crystals

MDPI

Article

The Enamelled Tiles of Olite's Castle (Spain): Characterization, Provenance, and Manufacture Technology

Iván Ruiz-Ardanaz [1,2,*], Esther Lasheras [1,2] and Adrián Durán [1,2,*]

[1] BIOMA Institute for Biodiversity and Environment, University of Navarra, Irunlarrea 1, 31008 Pamplona, Spain
[2] Chemistry Department, School of Science, University of Navarra, Irunlarrea 1, 31008 Pamplona, Spain
* Correspondence: iruiz.23@alumni.unav.es (I.R.-A.); adrianduran@unav.es (A.D.)

Abstract: The objective of this study was to determine the authorship, provenance, and technology of the *mudejar* enamelled tiles from the Olite Castle (northern Spain, 14th century). According to previous knowledge, Olite's enamelled tiles had been manufactured in Manises (Valencia, Spain). The analysis of ceramic pastes revealed the existence of two different chemical compositions, suggesting the use of two different clay sources, probably one from the Tudela area, and another from the Tafalla–Olite area. Those probably made in the Tudela area stood out with a higher diopside ($CaMgSi_2O_6$) content. Those probably made in the Tafalla–Olite area stood out for their calcium-bearing minerals, such as calcite ($CaCO_3$) or gehlenite ($Ca_2Al(AlSi)O_7$). On this basis, production in Manises has been ruled out. However, it is highly probable that the artisans of Manises would have led the production from Tudela. The study of the firing temperatures and composition of the enamels indicated that the production methods and materials used in Tafalla–Olite (800–850 °C) and Tudela (higher than 900 °C) were different, reflecting the influence of local and Manises artisans, respectively. In Olite tiles, enamel was applied following recipes from the 14th and 15th centuries.

Keywords: ceramic tiles; archaeometry; 15th century; diopside; analcime; cobalt blue; tin glaze

check for updates

Citation: Ruiz-Ardanaz, I.; Lasheras, E.; Durán, A. The Enamelled Tiles of Olite's Castle (Spain): Characterization, Provenance, and Manufacture Technology. *Crystals* **2024**, *14*, 813. https://doi.org/10.3390/cryst14090813

Academic Editor: Ruikang Tang

Received: 26 August 2024
Revised: 8 September 2024
Accepted: 12 September 2024
Published: 14 September 2024

1. Introduction

The kingdom of Navarre, located in northern Spain, had many royal residences. The kings moved around the kingdom constantly while residing in them. The most frequent royal residences during the 12th and 15th centuries were Estella, Pamplona, Olite, Tafalla, Tiebas, and Tudela. Some kings such as Sancho VII of Navarra or Carlos III of Navarra had a clear predilection for some of them such as Tudela and Olite, respectively, and resided there almost permanently. The castle of Tudela was located on a previous *alcazaba*. During the reign of Sancho VII of Navarra (28 January 1194–12 February 1234), both castles were built (Figure 1) [1].

During the reign of Carlos III of Navarre (28 January 1387–8 September 1425), the castles of Tudela and Olite (Navarre, Spain) underwent a great transformation with reforms and successive extensions. In both cases, the best artisans from each guild worked to decorate the castles with the most luxurious elements of the time and transform them into residential palaces for royalty. Their names, assignments, and salaries were recorded in the historical documentation that was fortunately preserved [2,3].

Among the many artisans were the *orceros*, mudejar artisans whose profession was the production of glazed and enamelled ceramics [2,3]. In the documentation referring to the renovations of the castles of Tudela and Olite, the potters were commissioned to make *adrieillos barnizados*, a concept that included enamelled paving tiles, wall tiles, roof tiles, and bricks.

Figure 1. (**a**) A reconstruction drawing of the Tudela Castle in the 14th century by Iñaki Dieguez Uribeondo. (**b**) An image of the New Palace of Olite Castle today by Jorab (licenced under CC BY 3.0.) [4,5].

1.1. Enamelled Tiles from the Tudela Castle

Carlos III of Navarre, a year after being crowned, began a number of successful works in the castle of Tudela. These works lasted for at least six years, until 1394. These works consisted of reconditioning the previous castle and transforming it into a more palatial and luxurious style.

In 1389, the first expenditure related to enamelled tiles appeared in the royal accounts: . . .adrieillos pintados de muchas et distintas maneras. . . (. . .tiles painted in many ways. . .) [3]. This order consisted of a purchase of 6720 tiles from artisans in Zaragoza. The tiles were transported from Zaragoza to Tudela across the Ebro River, using pontoons. The tiles were used to cover the floors of the Bel Regart chamber, the Great Hall, the king’s chamber, and the chamber above the king’s chamber [3].

A second order was made for the floors of the galleries; tiles were ordered to Lope (very possibly Loppe Xedet), Mahoma Almucí, and Ybrahim de Valencia [3].

Unfortunately, only two fragments of the enamelled tiles that decorated the castle of Tudela remain currently. Nor have any remains of the castle structure or maps been preserved, only the ruins of the outer walls.

1.2. Enamelled Tiles from the Castle of Olite

A few years after the renovations of the Tudela castle, it was time to renovate the Olite castle. The previous castle of Olite (Old Palace) was one of the royal residences used by Sancho VII of Navarre. However, it was not until the reign of Carlos III when the palace reached its maximum extent and luxuriousness. Between 1398 and 1401, the palace was expanded to the southwest, with the building of the Queen’s Palace or Merino’s Palace, which had a chapel dedicated to San Jorge (Figure 2). Later, between 1402 and 1424, Olite’s New Palace was built as a second expansion towards the southwest. This New Palace had two constructive phases: in the first phase, a residential building was built; and in a second phase, several towers were added (Figure 2) [3,6].

Among the multiple documentaries mentioning Olite’s castle works, there are five referring to enamelled materials:

- In 1400, 21,000 bricks were purchased from Loppe Xedet, orceros from Tudela [7,8].
- In 1400, 6000 bricks were purchased from three other orceros from Valencia: Ahmed al-lah, Muhammad al-Yan, and Saad al-Bakr. The adrieillos were placed on the floor of the Galería Mayor and the chapel [3,7,8].
- In 1410, Audeilla, an orcero from Tudela, built some pipes of “varnished earth” that would carry the water from the Cidacos River to the cistern tower [3,8].

- On 26 March, 1413, Ybray Abotay and Loppe Xedet, two orceros inhabitants of Tudela, moved with their families to live in Olite to work in the manufacture of adrieillos. The king paid them extra money for the trip and for the construction of the kiln. These craftsmen built a pesquera (pond) in the king's gardens, next to the castle [2,3,7].
- In 1418, orceros from Tudela covered the king's cloister with enamelled tiles [3,7].

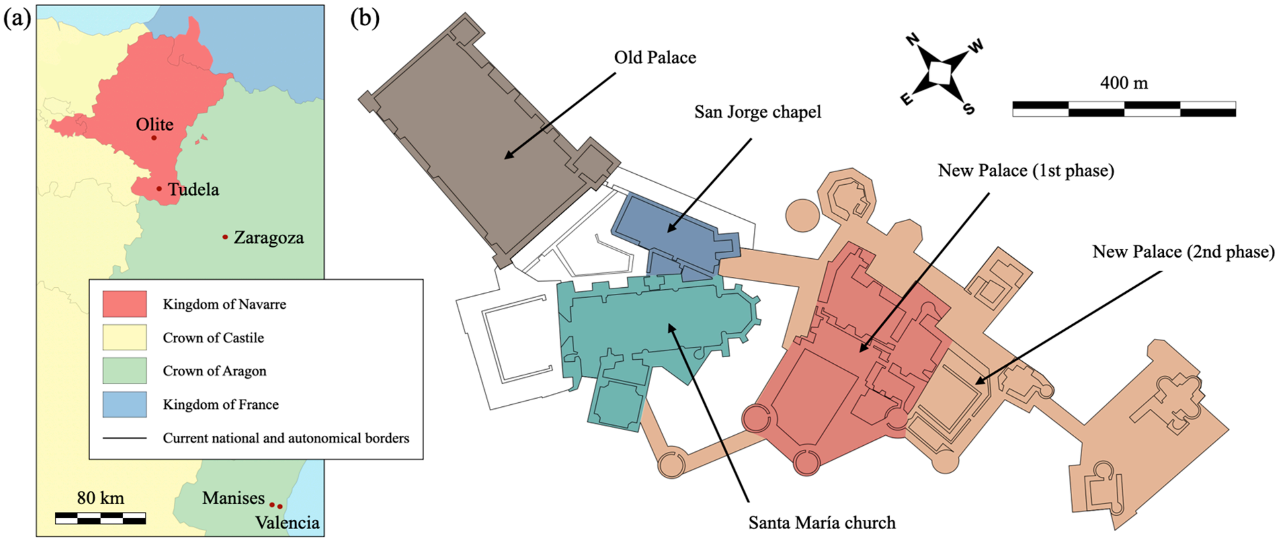

Figure 2. (**a**) The location of Olite and the rest of the places mentioned in the text in northeastern Spain at the beginning of the 15th century. (**b**) A map of Olite's castle with its differentiated areas [6].

1.3. Artisans and Place of Production (The Previous Historical Literature)

For both the castles of Tudela and Olite, all the orceros mentioned (Loppe Xedet, Mahoma Almucí, Ybrahim de Valencia, Ahmed al-lah, Muhammad al-Yan, Saad al-Bakr, Ybray Abotay, and Audeilla) were Mudejar. Some of them were expressly mentioned as being neighbours and residing in Tudela (Loppe Xedet, Ybray Abotay, and Audeilla). In the rest of the cases (Mahoma Almucí, Ybrahim de Valencia, Mahoma de Valencia, and Caet de Valencia) it was not expressly mentioned, although according to the published bibliography [3,6–8], they would come from Manises (Valencia). Some of the surnames of these possible Valencian artisans also appeared in the documentation preserved in the Arxiu del Regne de València (Archive of the Kingdom of Valencia) [9]. Azmet Albane (Ahmed al-lah) was mentioned as a master tile maker [9].

As interpreted in the referenced literature [3], enamelled adrieillos imported from Zaragoza and Manises were used for the castle of Tudela, as well as others produced in Tudela itself. In the case of the Olite castle, tiles imported from Manises and Tudela would have been used, as well as others manufactured in Olite by two orceros from Tudela (Loppe Xedet and Ybray Abotay) [3,6–8].

In both cases, it is thought that the Valencian tiles were manufactured in Manises and then transported to Tudela or Olite for installation. However, historical documentation does not mention this literally [3,6–8].

1.4. Materials Found in Archaeological Interventions

Unfortunately, archaeological interventions on the Tudela castle have barely provided two fragments of enamelled tiles that could be related to those mentioned in historical documentation.

On the other hand, numerous enamelled materials of different types and enamel colours have been found in the Olite castle. According to their type and size they could be classified into the following (Figure 3):

- Thin tiles (probably wall tiles): square base tiles with the following dimensions: 1.8 ± 0.1 cm (n = 43) thick and 13.5 ± 0.1 cm (n = 14) on each side. The enamel was white, blue, green, brown, or a combination of all of these, with some forming geometric motifs and others poorly preserved.
- Thick tiles (probably paving tiles): square base tiles with the following dimensions: 2.8 ± 0.1 cm (n = 6) thick and 12.3 ± 0.1 cm (n = 10) on each side. The enamel was white, blue, or green.
- Bricks: have a prismatic shape and the following dimensions: 3.7 ± 0.1 cm (n = 8) thick, around 12 cm wide, and around 40 cm long. The enamel was white, blue, or green.
- Roof tiles: with a flat shape and the following dimensions: 1.7 ± 0.1 cm (n = 7) thick, 14.4 ± 0.1 cm (n = 2) wide, and around 30 cm long. The enamel was white, blue, or green.
- The remains of a fountain [10]: an octagonal fountain with a central spout decorated with chestnut branches and a triple blue bow, on a green and white background.

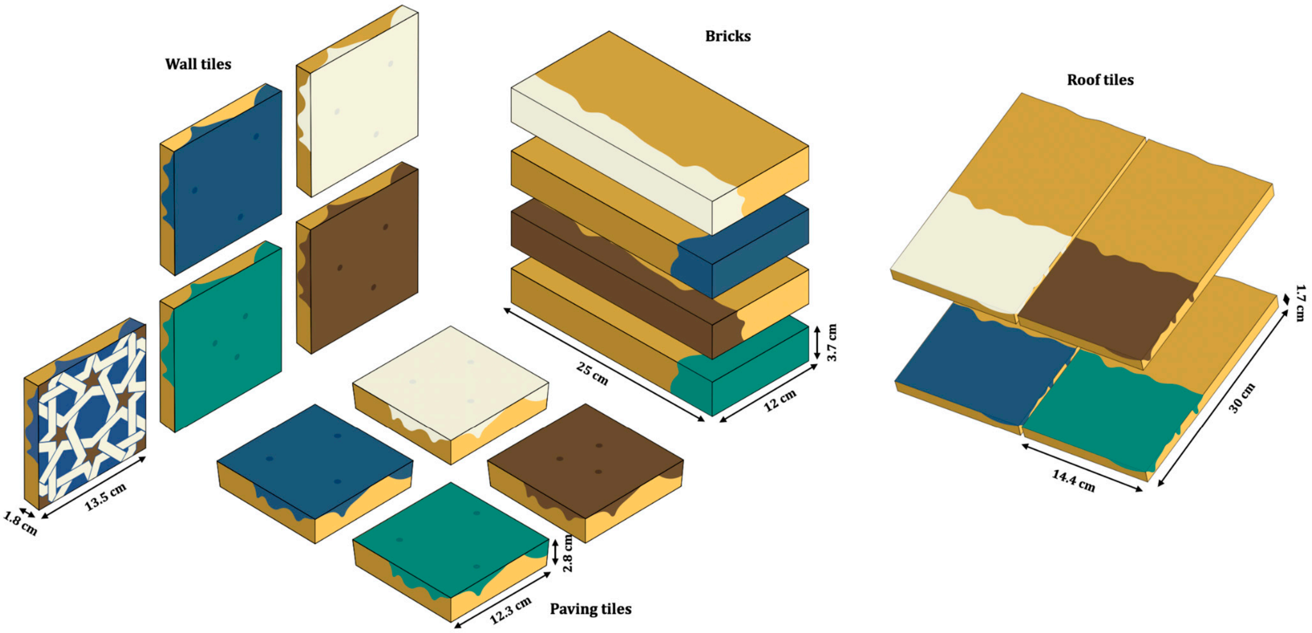

Figure 3. A digital reconstruction of the enamelled wall tiles, paving tiles, bricks, and roof tiles found in Olite's castle. Only two brown enamel thin tiles have been discovered, although they probably also existed in the form of thick tiles, roof tiles, and bricks.

According to their artistic and technical characteristics, experts in the field [6,7] have interpreted that the monochrome tiles (bricks, wall, paving, and roof tiles) and the octagonal fountain were made by the Tudela artisans Loppe Xedet and Ybray Abotay. As mentioned above, both artisans worked in both Tudela and Olite. On the contrary, polychrome tiles (geometric and others poorly preserved) were probably manufactured by Valencian artisans (Ahmed al-lah, Muhammad al-Yan, and Saad al-Bakr). Geometric polychrome tiles were found in situ in a wall between the San Jorge Chapel and Santa María Church (Figure 2) [6].

1.5. *The Manises Ceramics Technology*

The technology that was used in manufacturing the Manises pottery and tiles is well studied, according to the abundant literature [11–14]. The pastes were rich in Si, Ca, Al, and Fe, and with K, Ti, and Mg as minor elements [11–13]. The maximum temperature during firing was 1000–1050 °C in a single firing [14]. Regarding the enamel, it was composed mainly by Pb, Si, and Sn. The Sn was used as an opacifier with a white colour [15–17]. As for the pigments, pyrolusite and hausmannite were used for the brown colour; malachite for the green one; and asbolane, erythrite, and smaltite for the blue one [13,15–20].

The objectives of this study were to scientifically determine if the tiles from the Olite Castle comply with the interpretation of the documentary sources and the stylistic analysis. In a more specific way, they were to check if the tiles of the Olite castle were manufactured in Manises and Tudela, and whether their technical characteristics (firing temperature, composition, and thickness of the glazes) were compatible with the technique of the artisans of Manises (Valencia) during the 14th century. The study would help us to know the materials and the technology employed for manufacturing enamelled tiles in Southern Europe during the Middle Ages.

2. Materials and Methods

2.1. Materials

A total of 10 fragments of tiles and bricks from the Olite Castle were analysed (Table 1, Figure 4). The fragments were selected considering the availability of each type of material and their size, trying to minimise damage, as invasive analyses were carried out. Three of them (OM-1, OM-2, and OM-3) were thin tile fragments with polychrome enamel (white, blue, and brown) and geometric decoration. Four of them (OT-1, OT-2, OT-3, and OT-4) were thin tile fragments with monochrome (green or white) enamel. A single fragment (OT-5) was a thick tile with blue enamel. And two fragments (OT-6 and OT-7) were white or blue enamelled bricks. Unfortunately, it was not possible to collect samples from Tudela Castle or roof tiles from Olite.

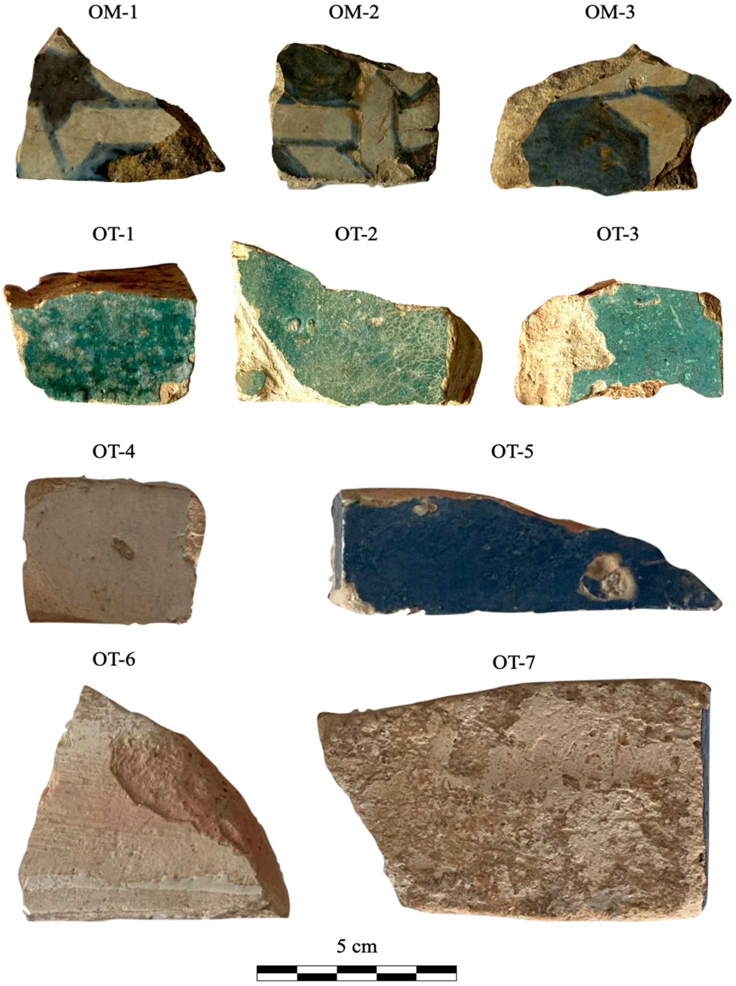

Figure 4. Analysed samples from Olite's castle: OM-1 to -3, polychrome thin tile; OT-1 to -3, monochrome green enamelled thin tile; OT-4, monochrome green enamelled thin tile; OT-5, monochrome blue enamelled thick tile; OT-6, white enamelled brick; and OT-7, blue enamelled brick.

Table 1. A classification of the analysed samples according to their typology and their hypothetical origin.

ID	Type	Original Size (cm)	Enamel Colour	Hypothetical Provenance
OM-1	Tile	1.8 × 13.5 × 13.5	White, brown, blue	Manises
OM-2	Tile	1.8 × 13.5 × 13.5	White, brown, blue	Manises
OM-3	Tile	1.8 × 13.5 × 13.5	White, brown, blue	Manises
OT-1	Tile	1.8 × 13.5 × 13.5	Green	Tudela/Olite
OT-2	Tile	1.8 × 13.5 × 13.5	Green	Tudela/Olite
OT-3	Tile	1.8 × 13.5 × 13.5	Green	Tudela/Olite
OT-4	Tile	1.8 × 13.5 × 13.5	White	Tudela/Olite
OT-5	Tile	2.8 × 12.3 × 12.3	Blue	Tudela/Olite
OT-6	Brick	3.7 × 12 × 40	White	Tudela/Olite
OT-7	Brick	3.7 × 12 × 40	Blue	Tudela/Olite

2.2. Methods

Archaeological samples (Table 1, Figure 4) were characterised using X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Optical Microscopy (OM), and a Field Emission Scanning Electron Microscope with Energy-Dispersive X-ray Spectroscopy (FE-SEM/EDS). All the paste samples were analysed in powder after grinding with an agate mortar. To study the enamel, some surface fragments were analysed in solid, without grinding. For OM and FE-SEM, small tile samples were cut vertically. The samples were laid in a mould of polymethyl methacrylate, which was filled with a resin. One of the faces of the sample preparation was polished (500-, 2000-, and 5000-grit sandpaper); in this form, cross-sections with the two layers (enamel and paste) were obtained.

For the XRF analyses, a Bruker S2 Puma (Bruker AXS, Karlsruhe, Germany) device was used, with a silver anode and helium atmosphere. The measurement conditions were triplicate scans at 20 kV, 40 kV, 50 kV, and a detector resolution of 10.8 eV (at 20 kV). The software Spectra Results Analysis (Spectra.Elements, version 2.3) was employed for quantification. XRD analyses were carried out with a Bruker D8 Advance (Bruker AXS, Karlsruhe, Germany) diffractometer, with a Cu-Kα1 tube (1.5418 Å, 40 kV, 25 mA) and a LYNXEYE detector. The experimental conditions have been the following: scans from 5° to 70° (2θ), at a speed of 2 s/step and a resolution of 0.02°/step. The software DIFFRAC.EVA (Bruker, version 4.3) was employed for the results interpretation. The samples were analysed in powder, for pastes, and in solid, for enamels.

A Optical PCE-MM200 (PCE Ibérica, Tobarra, Spain) was used for Optical Microcopy (OM). A ZEISS Sigma 300 VP FE-SEM/EDS (ZEISS, Jena, Alemania) coupled with an energy-dispersive X-ray analyser (Oxford Instrument Ultim Max 40) (Oxford Instruments, Abingdon, Reino Unido) was used for elemental punctual analyses and mappings performed on some of the cross-sections. The samples were previously metallised with gold. FE-SEM was used in the cross-sections to measure enamel thickness and inspect the morphology of the enamel/paste interface.

The results of the different samples groups were compared between them using the Kurskal–Wallis method. The Kurskal–Wallis method allowed us to determine if there were significant differences between two samples (non-normal) with a confidence level (95%) that allowed one to accept the alternative hypothesis (samples are significantly different) if the p-value was above a certain threshold (0.05). The Kurskal–Wallis method was applied by analysing the results with Matlab software (version R2023b, Update 7).

3. Results

3.1. Elemental Analysis

3.1.1. Paste

The results of the chemical elemental analysis of the pastes by XRF allowed us to identify three different compositions: group 1 (divided in subgroup 1-1 (samples OT-1, OT-2, OT-3, OT-4, and OT-7), and subgroup 1-2 (samples OM-1, OM-2, and OM-3)) and group 2 (samples OT-5 and OT-6) (Table 2). All of them stood out for being calcareous pastes (>5% Wt. in Ca). In all the cases, the majority components (>1%) were, in order from highest to lowest, as follows: Si, Ca, Al, Fe, K, Mg, and Ti. Na, Sr, Mn, Sc, and Zr were also detected as minor elements (<1%).

Table 2. The elemental composition (Wt%) of each group of pastes and *p*-values (95% confidence) obtained for the comparison between group of pastes. Values were expressed as the mean ± standard deviation. The applied statistical method was the Kruskal–Wallis method as the results were non-normal. Values in bold represent significant differences (<0.05).

Element	**Group 1-1**	**Group 1-2**	**Group 2**	***p*-Values (Kruskal–Wallis)**		
Samples	**OT-1, OT-2, OT-3, OT-4, OT-7**	**OM-1, OM-2, OM-3**	**OT-5, OT-6**	**1-1 vs. 1-2**	**1-1 vs. 2**	**1-2 vs. 2**
Si	31 ± 1	35.4 ± 0.9	28.8 ± 0.2	0.229	0.581	0.016
Ca	25 ± 1	23 ± 2	37.5 ± 0.7	0.949	0.083	0.039
Al	16.9 ± 0.9	16 ± 1	13.7 ± 0.6	0.848	0.017	0.237
Fe	12.7 ± 0.5	12.0 ± 0.4	11.5 ± 0.3	0.545	0.022	0.563
K	5.3 ± 0.5	4.6 ± 0.2	3.2 ± 0.7	0.613	0.003	0.204
Mg	6.1 ± 0.6	4.6 ± 0.2	2.6 ± 0.2	0.363	0.005	0.494
Ti	1.05 ± 0.02	1.08 ± 0.04	0.89 ± 0.01	0.986	0.025	0.021
Na	0.8 ± 0.2	1.1 ± 0.1	0.6 ± 0.2	0.298	0.606	0.027
Sr	0.20 ± 0.01	0.17 ± 0.01	0.16 ± 0.00	0.072	0.872	0.013
Mn	0.24 ± 0.02	0.18 ± 0.02	0.26 ± 0.03	0.059	0.012	0.986
Sc	0.12 ± 0.04	0.12 ± 0.02	0.31 ± 0.03	0.997	0.034	0.110
Zr	0.06 ± 0.00	0.07 ± 0.01	0.05 ± 0.01	0.153	0.278	0.002
n	6	4	5			

Regarding the differences between them, a clear difference was observed between group 2 and group 1: group 2 was poorer in Si, Al, K, Mg, Ti, Na, and Mn, while it was much richer in Ca, and in Sc. Between subgroups 1-1 and 1-2, the differences were not so significant, although Si was higher in subgroup 1-2 and Mg higher in 1-1 (Table 2).

From a statistical point of view (Table 2), the differences were only significant between group 1 and group 2, especially for Ca, Ti, and Sc, with p-values less than 0.05 (0.039 for Ca in 1-2 vs. 2, 0.025 for Ti in 1-1 vs. 2, 0.021 in 1-2 vs. 2, and 0.034 for Sc in 1-1 vs. 2). On the contrary, there were no significant differences between the composition of the pastes of subgroups 1-1 and 1-2, where all p-values were greater than 0.05.

3.1.2. Enamel

Regarding the composition of the enamels (Table 3), four types were differentiated according to their colours (white, brown, blue, and green). All of them presented a major composition of lead (50 ± 6% Wt.), probably the only type of flux (lead oxide).

As colouring agents or pigments, Sn appeared with an average concentration of 5 ± 2%, present in all samples and acting as an opacifier (Sn oxide) [15–18,21]. In the case of white enamels, the only chromophores detected were Sn-based compounds.

As for the rest of the elements, most of them appeared in much smaller amounts than in the pure paste, when diluted with the components provided for the enamel (mainly flux and pigments). For instance, Ca had a concentration of 23–38% in pastes and 6–10% in enamel, and Al 14–17% in paste and 3–4% in enamel. However, Si and K did not appear to be reduced by the same proportion as the rest of the elements of the paste. This was probably because some silica and K-feldspar were added as fine sand to the flux agents to help the Pb-O-Si polymerization [19,22]. The presence of Si is essential during enamel formation since it participates in the polymerization process and favours the formation of smooth and shiny enamels, especially in calcareous pastes [19,22]. This higher proportion of Si and K was reflected in all the enamel colours (Table 3), so the base of all of them (excluding the specific pigments of each one) could be a mixture of compounds such as PbO, SnO_2, SiO_2, and $KAlSi_3O_8$.

Table 3. The elemental composition (Wt%) of the studied enamels according to their colour. Values were expressed as the mean ± standard deviation.

Element	**White**	**Brown**	**Blue**	**Green**
Samples	**OM-1, OM2, OM-3, OT-4, OT-6**	**OM-1, OM-3**	**OM-2, OM-3, OT-5, OT-7**	**OT-1, OT-2, OT-3**
Si	30 ± 7	25 ± 1	22 ± 2	17 ± 4
Ca	6 ± 3	6 ± 1	7 ± 3	10 ± 5
Al	3 ± 1	3.7 ± 0.3	3 ± 1	3.1 ± 0.6
Fe	1.6 ± 0.8	1.9 ± 0.9	4 ± 3	1.1 ± 0.2
K	3.8 ± 0.5	2.8 ± 0.3	3.8 ± 0.8	2.6 ± 0.5
Mg	0.64 ± 0.09	0.58 ± 0.06	0.7 ± 0.2	0.49 ± 0.08
Ti	0.13 ± 0.09	0.14 ± 0.06	0.12 ± 0.07	0.09 ± 0.02
Na	0.18 ± 0.02	0.05 ± 0.06	0.07 ± 0.08	0.00 ± 0.01
Sr	0.06 ± 0.04	5.6 ± 0.7	0.2 ± 0.1	0.02 ± 0.02
Mn	0.05 ± 0.05	0.06 ± 0.02	0.04 ± 0.02	0.03 ± 0.01
Sc	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Zr	0.02 ± 0.03	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Pb	48 ± 9	47 ± 2	50 ± 6	55 ± 2
Sn	4.9 ± 0.8	5.7 ± 0.9	6 ± 2	5 ± 1
Mn	0.06 ± 0.04	5.6 ± 0.7	0.2 ± 0.1	0.02 ± 0.02
Co	0.2 ± 0.1	0.29 ± 0.06	0.7 ± 0.3	4.1 ± 0.6
Cu	0.04 ± 0.08	0.2 ± 0.1	1.0 ± 0.7	0.00 ± 0.01

The presence of Ca (6–10%) and Al (3–3.7%) in the enamels could be explained by the interference of the paste in the measurements. A few X-rays could penetrate deeper than the enamel layer and reach the paste. As the paste was composed by Si, Ca, Al, and Fe as major elements, the quantification of the enamel could be influenced by the composition of the underlayer paste. Si was also present in the enamel, coming from silica.

Si and Pb presented very high standard deviations (±7 for Si and ±9 for Pb). A possible explanation could be that the change in the paste depended on the thickness of the enamel and the heterogeneity of the enamels.

As for the pigments used for obtaining the white colour, only the previous components would have been used (PbO, SnO_2, and fine sand rich in SiO_2 and $KAlSi_3O_8$). On the other hand, for the brown enamel, the manganese concentration (5.6 ± 0.7%) was much higher than the rest (0.1 ± 0.1%) and responsible for the colour (Table 3). The rest of the elements did not show a correlation with manganese, so the pigment was surely applied alone and had a high purity. The green enamel only showed a higher proportion of copper (4.1 ± 0.6%), while the other enamels had values of 0.21 ± 0.12% (Table 3). The rest of the elements did not show a correlation with copper, so the pigment was probably malachite, based on its greenish tone. The blue enamel showed a high concentration of iron (4 ± 3%), copper (0.7 ± 0.3%), and Co (1.0 ± 0.7%) (Table 3). Nickel was also detected (0.3 ± 0.3%) (Ni contents were 0.68% for the OM-2 sample, 0.26% for OM-3, 0.21% for OT-5, and 0.00% for OT-7) but very close to the limit of quantification. In this case (blue enamels), the pigment or pigments used had to combine these four elements (Fe, Cu, Co, and Ni), some probably as impurities (see Section 4.3).

3.2. Mineral Analysis

3.2.1. Paste

The mineral analysis of the pastes (Table 4, Figure 5) allowed us to identify some common minerals in all the samples: mainly quartz and Ca-bearing minerals as major minerals, and to a lesser extent haematite. Quartz (SiO_2; trigonal-trapezohedral; a = 4.91 Å, c = 5.40 Å; PDF 33–1161) was identified by the following reflections at 2θ values: 20.8° (100), 26.5° (101), 36.5° (110), and 50.1° (112). Haematite (Fe_2O_3; trigonal-hexagonal; a = 5.03 Å, c = 13.74 Å; PDF 33-0664) was identified by its reflections at 33.1° (104) and 35.6° (110).

Table 4. The mineral composition of the tile paste samples. Abun- dance: +++: abundant; ++: moderate; +: minority; nd: not detected.

Mineral	Group 1-1	Group 1-2	Group 2
Samples	**OT-1, OT-2, OT-3, OT-4, OT-7**	**OM-1, OM-2, OM-3**	**OT-5, OT-6**
Quartz (SiO_2)	+ + +	+ + +	+ + +
Haematite (Fe_2O_3)	+	+	+
Calcite ($CaCO_3$)	nd	+/nd	+ + +
Illite ($K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}]\cdot(OH)_2$)	+ +/nd	nd	+
Gehlenite ($Ca_2Al(AlSi)O_7$)	+ +/+	+/nd	+ + +
Diopside ($MgCaSi_2O_6$)	+ + +	+ + +	+
Anorthite ($CaAl_2Si_2O_8$)	+ +/+/nd	+ + +	nd
Analcime ($Na(AlSi_2O_6)\cdot H_2O$)	+ + +/+ +	+ + +	nd

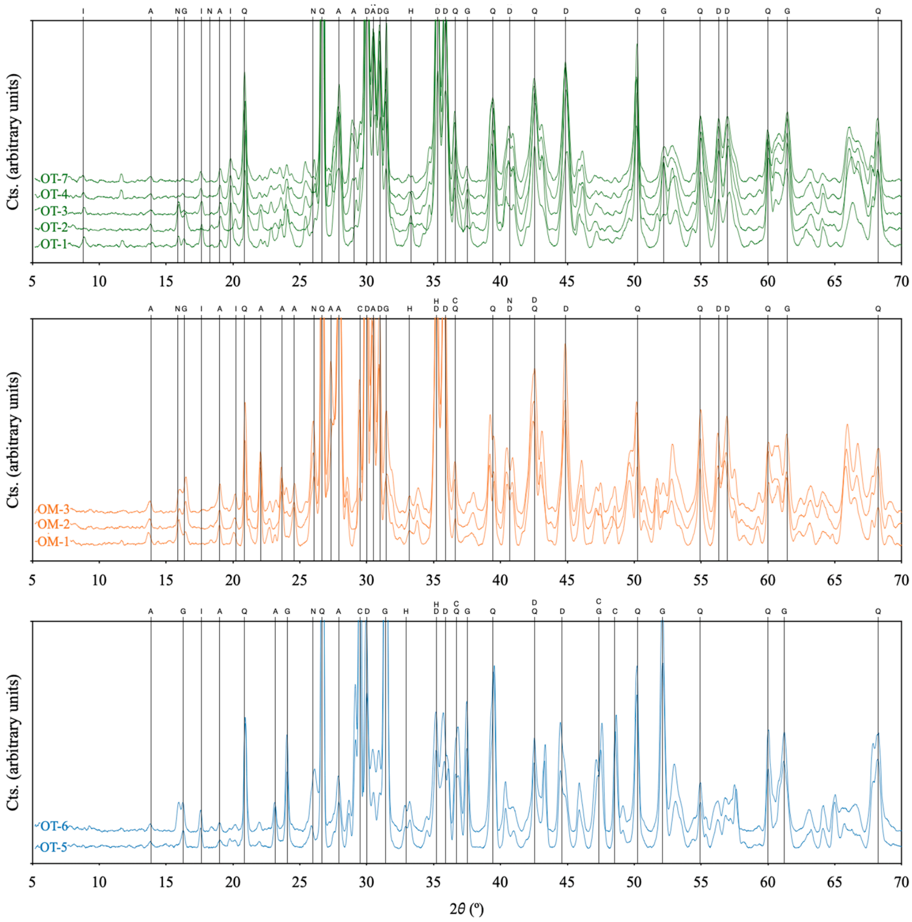

Figure 5. X-ray diffraction patterns of the pastes from Olite's castle. Abbreviations: I–illite; A–anorthite; N–analcime; G–gehlenite; Q–quartz; C–calcite; D–diopside; H–haematite.

The Ca-bearing minerals detected were different according to the groups. Subgroup 1-1 stood out for the presence of illite ($K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$; monoclinic-prismatic; a = 5.18 Å, b = 8.98 Å, c = 10.32 Å, β = 101.83°; PDF 70-3754) identified by reflections at 8.7° (002), and 19.7° (110); gehlenite ($Ca_2Al(AlSi)O_7$; tetragonal-scalenohedral; a = 7.69 Å, c = 5.07 Å; PDF 35-0755) reflections at 16.2° (110), and 31.3° (211); diopside ($CaMgSi_2O_6$; monoclinic-prismatic; a = 9.76 Å, b = 8.93 Å, c = 5.26 Å, β = 105.80°; PDF 17-0318) reflections at 40.8° (112), and 42.3° (−331); anorthite ($CaAl_2Si_2O_8$; triclinic-pinacoidal; a = 8.18 Å, b = 12.88 Å, c = 14.17 Å, α = 93.17°, β = 115.85°, γ = 91.22°; PDF 41-1486) reflections at 21.9° (−202), and 24.5° (130); and analcime ($Na(Si_2Al)O_6 \cdot H_2O$; triclinic-pedial; a = 13.71 Å, b = 13.70 Å, c = 13.71 Å, α = 90.16°, β = 89.57°, γ = 89.54°; PDF 41-1478) reflections at 15.9° (211), 18.3° (220), 26.0° (400), 30.6° (332), and 40.6° (661) (Table 4, Figure 5).

Subgroup 1-2 stood out for having no illite, less gehlenite, and more anorthite than subgroup 1-1 (Table 4, Figure 5). Calcite (CaCO3; trigonal-hexagonal scalenohedral; a = 4.99 Å, c = 17.06 Å; PDF 05-0586) was also detected (reflections at 29.4° (104), and 36.0° (110)) in some of the samples, but it was probably secondary calcite.

On the other hand, group 2 was characterised for having abundant calcite and gehlenite, and lesser diopside (Table 4, Figure 5). No illite, anorthite, or analcime were detected (Table 4, Figure 5).

3.2.2. Enamel

Regarding the mineral phases identified in the enamels (Figure 6), the main mineral phases include quartz, diopside, and cassiterite (Figure 7). The first two probably come from the paste or the fine sand added together with the flux (in the case of quartz). Cassiterite (SnO_2; tetragonal-ditetragonal bipyramidal; a = 4.74 Å, c = 3.12 Å; PDF 41-1445) was present in all the enamel samples analysed (reflections at 26.6° (110), 33.9° (101), 38.0° (200), 39.0° (111), 51.8° (211), 54.8° (220), 57.8° (002), 61.9° (310), 64.7° (112), and 65.9° (301)), and acted as an opacifier and chromophore [15–18,21], generating the white colour of the white enamels and lightening the green, blue, and brown enamels.

In the green, blue, and brown enamels, the pigments responsible for colour were not detected, although this was probably due to their low concentration.

Gypsum ($CaSO_4(H_2O)_2$; monoclinic-prismatic; a = 5.68 Å, b = 15.18 Å, c = 6.29 Å, β = 113.83°; PDF 33-0311) was detected in the samples OT-5-blue, OT-1-green, OT-2-green, OT-3-green, OM-2-white, and OT-4-white through reflections at 11.6° and 23.4°. This gypsum probably comes from the mortar used to adhere the tiles to the wall or to fill the joints between them.

3.3. Microscopy

Through the optical microscopy, SEM images, and the EDS mappings carried out with FE-SEM, it was possible to study the morphology of the pastes and enamels, and the distribution of the different elements within the enamel. Regarding the morphology of the samples, it could be seen how both pastes had a high porosity with a granulometry of less than 20 µm, although with scarce quartz crystals of around 70 µm (Figures 8 and 9).

In Figures 8 and 9, the thickness and uniformity of the enamels (identified by the colour (in optical microscopy) or abundance of Pb and Sn (in EDS mappings)) could be compared. The enamels of samples the 1-2 group (OM-1, OM-2) stood out for their very irregular and variable thickness of 170 ± 80 µm, with a variation for the same sample of up to 40%. On the contrary, the rest of the samples from group 1-1 (OT-1, OT-4, OT-7) and group 2 (OT-5, OT-6) showed great uniformity in the thickness of the enamel, with an average thickness of 160 ± 40 µm, with a variation for the same sample of 13%. The exception is the monochrome white enamels (OT-4 and OT-6), much thicker than the rest of the enamels, although also very uniform, with a 450 ± 80 µm thickness (Figure 8).

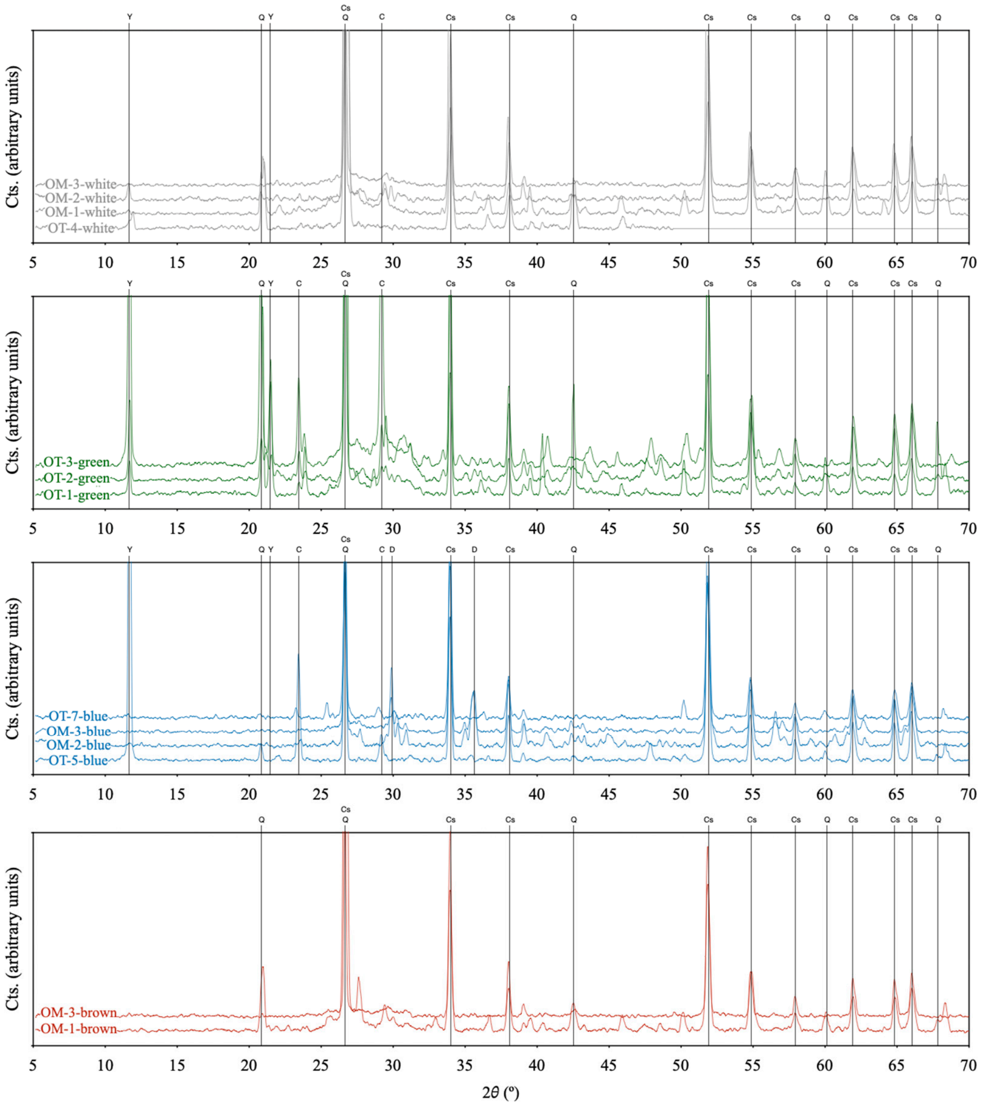

Figure 6. X-ray diffraction patterns of the enamels from Olite's castle. Abbreviations: Y–gypsum; Q–quartz; Cs–Cassiterite; C–calcite; D–diopside.

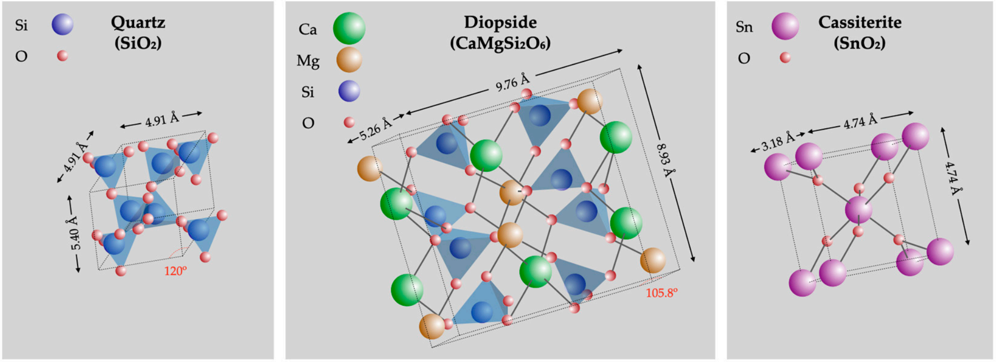

Figure 7. Visual schematic representation of quartz, diopside, and cassiterite structures. Modified from Webmineral.com [23].

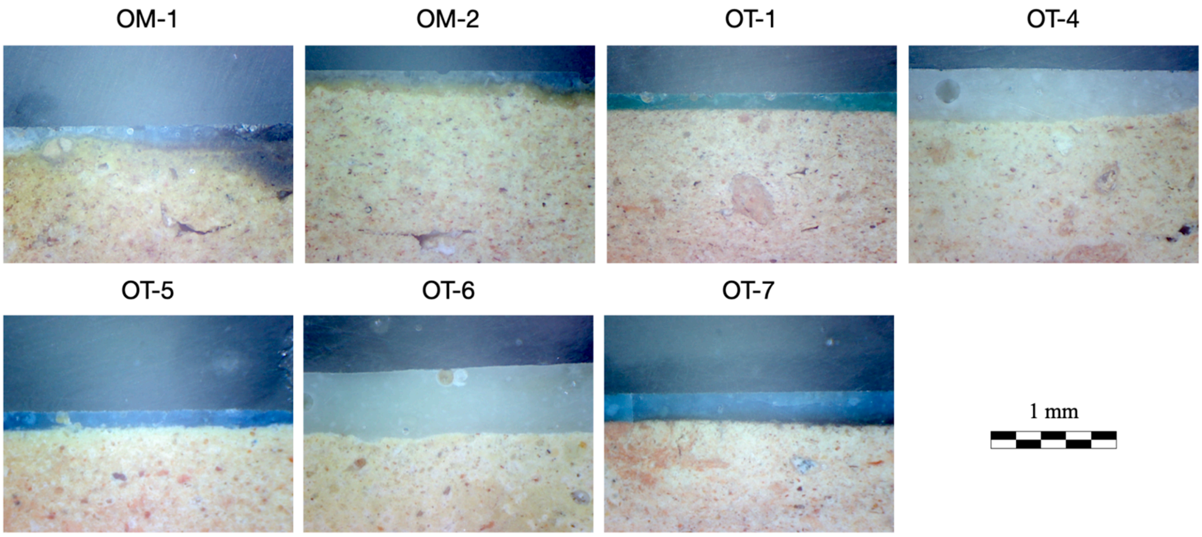

Figure 8. Optical microscope images of cross-sections of samples OM-1, OM-2, OT-1, OT-4, OT-5, OT-6, and OT-7.

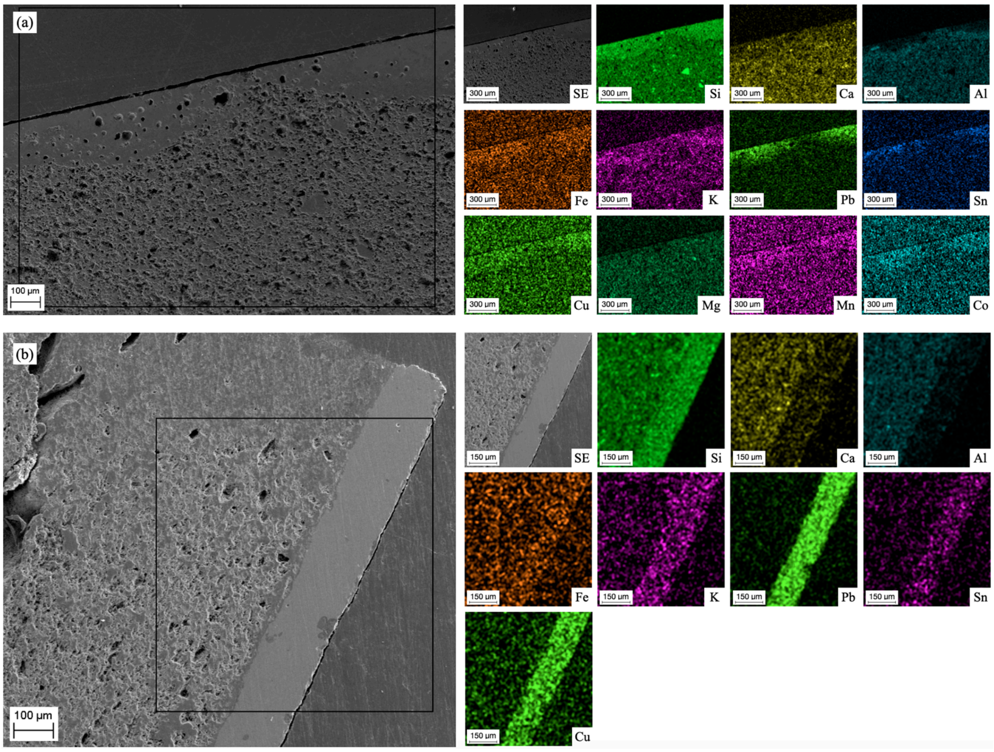

Figure 9. FE-SEM/EDS images of samples OM-1 (**a**) and OT-1 (**b**). Note that in Figure 9a, the enamelled surface is rotated 13° counterclockwise and Figure 9b is rotated 116° clockwise. Abbreviations: SE—secondary electron image.

In both samples of Figure 9 (OM-1 and OT-1), the enamel had a higher composition of lead, silicon, iron, potassium, and pigments (Cu, Co, Sn) than that of the paste. On the contrary, calcium and aluminium were present in a lower proportion. These results coincided with those obtained using XRF in Table 3.

Although the elements found in the enamel were the same in both samples, the distribution of these elements between the surface and the interface layer with the paste was totally different. In sample OM-1 (Figure 9a), it was possible to observe how the enamel, in addition to being more irregular, had a higher distribution of Pb and Sn on the surface and was lower the closer it got to the interface with the paste. In contrast, Cu, Mn, and Co appeared to be more homogeneously distributed within the enamel. In sample OT-1 (Figure 9b), the opposite case was observed: in addition to an enamel with a much more constant thickness, the distribution of all the elements (Pb, Si, K, Sn, and Cu) was homogeneous within the enamel.

4. Discussion

4.1. Provenance

The results of the analysis of the pastes have allowed us to distinguish two groups with significantly different compositions (group 1 and group 2). The main differences between them were in Si, Ca, K, Mg, and Ti. Therefore, at least two sources of clay were possibly used.

To delve deeper into this issue, the composition of these two groups was compared with those of the main production centres in Navarre during the Middle Ages (previously studied in Ruiz-Ardanaz et al., 2024 [24]).

The pastes of group 1 turned out to be very similar to those from the Tudela area. These pastes presented the following chemical composition [24] (Table 5): 33 ± 2% Si, 25 ± 5% Ca, 17 ± 2% Al, 12 ± 1% Fe, 4 ± 2% K, 5.0 ± 0.9% Mg, 1.05 ± 0.08% Ti, 0.9 ± 0.4% Na, 0.19 ± 0.02% Mn, 0.3 ± 0.1% Sr, 0.11 ± 0.04% Sc, and 0.06 ± 0.01% Zr. These pastes from Tudela stood out for being calcareous (25 ± 5%) and for having a certain sodium (0.9 ± 0.4%) and magnesium (5.0 ± 0.9%) content.

Table 5. Elemental composition (Wt%) of the paste of Olite Castle samples and the reference samples mentioned in the text (Tudela area, Tafalla area, La Falconera (Olite)).

Element	**Group 1-1**	**Group 1-2**	**Group 2**	**Tudela Area**	**Tafalla Area**	**La Falconera (Olite)**
Samples	**OT-1, OT-2, OT-3, OT-4, OT-7**	**OM-1, OM-2, OM-3**	**OT-5, OT-6**			
Si	31 ± 1	35.4 ± 0.9	28.8 ± 0.2	33 ± 2	25 ± 3	27
Ca	25 ± 1	23 ± 2	37.5 ± 0.7	25 ± 5	44 ± 5	42
Al	16.9 ± 0.9	16 ± 1	13.7 ± 0.6	17 ± 2	12 ± 1	12
Fe	12.7 ± 0.5	12.0 ± 0.4	11.5 ± 0.3	12 ± 1	9.9 ± 0.5	10
K	5.3 ± 0.5	4.6 ± 0.2	3.2 ± 0.7	4 ± 2	4.1 ± 0.7	4.2
Mg	6.1 ± 0.6	4.6 ± 0.2	2.6 ± 0.2	5.0 ± 0.9	2.2 ± 0.5	2.1
Ti	1.05 ± 0.02	1.08 ± 0.04	0.89 ± 0.01	1.05 ± 0.08	0.86 ± 0.06	0.93
Na	0.8 ± 0.2	1.1 ± 0.1	0.6 ± 0.2	0.9 ± 0.4	0.01 ± 0.01	0.21
Sr	0.20 ± 0.01	0.17 ± 0.01	0.16 ± 0.00	0.3 ± 0.1	0.29 ± 0.08	0.22
Mn	0.24 ± 0.02	0.18 ± 0.02	0.26 ± 0.03	0.19 ± 0.02	0.13 ± 0.01	0.17
Sc	0.12 ± 0.04	0.12 ± 0.02	0.31 ± 0.03	0.11 ± 0.04	0.24 ± 0.07	0.39
Zr	0.06 ± 0.00	0.07 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06
n	6	4	5	17	10	1

The pastes of group 2 turned out to be like to those from the Tafalla area, near Olite. These pastes presented the following chemical composition [24] (Table 5): 25 ± 3% Si, 44 ± 5% Ca, 12 ± 1% Al, 9.9 ± 0.5% Fe, 4.1 ± 0.7% K, 2.2 ± 0.5% Mg, 0.86 ± 0.06% Ti, 0.01 ± 0.01% Na, 0.13 ± 0.01% Mn, 0.29 ± 0.08% Sr, 0.24 ± 0.07% Sc, and 0.06 ± 0.01% Zr. These pastes stood out for being calcareous (44 ± 5%), but poorer in sodium (0.01 ± 0.01%) and magnesium (2.2 ± 0.5%). They also stood out for having a higher concentration of scandium (0.24 ± 0.07%).

To additionally verify that the clays from the Olite area were similar to those from the Tafalla–Olite area and to the pastes of group 2, clay samples were taken from the old tile kiln of La Falconera (latitude (φ) = +42.493°, longitude (λ) = −1.627°, 2 km from Olite), exhibiting the following composition, as in Table 5: 27% Si, 42% Ca, 12% Al, 10% Fe, 4.2% K, 2.1% Mg, 0.93% Ti, 0.21% Na, 0.17% Mn, 0.22% Sr, 0.39% Sc, and 0.06% Zr. The Olite clay is still like that of Tafalla, but it was more similar to that of group 2 pastes.

From the mineralogical point of view, the Tudela pastes (groups 1-1 and 1-2) were similar since they presented diopside and a certain amount of analcime, a specific characteristic phase that did not appear in other production centres in Navarra (Estella, Lumbier, Pamplona, and Tafalla).

Given the hypothetical attribution of the experts on the production in Manises of the samples of subgroup 1-2 (polychrome enamel with geometric decoration) [3,6,7], publications on materials from Manises were consulted in search of data on the composition of the pastes. In Pinto-Monte et al., 2021 [11], the elemental compositions of numerous pastes from mediaeval and modern times were published. None of them coincided with the composition of samples within subgroup 1-2. Another fact to consider is that the results of the mineral analysis did not present diopside or analcime in the samples originating from Manises [11–13], which those from Tudela and those from subgroup 1-2 did [24].

Based on all the above, it was determined that the tiles and bricks of group 2 were most likely manufactured in Olite in 1413 by Loppe Xedet and Ybray Abotay, as mentioned in the documentation [3]. The bricks and tiles of group 1 would most likely have been manufactured in the Tudela area, and not in Manises as had been hypothesised. They were probably made around 1400 by a combination of local artisans (Loppe Xedet and Ybray Abotay) and artisans from Manises (Ahmed al-lah, Muhammad al-Yan, and Saad al-Bakr).

4.2. Firing Temperature

In ceramic samples with a calcareous-based composition, the calcium minerals that form in the kiln are a good indicator of what the firing temperature was [14].

Based on these minerals, it could be estimated that the tiles and bricks of subgroup 1-1 were fired at 900–1000 °C given the presence of illite, gehlenite, diopside, anorthite, and analcime in different proportions. Subgroup 1-2 samples were heated from 1000 to 1100 °C given the abundance of diopside, anorthite, and analcime, and the almost complete disappearance of gehlenite. According to the literature, the artisans of Manises fired their tiles at 1000–1050 °C [20] and Tudela mediaeval artisans at temperatures higher than 1000 °C [24]. These firing temperatures were very high for the time, although they did not reach the 1200–1300 °C of some mediaeval productions in China [25,26]. Group 2, on the other hand, would present a lower firing temperature between 800 and 850 °C, given the absence of anorthite, low concentration of diopside, and the abundance of secondary calcite. Perhaps it is because the oven built in Olite in 1413 was not as powerful as the ones from Tudela.

Another relevant fact to highlight was the difference between the uniformity of the thickness of the enamel of monochrome tiles, such as OT-1 (Figure 9b), and the irregularity in the thickness of polychrome tiles, such as OM-1 (Figure 9a). This is most likely because some would have been fired twice (the monochrome ones), once before glazing, and a second time for glazing, and others would have had a single firing (in which both the paste and the enamel were fired simultaneously). In the first case, during the second firing the enamel was unable to penetrate already-sintered pastes and this resulted in a thicker, more regular, and homogeneous enamel. On the contrary, in the second case, the enamel was able to penetrate through the pores of the clay even without firing, generating a gradual heterogeneity from the surface to the interior.

Research referring to the tile production centres of Manises mentions that the technique used was single firing [20], so it would fit that those artisans from Manises participated in its production (even though it was in Tudela production centres).

4.3. Enamel Raw Materials and Enamelling Process

As for the enamels, we found an absence of publications referring to the enamels of the artisans of Tudela and a very wide range of publications on the enamels of the artisans of Manises [13,15–18,27].

The comparison of the enamels from the Olite castle with those from the Manises workshops shows a high similarity between cases with a high Pb and low Sn content, and is characteristic of the first enamel productions [15,21,27]. The high concentration of Si and K also coincides, probably due to the addition of fine silica sand and feldspar next to the flux.

The raw materials used to produce enamels would be high-purity tin for all types of enamel. For the brown enamel, pyrolusite (MnO_2) or hausmannite ($Mn^{2+}Mn^{3+}O_4$) was probably used [21]. For the green enamel, the pigment was probably malachite ($Cu_2CO_3(OH)_2$) [15]. And for the blue enamel there are two possibilities: that it was asbolane ($(Ni,Co)^{2-x}Mn^{4+}(O, OH)_4(H_2O)n$) brought from Saxony (Germany) via Venetian traders or from local mines such as those in Villamarchante (Valencia, Spain); or that it was erythrite ($(Co, Ni)_3(AsO_4)_2{\cdot}(H_2O)_8$) or smaltite ($(Co, Ni)As^{3-2}$) [13,15–18]. The absence of As in the enamels could be due to the fact that it would be eliminated during firing as a gas and therefore would not leave a trace of its presence in the enamel [18].

The use of some cobalt blue pigments or others has changed over the centuries. During the 14th century, the blue enamel was richer in copper. Later, at the end of the 14th century and the beginning of the 15th century, asbolane was the most used. Later, during the 16th and 17th centuries, minerals with Co and As were used. For the latter, the amount of As was such that it could not be eliminated during firing and traces remained in the enamel that have been detected and allow them to be dated [13,15–18].

The average thickness of the monochrome glazes was about 160 ± 40 µm, except for the white glazes, which were much thicker. One possible explanation is that for the green, blue, and brown glazes, the chromophoric capacity of the pigments responsible for the colour was sufficient to allow them to be applied in a thin layer. However, the white glaze may have required a greater thickness to avoid a certain transparency of the paste and to achieve a purer white.

Finally, it is worth mentioning that there was also an evolution in the order used when applying the cobalt blue pigment and the flux. During the 14th and 15th centuries, the pigment was applied to the paste, and then covered with the flux. Later (16th and 17th centuries), the process was reversed and first it was applied in flux and then painted with the pigment on top. In the case of the polychrome Olite tiles (Figure 9a), Co, Mn, and Cu were dispersed homogeneously in the enamel, while lead and tin were more abundant in the upper part. Therefore, this technical aspect would also coincide with the estimated date (1400) and with the technology used in the Manises workshops [17,20,21].

5. Conclusions

The analysis of the ceramic pastes of Olite's castle revealed the existence of two groups with significantly different chemical compositions, suggesting the use of at least two different clay sources. The similarities found between the pastes of group 1 and those previously studied in the Tudela area, as well as between those of group 2 and those previously studied from the Tafalla–Olite area, allowed the production of tiles and bricks to be attributed to these areas instead of to Manises, as had been previously hypothesised from an historical and stylistic point of view. Those probably made in the Tudela area stood out for a higher diopside ($CaMgSi_2O_6$) content. Those probably made in the Tafalla–Olite area stood out for calcium-bearing minerals, such as calcite ($CaCO_3$) or gehlenite ($Ca_2Al(AlSi)O_7$).

The study of the firing temperatures and composition of the enamels indicated that the production methods and materials used in Olite (800–850 °C) and Tudela (higher than 900 °C) were different, reflecting the influence of local and Manises artisans.

The evolution of glazing techniques and pigment composition over time also provided valuable context for understanding the ceramic production of the period. In Olite tiles, enamel was applied following recipes from the 14th and 15th centuries. The enamel was composed mainly of Pb, Si, and Sn. The Sn was used as an opacifier with white colour. The most probable pigments were pyrolusite and hausmannite for the brown colour; malachite for the green one; and asbolane for the blue one. The monochrome tiles were made using two firings (one for the paste and one for the glaze), while the polychrome ones were fired in one unique firing process.

Together, these findings not only enrich our knowledge of mediaeval ceramics in Navarra, but also highlight the importance of collaboration between different regions in the creation of these works of art.

Author Contributions: Conceptualization, I.R.-A., E.L. and A.D.; methodology, I.R.-A., E.L. and A.D.; software, I.R.-A.; validation, I.R.-A.; formal analysis, I.R.-A.; investigation, I.R.-A., E.L. and A.D.; resources, I.R.-A.; data curation, I.R.-A.; writing—original draft preparation, I.R.-A.; writing—review and editing, E.L. and A.D.; visualisation, I.R.-A.; supervision, E.L. and A.D.; project administration, E.L. and A.D.; funding acquisition, E.L. and A.D. All authors have read and agreed to the published version of the manuscript.

Funding: The research has the support and financing of the General Directorate of Historical Heritage-Príncipe de Viana of the Government of Navarre under the following projects: "Thibalt. Caracterización arqueométrica de Carreaux de Pavement procedentes del Castillo de Tiebas (Navarre)" and "Aplicación del arqueo- magnetismo y otras técnicas fisicoquímicas para el estudio de la tecnología de fabricación de azulejos medievales navarros", as well as of Ayuntamiento de Tiebas-Muruarte de Reta and the Fundación Sierra de Alaiz. I.R.-A. thanks the Asociación de Amigos de la Universidad de Navarre for its doctoral scholarship.

Data Availability Statement: Data will be made available on request.

Acknowledgments: SEM micrographs and EDS analysis were performed by Mikel Domeño Pérez in an FE-SEM Sigma 300 VP. The authors also thank Aitor Iriarte Cortazar, Javier Corcín Ortigosa, and Maite Garbayo Valencia for their knowledge of Olite's castle's history. The authors also thank Iñaki Dieguez Uribeondo for allowing the use of his illustration in this article. The authors also thank Alzahraa Mohamed, Mohamed Essaouari, and Rafael Sánchez García for their help with the translation.

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

References

1. Fortún-Pérez de Ciriza, L.J. *Sedes Reales de Navarra*; Gobierno De Navarra: Pamplona, Spain, 1991.
2. Ozaki, A. El régimen tributario y la vida económica de los mudéjares de Navarra. *Príncipe Viana* **1986**, *47*, 437–484.
3. Martínez de Aguirre, J. *Arte y Monarquía en Navarra (1328–1425)*; Gobierno de Navarra: Pamplona, Spain, 1987.
4. Idu Ilustración. Available online: https://idu-ilustracion.com/ (accessed on 25 August 2024).
5. Turismo de Navarra. Gobierno de Navarra. Olite. Available online: https://www.visitnavarra.es/es/olite (accessed on 25 August 2024).
6. Iriarte-Cortazar, A.; García-Purroy, J.; Ramos-Aguirre, M.; Narbona-Cárceles, M.; Zuza-Viniegra, M.; Serrano-Larráyoz, F.; Menéndez-Aldave, B.; Setuain-Chorraut, K. *Palacio de los Reyes de Navarra—Olite: Exotismo y Vanguardia en la Corte de Carlos III*; Editorial Mintzoa: Pamplona, Spain, 2024.
7. Iriarte-Kortazar, A. Los palacios dorados de nuestro señor el rey Don Carlos. In Proceedings of the Tercer Congreso General de Historia de Navarra, Pamplona, Spain, 20–23 September 1994.
8. Pérez-Marañón, J.M. *Olite. Historia, Arte y Vida*; Editorial EcoHabitar: Madrid, Spain, 2010.
9. Llibrer-Escrig, A. Relaciones protoindustriales en la producción cerámica. Manises y Paterna en la segunda mitad del siglo XV. *Medievalismo* **2014**, *24*, 213–239.
10. Iriarte-Kortazar, A. Nuevas representaciones de emblemas reales de Olite. In *Mito y Realidad en la Historia de Navarra*; Sociedad de Estudios Vascos: Pamplona, Spain, 1998; p. 483.
11. Pinto-Monte, M.; i Fernández, M.M.; i Garrigós, J.B.; Coll-Conesa, J. The medieval and post-medieval ceramics from Manises (Valencia). A reassessment from the new excavations at Barri d'Obradors. *J. Archaeol. Sci. Rep.* **2021**, *39*, 103135. [CrossRef]
12. Sánchez-Ramos, S.; Bosch-Reig, F.; Gimeno-Adelantado, J.V.; Yusá-Marco, D.J.; Doménech-Carbó, A. Application of XRF, XRD, thermal analysis, and voltammetric techniques to the study of ancient ceramics. *Anal. Bioanal. Chem.* **2002**, *373*, 893–900. [CrossRef] [PubMed]
13. Pérez-Arantegui, J.; Montull, B.; Resano, M.; Ortega, J. Materials and technological evolution of ancient cobalt-blue-decorated ceramics: Pigments and work patterns in tin-glazed objects from Aragon (Spain) from the 15th to the 18th century ad. *J. Eur. Ceram. Soc.* **2009**, *29*, 2499–2509. [CrossRef]
14. Ruiz-Ardanaz, I.; Úriz-Asiáin, O.; Lasheras, E.; Durán, A. Tiebas Castle' tuiles vernissées: Characterization, raw clay provenance, and manufacturing technology. *Appl. Clay Sci.* **2024**, *260*, 107552. [CrossRef]

15. Romero-Pastor, J.; García-Porras, A.; Grieken, R.V.; Potgieter-Vermaak, S.; Coll-Conesa, J.; Cardell, C. New insights in technology characterization of medieval Valencia glazes. *X-ray Spectrom.* **2015**, *44*, 426–435. [CrossRef]
16. Molera, J.; Coll, J.; Pradell, T. The blue ceramic from Manises' obradors quarter: Technology of production. In *Tecnología de los Vidriados en el Oeste Mediterráneo: Tradiciones Islámicas y Cristianas*; Ministerio de Cultura y Deporte: Madrid, Spain, 2021; Volume 12, pp. 255–272.
17. Pérez-Arantegui, J.; Resano, M.; García-Ruiz, E.; Vanhaecke, F.; Roldán, C.; Ferrero, J.; Coll, J. Characterization of cobalt pigments found in traditional valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry. *Talanta* **2008**, *74*, 1271–1280. [CrossRef] [PubMed]
18. Roldán, C.; Coll, J.; Ferrero, J. EDXRF analysis of blue pigments used in valencian ceramics from the 14th century to modern times. *J. Cult. Herit.* **2006**, *7*, 134–138. [CrossRef]
19. Hess, P. PbO-SiO2 melts: Structure and thermodynamics of mixing. *Geochim. Cosmochim. Acta* **1975**, *39*, 671–687. [CrossRef]
20. Pérez-Camps, J. *Sobre la Manera de Fabricar la Azulejería en Manises Durante los Siglo XIV al XVI*; Museu de Ceràmica de Manises: Valencia, Spain, 2008; pp. 83–96.
21. Coentro, S.; Alves, L.; Coll-Conesa, J.; Ferreira, T.; Mirão, J.; da Silva, R.; Trindade, R.; Muralha, V. White on blue: A study on underglaze-decorated ceramic tiles from 15th-16th-century Valencian and Sevillian productions. *J. Archaeol. Sci. Rep.* **2020**, *30*, 102254. [CrossRef]
22. Colomban, P.; Tournié, A.; Bellot-Gurlet, L. Raman identification of glassy silicates used in ceramics, glass and jewellery: A tentative differentiation guide. *J. Raman Spectrosc.* **2006**, *37*, 841–852. [CrossRef]
23. Webmineral. Available online: https://www.webmineral.com/ (accessed on 8 September 2024).
24. Ruiz-Ardanaz, I.; Araiz-González, S.; Lasheras, E.; Durán, A. The ceramic production and distribution network in the ancient Kingdom of Navarre (Spain) during the 12th–15th centuries. *Heritage* **2024**, *7*, 4814–4828. [CrossRef]
25. Liu, C.; Xie, H.; Nie, L.; Wang, H.; He, Y. A Study of the Composition and Dissolution of Jianshui Purple Pottery in Yunnan, China. *Crystals* **2021**, *11*, 1034. [CrossRef]
26. Tao, S.; Zhu, Y.; Liu, S.; Dong, J.; Yuan, Y.; Li, Q. Morphology and Structure Characteristics of the Rare Black-Glazed Porcelains Excavated from the Jian Kiln Site of Song Dynasty. *Crystals* **2023**, *13*, 632. [CrossRef]
27. García Porras, A.; Coll Conesa, J.; Romero Pastor, J.; Cabella, R.; Cardell, C.; Capelli, C. Nuevos datos arqueométricos sobre la producción cerámica de Paterna y Manises durante el siglo XIV. In *En I Congreso Internacional Red Europea de Museos de Arte Islámico*; Patronato de la Alhambra y Generalife: Granada, Spain, 2012; pp. 419–436. [CrossRef]