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Blue Shades in Plasters: Archaeometric Role in Dating of the Casamassima (Southern Italy) Historical Facades

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Abstract: Casamassima old town, locally known as "blue town", is widespread stratified blue paint covering the facades of the historical buildings, not reported in the archival data and historical sources. The archaeometric results presented in this study aimed to investigate raw materials, in particular pigments, used to cover the facades to contribute more precisely to the historical reconstruction of this local custom. A set of nine samples was collected from two representative historical buildings and observed by reflected light optical microscopy and scanning electron microscope (SEM-EDS) and their mineralogical characterisation was carried out by means of X-ray powder diffractometry (XRPD). The comparison of the mineralogical and elementary results and the stratigraphic, morphological, and microstructural observations made it possible to highlight a significant stratification of these plasters and to recognize the artificial ultramarine blue applied with lime, as the main mineral pigment, together with red ochre and blanc fixe. The identification of pigments was crucial to date the blue plasters.

Keywords: ultramarine blue; blue; plasters; pigment; XRPD; Apulia

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1. Introduction

In the second half of the last century, Casamassima city (Southern Italy) became famous with the denomination of "blue town", coined by the Italian painter Vittorio Viviani who, fascinated by the Apulian village colouring, portrayed the historic centre with cerulean colour in some paintings in 1976 [1]. According to the oral tradition and photographic traces of the second half of the twentieth century, in fact, the buildings of the old town showed facades built with irregular limestone blocks painted with different shades of blue.

On the origin of this chromatic choice and the use of blue lime everywhere in the urban landscape, there are no historical sources or archival data. This feature seems to be unique as the whole Apulia region is marked by historic centres where the facades of the buildings are plastered with white lime, among which the famous Itria valley [2]. Other evidence of "picturesque cities" are widespread in Italy (the Burano Island in Veneto and the Procida Island in Campania are noteworthy) but they are characterised by multicolour facades.

A local historiography hypothesis connects the blue painting colours to a devotion act to the Virgin of Constantinople, who allegedly protected the town from the plague that afflicted all the nearby villages in 1655 [3]; a second trend leads the choice back to a Byzantine custom, aimed at keeping insects away and disinfecting unhealthy places.

In addition, the blue painting combines the advantages of low cost and disinfectant power of lime with the attenuation of dazzling reflections of white under the sun, since the colour choice for the architectural built environment is usually connected to a specific purpose [4].

This feature is today strongly altered because only discontinuous fragments of the ancient layers of the blue painting are preserved along limited portions of the public monuments or in restricted layers on frames and windowsills less exposed to atmospheric agents [5].

Furthermore, Casamassima seems to show analogies with other cities marked by blue colours for their old town, in the Mediterranean area, such as Chefchaouen in Morocco and Sidi Bou Said in Tunisia [6], and Jodhpur in India [7,8]. Blue paintings are also found in Jùzcar (Spain), where its recent introduction was based only on marketing and touristic reasons [9].

However, comparable occurrences of blue facades in historical centres are not present in the region, even if blue paintings were frequently used in the local artistic tradition throughout the centuries [10–14].

The aim of the presented research is to contribute to the study of this custom in the territory and to describe its materials and painting techniques, in order to confirm or rebut the historical hypotheses advanced so far on the basis of legends. Through the archaeometric characterisation of raw materials, in particular of the blue pigment, it was possible to state that the Casamassima blue plasters are dated to the 19th century and then to a considerably more recent period than advanced by historical assumptions.

2. Blue Plasters

For the investigation of the plasters of Casamassima's old town, the St. Chiara's Monastery and the castle were considered (Figure 1). In fact, throughout the old centre, even if traces of blue plasters are still visible on several buildings, they showed a visible alteration of the historical stratigraphies, above all caused by neglect or by recent restorations which have canceled them. Compared to private buildings, the castle, and St. Chiara's monastery are the buildings in which the phenomenon of blue plasters is best represented as there are more significant stratigraphies and fewer renovations. Specifically, in the Monastery, 5 samples (M1, M2, M3, M4 e M5) and other 2 samples (CH1 e CH2) were collected from an outside wall and the cloister, respectively. In the castle, sampled plasters (C1, C2) belonged to two different outside walls. Origin, colour, and general description of the 9 collected samples were reported in Table 1. Fragments appeared as multilayered plasters, which colour showed several shades of blue, sometimes interrupted by white layers. In some samples, a single layer of a greenish blue and another single layer of brownish red were identifiable.

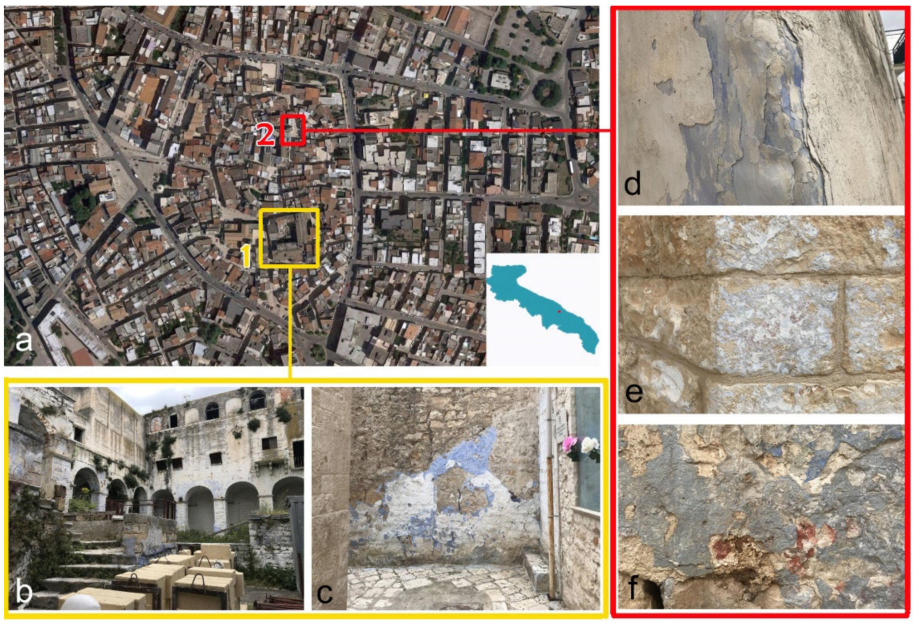

Figure 1. Geographic localisation of Casamassima (**a**) and of sampling points: the St. Chiara's Monastery (**b**,**c**) and the castle (**d**–**f**).

Table 1. Report of samples and their sampling points and macroscopic colour.

Sample	Sampling Area	Macroscopic Colour
M1	St. Chiara's monastery, outside wall	blue, greenish-blue, white
M2	St. Chiara's monastery, outside wall	blue, greenish-blue, white
M3	St. Chiara's monastery, outside wall	blue, brownish-red
M4	St. Chiara's monastery, outside wall	blue, greenish-blue, white
M5	St. Chiara's monastery, outside wall	blue, brownish-red
CH1	St. Chiara's monastery, cloister, left wall	blue, brownish-red
CH2	St. Chiara's monastery, cloister, left wall	blue, greenish-blue
C1	Castle, outside wall	blue, white
C2	Castle, outside wall	blue, brownish-red, white

3. Methods

The choice of the investigation methods was based first on the need to preliminarily observe the stratigraphy of samples and the homogeneity of the overlapped plaster layers, to evaluate the presence of one or more pigments in each layer, and to describe the thickness and morphological feature of pictorial layers and microscopic parameter of pigment particles (colour, shape, size, etc.) [15]. For this reason, plaster samples were observed by means of a stereomicroscope.

Moreover, SEM-EDS and XRPD were considered for the evaluation of the chemical-mineralogical composition of pigments and binders. Even if the application field of the latter technique is strictly limited to mineral pigments, the comparison with the chemical data has allowed us to obtain additional information.

The laboratory workflow and the experimental conditions are described below.

A small amount of pictorial layer was ground and used for the mineralogical analysis, which was conducted using an X'Pert pro MPD diffractometer with CuKα radiation at a wavelength of 1.54178 Å. The remaining part of fragments were incorporated in epoxy resin and transformed into cross sections which were observed under a Nikon Eclipse80i microscope equipped with a Nikon camera for digital image acquisition and Elements 3.1 software.

The microstructural features and the composition of coloured plasters, in terms of binder and pigments, were evaluated by a scanning electron microscope equipped with X-ray analysis (SEM-EDS, LEO, EVO50XVP model coupled with an X-max Silicon drift Oxford equipped with a Super Atmosphere Thin Window; operation conditions: 15 kV accelerating potential, 500 pA probe current and 8.5 mm working distance).

4. Results

4.1. Stratigraphy and Microscopic Observation

The considered samples consisted largely of blue layers and, secondary, white layers. In some cases, and any case only once in each sample, greenish-blue and red-brown layers were identified.

The microscopic observation, by means of a transmitted-light optical microscope, highlighted a considerable heterogeneity of the stratigraphy, therefore the number of layers varied greatly from sample to sample. In the case of blue layers, pigment consisted of very fine (<5 μm) and equidimensional blue particles, showing unimodal texture and dispersed in a white binder (Figure 2).

The pigment-binder ratio was highly variable, and the pigment concentration affected the colour rendering and hiding power of the final painting layer.

In fact, seeming to be equal to the pigment, the stratigraphic analysis highlighted both layers characterised by a rather limited amount of pigment and then by very light colour and layer where the blue pigment is considerably present thus determining an intense blue pictorial layer.

A representative sample of this complex stratigraphy was M4 (Figure 3), as it showed 30 pictorial layers characterised by different thicknesses (from about 20 to 400 μm) and by different pigment/binder ratios. In some layers, slightly different size of the blue pigment particles was observed.

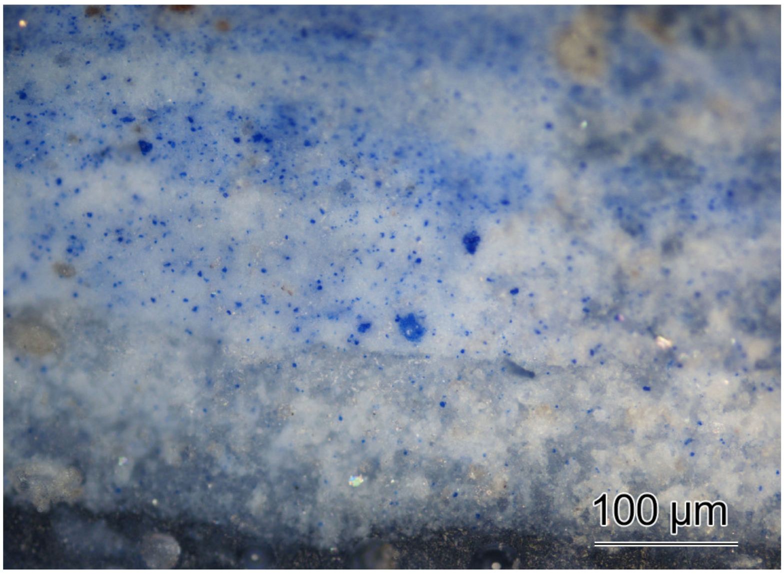

Figure 2. Photomicrograph of blue painting layers.

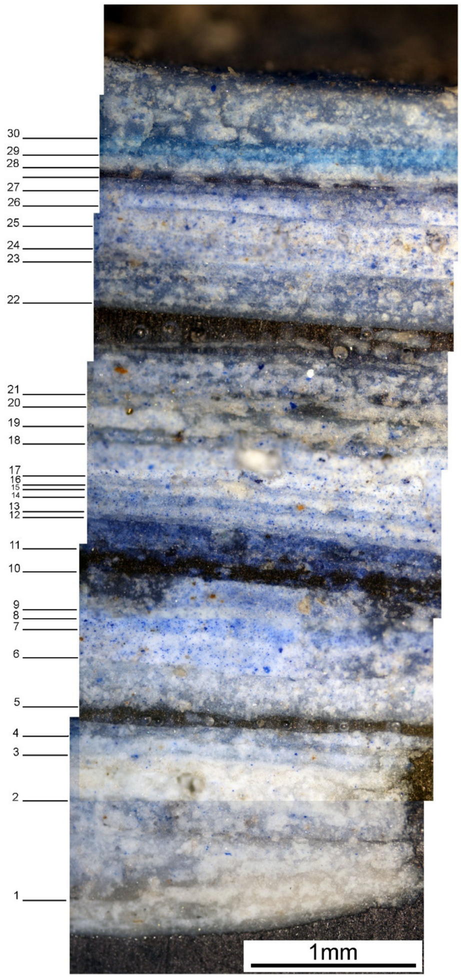

Figure 3. Photographic reconstruction of the stratigraphy of sample M4, showing 30 overlapped layers, obtained after matching of six photomicrographs.

Furthermore, in some layers of the sample, the presence of rare particles of yellow pigment between 5 and 15 μm in size, massive, and high roundness, was detected. White paint layers were also visible in the stratigraphy.

The greenish-blue layer, on the other hand, was recognised only in samples M1, M2, M4, and CH2. In this colour, the chromatic effect of this pigment was different from those of blue. The pigment particles were not distinguishable under optical microscopy.

The brownish-red layer, visible in samples M3, M5, CH1, and C2, included dark red particles with bimodal texture and then composed by a finer fraction that determined the background opacity and by a coarser fraction (about 20–30 μm). In addition, rare and rounded particles of black pigment (about 30–100 μm) were identified.

Lastly, although identical to the binder for their chromatic analogy, the white-coloured layers appeared to be constituted by an extremely fine (<5 μm) and dispersed white pigment.

Table 2 shows the main microscopic parameters useful for comparison with the compositional results for the recognition of pigments.

Table 2. Microscopic parameters of pigments included in the four groups of colours.

Macroscopic Colour	Sample	Microscopic Parameters				
		Pigment(s)	**Texture**	**Size (Moda)**	**Shape**	**Roundness**
Blue	M1, M2, M3, M4, M5, CH1, CH2, C1, C2	Blue	Unimodal	<5 μm	Massive-prismatic	Medium
		Yellow	Unimodal	5–15 μm	Massive	High
Greenish-blue	M1, M2, M4, CH2	Greenish-blue	Unimodal	n.v.	n.v	n.v.
Brownish-red	M3, M5, CH1, C2	Red	Bimodal	<5 μm	n.v.	n.v.
				20–30 μm	Massive	High
		Black	Unimodal	30–100 μm	Massive	Medium
White	M1, M2, M4, C1, C2	White	Unimodal	<5 μm	n.v.	n.v.

4.2. Mineralogical and Compositional Investigation

The mineralogical compositional analysis carried out using XRD and SEM-EDS respectively, made it possible to identify the pigments used in the plasters of the historical buildings Casamassima (Table 3).

Table 3. Report of mineralogical pattern (XRPD), elemental composition (SEM-EDS), and the attribution of pigments.

Macroscopic Colour	Sample	Pigment Colour	Mineralogical Pattern (XRPD)	SEM-EDS		Pigment Attribution
				Elemental Composition	**Compound Attribution**	
Blue	M1, M2, M3, M4, M5, CH1, CH2, C1, C2	Blue	Calcite, gypsum, lazurite, quartz, anhydrite	Si(+), Al(+), Na(+), S(+), Ca(−), K(−), Mg(−), Cl(tr)	Lazurite, sulfates, chlorides, lime	Ultramarine blue
		Yellow	-	Fe(+), Cl(−), Ca(−), Si(−), S(tr), Al(tr), Mg(tr), Na(tr), K(tr), Cl(tr)	Iron hydroxides, clay minerals, chlorides	Yellow ochre
Greenish-blue	M1, M2, M4, CH2	Greenish-blue	Calcite, gypsum, halite, graphite	Si(+), Al(+), Ca(+), Mg(−), K(−), Fe(−), Na(tr), S(tr), P(tr), Cl(tr)	Aluminosilicates, iron phosphate, chlorides, sulphates, lime	-
Brownish-red	M3, M5, CH1, C2	Red	Hematite	Fe(+), Si(−), Ca(−), Na(tr), Al(tr), Cl(tr), P(tr), K(tr)	Iron oxides, clay minerals	Red ochre
		Black	Carbon	-	-	Carbon black
White	M1, M2, M4, C1, C2	White	-	S(+), Ca(+), Ba(+), Si (−), Al (−), Mg(−), Na(−), K(tr), Cl(tr)	Barium sulphate, clay minerals	Blanc fixe

The colour of the most common pictorial layer was blue. The XRD spectrum (Figure 4a) generally indicates the presence of calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), lazurite ($Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3){\cdot}H_2O$), quartz ($SiO_2$) and anhydrite ($CaSO_4$): calcite and quartz referred to the binder [16], lazurite to the mineral present in the blue pigment [17,18], and gypsum and anhydrite to the salts crystallised on the pictorial surfaces. It was also present hematite (Fe_2O_3), referable to the brownish-red paint contribution [15,19,20].

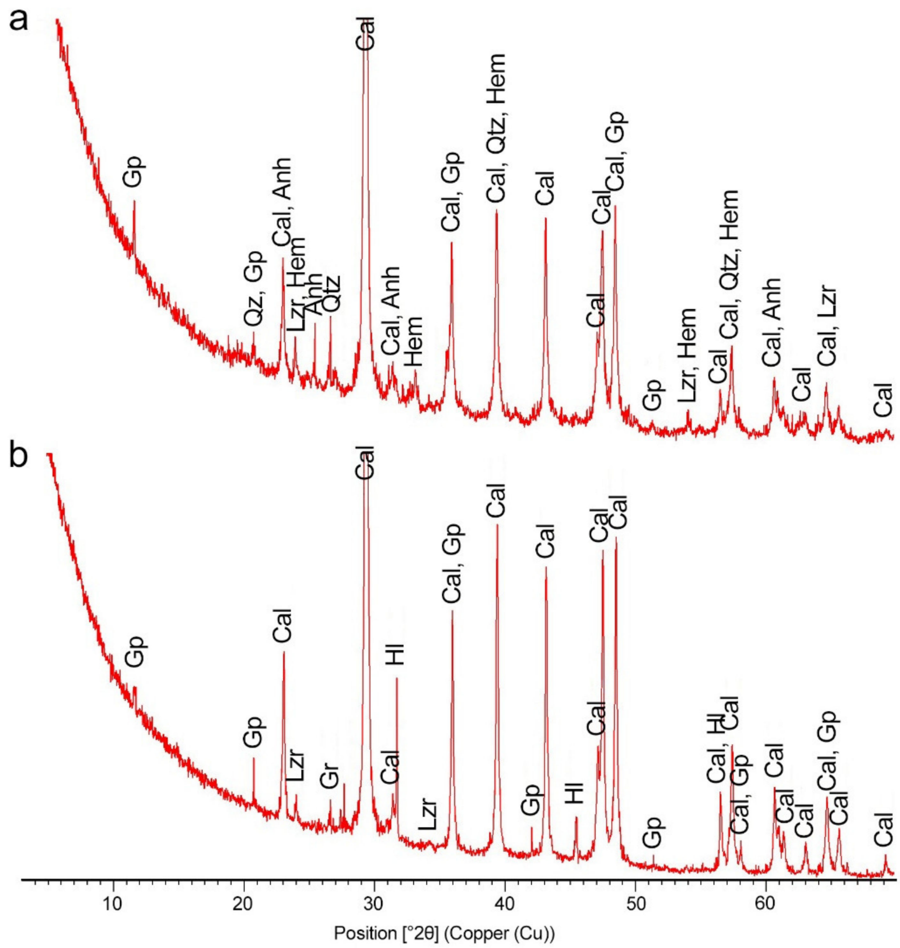

Figure 4. XRD spectrum of blue (**a**) and greenish-blue (**b**) colour. Cal: calcite; Gp: gypsum; Qtz: quartz; Hem: hematite; Lzr: lazurite; Ahn: anhydrite; Hl: halite.

The EDS spectrum of the blue layer (Figure 5) indicated the presence of Si, Al, Na, S, Ca, K, Mg, and Cl confirming the calcic binder and, according to the XRD pattern of lazurite, revealing the use of ultramarine blue ($Na_{8\text{-}10}$ Al_6 $Si_6O_{24}S_{2\text{-}4}$) [17,21–23].

In some painting layers, a limited amount of yellow pigment was added to the ultramarine. In this case, the EDS spectrum showed Ca, Fe, Si, Al, Mg, and K lines, proving the presence of silicoaluminates and iron oxides generally ascribable to the yellow ochre [15,19,20].

The greenish-blue painting layer did not show significant features under the microscope. In this case, the XRD spectrum (Figure 4b) showed calcite as the main phase and secondary gypsum and halite (NaCl). The first was related to the calcic binder, whereas the last referred to the salt crystals formed on the surface. Traces of lazurite were probably due to the ultramarine blue contribution by virtue of the high incoherence of the pictorial layers.

The compositional fingerprint of the greenish-blue layer obtained by EDS analysis highlighted the absence of elements, such as Co and Cu, typical of the well-known blue pigments. Some detected elements (Si, Al, Ca, Mg, K) could be ascribable to clay minerals and sulphides and chlorides crystallised on the painting surface.

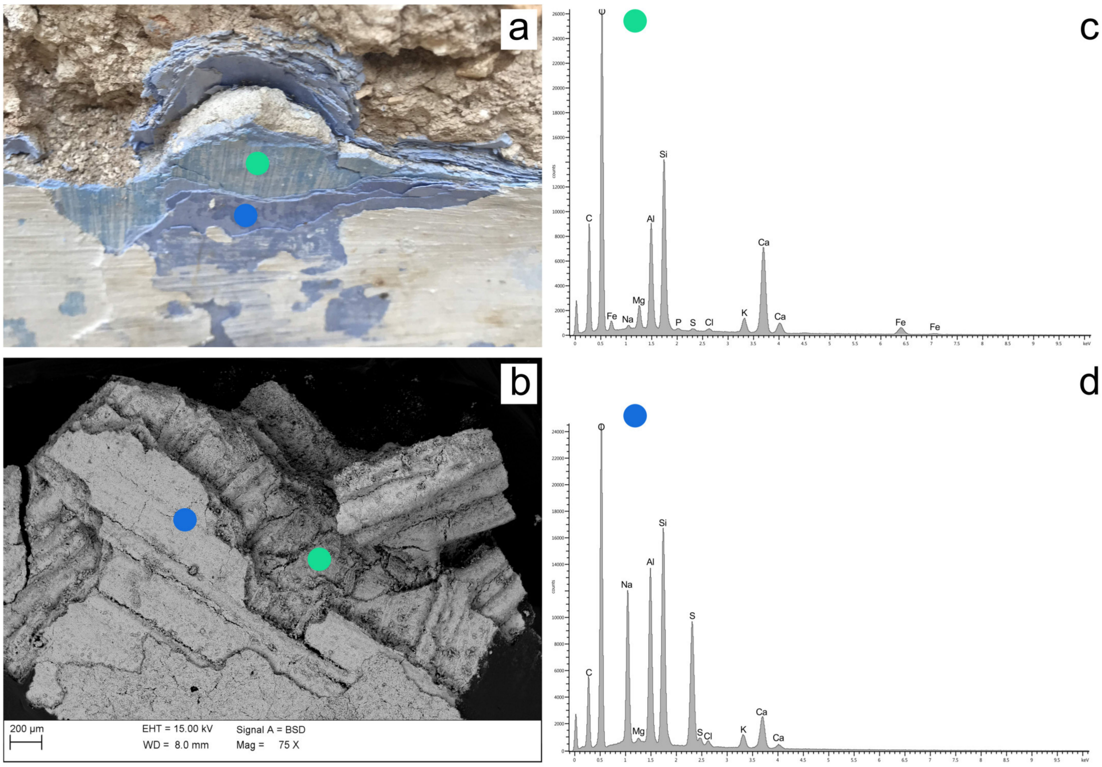

Figure 5. Sample before sampling (**a**), SEM-EDS (SE) photo (**b**), and EDS spectra of greenish-blue (**c**) and blue (**d**).

The brownish-red layers included a red pigment and rare particles of a black pigment (Figure 6). The mineralogical characterisation indicated the use of hematite (Figure 4a), confirmed by the EDS spectrum (Figure 6), which showed peaks of Fe, as the main element, and Si, Ca, Al, and Na, thus suggesting the presence of red ochre [15,19,20,24].

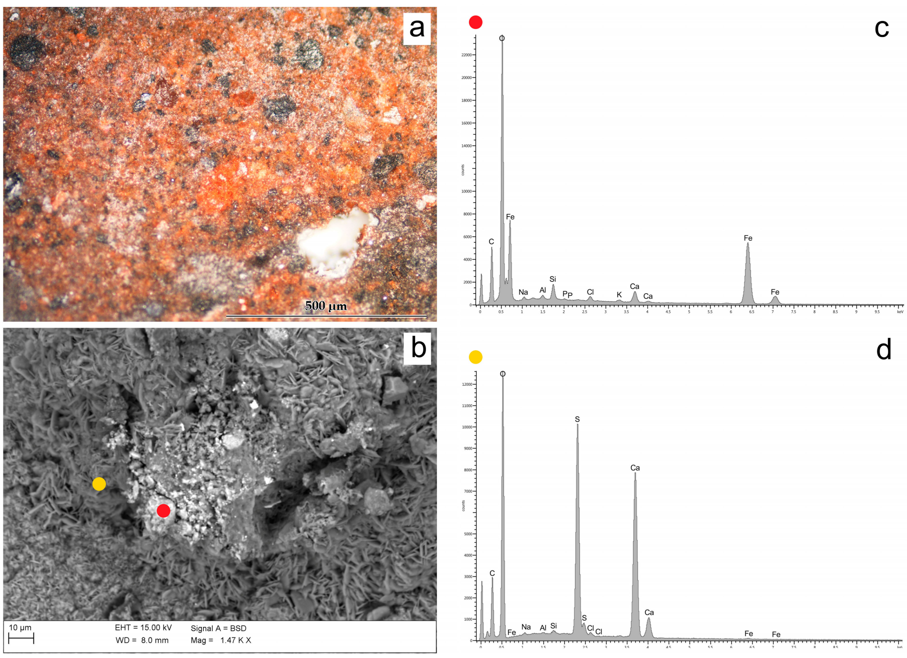

Figure 6. Photomicrograph of brownish-red layer (**a**), SEM-EDS (BS) photo (**b**), and EDS spectra of brownish-red pigment (**c**) and sulphates of salt deposit (**d**).

5. Discussion

The comparison of microscopic features, mineralogical patterns, and compositional data of coloured plasters of the historical buildings of Casamassima, made it possible to identify the pigments within. Generally, in the blue painting layers, the main pigment found was ultramarine blue. It was dispersed in lime in variable amounts to obtain different shades and brightness of blue. It is known that ultramarine blue is an artificial pigment introduced in the early 19th century (1828) and it is composed of lazurite [17,21]. The same mineral also constitutes the most precious lapis lazuli [21,25], known since ancient times and throughout the 17th century. The mineralogical and chemical analogy of ultramarine blue and lapis lazuli makes their distinction difficult. However, microscopic observation, above all by means of an optical microscope, allows us to identify in the Casamassima samples a blue pigment, regular in shape and equidimensional and micrometric in size [16–18]. Such an aspect would suggest its artificial production and then allow us to recognise the artificial ultramarine blue as a colouring pigment. The hypothesis of lapis lazuli can be completely removed, also because its use would have been excessively expensive to plaster large surfaces. Moreover, a similar application of artificial ultramarine blue was found in coloured plasters of Central European folk architecture dated to the 19th century [26].

Referring to the greenish-blue layer, the absence of mineralogical pattern and compositional fingerprint ascribable to the most used blue pigments, allowed us to consider the possibility of an organic dye, among which the common phthalocyanines blue. For its identification, a deeper investigation with other spectroscopic techniques, such as Raman or FORS, would be desirable.

Even the white layers contributed to reconstructing the historical setting, as the archaeometric results affirmed the presence of blanc fixe (litopone, barium sulphate), which was introduced only at the beginning of the 20th century [27].

Differently from the pigments of blue and white layers, the brownish-red layers were composed of red ochre, widespread in all historical periods and used in wall painting from antiquity to date [24].

The presence of a single layer of greenish-blue as well as of a layer of brownish-red, common to all the samples would suggest that in a specific historical moment the facades of the two buildings considered and presumably of the entire historical centre were plastered with a different colour. The reason for this choice is unknown, and probably of little importance, since it is limited in time, and the immediately following layers are once again made with ultramarine blue.

The identification of the artificial ultramarine blue and the blanc fixe even in the most ancient pictorial layers, allowed to date the realisation of the plasters in a period between the beginning of the 20th century, when the blanc fixe was introduced for the first time, and 1976, when the painter Viviani painted the blue old town of Casamassima [1]. This evidence would rebut the historical hypotheses that would connect the phenomenon of the blue plasters of Casamassima to the plague of 1655 or, worse, to a Byzantine custom [3].

Moreover, the presence of a single layer of greenish-blue as well as of a layer of brownish-red, in all the samples would suggest that on a specific date the facades of the two considered buildings, and seemingly of the entire historical centre, were plastered with a different colour. The reason for this choice is unknown, and probably poorly important since it is limited in time.

The stratigraphy observed under the optical microscope highlighted the presence of numerous (at most 30) blue pictorial layers, however, it is not certain that each layer was created at a different time. It is probable that two or more layers of paint were applied at the same moment, to intensify the final chromatic effect. From stratigraphic observations, it emerged that some groups of layers show very adherent contact surfaces and very similar pigment/binder ratios, sufficient reason to confirm their almost contemporary execution and application. In addition, the presence of salt deposits, mainly chlorides and sulphates due to capillary rising damp and saline precipitation phenomena frequent in urban environments, between groups of layers would confirm this belief.

Unfortunately, the lack of historical data on coloured plasters of the historical buildings of Casamassima makes it difficult to understand in depth the blue plaster phenomenon and the reason why in a specific unknown historical time different colours (greenish-blue and brownish-red) were used, nor the historical reasons for the exclusive use of ultramarine blue. Moreover, Nevertheless, the archaeometric research allowed us to identify the painting materials and then add a piece for the historical reconstruction of this architectural painting practice.

6. Conclusions

The archaeometric investigation carried out on the blue plasters of Casamassima made it possible to identify the pigments used for the realisation of the pictorial layers. This identification was essential in contributing to the historical reconstruction of the blue plaster phenomenon in the historic centre. Experimental results revealed a rather recent (20th century) use of the blue paintings, opposing the historical hypothesis.

Moreover, although the use of ultramarine blue, and in general of blue pigments or dyes in the local artistic tradition is frequent, this case seems to be an isolated occurrence, as no other towns in the region have seen a similar trend.

Finally, this study has highlighted that archaeometric investigations of the raw materials used in the pictorial layers, in this case, chemical, mineralogical, and microstratigraphic analyses, are essential to obtain significant information for the historical dating of artistic sites. The challenge for the future is that archaeometry and art history or archaeology specialists establish an increasingly dense and profitable dialogue for the knowledge, and therefore for the protection, of the cultural heritage.

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