

Fabrication of a suit of armour at the end of Middle Ages: an extensive archaeometallurgical characterization of the armour of Laval

Emilie Bérard, Philippe Dillmann, Olivier Renaudeau, Catherine Verna, Valérie Toureille

▶ To cite this version:

Emilie Bérard, Philippe Dillmann, Olivier Renaudeau, Catherine Verna, Valérie Toureille. Fabrication of a suit of armour at the end of Middle Ages: an extensive archaeometallurgical characterization of the armour of Laval. Journal of Cultural Heritage, 2022, 53, pp.88-99. 10.1016/j.culher.2021.11.008. hal-03599699

HAL Id: hal-03599699

https://hal.science/hal-03599699

Submitted on 24 Dec 2022

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.

Fabrication of a suit of armour at the end of Middle Ages: an extensive archaeometallurgical characterization of the armour of Laval

Emilie Bérard^{a*}, Philippe Dillmann^a, Olivier Renaudeau^b, Catherine Verna^c, Valérie Toureille^d

- a : LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France.
- b : Musée de l'Armée, Hôtel national des Invalides, 129, rue de Grenelle, 75007 Paris, France
- c : ArScAn UMR 7041, Université Paris 8 Vincennes-Saint-Denis, 2 Rue de la Liberté, 93526 Saint-Denis Cedex, France
- d : Héritages : Culture/s, Patrimoine/s, Création/s UMR 9022, CY Cergy Paris Université, 33 Boulevard du Port, 95011 Cergy-Pontoise Cedex, France
- * corresponding author : e-mail: e.berard75@laposte.net

Abstract

This study focuses on the extensive archaeometallurgical characterization of a suit of an exceptional armour belonging to the "Musée du Vieux-Château" in Laval (France). Except for the helmet, its morphological features correspond to a rare Italian-style equipment dated from the 15thcentury. However, its exact origin is unknown. Metallurgical investigations made on a set of samples revealed that the armour was made of various ferrous alloys, submitted to different heat treatments. Particular craftsmanship has been implemented on some elements of the armour such as the backplate involving both quenching to harden the metal and the use of a "banded steel", combining several sheets of metal with different properties, which could have been achieved to provide better defensive properties. These results were combined with a thorough provenance analysis of the metal by considering the composition of Slag Inclusions (SI), revealing three different metal supply sources for the different pieces of the suit. Two defences were made of a metal whose chemical signature is compatible with the Italian Alps while three others have a common chemical signature, compatible with another group of Italian-style defences, already studied. The provenance study reinforces the hypothesis of a link between several parts of the armour. More broadly, the results give new insight in the fabrication of Italian-fashion suit of armour and provide crucial data for establishing the chemical signature of metal supplies employed by the armourers' workshops.

Keywords: Archaeometallurgy, armour, ferrous alloys, provenance study, Middle Ages

1. Introduction

At the end of Middle Ages, armour was still essential to war practices which gave it a prominent place in the fighting. The best protection was a complete suit of armour [1–3]. While the adjustment of the armour to its wearer was crucial to guarantee its protection, other aspects, especially metallurgical ones, were also of paramount importance. Indeed, the nature and heat treatment of the metal played a key role on its mechanical properties, and thus on the effectiveness of an armour.

Written sources give valuable information regarding the workshops organisation [4–6], however they often remain silent on the ancient technical skills or choices made by the armorers when making such pieces. Archaeometallurgical studies can provide crucial information on these issues. Investigations were already made on single pieces of European armours dated from the Middle Ages and the Modern Period for several decades [7,8,17,9–16], mostly on isolated pieces as homogenous complete armour is rare [18]. That being said, some studies were performed on complete suits of armour [7,9,14,15] but very few on suits of armour dated from the 15th century due to the scarcity of pieces from this period.

Another interesting aspect, not covered previously on suit of armour, relies on the origin of the metal used. Ancient processes and especially the bloomery process for transforming ore into metal have been thoroughly studied. It has been demonstrated that the chemical signature of a production area can be characterized by the chemical composition of the ore and slag, this latter found as waste at the production site. A small part of this slag remains entrapped in the metal in the form of non-metallic inclusion called "Slag Inclusion", still carrying the chemical signature of the production area [19,20]. Thus, by studying the chemical composition of SI both in major [21–23] and lithophile trace elements [24–29], it is possible to investigate the provenance of ferrous alloys. This approach has been recently tailored to the particularly small SIs found in armour [30] allowing henceforth to shed light on the choices made by the armourers with regards to raw supplies.

The study focuses on the investigation of a composite horseman armour (see Figure 1) belonging to the "Musée du Vieux-Château" (Laval, France), and currently on display at the "Musée de l'Auditoire" (Sainte-Suzanne, France). The armour is associated with the siege imposed on the fortress of Sainte-Susanne in 1425 by Salisbury however its origin is unknown [31]. The armour was restored and reassembled at the Musée de l'Armée in 2005-2006 to improve its overall consistency, although it is likely to be composed from parts that did not belong together originally and some of the elements like the upper plate of the breastplate are unfortunately missing. Morphological features of the helmet refer to a defence dated from the first half of the 14th century while the other parts seems rather to correspond to an equipment dated around 1440, slightly posterior to the siege [31]. Nevertheless, the armour of Laval constitutes a valuable and rare defensive equipment of the end of Middle Ages. Furthermore, if the piece did not bear any recognizable mark of a workshop, its style could be related to an Italian and possibly a Milanese production [31]. However, during the Middle Ages, the style of famous production centres (such as the one of Milanese armour), was deliberately imitated in other European armourer centres, highlighting a renowned production technique or a particular shape of the piece [32]. Hence, the armour of Laval could also be an imitation of Italian production or made by Italian armourers established outside of northern Italy. Indeed, armorers from Lombardy, were strongly encouraged to come to settle in other centres, such as in Tours at the instigation of Charles VII, to develop the arms production during the 15th century [33,34]. Ambroise de Loré, a prestigious captain of Charles VII, defended the fortress of Sainte-Suzanne [35]. It seems likely that he may have found supplies of arms and armour in Tours. Consequently, in the absence of written sources on the history of the armour of Laval, the question of its origin remains.

2. Research aim

Although incomplete and at least partly composite, according to its morphological features the armour of Laval is one of the rare evidences of the 15th century defensive equipment preserved in France. However, there is no historical data or workshop mark to specify its origin and manufacturing

process. Thus, our objective was to study both the nature and the chemical signature of the metal to provide new information regarding the consistency of this artefact as a whole and expand our knowledge of the history of 15th century armour making. Specifically, the study presents first the results of metallographic analyses and hardness measurement on a broad set of samples aimed to give insight into the quality of the material used. It, then, combines these results with a thorough provenance analysis, of the metal involving the quantification of trace elements in SI.

3. Material and methods

Eleven samples were taken (see Figure 1), at least one on each defence, with a diamond-coated blade using a rotary cutting tool and avoiding applying the cutting wheel with excessive force or during long passes while checking that no colour change of the metal was visible to prevent overheating the metal. Sampling size and location were decided to best preserve the integrity of the armour while ensuring the representativeness of the results. Thus, the most damaged places have been avoided and sample size was fixed about 7mm long and 3mm wide, the thickness of the sample corresponding to the thickness of the armour plate. On the backplate made in three parts (two lateral plates covering the flanks, and a central one), three different samples were collected.

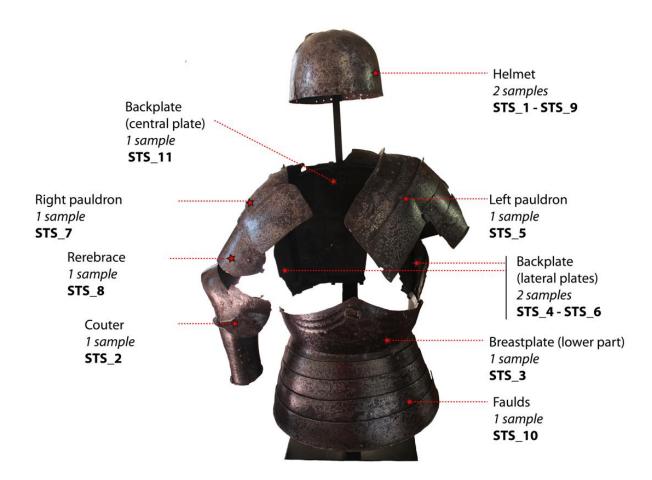


Figure 1 – Armour of Laval, number of samples and elements of the armour sampled

3.1. Metallographic analysis

Samples were mounted in cross section in epoxy resin and polished using SiC abrasive papers (grade 180-4000), followed by a final polishing using Struers diamond polishing medium 3 μ m and 1 μ m. Then, metallographic etching with Nital 3% and Oberhoffer's reagent were performed, to reveal possible welding lines, carbon and phosphorus contents. Microstructures were studied by using an OLYMPUS optical microscope (model BX51). Carbon content was evaluated by image analysis using Adobe Photoshop and Adobe Illustrator, excluding quenched structures where this parameter can't be accurately estimated by metallography. An average carbon content weighted by the surface (\bar{X} , see Eq.1) and its relative standard deviation (σ , see Eq.2) were calculated following the protocol proposed by Pagès et al., and completed by Leroy et al., [36,37].

$$\bar{X} = \sum_{i=1}^{n} Wi \times xi$$
 (Eq.1)

$$\sigma = \sqrt{\sum_{i=1}^{n} Wi \times (xi - \bar{X})^2} \text{ (Eq.2)}$$

Where Wi is the proportion assigned to each of the carbon rate groups on the sample surface and xi the mean value of each carbon rate groups (0.02 < wt%C < 0.1, 0.1 < wt%C < 0.3, 0.3 < wt%C < 0.5, 0.5 < wt%C < 0.7). To describe the carbon content heterogeneity four categories were defined: very homogeneous (σ = 0), homogeneous (σ between 0 and 0.1), slightly heterogeneous (σ between 0.1 and 0.2) and heterogeneous (σ above than 0.2).

Depending of the their content and size, SI are likely to weaken the microstructure locally and consequently influence the mechanical behaviour [38]. The amount of SI (PI) in the metal is then an important parameter linked to the quality of the metal. It was estimated by quantifying the surface fraction of SI on micrograph of the entire sample before etching using Adobe Photoshop. Following the method developed by L'Héritier et al., [39] (see Eq.3), the relative error of the calculation was estimated to be lower than 20%.

$$PI = \frac{S_i}{S_{tot}}$$
 (Eq.3)

Where S_i is the proportion of SIs, S_{tot} the total surface of the sample.

Vickers microhardness analyses were performed using a tester (BUEHLER VH3300 model) load 200 g during 10 sec, unless otherwise specified. Profiles of at least 10 measurements were made on each sample. An average (Hv_{mean}), and the standard deviation (Hv_{sd}) were calculated.

WDS measurement were also conducted on the metallic part (SX 100 CAMECA, accelerating voltage 15kV, current probe about 200nA at ICMPE lab, Thiais, France), to confirm the presence of phosphorus and other minor elements (As, Si, Mn, Co, Ni, Cr, Cu).

3.2. Slag Inclusions analysis

After a repolishing of the sample, the major compositions of the SI were estimated using Energy Dispersive Spectrometry (EDX with silicon drift detector - SDD) coupled to a Scanning Electron Microscope (SEM-FEG JEOL 7001-F). A probe current of about 8 nA and a 15 kV accelerating voltage were used. The protocol described in Bérard et al, [30] was followed to detect the SI by image

analysis using the software Aztec (Oxford company), and measure the compositions of each SI on the whole surface of the sample. Concentrations were estimated after normalization of the total signal (considered to be 100%), of the set of major elements known as major components of iron slags (O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Fe, Mn). Then, according to the procedure proposed by Dillmann and L'Héritier [19] and completed by Disser et al [40], only SI related to the smelting slag were selected. Those SI present constant "Non Reduced Coupounds" (NRCs) ratios (%K₂O/%CaO, %MgO/%Al₂O₃, %Al₂O₃/%SiO₂) [19], contrary to other inclusion families created by the use of fluxes during forging stages or by fragmentation of the SI. After identifying SI coming from the smelting, an average weighted major element content was calculated per artefact [19]. By considering the area of each SI, this transformation evaluates a "surface weighted average composition" of all the inclusions coming from an entire sample, hence facilitating the comparisons between the samples (see Eq.4).

$$\%E^* = \sum_{i=1}^{n} (\%E_i \times \frac{Si}{St})$$
 (Eq.4)

Where ${}^{\otimes}E^{*}$ the average weighted content for all the inclusions of an artefact coming from the smelting stage, ${}^{\otimes}E_{i}$ is the composition of a given inclusion, Si the surface of the inclusion analysed, St the sum of all the inclusion surfaces. Then, to avoid disturbance due to matrix effects (overrepresentation of Fe), a sub compositional ratio was calculated for each oxide [40] according to the following formula (see Eq.5).

$$\%E^{**} = \frac{100 \times \%E^*}{100 - FeO^*}$$
 (Eq.5)

After checking that the identified SI families have a composition compatible with the bloomery process (see Supplementary Information)[19,40], a dozen of SI per cross section were selected to be analysed by LA-ICP-MS. Analyses were performed at the Centre Ernest- Babelon-IRAMAT (Orleans, France) with a sector field ICP-MS Element XR (Thermo Scientific) coupled to an excimer laser (ArF*, 193 nm, RESOlution S155-E, Resonetics). We followed the methodology described in Bérard et al. [30], proposed for the calculation of relative concentration of trace element in small slag inclusions (<30μm) commonly found in armour samples.

3.3. Methodology for identifying a provenance

Among the trace elements measured, only a restricted set could be quantified with an acceptable accuracy of measurement at the concentrations observed in the samples: Y, Nb, La, Ce, Nd, Sm, Eu, Yb, Hf, Th, U. This set of elements was selected to compare the chemical signatures between the samples using multivariate analyses. SIs that contain at least one of these elements below the quantification limit $(10 \times SD)$ have been excluded. To ensure scale-invariant representations of trace elements, a log-ratio data transformation already used for the purpose of ancient ferrous alloys provenance study [25,26] was applied (see Eq.6)

$$X_{E} = Log([E]) - \frac{1}{N} \sum_{k=1}^{N} Log([E_{k}])$$
 (Eq.6)

Where: X_E is the transformed value for each element, [E] is the measured element concentration and N = 11

To compare the trace element compositions, a multivariate approach implementing a Principal Component Analysis (PCA) [23,26] was used. To determine the provenance of the armour pieces

supposed to be of Italian manufacture, comparisons were made with two dataset: the ores and slags from the Lombard area studied by Leroy [41] and the group of Italian-style armour published in Bérard et al., [30] with the Italian Alps data. The dataset corresponding to the artefacts from Italian Alps and the one corresponding to SI in armour present different kind of material analysed (ores and slags versus SI) and size (a dozen of SI analyses for each armour sample, up to about fifty analyses of slags and ores for the Lombard area). Furthermore, the results of the PCA analysis may be dominated by the largest dataset (Lombard area). Consequently, it was decided to compare interpretations made with PCA with another approach [23,25,37]: Linear Discrimination Analysis (LDA). Contrary to PCA, this method is a supervised classification approach and has been used, in this study, to graphically maximize the separation between the groups. Calculation and graphs were made using R software and the "factoextra" and "MASS" libraries for the implementation of the PCA and LDA methods.

4. Results

4.1. Nature of the metal

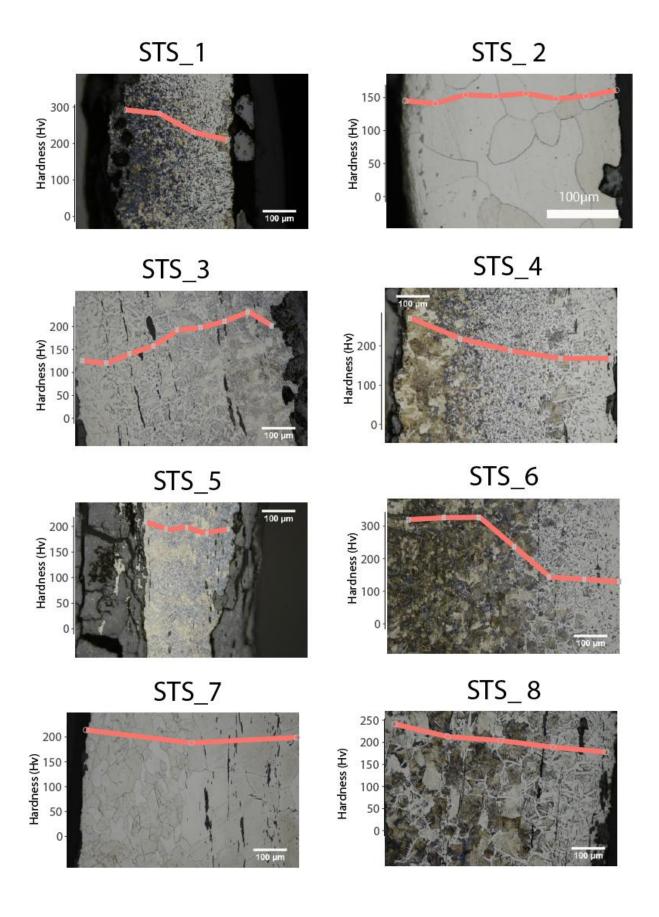
The microstructures of the samples studied are presented on Figure 2, a summary of the results is presented on Table 1. The different pieces of the armour present various metallurgical microstructures. Samples STS_1 (helmet), STS_3 (breastplate), STS_4 (backplate), STS_5 (left pauldron), STS_6 (backplate), STS_8 (rerebrace) present a ferrito-pearlitic steel structure with variable carbon contents. The pearlite, mostly spheroidized for sample STS_1, and partly spheroidized for samples STS_3 and STS_5 (Figure 3) shows that the metal was heated during an extended period of time around 700°C. Widmanstätten structures, appearing in medium carbon steel as a result of overheating the metal at high temperature (austenitic domain) followed by a fairly rapid cooling, were found on samples STS_1, STS_3, STS_4, STS_6, and STS_8.

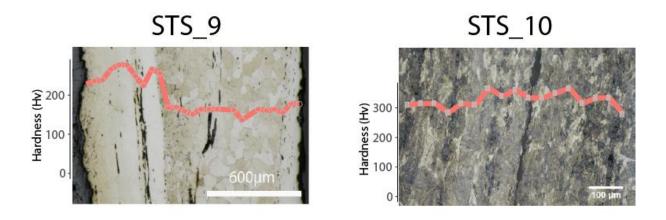
Samples STS_4 and STS_6 present similar microstructures, composed of two bands of different carbon content. The transition between the two areas is highlighted by a carbon gradient running from 0.8% to 0.1% and a clear drop in hardness. It could be a "randomly" arrangement of the initial heterogeneity of the bloom transformed into sheet. Another hypothesis is that a case carburisation has been made. Lastly, it could also be related to a voluntary welding made between two sheets of metal. Arguments in favour of the latter hypothesis are available in the Supplementary Information presenting the analyses of the compositions of the SI.

Table 1 - Main results of the metallographic investigation

Sample number	Defence	Microstructure	X	σ		PI (%)	Hv _{mean}	Hv _{sd}	Quench	Phosphoric iron
STS_1	Helmet	Ferrite and mostly spheroidized pearlite Widmanstätten structures	0.31	0.15	Slightly heterogeneous	0.2	261	47		
STS_2	Couter	Ferrite and carbides	0.06	0	Very homogeneous	1.8	148	10		
STS_3	Breastplate	Ferrite and partly spheroidized pearlite Widmanstätten structures	0.54	0.21	Heterogeneous	1.0	172	40		
STS_4	Backplate (lateral plate)	Ferrite and pearlite Widmanstätten	0.54	0.22	Heterogeneous	1.1	219	55		

		structures								
STS_5	Left pauldron	Ferrite and partly spheroidized pearlite	0.4	0	Very homogeneous	1.6	191	13		
STS_6	Backplate (lateral plate)	Ferrite and pearlite Widmanstätten structures	0.55	0.27	Heterogeneous	0.5	238	80		
STS_7	Right pauldron	Ferrite and carbides	0.06	0	Very homogeneous	1.5	198	13		
STS_8	Rerebrace	Ferrite and pearlite Widmanstätten structures	0.54	0.09	Homogeneous	1.8	203	24		
STS_9	Helmet	Ferrite and pearlite Ghost structures	0.06	0	Very homogeneous	1.5	222	48		x
STS_10	Faulds	Pearlite	0.8	0	Very homogeneous	0.6	327	26		
STS_11	Backplate (central plate)	Ferrite, pearlite, bainite and/or martensite	>0.3	-	-	0.6	390	109	х	





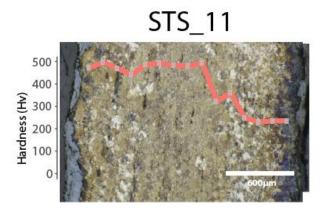


Figure 2 – « STS_1 », « STS_2 », « STS_3 », « STS_4 », « STS_5 », « STS_6 », « STS_7 », « STS_9 », « STS_10 », « STS_11 », microstructures observed and hardness profile (m=200g) observed after etching with Nital reactant 3%, « STS_9 » microstructure observed and hardness profile (m=20g) after etching with Oberhoffer reactant.

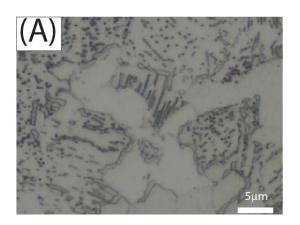
Sample STS_10 taken from the faulds, has a microstructure with a higher carbon content (around 0.8%), showing a distortion of grains. This suggests that the metal was not annealed to allow a grain recrystallisation after shaping the plate.

Samples STS_2 (couter) and STS_7 (right pauldron) show both a structure of ferrite with a few globular carbides. Given its mainly ferrite microstructure, the sample STS_7 presents a relatively high hardness (around 200 Hv for an expected value around 80). Unexpected high hardness of ferrite was also highlighted by other authors in armour samples [9,42]. In our case, it could be explained by the presence of hardening elements inside of the metal, however WDS measurements conducted revealed very low concentrations for the minor elements sought in the metal (%wt<0.1 for P As, Si, Mn, Co, Ni, Cr, Cu). Another hypothesis is that a quenching was made followed by an age-hardening (quench aging). Such heat treatment could lead to the formation of sub-micrometric hardening carbides [43–45]. However, it remains conjectural and will need to be confirmed by further research. The sample taken from the central plate of the backplate (STS_11) presents quenched structures (martensite and bainite) observed in the middle (Figure 3), while the extremities are composed of a ferrito-pearlitic microstructure. The interface between the bands is clearly marked on one side by a sharp drop in hardness from 450 to 300Hv. The precise mode of heat treatment leading to such heterogenous structure remain conjectural. It may be attributed to the heterogeneity in carbon content of the steel quenched [16,46].

Finally, the last sample STS_9 (helmet -) is classified as a phosphoric iron. The etching made with Oberhoffer's reagent revealed two main banded structures, one richer in phosphorus than the other

(see Figure 2). The separation between the two areas is showing by a net drop in hardness of about 250 to 150Hv, as well as a difference in grain size (>200 μ m in the phosphorus part and <100 μ m in the other part of the sample). At the extreme edge of the sample the hardness increases again, entering a new phosphorus-rich area.

Overall, the average hardness values range between 148 and 390Hv. The highest values were found on samples taken from the faulds (Hv= 327), showing a distortion of grain (STS_10) and from the central part of the backplate (Hv= 390), quenched (STS_11). The amount of SI (PI) in the metal is systematically below 2%, as it could be expected for artefacts highly manufactured as sheets [15].



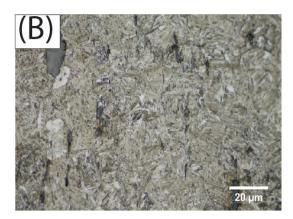


Figure 3 -« A » detail showing ferrite and partly spheroidized pearlite for sample STS_3, « B » detail showing martensite and/or bainite for sample STS_11

4.2. Metal provenance

Six samples (STS_3, STS_4, STS_6, STS_7, STS_8, STS_10) met the conditions necessary to identifying provenance based on a multivariate approach i.e., they were compatible with the bloomery process and had a sufficient number of slag inclusions that could be analyzed to perform a statistical analysis. For the other samples the reduction process is undetermined (STS_1, STS_2, STS_5) or trace element quantification was possible on a too low number of SI (\leq 3 SI for STS_9, STS_11).

Figure 4 summarizes the main results of the Principal Component Analysis made on the analysed SIs. Only the two first components, showing more than 90% of the variance are presented (other components are available in Supplementary Information. Three groups are distinguished. Samples STS_7 and STS_8 are isolated from each other and from the rest of the samples STS_3, STS_4, STS_6 and STS_10 taken respectively from the breastplate, the backplate and the faulds, and forming a cluster (despite some inclusions of STS_10 are out of this cluster).

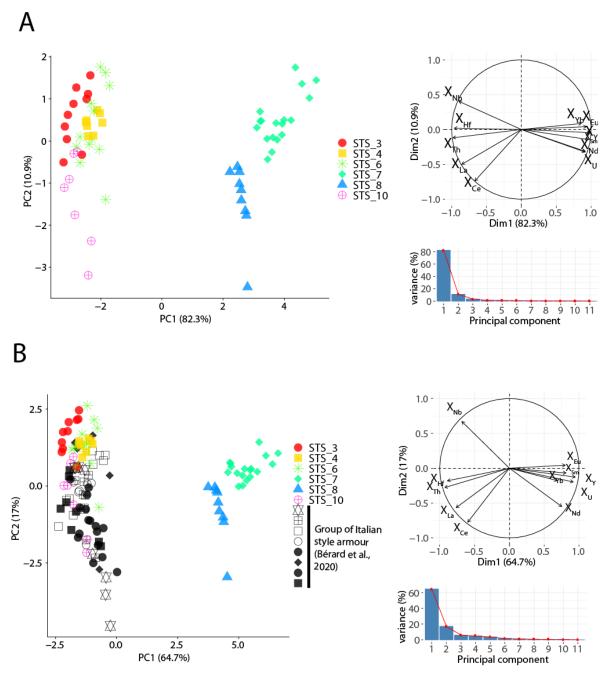


Figure 4 – "A": PCA carried out on the transformed data of SI projected onto PC1 and PC2, "B": PCA carried out on the transformed data of SI for the armour of Laval and the Italian armour samples projected onto PC1 and PC2

Then, we tested by PCA the compatibility of the chemical signature of the different pieces of armours with the Italian-style armour dataset analysed by Bérard et al. [30] (both data from the Laval armour and from Italian-styles armours are considered together in the PCA analysis). The chemical signature of samples STS_3, STS_4, STS_6 and STS_10 cannot be separated from the group of Italian armour on all the PCA projection planes (see Figure 6 and supplementary Information).

Slag and ores from the Lombard area as published by Leroy et al [41] are characterised by rich Ba (average: $4690 \mu g.g^{-1}$) and Mn (average: 5 wt%) contents. As shown on Figure 5, the composition of SI from the Laval armour samples shows comparable amounts for these two elements with the

Italian Alps. This is a first indication of chemical compatibility with this area which needs to be confirmed by comparing trace elements ratios.

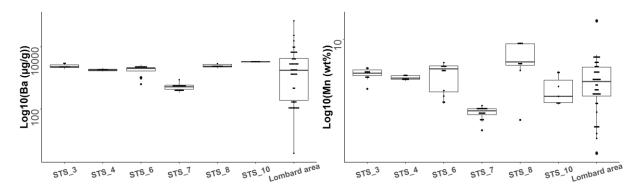


Figure 5 -Comparison of Ba and Mn contents of the SI originating from the Laval armour samples and from the Lombard area.

Following the same PCA approach the chemical signatures of the Laval armour samples have been compared with the Lombard area. As described in Bérard et al. [30], samples from the Lombard database present unfortunately one or several elements below detection limits. In order to avoid eliminating analyses bearing important information regarding the provenance, we chose to replace the non-quantified element by half their limit of detection. Figure 6 shows the projection of the PCA results on the two first components. The chemical signature of samples STS_7 and STS_8 are mixed with the Lombard area, while samples STS_3, STS_4, STS_6 and STS_10 are distinguished from the latter.

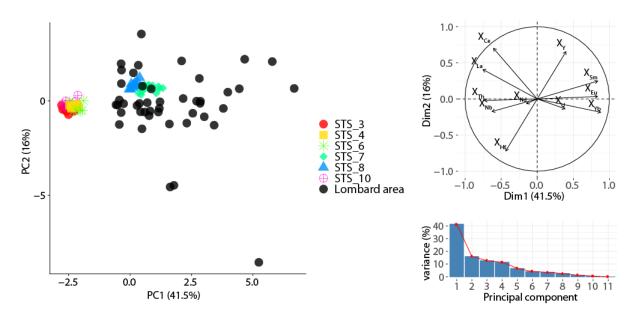


Figure 6 –PCA carried out on the transformed data of SI for the armour of Laval and the slags and ores from the Lombard area projected onto PC1 and PC2.

Consequently, the Lombard area may be considered as potential iron supplier for samples STS_8 and STS_7. To confirm this hypothesis, a PCA and LDA were carried out on the Lombard area and the samples STS_7, then STS_8 alone. Results on Figure 7 show that SI from samples STS_7 and STS_8 are compatible with the production area on all the PCA projection planes (see Figure 7 and

Supplementary Information). LDA confirms this result for sample STS_7. Despite LDA tends to maximize group separation, it is not possible to separate the data of the SI from the one of the Lombard area. Sample STS_8 remains relatively close, by comparison to those of samples already determined as being incompatible with the Lombard area, such as sample STS_10. Consequently, given the results of both PCA and LDA, the chemical compatibility of STS_8 with the Lombard area was considered as likely.

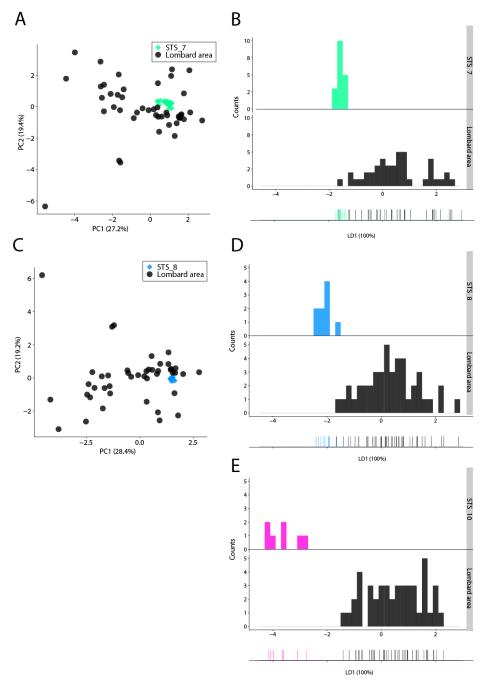
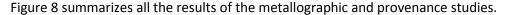


Figure 7 – "A": PCA carried out on the transformed data of SI for the sample STS_7 and the Lombard area projected onto PC1 and PC2; "B": LDA carried out on the transformed data of SI for the sample STS_7 and the Lombard area projected onto LD1; C": PCA carried out on the transformed data of SI for the sample STS_8 and the Lombard area projected onto PC1 and PC2; "D": LDA carried out on the transformed data of SI for the sample STS_8 and the Lombard area projected onto LD1; "E": LDA carried out on the transformed data of SI for the sample STS_10 and the Lombard area projected onto LD1

5. Discussion



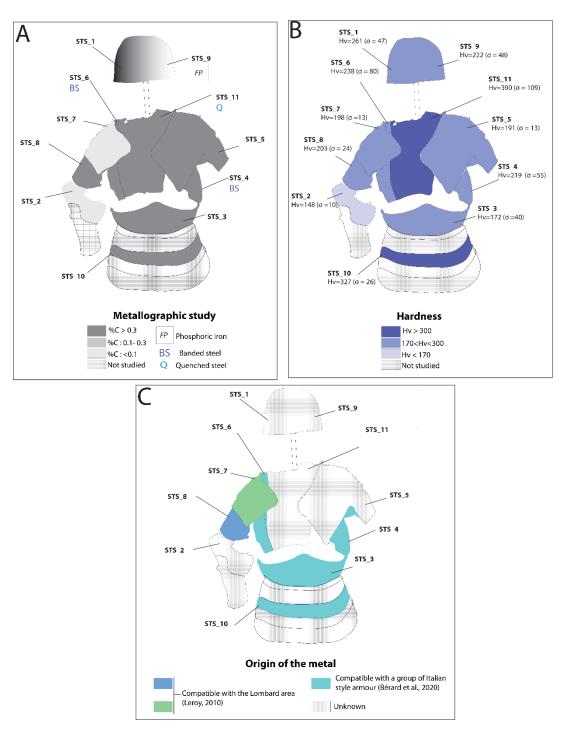


Figure 8 – Summary of the metallographic («A»), hardness («B») and provenance («C») results (ie., ore and slags from the Lombard area and SIs from Italian style armour pieces, see [30])

The helmet, which is supposed to be more ancient (14th century [31]) than the other parts of the armour given its morphological features, differs from the other elements, as it was made with phosphoric iron. However, the other sample taken (STS_1) on the same piece but at a different location do not show evidence of phosphorus. This suggests that the sheet of metal used to shape

the helmet was not necessarily homogeneous and may have been realized by combining several initial pieces of metal from different provenances welded together.

For the other pieces of the suit, all stylistically dated from the same period, all the samples are composed of carburized material (%C>0.2), except two defences (right pauldron and couter). The backplate of the armour have been forged with a particular craftsmanship. The two samples located on the lateral parts (samples STS_4 and STS_6) show a specific microstructure, combining two sheets of metal with different ductility called in this study a banded steel. Banded metal structures have already been identified in others studies focusing on metallographic examinations on armour plates [7,9,15]. They could be related to the heterogeneity of the semi product used to make the sheet. However, in our case, the carbon gradient running from 0.8% to 0.1% strongly suggests that a deliberate act has been made such as a case carburisation or welding two sheets of metal. This fabrication choice could have been made for technical reasons or for recycling purposes in the case of the welding [39,47]. Ideally, to improve the effectiveness of the armour, the metal should have combined two properties: being hard enough to deflect the cut of edged weapons and ductile enough to absorb the impact of projectiles weapons. Thus, this structure could be the result of a compromise made by the armourer between ductility and hardness. De Reuck et al., [48], had already highlighted this dilemma on breastplates made in the 17th century constituted of several "thin sheets of wrought iron, kept separate but forged together" to protect against firearms. Others mentions in written sources dated from the end of Middle Ages could refer to layered metal structures. The armorers regulations in Nuremberg specified that the armour should be made from "not less than half-steel material" ("nicht anders denn von halb stählernem Zeug")[49]. Although further studies must be conducted to conclude, it is possible that this "half-steel material" corresponds to a particular product, composed of a mixture of iron and steel, used for armour making. Another, term "harnoys complet souldé" ("complete welded harness") was noted by several authors [33,50,51]. The interpretation of this term should be considered with caution, but it could refer to a specific type of suit of armour, or armour-making. Baptiste assumed that it could be related to an armour made with material consisting of several sheets of metal welded together [51]. His hypothesis is supported by delamination observed over the entire surface of some pieces of armour which could be evidence of a welding revealed by the corrosion process over time. While the metallographic study realized on the backplate of the armour of Laval could illustrate such practice, further research should be made on a broader number of armours showing such structures to confirm this hypothesis, by examining the metallographic structure of the metal.

Contrary to the lateral parts, the central plate of the backplate (STS_11) is constituted of a quenched structure showing the highest hardness (>300) of the suit with the faulds (STS_10, Figure 8, «B»), constituted of carburized material showing a significant distortion of grains. This result illustrates that a similar hardness could be reached by different means (the selection of metal and/or its heat treatment). The same argument could be put forward for the helmet (where phosphorus acts as a hardener to reach the hardness of steel structures) and the pauldrons. The benefits of a high hardness (>300) for the backplate and the faulds are not obvious, the same for the selection of metal regarding the pauldrons. Indeed, the left one was most exposed during a charge, and if it is made of steel, the hardness of the metal is of the same rough size as the right pauldron composed mostly of ferrite and carbides. In the case of the horseman "AVANT" armour (preserved at the Glasgow City Museum) studied by Williams and dated from the same period [9], the contrary was observed from the metallographic structure. Thus, more comparisons with pieces of the same type would be needed to conclude.

The heterogeneities of microstructure and heat treatment observed may, in a first approach, suggest the involvement of several armourers and/or workshops to produce the suit of armour. This hypothesis is also supported by the presence of at least three metal supplies.

The involvement of several craftsmen for the manufacture of a complete armour seems likely, whether they work in the same workshop or in several, in the case of a contractual arrangement. In northern Italy, this hypothesis is supported by the presence of different stamped marks on the various parts of an homogeneous armour, which indicate the work of different craftsmen [4,5]. The Laval armour do not unfortunately bear any mark. Thus, another hypothesis is that the armour is not a made-to-measure suit of armour and the different parts have been acquired in different places or time by its owner(s) or assembled later in the museum collection. In that case, the right pauldron and the rerebrace might not originally belong to the rest of the armour. The right pauldron of the armour being fragmentary, a more detailed typological comparison could not be made with the left one to draw broader conclusions on the homogeneity of the armour.

However, some evidences linked the armour with northern Italy. The right pauldron and the rerebrace have two different chemical signatures but both compatibles with the Lombard area. This result could reinforce the hypothesis of a Lombard origin of several parts of the armour. Nevertheless, it remains conjectural as Lombard steel was also traded outside Lombardy [5,52]. Furthermore, the two lateral plates of the backplate, the breastplate and faulds form a single provenance group, suggesting that they may have been manufactured in the same area of production. Their chemical signature is compatible with the group of Italian-style armour studied by Bérard et al., but distinct from the Lombard area defined by Leroy et al., from slags and ores. As suggested by the authors, this does not exclude a Lombard origin for the metal as the low number of analysed slags for this area of production could be not completely representative of the chemical variation for the whole Lombardy. Furthermore, the fact that both sources (the one compatible with Italian-style armour and the ones compatible with ores and slags from Lombardy) is found on a same armour strengthens the hypothesis of a Lombard origin for the backplate, the breastplate and faulds. These metal supplies (and consequently the group of Italian-style armour studied by Bérard et al.) could thus reflect another part of the Lombard chemical signature.

Finally, the difference in the nature of the metal, heat treatment and sources of supply observed for the Laval armour highlights the composite aspect of such pieces, not only in museum collections but also during its period of use. Indeed, an armour could have been made by several craftsmen, workshops and even acquired at different times and places by its owner on a second-hand market.

6. Conclusions

In the 15th c., a complete suit of armour was the best protection available, and its fabrication required a specific technical craftsmanship. However, pieces dated from this period are rare and therefore poorly studied from a metallurgical point of view. This study focused on the material characterization of a composite suit of armour belonging to the « Musée du Vieux Château Laval » (France) and corresponding, except for the helmet , to an Italian-style equipment dated around 1440. Metallurgical investigations have revealed various microstructures suggesting several metal supplies and heat treatments. Particular craftsmanship was noted on some parts of the armour, especially on the backplate, involving quenching to harden the metal and the use of a banded steel, combining several sheets of metal with different mechanical properties that may have provide better defensive properties.

Despite the heterogeneities revealed from the nature of the metal, the provenance study reinforces the hypothesis of a link between several parts of the armour and northern Italy. Indeed, the right pauldron and the rerebrace have two different chemical signatures but both compatibles with the Lombard area defined by former studies, while the two lateral plates of the backplate, the breastplate and faulds form a single provenance group, compatible with the group of Italian-style armour studied by Bérard et al. This could suggest that these three elements were made in the same production area, linked to the manufacture of Italian-style armour, the exact location of which is unfortunately still unknown. Nevertheless, these results suggest that by tracking the sources of metal used by the armourer, it may be conceivable to establish, in the future, the types of metal supplies employed by a workshop and ultimately the chemical signature of a workshop or a set of workshops.

Acknowledgements

We would like especially to thank: Antoinette Le Falher (Musées de Laval) for the stimulating exchanges and allowing sampling the armour, Stéphane Lemoine (Arc'Antique) and Enrique Vega (LAPA-IRAMAT) for their help on the sampling campaigns, Bernard Gratuze (CEB—IRAMAT) for hosting the LA-ICP—MS analyses, Stéphane Urvoy (LA2M, CEA Saclay), Eric Leroy (ICMPE), Ivan Guillot (ICMPE) and Ivan Cotrebil (ICMPE) for their help in the microhardness and WDS measurements, Alexandre Disser (LAPA-IRAMAT) for the fruitful discussion on the SI analyses, Jean-Pierre Morteveille and Gérard Morteveille for their support, all the team members of LAPA, Arc'Antique, IPREM, and CEB labs for their contributions to this work and reviewers for the stimulating exchanges and remarks.

Funding: This work was supported by the LabEx PATRIMA ANR-10-LABX- 0094-01 and the Fondation des Sciences du Patrimoine, Paris Seine Graduate School Humanities, Creation, Heritage, Investissement d'Avenir ANR-17-EURE-0021 – Foundation for Cultural Heritage Sciences.

7. References

- [1] P. Terjanian, The currency of power. The central place of Armor in the ambitions and life of Mawimilian I, in: Last Kn. Art, Armor, Ambition Maximilian I, The Metropolitan Museum of Art, 2019: pp. 17–38.
- [2] C. Gaier, L'industrie et le commerce des armes dans les anciennes principautés belges du XIIIeme à la fin du XVeme siècle, Société d'édition "les Belles Lettres," Paris, 1973.
- [3] P. Contamine, Armes et Armures, in: C. Prigent (Ed.), Art Société En Fr. Au XVe Siècle, Maisonneuve et Larose, Paris, 1999: pp. 544–553.
- [4] S.W. Pyhrr, J.-A. Godoy, S. Leydi, Heroic armor of the Italian Renaissance Filippo Negroli and his contemporaries, The Metropolitan Museum of Art, New York, 1998.
- [5] F. Menant, La métallurgie Lombarde au Moyen Âge, in: P. Benoit, D. Cailleaux (Eds.),

- Hommes Trav. Du Métal Dans Les Villes Médiévales, Association pour l'édition et la diffusion des études historiques, Paris, 1988: pp. 127–161.
- [6] S. Leydi, Les armuriers milanais dans la seconde moitié du XVIème siècle, in: Parures Triomphales Le Maniérisme Dans l'art l'armure Ital., 5 continents et Musées d'art et d'histoire de la ville de Genève, Milan et Genève, 2003: pp. 25–46.
- [7] J. Kraner, T. Lazar, B. Zorc, P. Fajfar, M. Knap, Archaeometallurgical characterization of a 16th century suit of armour made by Valentin Siebenbürger, J. Cult. Herit. 39 (2019) 49–56.
- [8] C.W. Brewer, Metallographic examination of medieval and post-medieval iron armour, Hist. Metall. 15 (1981) 1–8.
- [9] A. Williams, The knight and the blast furnace: a history of the metallurgy of armour in Middle Ages and the Early Modern period, Brill, London, 2003.
- [10] S. Leever, For show or safety? A study on structure, ballistic performance and authenticity of seventeenth century breastplates, Master thesis, Mechanical, Maritime and Materials Engineering, 2005.
- [11] A. Williams, A. De Reuck, The Royal Armoury at Greenwich, 1515-1649 a history of its technology, Trustees of the Royal Armouries, London, 1995.
- [12] A. Williams, D. Edge, T. Capwell, S. Stanzl-Tschegg, A technical note on the armour and equipment for jousting, Gladius. 32 (2012) 139–184.
- [13] E. Imiołczyk, G. Żabiński, T. Goryczka, K. Aniołek, A. Balińska, E. Miśta-Jakubowska, An Armour from a finery?—a late medieval couter from Ogrodzieniec Castle in the Kraków-Częstochowa Jura, Archaeol. Anthropol. Sci. 12 (2020) 1–20.
- [14] A. Williams, Further metallurgical studies on Early Armour from Churburg, in: J. Hošek,
 H. Cleere, L. Mihok (Eds.), Archaeometall. Iron. Recent Dev. Archaeol. Sci. Res. Dedic.
 to Profr. Radomir Plein., Institute of Archaeology of the ASCR, Praha, 2011: pp. 163–172.
- [15] E. Bérard, L'armure du XIIIe au XVIIe siècle en Europe : une approche matérielle.

- Production, nature et circulation du métal, PhD thesis, Université de Cergy-Pontoise, 2019.
- [16] A.R. Williams, On the Manufacture of Armor in Fifteenth-Century Italy, Illustrated by Six Helmets in the Metropolitan Museum of Art, Metrop. Museum J. 13 (1978) 131–142.
- [17] C. von Böhne, Werkstofftechnische Fragen bei deutschen Plattnerarbeiten, Waffen-Und Kostümkd. 1 (1961) 47–53.
- [18] D. La Rocca, How to Read European Armor, The Metropolitan Museum of Art, New York, 2017.
- [19] P. Dillmann, M. L'Héritier, Slag inclusion analyses for studying ferrous alloys employed in French medieval buildings: supply of materials and diffusion of smelting processes, J. Archaeol. Sci. 34 (2007) 1810–1823.
- [20] P. Crew, The experimental production of prehistoric bar iron, J. Hist. Metall. Soc. 25 (1991) 21–36.
- [21] E. Blakelock, M. Martinón-Torres, H.A. Veldhuijzen, T. Young, Slag inclusions in iron objects and the quest for provenance: an experiment and a case study, J. Archaeol. Sci. 36 (2009) 1745–1757.
- [22] V.F. Buchwald, H. Wivel, Slag analysis as a method for the characterization and provenancing of ancient iron objects, Mater. Charact. 40 (1998) 73–96.
- [23] M. Charlton, E. Blakelock, M. Martinón-Torres, T. Young, Investigating the production provenance of iron artifacts with multivariate methods, J. Archaeol. Sci. 39 (2012) 2280–2293.
- [24] M.P. Coustures, D. Béziat, F. Tollon, C. Domergue, L. Long, A. Rebiscoul, The use of trace element analysis of entrapped slag inclusions to establish ore Bar iron links: examples from two Gallo-Roman iron-making sites in France (Les Martys, Montagne noire, and les Ferrys, Loiret), Archaeometry. 45 (2003) 599–613.
- [25] S. Leroy, S.X. Cohen, C. Verna, B. Gratuze, F. Téreygeol, P. Fluzin, L. Bertrand, P.

- Dillmann, The medieval iron market in Ariège (France). Multidisciplinary analytical approach and multivariate analyses, J. Archaeol. Sci. 39 (2012) 1080–1093.
- [26] A. Disser, P. Dillmann, M. Leroy, M. L'Héritier, S. Bauvais, P. Fluzin, Iron supply for the building of Metz cathedral: new methodological development for provenance studies and historical considerations, Archaeometry. 59 (2016) 493–510.
- [27] M. L'Héritier, S. Leroy, P. Dillmann, Bernard Gratuze, Characterization of Slag Inclusions in Iron Objects, in: L. Dussubieux, M. Golitko, B. Gratuze (Eds.), Recent Adv. Laser Ablation ICP-MS Archaeol., Springer, Berlin, 2016: pp. 213–228.
- [28] A.-M. Desaulty, P. Dillmann, M. L'Héritier, C. Mariet, B. Gratuze, J.-L. Joron, P. Fluzin, Does it come from the Pays de Bray? Examination of an origin hypothesis for the ferrous reinforcements used in French medieval churches using major and trace element analyses, J. Archaeol. Sci. 36 (2009) 2445–2462.
- [29] M.-P. Coustures, C. Rico, D. Béziat, D. Djaoui, L. Long, C. Domergue, F. Tollon, La provenance des barres de fer romaines des Saintes-Maries-de-la-Mer (Bouches-du-Rhône), Gallia. 63 (2006) 243–261.
- [30] E. Bérard, C. Pécheyran, P. Dillmann, S. Leroy, E. Vega, A. Williams, C. Verna, V. Toureille, Ancient armour provenance by LA-ICP-MS analysis of microscopic slag inclusions, J. Anal. At. Spectrom. (2020) 2582–2593.
- [31] O. Renaudeau, L'armure et les armes du musée de l'Auditoire de Sainte-Suzanne, in:
 C. Davy, N. Foisneau (Eds.), Sainte-Suzanne Un Territ. Remarq. En Mayenne,
 Association 303 Arts Recherches et Créations, 2014: pp. 157–165.
- [32] P. Dillmann, L. Pérez, C. Verna, Les aciers avant Bessemer, in: P. Dillmann, L. Pérez, C. Verna (Eds.), L'acier En Eur. Avant Bessemer, CNRS-Université de Toulouse-Le Mirail, Toulouse, 2011: pp. 6–56.
- [33] S. Painsonneau, Fabrication et commerce des armures l'armurerie tourangelle au XVe siècle, Association pour l'édition et la diffusion des études historiques, Paris, 2004.
- [34] E. Reppel, Minorités et circulations techniques : la confection des armures à Tours (XVe-XVIe siècles), Doc. Pour l'histoire Des Tech. (2008) 24–31.

- [35] V. Toureille, Jeanne d'Arc, Perrin, France, 2020.
- [36] G. Pagès, P. Dillmann, P. Fluzin, L. Long, A study of the Roman iron bars of Saintes-Maries-de-la-Mer (Bouches-du-Rhône, France). A proposal for a comprehensive metallographic approach, J. Archaeol. Sci. 38 (2011) 1234–1252.
- [37] S. Leroy, M. Hendrickson, S. Bauvais, E. Vega, T. Blanchet, A. Disser, E. Delque-Kolic, The ties that bind: archaeometallurgical typology of architectural crampons as a method for reconstructing the iron economy of Angkor, Cambodia (tenth to thirteenth c.), Archaeol. Anthropol. Sci. 10 (2017) 2137–2157.
- [38] M. L'Héritier, I. Guillot, P. Dillmann, Microstructural Characterization and Mechanical Properties of Iron Reinforcements in Buildings from the Medieval and Modern Periods in France, Int. J. Archit. Herit. 0 (2019) 1–13.
- [39] M. L'Héritier, P. Dillmann, S. Aumard, P. Fluzin, Iron? Which iron? Methodologies for metallographic and slag inclusion studies applied to ferrous reinforcements from Auxerre Cathedral, in: J. Humphris, T. Rehren (Eds.), World Iron, Archetype Publications, London, 2013: pp. 409–420.
- [40] A. Disser, P. Dillmann, C. Bourgain, M. L'Héritier, E. Vega, S. Bauvais, M. Leroy, Iron reinforcements in Beauvais and Metz Cathedrals: from bloomery or finery? The use of logistic regression for differentiating smelting processes, J. Archaeol. Sci. 42 (2014) 315–333.
- [41] S. Leroy, Circulation au moyen âge des matériaux ferreux issus des Pyrénées ariégeoises et de la Lombardie. Apport du couplage des analyses en éléments traces et multivariées, PhD thesis, Université Technologie Belfort-Montbeliard, 2010.
- [42] M. Fulford, D. Sim, A. Doig, J. Painter, In defence of Rome: a metallographic investigation of Roman ferrous armour from Northern Britain, J. Archaeol. Sci. 32 (2005) 241–250.
- [43] W.C. Leslie, Recent observations on quench-aging and strain-aging of iron and steel, Mater. Sci. Res. (1963) 208–250.
- [44] H. Abe, Carbide precipitation during ageing treatments, Scand. J. Metall. (1984).

- [45] K. Ushioda, K. Takata, J. Takahashi, K. Kinoshita, H. Sawada, Changes in States of Carbon and Mechanical Properties with Aging at 50°C after Quenching in Low Carbon Steel, Mater. Trans. 61 (2020) 668–677.
- [46] J. Piaskowski, The manufacture of medieval damascened knives, J. Iron Steel Inst. 202 (1964) 561–568.
- [47] M. L'Héritier, P. Dillmann, Récupération et remploi du fer pour la construction des monuments de la période gothique, in: J.-F. Bernard, P. Bernardi, D. Esposito, P. Dillmann, L. Foulquier, R. Mancini (Eds.), Reimpiego Archit. Recuper. Trasformazione, Uso, Ecole Française de Rome, Rome, 2009: pp. 157–176.
- [48] A. de Reuck, D. Starley, T. Richardson, D. Edge, Duplex armour: an unrecognised mode of construction, Arms Armour. 2 (2005) 5–26.
- [49] A.F. von Reitzenstein, Die Ordnung der Nürnberger Plattner, Waffen- Und Kostümkd. 1 (1959) 54–85.
- [50] P. Contamine, Les Gens de guerre et la ville. Achats d'armures à Orléans, 1434-1438, in: M. Bourin (Ed.), Villes, Bonnes Villes, Cités Capitales. Mélanges Offer. à Bernard Cheval., Université de Tours, Tours, 1989: pp. 3–11.
- [51] N. Baptiste, Des artisans spécialistes : l'art des armuriers, in: N. Baptiste (Ed.), Armatus Corpus Princes Cheval. 600 Ans Du Duché Savoie, Infolio, Gollion, 2016: pp. 199–209.
- [52] P. Braunstein, L'acier de Brescia à la fin du XIVe siècle : l'apport d'une correspondance d'affaires, in: P. Braustein (Ed.), La Sidérurgie Alp. En Ital. (XIIe XVIIe Siècle), École française de Rome, Rome, 2001: pp. 455–479.