heritage

MDPI

Article

Microanalytical Determinations to Distinguish Maiolica and Mezza Majolica Ceramics from Faenza (Emilia-Romagna Region, Italy)

Elena Marrocchino [1,2,*], Maria Grazia Paletta [1] and Chiara Telloli [3]

1 Department of Environmental and Prevention Science, University of Ferrara, C.so Ercole I D'Este 32, 44121 Ferrara, Italy
2 CNR—Istituto di Geologia Ambientale e Geoingegneria—Sede di Roma, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy
3 ENEA—Italian National Agency for New Technologies, Energy and Sustainable Economic Development Fusion and Technology for Nuclear Safety and Security Department Nuclear Safety, Security and Sustainability Division, Via Martiri di Monte Sole 4, 40129 Bologna, Italy
* Correspondence: mrrlne@unife.it; Tel.: +39-3-393-807-477

Abstract: Post-Renaissance ceramics (XVI–XIX) obtained in the Emilia Romagna region (north of Italy) demonstrate the difficulty in correctly identifying two different main types of artifacts: (i) enamel terracotta (or majolica) and (ii) glazed engobed terracotta (or mezza-majolica). This problem arises from the fact that the two different artifacts have the same shape, mixture, and even the same decoration in terms of color and style. Based only on macroscopic observation, the distinction between majolica and mezza-majolica could be problematic. This study aims to propose an immediate identification of the finds by diagnostic investigations to achieve identification of the type of coating applied. Different kinds of archeological finds were collected during a restoration of an important building in the city center of Faenza, Italy, and were analyzed by optical transmitted light polarized microscopy on thin sections, scanning electron microscope (SEM-EDS), and colorimetry analysis. The results identified two types of clayey material; one was Fe enriched carbonate clay and the other had Fe enriched non carbonate clay used in the production of the ceramic artifact. The analysis also distinguishes the different techniques by which the artifacts were produced, either by single firing or by double firing.

Keywords: ceramic finds; petrographic investigations; optical transmitted light polarized microscopy characterization; SEM-EDS; colorimetry analysis

Citation: Marrocchino, E.; Paletta, M.G.; Telloli, C. Microanalytical Determinations to Distinguish Maiolica and Mezza Majolica Ceramics from Faenza (Emilia-Romagna Region, Italy). *Heritage* **2022**, *5*, 3515–3529. https://doi.org/10.3390/heritage5040182

Academic Editor: Silvano Mignardi

Received: 16 October 2022
Accepted: 14 November 2022
Published: 17 November 2022

1. Introduction

Ceramic is identified as a hard, brittle, heat and corrosion-resistant material made by shaping and firing a nonmetallic mineral (such as clay) at a high temperature [1,2]. Common examples are terracotta [3,4], porcelain [5,6], and brick [7,8].

In Italy and the Mediterranean basin, vast ceramic production took place thanks to an abundance of clay deposits and the high level of skillfulness of local artisans established over centuries. Ceramic shards have been found in numerous archeological excavations in Italy, as in the case of the Villa dei Quintile (Rome) [9], Urbino and Pesaro [10] in Laterza (Taranto) [11], and the flooring of San Sebastiano in Venice [12].

All the post-Renaissance ceramics in Italy and the Emilia Romagna region (Italy) during the XVI-XIX century were characterized by a white, glossy surface and decorated in mono- or polychrome: majolica or engobed terracotta, and mezza-majolica or glazed engobed terracotta [13,14].

A large number of publications have been devoted to the study of the origin and development of the laviano [9–12,15,16]. Among these, much research has been devoted to the study of the technological aspects of Italian production [17,18] to better distinguish between majolica and mezza-majolica.

Generally, it is not easy to correctly distinguish between majolica and mezza-majolica [19]. This is because two different artifacts can have the same characteristics, shape, mixture, and even the same decoration, and sometimes the same color and style. In these cases, identification on a photographic basis only makes documentation more difficult. For this reason, the following study analyzes different types of majolica and mezza-majolica samples to identify their differences in order to better understand archeological ceramic finds.

When the ceramic products have a graffiti decoration, identification is far easier, as this technique highlights the contrasts between the reddish color of the earth that constitutes the body of the artifact and the white of the engobed lining. In contrast, when graffiti decoration is not present, an incorrect evaluation is possible.

The ceramic finds investigated in this work could be assigned to two types of ceramic materials:

- "majolica" or engobed terracotta, where the color of the ceramic body is hidden by a white or colored glass that waterproofs it on one side and highlights the painted decorations on the other side [20];
- "mezza-majolica" or glazed engobed terracotta, where the color of the earthy body is hidden by a white earth called engobed, generally painted and later made waterproof by a transparent showcase [21,22].

This work aims to facilitate the identification of finds and their attribution to the correct technical preparation. When based only on macroscopic observation, the distinction between majolica and mezza-majolica could be problematic. By subjecting them to diagnostic investigations, it could be possible to achieve more precise recognition of the type of coating applied. For this reason, all the finds were subjected to investigation through microscopic observations to define their structural aspect. In addition, morphological and chemical characterization on the surface of the fragments was carried out by a scanning electron microscope (SEM), and, finally, colorimetric analyses was used to define their color through data and precise references. This approach makes it possible to distinguish between the majolica samples from those of mezza-majolica, to better characterize archeological finds, and to distinguish the two different firing procedures.

2. Sampling and Analytical Methods

2.1. Samples and Sampling Site Description

Sampling of the archeological finds (bones, shells, glass, metals, ceramics, coals, plasters) was carried out by the Archeological Superintendence of the Emilia Romagna region, in collaboration with the Municipality of Faenza, during the restoration of an important building in the city center of Faenza, near Ravenna city, in the eastern part of the Emilia Romagna region (north-east of Italy, as shown in the map in Figure 1).

The sampling site was located in the basement of rooms 1 and 2 of the private building situated at 33 and 35, Corso Matteotti, on the corner of Vicolo Gottardi, in the city center of Faenza.

Of all the materials found, only ceramics were analyzed in this research work, which represented the most quantitatively significant fraction.

The ceramic samples, characterized by a colored and porous body, symbolized the style of the post-Renaissance period of the Emilia Romagna region (XVI–XIX) [23], and it was possible to classify them into engobed terracotta and glazed engobed terracotta:

- Engobed terracotta: CM1s (plate of about 40 cm diameter—Figure 2a), CM2s (plate of about 30 cm diameter—Figure 2b), CM3s (jug or pit of about 40 cm diameter—Figure 2c);
- Glazed engobed terracotta: CM1i (plate of about 40 cm diameter—Figure 2d), CM2i (plate of about 40 cm diameter—Figure 2e), CM3i (jug or pit of about 40 cm diameter—Figure 2f).

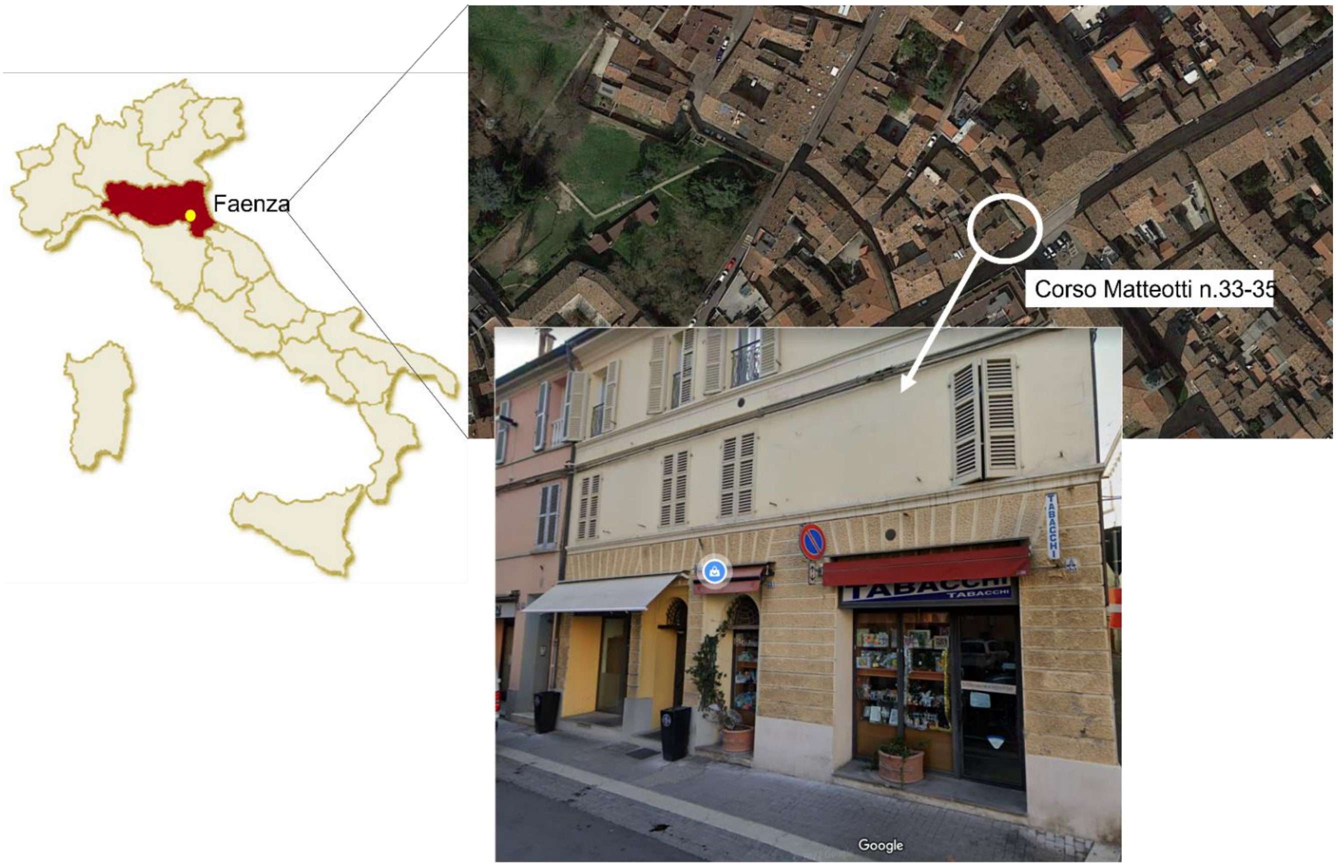
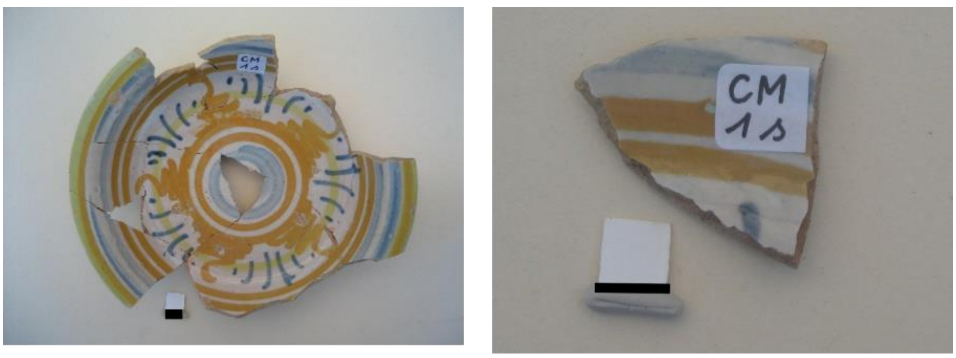


Figure 1. Picture of the sampling site in the building located in Corso Matteotti n. 33–45 in the city center of Faenza (on the **right** side) in the Emilia-Romagna region (colored in red in the map on the **left**). The detailed building located in Corso Matteotti n. 33–45 in the below section of the figure.

The ceramic finds of the two types of samples selected showed either the same formal characteristics (as for the samples CM3i and CM3s) or the same decorations (as for the samples CM1i and CM1s) or a clearly different coating (e.g., between the samples CM2i and CM2s).



(**a**)

Figure 2. *Cont*.

Figure 2. Photographs of the different types of ceramic samples selected for the analyses: (**a**) engobed terracotta CM1s; (**b**) engobed terracotta CM2s; (**c**) engobed terracotta CM3s; (**d**) glazed engobed terracotta CM1i; (**e**) glazed engobed terracotta CM2i; (**f**) glazed engobed terracotta CM3i. The black line indicates a scale bar of 2 cm.

2.2. Analytical Techniques

All the ceramic finds were macroscopically observed and described in detail.

Preparation of the samples and the analyses were carried out in the laboratories of the Department of Physics and Earth Sciences of the University of Ferrara (Emilia Romagna region, northeast of Italy), close to Faenza city.

Firstly, macroscopic investigations were carried out on all the ceramics samples to define their physical features (grain size and texture), color, and cohesion.

Microscopic observations were carried out using optical transmitted light polarized microscopy (BX51 Olympus) on thin sections (30 µm thickness) [24] to define the structural aspect (grain size and texture), clast dimensions, and morphological aspects of their state of conservation [25].

The morphological and chemical characterization on the surface of the fragments were carried out using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) INCA 300 (Oxford Instruments, Abingdon, UK) for X-ray microanalysis. The SEM instrument was a Zeiss EVO MA15 Basic Instrument (Carl Zeiss AG, Oberkochen, Germany) with a magnification range between <5–1.000.000× and a chamber dimension of 365 mm (Ø) × 275 mm (h). The accelerating voltage was from 0.2 to 30 kV. EDS analysis was carried out using air and water as the charge compensating gas, with pressures ranging from 10 Pa to 100 Pa. Electron beam energy of 20 keV and a probe current of 200 pA were used for all measurements. The SEM-EDS high magnification images of the fragment surfaces were performed using SmartSEM software (Zeiss) [26,27]. A non-metalized piece of each fragment from selected areas of uniform thickness (away from the edge) was firmed on an SEM stub utilizing double-sided conductive adhesive tape.

To define a color through data and precise references, analysis was carried out through visual comparison methods with color atlases or standard samples, or with instrumental reflectance measurements [28]. The color of our samples was evaluated using a Hunter Lab colorimeter (MiniScan XE Plus, Hunter Associates Lab Inc., Reston, VA, USA). The portable color measurement detector quickly and easily quantifies the color of the materials analyzed, producing numeric results indicative of the color of the sample by measuring L* (degree of lightness; black was 0 and white 100), a* (degree of redness when the value was positive, or greenness when it was negative), and b* (degree of yellowness when the value was positive, or blueness when it was negative) [29–31]. The device is self-contained with a liquid crystal display and keypad, and is powered by a rechargeable battery pack. It displays color and color difference values based on the red color (dark colors) and light colors.

3. Results and Discussion

3.1. Macroscopic Observation of the Collected Ceramic Samples

The majority of the ceramic samples observed were represented by plates of different sizes and depths, as shown in Figure 2a,b,d,e. The bowls found showed flared walls and, in some cases, they were equipped with trefoil handles (e.g., Figure 2c,f).

Based on the hypothetical daily use of the ceramic material collected, the samples could be divided as follows, and as detailed in Table 1 [32]:

- Tableware for domestic use consisting of containers (Figure 2c,f). These samples were glazed engobed terracotta. The body was colored, and it seemed more porous than those of the other samples. The coating was a white engobed covered with a yellowish lead glaze.
- Terracotta tableware for consuming food on a table, such as plates (Figure 2a,b,d,e). The bodies were porous, sometimes very crumbly, light yellow in color, and rarely pink in color. The coating was sometimes a white enamel or of bluish tones, or with a white engobed and with a glazed layer. In both cases, it completely covered the body. There were two different types of enamel: white (sometimes bluish) of considerable thickness (sometimes up to 2 mm) with a thin mesh; whitish of considerably less thickness than the other type with a much finer mesh. The first type was characterized

by the engobed terracotta of the seventeenth century, and probably later production (Figure 2a–c). The second type of coating was influenced by an older production method (Figure 2e); the coating was probably not a unique layer, but it was a painted enamel and subsequently covered by a glazed layer, a technique probably used in the last 1300 years [33].

Table 1. Macroscopic observation of the samples collected and analyzed [32].

Sample Name	Figure Reference	Classification	Daily Use	Engobed Color	Coating	Porous Body
CM1i	Figure 2a	engobed terracotta	Plats	White	white enamel	X
CM2i	Figure 2b	engobed terracotta	Plats	White	white enamel	X
CM3i	Figure 2c	engobed terracotta	containers (jug or pit)	White	yellow lead glaze	Less intense
CM1s	Figure 2d	glazed engobed terracotta	Plats	White	white enamel	X
CM2s	Figure 2e	glazed engobed terracotta	Plats	White	white enamel	X
CM3s	Figure 2f	glazed engobed terracotta	containers (jug or pit)	White	yellow lead glaze	Less intense

All the ceramic samples analyzed showed similar characteristics:

- the color surface was generally white, milky, or blue;
- the surface appeared brilliant;
- the coating completely and homogeneously covered both the front and the back sections, except the foot;
- if there were decorations, they were always painted in blue, yellow, orange, green, or manganese violet.

In addition, they were covered by an earthy coating combined with a transparent glassy coating. Except for some fragments of dishes.

By studying the findings in more detail, we realized that if the decorations belonged to the glazed ceramics, they were not made of enamel.

Regarding the engobed terracotta and the glazed engobed terracotta samples collected, they were classified following the scheme shown in Table 2, which allowed us to understand that the materials were created using different techniques. The major differences between the two types of ceramics, as expressed in Table 2, were:

- Coating thickness: This was thicker in the engobed terracotta samples;
- Coating color: The color of the engobed terracotta samples appeared milky white when the thickness of the enamel was thicker (Figure 3a) and pink where the thicknesses were thinner (Figure 3b). In the glazed engobed terracotta samples, the color was yellowish-ivory and none had pink tones (Figure 3c);
- Coating luster: This was more visible in the glazed engobed terracotta;
- Touch sensitivity on the painted ornaments: No sensitivity was detected in the engobed terracotta samples, except for the orange color. The opposite was true for the glazed engobed terracotta samples, in which the color had touch sensitivity.
- Even alterations and degradation due to wear and/or laying in the subsoil could be used as indicators to identify the materials, for example:
- In the engobed terracotta samples, the quibble appeared always with a rounded mesh, but in the presence of a thick enamel quibble, it appeared thin (as shown in Figure 3a); with a thin enamel, the quibble appeared denser (Figure 3b);

Table 2. Differences detectable by macroscopic observation between the two different types of ceramic samples analyzed: engobed terracotta and the glazed engobed terracotta. In the table below, thickness, color, and luster of the coating are shown, as well as the touch sensitivity on the painted ornaments and the quibble.

	Coating Thickness	Coating Color	Coating Luster	Touch Sensitivity on the Painted Ornaments	Quibble
Engobed terracotta	Thick	Milky white with thick enamel and pink with thin enamel	Less visible	Never, except for orange color.	Thin or thick depending on the thickness of the glaze. Always with round mesh
Glazed engobed terracotta	Thin	Yellowish-ivory	More visible	Always	Mesh with geometrical trend and always blackened

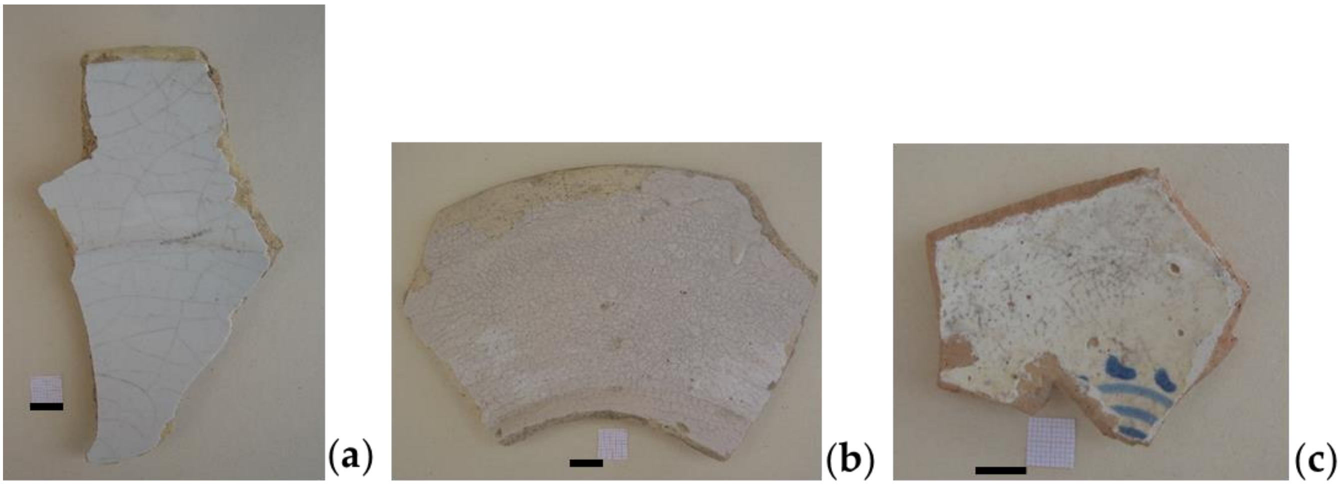


Figure 3. Photographs of some examples of the observed ceramic finds: (**a**) engobed terracotta with thick enamel and quibble with thin and rounded mesh; (**b**) engobed terracotta with thin enamel and quibble with denser and rounded mesh; (**c**) glazed engobed terracotta and quibble with a blackened mesh with a geometrical trend. The black line indicates a scale bar of 2 cm.

Conversely, in the glazed engobed terracotta samples, the quibble was blackened with a mesh following a geometrical trend (Figure 3c).

3.2. Microscopic Observation of the Selected Ceramic Samples

The thin sections of the selected samples (CM1s, CM2s, CM3s, CM1i, CM2i, CM3i) were observed by optical transmitted light polarized microscopy at 4× magnification and parallel Nicols.

3.2.1. Engobed Terracottas

The sample CM1s shows a very similar mixture to the other samples (Figure 4a), having an isotropic portion closest to the surface, while the presence of secondary material in the central part is highlighted. The skeleton, more than 100 µm, is characterized by quartz, plagioclase, mica, and iron oxides, and the macro-porosity is extremely low. There is a layer of glassy coating characterized by a high presence of granules of silicate material (mainly quartz) in contact with the mixture. The area with the greatest abundance of silicate inclusions is also characterized by the presence of a dense blackish dot (most likely SnO_2 granules). In general, the glassy layer is characterized by bubbles, especially concentrated in the transition area between the glassy portions and the more limpid and transparent ones. There is no clear area on the mixture-glaze interface. The total thickness of the entire layer is about 380 µm.

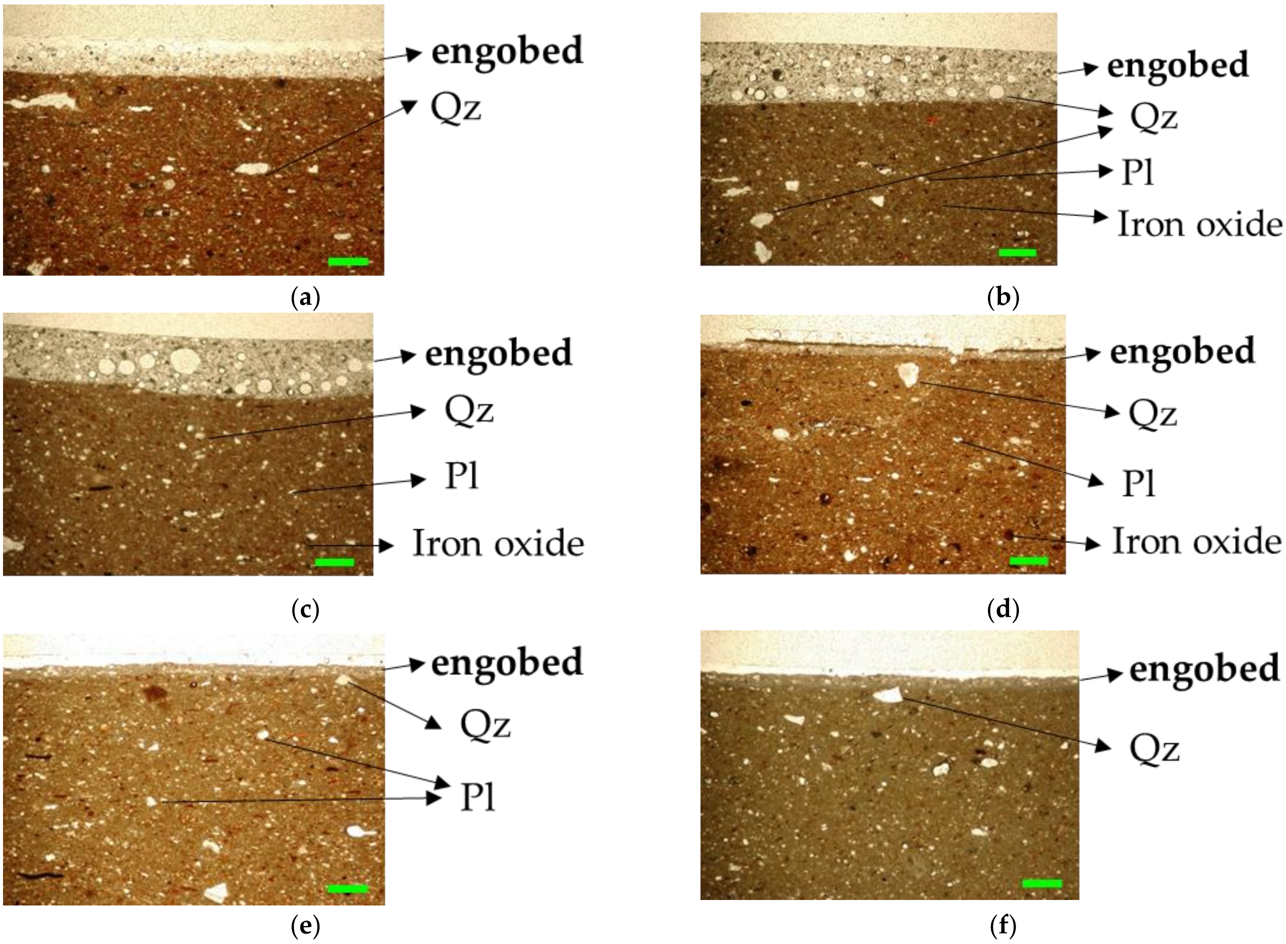


Figure 4. Imaging obtained by optical transmitted light polarized microscopy at 4x magnification and parallel nicols on the different type of samples analyzed: (**a**) engobed terracotta sample CM1s; (**b**) engobed terracotta sample CM2s; (**c**) engobed terracotta sample CM3s; (**d**) glazed engobed terracotta sample CM1i; (**e**) glazed engobed terracotta sample CM2i; (**f**) glazed engobed terracotta sample CM3i. Scale bar colored green in each figure corresponds to 0.2 mm. Qz = quartz particles; Pl = plagioclase particles.

Figure 4b shows the imaging of the sample CM2s. The sample is characterized by a mixture similar to the previous one; fine, isotropic, and homogeneous, with rare quartz grains with a diameter more than 100 µm. The coating layer is present on the surfaces of the sample. The thickness reaches between 500 and 720 µm. The appearance is extremely bullous; the bubbles are distributed along the entire enamel layer and range from small dimensions, with a maximum diameter of 20 µm, up a dimension of about 200 µm. Conversely, undissolved quartz grains are rare, along with other materials of small size (less than 100 µm in diameter). Additionally, in this case, a well-developed interface zone is not observed.

The sample CM3s shows a very similar mixture to the previous one, without an overprint of secondary material (Figure 4c). The layer of glass coating, present on both surfaces, is similar in structure. The average thickness is about 480 µm and 600 µm.

3.2.2. Glazed Engobed Terracottas

The sample CM1i shows a bright red mixture characterized by a very micaceous isotropic groundmass (Figure 4d). The skeleton is composed of iron oxides and rare quartz grains with a diameter of less than 250 µm. The coating is characterized by an engobed layer and a glazed layer. The engobed layer shows a lighter color than the mixture. It has a fibrous appearance, with some grains of quartz and plagioclase, some micas, and some ferrous nodules. The thickness is around 80 µm. The glazed layer is characterized by the presence of undissolved quartz granules. Therefore, it does not have a very clear appearance, but has numerous bubbles and the presence of oxides.

Figure 4e shows imaging of the sample CM2i. The sample is characterized by a mixture with an isotropic and homogeneous base mass with a low quantity skeleton. Fragments of quartz (around 400 µm) and plagioclase are observed, as are many grains of badly cooked calcite and micas. A coating, consisting of a layer of glazed engobed, is present on the surfaces of the fragment. The engobed layer presents an average thickness of about 120 µm. Quartz granules immersed in a clayey illitic matrix are also observed, lighter in color than that of the mixture. The glassy layer is similar on both surfaces of the sample, with an average of thickness of about 120 µm and with some inclusion of undissolved quartz and some micro-cracks.

The sample CM3i shows a mixture similar to the previous one, but slightly finer (Figure 4f). Quartz and k-feldspar granules are observed with a maximum diameter of about 250 µm. The coating is characterized by a layer of engobed and one of the showcases. Small quartz grains with a diameter of less than 100 µm are also observed in the engobed layer, immersed in a fibrous clayey matrix. Overprints of secondary material are noted. The average thickness of this layer is about 100–140 µm. The layer of glass, about 180 µm thick, is extremely clear and transparent with little cracking and few bubbles. There are some traces of devitrification. Rare undissolved quartz crystals do not exceed 100 µm in size.

The microscope analysis allowed for the highlighting of small differences between the two different types of samples: engobed terracotta and glazed engobed terracotta. These differences allow for the recognition of the majolica in the engobed terracotta samples and the mezze-majolica in the glazed engobed terracotta samples.

3.3. SEM-EDS Analyses of Selected Samples

The results of the chemical analyses carried out by SEM-EDS are reported in Table 3. For each sample, different parts were analyzed: glazed, enamel, and ceramic body in the engobed terracotta samples; glazed, engobed, and ceramic body in the glazed engobed terracotta samples.

Table 3. SEM-EDS data of the engobed terracotta and glazed engobed terracotta samples selected and expressed in oxide (%). G = glazed; Eng = engobed; Ena = enamel; CB = ceramic body.

		SiO_2	PbO	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	SnO_2	TOT
CM1s	G	61.11	17.10	6.20	2.95	1.21	0.23	2.10	1.87	7.23	0.00	0.00	100
	Ena	66.24	14.11	0.00	0.17	0.53	0.17	3.66	1.84	6.61	0.00	6.67	100
	CB	55.66	0.00	0.65	14.79	6.03	3.67	14.86	1.16	3.18	0.00	0.00	100
CM2s	G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
	Ena	56.39	25.31	0.00	4.15	0.38	0.28	1.53	1.42	4.51	0.00	6.03	100
	CB	51.89	0.00	0.76	14.20	6.60	4.47	18.56	1.41	2.11	0.00	0.00	100
CM3s	G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
	Ena	55.57	24.14	0.00	4.35	0.61	0.21	1.74	1.39	5.43	0.00	6.56	100
	CB	51.50	0.00	0.73	14.65	7.26	3.90	17.71	1.37	2.88	0.00	0.00	100
CM1i	G	59.69	22.85	0.00	4.64	0.74	0.42	3.97	1.86	5.83	0.00	0.00	100
	Eng	53.83	0.00	0.68	16.53	1.80	5.86	11.04	2.00	5.93	2.33	0.00	100
	CB	51.36	0.00	0.59	15.27	6.43	4.38	16.58	1.65	3.74	0.00	0.00	100

Table 3. *Cont.*

		SiO_2	PbO	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	SnO_2	TOT
CM2i	G	58.30	27.70	0.00	3.97	0.35	0.45	2.73	1.57	4.93	0.00	0.00	100
	Eng	49.90	0.00	0.69	16.27	0.99	5.12	15.10	1.04	6.49	4.40	0.00	100
	CB	53.13	0.00	0.63	14.23	5.19	4.11	17.85	1.15	3.71	0.00	0.00	100
CM3i	G	60.26	24.95	0.00	3.36	0.63	0.68	3.74	2.27	4.11	0.00	0.00	100
	Eng	56.00	0.00	0.70	15.27	1.60	5.51	11.19	2.94	5.03	1.76	0.00	100
	CB	56.75	0.00	0.72	15.37	3.82	4.91	12.64	2.91	2.88	0.00	0.00	100

3.3.1. Engobed Terracotta Samples

The ceramic bodies of the three analyzed samples are not very different from each other. They are characterized by material rich in calcium (from 15 to 18%) with an iron percentage of around 7%. The magnesium content (about 4%) is also quite high, while the amount of alumina is around 15%. As for the coating, two samples have a vitreous enamel layer with a percentage of opacifier of around 6% of SnO_2, lead content of around 25%, and silica content of around 55%. Only one sample differs from the others, in that the coating layer is characterized by two portions: the lower one directly in contact with the mixture is characterized by a SnO_2 content of around 2%, while the PbO content is approximately 15%, against 60% of SiO_2; the more superficial part, on the other hand, is completely free of tin, characterized by a small amount of lead (about 14%) and silica around 65%. Remarkably, the percentage of potassium in both portions is around 7%. The images of Figure 5a–c appear different with respect to the imaging regarding the glazed engobed terracotta samples (Figure 5d–f). In the engobed terracotta samples, it is possible to note a clear separation between the two layers of the product and, above all, the presence of bubbles in the upper layer. This feature could be related to the single-stage firing technique.

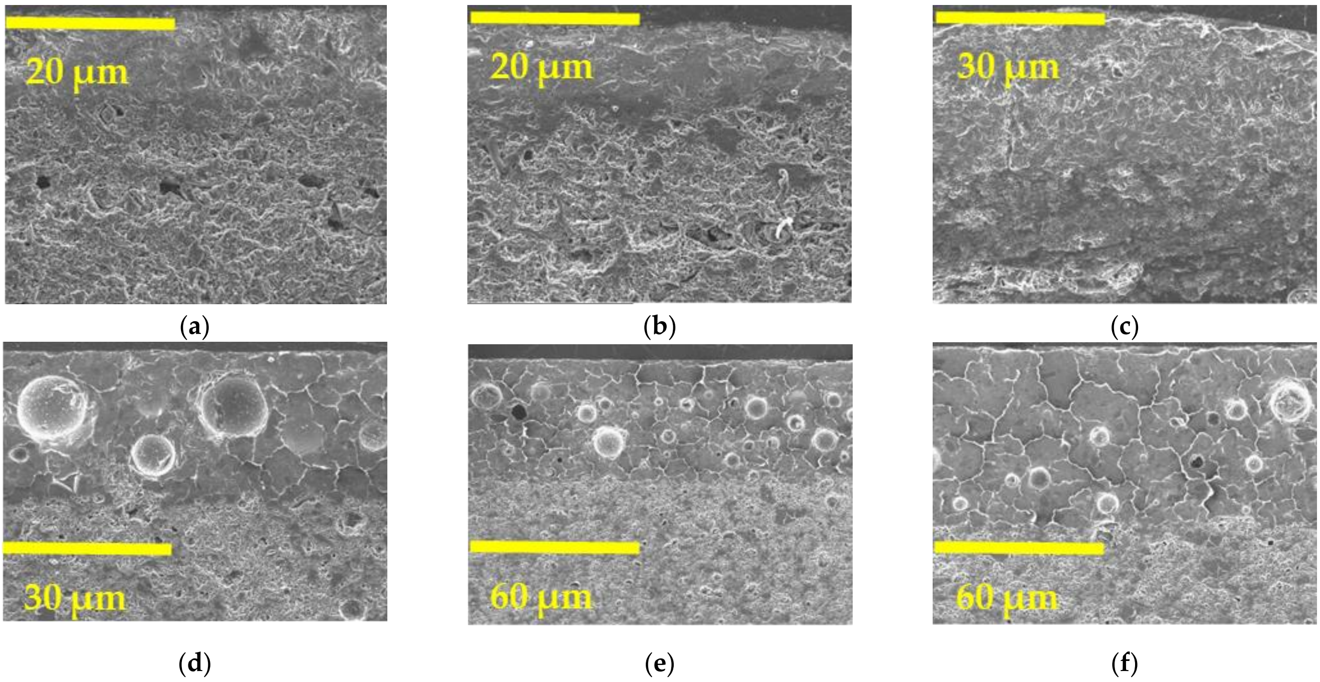


Figure 5. Imaging obtained by SEM-EDS analyses on the different types of samples analyzed: (**a**) engobed terracotta sample CM1s; (**b**) engobed terracotta sample CM2s; (**c**) engobed terracotta sample CM3s; (**d**) glazed engobed terracotta sample CM1i; (**e**) glazed engobed terracotta sample CM2i; (**f**) glazed engobed terracotta sample CM3i.

3.3.2. Glazed Engobed Terracotta Samples

The chemical data highlight that these samples are ceramics made with calcium raw materials (15% CaO), probably calcium carbonate for the majority, and also dolomite too. The percentage of iron is typical of this type of ceramic body. No major differences between the three samples analyzed were observed. As for the chemical composition of the engobed layer, it is difficult to define the composition of the raw material used due to the high percentage of SO_2 present in all three analyzed fragments. However, it is possible that sulfur is present in the engobed terracotta as a primary component, even if it is difficult to explain its presence. In general, these types of samples are characterized by raw materials rich in potassium (about 5–6%), calcium (11–15%, which would seem in relation to sulfur), and also with barely negligible magnesium content (around 5%). A percentage of around 1% of Fe_2O_3 is typical of iron oxide. The glazed is a lead type, with a percentage of SiO_2 around 60% and PbO from 22 to 27%, with 1:2 ratios between them. The silica content remains fairly constant, while the lead content varies from one to another. The level of potassium and calcium is also quite high, probably deliberately introduced in the glazed blends. Regarding alumina, the percentage probably justifies its introduction as an impurity of silica sands. The images of Figure 5d–f show a quite homogeneous upper layer without bubbles or unconformities. Moreover, it is difficult to note a clear separation between the two layers of the product.

The SEM-EDS analyzes could confirm the results obtained by the microscope analysis identifying majolica in the engobed terracotta samples and the mezza-majolica in the glazed engobed terracotta samples.

3.4. Colorimetric Analyses

The samples were also subjected to colorimetric analysis to define their coatings. The analyses were performed in all samples in the section without colored decorations. Three absolute values were considered: L*, a*, and b*.

The L* expressed the lightness, which could take values from 0 (minimum lightness corresponding to black) to 100 (maximum lightness corresponding to white in the gray scale).

The a* represented the red color when the value was positive and green when it was negative, it could take on values infinitely ranging from plus to minus.

Finally, b* represented yellow when the value was positive and blue when it was negative. As for the a*, it could take on values infinitely ranging from plus to minus [34].

Analyzing the values reported in Table 4, it can be noted that the lightness (L*) is higher in the engobed terracotta samples CM2s and CM3s than in the glazed engobed terracotta samples.

Table 4. Data values obtained through the colorimetric analyses on the collected samples. In the columns: L* = lightness; a* = red color; b* = light colors.

	L*	**a***	**b***
CM 1s	66.61	3.95	10.01
CM 2s	78.63	1.04	6.47
CM 3s	78.35	1.85	8.36
CM 1i	76.38	2.10	14.69
CM 2i	77.17	0.80	13.51
CM 3i	75.39	1.89	12.31

The CM1s sample, despite being engobed terracotta, shows a different L* value from the other two engobed terracotta samples, probably due to the double vitreous coating consisting of an enamel and glazed layer.

In relation to the value a*, CM1i and CM1s show the highest values (CM1s has the absolute higher value).

For b*, the glazed engobed terracotta samples (CM1i, CM2i, CM3i) show the highest yellow color. The engobed terracotta CM1s sample distinguishes itself from the two other engobed terracotta samples with more yellow color, placing itself in a clearly intermediate position.

Finally, colorimetric analyses also confirmed the previous results, verifying that the majolica is represented by the engobed terracotta samples and the mezze-majolica by the glazed engobed terracotta samples.

Overall, all the ceramic samples collected for this study, with or without coating, were attributable to two types of clayey material:

- Fe-enriched calcareous clay is characterized by a more or less fine structure, free of inclusions and vacuoles, with a color ranging from light pink to more intense shades, but never reaching the intense red color [35,36];
- Fe-enriched non-calcareous clay is characterized by a porous structure with a sandy appearance with regular inclusions and vacuoles. It is characterized by a reddish-brown color.

While calcareous clay was generally used in the production of all ceramic artifacts, not for firing use [37,38], the non-calcareous clay was exclusively used for all the materials intended to withstand thermal changes [39].

Although the raw materials used and the manufacturing techniques (as shown in Table 5) were different [21], and despite the macroscopic observations and the obtained information, as identified in Table 2, it was not easy to distinguish these two types of ceramics.

Table 5. Manufacturing techniques for the engobed terracotta (majolica) and glazed engobed terracotta (mezza-majolica) realization.

	Engobed Terracotta (Majolica)	Glazed Engobed Terracotta (Mezza-Majolica)
1	Molding of the clay in a plastic state	Molding of clay in a plastic state
2		Engobed application on the raw artifact
3	First firing	First firing
4	Enable application and decoration	Decoration
5		Glazed application
6	Second firing	Second firing

For the realization of mezza-majolica objects, however, single firing should not be excluded, which would have involved adding the decoration to the still raw object.

It was generally less problematic to distinguish the two products (majolica and mezza-majolica) when their state of conservation was altered and highlighted the defects due to the different origins of the covering coating. The mezza-majolica finds had always raised the doubt that they were real majolica; so much so that with the eye you cannot distinguish the real from the counterfeit. The product obtained using cheaper raw materials turned out to be of inferior quality compared to the majolica that still wanted to imitate both in terms of aesthetic quality and durability [40]. This type of process was due to the non-use of stanniferous enamel, which to produce it was necessary to calcinate the respective oxides of lead and tin in the appropriate burner for calcinations [41]. The replacement of the glaze with the engobed was aimed at cost-effectiveness derived from the non-use of the glaze itself; fuel for the calcination of the oxides and skilled labor was no longer necessary.

From macroscopic observations of these ceramic products, it may be problematic to distinguish them from majolica. By subjecting them to targeted diagnostic investigations, it is possible to arrive at a precise recognition of the type of coating applied.

The analyses carried out have shown that it is possible to distinguish three different techniques by which to determine ceramics painted in mono- or polychrome on white or whitish glazing:

- with a double coating consisting of an engobed (earthy, covering) and a colorless showcase (vitreous, transparent); the decoration was between the two coatings (samples CM1i, CM2i, CM3i represented the mezza-majolica finds);
- with a double coating consisting of an enamel (vitreous, covering); the painted ornamentation was between the two coatings (as for the majolica sample CM1s);
- with a single coating consisting of an enamel (vitreous, covering) on which the painted decoration was carried out (as for the majolica sample CM2s).

The first group included artifacts characterized by an engobed and a showcase which, on the one hand, made the earthy coating waterproof, and on the other hand, incorporated the colors and enhanced the decorative system. The ceramics belonging to this group were easily confused with those of the third group if the analysis was only an autopsy.

The second group of ceramics was characterized by an enamel that had the purpose of incorporating the colors of the painted ornament onto the enamel, enhancing the shades. This practice is described in detail by Piccolpasso [33] who associated transparent glazing with the term "blanket". The use of the blanket seems to disappear in the century XVIII, and then reappears at the end of the century XIX, perhaps following the publication of the manuscript of the architect with the term "crystalline".

The third group included artifacts that had an enamel with good opacifier content (SnO_2 6.03%), obtained by calcifying the tin and metal lead in the appropriate stove and subsequently added to the marzacotto, which in turn was obtained by cooking silica sand, sodium, and potassium salts. The limestone (together with tin oxide and lead oxide) was mixed with marzacotto and any other substances, then ground in a mill. This practice, as reported by Piccolpasso [33], was in use until almost the middle of the last century [42].

From an economic perspective, the ceramics engobed with showcase were certainly less expensive than the enameled ones. Opaque stanniferous glazing required having appropriate equipment (stove), materials (fuel, tin, and lead), and skilled workers; these were not seen in the first group of ceramics [43].

This subdivision is confirmed by the analyses that have shown that the majolica ceramics with their own glaze (CM1s, CM2s, CM3s) had thicker glazing than the mezza-majolica samples (CM1i, CM2i, CM3i) highlighted by the high tin oxide value (samples CM1s, CM2s, CM3s, with SnO values between 6.03 and 6.67 wt%).

The ceramics with coating consisting of an engobed and a showcase (mezza-majolica, samples CM1i, CM2i, CM3i) were free of tin oxide.

4. Conclusions

The purpose of this work was, through a microscopic and microanalytical study, to highlight the differences between the two types of material in order to facilitate the identification of the artifacts and their correct attribution to technical preparation for a better understanding of archeological ceramic finds and processing techniques. The finds were subjected to colorimetric analysis to define their color through precise data and references, and an investigation, through OMPTL observation on thin sections, to define the structural (grain size and texture) and dimensional aspects of the clasts and morphological aspects of their state of preservation. In addition, using SEM-EDS, morphological and chemical characterization of the surface of the samples were performed. All the collected ceramic samples, with or without coating, were attributable to two types of clay material:

- Fe-enriched carbonate clay, characterized by a more or less fine structure, free of inclusions and vacuoles, with a color ranging from light pink to more intense shades, but never reaching the deep red color;
- Fe-enriched non-carbonate clay, characterized by a porous structure of sandy appearance with regular inclusions and vacuoles. It is characterized by a reddish-brown color.

SEM-EDS analyses revealed a clear separation between the two layers of the material in the engobed terracotta samples. The presence of bubbles in the upper layer could be related to a single-stage firing technique. In the glazed engobed terracotta, a quite homogeneous upper layer without bubbles and unconformities was observed without clear separation between the two layers of the material.

From the analyses carried out, it was possible to distinguish three different techniques used to obtain mono- or polychrome painted ceramics on white or whitish glazing:

- one with a double coating consisting of an engobe (earthy, covering) and a colorless glaze (vitreous, transparent);
- one with a double coating consisting of a glaze (vitreous, opaque); the painted ornament was between the two coatings;
- another with a single coating consisting of an enamel (vitreous, opaque), on which the painted ornament was executed.

The results of this study showed how the economic aspect strongly influenced the production of coated ceramic materials in the post-Renaissance period, leading artisans to refine half-maiolica processing techniques in order to produce materials that increasingly approached the production standards of the finest majolica.

Author Contributions: Conceptualization, E.M. and C.T.; methodology, E.M. and C.T.; formal analysis, E.M. and M.G.P.; investigation, E.M.; resources, E.M. and C.T.; data curation, E.M. and C.T.; writing—original draft preparation, E.M., M.G.P. and C.T.; visualization, E.M. and C.T.; supervision, E.M. and C.T.; project administration, E.M. and C.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

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

References

1. Fabbri, B.; Ravanelli Guidotti, C. *Il Restauro della Ceramica*; Nardini Editore: Firenze, Italy, 2003.
2. Akgun, O. Damage Detection in Ceramic Materials Using Bicoherence Analysis. *Balk. J. Electr. Comput. Eng.* **2000**, *8*, 300–306. [CrossRef]
3. Tirado-Hernandez, A.; Becerra, J.; Ortiz, R.; Ortiz, P.; Gomez-Moron, A.; Ghervase, L.; Cortea, I.; Angheluta, L.; Radvan, R. Non-destructive techniques applied to the study and diagnosis of ceramic and glazed terracotta tombs in Omnium Sanctorum church (Seville, Spain). In *Science and Digital Technology for Cultural Heritage—Interdisciplinary Approach to Diagnosis, Vulnerability, Risk assessment and Graphic Information Models*; CRC Press: Boca Raton, FL, USA, 2019.
4. Quinn, P.; Yang, Y.; Xia, Y.; Li, X.; Ma, S.; Zhang, S.; Wilke, D. Geochemical evidence for the manufacture, logistics and supply-chain management of Emperor Qin Shihuang's Terracotta Army, China. *Archaeometry* **2021**, *63*, 40–52. [CrossRef]
5. Gültekin, E.E.M.; Topates, G.; Kurama, S. The effects of sintering temperature on phase and pore evolution in porcelain tiles. *Ceram. Int.* **2017**, *43*, 11511–11515. [CrossRef]
6. Fontes, W.C.; de Carvalho, J.M.F.; Andrade, L.C.R.; Segadaes, A.M.; Peixoto, R.A.F. Assessment of the use potential of iron ore tailings in the manufacture of ceramic tiles: From tailings-dams to "brown porcelain". *Constr. Build. Mater.* **2019**, *206*, 111–121. [CrossRef]
7. Martin, D.; Aparicio, P.; Galan, E. Time evolution of the mineral carbonation of ceramic bricks in a simulated pilot plant using a common clay as sealing material at superficial conditions. *Appl. Clay Sci.* **2019**, *180*, 105191. [CrossRef]
8. Vakalova, T.V.; Revva, I.B. Use of zeolite rocks for ceramic bricks based on brick clays and clay loams with high drying sensitivity. *Constr. Build. Mater.* **2020**, *255*, 119324. [CrossRef]
9. Ricca, M.; Paladini, G.; Rovella, N.; Ruffolo, S.A.; Randazzo, L.; Crupi, V.; Fazio, B.; Majolino, D.; Venuti, V.; Galli, G.; et al. Archaeometric Characterisation of Decorated Pottery from the Archaeological Site of Villa dei Quintili (Rome, Italy): Preliminary Study. *Geosciences* **2019**, *9*, 172. [CrossRef]
10. Antonelli, F.; Ermati, A.L.; Verita, M.; Raffaeli, G. An archaeometric contribution to the characterization of Renaissance maiolica from Urbino and a comparison with coeval maiolica from Pesaro (the Marches, Central Italy). *Archaeometry* **2014**, *56*, 784–804. [CrossRef]
11. Dell'Aquila, C.; Laviano, R.; Vurro, F. Chemical and mineralogical investigations of majolicas (16th–19th centuries) from Laterza, southern Italy. *Geol. Soc.* **2006**, *257*, 151–162. [CrossRef]
12. Fabbri, B.; Fassina, V.; Rattazzi, A.; Salvioni, D. The maiolica flooring of S. Sebastiano in Venice; an attempt of attribution by means of its composition and technology. In Proceedings of the 4th European Ceramic Society Conference, Riccione, Italy, 2–6 October 1995.
13. Borzacconi, A. Technological Aspects of 16th Century Ceramics Production in Castelnovo del Friuli, Italy. *Mater. Manuf. Process.* **2009**, *24*, 1041–1047. [CrossRef]
14. Law, J.E.; Østermark-Johansen, L. *Victorian and Edwardian Responses to the Italian Renaissance*; Routledge: London, UK, 2017.

15. Matejkova, K.; Blazkova, G. *Europa Postmediaevalis 2018: Post-Medieval Pottery between (Its) Borders*; Archaeopress Publishing: London, UK, 2019; 310p.
16. Ricci, C.; Borgia, I.; Brunetti, B.G.; Sgamellotti, A.; Fabbri, B.; Burla, M.C.; Polidori, G. A study on late medieval transparent-glazed pottery and archaic majolica from orvieto (central Italy). *Archaeometry* **2005**, *47*, 557–570. [CrossRef]
17. Padeletti, G.; Fermo, P.; Bouquillon, A.; Aucouturier, M.; Barbe, F. A new light on a first example of lustred majolica in Italy. *Appl. Phys. A* **2010**, *100*, 747–761. [CrossRef]
18. Kingery, W.D. Painterly Maiolica of the Italian Renaissance. *Technol. Cult.* **1993**, *34*, 28–48. [CrossRef]
19. Falke, J. Majolica. In *The Workshop: A Monthly Journal Devoted to Progress of the Useful Arts*; Baumer, W., Schnorr, I., Eds.; E. Steiger: New York, NY, USA, 1869; Volume 2, pp. 145–148.
20. Dias, M.I.; Prudencio, M.I.; Kasztovsky, Z.; Maroti, B.; Harsanyi, I.; Flor, P. Nuclear tech-niques applied to provenance and technological studies of Renaissance majolica roundels from Portuguese museums attributed to della Robbia Italian workshop. *J. Radioanal. Nucl. Chem.* **2017**, *312*, 205–219. [CrossRef]
21. Douglas, R.L. The majolica and glazed earthenware of Tuscany. *J. Soc. Arts* **1904**, *52*, 853–862.
22. Solon, M.L. The Ceramic Art of Orvieto during the Thirteenth and Fourteenth Centuries. *Burlingt. Mag. Connoiss.* **1909**, *16*, 10–13, 16–17.
23. Bersani, D.; Lottici, P.P.; Virgenti, S.; Sodo, A.; Malvestuto, G.; Botti, A.; Salvioli-Mariani, E.; Tribaudino, M.; Ospitali, F.; Catarsi, M. Multi-technique investigation of archaeological pottery from Parma (Italy). *J. Raman Spectrosc.* **2010**, *41*, 1556–1561. [CrossRef]
24. Marrocchino, E.; Telloli, C.; Pedrini, M.; Vaccaro, C. Natural stones used in the Or-si-Marconi palace façade (Bologna): A petro-mineralogical characterization. *Heritage* **2020**, *3*, 62. [CrossRef]
25. Cuomo di Caprio, N. *La Ceramica in Archeologia, Antiche Tecniche di Lavorazione e Moderni Metodi d'Indagine*; Erma di Bretschneider: Rome, Italy, 1988.
26. Telloli, C.; Chicca, M.; Pepi, S.; Vaccaro, C. Saharan dust particles in snow samples of Alps and Apennines during an exceptional event of transboundary air pollution. *Environ. Monit. Assess.* **2018**, *190*, 37. [CrossRef]
27. Marrocchino, E.; Telloli, C.; Caraccio, S.; Guarnieri, C.; Vaccaro, C. Medieval Glassworks in the City of Ferrara (North Eastern Italy): The Case Study of Piazza Municipale. *Heritage* **2020**, *3*, 45. [CrossRef]
28. NORMAL-43/93. *Misure Colorimetriche di Superfici Opache. Raccomandazioni Normal*; Comas Grafica Srl: Rome, Italy, 1994.
29. Parvathy, U.; Nizam, K.M.; Zynudheen, A.A.; Ninan, G.; Panda, S.K.; Ravishankar, C.N. Characterization of fish protein hydrolysate from red meat of Euthynnus affinis and its application as an antioxidant in iced sardine. *J. Sci. Ind. Res.* **2018**, *77*, 111–119.
30. Bautista-Ruiz, J.; Torres, N.; Aperador, W. Effect of the application technique on the colorimetric coordinates for a ceramic enamel. *J. Phys. Conf. Ser.* **2020**, *1708*, 012004. [CrossRef]
31. Echarri-Iribarren, V.; Rizo-Maestre, C. Gloss, Light Reflection and Iridescence in Ceramic Tile Enamels Containing ZrO_2 and ZnO. *Coatings* **2020**, *10*, 854. [CrossRef]
32. Miller, G.L.; Samford, P.; Shlasko, E.; Madsen, A. Telling Time for Archaeologists. *Northeast Hist. Archaeol.* **2000**, *29*, 2. [CrossRef]
33. Piccolpasso, C. *I Tre Libri dell'Arte del Vasaio*, 3rd ed.; Arnaldo Forni Editore: Sala Bolognese, Italy, 1879.
34. Burzacchini, B. *Colore, Pigmenti e Colorazione in Ceramica*; Cierre Grafica: Verona, Italy, 2003.
35. Amraoui, M.E.; Haddad, M.; Bejjit, L.; Ait Lyazidi, S.; Lakhal, R. On-site XRF characterization of archaeological materials in CERA center of Rissani (Morocco). *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *186*, 012029. [CrossRef]
36. Aloupi-Siotis, E. Ceramic technology: How to characterise black Fe-based glass-ceramic coatings. *Archaeol. Anthropol. Sci.* **2020**, *12*, 191. [CrossRef]
37. Quinn, P.S. *Ceramic Petrography: The Interpretation of Archaeological Pottery & Related Artefacts in Thin Section*; Archaeopress: Oxford, UK, 2013.
38. Kazakou, T.; Zorba, T.; Vourlias, G.; Pavlidou, E.; Chrissafis, K. Combined studies for the determination of the composition and the firing temperature of ancient and contemporary ceramic artefacts. *Thermochim. Acta* **2019**, *682*, 178412. [CrossRef]
39. Carretero, M.I.; Dondi, M.; Fabbri, B.; Raimondo, M. The influence of shaping and firing technology on ceramic properties of calcareous and non-calcareous illitic–chloritic clays. *Appl. Clay Sci.* **2002**, *20*, 301–306. [CrossRef]
40. Ryan, W. *Properties of Ceramic Raw Materials*, 2nd ed.; Pergamon Press: Oxford, UK, 2013.
41. Pereira, S.L.C. The production of faience in Portuguese workshops (15th–18th century). *E-J. Port. Hist.* **2019**, *17*, 49–150.
42. Baldisserri, G. *Rilievo delle Tecniche Ceramiche in Uso a Castelli tra le Due Guerre*; Istituto Statale d'Arte per la Ceramica "G. Ballardini": Faenza, Italy, 1988.
43. Liverani, G. Una nota sulla "Mezzamaiolica". *Boll. Del Mus. Int. Ceram. Faenza* **1977**, *63*, 99–107.