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# War and commercial exchanges in the late medieval Aegean: investigating the metal provenance of the Chalcis hoard

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## Abstract

At the end of the Middle Ages the Aegean was an active trade area, connected to numerous exchange networks. Arms and armor were strategic products, exchanged over extra-regional distance through the Mediterranean trade. To shed light both on military goods manufacturing and Aegean trade networks, this paper focuses on the archaeometric examination of thirteen medieval pieces of armor found in Chalcis (Euboea Island, Greece), then a Venetian hub. Our aim was to perform a provenance study of the metal, based on the LA-ICP-MS analysis of trace rare earth elements in the slag inclusions of the metal artefacts, combined with statistical approaches to compare the chemical signatures with published reference groups. Until now most of these objects were considered imported from northern Italy, whereas the chemical approach highlighted several subsets. Seven samples have a chemical signature compatible with a reference group of Italian style defenses, while others present different chemical tracers such as high Titanium content, that could indicate the use of regional metal resources (Macedonia). These results bring new insight into the Aegean trade network opening the door to more extensive studies in the area.

Keywords : Archaeometallurgy, iron artefacts, arms and armor, provenance study, Middle Ages

## 1. Introduction

31  
32

33 The late medieval Aegean was marked by multiple conflicts for the control of land and sea territories  
34 and saw encounters between various communities (Byzantine, Latin, Turkish...). In this context, arms  
35 and armor were commodities of crucial importance, exchanged through the Mediterranean trade but  
36 also through the looting and reuse of weapons collected by the soldiers on the battlefield. While  
37 written sources provide crucial information on the trade routes (Sprandel, 1970; Valérian, 2017), they  
38 remain insufficient to assess the importance of these exchanges on a regional scale. Hence artefacts  
39 are precious witnesses, whose study is essential to detail the morphology of exchange networks.  
40 Although archaeometric investigations have been performed on European armor for several decades  
41 (Bérard, 2019; Bérard et al., 2020; Böhne, 1961; Brewer, 1981; Imiołczyk et al., 2020; Kraner et al.,  
42 2019; Leever, 2005; Williams, 2011, 2003; Williams et al., 2012; Williams and De Reuck, 1995), few  
43 were made on medieval ones. Hence, the hundreds of armor discovered at Chalcis (Ffoulkes and  
44 Traquair, 1911; Kontogiannis, 2012) constitute valuable evidence to document the eastern  
45 Mediterranean network exchanges and the history of armor making.

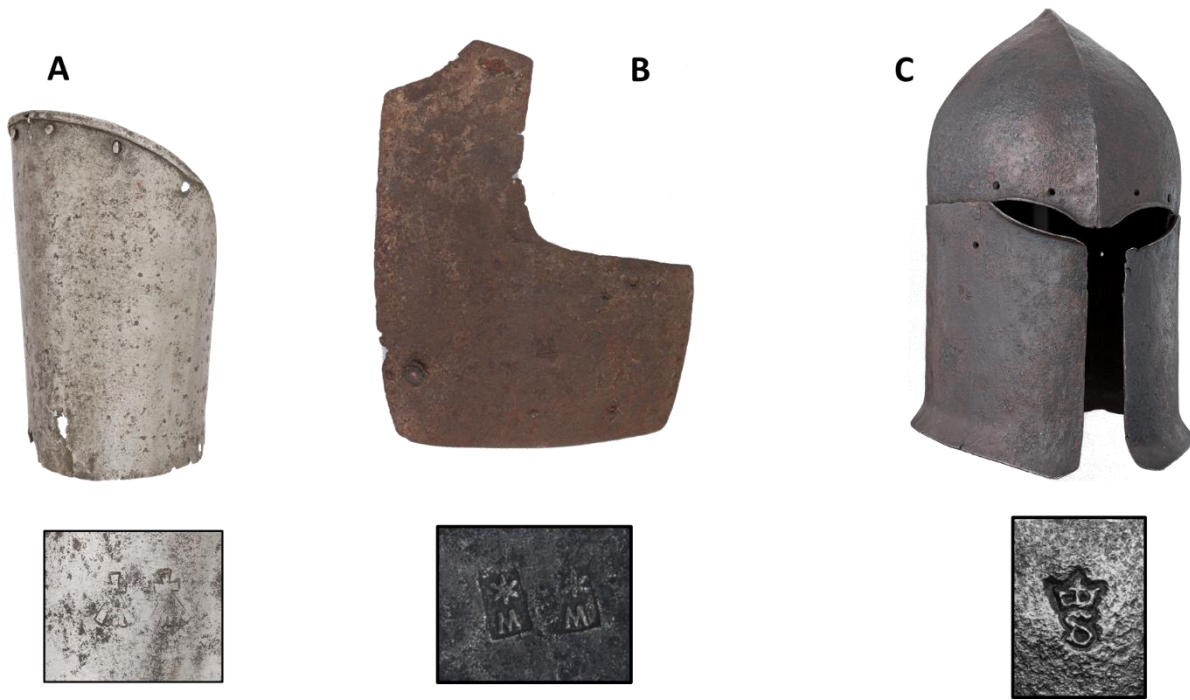
46 This set of artefacts includes over 400 objects, the majority of which are typo-chronological dated to  
47 the 14th and early 15th centuries. The set was discovered in 1840 in the ancient fortress of Chalcis  
48 (Euboea Island) when, according to the historian Jean-Alexandre Buchon, a wall (whose present  
49 location is unknown) collapsed. At the end of the Middle Ages, Chalcis was a Venetian hub named  
50 Negroponte. The terminus ante quem of the hoard is dated to 1470, when the city fell to the Turks  
51 (Ffoulkes and Traquair, 1911; Kontogiannis, 2012). Soon after their discovery they were first stored in  
52 Athens in the Ethnological Museum where in 1919-1920, Bashford Dean, curator at the Metropolitan  
53 Museum of Art (New York), acquired about two hundred pieces (Dean, 1925). Following his death in  
54 1928 they were kept in the MET. Today the hoard is dispersed among several collections, most of the  
55 pieces being kept in the MET and in the National Historical Museum (Athens).

56 The majority of the pieces were originally identified by scholars as of western European manufacture  
57 (Dean, 1925). Of important interest are the armorers marks still preserved on some pieces, attributed  
58 to Italian workshops (see an example Figure 1, "A" showing a mark attributed to the Milanese Missaglia  
59 workshop), leading to assume that almost all of the hoard was Italian made and imported by the  
60 Venetians. Nevertheless, this Italian-centric perspective needs to be reexamined. Some of the marks  
61 applied has not been linked to any known workshop or armorer. Furthermore, the mobility of skilled  
62 Italian craftsmen is attested in many parts of Europe (La Rocca, 2017; Painsonneau, 2004, p. 25; Reppel,  
63 2008) but also in the Aegean, notably in Genoese and Venetian territories (Balard, 1978; Racine, 1995;

64 Thiriet, 1975). In addition, it is possible that Italian-style objects not bearing marks were made by local  
65 craftsmen reproducing the Italian style. Part of the artefacts shows particular stylistic features only  
66 known from Chalcis and other Aegean sites, that do not fit an Italian-style, (such as the two pieces  
67 sallet shown on Figure 1, "C"). Their distinctive morphology and multi-piece assemblage have led to  
68 the assumption of a regional production, especially in Dalmatia (Blair, 1982), while some objects of  
69 Turkish style (kept at the National Historical Museum in Athens) would rather suggest a Middle East  
70 origin (Kontogiannis, 2012). The complexity of the hoard also underlines its historical importance, as it  
71 reflects war practices (such as looting), the mobility of weapons and soldiers and the variety of  
72 communities involved in the medieval Aegean.

73 Investigations of the ferrous alloys can provide answers to these open questions. Although a first  
74 metallographic examinations has been already published on a few Chalcis samples (Williams, 2003),  
75 crucial questions regarding the nature and origin of the metal used remains unexplored. Several  
76 methodologies have been proposed to shed light on the metal provenance based on the comparison  
77 of isotopic signature (Brauns et al., 2020, 2013; Degryse et al., 2007; Dillmann et al., 2017; Milot et al.,  
78 2021, 2016; Schwab et al., 2006), major (Blakelock et al., 2009; Buchwald and Wivel, 1998; Charlton et  
79 al., 2012) and lithophile trace elements ratios (Coustures et al., 2006, 2003; Desaulty et al., 2009; Disser  
80 et al., 2016; Leroy et al., 2012, 2011; L'Héritier et al., 2020, 2016; Pagès et al., 2022) in slag inclusions  
81 (SI). The latter approach is based on the follow-up of the chemical signature from the initial ore to the  
82 SI that remains entrapped in the metal artefact. During the bloomery process used to transform ore  
83 into metal, some of the chemical elements ("non reduced compound' NRC) are not reduced and  
84 remain in the same proportion in the slag left as a waste at the ironmaking site. This chemical signature  
85 is also preserved in the small parts of the slag entrapped in the metallic matrix, under the form of  
86 inclusions. Thus, by determining the chemical composition of SI both in terms of major and lithophile  
87 trace elements and by comparing it with available reference data, it is possible to evaluate the  
88 compatibility of the ferrous alloys. Several analytical techniques have been used, tailored to those SI  
89 (< 30µm, see Figure 2) found in armor, such as µ-XRF (Leroy et al., 2011) and LA-ICP-MS (Bérard et al.,  
90 2020). The latter methodology has recently allowed to quantify about fifteen trace elements in armor  
91 samples, highlighting ancient exchange networks and trade, such as in Lombardy, a reputed area of  
92 steel and arms and armor manufacture(Bérard et al., 2020), and from which some of the Chalcis pieces  
93 may have been produced.

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*Figure 1 – Examples of armor from Chalcis examined, “A” upper arm defense with an Italian mark detail (Milanese Missaglia workshop) shown on the reverse side (MMA 29.150.57), “B” brigandine plate (MMA 29.150.90ii) with a mark M surmounted by a star, “C” Helmet defense (MMA 29.158.42) with specific stylistic features different from Italian-style armor of the same period and a mark S surmounted by a crown*

100 In this paper, we present a first provenance study of thirteen armor from Chalcis in the collection of  
101 The Metropolitan Museum of Art (New York), based on the analysis of lithophile trace elements in SI,  
102 combined with statistical approaches. Our aim is to estimate the variability of the supply sources  
103 through the investigation of the metal and compare their chemical signature with reference sets of  
104 European armor previously defined (Bérard et al., 2022, 2020).

105

## 106 2. Set of artefacts

107

108 Thirteen artifacts were selected for analysis (see Table 1), according to the condition of their metal  
109 surfaces. Three of the marks applied on the pieces studied (MMA 29.150.57, MMA 29.150.18, .115,  
110 and MMA 50.160) have been identified in the literature devoted to Italian armor (Boccia, 1982). The  
111 others remain unidentified but the brigandine breastplates marks (MMA 29.150.90ii, MMA  
112 29.150.90oo, MMA 29.150.90t) and mark on piece MMA 29.158.42 are assume to be of Lombard origin  
113 (Eaves, 2014 ; Boccia et al., 1980). Piece MMA 29.150.18, .115 is a composite piece of the lower  
114 vambrace (forearm defense) 29.150.18 and the couter (elbow defense) 29.150.115. The two elements  
115 belonging to the Chalcis hoard were united in the MET.

116 As ancient ferrous alloys can be heterogeneous and likely to present several chemical families of SI,  
 117 sampling size and location were chosen to ensure a minimum alteration for the artefact while  
 118 guaranteeing the representativeness of the results. Thus, delamination areas on the plates have been  
 119 avoided and sample size was fixed to about 6mm long and 2mm wide, the thickness of the sample  
 120 corresponds to that of the armor plate. Samples were collected with a small rotary cutting tool and a  
 121 diamond-coated blade.

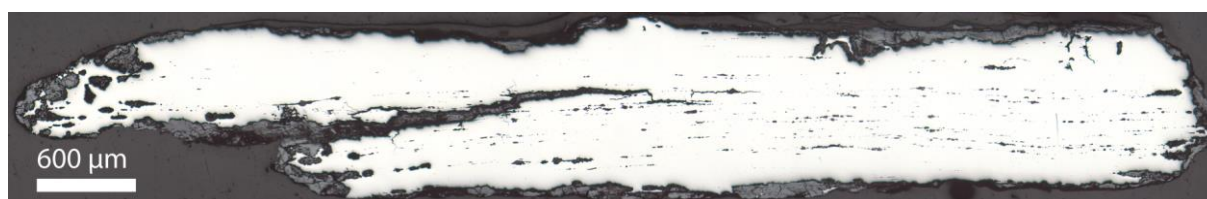
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*Table 1 – Pieces selected for study*

Identification Number	Category	Sub-category	Date	Type of mark	Sample(s) number	Additional information
<b>MMA 2005.466.4</b>	Torso defence	Small plate from brigandine	ca. 1450	-	2005-466-4	
<b>MMA 29.150.105</b>	Torso defence	Coat of Plates, or Brigandine	ca. 1400	-	29-150-105	
<b>MMA 29.150.18, .115</b>	Arm defence	Forearm defense (Vambrace)	15th century	Split cross with double S	29-150-18.22	
	Arm defence	Elbow defense (Couter)	15th century		29-150-18.1	
<b>MMA 29.150.57</b>	Arm defence	Upper arm defense (Rerebrace)	ca. 1430–40	M with cross and split leg (attributed to Missaglia)	29-150-57	
<b>MMA 29.150.90ii</b>	Torso defence	Large plate from brigandine	1400–1450	M surmounted by a star	29-150-90ii	
<b>MMA 29.150.90oo</b>	Torso defence	Large plate from brigandine	1400–1450	M surmounted by a star	29-150-90oo	
<b>MMA 29.150.90t</b>	Torso defence	Large plate from brigandine	1400–1450	Letter B mark	29-150-90t	
<b>MMA 29.158.42</b>	Head defence	Great sallet	possibly 1420–50	S surmounted by a crown	29-158-42	stylistic features only known from Chalcis and the Aegean
<b>MMA 49.120.7</b>	Head defence	Lower plate of a bascinet	early 15th century	-	49-120-7	stylistic features only known from Chalcis and the Aegean
<b>MMA 50.160</b>	Arm defence	Left vambrace	ca. 1400	YO with cross and split leg	50-160g	
<b>MMA 49.120.5</b>	Head defence	Lower plate of a bascinet	early 15th century	-	49-120-5	stylistic features only known from Chalcis and the Aegean
<b>MMA 49.120.8</b>	Head defence	Lower plate of a bascinet	early 15th century	-	49-120-8	stylistic features only known from Chalcis and the Aegean

MMA unacc#1	Torso defence	Small plate from brigandine	ca. 1450	-	unacc1	
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125 *Figure 2 – Optical micrograph of a sample cross section (29.150.90t) showing slag inclusions entrapped in the metallic matrix.*

126

### 127 3. Materials and methods

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129 Samples were embedded in epoxy resin and studied in cross section. They were grinded using abrasive  
 130 papers (MICRO-MESH™ REGULAR, grade 1800-4000). Final polishing was performed using diamond  
 131 polishing media of 9μm, 3μm and 1μm. The major compositions of the SI were determined using  
 132 Energy Dispersive Spectrometry (EDX with silicon drift detector) coupled with a Scanning Electron  
 133 Microscope (SEM-FEG JEOL 7001-F) at the LAPA-IRAMAT-NIMBE laboratory (France). A probe current  
 134 of about 8 nA and a 15 kV accelerating voltage were used. To pursue a provenance study using  
 135 lithophile elements in SI, it is necessary to determine the major elements compositions of a statistically  
 136 representative number of SI (a minimum of 40 SI is recommended (Dillmann and L’Héritier, 2007)). In  
 137 our case, this condition was met by analyzing the chemical composition of the SI on the entire cross  
 138 section of the samples. The protocol described in Bérard et al., (Bérard et al., 2020) was followed to  
 139 both detect the SI by image analysis using the Aztec particle analysis software (Oxford company), and  
 140 estimate the compositions of each SI on the whole surface of the sample. Concentrations were  
 141 determined after normalization of the total signal (considered to be 100%), of the set of elements  
 142 known as major components of iron slags (O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Fe, Mn).

143 Phosphorus is a strong chemical marker frequently found in ancient iron alloys (L’Héritier et al., 2019;  
 144 J. W. Stewart et al., 2000, 2001). Its presence in significant amount (> 0.1 wt.%) in the metal matrices  
 145 was checked on samples showing significantly elevated levels in some SI (> 2wt.%), using a microprobe  
 146 with a wavelength dispersive X-rays spectrometer (SX 100 CAMECA, accelerating voltage 15kV, current  
 147 probe about 200nA, ICMPE, Thiais, France).

148 In Europe, during the late Middle Ages, two main ironmaking processes were used: the direct (single  
 149 step: bloomery furnace) and indirect (two steps : blast furnace and finery) processes. However, no  
 150 provenance study based on the analysis of lithophile trace elements in SI can be pursue for metal

151 associated with the indirect process, as the NRC-based signature of the ore (smelting system) is lost  
152 during the separation between the metallic phase and the blast furnace slag during smelting. (Dillmann  
153 and L'Héritier, 2007; Disser et al., 2014). In order to determine if the SI families related to the smelting  
154 slag have a composition compatible with the bloomery process, the procedure proposed by Dillmann  
155 and L'Héritier (Dillmann and L'Héritier, 2007) and completed by Disser et al., (Disser et al., 2014), was  
156 followed. Contrary to other inclusion families generated by the use of fluxes during forging or by  
157 fragmentation of the SI, SI related to the smelting slag are characterized by constant NRC ratios  
158 (Dillmann and L'Héritier, 2007) (in particular %Al<sub>2</sub>O<sub>3</sub>/%SiO<sub>2</sub>, %MgO/%Al<sub>2</sub>O<sub>3</sub>, %K<sub>2</sub>O/%CaO).

159 Recycling practices, by welding several pieces of metal, also need to be addressed. Recent work has  
160 shown that, in cases where the metal is derived from the direct reduction process, recycling does not  
161 irreparably alter the chemical signature of the objects, thus allowing provenance studies to be carried  
162 out (M. L'Héritier and P. Dillmann, 2009). Such practices can be identified by the presence of spatially  
163 distinct SI families in the sample. Hence, the following procedure has been applied for each SI family  
164 identified in the samples, representative of one or more smelting slags in case of welding.

165 After selecting SI coming from the smelting stage, an average weighted major element content was  
166 calculated for each sample (Desaulty et al., 2009; Dillmann and L'Héritier, 2007; Leroy et al., 2012).  
167 This transformation evaluates a "surface weighted average composition" of all the inclusions analysed  
168 on a cross section to facilitate comparisons between the samples.

169

$$\%E^* = \sum_{i=1}^n (\%Ei \times \frac{Si}{St})$$

170 Where %*Ei* is the composition of a given inclusion, *Si* the surface of the inclusion analysed, *St* the  
171 sum of all the inclusion surfaces.

172 Discrimination between the two smelting processes (bloomery or indirect process) was made using a  
173 reference database (see Supplementary materials) (Dillmann and L'Héritier, 2007; Disser et al., 2014).

174 For each sample compatible with the bloomery process, a dozen of the biggest SI was chosen for  
175 analysis by LA-ICP-MS. Analyses were made at the Centre Ernest- Babelon-IRAMAT (Orleans) with a  
176 sector field ICPMS Element XR (Thermo Scientific) coupled to an excimer laser (ArF\*, 193 nm,  
177 RESolution S155-E, Resonetics). The methodology published in Bérard et al., (Bérard et al., 2020), was  
178 followed to calculate relative concentrations of trace elements in small slag inclusions (<30µm) found  
179 in armor samples, especially Y, Nb, Ba, La, Ce, Nd, Sm, Eu, Yb, Hf, Th, U. SI containing at least one of  
180 these elements below the quantification limit (10 × SD) were excluded for provenance analysis  
181 comparison by statistical approaches (Bérard et al., 2020).



182 Iron oxides are differentially reduced during smelting, according to the thermodynamic conditions in  
183 the furnace. Therefore, their absolute concentrations in the slag and in the SI being variable, they  
184 cannot be directly compared, and a transformation of the data is required. We have chosen to apply a  
185 log-ratio data transformation already used for the purpose of ancient ferrous alloys  
186 provenance study (Dillmann et al., 2017; Disser et al., 2016; Leroy et al., 2012).

$$187 \quad X_E = \text{Log}([E]) - \frac{1}{N} \sum_{k=1}^N \text{Log}([E_k])$$

188 Where:

189  $X_E$  is the transformed value for each element

190  $[E]$  is the measured concentration for each element

191

192 Finally, chemical signatures were compared by combining unsupervised multivariate approach  
193 (Principal Component Analysis, PCA, and PCA combined with Hierarchical Clustering Analysis, HCA) and  
194 a supervised approach (Linear Discriminant Analyses, LDA), using R software (MASS FactoMineR and  
195 gg dendro packages). The potential advantages and drawbacks of each method for provenance analysis  
196 in archaeometallurgy have been widely discussed previously (Disser et al., 2016; Leroy et al., 2012;  
197 Tomczyk et al., 2023). PCA analysis aims at representing the global dispersion of multidimensional  
198 clusters and provide information regarding the influence and relations of the variables on the cloud  
199 projection. As the last principal components are likely to contain noise, PCA can be combined with HCA  
200 to consider only the principal components that contain relevant information (approximately 90% of  
201 the total variance) (Disser et al., 2016). In this study we choose to conduct HCA based on Euclidian  
202 distance using the Ward method of agglomeration, as advised by previous studies focusing on iron  
203 provenance (Dillmann et al., 2017; Disser et al., 2016). Nevertheless, PCA results may be dominated by  
204 variables or dataset with highest variance, leading to an important overlapping. On the contrary,  
205 supervised analysis such as LDA may improve discrimination between the clusters, providing that  
206 reference data of chemical signatures have been thoroughly established (Disser et al., 2016; Leroy et  
207 al., 2012). L'Héritier et al., 2020 (L'Héritier et al., 2020) showed the interest to cross several approaches  
208 (supervised and unsupervised) to discriminate between several hypotheses in the case of ferrous alloys  
209 provenance study. Building on this work we choose to compare the results given by both LDA, PCA and  
210 PCA-HCA approaches to establish three levels of provenance compatibility between two clusters:

- 211 • high compatibility: clusters are not separable by both PCA and LDA approaches;
- 212 • compatibility probable (clusters presenting chemical similarities) : clusters separable by a LDA  
213 approach but not with PCA approach;

- incompatibility: clusters separable by both LDA, PCA and PCA-HCA approaches.

#### 4. Results and discussion

First, we will consider the major elements chemical tracers such as phosphorus and manganese. As shown in Table 2, phosphoric iron was evidenced for two samples (unacc1 and 49-120-5). The majority of the samples are characterized by low phosphorus content ( $\%wt.P^* < 0.5$ ) and high manganese content ( $\%wt.Mn^* > 1$ ) in the SI. Two samples (unacc1, 2005-466-4) are also distinguished by a high titanium content ( $\%w.Ti^* > 1$ )

Trace element ratios were compared for samples compatible with the bloomery process and exempt from values below the quantification limit ( $10 \times SD$ ) for each measured trace element (dataset are available in Supplementary materials). Thus samples 49-120-5, unacc1 and 49-120-8 that did not meet these conditions are excluded in the following.

A Principal Component Analysis made on the transformed value of the trace elements concentration confirmed that one sample (2005-466-4), present a different chemical signature from the other samples, in particular in terms of Th, U and Hf contents (see Figure 3). The other principal components are shown in Supplementary materials.

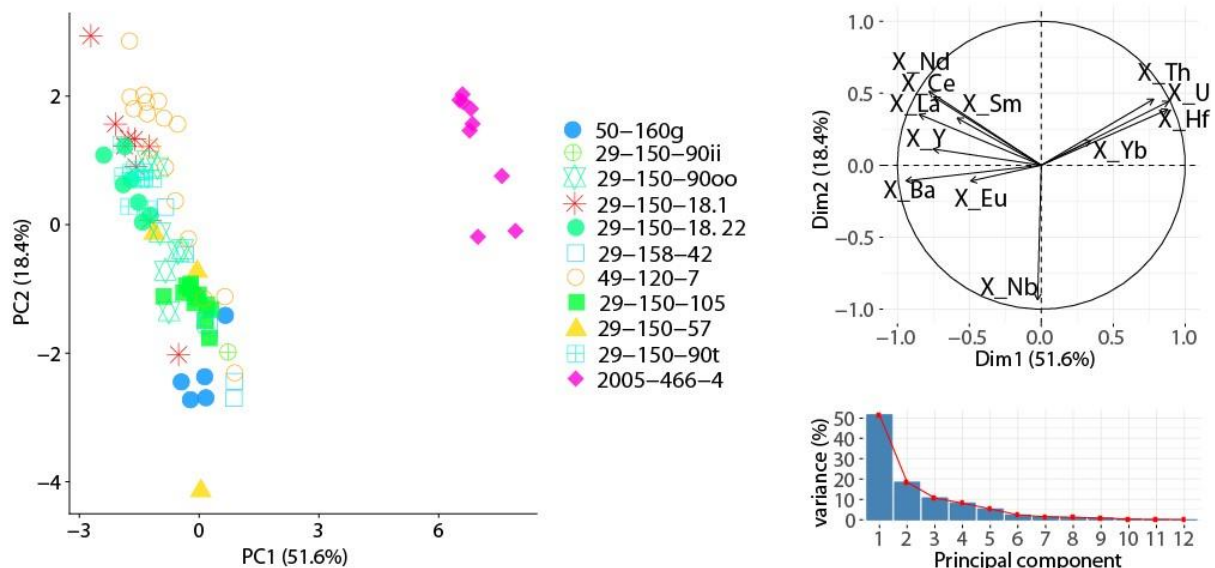
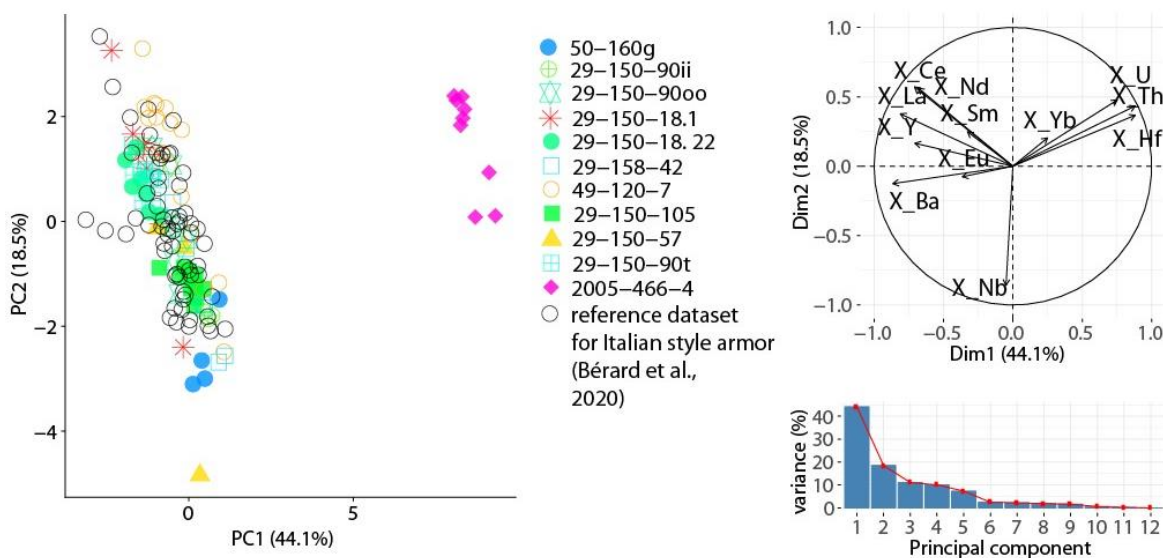


Figure 3 - PCA carried out on the transformed data of SI originating from Chalcis armor projected onto PC1 and PC2 (other components are available in Supplementary materials)

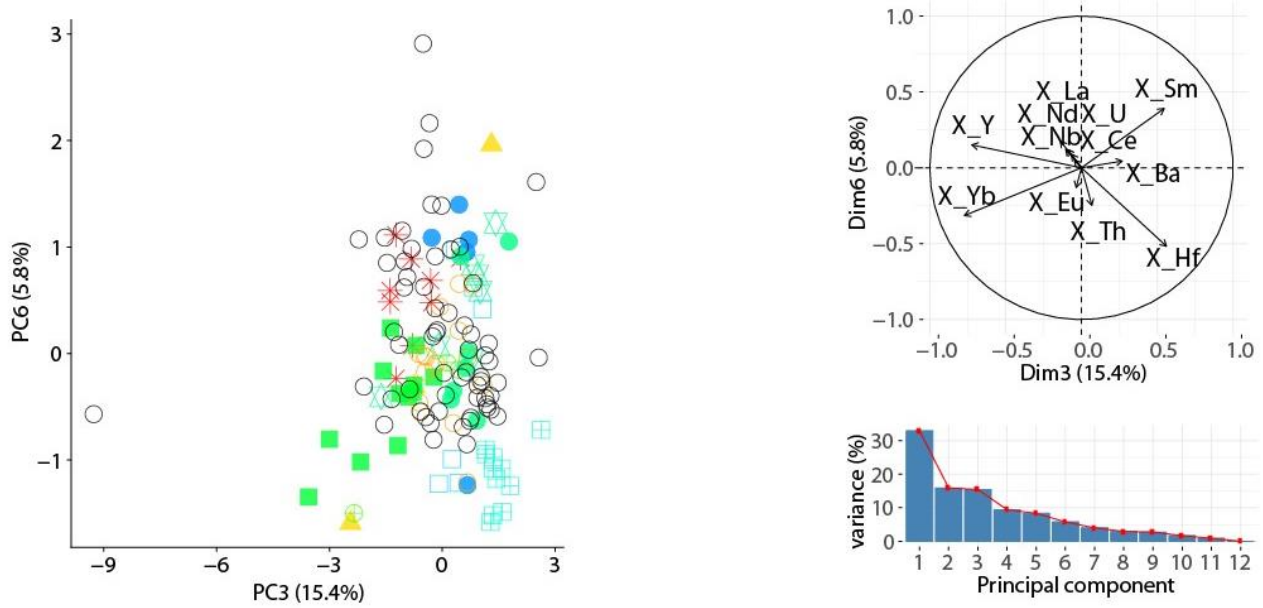
As the majority of the Chalcis armor was assumed to be of Italian manufacture, their chemical signature has been compared with a reference dataset of Italian-style armor analyzed by Bérard et al., (Bérard et al., 2020). The chemical signature of this group has been fully characterized and constitutes a first

237 reference set associated with an Italian armor style. Except for two samples, PCA results show that the  
 238 Chalcis armor and the reference dataset of Italian-style armor overlap into the same cluster, suggesting  
 239 a common provenance of the metal. Sample 2005-466-4 is clearly isolated and characterized by the  
 240 presence of X\_Th, X\_U and X\_Hf, opposed to X\_Ba variable(see Figure 3). After excluding sample 2005-  
 241 466-4, sample 29-150-90t is slightly detached from the reference dataset of Italian-style armor,  
 242 particularly by the X\_Hf variable (see Figure 5). To confirm this observation, a HCA was made on the  
 243 principal components of the PCA that cumulate about 90% of the variance, using the Ward's method.  
 244 Sample 29-150-90t is isolated on one main branch (see Figure 6).



245  
 246 *Figure 4 - PCA carried out on the transformed data of SI originating from Chalcis armor and the reference dataset for Italian*  
 247 *style armor (Bérard et al., 2020) projected onto PC1 and PC2*

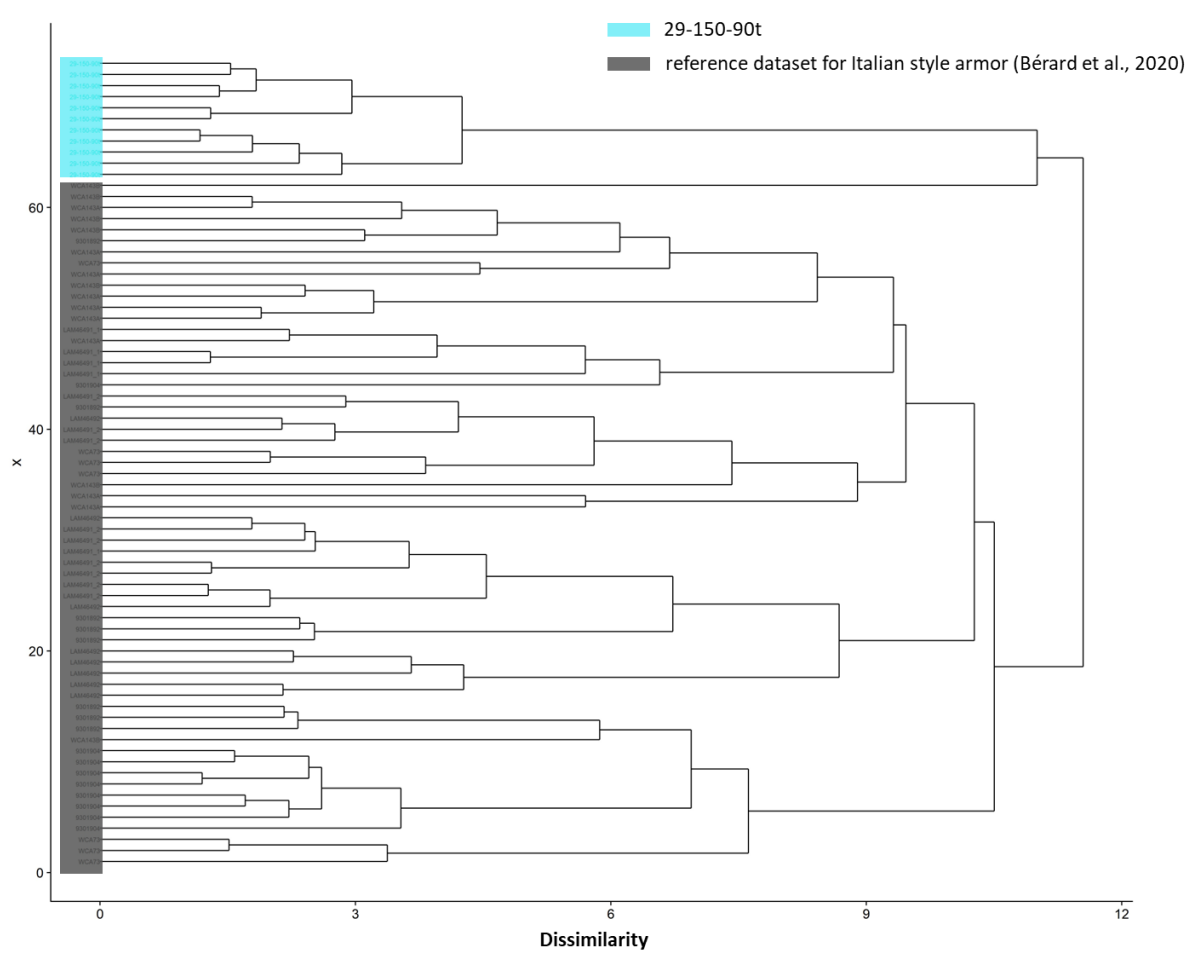
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Figure 5 - PCA carried out on the transformed data of SI originating from Chalcis armor (sample 2005-466-4 excluded) and the reference dataset for Italian style armor (Bérard et al., 2020) projected onto PC3 and PC6



252

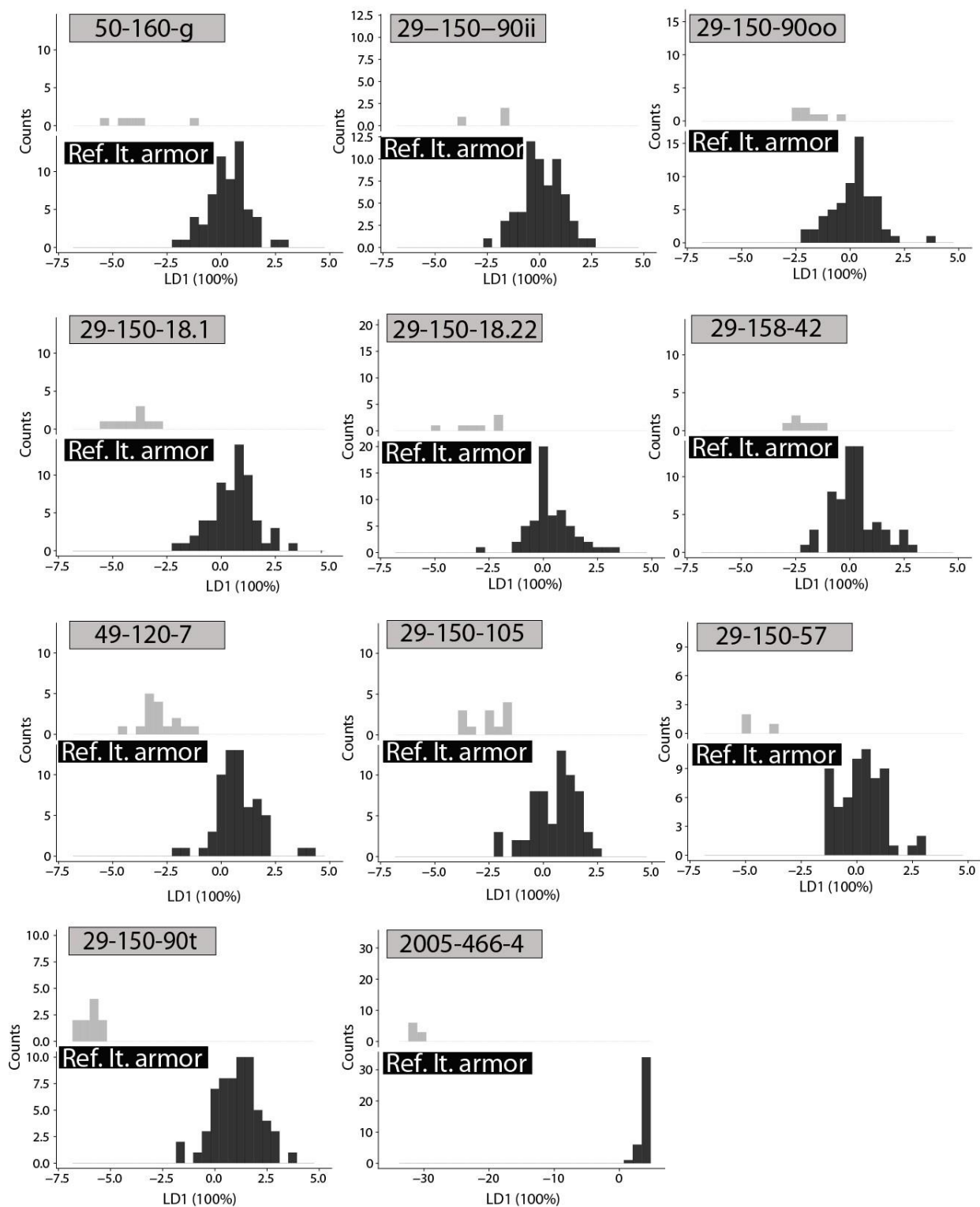
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Figure 6 - dendrogram showing the clustering performed on the results of the PCA on sample 29-150-90t and the reference dataset for Italian style armor, by taking into account the first seven PC which express 90% of the variance.

255

256 LDA confirms these observations. Inclusion of each sample was individually compared with the  
257 reference dataset for Italian style armor (Figure 7). Sample 2005-466-4 is the most distant from the  
258 reference dataset, followed by sample 29-150-90t. Two other samples are clearly separated from the  
259 reference set by LDA: samples 29-150-18.1 and 29-150-57. On the contrary other samples cannot be  
260 separated from the reference dataset for Italian style armor. A summary of the provenance  
261 compatibility considering both LDA and PCA-HCA results is presented in Table 2.

262



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Figure 7 - LDA carried out on the transformed data of SI originating from Chalcis armor plates and from the reference dataset of Italian style armor published in Bérard et al. 2020.

266

267 *Table 2 – Summary of the provenance study: LDA and PCA approach comparison, Comparison of average weighted Mn, P*  
 268 *and Ti content (E\* see Methodology) of the SI originating from the Chalcis armor, phosphorus presence in significant amount*  
 269 *(>0.1 wt.%) in the metallic matrix.*

270 *Column 6 : High compatibility with reference dataset of Italian style armor (not separable by a LDA or PCA approach)*  
 271 *Column 7 : Chemical similarities with reference dataset of Italian style armor : compatibility probable (Separable by a LDA*  
 272 *approach but not with PCA approach)*

273 *Column 8 : Not compatible with reference dataset of Italian style armor (Separable by a LDA and PCA approaches or*  
 274 *composed of phosphoric iron)*

Sample number	%wt. Mn*	%wt. P*	%wt. Ti*	Phosphoric iron (%wt.P > 0.1 in metallic matrix)	Column 6	Column 7	Column 8
50-160g	5.4	0.6	0.1		X		
29-150-90ii	6.3	0.1	<LD		X		
29-150-90oo	5.5	<LD	0.2		X		
29-150-18.1	10.6	0.2	0.3			X	
29-150-18.22	1.5	<LD	0.2		X		
29-158-42	6.7	0.6	0.2		X		
49-120-7	4.6	<LD	0.2		X		
29-150-105	3.7	0.2	0.1		X		
29-150-57	5.9	0.2	0.2			X	
29-150-90t	2.0	<LD	0.2				X
2005-466-4	0.4	0.2	2.8				X
unacc1	0.6	2.5	1.4	X			X
49-120-5	7	0.2	0.1	X			X
49-120-8	0.2	0.8	0.2				

275  
 276 The provenance study conducted here strengthens the hypothesis of an Italian manufacture for five  
 277 marked armor elements (MMA 50.160.g, MMA 29.150.90ii, MMA 29.150.90oo, MMA 29.150.18, .115  
 278 forearm defense, MMA 29.158.42), as they share a common chemical signature, compatible with a  
 279 reference dataset for Italian style armor according both to PCA and LDA analysis. Two other pieces,  
 280 unmarked, have also a chemical signature compatible with this group (MMA 49.120.7, MMA  
 281 29.150.105), while two pieces (sample 29-150-57 and sample 29-150-18.1), show chemical similarities  
 282 with this group (PCA compatibility), consequently their compatibility was deemed probable. This slight  
 283 difference in chemical signature for piece MMA. 29.150.57, bearing a Missaglia mark (Milanese  
 284 workshop) could illustrate the chemical variability of the Lombard iron-making production area. The  
 285 variation of chemical signature for samples 29-150-18.22 and 29-150-18.1 is in good accordance with  
 286 the history of the whole piece (MMA 29.150.18, .115). As specified in the “Set of Artefact” section,

287 piece MMA 29.150.18, .115 is an assemblage of two Chalcis pieces: a forearm bearing an Italian mark  
288 (sample 29-150-18.22), whose chemical signature have a high compatibility with the reference dataset  
289 of Italian style armor and an unmarked couter (sample 29-150-18.1).

290 Further research is needed to identify precisely the provenance of the metal, although several  
291 hypotheses can be made. Chalcis being a strategic location for Venice in the Aegean, the city received  
292 war material from the Republic particularly during the expansion phase of the Ottoman Empire  
293 (Braunstein, 1966; Mazou, 2018). The manufacture and commercial exchanges of weaponry was a  
294 twofold challenge for Venice. Their sale was highly lucrative, encouraging trade that was not, however,  
295 in line with the imperatives of defense. Venice imported iron from various regions, in particular for the  
296 Arsenal's imposing needs. Iron from regional resources (in particular Belluno, Zoldano and Agordino)  
297 and more distant iron-producing areas such as Styria and Carinthia manufactured in Frioul, are  
298 mentioned in historical sources (Braunstein, 1965). During the 15th century, Venice also extended its  
299 influence over the valuable Lombardy iron resources of Bergamo and Brescia, which produced highly-  
300 quality steel (Braunstein, 2001). The Republic encouraged the development of metallurgical and arms  
301 and armor manufacturing activities in the area to secure regular supplies of iron and military  
302 equipment (Gaier, 1995). Northern Italy constituted an important arms and armor manufacturing  
303 area, Milan being the most renowned, but in competition with Brescia, especially under Venetian  
304 influence. Milanese and Brescia arms manufacturers had a privileged relationship with Lombardy's iron  
305 producers (Braunstein, 2001; Menant, 1988; Pyhrr et al., 1998; Verna, 2001). One of the most  
306 important outlets for Lombardy steel was the arms industry, nevertheless, supplies coming from  
307 elsewhere may have been used by Italian armorers.

308 Styria, Carinthia and Italian Alps are iron-making areas where the practice of direct reduction is  
309 attested, exploited manganese-rich deposits (Dillmann et al., 2011; Sprandel, 1968). In addition,  
310 Lombardy is characterized by high levels of manganese (average: 5 wt%), barium (average: 4690  $\mu\text{g.g}^{-1}$ )  
311 but also low phosphorus content (average <0.3 wt%) ores (Bérard et al., 2020; Leroy, 2010). Those  
312 chemical tracers were also highlighted by the provenance study of the Chalcis pieces compatible with  
313 the reference dataset of Italian style armor (see and Table 2). Therefore, Lombardy is a prime candidate  
314 for iron supply of those Chalcis pieces, testifying to Venice's influence in northern Italy and the  
315 shipment of military equipment from this region to the Venetian Aegean territories.

316 The statistical approaches highlighted two isolated chemical signatures (MMA 2005.466.4 and MMA  
317 29.150.90t), whereas armor MMA 29.150.90t shows some chemical similarities with the reference  
318 dataset of Italian style armor. If the attribution of the pieces' mark to an Italian workshop is correct,  
319 the provenance study could illustrate the use of metal supplies outside Lombardy by Italian craftsmen,  
320 derived from manganese rich ores. The other piece (MMA 2005.466.4) is characterized by specific  
321 chemical tracers very different from Italy, such as high amount of Ti in SI (>2%wt) as well as by X<sub>Hf</sub>,



322 X\_U and X\_Th variables (see Figure 3). Important quantities of Ti were also found in another small plate  
323 brigandine (MMA unacc#1). The use of titanium-rich magnetite sands as iron ore source for bloomery  
324 furnaces were already reported. Most of the references point to Africa and Asia (Ige and Rehren, 2003;  
325 Iles and Martínó N-Torres, 2009; Killick and Miller, 2014; Park and Rehren, 2011) the Black Sea  
326 (Tylecote, 1981) and to northern Greece (Nerantzis, 2009; Nerantzis et al., 2022; Photos, 1987),  
327 suggesting Ti as a chemical tracer in the SI. Studies of northern Greece black sands mineralogy have  
328 highlighted the enrichment of certain elements (Filippidis et al., 1997; Peristeridou et al., 2022), such  
329 as Hf, Th, U and Ti (several hundreds of  $\mu\text{g}\cdot\text{g}^{-1}$  for Th, U and  $5076 \mu\text{g}\cdot\text{Hf g}^{-1}$  in zircon mineral fraction  
330 (Filippidis et al., 1997)). These chemical tracers, also observed in sample 2005.466.4, could constitute  
331 a first indication of provenance. In the late Byzantine period, magnetite sands were important iron  
332 sources (Photos, 1987). Numerous slag heaps in the Vrontou attest to the continuation of iron mining  
333 and smelting activities in Macedonia during the Ottoman period (Nerantzis, 2009; Photos, 1987).  
334 Therefore, Macedonia could be potential candidate for iron supply for those pieces. Further analyses,  
335 involving the comparison of trace elements, currently lacking for the Macedonian iron slags will be  
336 required to validate this hypothesis and attest the use of Balkans ores resources in the production of  
337 these pieces. If confirmed it would give new insights on arms manufacturing activities in the Balkans  
338 and the Aegean, far less documented than those in Western Europe during the late Middle Ages. Iron  
339 smelting activities continued in Macedonia during Ottoman times therefore an oriental origin should  
340 not be excluded, especially since Turkish style pieces (kept at the National Historical Museum in  
341 Athens) are reported among the Chalcis Hoard (Ffoulkes and Traquair, 1911; Kontogiannis, 2012). If  
342 confirmed, it could testify not only to the mobility of armor and soldiers, but also to the reuse of  
343 military equipment as war-booty by late Middle Ages armies.

344 Among the Chalcis pieces studied, four helmets (MMA 49.120.5, MMA 49.120.7, MMA 49.120.8, MMA  
345 29.158.42) share common morphological features, known only from Chalcis and other Aegean sites,  
346 leading to suspicion of a common provenance. Claude Blair suggested a Dalmatian origin for those  
347 pieces supported by the comparison of a high relief in Sibenik showing helmets with similar  
348 morphological features. He pointed out the importance of Dubrovnik manufacturing center,  
349 renowned for its firearms production, to support his hypothesis (Blair, 1982; Petrovic, 1975). Based on  
350 the composition of the metal and the provenance analysis, one single piece (MMA 49.120.5) is made  
351 with phosphoric iron derived from the use of a phosphoric ore. Two of them (MMA 49.120.7 and MMA  
352 29.158.42) shows a chemical signature with the reference dataset of Italian style armor. (Bérard et al.,  
353 2020). The last piece of this group, MMA 49.120.8, did not met the conditions to pursue a provenance  
354 study based on the comparison of trace elements ratios but may also have a different provenance  
355 characterized by low manganese content (<1wt.%). Despite having common morphological features,  
356 the provenance study demonstrates that these four helmets were not made with the same raw

357 material. It may suggest that they were made in a workshop using various metal supplies or in different  
358 workshops. Further research would be needed to decipher whether a Dalmatian provenance for those  
359 pieces, as suggested by Claude Blair, could be confirmed. The presence of phosphorus, as chemical  
360 tracer for piece MMA 49.120.5, could be a first indication in the future for dataset comparison.  
361 Furthermore, the compatibility with reference dataset of Italian style armor for pieces MMA 49.120.7  
362 and MMA 29.158.42 could point to Italian workshops or could also evidence a use of Italian metal  
363 supply in the Aegean or Balkan areas. Italian merchants, in particular Venetians, had indeed a very  
364 active role in the eastern Mediterranean iron trade routes (Sprandel, 1970). The provenance study  
365 brings thus new insight on the medieval network's exchanges in this region.

## 366 5. Conclusions

367

368 The provenance study of the Chalcis armor reinforces the hypothesis of the existence of different  
369 subsets within the large medieval Chalcis defense hoard and suggest that several manufacturing  
370 workshops or areas were involved. Seven samples have a common chemical signature compatible with  
371 a reference dataset for Italian style armor. This result strengthens the hypothesis of an Italian  
372 manufacture for these pieces, whose two of which are unmarked. Lombardy appears to be a prime  
373 candidate for the metal's origin underlining the influence of Venice in this area. Another sample taken  
374 from small plate brigandines show a different chemical signature characterized by high Ti content.  
375 Comparison with literature indicate that Ti-rich iron sources occur in northern Greece (Macedonia)  
376 suggesting the possible use of local ores in the production of these pieces. If confirmed, it would  
377 constitute a first step towards future research aiming at understanding workshop practices, arms  
378 manufacture and trade in the Aegean region during the Middle Ages. To that end, these first results  
379 will serve as a basis for a more extensive study on the Chalcis Hoard which will gather a thorough  
380 investigation on the nature, heat treatments and origin of the metal combined with other type of  
381 historical sources.

382

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