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1 Seal the deal: an extensive study of European historical copper- 2 based seal matrices using a multimodal protocol.

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13 Highlights

- 14 – Overview of medieval and early modern European seal matrices technical practices
- 15 – 466 objects analysed by pXRF in order to document the alloys
- 16 – Engraving techniques of 142 objects documented using binocular
- 17 – 6 cross sections of seal matrices examined under microscope
- 18 – Crucial information provided on workshops diachronic tradition and specificities

19 Abstract

20 Seal matrices have been used in many civilizations across the globe for thousands of years. In Europe,
21 during the late medieval and early modern periods, they were made of a resistant material such as
22 metal, frequently copper-based alloys, and were an essential attachment of official documents, serving
23 as personal signatures. By investigating an exceptional body of objects, this work contributes to throw
24 some light on the technical landscape of copper-based seal matrix production which has remained
25 undocumented until now. A multi-modal approach was carried out in order to document the materials
26 and techniques involved. More than four hundred objects were analysed using a recently developed
27 portable XRF protocol for copper-based alloy analysis. In addition, more than one hundred were
28 carefully examined on a micro scale in order to determine the engraving techniques. Cross sections
29 were obtained from six broken seal matrices, allowing the manufacturing process of the objects to be
30 revealed. First, although a wide range of copper-based alloys were documented, namely bronze, red
31 brass and brass, two groups of objects could be identified based on the Pb content, suggesting two

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32 levels of quality. Second, three different successive engraving techniques could be identified dating
33 from between the 13th c. and the 17th c: engraving, simple stamp combination and letter punches.
34 Finally, similarities in terms of the fabrication process and the alloys used in French and Italian ways
35 of production could suggest a transborder practice. Apart from providing insights into historical seal
36 matrices production, these results also contribute to the documentation of medieval and early modern
37 copper-based workshops practices.

38 Graphical Abstract



39

40 **Keywords:** Seal matrices; copper-based alloys; Medieval and Modern Periods; Western Europe;
41 Technical knowledge; pXRF; Metallographic study

42 1. Introduction

43 The context of production of small copper-based objects from Medieval and Early European Modern
44 periods remains largely undocumented despite some pioneer works addressing the technical
45 knowledge associated with copper-based domestic objects (Blades, 1995; Brinklow, 1975; Heyworth,
46 1991; White, 1982). Written sources provide crucial but yet incomplete information on organisation of
47 craftsmanship and processes (Boileau, 1879; Cennini and Herringham, 1922; Theophilus, 1979). From
48 an archaeological point of view, one can mention in particular the study of a Parisian copper-based
49 workshop excavated in the centre of the city (Bourgarit, 2012; Thomas, 2009; Thomas and Bourgarit,
50 2006). However, the deficit of data remains particularly persistent for European medieval and Early
51 Modern small size productions.

52 Among these productions, seal matrices were widely used by institutions and towns as well as a large
53 portion of the population of high and intermediate status, from rich local farmer to royalty. The
54 matrices, predominantly made of copper-based alloys, accompanied the *sigillant* throughout his life, as
55 he carried it often on his belt, visible for everyone (Vilain, 2015).

56 This work aims at gaining insight into the technical landscape of seal matrix production during the
57 European Middle Ages and Early Modern periods. The objective is to provide an overview of the
58 range of alloys employed for their fabrication, to reveal their context of production and associated
59 technical knowledge, and to discuss their specificities in relations with the larger ensemble of small
60 copper-based objects produced during this period.

61 Our study focuses his attention on the collections kept at the French National Archives (Archives
62 Nationales: AN) institution and at the Fine Arts Museum (Musée des Beaux Arts: MBA) of Lyon
63 which constitute a unique group of objects from the 13th c. to the 17th c. The corpus under investigation
64 in this study is part of a large production representing probably several tens of thousands of objects, as
65 the number of objects kept in the collections, about ten thousands, only represents a small percentage
66 of the objects produced (Pastoureau, 2015). Thus, in order to identify trends and specificities within
67 this large-scale production, it appears essential to characterize a sufficient number of objects in order
68 to get a representative view of the 13-17th c. seal matrix production.

69 To achieve this, and because of the large number of artefacts, portable X-ray fluorescence analyser
70 (pXRF) was used for systematic elemental analysis of the seal matrices alloys using a methodology
71 specifically developed for copper-based alloy and adapted to the very specific characteristics of the
72 collections under investigation (Heginbotham and Solé, 2017). It allowed a non-invasive in situ
73 analysis of the objects: an essential constraint when studying cultural heritage objects (Bonizzoni et
74 al., 2007; Bottaini et al., 2015; Colomban et al., 2012; Karydas, 2007; Šatović et al., 2013). Two main
75 problems must be addressed when analysing cultural heritage copper-based objects using pXRF
76 methods. First, due notably to their detection and quantification limits but also its associated
77 uncertainty, those techniques do not offer the analytical precision of, for example, ICP set ups.
78 Second, pXRF (and XRF in general) only probe a limited depth of the analysed object. This is
79 particularly important regarding analyses of Cu-alloys which are often covered with patina layers
80 (artificial or natural). Thus, it is necessary to carefully consider the depth probe according to both the
81 matrix and the patina layer composition / thickness. Having said that, pXRF, when rigorously
82 performed, allows the determination of the Cu-alloys main constituents with confidence. Indeed,
83 regarding the quality of provided quantitative data, progress has been made through the careful control
84 of data treatment and the development of a calibration procedure dedicated to copper-based alloys
85 (Heginbotham and Solé, 2017). Moreover, for relatively thin patinas, of a few microns, recent work by
86 different teams have allowed producing more trustworthy bulk metal composition data by giving a
87 reliable overview of both the applicability of the method (Karydas, 2007; Martín-Torres et al.,
88 2014) and bias of the analysis (Nørgaard, 2017; Orfanou and Rehren, 2015; Smith, 2012). This
89 provides several tracks for good pXRF data treatment and interpretation.

90 In addition, fabrication techniques were documented for the first time by metallographic approaches
91 and extensive observation of the engraving techniques including identification of tool marks. By
92 careful visual characterisation of the objects, insights into the different steps and the organisation of
93 the production were made possible.

94 **2. Materials and Method**

95 *2.1. Studied corpus*

96 In this work, a total 466 seal matrices (see example Figure 1) were investigated: 394 from the French
97 National Archives, 71 from the Fine Arts Museum of Lyon and one archaeological object (Table 1).
98 As French institutions were targeted, most of the objects have been collected in France where they
99 originate (79%) but 15% have been produced in Italy, and 6% from other European areas such as
100 Holy Roman Empire or Spain. The chronological repartition of the corpus ranges from the 13th c. to
101 the 17th c. Objects from the 14th c. – a period of important production – are among the most numerous
102 (49% of the corpus), followed by objects from the 13th c. (18 %) and 15th c. (17%). A few objects are
103 dated from intermediary periods (e.g. late 13th c - early 14th c.). Dating and provenance identification
104 are based on several stylistic criteria, helped by the inscriptions found on the objects themselves. Some
105 of the *sigillants* are well known and their seal matrices can thus be precisely dated according to their
106 assumption of duty for example. Those seal matrices constitute references for other dating. When in
107 doubt, the objects were not included in this study as the main objective was first to constitute a
108 reference database for this kind of metal production. The seal matrices measure typically a few
109 centimetres in diameter, and weight between a few tens of grams and two hundred grams. Almost all
110 the objects from the collections are in a very good state of conservation. Only a few of them have been
111 broken, most probably just after the death of the *sigillant* in order to avoid later use of the matrices to
112 produce false seals (Nieus, 2011; Vilain, 2016).



113

114
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Figure 1 : Seal matrix of the « Bailliage royal de Corbie », French National Archives, inv. Mat. 124, second half of 13th century, France. H.: 13; D.: 46; th.: 4, Weight: 45.3g. © M Castelle LAPA/AN/DYPAC

Total: 466 pXRF / 142 BM	Period								
	13th c.	13th-14th c.	14th c.	14th-15th c.	15th c.	15th-16th c.	16th c.	16th-17th c.	17th c.
	83 / 3	10 / 3	227 / 48	11 / 10	79 / 35	1	38 / 8	7 / 2	10 / 3
Origin									
	France		Italy		Other				
	372		68		26				
Collection									
	French National Archives		Fine Arts Museum Lyon		INRAP				
	394 / 142		71		1				

116 Table 1 : Overview of the seal matrices investigated for the present study. A total of 466 objects have been analysed by pXRF
117 / A total of 142 objects have been observed under binocular magnifier (BM). More details are to be found in supplementary
118 material.

119 2.2. Fabrication process investigation

120 Metallic cross sections were obtained from six already broken seal matrices by taking a sample of a
121 few square millimetres by means of a diamond saw. These cross sections were prepared by mounting
122 the samples in resin and then grinding and polishing the mount. Images were obtained using both
123 optical microscope (OM) and Scanning Electron Microscopy (SEM) in order to not only question the
124 seal matrices fabrication process but also estimate the chemical heterogeneity between the core metal
125 and the surface areas – the patina – of the objects. Chemical ferric chloride etchant was used in order
126 to reveal the microstructure under OM.

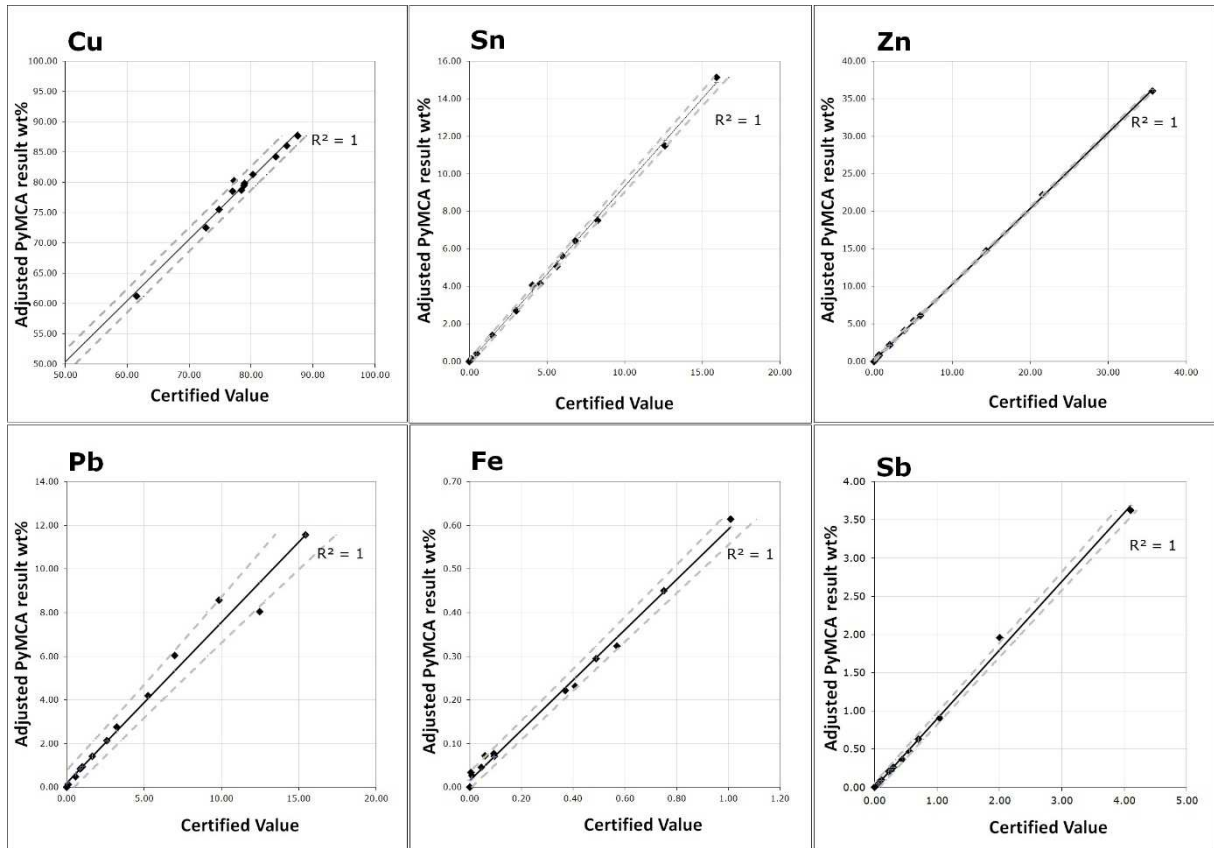
127 In addition, 142 seal matrices were observed under a binocular microscope in order to characterise the
128 engraving techniques. Both the inscriptions and the central motifs were carefully documented.

129 2.3. *Metal analyses (pXRF)*

130 466 seal matrices were selected to be analysed by portable-X-ray fluorescence (pXRF) with a Niton
131 XL3t spectrometer coupled with a 50 kV X-ray tube and a GOLDD Detector. These objects are
132 covered by a range of patina, from fine, almost visually inexistent, to medium, revealing the
133 underpinned metal. Seal matrices presenting a dark, powdery and inhomogeneous patina (approx. 10
134 % of the collections), or remains of gilding (only a few objects) were excluded, as only analyses of the
135 surfaces of the objects were possible.

136 Spectra acquisition were performed using a metal alloy mode including both light and main ranges of
137 elements for a total counting time of 60 seconds and a 6 mm spot. Three measurements were taken at
138 different places on the object in order to avoid possible heterogeneity issues of the materials. These
139 measurements were averaged taking into account the associated standard deviation in order to
140 appreciate the degree of homogeneity of the measurements. The consistency of the quality of each
141 measurement was controlled by systematically analysing a set of four reference standards during the
142 analyses carried out at the location of the collections.

143 Spectra were treated for quantification using the open-source, PyMca software (Solé et al., 2007) by
144 mean of the fundamental parameters (FP) approach based on the spectrometer characteristics allowing
145 total transparency during the process. Calibration was carried out based on the so-called CHARMed-
146 PyMca protocol. This protocol is based on previous work showing not only good but also
147 reproducible results on pXRF analysis of Cu-alloys. The Cu-CHARM set of 12 reference materials
148 was used for calibration of the standard-less XRF measurements (Heginbotham et al., 2015). The
149 calibration coefficients were calculated for each considered element using standard reference values
150 both calculated (PyMca) and certified and through the MECS (Multi-Element Calibration
151 Spreadsheet) file proposed by these authors. The complete description of the calibration protocol has
152 been previously detailed (Heginbotham and Solé, 2017). Calibration curves obtained on four of the
153 main constituents (Cu, Sn, Zn, Pb) as well as on two minor components (Fe, Sb) of copper-based
154 alloys are presented in Figure 2. Calculated data are plotted together with certified values. Very good
155 calibrations are obtained for the considered elements. Only Pb exhibits a slightly less narrow
156 calibration. This is mainly due to the fact that Pb is not miscible into copper-based alloys and is
157 heterogeneously distributed within the matrix.



158

159 *Figure 2 : Cu, Sn, Zn, Pb, Fe and Sb calibration plots using the CHARMed PyMca protocol (raw data are obtained using a*
 160 *NITON GOLDD with an Ag tube). The 12 reference materials were analysed three times. The black line represents the linear*
 161 *regression for each series of measurements, the grey lines represent the standard error at the prediction at 95% confidence*
 162 *and R2 is the coefficient of determination of the linear regression.*

163 The depth penetration of incident X-rays during the analysis has been calculated using linear
 164 attenuation coefficients (Chantler et al., 2005; Markowicz, 2011) for several unpatinated copper-based
 165 alloys. Corresponding data for CuZn15Sn6Pb2, CuZn15, Cu, CuSn10 and CuSn10Pb5 are reported in
 166 Table 2. This made possible the control of the X-ray penetration for a good representativity of the
 167 measurement, considering the presence of a thin patina layer.

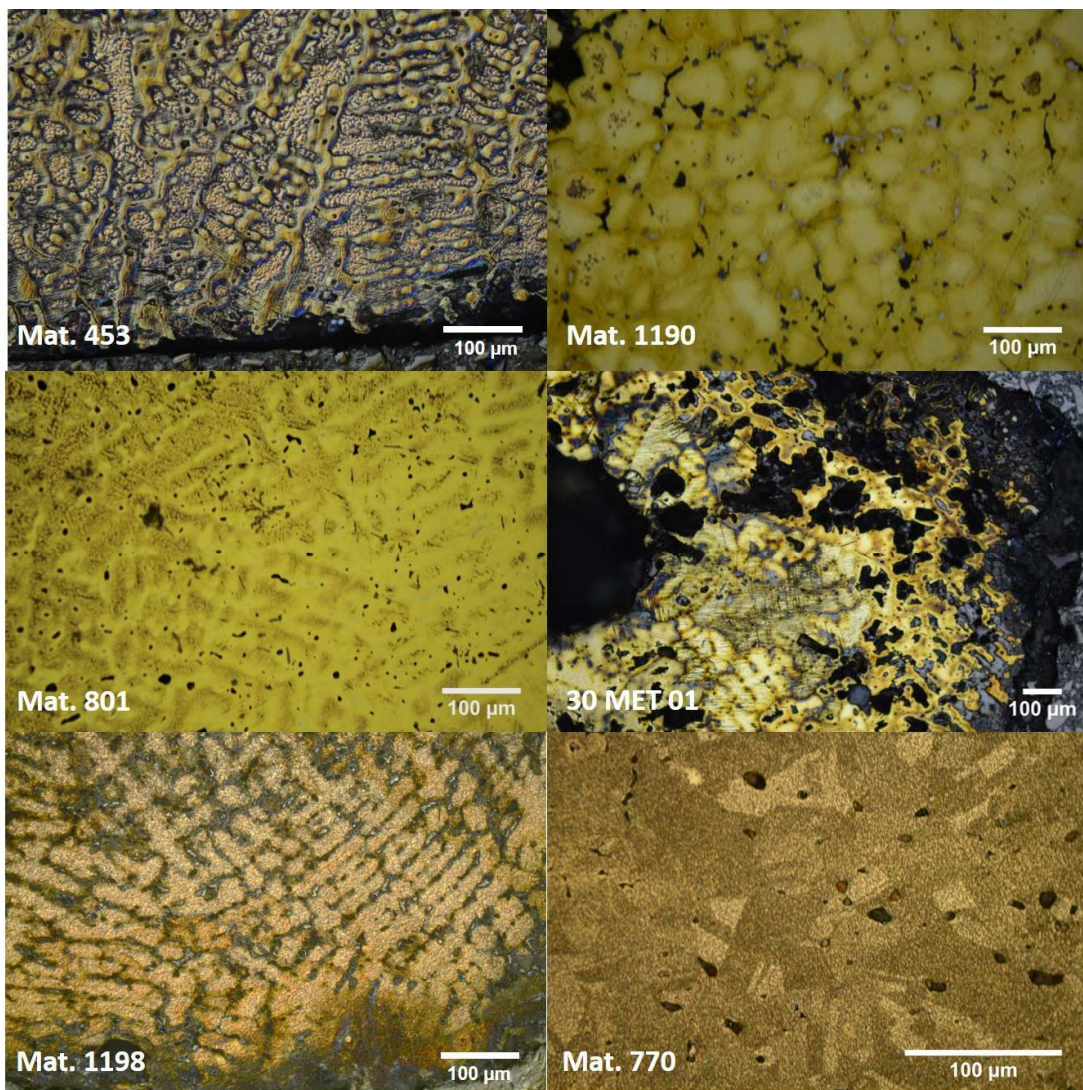
		CuZn15Sn6Pb2		CuSn10		Cu		CuSn10Pb5		CuZn15	
X-ray lines	E	95% Xray	90% Xray	95% Xray	90% Xray	95% Xray	90% Xray	95% Xray	90% Xray	95% Xray	90% Xray
	KeV	μm									
Sn-L	3.44	6	5	6	5			5	4		
Cu-K	8.91	57	44	55	42	92	71	44	34	65	50
Zn-K	9.57	18	14							87	67
Pb-L	12.61	31	24					34	26	17	13
Sn-K	25.27	205	157	196	151			158	121		

168 *Table 2 : Depth penetration of several X-ray lines according to four different types of copper-based alloys (μm). Provenance*
 169 *depths are provided in μm for respectively 90% and 95% of the X-ray*

170 **3. Results**

171 *3.1. Seal matrices fabrication process*

172 Micrographs of chemically etched cross sections taken from six seal matrices are presented in Figure
173 3. For five of them, observations under optical microscope after chemical etching revealed as-cast
174 microstructures. No thermal treatment could be identified and only a few mechanical twins resulting
175 from a superficial mechanical treatment are observable, performed in order to prepare the surface to be
176 engraved. As an exception, only one unalloyed copper seal matrix (Mat. 770) exhibits an annealed
177 microstructure attesting to a thermal treatment, which might have occurred just after a work hardening.
178 Such a process must have probably been reserved for some unalloyed copper objects – representing
179 only 2.6% of the objects analysed in the framework of this study (see below). Thus, it can be
180 confidently argued that all the alloyed copper objects of our corpus were manufactured by casting
181 process using refractory material moulds.

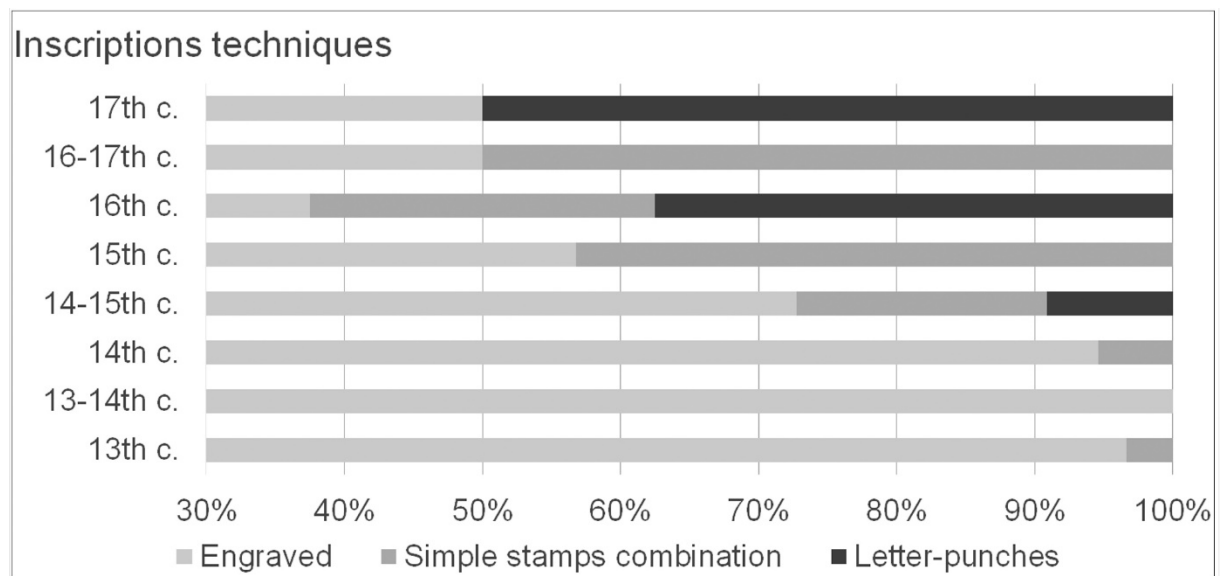


183 *Figure 3 : Metallographic cross section of samples taken from six seal matrices, observation under optical microscope after*
 184 *etching of the surface with ferric chloride.*

185 The central motifs of the observed seal matrices, from all periods, all show traces of direct engraving
 186 at the surface of the metal, with a few examples of punches from the 15th c. Had the motifs been
 187 partially moulded, they were largely reworked afterwards. Yet, the hypothesis of direct engraving of
 188 these motifs seems here convincing. The observation of the inscriptions on the other hand, reveals
 189 three successive technical knowledges involved over the period considered (Figure 4 and Figure 5).
 190 Indeed, before the 14th c. the inscriptions were systematically achieved by direct engraving (Figure 4-
 191 A). Examples of the use of simple stamps combined to produce each letter could then be found (Figure
 192 4-B). By the 16th c., letter-punches were more often employed (Figure 4-C) whereas engraved letters
 193 tended to disappear.



194 *Figure 4 : Different techniques to realise the letters on the seal matrices: (A) engraving, (B) simple stamps combination, (C)*
 195 *letter-punches*
 196



197
 198 *Figure 5 : Chronological evolution of the seal matrices inscriptions techniques (142 objects distributed as follow, 13th c.:33;*
 199 *13-14th c. :3; 14th c. 48; 14-15th c.:10; 15th c.: 35; 16th c.:8; 16-17th c.:2, 17th c.:3*

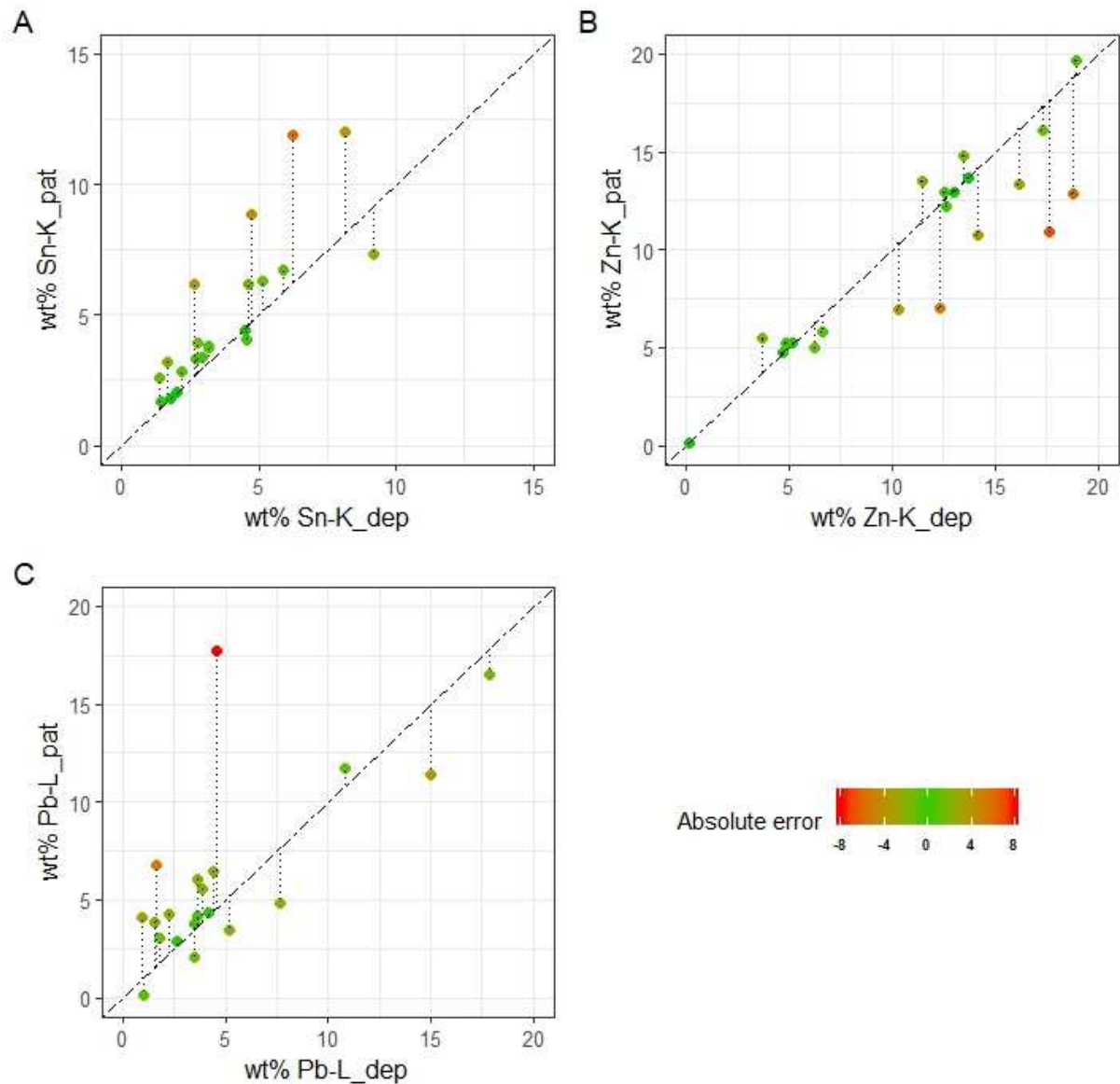
200 *3.2. Alloy characterization*

201 *3.2.1. Evaluation of the pXRF error due to the presence of patina*

202 Patina layers of the six cross sections mentioned above seem to result from a natural mechanism of
203 alteration and have been formed by corrosion of the metal surface. They are composed by typical Cu-
204 oxides and salts resulting from an indoor conservation of the objects (Nørgaard, 2017; Robbiola et al.,
205 1998). These patina layers observed by means of SEM imaging on seal matrices cross section ranges
206 from a few microns to locally a few tens of microns. On the millimetric scale of the XRF spot, the
207 patina thickness mean values do not exceed 10-15 μm (Mat. 453 and Mat. 801) and are generally
208 about 6-7 μm (Mat. 770, Mat. 801, Mat 1190). No specific trends were observed regarding a possible
209 correlation between patina thickness and the age of the matrix, or alloy type.

210 The determination of differences in elemental composition between surface and metallic core was
211 undertaken by means of chemical EDS-SEM mapping of the cross sections. Additionally, 21 seal
212 matrices were unpatinated on a surface of a few mm^2 by means of polishing; pXRF analyses were
213 performed on both patinated and unpatinated areas. Results were compared in order to evaluate the
214 error induced by the presence of patina layers on main elements' quantitative data. The results of this
215 approach, combined with the SEM observations and analyses previously described, made it possible to
216 highlight that when in the presence of a natural patina formed at the seal matrix surface, Sn and Pb
217 contents tend to be overestimated as the patina results from a decuprification of the metallic surface
218 and the formation of superficial Pb and Sn enriched oxides. Moreover, when in presence of Zn, the
219 surface of the object typically suffers from a dezincification which results in underestimating the Zn
220 content. These phenomena must be taken into consideration when performing pXRF analysis at the
221 surface of the objects.

222 Thus, the comparison of data obtained on patinated and unpatinated areas shows that for a large
223 majority (75%) of the objects, the presence of patina generates an absolute error on quantitative data
224 inferior to +/- 3%. This value has little or no impact on the alloy identification (if it is a bronze, a brass
225 or a red brass, or does it contain Pb). The remaining cases (25%) fall into the statistical error of the
226 method and are compensated by the analysis of a large number of objects. With an associated error
227 between 3 and 7%, they do not affect the general distribution of the obtained data. Nevertheless, a
228 possible under (Zn) or over (Sn and Pb) estimation of the alloy's constituents described above should
229 be taken into account.



230

231 *Figure 6 : Comparison of elements quantitative data obtained on both patinated and unpatinated area of seal matrices. A)*
 232 *Pb, B) Zn, C) Sn. The numbers on the plots correspond to the inventory numbers AN. Mat. Absolute errors correspond to the*
 233 *difference between the composition measured on the unpatinated area and the composition measured on the patinated area.*

234 3.3. Alloy recipes: a general overview

235 The alloys nomenclatures defined by Bourgarit and Thomas (Bourgarit, 2012) and Bayley (Bayley,
 236 1991) for medieval alloys were used as a starting point to define a new nomenclature adapted to the
 237 alloys characterised in the framework of the present study. Bronze and brass alloys are defined by their
 238 main alloying elements, respectively Sn and Zn. For Cu-Sn-Zn ternary alloys, as suggested by Bayley
 239 (Bayley, 1991), subdivisions into Zn-rich and Sn-rich alloys were adopted. However, the term “red
 240 brass” employed by Bourgarit and Thomas (Bourgarit, 2012) was preferred instead of “gunmetal”
 241 which refers to the gun-making. Unalloyed copper might naturally contain low level of Zn and Sn,
 242 hence the tolerance threshold including a few percent of these elements. This threshold is here based
 243 on discontinuities in the data.

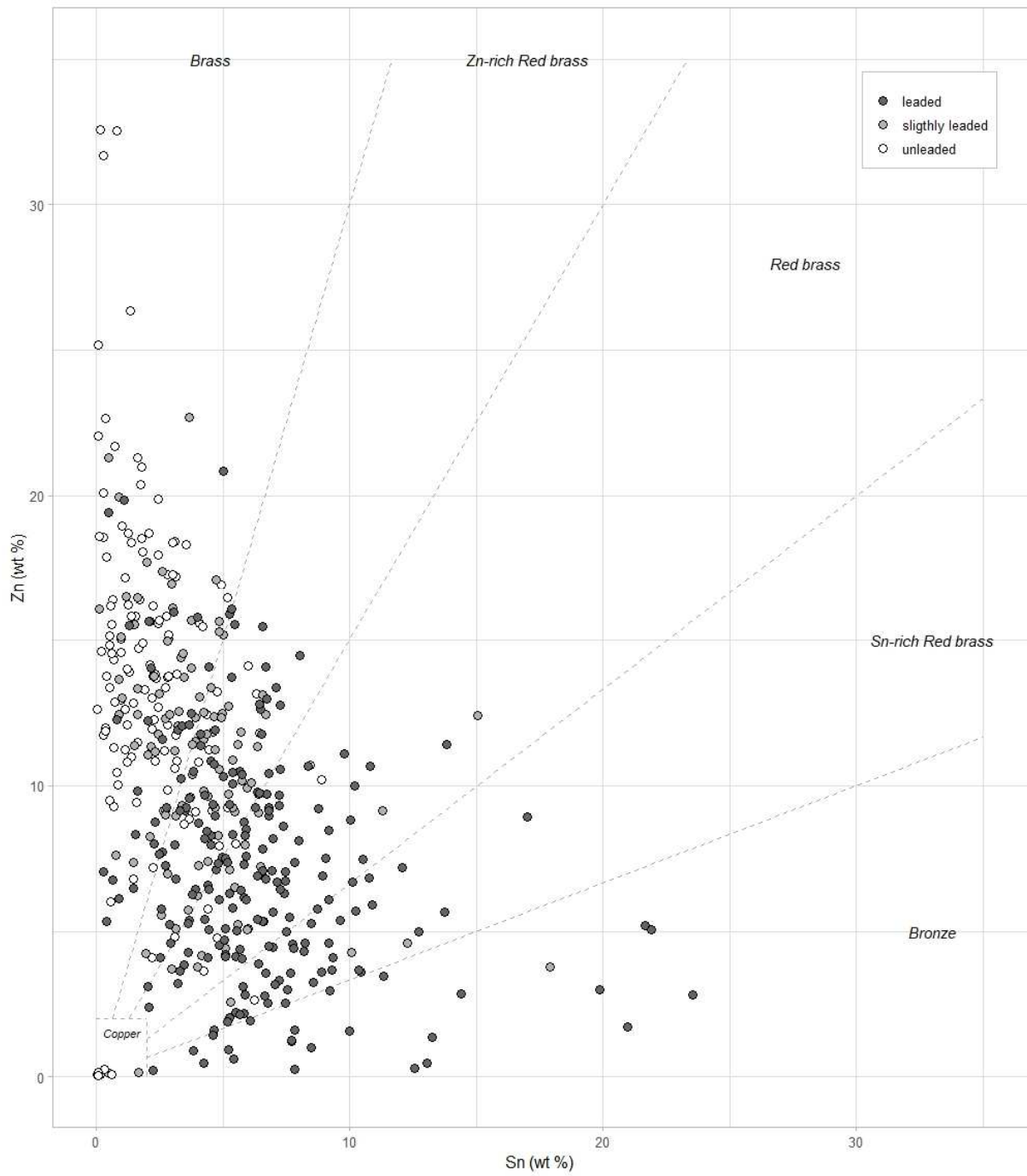
244 The nomenclature should be considered more as a description tool, a guide, than a clustering tool,
245 considering the continuum of the results and the constant overlapping of the categories which are
246 defined as follows:

- 247 – *Unalloyed copper*: containing both less than 3 wt% Sn and 2 wt% Zn
- 248 – *Bronze*: alloys with $\text{Sn} \geq 3\text{Zn}$ wt%.
- 249 – *Sn-rich red brass*: alloys ranging between $\text{Sn} \geq 3\text{Zn}$ wt% and $2\text{Sn} \geq 3\text{Zn}$ wt%
- 250 – *Red brass*: alloys ranging between $2\text{Sn} \geq 3\text{Zn}$ wt% and $2\text{Zn} \geq 3\text{Sn}$ wt%.
- 251 – *Zn-rich red brass*: alloys ranging between $2\text{Zn} \geq 3\text{Sn}$ wt% and $\text{Zn} \geq 3\text{Sn}$ wt%.
- 252 – *Brass*: alloys with a ratio $\text{Zn} \geq 3\text{Sn}$ wt%.

253 Additional subdivision is made based on the Pb content of each alloy (e.g. leaded bronze): when $3 <$
254 $\text{Pb} < 6$ wt%, the alloy is considered as “slightly leaded”, below this limit, the alloy is “unleaded”, and
255 when $\text{Pb} > 6$ wt%, it is considered as “leaded” (Bourgarit, 2012).

256 Major elements compositions of the matrix are plotted in Figure 7 in which these categories are
257 indicated by means of dashed lines. The compositions are distributed continuously from one type of
258 alloy to another. No specific group of objects can be derived solely from the alloying elements.
259 Despite this observation, in order to evaluate the distribution of the objects into this continuum, they
260 have been sorted out according to the nomenclature defined above (Figure 9). Thus, seal matrices from
261 the corpus are spread as follow: brass (40 %), Zn-rich red brass (25 %), red brass (20%), Sn-rich red
262 brass (8%) and bronze (4.4%). A few unalloyed copper objects (2.5 %) were also characterized
263 (Figure 9). This distribution reflects a significant representation of Cu-alloys containing Zn.
264 Chronological and geographical specificities are discussed below.

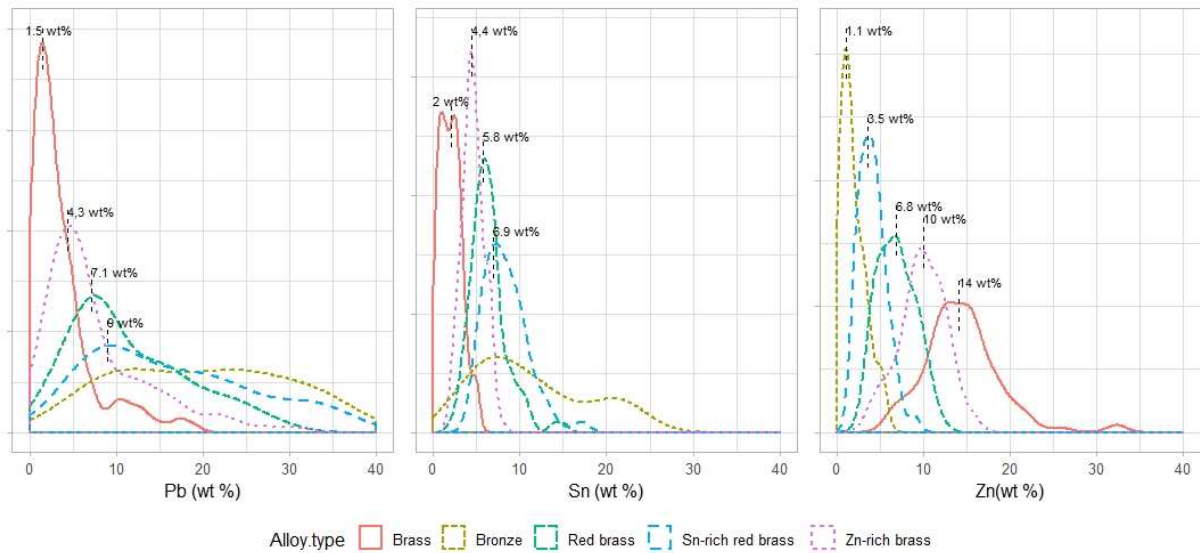
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Figure 7 : Scatter plot of Sn and Zn contents of the analysed seal matrices (wt %), the alloys types areas appear delimited by dashed lines.



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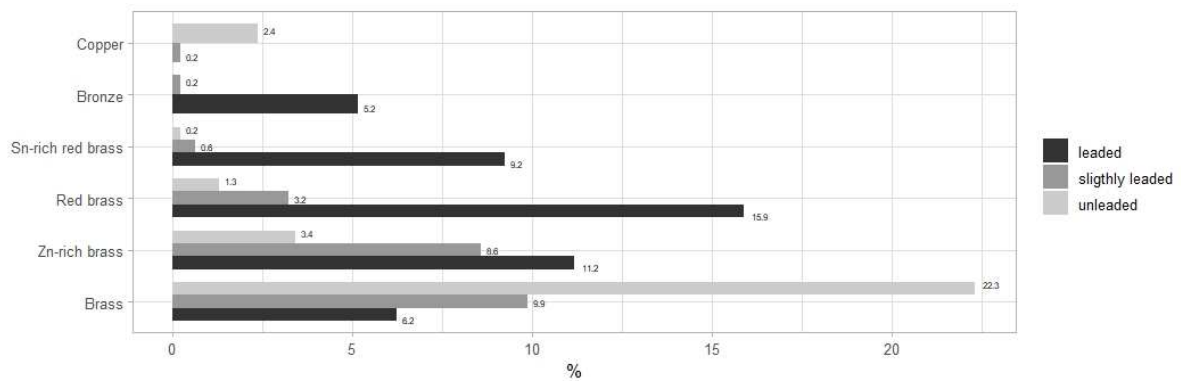
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272

Figure 8 : Kernel density plots representing the distribution of Pb, Sn and Zn contents according to the alloys types brass, bronze and red brass. Density peaks or modes for each plot are expressed as percentages and provide information on where values are concentrated over the interval.

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Figure 9 : Bar plots of the seal matrices distribution according to alloys types and Pb content. Data are expressed as percentage of the objects total.

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Despite this apparent continuum, Pb content can be used as a criterion to distinguish three classes of alloys despite the constant overlapping (Figure 8). First, objects made of unleaded Cu-alloys with no or negligible quantities of Pb constitute a first group including a majority of the brass (54%) and unalloyed copper (91%) objects, as well as 14% of the Zn-rich red brass objects. Second, objects made of leaded copper-based alloys form a second group which encompasses a large majority of the bronze (90%), Sn-rich red brass (85%), red brass (75%) and Zn-rich red brass (52%) objects. Finally, slightly leaded copper-based alloys constitute an intermediary group including 27% of the brass objects, 33% of the Zn-rich objects, 16% of the red brass objects, and a few bronze, Sn-rich red brass objects, with only one unalloyed copper object being slightly leaded.

286

287 **4. Discussion**

288 *4.1. Seal matrices fabrication*

289 As for the few Cu-alloyed objects for which the metallographic investigations were carried out, it is
290 most likely that all the bronze, brass, Sn-rich red brass, red brass and Zn-rich red brass objects have
291 been cast. Interestingly, Cennino Cennini 1437 treatise on arts offers a brief description of a possible
292 process performed to take impression of either a seal or a coin (Cennini and Herringham, 1922, chap.
293 189), using a moulding material, made of ashes, salt and water:

294 *“Then on this paste take impression of seals, medals, figurines, coins, or in general of anything of*
295 *which you desire impressions. This done, let the paste dry gradually without sun or fire. You may*
296 *pour on this paste the melted lead, silver, or any metal you please, for the paste is sufficiently*
297 *tenacious to bear a great weight.”*

298 This description actually refers to the first step of matrices fabrication process. This consists of casting
299 a primary form, the semi-finished object, to be then decorated using engraving techniques. At this step
300 of the process, some of the details of the central motifs might have been moulded, even if this remains
301 difficult to confirm as traces of engraving were observed on all the central motifs of the objects. The
302 mould, here described as a mixture of ashes, salt and water might also well have been in stone, metal
303 or clay.

304 Thus, three distinct steps of the production process were most probably carried out to produce the final
305 object. The semi-finished matrix is first cast and prepared, including a light hammering of the surface
306 in order to obtain a perfectly regular and flat surface, as exemplified by the cross sections observed in
307 the framework of this study (Figure 4). The drawing composition is then set up and the central motif
308 engraved or enhanced by engraving if pre-moulded. Finally, as exemplified by the two incomplete seal
309 matrices shown by Figure 10, the inscriptions, including most of the time the name of the owner, were
310 realized all around the edge. The question of the craftsmen in charge of the fabrication process is
311 beyond the scope of the present paper and will be discussed in a forthcoming publication.

312



Figure 10 : Incomplete seal matrices (Mat. 649 and Mat.763) revealing that the central motif is realised prior to the inscriptions.

4.2. Alloys technical specificities

We can say with confidence that none of the alloys encountered in our study would bring any difficulty during the fabrication process of the semi-finished product. Indeed, small size objects are relatively easy to cast regardless the nature of the copper-based alloy employed.

That said, the addition of Pb can reasonably be associated to a low level of alloy quality. Indeed, even if it reduces its fusion temperature, improves the castability of the metal when added in significant amount (from 10-15%) (Mille et al., 2010) and has the property to make the metal softer, this addition might have been decided upon for economic reasons rather than technical constraints. The addition of Pb could make the objects difficult to engrave as it is not miscible in the Cu-alloy and forms nodules at the grain boundaries, resulting in hardness heterogeneity in the metal. Furthermore, a metal too soft would also produce fuzzy engravings. This aspect will be explored in a forthcoming publication.

Conversely, the addition of Zn reduces the alloy porosity. Since fusion of Zn occurs at relatively low temperature (420° C) compared to Cu(1085° C), Zn vapours escape from the molten metal, carrying impurities and gas : the alloy obtained is purified and deprived from asperities (Campbell, 2015, p. 7). Due to this Zn loss, it is impossible to estimate the initial Zn content before the fusion of the metal takes place. This cleansing property of Zn is of particular interest when engraving as it provides a

332 homogeneous material, free from irregularities. This is even more noticeable if the alloy is deprived of
333 Pb as it is the case for a large majority of brass objects in our study. However, Zn also has the property
334 to form a barrier at the surface of the molten metal, therefore, when small crucible are used, the Zn
335 loss is moderate (Gaffiero et al., 2011). Craftsmen might have found a good compromise between a
336 clean metal, a sufficient amount of Zn remaining in the metal and production costs.

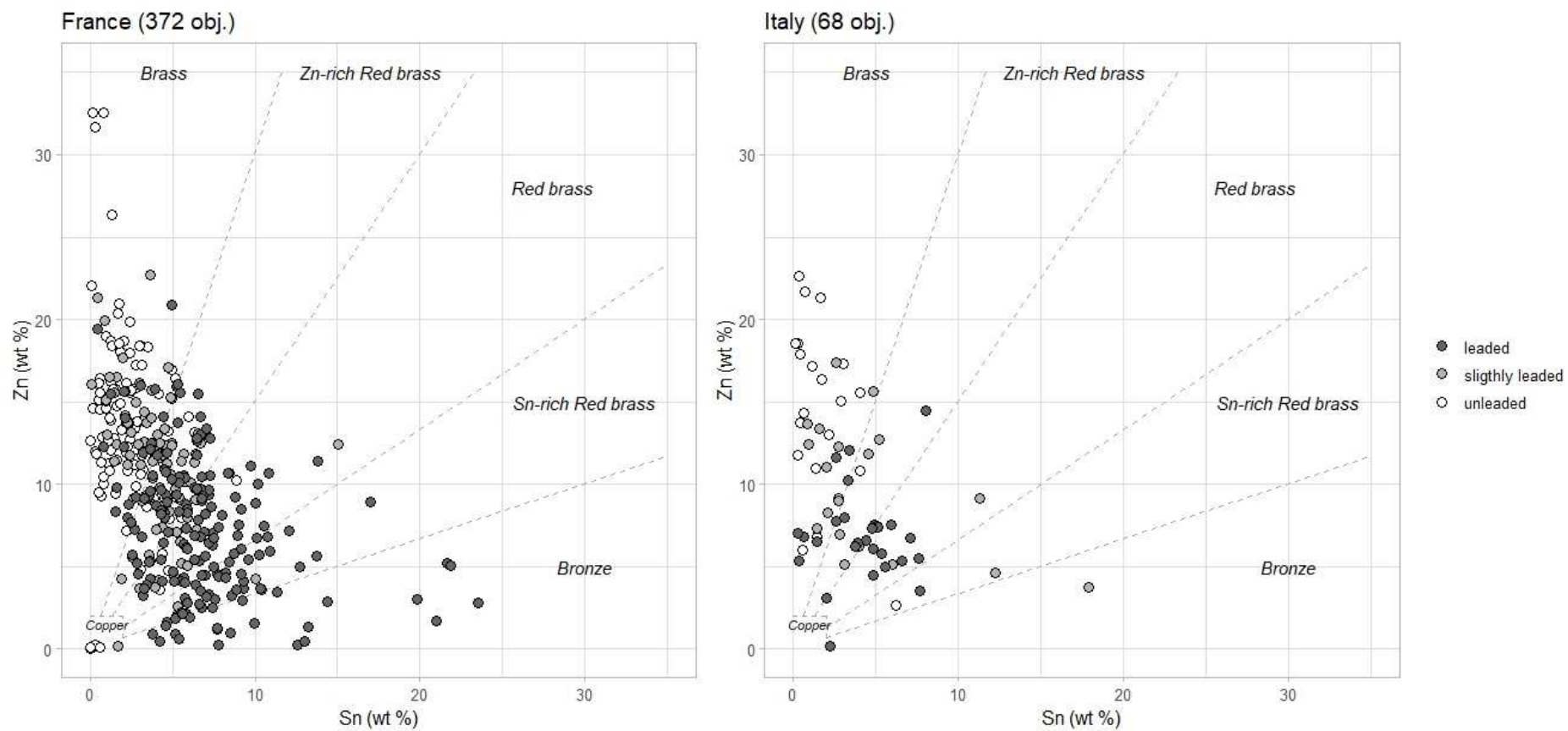
337 Although the type of alloy does not affect the semi-finished matrix fabrication, it induces variation of
338 colour and, by consequence, influence the general aspect of the objects. Indeed, brass alloys would
339 produce a bright goldish colour whereas bronze alloys a brown-grey one (Bourgarit, 2003).
340 Considering that the matrices were often openly carried by the *sigillant* as an ornamental accessory,
341 the colour would have most likely been of great importance.

342 4.3. Particularities in question: typology, chronology, geography

343 With regard to other small medieval artefacts, the wide range of alloys documented by the present
344 study demonstrates the absence of specificity related to the typology of the seal matrices. High and
345 late medieval small copper-based objects, including mounts, buttons, and other fittings items,
346 excavated at Leopoli-Cencelle, Italy (Gaudenzi Asinelli and Martínón-Torres, 2016), were made of
347 some of the alloys identified in our study, namely, on one hand, unleaded and leaded brass and Zn-rich
348 red brass, and, on the other hand, slightly leaded bronze, with only a few exception being made with
349 leaded brass and unleaded bronze. Therefore, in this case, slightly leaded bronze could be associated
350 with bell casting, an already established alloy specificity linked to the typology of the objects (Neri,
351 2018). This does not exclude the use of this alloy for other productions. The medieval dress
352 accessories analysed in the 90's (Heyworth, 1991) enables further questioning the correlation between
353 the composition of the alloy and the typology of the objects. For most of the objects analysed,
354 including similar objects as those found at Leopoli-Cencelle, compositions do not seem to be
355 correlated to the object categories: a wide range of copper-based alloys was documented, echoing the
356 results of the present study. In addition, if the material excavated in a late medieval Parisian workshop
357 (Bourgarit, 2012) had revealed some specificities of the alloys linked to the shaping techniques, and so
358 the typologies of objects, small cast objects constitute a coherent group, either made of low leaded red
359 brass or brass, two alloys encountered within the group of seal matrices.

360 The comparison between French and Italian seal matrices showed no regional specificities according
361 to the metal composition (Figure 11). The same range of composition was documented for both French
362 and Italian productions, suggesting a transborder practice which took advantage of the available
363 copper-based alloys. This produces very interesting considerations in relation to workshop technical
364 knowledge and attribution. Indeed, the nature of the alloy should not be used to support any argument
365 on provenance of the object; however, it does provide a new vision of a common tradition developed
366 in several European areas during Medieval and Early Modern times.

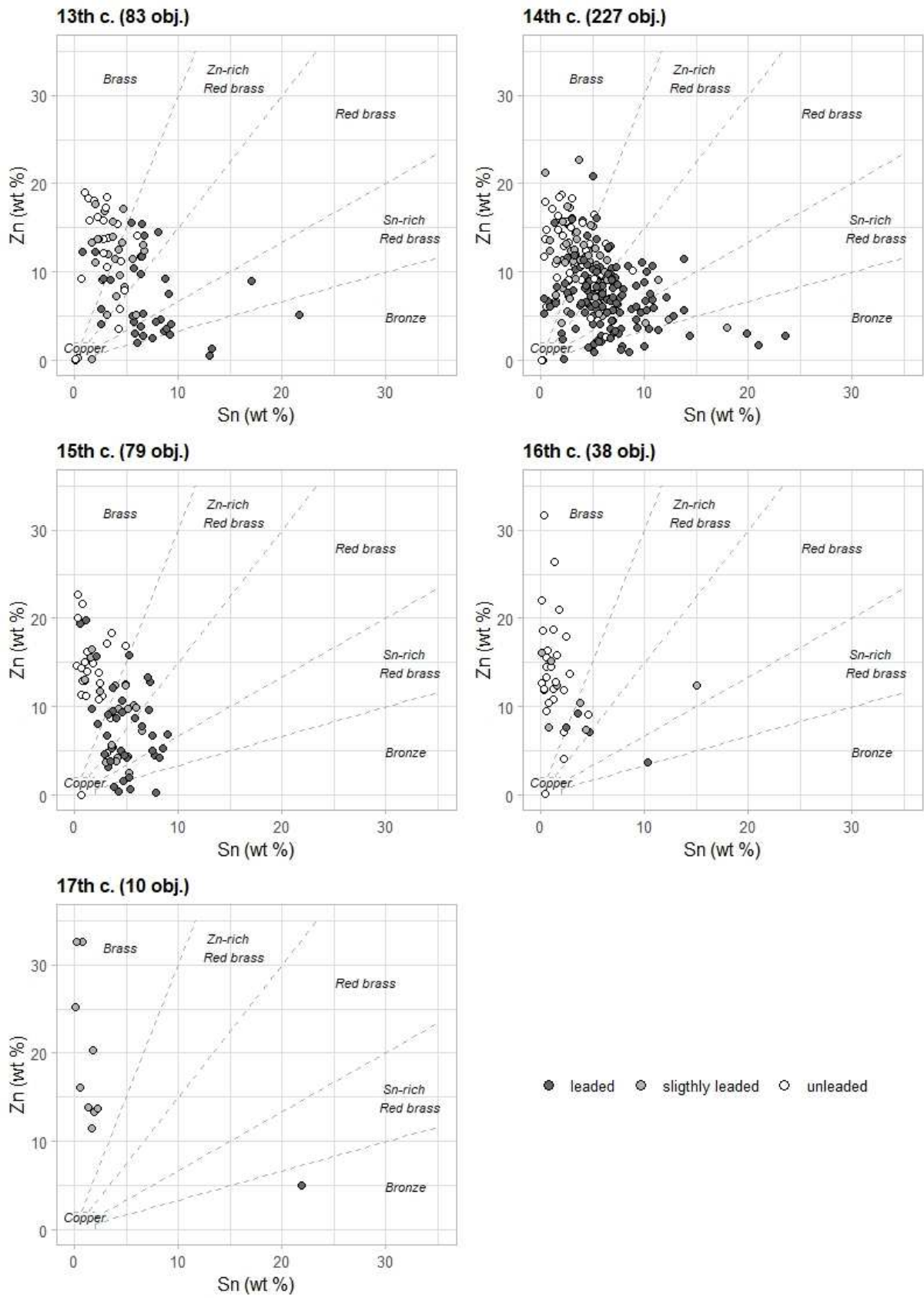
367 Regarding the chronology (Figure 12), similar alloy distributions were highlighted for the 13th and the
368 14th c., in the form of a continuum ranging from brass to bronze alloys. From the 15th c., bronze alloys
369 tended to be rare, with only a few exceptions, leading to a more important representation of Zn-
370 containing alloys, and in particular brass from the 16th c. onward. The ten matrices dated from the 17th
371 c., are all made of unleaded and slightly leaded Cu-Zn alloys, predominantly brass, with one matrix
372 being made of Zn-rich brass. That said, this later distribution should only be considered with caution
373 due the lower number of objects analysed from the 16th and 17th c.



374

375

Figure 11 : Sn, Zn and Pb contents (wt%) of the seal matrices from France (A) and Italy (B)



376

377

Figure 12 : Sn, Zn and Pb contents (wt%) of the seal matrices produced during the 13th -17th century period.

379 Brass alloy compositions reveal a clear willingness to keep these alloys free of Pb, whose contents
380 rarely exceed 6 wt% for 83% of the brass objects, with a very narrow 1.5 wt% mode (Figure 8). Such
381 a specific selection of brass alloys with about 14 wt% Zn (Figure 8) could be linked to the constraint
382 of valuable commissions requiring very specific aspects for the objects, and thus a very specific
383 composition. In addition, this rather narrow composition could indicate that the metal was freshly
384 prepared, as other authors have proposed (Gaudenzi Asinelli and Martín-Torres, 2016).

385 Conversely, bronze alloys exhibit a wider range of Sn and Pb contents compared to Zn contents in
386 brass alloys (Figure 8). This suggests that bronze alloys were less strictly controlled than Cu-Zn
387 alloys. Several hypotheses can be built on this. First, bronze alloy compositions may vary between
388 several workshops according to the local technical tradition of foundry-men. Second, depending on
389 economical constraints, e.g. the budget of the customer, the alloy composition might have been
390 adapted in order to reduce the cost of the seal matrices, adding more or less Sn and Pb. Finally, bronze
391 alloys could originate from the recycling of various bronze objects in which Sn and Pb contents may
392 vary.

393 Regarding red brass alloys, whether rich in Zn or Sn, the hypothesis of recycling objects as raw
394 materials seems particularly convincing given the wide range of composition encompassed by the
395 group, from (0-30 wt% Pb, 3-15 wt% Sn, 3-15 wt% Zn). This could constitute an intermediary state
396 resulting from the mixing of controlled brasses and random bronzes – sometimes leaded bronzes.

397 As all steps of seal matrix fabrication are identical whatever the alloy used, this latter can be
398 considered as the main factor in price variation, notwithstanding the relatively small size of the objects
399 and so the relatively small amount of materials required, as well as the possible low share of the
400 material costs compared with the cost of engraving. Despite the lack of sources documenting prices of
401 metals and alloys during the production period of the studied seal matrices, a few considerations help
402 the understanding of the relative price of one alloy type in respect to the others. First, as a result of the
403 cementation process, brass alloys were more expensive due to the very technical nature of their
404 production and involve complex technical knowledge (Bourgarit and Thomas, 2011; Pollard and
405 Heron, 2008, p. 20; Thomas and Bourgarit, 2018). Second, bronze alloys were relatively easily
406 produced and less expensive, despite the fact that Sn was probably more expensive than Cu. Finally,
407 leaded alloys, and especially leaded bronze, were among the cheapest Cu-alloys, as Pb was an
408 available resource and principally used to reduce the production cost of Cu-alloys. Consequently, seal
409 matrices with high Zn and low Pb contents constituted most in all probability the most expensive
410 objects. Interestingly, Etienne Boileau *Livres des métiers* (Boileau, 1879, pp. 79–80) talks about “*bon*
411 *lato*” in a sense of “good brass” that neither contains Pb or Fe and designates seal matrices and other
412 kind of buckles under the term “*menue oeuvre*”, small objects made of Cu-alloys by foundry-men. But

413 this book does not specify why such an alloy should be considered as good, and what its composition
414 was. Indeed, as far as Cu-Zn alloys are concerned, Zn ores naturally contain impurities that migrate
415 together with Zn into the final Cu-metal (Bourgarit, 2012). As Pb can be one of those impurities, it is
416 safe to assume that under a few percent, the presence of Pb, although well known by craftsmen based
417 on the ore colour, as for Fe, could not have been intentional. Thus, brass alloys employed to cast seal
418 matrices should be considered as “good brasses” whereas bronze and red brass objects, whether rich in
419 Sn or Zn, might correspond to lower value productions in particular when leaded.

420 This question of alloys values during Medieval periods has been raised by the study of both everyday
421 objects such as cauldrons and more prestigious productions such as lecterns, candlesticks, aquamaniles
422 and (Dandridge, 2006; Thomas and Bourgarit, 2014). Brass alloys are reserved for the latter, whereas
423 bronze alloys possibly leaded, are used for the former. The economic criterion is perhaps one of the
424 most important issues in the choice of alloys. In this sense, the investigation of the remains of a late
425 medieval workshop excavated in Paris (Bourgarit, 2012) reveals another economic constraint probably
426 linked to the typology of the objects produced: the small cast artefacts are either made of brass or
427 slightly leaded red brass (Sn-rich or Zn-rich red brass), whereas middle size castings are made of
428 leaded metals, either red brass, brass or copper. Thus, within the corpus of seal matrices, different
429 levels of quality of alloys are encountered. Unleaded alloys (mostly unleaded brass and Zn-rich red
430 brass) presenting a goldish aspect could have been used to cast more expensive copper-based objects.
431 These objects might constitute an intermediary production, less expensive than silver objects. On the
432 contrary, leaded alloys (mostly leaded bronze, Sn-rich red brass and red brass) were most probably
433 cheaper. Finally, the question of objects made of unalloyed copper remains difficult to answer,
434 considering the poor representativity compared to the large number of studied seal matrices. Whether
435 these objects – soft, easy to corrode – were rare because of the colour and the properties of the alloy
436 remains unclear.

437 Therefore, despite the control by official instance operated over the production of seal matrices
438 (Vilain, 2015), it appears clear that some adjustments regarding the materials employed were made
439 possible. These adjustments were probably influenced by the wealth of the *sigillant*. This will be
440 further discussed in a forthcoming publication.

441 **5. Conclusion**

442 A large number (466) of Cu-based seal matrices from the French National Archives and the Fine Arts
443 Museum of Lyon was analysed during this study. This paper offers an extensive view of the technical
444 landscape of seal matrix production during European Middle Ages and Early Modern periods, from
445 the perspective of the materials and techniques involved.

446 The objects had made of a large range of unleaded and leaded Cu-based alloys including unalloyed
447 copper, bronze, brass and red brass, more or less rich in Sn and Zn, and their leaded counter parts.
448 That said, looking at the Pb contents produces interesting considerations regarding the level of quality
449 of the matrices. Different levels could be identified within the body of objects. On one hand, unleaded
450 alloys (mostly brass) could have been used for high level quality productions. On the other hand,
451 leaded alloys (mostly bronze but also Sn-rich red brass, red brass and Zn-rich red brass) could have
452 been reserved for a lower level quality production. Adjustments regarding the materials employed had
453 certainly been made according to the budget of the commissioner, local traditions of the production
454 workshop and availability of raw materials. As for the fabrication techniques, a multi-step process was
455 documented. In all probability, the Cu-alloyed semi-finished objects had all been cast. Central motifs
456 had then been engraved, and finally lettering had been placed all around. Within the investigated body
457 of objects, comparison between French and Italian productions made possible to document transborder
458 practices, regarding both the materials employed and the fabrication techniques involved. With regard
459 to the chronology, similar ranges of alloys were documented for the period between the 13th and the
460 14th c. From the 15th c. to the 17th c., despite the lower number of objects investigated, alloys
461 containing Zn are well represented, whereas bronze alloys become progressively rare. In addition, for
462 the earliest objects investigated, the legend was always engraved, letter by letter and the traces of
463 engraving tools are easily observable at high magnification. Starting from the 14th c. and becoming
464 more common through the 15th c., letters had been formed by combination of simple stamps
465 associated together to form each letter. Then, during the 16th c. it became more common to have letters
466 formed with letter-punches, one punch corresponding to one letter of the alphabet. This evolution of
467 practices not only implies a modification of technical knowledge, but also the development of new
468 tools within the workshops.

469 From a methodological point of view, this study confirms the potential of pXRF methods for the
470 characterisation of copper-based alloys by implementing a rigorous calibration protocol of the device,
471 and a careful control of the post-acquisition treatment. In addition, this work underlines the possible
472 bias of analyses carried out on altered objects, covered by a natural patina.

473

474

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483 **Competing interests**

484 The authors declare that they have no competing interests.

485 **Availability of data and materials**

486 All experimental details can be available from the corresponding author on reasonable request.

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