 1), the latter being prepared by applying a very thin varnish or protein-based layer over the silver [3]. On most decors, polychromy was also added on top. Nowadays it is difficult to date and attribute gilt leathers as they are not signed, and assumptions concerning their provenance are only based on stylistic studies [4].

Identification of the constitutive materials could provide some clues regarding the decor manufacturing process or reveal physical or chemical markers specific

of a period, a country or a workshop. Historical texts on the manufacture of these decors mention variation in the practices, recipes or quality of the materials depending on the countries. For example, it was reported that French workshops, to reduce the cost of the decor manufacturing, sometimes employed thinner leaves or used other metal leaves [5].

The identification and comparison of chemical elements composing a metal object is a common approach to determine its provenance [6,7]. In a former study, Talland compared the silver leaf composition obtained by PIXE (Particle Induced X-ray Emission), in five gilt leather samples, two attributed to the Netherlands and three to Spain/Italy, and made the hypothesis that the differences in the chemical composition could be related to the country of origin [8]. These analyses showed a lower percentage of silver (close to 90 %) and a higher percentage of lead (4 to 7 %) in the Netherlands samples compared to the Spanish/Italian ones which contained more than 95 % of silver and less than 1 % of lead. This hypothesis is based on a limited number of samples and needs to be verified over a larger corpus. Recently,



**Figure 1.** Photograph of the wall hanging the “Battle of Gelboé” (made in The Netherlands, 17<sup>th</sup> c., exhibited in the musée national de la Renaissance, Ecouen, France) and a detail of this decor showing “gilt” and “silvered” areas (© C. Bonnot-Diconne 2017).

an analytical methodology was developed to characterize the main components within gilt leather decors that is the leather, the silver leaf and the varnish, to increase knowledge on the manufacturing technique and degradation processes [9]. For the analysis of the silver leaf, this methodology combined two ion beam analyses (IBA), first the non-invasive PIXE analyses, to characterize the elemental composition, and secondly, the RBS (Rutherford Backscattering Spectrometry) to localize the different chemical elements in the depth of the considered layer which, by assuming its density, gives access to the thickness of the metallic leaves [10]. Based on these measurements, it was hoped to find chemical and/or physical markers in these silver leaves that could lead historians towards the provenance of the objects.

The present paper comes in the continuity of this research by applying this analytical methodology to analyze the silver leaves in a corpus of 58 historical samples originating from different geographic areas in Europe, as well as on mockup samples made according to a 18<sup>th</sup> c. recipe [5]. The specific issues encountered during these analyses and the processes implemented in response are discussed. IBA analyses of ancient artifacts always present complicated data processing and interpretations, mainly due to the representativeness of the area analyzed, and the heterogeneity, roughness or porosity inherent to the material. Ager study recently examined the accuracy of this non-invasive technique to measure thicknesses of thin metallic layers, and concluded that the results gained from this technique on gold leaves were close to expectations [11]. In the case of silver leaves, we will see that several factors could play a role in the measurement of their thickness and disturb the reproducibility of the data obtained.

## 2. Materials and methods

### 2.1. Studied materials

The methodology was assessed with modern silver leaves bought from three suppliers: Dauvet (France) dimension 80 × 80 mm, Manetti (Italy) dimension 95 × 95 mm and Berta (Italy) “thickness 30” reference dimension 85 × 85 mm. Whilst Dauvet and Manetti leaves are manufactured by pneumatic beating, Berta leaves are made by hand beating. The leaves from the three suppliers were prepared in different ways: 1) fixed with water on a glass slide, 2) glued using rabbit skin glue on a modern vegetable leather (Azais, France) and partly burnished with an agate stone, 3) used in a gilt leather mockup prepared according to a 18<sup>th</sup> century recipe [5].

The 58 ancient gilt leathers analyzed belong to public or private collections in France and Italy. Based on their stylistic characteristic, these were dated from the 16<sup>th</sup> to the 18<sup>th</sup> century and attributed to four countries: Spain, Italy, France and the Netherlands. All the decors selected had experienced no or minimal restoration. Some of these objects were assigned to two known manufacturers, André Reynier (France) and Agostino Nespola (Italy), thanks to documents present in local archives. Analyses were performed either directly on the decor or fragments of the decor, as well as on samples taken during conservation treatment.

### 2.2. Methodology

Ion beam analyses were directly carried out on objects without any preparation, simultaneously measuring PIXE (Particle Induced X-ray Emission) and RBS (Rutherford Backscattering Spectroscopy) at atmospheric pressure at the AGLAE facility (C2RMF). The beam was 30 μm in size and composed by protons for PIXE or alpha particles for RBS at 3 MeV for each

beam [12]. For each technique, three to six measurements per sample were performed. In few occasions, samples showed a high sensitivity to the ion beam analyses, therefore in these cases the number of measurements was reduced.

PIXE spectra were collected with one SDD Low Energy X-ray (LE) detector and two SDD High Energy X-ray (HE) detectors, positioned respectively at 45° and 50° relative to the beam axis [12]. The LE detector, that had no filter, enabled the detection of light elements thanks to a helium flow, whereas each one of the HE detectors was covered by a 50 µm thick aluminum filter. PIXE data were processed using the GUPIXWIN calculation engine [13] coupled to the homemade TRAUPIXE software [14]. The composition of the target obtained from the LE and the HE detectors can be combined by using iron as the *pivot* element, which means that it contributes to both types of X-rays. The quantitative composition of the analyzed materials is obtained for matrix and trace elements. For the results presented here, only elements quantified as being above the detection limit were considered.

RBS measurements were performed with a particle detector collecting backscattered protons set at 130° with respect to the incident beam. RBS data were processed using the SIMNRA software V6.05 [15].

Imaging of the silver leaves surfaces was performed using a scanning electron microscope with a field emission gun (SEM-FEG) at 4 kV and a working distance of 6 mm. A small silver leaf was attached on carbon tape and a bridge between the leaf and the tape was made with carbon lake. Estimation of the surface occupied by microporosities was made by a pixel calculation after an image treatment using the GIMP software.

### 3. Results and discussion

#### 3.1. Analysis of the composition of silver leaves

IBA measurements in ancient gilt leathers were carried out as much as possible away from pictorial layers, therefore the chemical elements detected are expected to come from the combination of the varnish, the silver, the glue and the leather. For each object, an analysis was also performed on the leather on its own, either from the front, if accessible, or from the back of the object, and the data were compared (Table 1).

In all the decors analyzed, only silver leaves are encountered and their composition is relatively pure in silver (with over 98 at%). Variability in the quantification of chemical elements is sometimes observed in a single sample and this may be associated with the surrounding components of the decor. Many elements were detected in the leaves in different proportions but none of these could be directly correlated with the object provenance. In particular the

**Table 1.** Chemical elements identified by PIXE in the leather alone and in the silver attached to the leather for the gilt leather wall hanging of L'Isle (Switzerland), made in The Netherlands in the 17<sup>th</sup> c. Element quantification is provided by “X” and “x” corresponding respectively to more and less than 3 times the limit of detection and “-” indicates the absence of the element considered.

Element	Leather	Silver
Na	x	-
Mg	X	-
Al	X	x
Si	X	X
P	X	X
S	X	X
Cl	X	X
K	X	X
Ca	X	X
Ti	X	x
Cr	x	-
Mn	X	X
Fe	X	X
Ni	x	x
Cu	X	X
Zn	X	X
Ga	x	x
Ge	x	-
As	x	x
Se	x	x
Br	X	-
Rb	x	x
Sr	X	X
Ag	-	X
Au	-	X
Hg	-	X
Pb	X	X

**Table 2.** Percentages of lead calculated from PIXE analyses of silver leaves in 11 gilt leathers (only considering the presence of silver, gold and mercury next to lead).

Provenance	Date	Reference	Pb (at%)
Spain	16 <sup>th</sup>	DEC9	0.07
	17 <sup>th</sup>	CBD6	0.54
Italy	17 <sup>th</sup>	Montalzat	0.11
	17 <sup>th</sup>	AR4.1	2.33
	18 <sup>th</sup>	Béceleuf	0.41
France	17 <sup>th</sup>	Golleville	0.30
	17 <sup>th</sup>	DEC4.1	0.12
	17 <sup>th</sup>	EC3	0.97
The Netherlands	17 <sup>th</sup>	Scipion	0.28
	17 <sup>th</sup>	L'Isle	0.07
	18 <sup>th</sup>	Maintenon	1.85

**Table 3.** Quantification of silver, gold and mercury in gilt leathers attributed to two well-known manufacturers.

Manufacturer	Provenance	Date	Reference	Ag (%)	Au (%)	Hg (%)
André Reynier	France	1670	AIX2	99.874	0.119	0.007
		17 <sup>th</sup>	CBD7	99.938	0.053	0.009
		17 <sup>th</sup>	AIX1	99.921	0.052	0.027
Agostino Nespola	Italy	ca. 1670	AR5	99.963	0.037	0
		ca. 1670	AR6	99.977	0.009	0.014
		ca. 1670	AR11	99.943	0.057	0
		17 <sup>th</sup>	AR3	99.912	0.073	0.015

lead content, raised by Talland as a provenance marker, was compared in the 58 decors, but our results did not display a higher lead content in gilt leathers from the Netherlands, nor a correlation between the lead content and the geographical origin of the decors (Table 2). In gilt leather decors, lead can be encountered in leather (Table 1), in varnish or in polychromy, and is related to the use of lead based products, either as dryers for the “gold varnish” [3,5] or pigments in the polychromy. For that reason, it is not possible to rely on the lead content to make attribution.

Although copper was also suggested in previous study as a possible marker of provenance [8,9], it was often detected by PIXE in areas where silver was not present (eg. leather only areas), therefore this element was also discarded. Thus, among all the chemical elements identified in the decors (see an example in Table 1), we focused on the two elements that seemed to be present concurrently with silver in most of the samples: gold and mercury.

Several hypotheses can explain the presence of gold and/or mercury in the silver leaves. One concerns the silver extraction process, as mercury amalgam was used to recover the gold usually present in the same ores. Another explanation can be found in ancient French regulation texts stating that the use of “sublimé corrosif”, corresponding to mercury (II) chloride (HgCl<sub>2</sub>), was authorized in beating workshops to pack silver bar [16]. Following the decor manufacture, other sources can possibly explain the presence of mercury in the silver leaves. In decors containing vermilion pigment (HgS), traces of pigment particle may have detached, contaminating the surface in other areas. In this case, it would be detected on the beam path, but would not be incorporated to the silver leaf. Also, mercury vapor either emitted from the vermilion [17] or present in the atmosphere can form amalgam with the silver [18]. In our case, this hypothesis appears less likely since the varnish at the surface of the silver was shown to acts as a protective barrier towards the pollutants in the atmosphere [19]. Finally, adding some gold during the preparation of silver leaves was known to improve their mechanical qualities. Indeed, the formation of an Ag-Au alloy is more favorable because of the partial charge transfer from Au atoms to Ag

atoms, providing significant electrostatic stabilization. The consequence is that adding gold in silver increase the ductility of the material, making the silver leaf manufacturing process easier than with pure silver [20].

Silver, gold and mercury were quantified in the silver leaves for all the objects. In the ancient gilt leather corpus, 84 % contained gold, 62 % contained both gold and mercury and only 6 % contained neither of these two elements. As a comparison, all three modern silver leaves contained gold but no mercury.

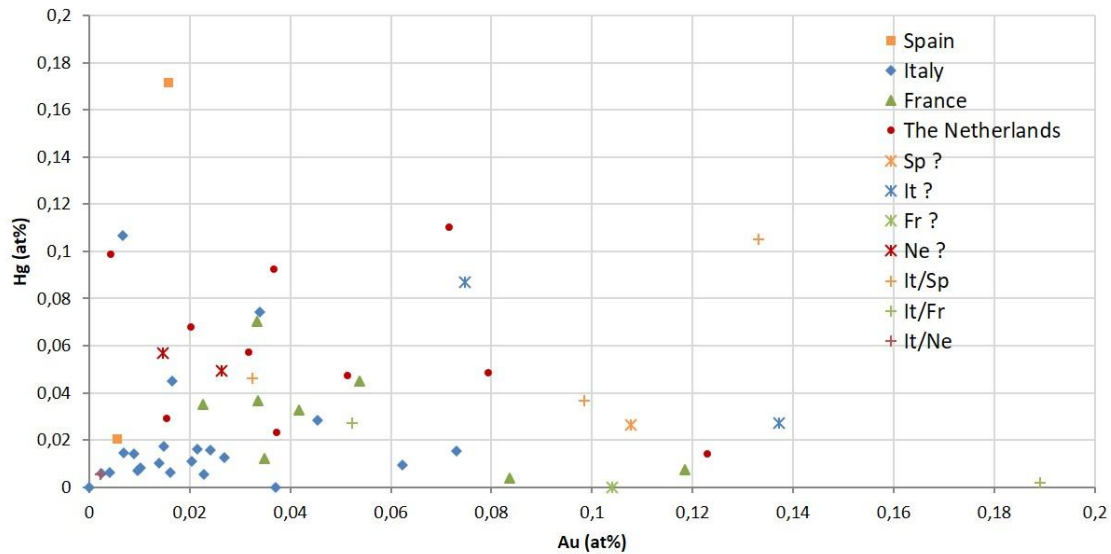
The quantification of the three elements in gilt leathers attributed to two well-known manufacturers, André Reynier and Agostino Nespola are presented in Table 3, but it showed no clear correlation. Very high mercury contents were found in some decors containing mercury based pigments (from few at% up to 15 at% in one decor) although the analysis was performed far from the polychromy.

The gold and mercury contents were plotted for all the gilt leather samples according to the decor firm or hypothetic provenance, with the exception of the 4 decors containing more than 0.2 at% Hg or Au (Figure 2). Although no direct correlation could be established, it seems that decors coming from Italy present in average very low gold and mercury contents compared to the other decors (Figure 2). This hypothesis would need to be confirmed by increasing the number of decor analyzed and by increasing the Spanish decor representation. If the hypothesis was verified, it could lift the uncertainty for the decors where Italy provenance was suggested.

### 3.2. Analysis of the thickness of silver leaves

#### 3.2.1. Model samples

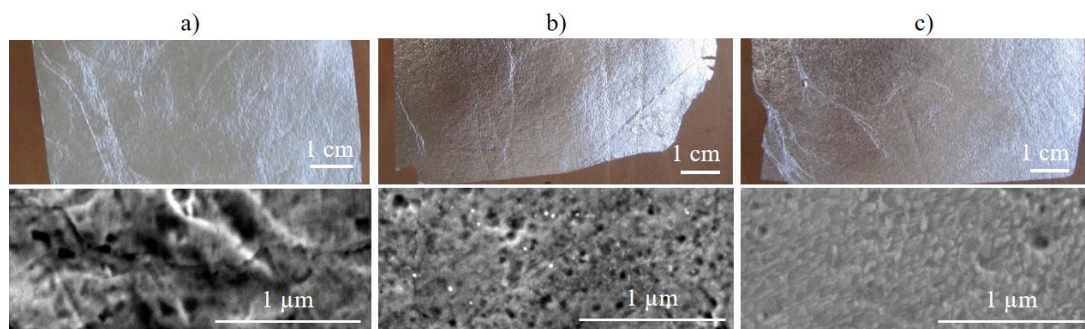
The methodology of RBS analyses was implemented first using the mockups in order to assess the impact of the leaf characteristics and preparation. For the modern leaves, the thickness of the leaf could be estimated thanks to the information given by the supplier or determined from its weight. In the case of Dauvet, one leaf composed mostly of silver weighted 0.015 g and measured 80 × 80 mm, therefore the calculated thickness was 223 nm. These values were then compared with the thickness estimated from RBS



**Figure 2.** Elemental composition calculated from PIXE analyses for ancient gilt leathers from the corpus presented according to their country of attribution. The percentages are calculated considering only the presence of mercury and gold together with silver. The values indicated with “?” or “/” correspond to undefined provenance respectively attributed with no certainty to one country or with hesitation between two countries (Sp = Spain; It = Italy; Fr = France; Ne = The Netherlands).

measurements of the silver leaf deposited on a glass slide. In the case of Dauvet leaves, the thickness estimated over five measurements ranged from 193 nm to 219 nm and the average value was  $207 \pm 26$  nm. The uncertainty of 0.6 % due to the instrument and the data process of RBS analyses at the AGLAE facility is negligible next to the one due to the roughness of the sample surface, therefore only the later one will be expressed next to the thickness values in this paper. Indeed, the roughness of the surface induces a change in the profile of the RBS spectrum, increasing as a result the uncertainty of the analysis (the details about this question can be found elsewhere [15]). This parameter might then be a factor playing a role in the variability of the thickness measurements. All the silver leaves analyzed by RBS displayed a variability in thicknesses more or less important over a single leaf or area. Surface roughness and silver

corrosion might have a role to play in this variability [21], however another factor should be considered, the presence of microporosities greatly smaller than the beam size in the metallic layer. Considering that the RBS spectrum obtained is an average of the materials encountered by the beam in each layer, if microporosities are present, the intensity of the peaks coming from the elements present in this layer will decrease, therefore reducing the calculated thickness. In an attempt to examine this question, the silver leaf surfaces were analysed by SEM-FEG, and the technique revealed the presence of microporosities in different proportions: 10.2 % of the surface occupied by microporosities for Dauvet leaves (probably combined to a significant roughness according to the SEM-FEG image), 2.0 % for Manetti leaves and 0.4 % for Berta leaves (Figure 3). The manufacturing process of the leaves (pneumatic beating for Dauvet and



**Figure 3.** Photographs of modern silver leaves (top) from a) Dauvet, b) Manetti and c) Berta, and corresponding SEM-FEG images (bottom).

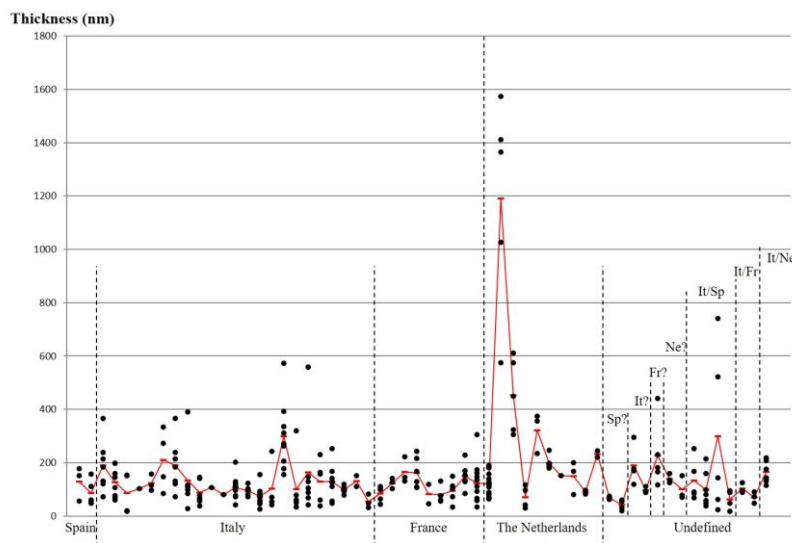
Manetti, hand beating for Berta) and the corrosion might affect the leaf properties and its surface appearance. At this stage, it is difficult to establish a direct correlation between the presence of these microporosities and the variability in the thickness measurements, as suggested by Ager [11], however more samples should be systematically observed by SEM and analyzed by RBS to examine this hypothesis. In relation to the manufacturing of gilt leather, the influence of different factors on the measurements was assessed: the nature of the supporting material, the leaf overlap that can occur when the leaf is deposited on the leather, and the burnishing step. A leaf from Dauvet was folded in two on a glass slide and its thickness was estimated by RBS measurement to be  $220 \pm 50$  nm in the single leaf area and  $415 \pm 50$  nm in the folded area. When the same leaf was glued on leather and analyzed by RBS, its thickness was estimated at  $222 \pm 44$  nm in an unburnished area, but decreased to  $170 \text{ nm} \pm 45$  nm in the burnished area. From these results, it can be concluded that the supporting material has no influence on the thickness measurement. The mechanical action from the burnishing, however, seems to modify the thickness value calculated by the software, and this is an important parameter to bear in mind for the data interpretation. This effect might be explained by the slimming of the leaf or the increase of the size or the number of microporosities. Although this has not been assessed here, we may expect the thickness value calculated to vary depending on the burnishing method used or the person doing the burnishing. The influence of this factor will be investigated in the future as part of another project.

### 3.2.2. Ancient gilt leather

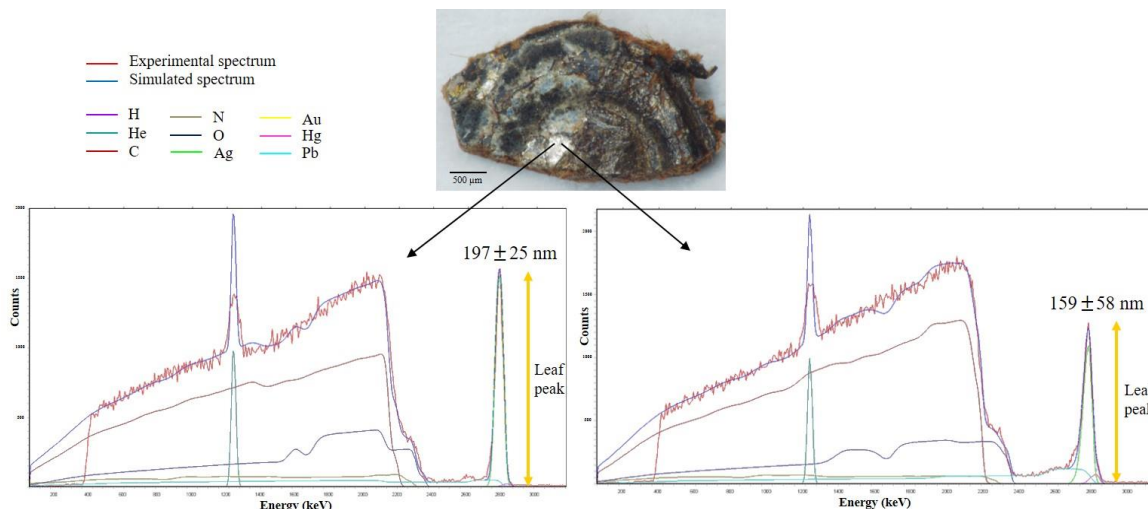
The thicknesses values calculated over all the ancient samples analyzed spread from 19 to 1574 nm, but most of the values are centered around 100 nm (Figure 4).

For several decors, the variability in thickness values within a single sample was very high, even in a same area (Figure 5). Different factors could explain this scattering in the thickness values. As mentioned earlier, intrinsic factors linked to the silver leaf properties, such as the leaf roughness, porosity or homogeneity in the beating can induce variable values, as well as the manufacturing of the decor, and in particular the silver leaf laying and the burnishing.

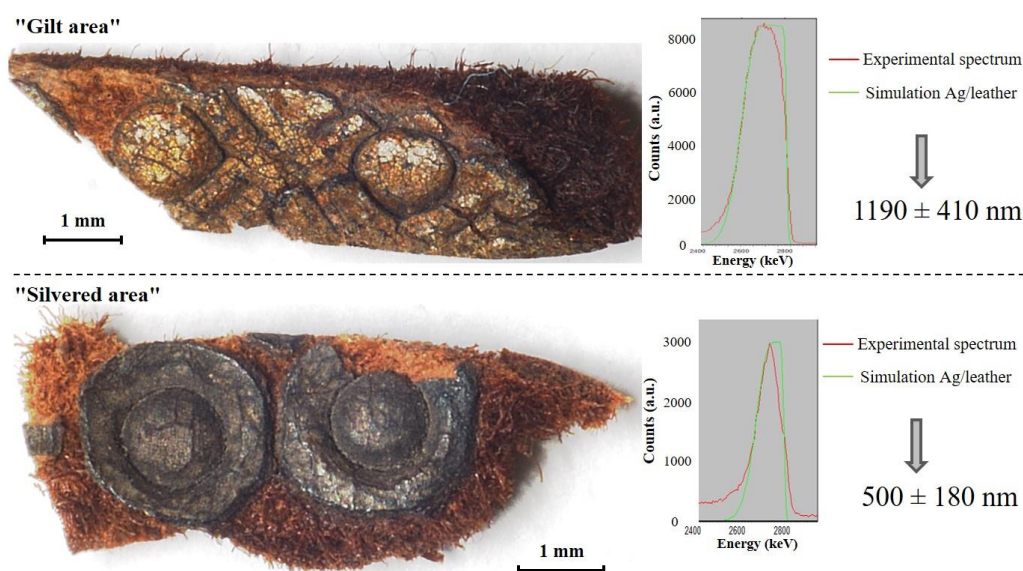
The high thickness values might represent a superposition or folding of silver leaves in the object, nevertheless this would appear as isolated values when several measurements are carried out. The low thickness values might result from the effect of different factors or combination of these factors that are the presence and the ratio of microporosities and the burnishing step, but also factors associated with the life of the object. In ancient gilt leather decors, the corrosion of the silver by endogenous or exogenous compounds could reduce the thickness and increase the surface roughness, and mechanical action like cleaning may cause abrasion of the leaves resulting in the removal of materials from the object surface [19]. A good illustration is provided by the measurements made on samples of the “gilt” and “silvered” areas from the “Battle of Gelboé” gilt leather wall hanging belonging to the musée national de la Renaissance in



**Figure 4.** Thicknesses calculated from RBS analyses for the corpus of ancient gilt leathers presented chronologically and according to their country of provenance. The values indicated with “?” or “/” correspond to undefined provenance (Sp = Spain; It = Italy; Fr = France; Ne = The Netherlands). In each column the black dots represent the different measurements for one single sample, and the red dash shows the average of thickness for each sample. The thin red line links all the average values.



**Figure 5.** Simulation (blue curve) on two RBS spectra (red curve) collected from the same area in the sample (REG1.3, made in Italy, 16<sup>th</sup> c.), giving leaf thicknesses (peak on the right of each spectrum) at  $197 \pm 25$  nm and  $159 \pm 58$  nm.



**Figure 6.** Thicknesses of silver leaves calculated using the simulation of a silver leaf glued on leather on the RBS spectra collected on two different samples of the “Battle of Gelboé” gilt leather wall hanging (made in The Netherlands, 17<sup>th</sup> c., exhibited in the musée national de la Renaissance, Ecoeu, France), one from a “gilt area” (GEL9-top) and the other from a “silvered area” (GEL10-bottom).

France (Figure 6). Silvered areas are often most exposed to both factors as they were only covered with a thin organic protective layer. Thus, the reduced thickness observed in the silvered area might originate from the silver corrosion and/or abrasion from repetitive cleaning. The manufacturing and conservation treatment can have an impact on the corrosion of silver in gilt leathers [19] therefore this evolution should also be considered when assessing the thickness of silver leaves. Despite all the variation observed in the values, the average thicknesses of silver leaves in ancient gilt leathers coming from The

Netherlands are greater than the ones from the other countries (Figure 4). No tendency was observed between the thicknesses and the date of manufacture of the objects. All these results stress the necessity to expand the corpus by increasing the number of gilt leather decors analyzed, so that firmer conclusions could be drawn.

#### 4. Conclusion

This project is the first study aiming at obtaining a fine measurement of the composition and the thickness of silver leaves on a large corpus of gilt leather



decorations. The methodology implemented, with PIXE and RBS analyses, is adapted to the specificity of silver leaves and of these objects, as sampling, when permitted, might locally change the thickness of these thin metal leaves. However, the composite nature of this kind of artefact with the presence of different organic materials makes the analysis of the silver leaves and the interpretation of the data complex. For that reason, only chemical elements solely associated with the metallic leaf, that is silver, gold and mercury were considered although multiple elements were identified by PIXE analyses. The observation seems to indicate that the silver leaf in the decors from Italy are generally characterized by a low gold and mercury content, but this has to be confirmed by expanding the corpus. Regarding the thicknesses calculated from RBS analyses, the data seemed to show that silver leaves from the Netherlands are thicker than the ones from Spain, Italy or France. An important variability was seen in the thickness values, even for modern leaves coming from the same book, which can be due to different factors: surface roughness, microporosities, mechanical actions during manufacturing or cleaning, and silver corrosion. For the two former ones, an instrumental development implemented during this project, RBS cartography, will help calculating an average of the thickness of the leaf on a large surface, reducing the impact of these factors or visualizing leaf heterogeneity or overlap.

This study allowed an assessment of the sensitivity of the analytical techniques used and showed the variability of the chemical composition and the thickness of the silver leaves in gilt leather decors, which are related to several factors linked to the materials, the manufacturing or the life of the objects.

In the future, the corpus analyzed will be expanded to confirm the different hypotheses raised by the composition and the thickness measurements. In parallel, archives should also be studied to know if workshops always used local silver leaves or if they might have come from a different geographical area. Beyond the silver leaf, we should continue to increase our knowledge on the other materials present in gilt leathers so that all the information could be combined and may reveal clearer trend in the provenance attribution.

#### Acknowledgements

This study was performed under the scope of the CORDOBA project, funded by the Fondation des Sciences du Patrimoine (LabEx PATRIMA), and as part of the New AGLAE project (grant ANR-10-EQPX-22). The authors are grateful to Eric Laval for the SEM-FEG analyses at C2RMF, to Mariabianca Paris and Marcella Ioele (ISCR Roma) and to all the owners of the collections for providing the samples of

gilt leathers.

#### References

- [1] E.F. Koldeweij, "Gilt Leather, An Important Craft and a Little Known Luxury", *The European Fine Art Fair Handbook*, Maastricht, 10-18 March 1990, pp.146-151.
- [2] C.Bonnot-Diconne, *Method of Use and Importance of Gilt Leather in Three Italian Palaces during the 16th and the 17th Century through the Study of Inventories*, ICOM-CC Interim Meeting of the Leather Working Group, Offenbach, 28-29 août 2012, pp.15-22.
- [3] A. Schulze, *Goldleder zwischen 1500 und 1800 – Herstellung und Erhaltung*, Arbeitsheft 17 des Landesamtes für Denkmalpflege Sachsen, Dresden : Ed. Sax-Verlag, 2011.
- [4] J.P. Fournet, *Les cuirs dorés anciens en France*, Mémoire de Recherche approfondie, PhD thesis, Ecole du Louvre, Paris, 2004.
- [5] A.D. Fougeroux de Bondaroy, *L'art de travailler les cuirs dorés et argentés*, Description des arts et métiers, Paris: Guérin et Delatour, 1762, 42pp.
- [6] M. Blet-Lemarquand, S. Nieto-Pelletier, G. Sarah, *L'or et l'argent monnayés*, Circulation et provenance des matériaux dans les sociétés anciennes, ed. des archives contemporaines, 2014, pp.133-159.
- [7] M.F. Guerra, *La circulation des objets en or*, Circulation et provenance des matériaux dans les sociétés anciennes, ed. des archives contemporaines, 2014, pp.161-173.
- [8] V. Talland, C.M. Tsu, D. Fullick, B. Mangum, *The Conservation of Leather Wallhangings at the Isabella Stewart Gardner Museum*, ICOM-CC Interim Meeting on the Conservation of Gilt Leather, Bruxelles, 25-27 March 1998.
- [9] C. Bonnot-Diconne, L. Robinet, C. Pacheco, M. Iole, M. Paris, *Multi-technique analysis of gilt-leather wall coverings (16<sup>th</sup>-18<sup>th</sup> centuries)*, ICOM-CC 17<sup>th</sup> Triennial Conference Preprints, Melbourne, 15-19 September 2014, ed. J. Bridgland, art. 0701, Paris: International Council of Museums (ISBN 978-92-9012-410-8), 2014, 8pp.
- [10] L.C. Feldman, J.W. Mayer, *Fundamentals of surface and thin film analysis*, North-Holland, Elsevier Science Publishing Co., Inc, 1986, 354pp.
- [11] F.J. Ager, M. Ferreti, M.L. Grilli, D. Juanes, I. Ortega-Feliu, M.A. Respaldiza, C. Roldan, S. Scrivano, *Reconsidering the accuracy of X-ray fluorescence and ion beam based methods when used to measure the thickness of ancient gildings*, Spectroc. Acta B 135, 2017, pp.42-47.
- [12] L. Pichon, B. Moignard, Q. Lemasson, C.

- Pacheco, P. Walter, Development of a multi-detector and a systematic imaging system on the AGLAE external beam, *Nucl. Instr. and Meth. in Phys. Res. B.* 318, 2014, pp.27-31.
- [13] J.L. Campbell, N.I. Boyd, N. Grassi, P. Bonnicks, J.A. Maxwell, The Guelph PIXE software package IV, *Nucl. Instr. and Meth. in Phys. Res. B* 268, 2010, pp.3356-3363.
- [14] L. Pichon, Q. Lemasson, B. Moignard, C. Pacheco, Programs for visualization, handling and quantification of PIXE maps at the AGLAE facility, *Nucl. Instr. and Meth. in Phys. Res. B* 363, 2015, pp.48-54.
- [15] M. Radepon, L. Pichon, Q. Lemasson, B. Moignard, C. Pacheco, Towards a sharpest interpretation of analytical results assessing the uncertainty of PIXE/RBS data at the AGLAE facility, *Measurement* 114, 2018, pp.501-507.
- [16] Arrêté de jurisprudence sur la réglementation des batteurs français, Paris, 1776.
- [17] D. Strahan, M. Tsukada, Measuring mercury emissions from cinnabar lacquer objects, *Stud. Conserv.* 61, 2016, pp.166-172.
- [18] R. Nowakowski, J. Pielaszek, R. Dus, Surface mediated Ag-Hg alloy formation under ambient and vacuum conditions - AFM and XRD investigations, *Appl. Surf. Sci.* 199, 2002, pp.40-51.
- [19] M. Radepon, C. Bonnot-Diconne, L. Robinet, S. Thao, C. Pacheco, M. Bouttemy, E. Delbos, The impact of manufacturing and conservation on silver leaf tarnishing in gilt leather, *ICOM-CC 18<sup>th</sup> Triennial Conference Preprints*, Copenhagen, ed. J.Bridgland, art. 0603. Paris: International Council of Museums, 4-8 September 2017.
- [20] H.M. Lee, M. Ge, B.R. Sahu, P. Tarakeshwar, K.S. Kim, Geometrical and electronic structures of gold, silver, and gold-silver binary clusters: origins of ductility of gold and gold-silver alloy formation, *J. Phys. Chem. B* 107, 2003, pp.9994-10005.
- [21] Q. Wu, K. Soppa, N. Sherrer, B. Watts, T. Yokosawa, L. Bernard, T. Araki, M. Döbeli, M. Meyer, E. Spiecker, R.H. Fink, Investigation of the foil structure and corrosion mechanisms of modern Zwischgold using advanced analysis techniques, *J. Cult. Herit.* 31, 2018, pp.122-132.