

Article

An Archaeometric Study of Lead-Glazed Medieval Ceramics (13th–14th Century) from Santarém, Portugal

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Abstract: Ceramic sherds from approximately 20 samples of lead-glazed tableware, recovered from diverse archaeological sites, including three repurposed storage pits transformed into dumpsters within the medieval city of Santarém (13th–14th century), underwent a meticulous examination. This investigation utilised techniques such as micro-Raman, ground-state diffuse reflectance absorption, and X-ray fluorescence spectroscopies, in addition to X-ray diffraction and stereomicroscopy. A parallel study was conducted on contemporaneous European ceramics (glazed sherds) sourced from archaeological sites dating back to the 13th–15th centuries in Saintonge (France), Ardenne, Zomergem, and Bruges (Belgium), as well as Surrey–Hampshire, Kingston, and Cheam (England). The first premise for comparing the Santarém samples with European production locations was their frequent commercial relations with Portugal and the frequency of these productions being found in Portugal. The colour of the ceramic bodies is predominantly white or whitish, with a few exhibiting a vivid red hue. Analyses of the fabric, mineralogical, and elemental composition of the sherds suggest that the majority of Santarém’s glazed ceramics were locally or regionally produced, potentially derived from a Pliocene kaolin-rich sand formation. However, this conclusion is not supported by the absence of discovered lead glaze kilns or workshops in Santarém for the late Middle Ages.

Keywords: medieval ceramics; Santarém; micro-Raman; GSDR; XRD; XRF; SM



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1. Introduction

Santarém was one of the most important cities in late Medieval Portugal. This importance needs to be observed from many different perspectives. One of the most important was related to its cereal production capacity, which granted this urban centre the nickname of “Portugal’s barn”. Santarém could produce large quantities of cereal and its location less than 100 km from Lisbon and close to the Tagus River made it fundamental in the wider Portuguese urban strategy [1,2]. The centralisation of cereal in communal barns only started to happen in the late 16th century [3]. Until then, cereals were kept underground in pits excavated into the bed rock. These can be found in many shapes but the most common were excavated shaped like a bag [4], and some of them date back to the Muslim occupation of the city (8th–12th centuries). Archaeological information obtained from many parts of the country reveals that these were located inside houses as much as on open fields. When these underground structures were out of use, independently of the reason behind this, they

were filled with garbage either obtained from demolitions or just domestic refuse. Their abandonment occurred for many reasons but when some areas of the city were refurbished (construction of new roads or buildings), large areas of these storage pits were filled with domestic garbage. Although ceramics are the most abundant, all types of domestic refuse are frequently found inside.

The ceramics studied in this paper were found in some of these storage pits during an archaeological intervention carried out in Santarém in 2014, and they distinguish themselves from most other pottery objects due to their surfaces covered in glaze. These are what we can consider tableware. Their shapes correspond essentially to pitchers used to serve wine and can be dated (through information retrieved from archaeological stratigraphy and style) to the 13th and 14th centuries.

Although lead-glazed ceramics were common during the Muslim occupation and used in the majority of Santarém households [5–7] and other places where Muslim communities were, these tended to disappear from the set of household ceramics in the following centuries. In 1147, the city of Santarém was conquered by Christian forces, together with many other towns in the Tagus Valley. Although political and military elites disappeared, the local population continued to live there, including potters. This continuity can be seen in their production with the continuation of the use of similar shapes and decorations. Local production of redwares is confirmed by the existence of kilns dated to the 12th and 13th centuries [8–10]. However, this did not occur with glazed wares, which seemed to disappear completely in the second half of the 12th century and the first half of the 13th century. Nevertheless, these started to reappear in the archaeological context in the second half of the 13th century, although in small amounts.

The lack of published evidence of any kiln producing lead-glazed wares in the Tagus region in the 13th and 14th centuries made us believe initially that all these vessels were imported from Northern Europe, an area with whom the Portuguese kingdom had commercial relations [11]. These glazed vessels have been identified in many parts of the country but are seldom published [12–14] and demonstrate a relationship between Portugal and the Northern European markets.

Building upon the premise that these objects are imported, this paper will initially analyse a collection of such vessels unearthed in Santarém and juxtapose them with lead-glazed ceramics confidently crafted in Northern European workshops.

A detailed comparison of both ceramic bodies and glazes originating from Santarém and from the different coeval kilns in different European countries (countries with which Portugal had frequent commercial relations) aims to clarify the local or imported origin of all the earthenware samples under study. Upon noting substantial compositional disparities between the two sets of sherds under scrutiny, the proposal is to ascertain a plausible local or regional geological source for the clay deposits that provided the raw materials.

2. Geological Framework

The Santarém region is situated in Cenozoic formations, with ages ranging from ancient Miocene to modern Quaternary. Geomorphologically, the region is characterised by two Miocene–Pliocene plateaus with horizontally stratified layers and extensive lateral extent. These plateaus confine the Tagus River and its respective floodplains and river terraces. Detrital rocks, ranging from clayey sediments to large rounded pebbles, prevail, but locally, there are lithotypes of carbonate composition or transitional nature. Various geological resources exist in the region, particularly some clayey or sandy formations with suitability for the ceramic industry, continuing in use until recent times [15,16].

Kaolinite-bearing formations are less common but can be found in the Pliocene complex at various points along the Lisbon to Santarém railway line. Primarily used for ceramics (whitish bodies), they have led to exploitation at the site called Fonte da Pipa, west of the Vale de Santarém railway station. Clays used to produce tiles and bricks (red bodies) are also present at various points in the region.

The provenance of ceramic raw materials and the ceramic technology employed was studied in a recent publication [17], focused on the analysis of Islamic ceramics from the Alcáçova of Santarém. The authors collected samples from locations with historical records or of a more recent exploitation, as previously referenced for Miocene and Pliocene formations. In some cases, the authors conducted purification of the collected clays and sandy materials, providing detailed chemical and mineralogical characterisation to establish the local or external origin of those Islamic ceramics. The composition of those materials is mainly quartz, illite/muscovite, and minor feldspars (K feldspars and plagioclase). Calcite and chlorite can be also present in some layers. Based on various indicators, these authors concluded that both local production and imported objects existed in the Alcáçova of Santarém. Given the highly sandy-silt (siliceous) composition prevalence, they conclude that all raw materials were treated before use. This information is, therefore, highly relevant to the present study, which seeks to investigate whether there is temporal continuity in ceramic production, based on local mineral resources and marked stylistic similarities, or whether, conversely, medieval materials originate from European production centres.

3. The Ceramic Sample Set—Selection Methodology

3.1. Archaeological Context

In 2014/2013, a large archaeological campaign was carried out in Santarém, taking advantage of the replacement of water and electricity infrastructures. Being a historical city, it is legally mandatory that an archaeological survey is performed. During the work developed both in Travessa das Capuchas—Largo António Monteiro, 22 abandoned underground storage pits were found. In Largo Pedro Alvares Cabral, that number was 20. Not all of them were filled with domestic waste and that process occurred in the 13th and 14th centuries. In the Capuchas area, this certainly happened before 1415, when the Hospital dos Inocentes was built, and in Largo Pedro Alvares Cabral, this action was most likely related to the construction of Igreja da Graça that started to be built in the 1380s [18].

The commercial nature of the archaeological excavation did not allow excavation of these underground structures, except for three cases that were only partially excavated. They presented different dimensions from small, just over 1 m deep, to large, almost 3 m deep. Still, this allowed the recovery of hundreds of ceramic objects, most of them unglazed red earthenwares produced locally. In addition to the ceramic evidence, a large quantity of food remains were also recovered, demonstrating that these abandoned storage pits were used for domestic refusal deposits.

In considering the significance of these storage pits within the Medieval Santarém cultural frame, it becomes evident that they not only served utilitarian functions but also embodied symbolic meanings within the social manufacture of the city and the social construction of space. Their presence in urban spaces reveals aspects of the organisation of domestic life, the management of resources, and the interconnectedness of economic, social, and cultural spaces. These archaeological findings within the pits can thus be contextualised and inserted into broader historical narratives, gaining a richer understanding of medieval Santarém and its inhabitants' daily experiences and practices. As one of the most productive areas of the kingdom of Portugal, Santarém had many wealthy inhabitants. Historical documents attest to that social reality [2] and when looking at the pottery used in tables, when compared to the other Portuguese cities mentioned below, the consumption of pottery reveals the same reality.

3.2. Samples

Figure 1 presents 20 sherds recovered from two underground cereal storage pits transformed into dumpsters excavated in Santarém and dated to the late medieval period (13th–14th-century archaeological context). Only glazed ceramics were selected for the archaeometric analyses presented in this paper.

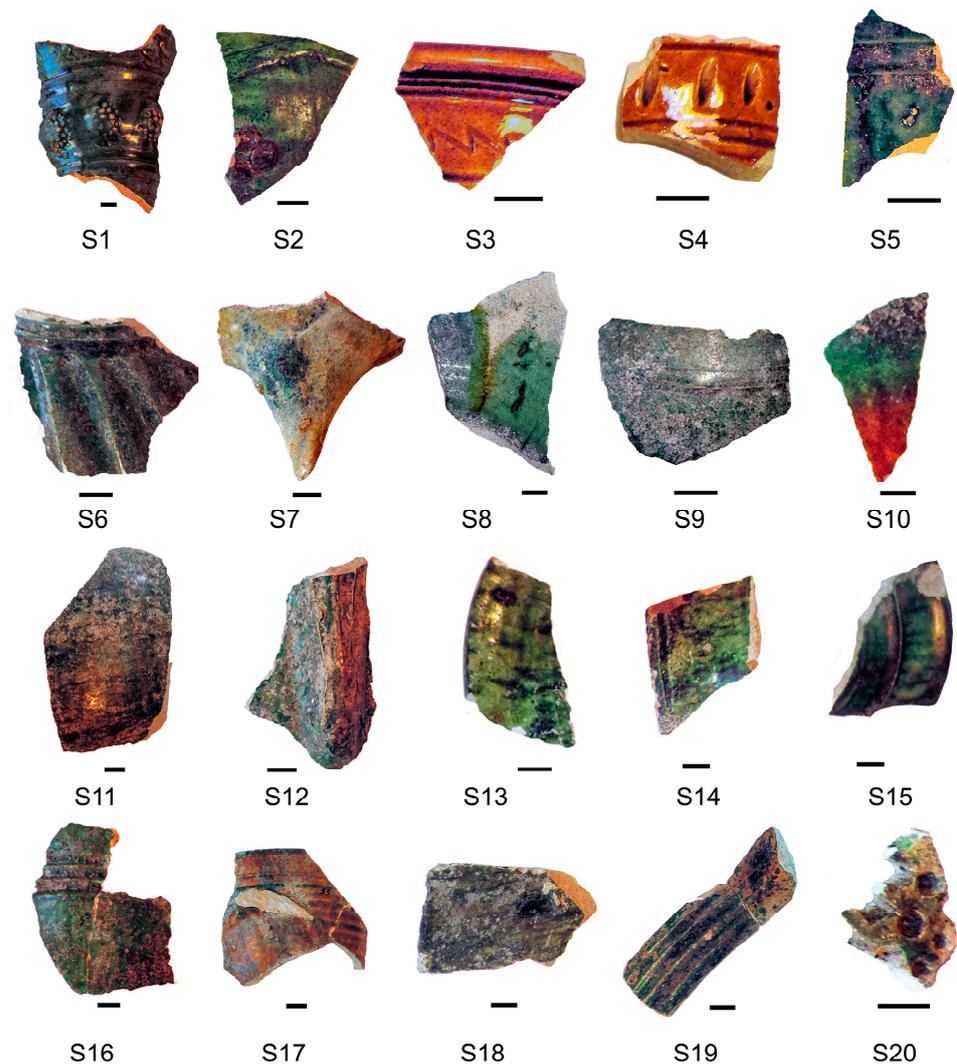


Figure 1. Glazed ceramic sherds collected from two storage pits, dated to the 13th–14th centuries, Santarém. S stands for Santarém. Scale bar: 10 mm.

As Figure 1 shows, green glazes are predominant, but some sherds exhibit amber or light brown glazes. In some cases, all sherd surfaces are glazed, but there is no pigment in some areas, and the glaze simply covers the ceramic body. As it is possible to observe through the sherd's images, the samples can be considered quite heterogeneous. Samples S1 and S2 are particularly interesting since they belonged to jugs decorated with green grapes in the S1 sample and black 'grapes' in the case of S2. S1 exhibits a red ceramic body, while all the other Santarém samples exhibit a whitish paste. All sherds are small, not exceeding about 10 cm in the longest dimension. The exception is sherd S1, which is about 15 cm high and 10 cm long.

Previous compositional studies of pottery ceramic pastes and clay raw materials from the region of Lisbon enabled us to establish a limited number of clay sources and formulations being used in the Lisbon workshops, where most of the ceramic production in the country was located [19–22]. Pliocene ceramic pastes (highly siliceous) or Miocene ceramic pastes (with a high content of calcium carbonate) were detected [23]. Potters settled preferentially in vicinity areas with clayey soils. We have to say, however, that there is no evidence of kilns producing lead-glazed pottery in the 13th and 14th centuries in the Tagus Valley (where Santarém is located). The production of glazed ceramics existed in the Muslim period until the 12th century and it was again proven from the 15th century onwards [24].

One should emphasise that in the Lisbon region, Miocene clays can be found in the North and South of the Tagus River, while Pliocene clays only exist on the South bank [16,21–23]. In the region of Santarém, Pliocene formations exhibit a more diversified composition, including predominantly illitic clayey facies, occasionally with calcretes (calcite-bearing formations) [17]. The only kaoliniferous formation referenced is the P1 level of kaolin sands [16].

In order to clarify this issue, many glazed (and some nonglazed) sherds from coeval European workshops were studied, and 20 samples are presented in Figure 2.

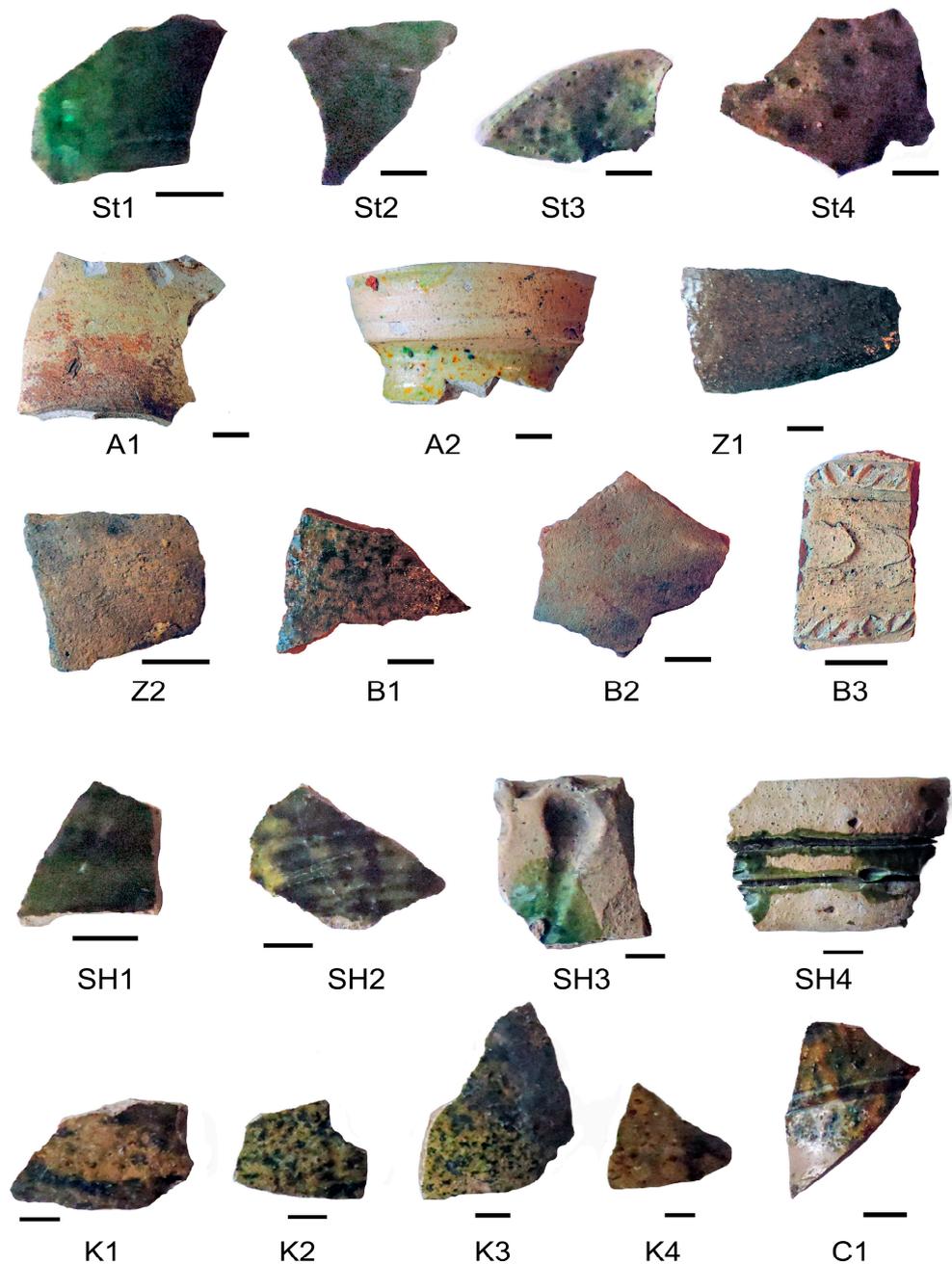


Figure 2. Glazed ceramic sherds collected from several European archaeological sites dated to the 13th–14th centuries. St—Saintonge; A—Ardenne; Z—Zomergem; B—Bruges; SH—Surrey–Hampshire; K—Kingston; and C—Cheam. Scale bar: 10 mm.

The suspicion that Santarém ceramics originated from different parts of Northern Europe is related to several factors: (a) 13th- and 14th-century ceramic productions are not

that well known in Portugal, and lead-glazed wares are proportionally rare in medieval collections; (b) the majority of these ceramics correspond to shapes and glazes which are very similar to Northern European productions; (c) Northern European glazed ceramics have been found in other archaeological contexts in Portugal and medieval lead-glazed ceramic production has never been confirmed—Figure 3. When observing some of the lead-glazed ceramics found in Portugal, these objects are very similar to Saintonge, Bruges, and English productions. It is known that ceramics previously identified as Northern European ceramics in 15th-century contexts were after all produced in Portugal [25]. The Santarém contexts are earlier and, thus far, no kiln before the 15th century is known to have produced any type of glazed ceramics.



Figure 3. Map with Santarém and European archaeological sites where all samples were collected.

The sherds analysed as comparative productions in this paper were obtained from different excavations in different parts of Northern Europe in sites possible to date to the 13th to the 15th century. The Saintonge, Surrey–Hampshire, Kingston, and Cheam types were all found in unstratified contexts in the greater London area and were classified by pottery specialists. As for the remaining types, these were obtained in the Ardenne, Zomergem, and Bruges areas. They were found associated with kilns and pottery wasters, and are thus considered local productions [26,27]. The choice of these areas as comparative productions was based on two basic premises. First, this area had frequent commercial relations with Portugal in the 13th and 14th centuries [11], and second, ceramics produced in this area are frequent finds in Portugal [12,13].

The Saintonge productions tend to present a light buff fabric glazed either green or dark yellow and are among the most widely distributed medieval glazed ceramics in Northern Europe [28]. The red fabric objects are usually glazed in green and are believed to be produced in the Bruges area (or the Netherlands) [29,30]. Finally, there are some objects that, by their characteristics, seem to have been produced in Britain [31].

Our archaeometric study of the glazed pottery found in the archaeological sites of medieval Santarém dated to the 13th to 14th centuries are, in this context, the first ones for such medieval glazed ceramics, and it is particularly interesting to determine whether they were locally produced or imported pottery.

4. Experimental Techniques under Use

Micro-Raman and ground-state diffuse reflectance absorption spectra spectroscopy (GSDR), stereomicroscopy (SM), and X-ray fluorescence (XRF) are non-invasive spectroscopies for glazes, while X-ray diffraction (XRD) analyses of the ceramic bodies involve the removal of ca. 10 to 15 mg of powder from each sherd. The use of powdered samples was mandatory for the equipment under use (described in the experimental section). The same powder was used for the X-ray fluorescence (XRF) experiments, enabling us to obtain results from more homogenous samples. This amount of 10 to 15 mg of powder is negligible since all sherds' weights vary between 5 and 75 g, and these two techniques can be considered as quasi-non-invasive methodologies for the study of ceramic bodies.

Micro-Raman investigations were carried out employing Renishaw InVia Confocal Raman equipment (manufacturer: Renishaw, London, UK), in a back-scattering configuration, using a 532 nm laser excitation.

GSDR experiments were conducted employing a home-built diffuse reflectance set-up, using an ICCD as a detector and a W-Hal lamp as the excitation source. Three standards, Spectralon white and grey disks and barium sulphate powder, were used to obtain the reflectance curves, and from them, the remission function was calculated.

For elemental composition information, XRF analyses were performed using a Niton XL3T GOLDD spectrometer from Thermo Scientific (manufacturer: ThermoFisher Scientific, London, UK).

To study the mineralogical and phase composition of the ceramic bodies of the sherds, XRD analyses were conducted utilising a Panalytical X' PERT PRO (Malvern Panalytical Ltd., Malvern, UK) diffractometer system equipped with a copper source.

The analysis conditions for the four methodologies under use were the same as in the references provided. Diffractograms were performed only one time for most samples as they were quite similar, as discussed in the text. However, in the cases where some differences were noted, they were repeated once or twice. All the other experiments were repeated at least three times.

In the stereomicroscopy (SM) experiments, tile sections' were observed using a Nikon SMZ645 stereomicroscope and representative images were acquired using a Moticam 10.0 MP digital camera.

XRF spectroscopy provides the elemental compositions of both ceramic bodies and glazes, diffractograms provide the mineralogical composition of pastes, and GSDR absorption spectra provide the colour characterisation. Finally, stereomicroscopy allowed us to perform a detailed comparison of cross-sections, which distinctly revealed that the fabric of light-coloured pastes in Santarém was quite distinct from the foreign fabrics.

Further details regarding all these techniques were previously described in [20–22].

5. Results and Discussion

5.1. Micro-Raman Studies

Micro-Raman spectroscopy is an excellent technique to identify the pigments used to decorate the surface of the glazed ceramic and to characterise the glaze itself [32]. All the white paste ceramics were made with highly siliceous clays; therefore, *quartz* was detected in many samples. In the white pastes, most samples exhibited *anatase* (TiO₂) and *carbon*

black on the darker surfaces. As expected, the red pastes were rich in hematite, as will be further demonstrated.

As previously referred to, sherd S1 has dimensions of about 15 cm × 10 cm and belonged to a wine jar, common in medieval pottery. Both the body of the jar and the grapes are covered with a green glaze, and it is interesting to point out that no specific copper signature (Cu^{2+}) was detected in the Raman spectrum of S1. The green colour of the lead-based glaze was certainly obtained with the use of copper oxide, as XRF data presented later in this paper for glazes will show. However, no Raman signature was detected because Cu^{2+} was dissolved in the matrix, as pointed out in previous publications [33,34].

Sherd S2 was probably also from a wine jug, in this case decorated with black grapes. Large amounts of hematite (Fe_2O_3) and magnetite (Fe_3O_4) were detected in that black decoration, as the micro-Raman spectra of Figure 4a show. The presence of a red paste beneath the substrate, covering the white paste, justifies the obtained results (see also Figure S1).

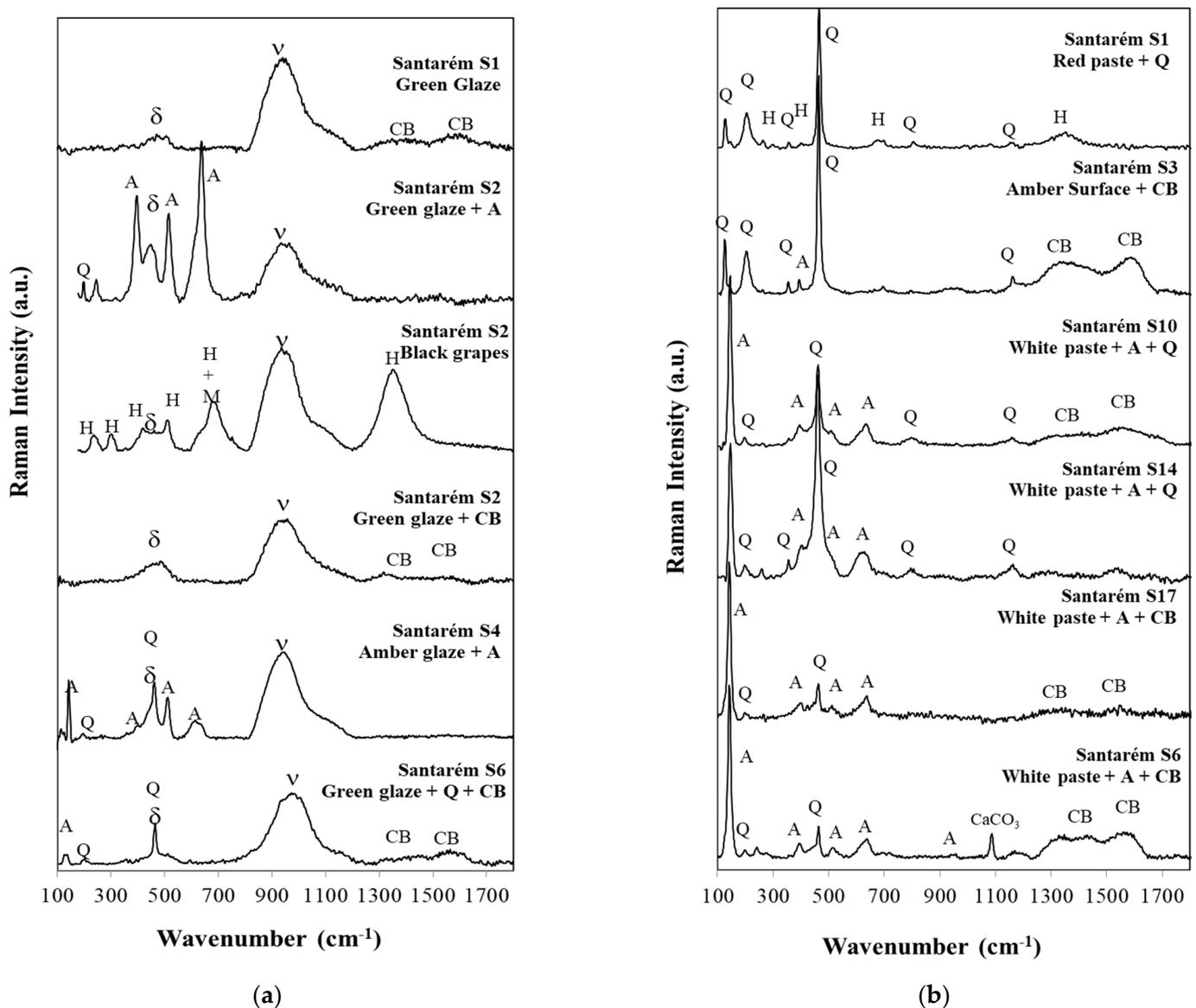


Figure 4. Micro-Raman spectra from the most significant glazed surfaces (a) and pastes (b) of the Santarém sherds. Quartz (Q), anatase (A), hematite (H), magnetite (M), carbon black (CB), stretching (v) and bending (δ) of Raman envelopes.

In samples S2 and S4 from Santarém, a clear signature of anatase was detected, showing that this mineral is dispersed in the glaze layer that covers the surface of the pottery. Anatase and quartz were also detected in most Santarém Raman spectra of the ceramic bodies, as Figure 4b shows.

One should also mention that, in all samples, there was a remarkable absence of calcium carbonate, as shown in Figures 4 and 5. The only exception was Santarém S6 white paste, although the amount of CaCO_3 (peaking at 1087 cm^{-1}) was certainly very low. The residual presence of calcite can be attributed to secondary calcite formed during burial, through impregnation or alteration of primary ceramic components, with the latter hypothesis being less likely, as will be shown subsequently using other methodologies.

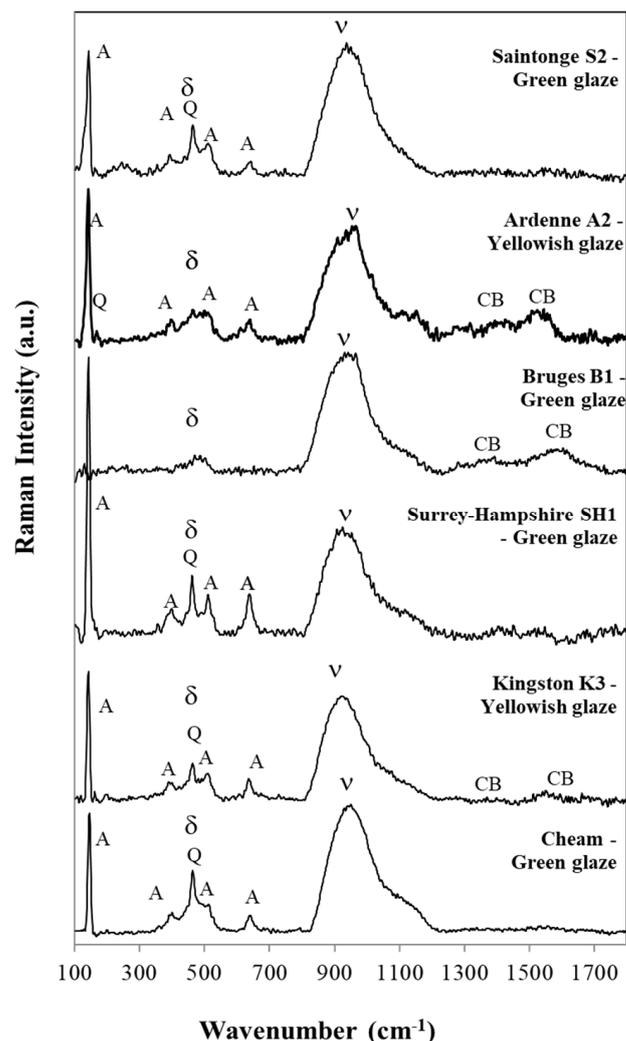


Figure 5. Micro-Raman spectra from the most significant glazed surfaces from the European sherds. Quartz (Q), anatase (A), carbon black (CB), stretching (v) and bending (δ) of Raman envelopes.

Micro-Raman spectroscopy was also used to obtain information about the nature of the glaze, even establishing correlations with the firing temperature of the kiln. Quartz is a crystalline form of SiO_2 and, in glassy structures, part of the covalent bonds between the SiO_4 tetrahedra is destroyed. The ratio of the stretching (i.e., $\sim 1000\text{ cm}^{-1}$) and bending ($\sim 500\text{ cm}^{-1}$) Raman envelopes can be correlated to the temperature of the kiln, the glaze composition, and the different fluxing agents. Colomban introduced a quantification using a ratio of band areas $I_p = A_{500}/A_{1000}$, where I_p is the polymerisation index [32]. Santarém glass types are lead-rich glazes with $I_p \sim 0.1$ to 0.2 , pointing to kiln firing temperatures below $700\text{ }^\circ\text{C}$.

The maximum wavenumber of the Si-O stretching bands (ν_{\max}) for the Santarém glazes lies in the 935 to 960 cm^{-1} range, a value typical of lead-rich glazes [32].

Figure 4b shows the Raman spectra found for most ceramic bodies for the Santarém sherds. Large amounts of anatase, quartz, and carbon black were detected.

A similar study was performed for the sherds of the European coeval production centres, and some significant cases are shown in Figure 5.

A striking similarity is observed in the micro-Raman spectra of the glazes depicted in Figures 4a and 5. Additionally, the I_p parameter exhibits slight variations, ranging from approximately 0.1 to 0.2. Consequently, discerning distinctive features indicative of different production centres proves challenging through this spectroscopic technique alone. No Raman spectra are presented for the ceramic bodies of the European sherds because the results are basically the same as those presented in Figure 4b. To ascertain the origins of Santarém pottery conclusively, we will proceed by presenting results derived from alternative spectroscopic and visual methods or techniques.

5.2. GSDR Studies

Ground-state diffuse reflectance absorption spectra for all coloured sherds in Figures 1 and 2 are presented in Figures 6 and 7, where the remission function is the ordinate and the wavelength in nm is the abscissa. Figure 6a shows the absorption spectra of sample S2, the one with black grapes. The green glaze presents two maxima, one at about 380 nm and the other in the visible region, maximising at ca. 700 nm. The absorption in the red region produces the observed green colour (the complementary colour of the red). The black grapes are characterised by a high value of the remission function both in the UV and visible regions of the spectrum. By contrast, the ceramic body absorbs primarily in the UV region.

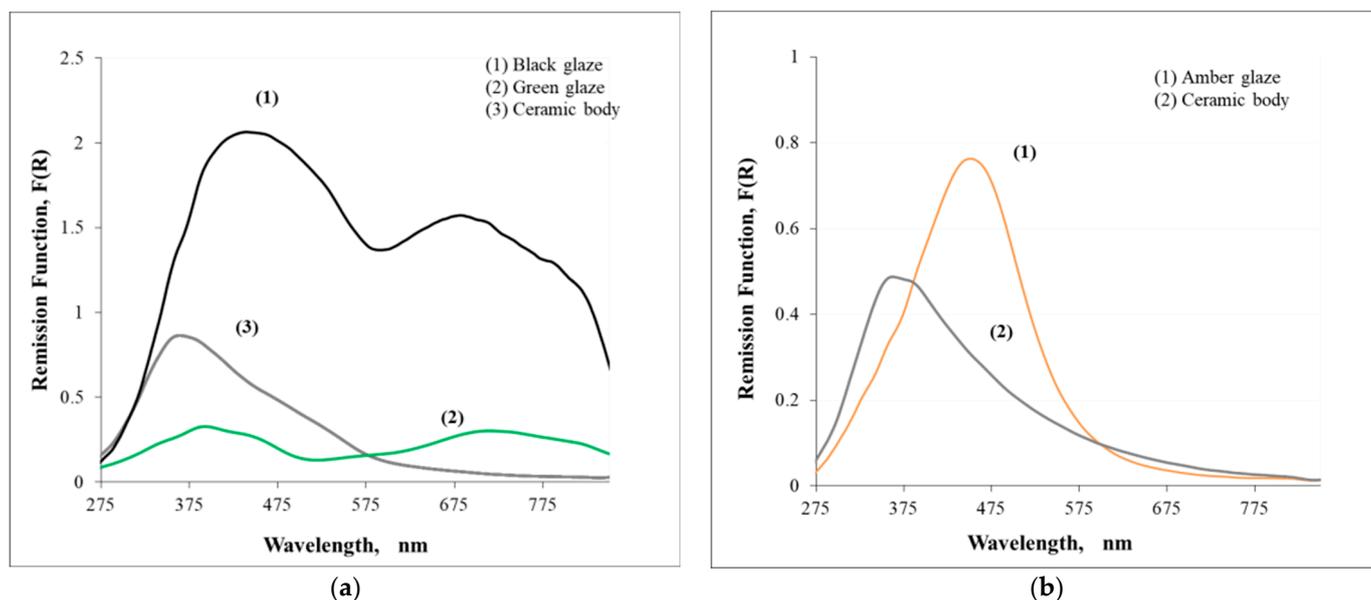


Figure 6. GSDR absorption spectra of S2 Santarém green and black glaze and ceramic body (a) and S3 Santarém amber glaze and ceramic body (b).

Figure 6b refers to the amber colour of sample S3. An absorption band maximising at about 470 nm is compatible with a higher concentration of iron oxide, as described in [33,34].

The GSDR absorption spectra of Figure 7 are like the ones presented in Figure 6, regarding the green and greenish glazes. The brown glaze of sherd Z1 is characterised by a broad absorption band, spreading from the UV to all visible regions and maximising at about 420 nm. The K2 sherd exhibits yellow and green spots, and the absorption

bands reflect blue and red absorptions. Finally, the yellow glaze of sample St3 exhibits an absorption, in the blue region, at about 380 nm, while the creamy glaze of the A2 sample absorbs in the UV region and has a small broad band in the visible region.

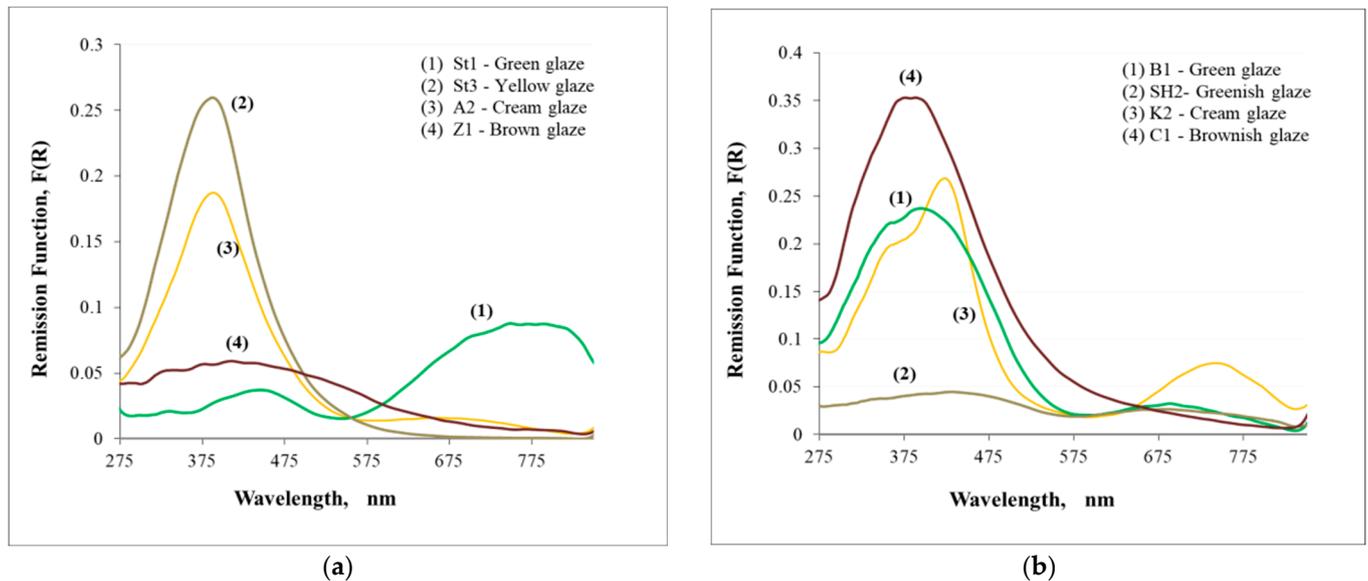


Figure 7. GSDR absorption spectra of European sherds: (a) St1—Saintonge green glaze; St3—Saintonge yellow glaze; A2—Ardenne cream glaze; Z1—Zomergem brown glaze; (b) B1—Bruges green glaze; SH2—Surrey–Hampshire greenish glaze; K2—Kingston cream glaze; C1—Cheam brownish glaze.

Again, the similarity of the GSDR absorption spectra for the glazes presented for the Santarém and European sherds is remarkable, and no clear differences in the production centres can be established using this spectroscopic technique.

5.3. XRD Studies

The ceramic bodies retrieved from both the Santarém pits and European archaeological sites underwent comprehensive analysis using X-ray diffraction (XRD powder method). As illustrated in Figure 8 (limited to whitish pastes), the striking resemblance between the two groups outweighs any noticeable distinctions. All pastes were crafted from siliceous raw materials, resulting in pronounced quartz (Q) signatures. Alongside amorphous/nanocrystalline phases, which XRD cannot fully characterise, a select number of minor minerals were identified, including muscovite, rutile, anatase, microcline, and plagioclase. Hematite was found only in the red pastes. Furthermore, the presence of muscovite or illite/muscovite thermal-derived phases was observed (see Table 1). This temperature-dependent phenomenon, primarily governed by dihydroxylation, is discernible in XRD pattern modifications, particularly evident in characteristic reflections at $2\theta = 8.9$ and $2\theta = 19.8$. These modifications facilitate the assessment of minimum kiln temperatures [22].

Table 1. Main XRD peaks used to identify the minerals in the diffractograms of all ceramic bodies.

Quartz—Q, SiO_2 , $2\theta^0 = 21.0, 26.7, 36.7, 46.0, 50.2, 60.0, 64.1, 68.2,$
Microcline—Mic, $\text{K Al Si}_3\text{O}_8$, $2\theta^0 = 20.9, 25.7, 27.5, 42.0, 50.8,$
Muscovite—M, $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, $2\theta^0 = 8.9, 17.8, 19.8, 25.7,$
Illite—I ($\text{K, H}_3\text{O})(\text{Al, Mg, Fe})_2(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2$ $2\theta^0 = 8.8, 17.8, 19.8, 25.7,$
Rutile—R, TiO_2 , $2\theta^0 = 27.3, 36.1, 54.3,$
Anatase—A, TiO_2 , $2\theta^0 = 25.3, 307.1, 47.9,$
Hematite—H, $\alpha\text{-Fe}_2\text{O}_3$, $2\theta^0 = 24.4, 35.7, 49.6, 54.2, 57.4$

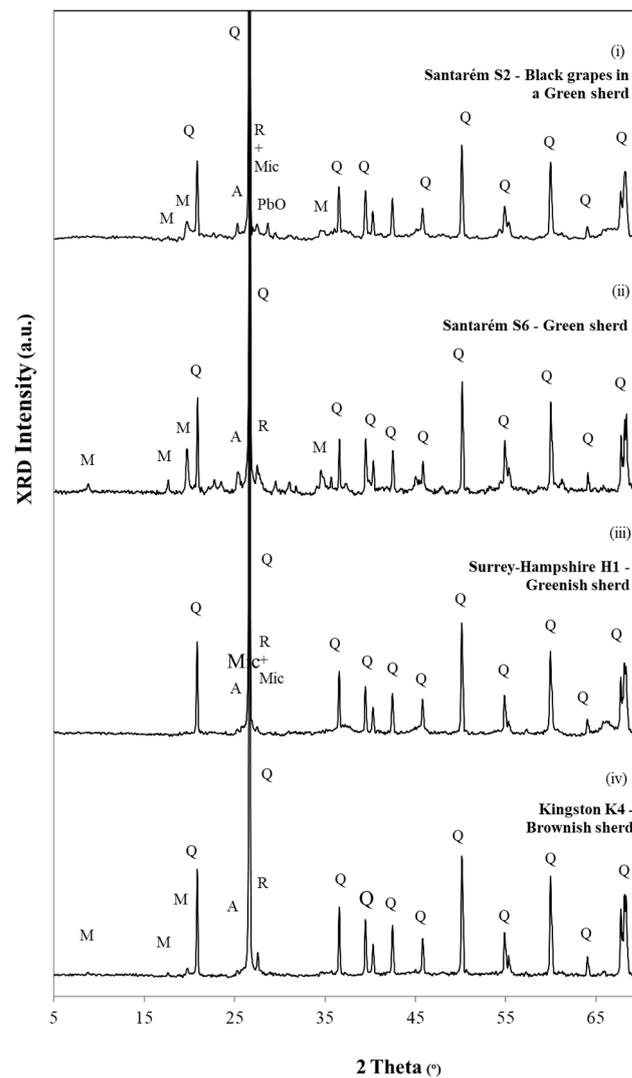


Figure 8. Representative XRD patterns for ceramic bodies of sherds from Santarém medieval archaeological site, all non-carbonaceous silicious-type pastes. XRD peaks: quartz (Q), anatase (A), rutile (R), muscovite (M), and microcline (Mic). (All diffractograms were normalised to the quartz peak at $2\theta^0 = 21.0$ (constant intensity), to allow comparisons of the relative amounts of all the other minerals).

5.4. XRF Studies

5.4.1. Ceramic Bodies

The XRF results achieved for the ceramic bodies of sherds from the Santarém archaeological site are presented in Table 2, and Table 3 presents similar data for the European sherds.

The data included in Tables 2 and 3 allow for establishing various types of ratios, commonly used for comparative analyses between materials. After an exploratory analysis of these data, it is found that one of the main ratios with discriminatory capacity among the samples under study is based on the concentration of the two main oxides, SiO_2 and Al_2O_3 , with which K_2O , CaO , and Fe_2O_3 can be associated. The observed differences/trends will be directly correlated with the original formulation of the paste, where, alongside the clay components and quartz, the aforementioned accessory minerals occur. Thus, Figure 9 was selected, elaborated on with the ratios of Al/Si vs. Ca/Si , to chemically describe all the samples under study.

Table 2. Chemical composition of the powdered ceramic bodies of the Santarém sherds, obtained by XRF. Data are presented as wt.% for major and minor constituents and ppm for trace elements. (nd: not detected; nq: not quantified).

	Samples	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Mn	Rb	Sr	Zr	Nb	R (*)
Santarém	S1	1.41	12.44	73.66	3.47	0.67	1.05	7.26	nd/nq	67	70	266	22	134
	S2	nd/nq	27.13	63.10	3.11	1.08	2.84	2.71	nd/nq	62	122	224	29	87
	S3	nd/nq	25.45	66.70	2.18	0.70	1.36	3.61	nd/nq	55	22	66	19	135
	S4	nd/nq	22.89	68.64	2.10	0.77	1.38	4.21	nd/nq	28	18	66	10	122
	S5	nd/nq	21.09	70.40	2.67	0.70	1.38	3.75	nd/nq	37	21	86	13	135
	S6	nd/nq	24.11	64.03	5.30	0.90	1.92	3.71	nd/nq	148	48	240	36	104
	S7	nd/nq	22.08	70.32	2.18	0.45	1.33	3.61	nd/nq	78	28	94	23	210
	S8	nd/nq	25.37	66.00	2.41	0.52	1.51	4.16	nd/nq	94	52	210	37	182
	S9	1.29	25.77	62.18	2.70	1.55	1.43	5.06	nd/nq	69	52	119	23	58
	S10	nd/nq	27.35	63.84	2.34	0.48	1.61	4.34	nd/nq	98	59	243	40	194
	S11	nd/nq	26.39	63.73	2.77	1.40	1.48	4.21	nd/nq	81	46	154	30	67
	S12	nd/nq	25.13	65.02	2.88	1.12	1.48	4.34	nd/nq	73	49	135	26	83
	S13	nd/nq	27.88	62.47	2.39	1.24	1.31	4.67	nd/nq	81	54	90	28	75
	S14	nd/nq	24.28	64.88	3.15	1.69	1.61	4.36	nd/nq	90	69	200	32	55
	S15	nd/nq	26.18	64.74	2.64	1.17	1.41	3.84	nd/nq	75	30	87	24	80
	S16	nd/nq	23.99	65.04	2.98	2.21	1.54	4.21	nd/nq	75	66	183	30	42
	S17	nd/nq	25.57	64.05	2.24	1.37	1.33	5.41	nd/nq	84	68	151	30	67
	S18	nd/nq	22.20	69.27	2.52	0.69	1.23	4.06	nd/nq	81	56	178	31	135
	S19	1.45	21.74	68.14	2.34	0.90	1.20	4.19	nd/nq	79	59	200	32	102
	S20	nd/nq	26.58	65.06	2.31	0.75	1.29	3.97	352	47	nd/nq	nd/nq	20	126

(The estimated error for major elements (Si and Al) was $\leq 3\%$, for minor elements (K, Ca and Fe) $\leq 4\%$ and for trace elements $\leq 8\%$). (*) Ratio R = (SiO₂ + Al₂O₃ + K₂O)/CaO.

Table 3. Chemical composition of the powdered ceramic bodies of European sherds, obtained by XRF. St, Saintonge; A, Ardenne; Z, Zomergem; B, Bruges; SH, Surrey- Hampshire; K, Kingston; C, Cheam. Data are presented as wt.% for major and minor constituents and ppm for trace elements. (nd: not detected; nq: not quantified).

	Samples	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Mn	Rb	Sr	Zr	Nb	R (*)
Saintonge	St1	nd/nq	23.07	67.51	2.91	0.92	1.73	3.82	nd/nq	64	63	170	21	101
	St2	nd/nq	16.95	74.51	2.79	1.09	1.30	3.30	nd/nq	43	203	210	18	86
	St3	nd/nq	18.42	72.03	4.24	0.83	1.74	2.71	nd/nq	46	55	149	20	115
	St4	nd/nq	19.78	71.76	2.04	0.67	1.82	3.91	nd/nq	40	38	168	19	141
Ardenne and Zomergem	A1	nd/nq	22.22	69.61	1.12	0.90	2.69	3.42	nd/nq	38	87	273	46	104
	A2	nd/nq	23.53	68.14	1.24	1.10	2.67	3.28	nd/nq	30	74	226	38	84
	Z1	1.55	11.27	73.21	3.37	0.64	1.08	8.83	nd/nq	63	58	325	20	138
	Z2	1.20	11.09	74.22	3.16	0.54	1.05	8.70	nd/nq	59	57	248	20	164
Bruges	B1	1.24	10.53	75.68	3.23	0.83	1.06	7.39	nd/nq	59	64	243	20	108
	B2	1.54	13.46	69.70	4.23	1.34	1.25	8.42	nd/nq	82	114	268	25	65
	B3	1.16	10.68	76.68	3.40	0.79	1.04	6.21	nd/nq	50	60	221	16	115
Surrey Hampshire	SH1	nd/nq	19.90	70.51	3.41	0.95	1.35	3.84	nd/nq	37	222	142	15	99
	SH2	nd/nq	15.19	73.69	2.63	2.89	0.92	4.58	360	46	162	87	13	32
	SH3	1.14	18.66	71.11	3.00	0.95	1.22	3.85	nd/nq	67	382	348	29	98
	SH4	1.28	15.98	73.63	2.87	0.80	1.09	4.27	nd/nq	46	383	165	18	115
Kingston	K1	nd/nq	12.45	80.03	2.00	0.18	0.88	4.43	nd/nq	35	22	125	11	531
	K2	1.15	17.24	72.70	1.68	0.81	1.28	5.11	nd/nq	33	39	126	20	113
	K3	1.17	15.93	74.62	2.35	0.71	1.05	4.14	nd/nq	34	39	178	17	131
	K4	nd/nq	15.62	76.53	2.26	0.40	1.01	4.14	nd/nq	37	45	244	21	237
Cheam	C1	nd/nq	18.67	71.99	2.53	0.91	1.40	4.48	nd/nq	45	76	217	24	102

(The estimated error for major elements (Si and Al) was $\leq 3\%$, for minor elements (K, Ca and Fe) $\leq 4\%$ and for trace elements $\leq 8\%$) (*) Ratio, R = (SiO₂ + Al₂O₃ + K₂O)/CaO.

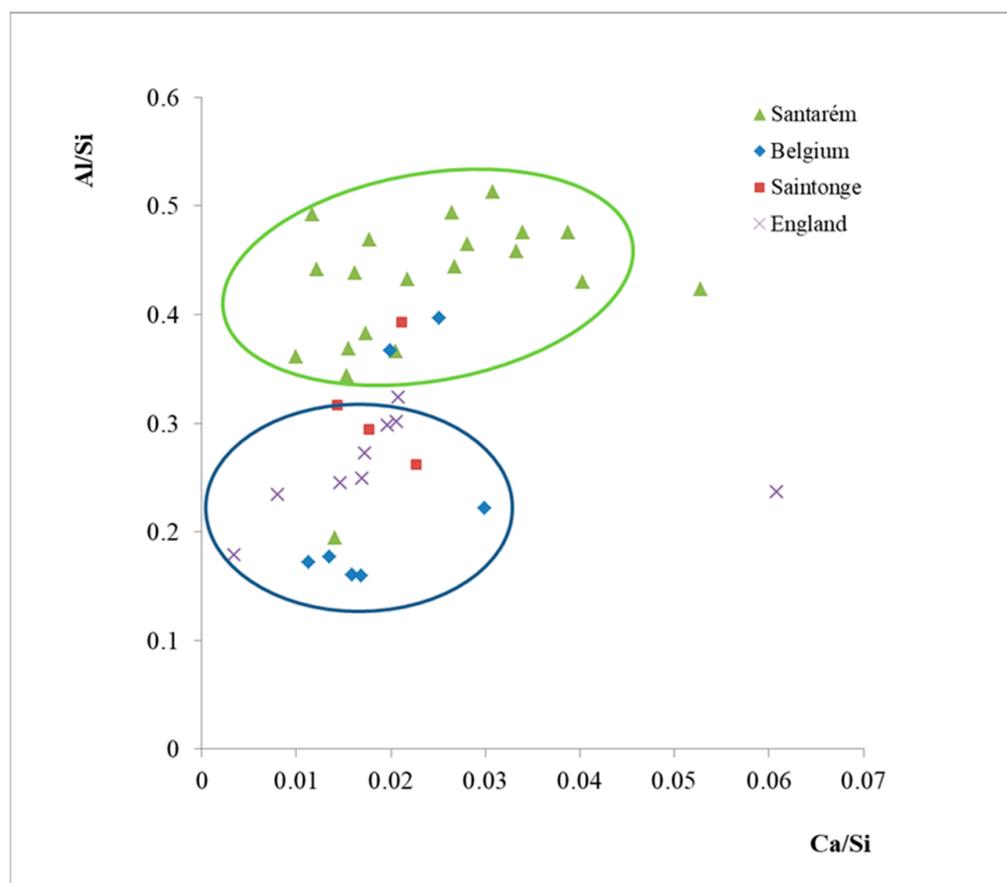


Figure 9. Scatterplot of Al/Si versus Ca/Si count ratios for the studied ceramic. The contents of Al and Ca measured by XRF were normalised to the Si content [35]. Green ellipse—light coloured pastes with lower quartz temper. Blue ellipse—light, reddish, and grey brownish pastes with higher quartz temper.

The scatterplot for Al/Si versus Ca/Si (% wt ratio) for all sherds (Figure 9) reveals two distinct clusters, with the upper one corresponding to Santarém samples and the lower one to the European group. There are a few samples that slightly deviate from this general clustering. The Santarém sample S1 (red paste), is positioned in the group of the blue ellipse, the European one. Saintonge St1 and Ardenne A1 and A2 are included in the Santarém green ellipse. Santarém samples exhibit a distinctly higher aluminium content, while the majority of European ceramic bodies are more quartz-rich. The Ca/Si ratio shows little variability as, in general, CaO contents are very low, and according to the XRD-identified mineralogy, they can be correlated with the presence of Na-Ca plagioclase.

This finding represents the initial spectroscopic evidence definitively delineating between Santarém and European samples. All preceding findings from Figure 9 gathered with the data of Tables 2 and 3 reinforce the non-calcareous nature of the ceramic bodies, with calcium contents less than 5% wt CaO [36,37], aligning with the Pliocene-like origin of the clays used from the Lisbon region [19].

Tables 2 and 3 present R values. R is defined by $R = (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O})/\text{CaO}$ and was used in previous papers by our group [19–22] to quantify the relative amounts of the structural components of the ceramic pastes ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}$), related to calcium fractions (CaO). As one could expect, all R values are characteristic of the Pliocene-like clays [19], and no significant difference exists between Santarém and the European cases.

Figure 10 depicts samples S1 (red paste) from Santarém and Belgium (B1, B2, and B3 from Bruges—red pastes and Z1 and Z2 from Zomergem—grey-brown pastes). These pastes are represented in the lower section of Figure 10, exhibiting notably low Al/Si

and Ca/Si ratios. All of them demonstrate a higher iron content (7–9% wt.). This aspect clearly indicates that Belgian pastes have a markedly distinct formulation from the other light-coloured pastes from Santarém. The similarity in chemical composition between sample S1 and the other coloured paste samples suggests a common origin. This aspect will be further evaluated by also considering the data from the ceramic's fabric.

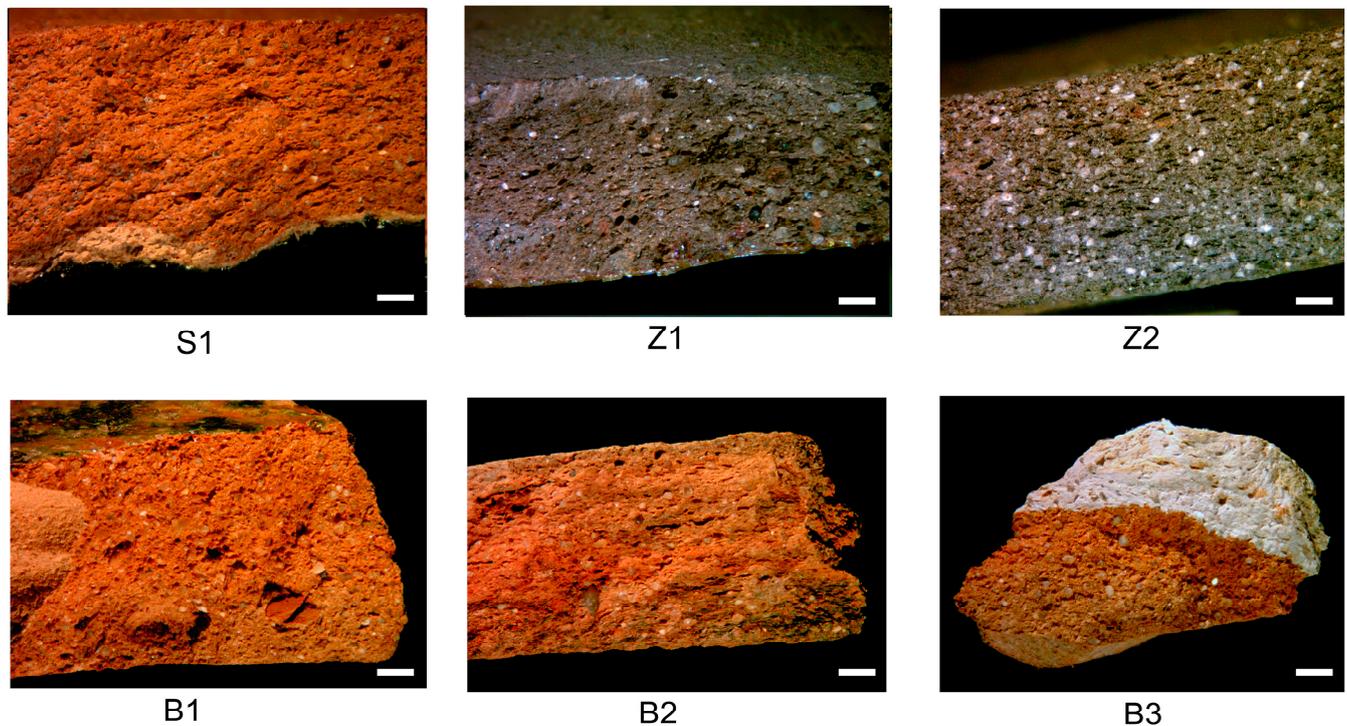


Figure 10. Selection of representative Santarém (S1, Santarém), and European red (Bruges—Belgium B1, B2, B3) and grey-brown (Zomergem Z1, Z2) fabric pastes. Scale bar: 1 mm.

5.4.2. Glazes

XRF results for glazes are presented in Tables 4 and 5. As mentioned before, all glazed sherds possess transparent lead glazes [38], and, for most samples, the PbO content of the Santarém samples (~50% wt.) is higher than the European ones (~40% wt.). The PbO/SiO₂ ratio is also different for the two groups, pointing to different technologies in the glaze-manufacturing process.

Table 4. Chemical composition of the glazed surfaces of Santarém sherds obtained by XRF, wt.%. (nd: not detected; nq: not quantified).

Samples	Colours	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	NiO	CuO	ZnO	As ₂ O ₃	SnO ₂	PbO	PbO/SiO ₂	
Santarém	S1	Green	nd/nq	7.03	20.20	0.42	nd/nq	0.28	0.28	1.13	0.05	3.76	0.51	6.33	0.15	59.87	3.0
		Green	nd/nq	8.97	32.33	1.57	3.40	0.34	0.22	0.42	0.07	3.12	0.02	4.86	0.20	44.49	1.4
	S2	Black (grape)	nd/nq	9.48	34.50	1.17	1.92	0.30	0.24	1.21	0.06	2.60	0.02	5.50	0.15	42.85	1.2
		Amber	nd/nq	9.31	20.68	0.35	nd/nq	0.05	0.28	4.40	0.07	0.03	0.02	6.51	nd/nq	58.31	2.8
	S3	Brown (scratch)	nd/nq	9.71	21.91	0.43	nd/nq	nd/nq	0.28	4.54	0.12	0.09	nd/nq	5.37	nd/nq	57.56	2.6
		Amber	nd/nq	9.72	23.58	0.51	nd/nq	nd/nq	0.28	4.57	0.09	0.03	0.02	5.61	nd/nq	55.59	2.4
	S4	Brown (scratch)	2.93	9.22	22.93	0.49	nd/nq	0.03	0.28	4.44	0.08	0.05	0.02	5.89	nd/nq	53.64	2.3
	S5	Green	nd/nq	9.70	34.83	1.26	1.63	0.07	0.24	0.57	0.07	2.95	0.02	5.19	nd/nq	43.48	1.2
	S6	Green	nd/nq	5.01	16.80	0.24	10.02	nd/nq	0.25	0.31	0.07	5.96	0.56	5.96	0.08	54.73	3.3
	S8	Green	nd/nq	9.35	29.46	0.77	nd/nq	0.06	0.31	0.77	0.11	1.96	nd/nq	5.45	nd/nq	51.76	1.8
		Green	nd/nq	9.43	25.93	1.04	6.58	0.07	0.24	0.93	0.08	1.67	0.02	4.74	0.02	49.26	1.9
	S10	Brown	2.48	9.28	25.54	0.68	nd/nq	0.05	0.27	3.72	0.07	0.22	0.02	5.78	nd/nq	51.89	2.0
	S19	Green	nd/nq	7.64	49.33	1.17	4.49	0.06	0.20	0.67	0.08	2.42	0.02	3.65	0.04	30.25	0.6

Figure 11 shows the correlation between the flux, PbO, and the SiO₂ content, suggesting a linear relation between them. Indeed, the flux content is higher in the Santarém samples (the green triangles).

Some authors [39–41] referred to the use of Sb-based opacifiers in the studied glazes (from Korchabad, Susa, Persepolis, and Tepe Rabat—8th and 6th centuries BC), present as lead antimonate, calcium antimonate, and/or sodium antimonate. In some cases [39], even no Pb was detected. This was not our case, because no Sb was detected in the samples studied by us.

The colouring agent of green-coloured sherds was copper, as is common in ancient coloured glazed ceramics [39,42,43], while brown and amber colours were obtained with the use of iron oxide. The black grape of sample S2, apart from the iron compounds revealed by the micro-Raman spectrum, also presents the addition of copper, perhaps used to reinforce the darkness [40].

Table 5. Chemical composition of the glazed surfaces of European sherds obtained by XRF, wt.% (nd: not detected; nq: not quantified).

	Samples	Colours	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	NiO	CuO	ZnO	As ₂ O ₃	SnO ₂	PbO	PbO/SiO ₂
Belgium	B1	Green	nd/nq	11.57	35.46	0.42	nd/nq	0.25	0.35	1.41	0.09	2.77	0.57	5.91	0.05	41.15	1.2
	B3	Yellow	1.91	19.19	29.67	1.78	nd/nq	0.09	0.23	1.19	0.08	nd/nq	0.02	5.10	0.13	40.60	1.4
	A2	Creamy	nd/nq	13.58	38.23	0.22	nd/nq	0.39	0.29	1.21	0.13	nd/nq	2.54	5.60	nd/nq	37.81	1.0
	Z1	Brown	2.62	8.96	37.52	0.58	nd/nq	0.20	0.23	3.34	0.09	nd/nq	0.03	5.50	nd/nq	40.93	1.1
	St1	Green	nd/nq	8.13	38.16	0.30	nd/nq	0.21	0.27	0.94	0.08	3.25	0.46	6.04	0.17	41.98	1.1
Saintonge	St2	Green	nd/nq	10.71	26.24	0.80	1.97	0.19	0.33	1.48	0.08	3.18	0.73	5.69	0.10	48.48	1.8
	St3	Creamy	nd/nq	11.93	45.68	0.73	nd/nq	0.26	0.25	0.99	0.08	0.60	0.02	5.77	nd/nq	33.69	0.7
	St4	Green	nd/nq	11.91	38.88	0.86	0.64	0.23	0.25	0.99	0.09	1.84	0.00	5.75	nd/nq	38.57	1.0
	St4	Green	2.38	13.23	35.16	0.52	2.90	0.37	0.28	1.64	0.06	2.43	0.03	5.36	nd/nq	35.64	1.0
Surrey-Hampshire	SH1	Green	2.53	12.15	21.79	0.98	0.44	0.17	0.25	1.00	0.09	4.15	0.07	4.92	0.28	51.21	2.3
	SH2	Green	nd/nq	9.57	28.34	0.58	0.66	0.14	0.30	1.48	0.11	2.26	0.21	7.26	0.39	48.70	1.7
	SH3	Green	2.11	14.28	29.77	1.36	1.95	0.22	0.21	0.99	0.08	3.17	0.02	4.79	0.03	41.02	1.4
Kingston	K1	Yellowish	nd/nq	11.14	30.45	0.50	nd/nq	0.14	0.27	1.34	0.10	1.25	0.03	5.79	0.09	48.90	1.6
	K2	Yellowish	2.44	12.39	30.77	1.44	nd/nq	0.17	0.23	1.24	0.08	5.01	0.68	4.33	0.17	41.04	1.3
	K3	Green	2.90	11.39	26.10	0.47	nd/nq	0.19	0.25	2.00	0.09	4.82	0.02	5.28	0.54	45.95	1.8
Cheam	K3	Colourless	nd/nq	11.99	32.81	0.41	nd/nq	0.19	0.27	1.61	0.10	0.91	0.02	6.16	0.46	45.07	1.4
	C1	Green	nd/nq	8.59	28.57	0.52	1.05	0.16	0.28	1.67	0.08	3.56	0.26	5.79	0.59	48.88	1.7

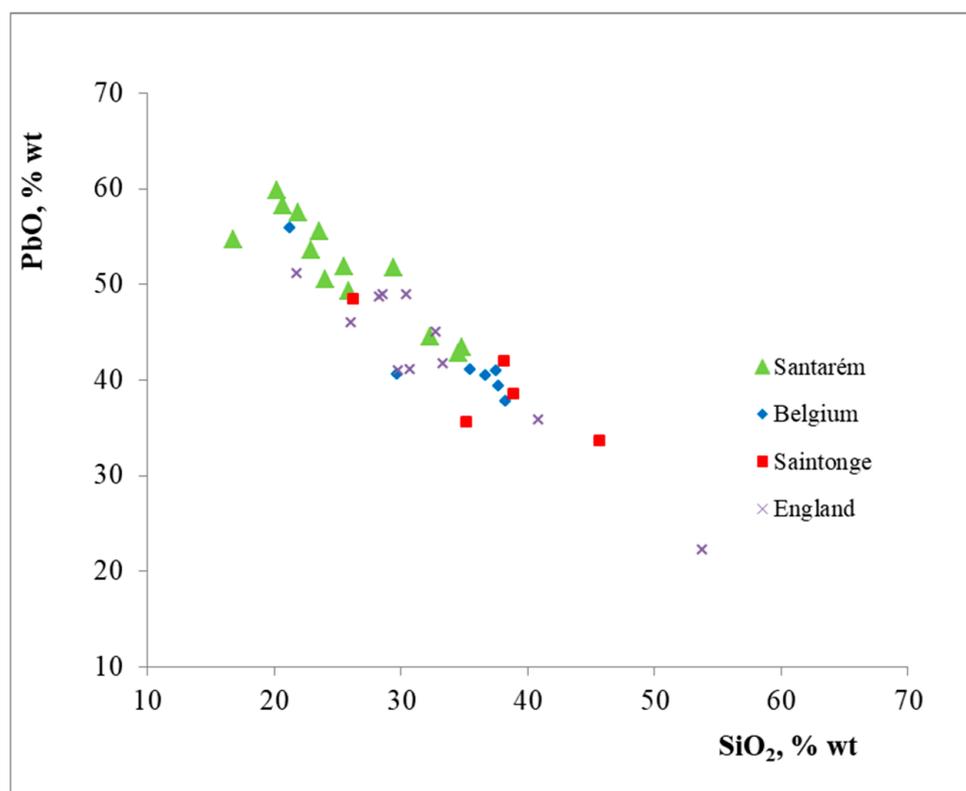


Figure 11. Scatterplot of PbO versus SiO₂ for glazed surfaces of Santarém and European samples.

5.5. Optical Microscopy (OM)

Given the limited variability in X-ray diffraction (XRD) analyses of light-coloured ceramic pastes, suggesting similarities in the components of raw materials and firing conditions, a clear trend emerges regarding the proportion of these components. This trend becomes more evident when considering major oxides (SiO_2 and Al_2O_3) as stated before. Despite previous evidence revealing a strong possibility of different origins for the light clay samples from Santarém compared to European ones, a visual inspection of their manufacturing was carried out, using various parameters, to validate this assumption. Particular attention was given to European samples whose composition fell within the domain of the Santarém group or vice versa, as well as to the group of coloured ceramics, namely those made of red clay.

Figures S1 and S2 (Supplementary Material) present cross-sections of Santarém samples S1 to S20 and all European samples. Tables S1 and S2 summarise the fabric paste characteristics of all samples used in this study.

The combination of chemical data (Tables 2 and 3) with the fabric analysis of the light sherds, including sample Z1, observed through stereomicroscopy, is represented in Figure 12. Alongside the Al/Si and Ca/Si values that determined the positioning of the samples in the figure, two parallel vertical axes were placed, aiming to establish a correspondence between the ceramic and the raw material that it originated from (clay–quartz mixture) for a given value of Al/Si. Given the aluminous and siliceous composition of the pastes, with a low content of K_2O , hypotheses of kaolinite–quartz and illite–quartz mixtures are considered based on their ideal chemical compositions. On the horizontal axis, we placed the slight trend of enrichment in CaO instead of the Ca/Si parameter, which, according to observations, is due to the presence of relic feldspar (Na–Ca plagioclase) in the ceramic paste (e.g., sample S16).

From top to bottom, the samples exhibit a decreasing $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio (indicating that they are more quartzose or siliceous), and from left to right, they show a slight enrichment in feldspar, possibly albite/oligoclase.

Visual analysis distinctly reveals that the manufacture of light-coloured pastes in Santarém is distinct from other foreign manufactures. Foreign light-coloured paste fabrics are also distinct from each other. Only the samples from SH exhibit two distinct manufactures (SH1, SH3, SH4 vs. SH2), revealing that they may have a different origin or formulation. The remaining samples show a notable origin homogeneity in both chemical composition and fabric.

In the formulation of pastes found in Santarém, it is evident that there is control over the quantity of quartz in the paste formulation. The fabric is globally dominated by an abundant plastic fraction, where the quartz temper is unimodal, tending to be fine, with occasional coarse grains. Some small compositional differences are observed in the content of muscovite and feldspar, still recognisable in XRD patterns and visual inspection. The overall composition suggests that the paste results from a source rich in kaolinite, where quartz is consistently present. Considering only quartz and kaolinite as paste constituents, the quartz content of Santarém light pastes varies between 15 and 30%, which is in good agreement with the visual analysis. The light colour of the pastes and the actual content of quartz exclude the hypothesis of an illite-bearing source, as can be seen in Figure 12.

The gathered information suggests that the origin of the ceramics found in Santarém are not of European import, as initially thought due to stylistic similarities. On the other hand, there are geological formations in the local area capable of providing ceramic raw materials, particularly a Pliocene or Pliocene-like formation rich in kaolinite (Pliocene sands P1 with approximately 30% kaolinite) [16,17].

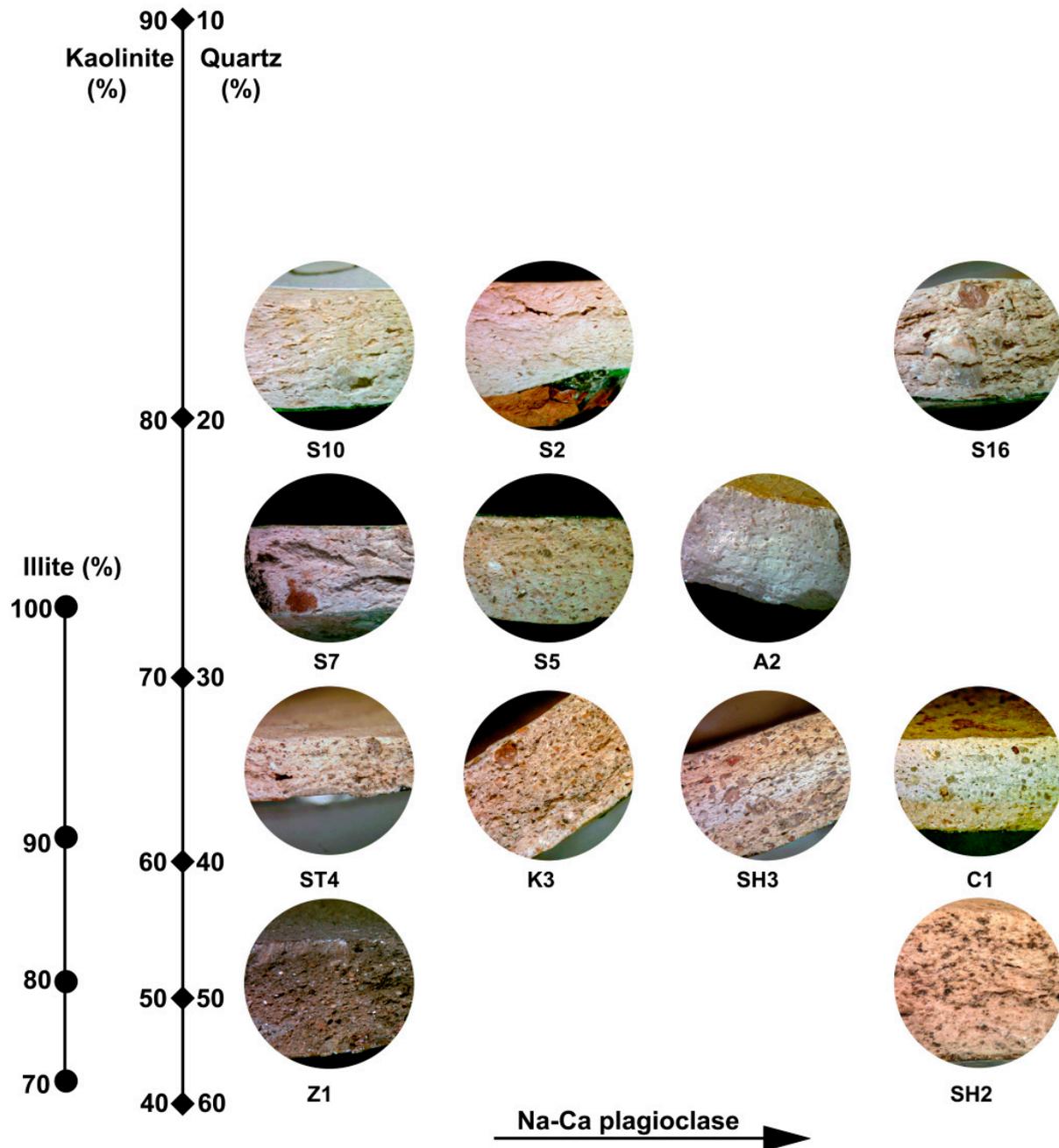


Figure 12. Selection of representative Santarém and European fabric pastes. From top to bottom, quartz temper increases. From left to right, feldspar slightly increases (Na-Ca plagioclase).

Upon initial visual observation, the entirely red ceramics appear similar due to the abundance of quartz and similarity in manufacturing. However, there is a noticeable trend towards a greater predominance of fine and rounded quartz in the Bruges samples. Another evident aspect, observed in the two selected pastes with red and white components, is that, in the case of Santarém (S2), there is a very plastic and compact white paste, almost devoid of quartz, onto which another very plastic red paste was added, the grape decoration. On the other hand, in Bruges, there is a coarser red paste in the interior and a more plastic and visibly porous white decorative layer—Figure 13.

Based on the comprehensive data collected, we can confidently assert that most identified Santarém ceramic fragments are likely of local origin. The production of light-coloured ceramics seems to have involved the utilisation of clay from Fonte da Pipa, specifically from the Pliocene formation P1 [16], known for its kaolin-bearing sands. In the refinement

process, the explored material underwent purification, with meticulous control over the temper proportion tailored to meet the specific requirements dictated by the intended function of each object. In contrast, the origins of the red ceramics appear more diverse, reflecting the multiple possibilities suggested by historical records. In this case, a more illite-bearing local clay is expected [17].



S2



B3



Figure 13. Selection of representative Santarém (S2—Santarém) and European (B3—Bruges—Belgium) red combined fabric pastes. Scale bar: 1 mm.

6. Conclusions

A multiple analytical approach using micro-Raman, ground-state diffuse reflectance absorption, and X-ray fluorescence spectroscopies, as well as the X-ray diffraction technique and stereomicroscopy, allowed us to establish the mineralogical and elemental composition of the Santarém and European coeval sherds. Most techniques did not allow us to determine a distinction between the two groups.

However, biplots of XRF data, both for ceramic bodies and glazes, seem to indicate that the majority of the Santarém ceramics were most probably produced locally. This assumption is validated by the visual analysis of the paste's fabric. Considering the results obtained, it seems possible to infer that the raw material could have been obtained from local or regional clay sources, particularly from the purification of kaolinitic siliceous sands of the Pliocene type.

Late medieval imported ceramics from Northern Europe have already been identified in Porto and Lisbon. However, these were two of the most prominent cities in the kingdom of Portugal whose economy was largely based on their Atlantic ports. Santarém had no direct access to the sea and all trade was made by river navigation. This may have motivated the production of objects resembling Northern European ceramics. The hypothesis that some of these objects were produced locally opens very interesting paths of discussion in terms of cultural influence. As aforementioned, several studies demonstrate that Muslim potters did not abandon the city and redwares continued to be made following the 8th–12th-century tradition. However, the same did not happen with lead-glazed wares. If made in Santarém, these were made following the patterns and styles of Northern European productions, revealing a confluence of influences and styles that permits us to conclude that, while daily used objects such as pots and pans were produced according to old traditions, glazed tableware production followed the most recent imported style.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/heritage7050105/s1>, Figure S1: Cross-sections of Santarém samples S1 to S20; Figure S2: Cross-sections of European sherds; Table S1: Santarém Stereomicroscope fabric sherd character; Table S2: European Stereomicroscope fabric sherd characterization.

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Conflicts of Interest: The authors declare no conflict of interest.

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