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In Situ Investigation of the Medieval Copper Alloy Door in Troia (Southern Italy)

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Abstract: This work describes experimental results concerning the chemical composition of the alloy patina and inlays from the medieval copper alloy door of the cathedral of Troia (southern Italy), dating back to 1127 CE. The analyses were conducted in situ with no sampling or sample preparation required, using a portable energy-dispersive X-ray fluorescence (ED-XRF) instrument. The compositional results show that the two door leaves were made using a binary alloy of copper and lead, while the nails, lion protomes, and handles have a different chemical composition. Moreover, the analyses revealed uniform concentrations of chlorine, probably due to cleaning treatments during the restoration. It is important to emphasise that the obtained results are the only ones related to this valuable masterpiece analysed.

Keywords: medieval door; copper alloy; patina; ED-XRF; portable apparatus

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1. Introduction

The final decades of the Western Roman Empire were the time when the majority of historical bronze doors were made. The plainness of the ornamental plant or animal designs that embellish these doors is what makes them distinctive. The Middle Ages saw a resurgence in bronze door production, with many doors being installed across Europe. Sadly, a significant number of these doors have been lost because of environmental agents' eroding effects, and many more since the valuable metal from which they were manufactured was repurposed for other applications.

There are currently just about thirty medieval copper alloy doors in Europe that can be visited, and, in particular, in Italy, it is possible to admire them in Amalfi (1060 CE), Monte Cassino (1066 CE), Rome (1070 CE), Monte Sant'Angelo (1076 CE), Atrani (1087 CE), Salerno (1085 CE), Benevento (1150–1151 CE), Canosa di Puglia (1111–1118 CE), Trani (1111–1118 CE), Troia (with two: 1119 CE and 1127 CE), Monreale (1140 CE), and Venice (with two: 1080 CE and 1112 CE) [1–8].

Such great works of art were mostly created in Constantinople and brought to Italy or were manufactured by Italian artisans using byzantine doors as inspiration.

Although commonly considered "bronze doors", byzantine doors were constructed using orichalcum, a form of brass composed of a copper alloy with a low zinc percentage. Since brass oxidizes to a greenish hue over time, similar to how bronze does, these doors were likely given the name "bronze". They include illustrations of sacred icons and were distinguished by priceless goldsmiths' embellishments done with inlay and niello techniques.

Byzantine doors are composed of panels, which are tiny modular orichalcum pieces that are nailed to a wooden core and used as the doors' structural building blocks. The creation of controllable, lightweight doors that were simple to move was made possible through this building technology.

In the Middle Ages, lost-wax casting was frequently employed for producing bronze (or brass) doors. In this technique, a chalk model of the artifact was covered in wax and buried under a layer of refractory soil. This type of mould was then baked in an oven. The dissolving of the wax induced by the temperature left a tiny gap between the chalk model and the refractory soil that was filled with molten metal, producing the final piece. For single-part doors, this process worked quite well, but it was costly and time-consuming for multi-part doors like the bronze ones used in Italy.

Regarding byzantine doors, some research shows that their leaves may have been cast using the so-called sand or mould casting process. Since it did not require wax, this approach is different from lost-wax casting. Using a frame known as a casting flask, moulds for the intended object were created. The model, which was typically constructed of wood and had the shape of the object to be cast, was set in the centre of the casting flask. The model was surrounded by sand, which was then compressed to form a chamber into which the casting could be done after the model was taken out.

The chemical composition, the colour, and the thickness of the patina vary depending on both the original composition of the metal and the post-deposition environment (air, soil, and water) [9]. The chemical composition of the deposition environment, and its temperature, humidity, and pH contribute to the formation of different patinas.

Moreover, it is important to evaluate the phenomenon of surface enrichment of certain elements, such as, for example, tin, which often appears in higher percentages in surface measurements. Cleaned copper has been shown to provide similar results between destructive methods and portable energy-dispersive X-ray fluorescence (ED-XRF) [10]. Some success has also come with the use of ED-XRF through the implementation of Monte Carlo simulations, as a way to circumvent the effects of the patina [11]. The issue with the implementation of Monte Carlo simulations is that it currently still requires knowledge of the cross-section of a corroded alloy [12].

There is another qualitative method that is often considered, that is, the evaluation of the ratio Sn-Kα/Sn-Lα of the X-ray intensities. If there is a uniform distribution of tin between the surface and the bulk of the alloy, it is expected that the analysis is free from any corrosive patinas. In these ways, the artefacts are cleaned to remove the patina, or the object is sectioned to analyse the bulk of the alloy.

Very often, however, destructive sampling of objects of antiquity is not possible due to the historical–artistic value of the object and its integrity [10]. Usually, the need for destructive sampling is assessed beforehand by a team of experts (researchers, restorers, and superintendents) to see if this is really necessary.

With this in view, portable ED-XRF has found wide use over the past decades as an in situ, non-invasive, fast, low-cost surface technique. Of course, the advantages and disadvantages of such equipment must be evaluated on a case-by-case basis, precisely because of the experimental difficulties that patinas create on the materials to be analysed.

It is clear that, for bronze samples that require specifically objective results, energy-dispersive X-ray fluorescence could be defined as not valid, but it is a very useful technique for the preliminary analysis of bronze artefacts and/or when it is not possible to perform destructive analyses on historical–artistic manufacts [13].

The objective of this research is to use portable energy-dispersive X-ray fluorescence to perform an in situ, non-destructive investigation of the medieval door of the Cathedral of Troia (Figure 1), on which very little information is available in the literature [14–16]. In particular, our aim was to investigate the patinas of these precious medieval doors using the portable ED-XRF instrument we had available. Moreover, we would also like to underline that the superintendent did not allow destructive analyses.

This study is the result of several years of investigation by the authors of this manuscript, who analysed different doors in Apulia, including those in Canosa di Puglia [17] and Monte Sant'Angelo [18], in an effort to ascertain the composition of these priceless examples of medieval art and aid future research to clarify the intricate processes involved in their manufacture.

Figure 1. Picture of the medieval door called "*Freedom Door*" in Troia (southern Italy) with the measurement points.

2. Materials and Methods

2.1. Description of the Analysed Door

Troia (Foggia, Apulia, Southern Italy) is considered the heir of an ancient city known as Aecae, and from 1031 CE it became a bishopric and one of the most important religious centres in southern Italy, culturally and politically linked to the Church of Rome. The actual cathedral of Troia stands on the site of a primitive church dedicated to the Blessed Virgin Mary Assumed into Heaven.

The work for its construction began under the episcopate of Girardo of Piacenza and in 1106 CE was refinanced by bishop William II, known as William the Norman, who decided to seal the importance of this sacred place by commissioning a bronze door to the master foundryman Oderisius of Benevento. Soon before the cathedral was completed in 1119 CE, the door was installed on the main entrance and was renamed the "*Door of Prosperity*" to honour the euphoric atmosphere created by the church and its bishop, who acted as a crucial mediator between the papacy and the Norman barons.

In 1127 CE, only eight years after the execution of the main door, bishop William II again commissioned Oderisius of Benevento to craft a bronze door for the side of the cathedral, which is the subject of this study.

The door, measuring 284 cm in height and 158 cm in width, is divided into twenty-four panels framed in bolted bronze frameworks and divided into six bands of four panels each, which narrate an important page in the life of the city of Troia: the liberation from Norman domination. For this reason, the studied manufact was called the "*Freedom Door*".

Starting from the left (Figure 2), the first band of panels has an epigraphic inscription in Latin that states:

PRINCEPS PATRONU(M) PETRE TROIA(M) SUSCIPE DONUM QUA(M) L(A)ETABUN DUS GUILELM(US) DONO SECUNDUS

which can be translated as:

O Peter, prince (of the apostles) and patron, receive as a gift the city of Troia, which I, William the Second, gladly offer to you.

Figure 2. Picture of the first twelve upper panels of the studied door.

Next to this phrase is in fact depicted the bishop William II, who commissioned the door, towering in the act of donating the "*Civitas Trojana*" to the Church of Rome symbolised in the next panels by the inlays depicting St. Peter and St. Paul.

On the left outer edge of the second and third panels' bands is engraved the phrase:

HIC FUIT NOVAE TROIAE

which means that this was of the new Troia.

To introduce, starting from the second band there is a series of eight panels engraved with eight flexuous and harmonious stylised figures with a bicorne mitre surrounded by a halo, which represent, in reverse chronological order, the first eight bishops who succeeded one another in the city of Troia:

GUILIELMUS PRIMUS EPISCOPUS, *HIC OCTAVUS* (William the First, eighth bishop);
UBBERTUS EPISCOPUS, *HIC SEPTIMUS* (Hubertus, seventh bishop);
GIRARDUS EPISCOPUS, *HIC SESTUS* (Girard, sixth bishop);
GUALTIERUS EPISCOPUS, *HIC QUINTUS* (Gualtiero, fifth bishop);

STEPHANUS EPISCOPUS, HIC QUARTUS (Stephen, fourth bishop);
IOHANNES EPISCOPUS, HIC TERTIUS (John, third bishop);
ANGELUS EPISCOPUS, HIC SECUNDUS (Angel, second bishop);
ORIANUS EPISCOPUS, PRIMUS EPISCOPUS (Horian, first bishop).

It is important to highlight that the panel with the inlay Horian, first bishop of Troia, is the only documented evidence of his existence.

In the fourth band, it is possible to read an engraving with the author's signature (Figure 3):

FACTOR PORTARUM FUIT ODERISIUS HARUM BENEVENTANUS

That means that the creator of this door was Oderisius of Benevento.

Figure 3. Photograph of the four leonine protomes of the door. On the lower frame, it is possible to read the engraving *"Factor portarum fuit Oderisius harum beneventanus"*, which represents the signature of Oderisius of Benevento, builder of the bronze door.

The fourth band also contains four lion protomes holding clapper rings between their teeth. The style of these lions is simpler than those of the "*Door of Prosperity*", but Oderisius did not fail to give them sufficient vigour to make them stand out, breaking up the uniformity of the composition. Some of the protomes have gaps, behind which the wooden support of the bronze door can be glimpsed. As an example, in Figure 4, two gaps are shown around the third leonine protome.

The last two bands are engraved with a Latin inscription (Figure 5):

AEQUITATIS MODERATOR/LIBERATOR PATRIAE/DOMINUSGUI/LIELMUS SECU (n)UDUS/DEI GRATIA/VENERABILIS HUJUSTROJANAE/SEDIS E(pisco)PU(u)S/NONUS/ HAS ETIAM/PORTAS AENEAS/DE PROPRIO ERARIO/LARG(e)DISPEN/SATOR FIERI IUSSIT/ANNO INCAR/NATIO(n)IS D(omi)NICAE MCXXVII ET/CIVITATIS HUJUS CON-DITIO(n)E/ANNO C(entesimo) AT(que) OCTAVO PONTIFICAT(us) VERO/D(omi)NI HON-ORII P(apae)/SEC(un)DI TERTIO ITEM/PONTIFCATUSD(omi)NI/GUILIELMI EPI(scopi)/SEC (un)DI XXI/INDIC(tione) V ANNO/Q(uo) GUILIELM(us) T(er)T(iu)/N(o)RMANN(o)R(um) DUX/SALERNI(s)OBIIT MORTE COMUNI/(Tun)C TROJANUS/POP(u)L(u)S PRO LIBER/ TATE TUENDA ARCEM SUB/VERTITETUR/BEM VALLO/MURISQ(ue)MUNIVIT

which can be translated as:

The moderator of equity, liberator of the homeland, William II by the grace of God, ninth bishop of this Trojan See, magnanimous dispenser, also had these bronze doors made with his own money in the year of the incarnation of the Lord 1127 CE, the eighth hundredth from the foundation of this city, the third of the pontificate of Pope Honorius II, the twenty-first of the pontificate of bishop William himself, the fifth indiction, in which year William, third duke of the Normans, died a natural death in Salerno. Then the people of Troia, to defend their freedom, pulled down the castle and fortified the city with walls and a moat.

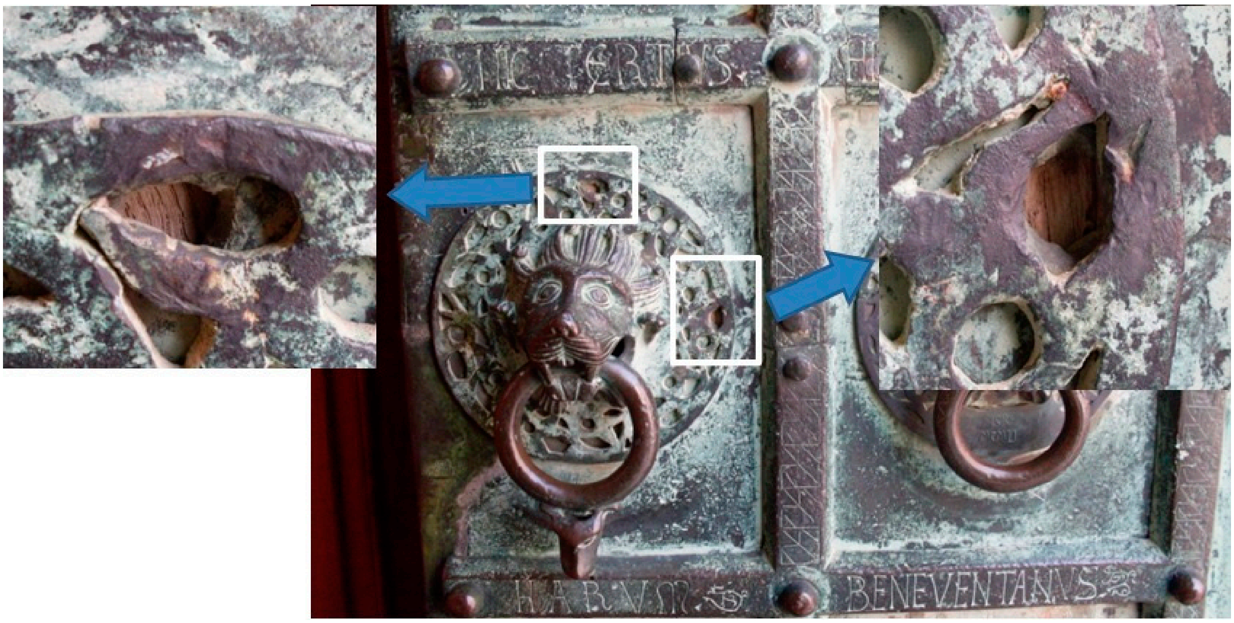

Figure 4. Pictures of the gaps near the third leonine protome, behind which the wooden support of the bronze door can be seen.

Figure 5. Photo of the bottom of the door.

This story engraved on the "*Freedom Door*" proudly and accurately summarises several historical events in the city: the year the gate was built (in 1127 CE) and who commissioned it, William II; the year Troia was founded (in 1019 CE); the year Pope Honorius II assumed the papal throne (in 1124 CE); the year William II took office as bishop (in 1106 CE); and the demolition of the castle on the death of Duke William III in 1127 CE to defend the freedom of the Trojan people.

A further constructive detail is that the neighbouring panels have complementary engravings, probably made to facilitate the correct assembly of the door. It is important to underline that these engravings are present in various parts of the door under the frame. An example of such engravings is shown in Figure 6.

Figure 6. Picture of three complementary engravings between two neighbouring panels, inscribed to facilitate the assembly of the door.

As stated on the door, the last restoration dates to 1951 CE [19], but oxidation on the bronze doors, clearly visible to the naked eye, is causing irreparable damage to the panels made by Master Oderisius. The experimental results obtained in this study could therefore represent a valuable resource in the now-necessary restoration of this priceless artefact.

2.2. ED-XRF Analysis

Energy-dispersive X-ray fluorescence (ED-XRF) analysis was performed using a portable instrument designed at the University of Salento [20,21]. It is composed of an X-ray tube produced by MOXTEK® (Orem, UT, USA) with a palladium anode operating at 1–40 kV voltage and 0–100 μA current, and a Si-PIN detector produced by AMPTEK® (Bedford, MA, USA), model XR_100CR, thermoelectrically cooled, with a beryllium window of 25 μm. It has a resolution of 150 eV at 5.9 keV, a resolution of about 250 eV in the range 10–15 keV, and a pocket multi-channel analyser produced by AMPTEK®, model MCA8000A, interfaced with a laptop. The diameter of the X-ray beam is an ellipse, whose axes are equal to 2 mm and 3 mm.

Cu, Pb, Zn and Fe were quantitatively determined at high energy: 20 kV voltage, 3 μA current, with an acquisition time of 60 s. Sn, S and Ag were determined at low energy: 6 kV voltage, 40 μA current, with an acquisition time of 60 s.

The calibration was carried out by analysing five standards, consisting of CuO, $CuCO_3$, Cu/Sn (80/20% *w*/*w*), Pb_3O_4, Zn, Fe, $CuCl_2$, $CuSO_4$, and SnO_2 in different ratios. The concentration of each standard was chosen in order to reproduce the chemical composition of the investigated patinas.

All chemical compounds were analytical grade and purchased from Sigma-Aldrich® (St. Louis, MO, USA), except the Cu/Sn (80/20% *w*/*w*) standard, which was purchased from Goodfellow® (Huntingdon, UK).

Each standard was prepared by mixing the compounds in different weight percentages. In particular, the chemical compounds were weighted using an analytical balance KERN® model ABT 100–5M (KERN & SOHN GmbH: Balingen, Germany), subsequently mixed and homogenised in an agate mortar for ten minutes, and finally compressed at 200 bar for ten minutes. The homogeneity of the elements in the standard meets the requirements for ED-XRF quantitative analysis [22].

Table 1 shows the quantitative chemical composition of the five analysed standards for ED-XRF analysis.

Table 1. Chemical composition of the standards used for calibration in ED-XRF analysis.

Standard	**Cu**	**Pb**	**Sn**	**Zn**	**Fe**
			(% wt)		
1	73.5	12.3	2.2	4.8	0.7
2	65.0	8.4	4.9	7.5	1.1
3	58.1	5.9	8.4	12.4	2.2
4	51.5	3.6	10.7	18.4	2.9
5	48.9	2.5	11.8	21.2	3.3
Standard deviation	*0.5*	*0.5*	*0.3*	*0.3*	*0.2*

The samples analysed were assumed to have "infinite thickness" [23–25] and the quantitative results are expressed in terms of weight percentage (% wt).

From a visual examination, the door does not show any corrosive phenomena in progress and the surface patina appears compact and homogeneous in the various regions. Before performing the ED-XRF analysis, cleaning of the metal surface was performed with Japanese paper and deionised water.

Both the calibration and analytical samples were analysed under the same instrumental conditions. For all the spectra obtained, the intensities of the different signals were determined by integrating the different signals using Gaussian curves.

The calibration curves were obtained by reporting the intensity of the signals as a function of the concentrations of the element under investigation.

Figure 1 shows the locations of all the measurement points, while Table 2 shows their brief description. The twenty-nine points were chosen to have enough measurements on both leaves. In particular, the choice of the various areas was performed to characterize as much as possible of the patinas of the alloys (points n. 1–11), the frame (points n. 12–13), the regions added in 1951 CE by the ICR (points n. 14–17), the different engravings (points n. 18–22), the different ornaments of the door (points n. 23–28), and an evident welding (point n. 29).

Table 2. Brief description of the analysed measurement points and their composition obtained using ED-XRF.

Sample	Description	Cu	Pb	Sn	Zn	Fe	Cl	S	Note
		(% wt)							
1	Alloy (dark)	63.8	16.5			3.9	13.7		
2	Alloy (dark)	68.5	13.0				16.7		
3	Alloy	63.6	12.2		9.6	2.5	11.5		
4	Alloy (dark)	62.8	16.5			0.9	12.8		
5	Alloy	65.2	14.2				15.1		
6	Alloy	65.0	15.8				11.8		
7	Alloy	62.8	13.7				13.8		
8	Alloy	66.0	13.6				14.5		
9	Alloy	65.0	14.5				12.1		
10	Alloy	64.1	15.0				13.2		
11	Alloy	69.6	10.2			3.5	11.2		
12	Frame	65.4	14.5			2.0	12.2		
13	Frame	66.0	14.0				13.1		
14	Addition	78.8	2.9				17.8		
15	Addition (rest 1951)	70.5	3.4	6.8	2.8	2.7	11.9		
16	Rawplug	41.4	5.2		38.2	6.4	8.4		
17	Addition (rest 1951)	73.2	2.9		2.1	2.9	18.8		
18	Inlay	48.8	13.1				5.2	5.3	Ag trace
19	Inlay	63.2	6.0	3.0	7.9		9.3	7.2	Ag trace
20	Inlay	45.1	12.7			0.7	11.9		Ag trace
21	Inlay	20.0	3.1				17.9		Ag
22	Inlay	10.0	1.1				15.4		Ag
23	Leonine protome	62.4	17.5	4.8			10.9		
24	Leonine protome	63.6	22.5	7.9			4.5		
25	Handle	70.8	6.1	6.4	7.7		7.2		
26	Handle	70.4	8.0	3.3	7.9	2.0	6.8		
27	Nail	70.3	2.0	13.2		2.0	12.4		
28	Nail	72.9	2.5	6.9		4.3	11.2		Ti
29	Welding	10.0	60.5	12.2					
	Detection limit	*2.0*	*1.0*	*2.0*	*1.0*	*0.5*	*3.0*	*3.0*	

3. Results and Discussion

The analysed door includes two wooden-core copper-based leaves covered with metal-framed panels fixed with nails. Table 2 shows a brief description of the analysed measurement points and their chemical composition obtained using portable energy-dispersive X-ray fluorescence.

Regarding the chemical composition, the two wings show no significant differences.

The panels' patina (samples n. 1–11) and the frames (n. 12 and n. 13) consist of a binary alloy of copper and lead with a Cu/Pb ratio for the thirteen samples of $4.7 \pm 0.8\%$ wt. The percentage of tin detected was always below the detection limit. The quantity of zinc was also always below the detection limit of the instrument, except for sample n. 3 where the zinc percentage was 9.6% wt.

The chemical composition of some areas (n. 1, n. 3, n. 4 and n. 11) differs from that typical of the door due to the presence of iron at between 0.9% wt and 3.9% wt. These are original areas, and the high iron content may suggest dripping. Other areas of the door were indeed restored (n. 14–17). For example, at point n. 14 there was certainly a gap that was filled during restoration by casting of an alloy consisting of copper (78.8% wt) and lead (2.9% wt). In contrast, at point n. 16, a repair was carried out during the restoration using a square dowel consisting of copper and zinc in a 1:1 ratio and with traces of lead (5.2% wt) and iron (6.4% wt).

As reported in the "*Bollettino dell'Istituto Centrale del Restauro, 1952*" these areas are the result of reconstruction processes during the 1951 CE restoration, which used a quaternary alloy composed of copper in high concentration, tin, lead, zinc, and small quantities of iron [19].

The analysed inlays depicting the bishops of Troia were mainly made of copper, lead, and silver. In particular, inlays n. 18, n. 19, and n. 20 are made of copper with a high lead content and traces of silver, while agemine n. 21 and n. 22 are made of silver with low copper and lead content. It is important to emphasise that the amount of silver has not been quantified, since the precious metal is not a constituent of the alloy of the panels but was used in the form of foils in the inlaying process to fill the grooves of the engravings. Therefore, the terms trace or high content, referring to silver, only indicate a qualitative estimation of the metal present in the ageminature, taking into account that most of the silver was removed over the centuries. Furthermore, very often, the dimensions of the agemine are smaller than the emission spot of the tube; therefore, the emission signal is not only due to the chemical composition of the silver, but also to the surface of the alloy patina.

Sample n. 19, somewhat darker in colour, showed the presence of tin (3% wt) and zinc (7.9% wt).

The protomes (n. 23 and n. 24) and handles (n. 25 and n. 26) were made of a different patina than the one used to make the door moulds and the door brim. For the protomes, this is a ternary alloy of copper, lead, and tin, while for the handles it is a quaternary alloy consisting of copper, lead, tin, and zinc.

The fasteners analysed (n. 27 and n. 28) are made of copper (70.3% wt–72.9% wt) and tin (6.9% wt–13.2% wt) and lower concentrations of lead (2% wt–2.5% wt) and iron (2.0% wt–4.3% wt). Therefore, the nails seem to be made of brass alloyed with iron. A lower amount of lead is understandable, since lead reduces to some extent the mechanical properties of the alloy, which is important for their functions.

All the regions analysed show the presence of chlorine in relatively high concentrations, ranging from 4.5% wt to 18.8% wt, except for region n. 29, in which is evident a solder showing high concentrations of lead (60.5% wt), as well as copper (10.0% wt) and tin (12.2% wt).

The chlorine concentration in the different investigated regions may be due to atmospheric corrosion; indeed, during wet and dry cycles, chlorides could concentrate in the surface, causing chlorine-rich patinas [26]. A further cause of the widespread presence of chlorine on the surface can be attributed to the reagents used to patinate the pieces crafted to repair the door during the 1951 CE restoration.

The chemical composition of the alloy patina was compared with that of the alloy used to make eight medieval bronze doors in Italy, as shown in Table 3. The table shows the average concentration values of copper, lead, zinc, and tin in nine Italian doors and, for further comparison among them, the ratio between the concentration of copper and the concentration of lead.

The patina analysed on the "*Freedom Door*" in Troia turned out to consist of a binary alloy of copper (65.2% wt) and lead (14.1% wt). Moreover, it has a copper-to-lead ratio of 4.6, which is very different from other manufacts.

Therefore, it is clear that the chemical composition of the alloy studied is quite different from that of the other doors; in fact, the remaining medieval doors are made up of ternary or quaternary alloys. For example, the Amalfi door has a ternary alloy consisting of copper (62% wt), lead (19% wt), and zinc (17% wt) and a copper/lead ratio equal to 3.3.

The Monte Cassino door has a quaternary alloy with the highest concentration of copper (80% wt) among the eight doors, in addition to lead (3% wt), zinc (10% wt), and tin (7% wt). The door in Monte Cassino also has the highest copper/lead ratio value (26.7).

The door in Rome S. Paul's outside the walls has a quaternary alloy with a high concentration of copper (73.5% wt), in addition to lead (8.48% wt), zinc (17.9% wt), and tin (0.12% wt) and a copper/lead ratio equal to 8.7. These values are very similar to the door in Monte Sant'Angelo; in fact, it has a quaternary alloy with a high concentration of copper (70.2% wt), in addition to lead (11.2% wt), zinc (14.2% wt), and tin (0.8% wt) and a copper/lead ratio equal to 6.3.

The door in Venice, S. Clemente, has a quaternary alloy with a high concentration of copper (72.4% wt), in addition to lead (8.6% wt), zinc (16.8% wt), and tin (2.2% wt) and a copper/lead ratio equal to 8.4.

The door in Salerno has a quaternary alloy with a high concentration of copper (77% wt), in addition to lead (11% wt), zinc (4.5% wt), and tin (3.5% wt) and a copper/lead ratio equal to 7.0.

The central door in Venice has a quaternary alloy with a high concentration of copper (78% wt), in addition to lead (8% wt), zinc (9% wt), and tin (5% wt) and a copper/lead ratio equal to 9.8.

The door in Canosa di Puglia has a quaternary alloy with a high concentration of copper (69.6% wt), in addition to lead (10.2% wt), zinc (0.3% wt), and tin (8.5% wt) and a copper/lead ratio equal to 6.8.

Table 3. Comparison between the chemical compositions of alloys obtained in this work and those of other Italian medieval copper-alloy doors.

Italian Medieval Door	Cu	Pb	Zn	Sn	Cu/Pb	Reference
	(% wt)					
Amalfi (1060 CE)	62	19	17	Traces	3.3	[3]
Monte Cassino (1066 CE)	80	3	10	7	26.7	[1]
Rome, S. Paul's outside the Walls (1070 CE)	73.5	8.48	17.9	0.12	8.7	[1]
Monte Sant'Angelo (1076 CE)	70.2	11.2	14.2	0.8	6.3	[18]
Venice, S. Clemente (1080 CE)	72.4	8.6	16.8	2.2	8.4	[1]
Salerno (1085 CE)	77	11	4.5	3.5	7.0	[3]
Venice, central door (1112 CE)	78	8	9	5	9.8	[1]
Canosa di Puglia (1111–1118 CE)	69.6	10.2	0.3	8.5	6.8	[17]
Troia, "Freedom Door" (1127 CE*)*	*65.2*	*14.1*	*<1.0*	*<2.0*	*4.6*	*This work*

4. Conclusions

The experimental results obtained have shown that the two wings and the frame of the medieval door in Troia have the same patina chemical composition. In these experimental situations, it is possible to correlate the patina's composition with the composition of the alloy because the same substrates are compared, and it can be assumed that the environmental conditions have been the same for the areas compared over the centuries.

Moreover, the results show that the door studied has a very different composition from the other Italian medieval doors investigated. In fact, the copper/lead ratio in the studied manufact, equal to 4.6, is different from eight medieval copper doors analysed in Italy.

The entire structure is uniformly covered in a patina of chlorine, probably added during the 1951 CE restoration, or it could be due to atmospheric phenomena; in fact, during wet and dry cycles, chlorides can concentrate in the surface of the manufact causing chlorine-rich patinas.

Even the leonine protomes, handles, nails, and parts added during the restoration are different from the original alloy. The few remaining agemine were also analysed, and the results showed that they are of two distinct types: copper-based agemine and silver-based agemine.

The data obtained from this work are the only date relating to this valuable manufact and may be of help for future research in the field of medieval copper alloy doors still present in Europe.

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