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Microscopic Analysis of Wall Painting Techniques: Laboratory Replicas and Romanesque Case Studies in Southern Switzerland

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ABSTRACT
The identification of painting techniques is an important aspect of any research related to historical, artistic, and conservation issues in the field of wall paintings conservation. There are a variety of different methodological approaches that can be used to identify wall painting techniques. In this study, the application of optical (PLM) and electron (SEM-EDX) microscopy was explored as they are complementary analytical techniques commonly used for micro-stratigraphic analysis of painted surfaces. Five replicas were prepared according to the technical procedures reported in medieval historical treatises, and the pigment was applied at different time intervals in order to monitor the modifications at the interface between the ground and pictorial layer. The comparison of data from the replicas with samples from Romanesque wall paintings in churches in Southern Switzerland and Northern Lombardy (Italy) allowed for an evaluation of the reliability of the proposed methodology and for the interpretation of the painting techniques.

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KEYWORDS
Painting techniques; pictorial layer; microscopy; Tessin Canton; Northern Lombardy; Romanesque wall paintings

Introduction and aim of the research

The identification of wall painting techniques is an essential task involving the study of the esthetic, formal, stylistic, and material aspects of the work of art. This includes the composition of the pigments and the binders, the method of their application, and the modality used to execute the artwork. In addition, the modifications induced by natural processes may substantially change the physical–chemical characteristics of the original materials and their stability over the centuries in such a way that the understanding of the painted surface can be rather difficult. The ability to properly consider all these aspects requires specific expertise, adequate archival and historic research, accurate visual examination of the painted surfaces using various light sources such as visible (Vis), infrared (IR), and ultraviolet (UV), and the use of analytical methods that are as much as possible non-invasive. Therefore, the understanding of the painting technique is a process where many professionals are involved and where the use of micro-invasive techniques requiring micro-sampling is only the final step (Plesters 1956; Ajo et al. 2004,; Mugnaini et al. 2006).

The terminology concerning painting techniques is often not well-defined and leads to misunderstandings. The term, *a fresco* means 'executed on a wet plaster' (Mora, Mora, and Philippot 2001), where pigments are dispersed in water and applied on a wet ground layer. This is the *pure fresco* technique mentioned by Cennini (2008). The carbonation process involves the development of a matrix that englobes the pigment grains, guaranteeing the complete adhesion of the pigment with the plaster. If the pigments are not mixed with pure water, but with lime water or diluted slaked lime instead, the painting technique is called *lime fresco*. The *a secco* techniques are defined as, 'all forms of painting made on a dry plaster or lime wash layer' (Mora, Mora, and Philippot 2001), where the pigments are mixed with organic and/or inorganic binders and then applied on the dry ground layer. This results in a thin pictorial layer adhered to the plaster layer below.

The main criteria for distinguishing between *a fresco* and *a secco* painting techniques on a microscopic scale are based on the appearance of the interface where the ground and the paint layer meet. A continuity between these layers suggests the use of the *a fresco* technique, whilst the presence of a clearly distinguishable break between the ground and the first paint layer suggests the use of the *a secco* technique. Published studies have shown that optical (reflected Vis and UV light; Lanterna et al. 2003) and scanning electron microscopy coupled with an energy-dispersive X-ray spectrometry (SEM-EDX) have already been used in distinguishing between *a fresco* and *a secco* painting techniques (Cornale et al. 2008) and *a fresco* and lime painting based on these criteria (Piovesan et al. 2012).

According to the authors' previous research (Cavallo and Biondelli 2013), the development of a 2–3 μm thick

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calcium carbonate-rich layer at the interface of the ground and paint layer was also observed in a few replica samples prepared when the pigment was used *a fresco* (these replicas were prepared for another issue as reported in Cavallo and Gianoli Barioni 2015). This evidence suggested that the presence of a calcium carbonate-rich interface, in some cases, cannot be the definitive criteria for identifying the use of the *a secco* technique as reported in Piovesan et al. (2012); whereas a continuity between the ground and paint layer is a reliable method to use in identifying the *a fresco* technique.

To understand the problem in greater detail, replicas of wall paintings were prepared controlling some variables (see the experimental session) and according to the indications reported in medieval historical treatises, aware of the complexity of the painting technique in a real case study but also of the fact that the interpretation of the analytical results is supported by other issues related to the direct inspection of the surface (when possible), the knowledge of the artistic painting technique in the region and in that particular period, and the properties of the materials used (compatibility, permanence, hiding power, and stability). Results obtained from this model (replicas) were used as a basis for the interpretation of the painting technique of samples collected from several Romanesque wall paintings in Tessin Canton (Switzerland) through microscopic techniques (PLM and SEM-EDX). The Romanesque period was chosen for three main reasons: first, it is well documented in Tessin Canton and Northern Lombardy (Italy); second, because wall paintings from this period often do not exhibit the characteristic features of the *a fresco* painting technique, such as incisions, *giornate* (corresponding to areas of plaster applied and painted within a working day), *pontate* (corresponding to the plaster applied over areas in relation to the scaffolding), and preliminary drawings; and third, the fact that Romanesque wall paintings were often partially covered with later paintings that makes the description of the painting technique through visual examination rather difficult.

The following objectives were defined to guide the research:

(1) make a careful assessment of the microscopic characteristics of micro-stratigraphy from *a fresco* and *a secco* painting techniques executed in the atelier;
(2) assess when the ground layer becomes dry by monitoring the time span of application of the paint layer;
(3) assess if the presence or absence of the calcium carbonate-rich interface separating the ground from the paint layer is really a distinctive characteristic of the painting technique; and
(4) understand the role of the thickness of the paint layer in terms of interpretation of the paint technique.

Romanesque painting technique: historical treatises

In order to construct a historical and artistic context for the study, two of the most important historical treatises from this period were consulted, *Theophilus* (Teofilo 2000) and the *Mappae Clavicula* (Smith and Hawthorne 1974). In addition, several other historical sources were also consulted, including *Heraclius* (Richards 1940), *Archerius* (Merrifield 2011), *Plinius* (Conte 2003), Cennini (2008), Vasari (1986) and Vitruvio (2006).

These sources suggest that the wall to be painted requires a preparation with two or three layers of lime-based plaster, with each subsequently applied layer having decreasing thickness.

The first layer, called *arriccio,* consists of a lime-based plaster created by mixing one part of lime with three parts of river sand (Vitruvio 2006; Cennini 2008), applied several centimeters thick on the masonry by *pontate* (Tsuji 1983; Vitruvio 2006). Visual observations confirmed the presence of *pontate* in important Romanesque paintings in Northern Lombardy (Churches of *San Pietro al Monte* in Civate, tenth century; *San Pietro* in Agliate; and *San Vincenzo di Galliano* in Cantù, eleventh century) (Zastrow 1982). The second layer, called *intonaco* consists of a lime-based plaster created by mixing one part of lime with two parts of river sand, applied over the *arriccio.* This is shown in eleventh-century archaeological Romanesque fragments found in the Church of *San Giovanni Battista* in Cevio, Tessin Canton (Cavallo et al. 2012). It is common to find a third layer called *intonachino,* which is few millimeters thick applied over the *intonaco,* having a compact and smooth surface.

Preparatory drawing is part of the Romanesque painting technique; the outline and the basic geometric shapes were usually sketched on the wet *intonachino* with red, yellow, or brown earths suspended in water (Swoboda 1993; Mugnaini et al. 2006).

Considering the extension of the *pontate* and according to the literature (Teofilo 2000) Romanesque painting is a composite technique (Swoboda 1993; Teofilo 2000; Mora, Mora, and Philippot 2001). In fact, the surface is painted *a fresco* mixing pigments with pure water (*buon fresco* technique) or with slaked lime. After several hours or days, the painting can be completed using the *a secco* technique. Details are added mixing slaked lime with pigments applied on a previously moistened *intonachino* (Teofilo 2000; Mora, Mora, and Philippot 2001; Merrifield 2003). Pigments that are unstable with lime alkalinity can be mixed with organic binders (Richards 1940; Mugnaini

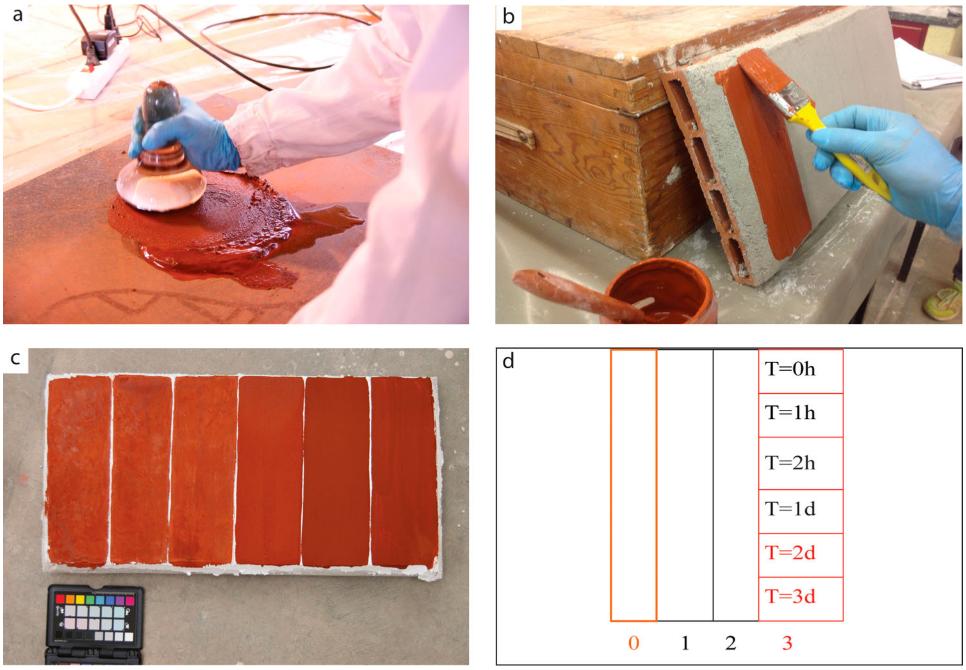

Figure 1. Execution of the replicas. (a) pigment preparation; (b) execution of the painting; (c) final appearance of the six sectors; and (d) scheme of the time of application of the individual painted sectors.

et al. 2006). Paintings can also be executed *a fresco* over a slaked-lime layer applied on the carbonated *intonachino* (Tsuji 1983); it is possible that this technique comes from the Roman period as the analyses in Etruscan tombs in Tarquinia (Cecchini and Adamo 2005) and eleventh-century paintings in the Santa Maria Antiqua church in Rome suggest (Bensi 1990). In Romanesque painting, the flesh tones were painted first and then the clothing was painted (Tosatti 2007). *Theophilus* (Teofilo 2000) suggests painting the background first *a fresco* by mixing red and/or yellow earth and cinnabar with lime, and then to define the volume or shapes *a secco* with *posc*, probably a green earth (Teofilo 2000; Mora, Mora, and Philippot 2001).

To paint the garments, *Theophilus* (Teofilo 2000) recommends the application of a base tone consisting of earth dispersed in lime on a wet *intonachino* and then to define the forms with white clay and *prasinus*, probably a mixture of green and black earths, or perhaps *verdaccio* (Tosatti 2007). Most of the examined Romanesque paintings seem to correspond to Cennini's indications (Cennini 2008) that explain how to model the garments starting from a base of *verdaccio* applied *a fresco*, then alternating geometric folds with three shades of one color obtained by adding different amounts of *Bianco di San Giovanni* often used to define the light tones as well.

Materials and methods

Replica preparation

A set of five replicas was prepared (Figure 1) according to the indications reported in the medieval treatises with particular emphasis on those found in *Mappae Clavicula* (Smith and Hawthorne 1974), Cennini (2008), and *Vitruvio* (by Barbaro 2006). In addition, the preparation of the replicas was executed taking into account several aspects trying to create a model that could match as far as possible with the characteristics of the wall painting in a real case, aware of the limitations that a model includes. For these reasons, the application of the color was done on large areas and the support was held vertical for simulating a real wall; this is very important in order to guarantee an adequate workability of the painting surface and for the right application of the pigment. The execution of the replicas was carried out monitoring the environmental variables (T°C and RH %) that influence the carbonation time of the plaster.

Replicas were executed with a 10 mm thick *arriccio* and 5 mm thick *intonaco*; the support consisted of a small lightweight brick ($3 \times 25 \times 50$ cm) that was first soaked in water. Details of the proportion of lime to aggregate used in the mortars are reported in Table 1. Ground plasters were prepared using mortars with binder/aggregate proportion close to those reported in the treatises but with slight modification in order to obtain a workable mix.

Red earth composed of kaolinite, hematite (and anatase; Cavallo and Zorzin 2014) was selected as a pigment. This choice was due to the fact that red earth was commonly used (as were other earth pigments) during the Medieval Age both *a fresco* and *a secco*. The pigment was prepared from the raw material through dry and wet grinding and final smoothing (Thompson 2007).

Table 1. Composition of the plaster used for the replicas.

	Binder (B)	Aggregate (A)	B/A Ratio
Arriccio	½ part calcitic lime putty ½ part dolomitic lime putty Dolomitic water lime qb	2 part of siliceous sands (grain size 0–2 mm) 1 part of siliceous sands (grain size 0–4 mm)	1:3 by weight
Intonaco	½ part calcitic lime putty ½ part dolomitic lime putty Dolomitic water lime qb	2 part of siliceous sands (grain size 0–2 mm)	1:2 by weight

Table 2. Composition of the replicas.

Replica ID	Binder of the painted layer	Painting technique
02CM-LC	Dolomitic wash lime	*A secco*: after 6 months
02CM-GC	Dolomitic slaked lime	
05CM	Dolomitic slaked lime	*A fresco:* $t = 0$; $t = 1$ h; $t = 2$ h; $t = 1$day; ($t = 2$ days; $t = 3$ days)
06CM	Pure water	
07CM	Dolomitic lime water	
08CM	Pure water	
10CM	Dolomitic slaked lime	

A two-year aged dolomitic lime putty obtained after calcination of a dolostone coming from Rossana quarries (Cuneo, Italy) was used for the *arriccio* and *intonaco* preparation because it was widely used in Tessin Canton (Cavallo et al. 2012) and Northern Lombardy (Fieni 2000); it was mixed with siliceous sand (0–4 mm). The preparation of the replicas was carried out during the summer in an atelier where the following thermo-hygrometric conditions were registered: $T = 17–23$ °C and RH = 35–55%.

The paint layer was applied using red earth dispersed in three binders: pure water (replicas ID 06CM and 08CM), dolomitic lime water (replica ID 07CM) and dolomitic slaked lime (replicas ID 05CM and 10CM) as reported in Table 2.

Each replica consisted of six test surfaces corresponding to the time span between the first color application when the plaster was still wet ($t = 0$ h) and the last color application ($t = 3$ days) as reported in Table 2. Hence, the first application corresponds to the *a fresco* technique in which the pigment was applied approximately 15 minutes after the application of the *intonaco*. After this time the plaster was still wet but sufficiently dry to be painted. The remaining applications were used to monitor when the plaster became dry. Five *a secco* replicas were prepared with pigment and dolomitic slaked lime, applied after six months of natural ageing of the ground (Table 2).

Historical samples

Six samples were selected from medieval wall paintings executed in the period between the eleventh and fourteenth centuries. A description of these samples is reported in Table 3. Several samples (samples 1, 2, and 3) come from archaeological excavations and were considered to be ideal for this research because they have not been affected by later restoration work. In order to make a direct comparison with the experimental replicas, samples were selected from pictorial layers where iron-based earth or iron oxides were used. The six samples collected from the wall paintings and those from the experimental replicas (32 samples) were first observed and documented with a Leitz Wild M420 stereomicroscope and then embedded in epoxy resin. Polished cross sections were examined in reflected light using a Leitz Ortholux microscope with a Ultrapack illuminator and a digital image capture system. A Zeiss Axioskop40 polarizing light microscope (PLM) combined with a digital camera for image capture and processing was used for polished thin section analysis. A JEOL 5910 LV scanning electron microscope equipped with an EDS 2000 X-ray spectrometer system was used to capture BSE images, create X-ray maps, and perform chemical elemental micro-analysis on carbon-coated samples. The investigation was performed using the following instrumental set-up: 20 KeV, Spot size 42, HV, 100 sec counts for analysis, and standard conditions for X-ray maps

Table 3. Samples from Romanesque wall paintings.

Samples ID	Type	Provenance	Notes
1	Cross section	Archaeological fragment, eleventh-century San Giovanni Battista church, Cevio	On the fragment are partially visible two faces
2	Thin section	Archaeological fragment, eleventh-century Sant'Ambrogio church, Cademario	On the fragment are visible traces of a red paint layer
3	Cross section	Archaeological fragment, fourteenth-century Sant'Ambrogio church, Cademario	On the fragment are visible traces of a green paint layer
4	Thin section	Wall painting, end of twelfth-century San Carlo church, Negrentino	The sample was taken from a red frame
5	Cross section	Wall painting, eleventh-century San Lorenzo Cathedral, Lugano	The sample was taken from a red frame
6	Cross section	Wall painting, end of twelfth-century San Nazario church, Dino	The sample was taken from a red drawing up

Table 4. Replica samples: chemical and morphological features.

Replica ID	Ca-rich interface ground/painted layer: BSE image	Ca-rich interface ground/painted layer: CaKα X-ray map	Ca-rich veil on the painted layer CaKα X-ray map	Penetration of the pigment into the plaster PLM and X-ray maps
***A fresco* application**				
Pictorial binder: dolomitic slaked lime				
05CM_0 h	NO	NO	NO	NO
05CM_1 h	NO	NO	YES	NO
05CM_2 h	YES	YES	NO	NO
05CM_1 d	YES	YES	NO	NO
10CM_0 h	NO	NO	YES	YES
10CM_1 h	NO	NO	YES	YES
10CM_2 h	YES	YES	YES	NO
10CM_1 d	YES	YES	NO	NO
Pictorial binder: pure water				
06CM_0 h	NO	NO	YES	NO
06CM_1 h	NO	NO	YES	YES
06CM_2 h	YES	YES	YES	NO
06CM_1 d	YES	YES	NO	NO
08CM_0 h	NO	NO	YES	YES
08CM_1 h	YES	YES	YES	NO
08CM_2 h	YES	YES	YES	NO
08CM_1 d	YES	YES	NO	NO
Pictorial binder: dolomitic lime water				
07CM_0 h	NO	NO	YES	NO
07CM_1 h	NO	NO	YES	NO
07CM_2 h	YES	YES	NO	NO
07CM_1 d	YES	YES	YES	NO
A secco application				
02CM_LC	YES	YES	NO	NO
02CM_GC	YES	YES	NO	NO

acquisition. The scientific section was carried out one year after the preparation of the replicas.

Results

Replicas

Table 4 reports the results obtained from PLM and SEM-EDX analysis with particular emphasis on noting the presence or absence of a calcium carbonate-rich interface layer, the calcium carbonate-rich veil on the painted layer, and the penetration of the pigment into the plaster; these are considered basic criteria for distinguishing *a fresco* and *a secco* replicas.

Results from the replicas made at application time two days and three days are not reported in Table 4 as they have the same characteristics of replicas executed at $t = 1$day. PLM and SEM-EDX observations of samples from the replicas reveal that the average thickness of the pictorial layers is around 100 μm for *a fresco* applications with water and lime water, between 100 μm and 300 μm with slaked lime, and up to 400 μm for *a secco* replicas.

All the samples executed using *a fresco* technique at $t = 0$ h (Figure 2) and $t = 1$ h do not show any interface between the paint layer and the *intonaco*; the sequence is characterized by a perfect continuity between the *intonaco* and pictorial layer while a thin calcium carbonate-rich layer is evident in the upper part of the pictorial layers as clearly visible in the CaKα X-ray maps (Table 4). However, replica 08CM at $t = 1$ h exhibits the presence of the interface between the ground and the paint layer (Table 4) indicating, in this specific case where the painting technique is known, the initial drying of the plaster (*intonaco stanco*). The absence of a calcium carbonate-rich interface and the presence of the thin layer on the painted surface were detected in all *a fresco* replicas where the pigment was dispersed with pure water, lime water, or dolomitic slaked lime. On the other hand, the amount of calcium and magnesium in the paint layers is negligible (see also elemental micro-analysis). After two hours (Figure 3), all the samples show a 2–3 μm thick calcium carbonate-rich and dense interface separating the ground and the paint layer indicating the complete drying of the *intonaco*. Unlike the previous *a fresco* samples, there is no evidence of the superficial calcium-rich layer with the exception of three samples (06CMt=2 h, 08CMt=1 h, where the pigment was applied with pure water, and 07CMt=1day where the pigment was applied with lime water; Table 4). The presence of the interface is clearly visible in all the replicas where the pigment was applied after the *intonaco* had set for at least two hours (Figure 3); this behavior is not dependent on the binder used for the pigment (Table 4).

Samples corresponding to *a secco* technique replicas (02CM-LC, 02CM-GC; Table 2) where the pigment was mixed with dolomitic putty or slaked lime and applied on a dry *intonaco* after six months (Figure 3), reveal similar morphological characteristics to those of the *a fresco* replicas where the pigment was applied at a time $t \geq 2$ h (Table 4). The presence of calcium carbonate enrichment at the interface between the two layers, and the absence of calcium carbonate enrichment on the surface of the pictorial layer was clearly detected in these samples.

Another interesting characteristic is that all *a fresco* applications do not exhibit any penetration of the pigment into the plaster regardless of the binding medium (pure water, lime water, and slaked lime). However, FeKα X-ray maps (samples 06CM $t = 1$ h; 08CM $t = 0$ h; 10CM $t = 0$ h; 10CM $t = 1$ h) show a slight migration of the pigment into the plaster.

Historical samples

Most of the examined historical samples show a ground layer made with dolomitic lime and siliceous sands (Table 5). They generally show (under PLM) one

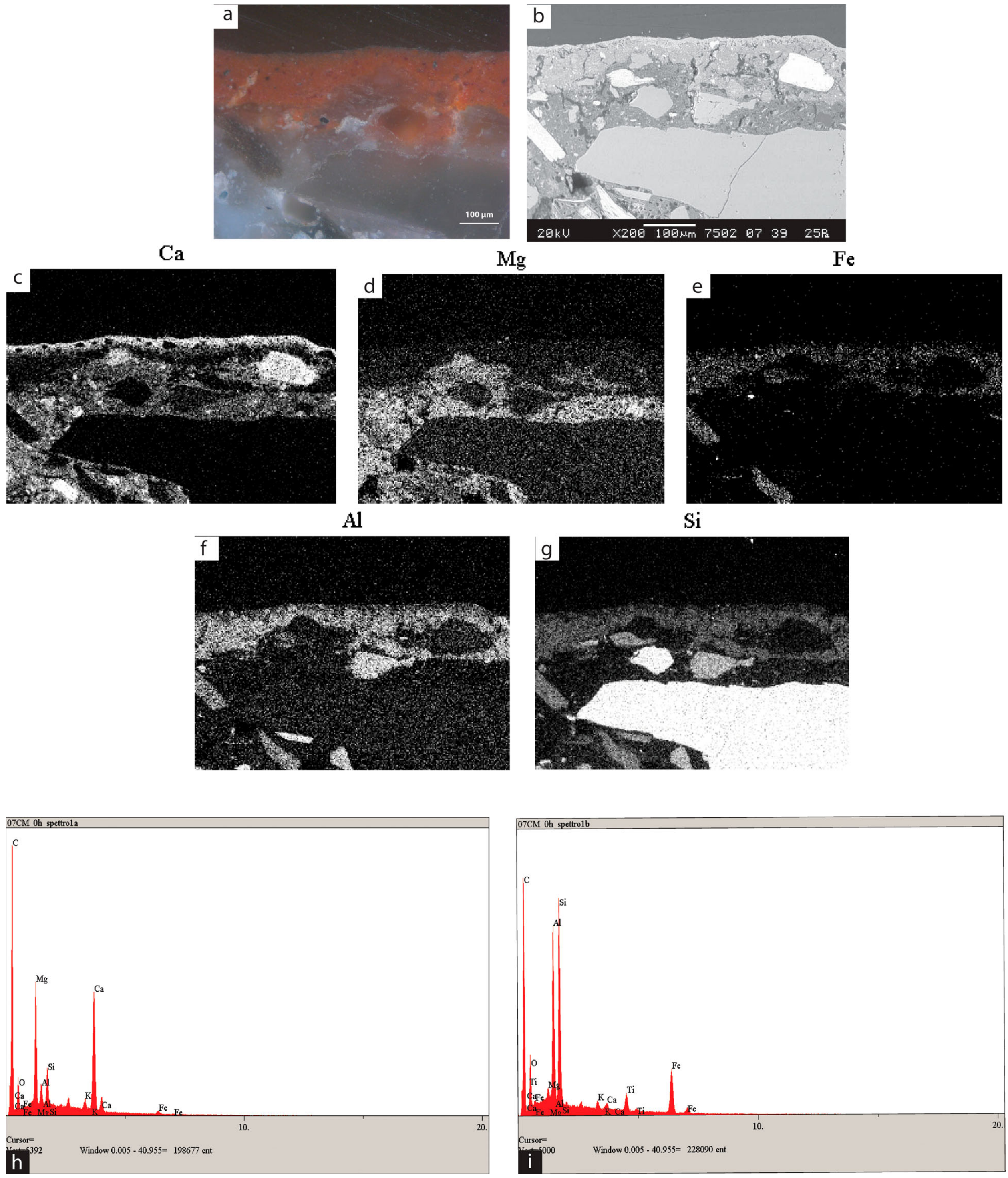

Figure 2. Optical and electron microscopy images, micro-analysis, and elemental X-ray mapping of replica sample 07CM at $t = 0$ h, where the pigment was mixed with dolomitic lime water: (a) PLM image of the sample; (b) BSE image of the sample, (c–g) X-ray maps. (h) micro-analysis of the *intonaco*'s binder in figure a (small area). (i) micro-analysis of the pictorial layer in figure a (small area). Optical and electron microscopy images, micro-analysis, and elemental X-ray mapping of replica sample 08CM at $t = 0$ h where the pigment was mixed with pure water: (l) PLM image of the sample; (m) BSE image of the sample; (n–r) X-ray maps.

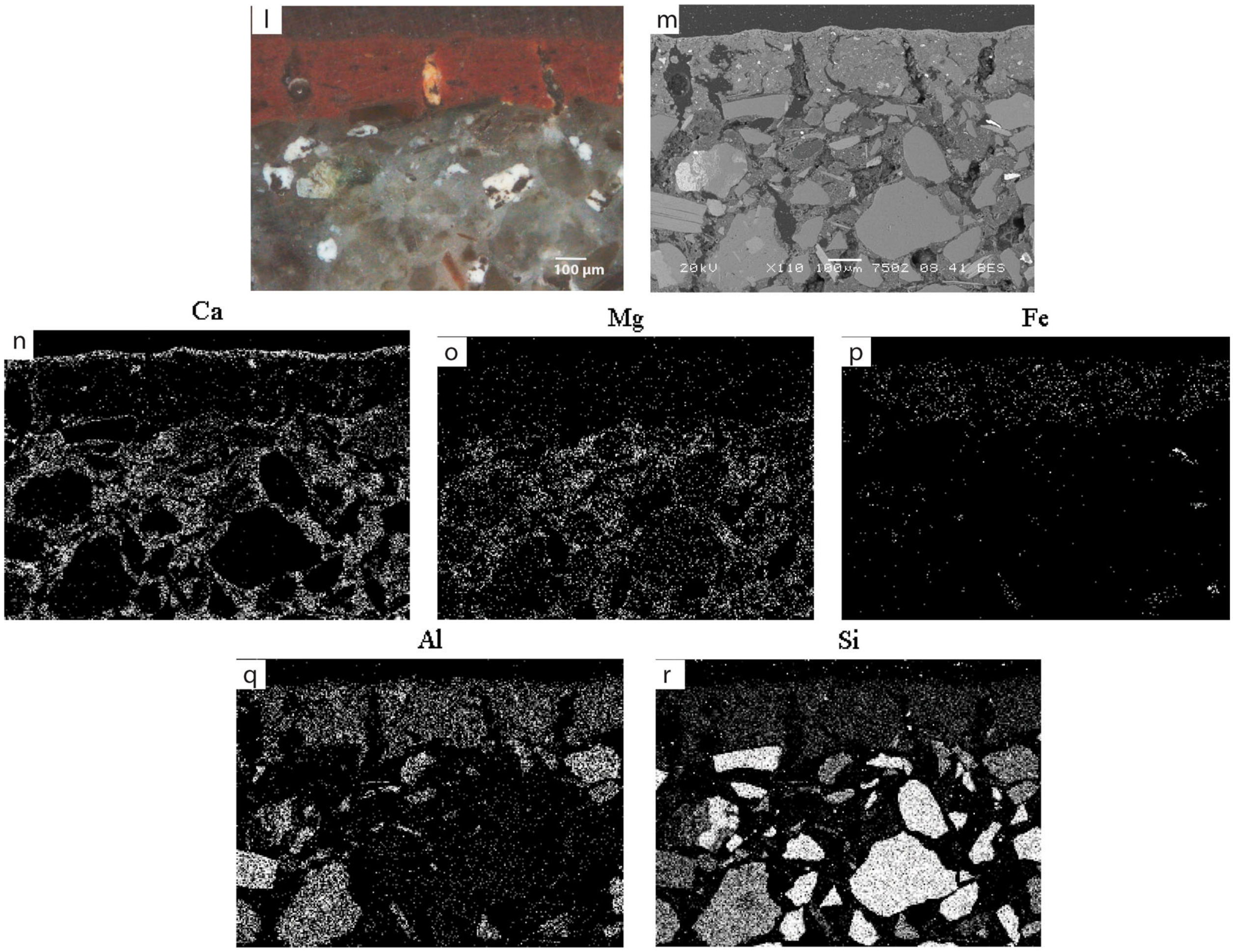

Figure 2. Continued.

red pictorial layer (samples 2, 4, 5, and 6) whose chemical composition (Table 5) indicates the use of iron oxides. In sample 6 mercury and sulfur were detected (Figure 4) suggesting the presence of cinnabar (HgS) mixed in a small amount with iron oxide pigments. The sample 1 shows a first red layer, a second yellow–orange layer, and a third green layer executed using iron-based pigments. Sample 3 shows two green layers composed of green earths (Table 5).

There are notable differences in terms of the thickness and morphology of the pictorial layers. The thickness (mean value) is around 100 µm for the application with red Fe-oxide pigment whilst the applications of green earth (samples 1 and 3) are less than 30 µm. According to the irregularity of the surface of the *intonaco*, thickness is not greater than 150 µm.

Samples 2, 4, and 6 show under the optical microscope an irregular contact between the plaster and the painting surface (Figures 5–7); for these samples the analysis of the BSE images show a continuity between the plaster and the paint layer. The absence of an interface also confirmed by the Ca distribution is clear evidence that the painting technique is a fresco.

In the remaining samples (no. 1, 3, and 5), the contact of the ground and the painted layer (first, for samples no. 1, 3) is rather sharp (Figures 8–10). BSE images do not show any evident interface (except for the sample 3) but Ca-Kα X-ray maps show Ca-carbonate enrichment. This behavior can be interpreted as the *a secco* technique or *a fresco* technique executed over an *intonaco stanco* indicating an early stage of the carbonation process.

Discussion

Many differences between *fresco* and *secco* paint were observed under PLM and SEM; these two instrumental techniques are complementary for understanding the painting technique. As a general rule, the identification of the Ca-rich interface between the support and the painting layer is well detected using BSE images and CaKα X-ray mapping; the same consideration is valid for the continuity between the ground layer and the first pictorial layer.

BSE images and X-ray maps show that all of the replicas executed at $t = 0$ h (pigment application after 15 min) and $t = 1$ h (pigment application after 1 h15 min) do not show any interface between the pictorial layer and the *intonaco* (except replica 08CM). In addition, a thin calcium carbonate-rich layer is evident on the painted surface attributable to the lime carbonation reaction (Beruto, Barberis, and

Botter 2005; Horgnies et al. 2015). These microscopic characteristics were detected in all of the replicas until $t = 2$ h (15 min) as reported in Table 4. After $t = 2$ hours and $t = 1$day, ($t = 2$days, $t = 3$days, and $t = 6$ months) the samples show a 2–3 µm thick calcium carbonate-rich and dense interface separating the *intonaco* from the paint layer.

The development of a dense calcium carbonate-rich layer in replica paintings occurred after four hours in other experimental research (Cornale et al. 2008; Piovesan et al. 2012). In the present study, it is demonstrated that the interface can be clearly detectable after about two hours; the difference in results is probably due to different environmental conditions (the mentioned articles do not report environmental values for a comparison) but also other variables can play an important role (Van Balen and Van Gemert 1994) including the exposure of the wall, the external climate and internal micro-climate, the typology and thickness of the masonry, the thickness of the plaster and the number of layers applied, the amount of water in the original lime putty and which was added in order to reach an adequate plasticity and workability, the proportion of lime to aggregates, and the nature of the air lime (calcitic or dolomitic). So, as reported by De Luca (2016) the drying time of the plaster is strongly variable.

The distinction between the *a fresco* and *a secco* technique in the replicas is rather satisfactory: the calcium carbonate-rich interface between the support and the pictorial layer is not evident in the case of the *a fresco* technique (until application time $t = 1$ h). After two hours, the presence of a calcium carbonate-rich layer indicates the beginning of the *intonaco* setting process (Beruto, Barberis, and Botter 2005). The presence of the enrichment in some cases cannot be a reliable criterion for the

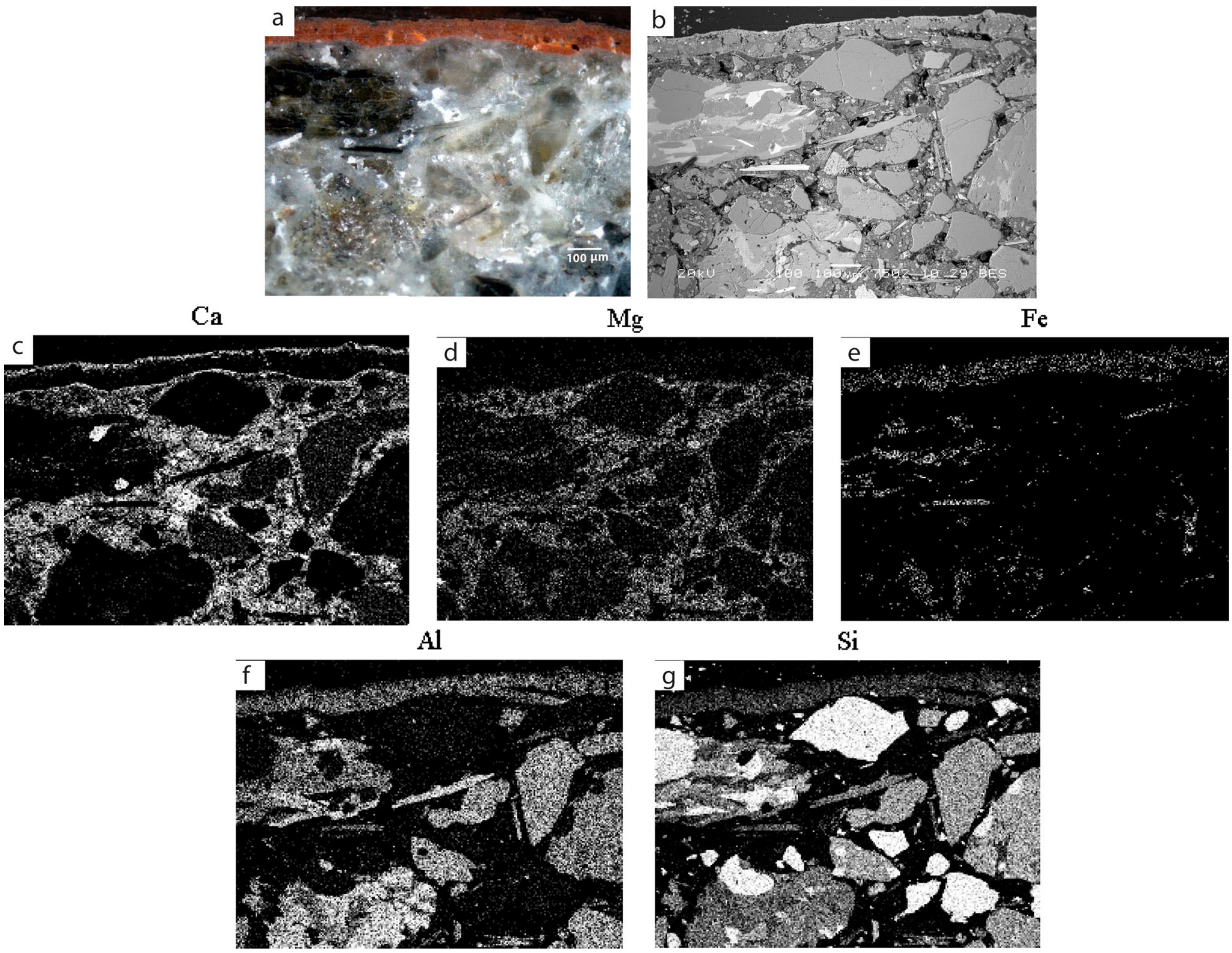

Figure 3. Optical and electron microscopy images, micro-analysis, and elemental X-ray mapping of replica sample 06CM at $t = 2$ h, where the pigment was applied with pure water: (a) PLM image of the sample; (b) BSE image of the sample; (c–g) X-ray maps. Optical and electron microscopy images, micro-analysis, and elemental X-ray mapping of replica sample 07CM at $t = 2$ h, where the pigment was applied with dolomitic lime water: (h) PLM image of the sample; (i) BSE image of the sample; (l–p) X-ray maps. Optical and electron microscopy images of the sample 05CM at $t = 2$ h, where the pigment was applied with dolomitic lime water: (q) PLM image of the sample; (r) BSE image of the sample. Optical and electron microscopy images of the sample 05CM at $t = 2$days, where the pigment was applied with dolomitic lime water: (s) PLM image of the sample; (t) BSE image of the sample; Optical and electron microscopy images of the sample 02 LC slaked lime, at $t = 6$months: (u) PLM image of the sample; (v) BSE image of the sample.

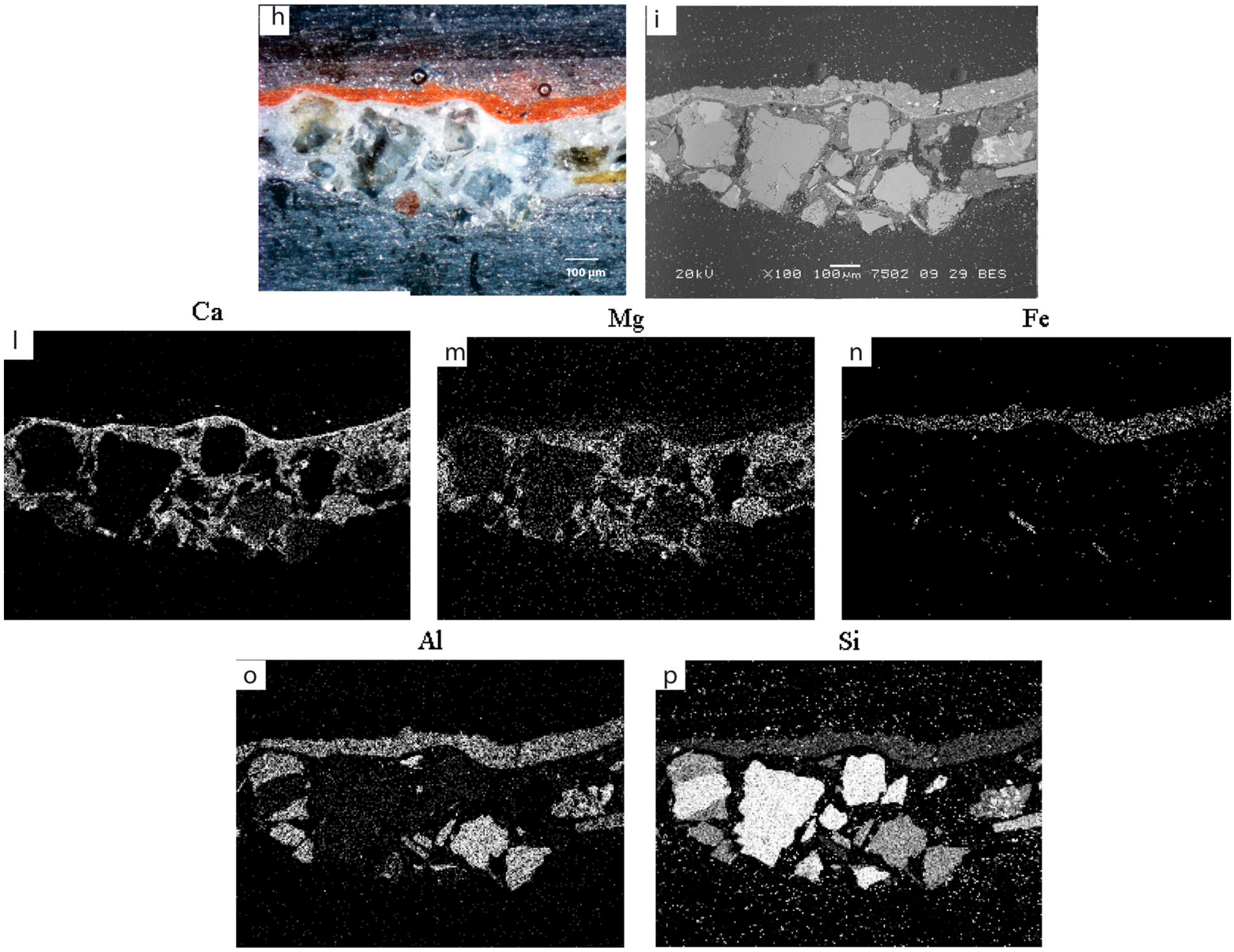

Figure 3. Continued.

a *secco* technique (Piovesan et al. 2012), because sometimes the dense calcium carbonate-rich interface is not clearly visible in all the samples, leading to a misinterpretation of the data (08CM $t = 1–2$ h in Table 4) where the drying process started earlier (*intonaco stanco*). This anomaly, already evidenced in our previous research (Cavallo and Biondelli 2013), indicates the possibility to execute *a fresco* paint when the plaster starts the setting process. It means that in the real cases (when the painting technique is unknown) the presence of the Ca-rich interface could be due to the *a secco* or *a fresco* technique when the plaster started the carbonation as observed in the real cases (samples 1, 3, and 5).

The thickness of the paint layer is not a valid criterion to use in the interpretation of the paint technique as it can be variable and dependent on numerous factors such as the type of binder, the pigment grain size, the painter's skill and wishes, and the period.

In the case of water and lime water as binder, the pigment layer thickness is in the range of 50–150 µm. *A secco* replicas made with slaked lime showed thickness around 400 µm whilst *a fresco* thickness was around 300 µm. The thickness does not depend on the application time. The higher uniformity in colour distribution and the opacity in the binder under PLM are probably due to the fine-grained fraction of particles dispersed in the red earth (Piovesan et al. 2012). The discrimination between the two techniques (pigment mixed with water and with lime water) is not possible.

Looking at the X-ray maps of all the *a fresco* experimental replicas (Figure 2), the relative amount of magnesium and calcium in the pictorial layers is related to the medium used: samples executed with pure or lime water display a relatively low amount of magnesium and calcium in respect to those made with slaked lime as binder. This aspect allows for the determination of the type of the binder employed (Ajo et al. 2004).

All of the *intonaco* of the Romanesque samples are composed of dolomitic lime and siliceous sands, in accordance with the composition of the traditional building mortars used in Tessin (Southern Switzerland; Cavallo and Biondelli 2012) and Lombardy (North-Western Italy; Fieni 2000). All of the pictorial layers are composed of natural yellow, red, and green iron-based pigments. Most of the pigments were mixed

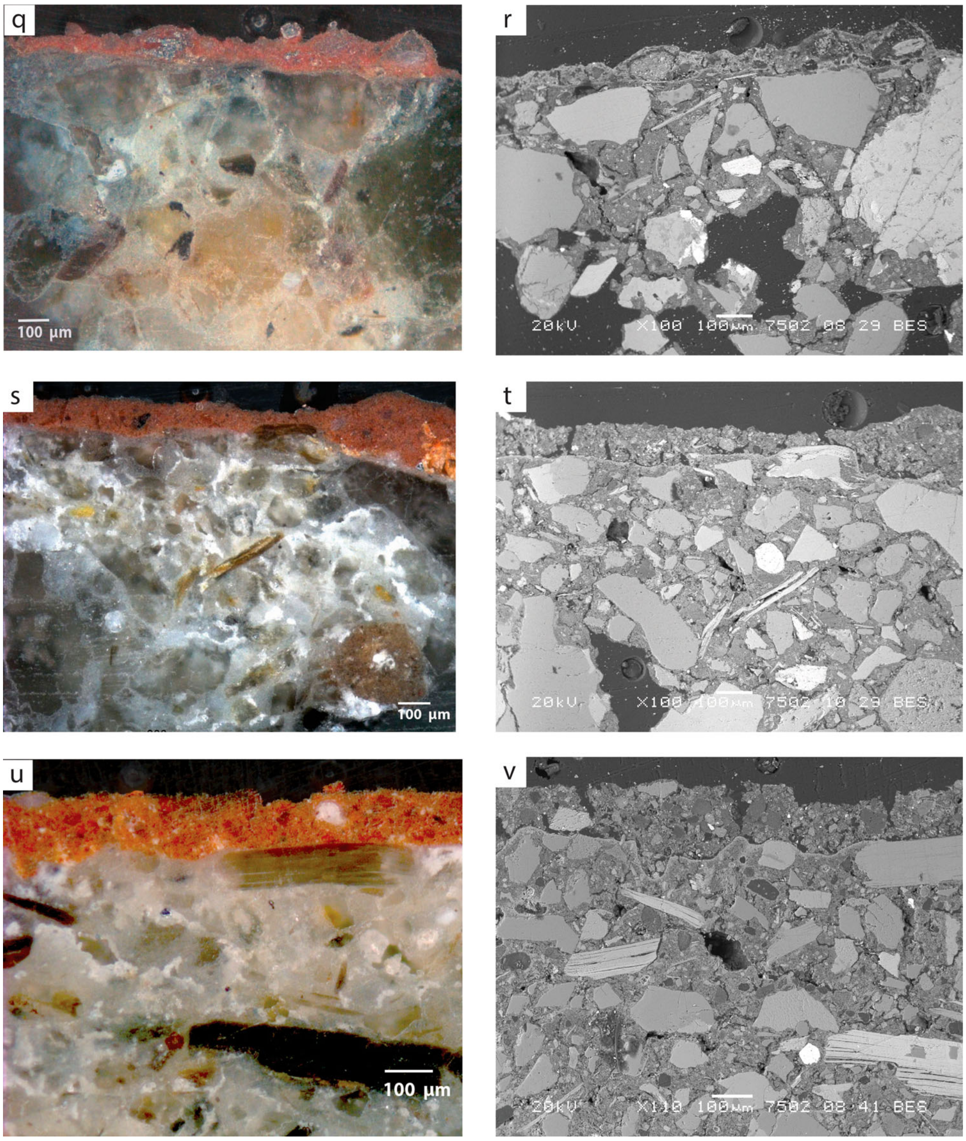

Figure 3. Continued.

Table 5. Romanesque wall paintings: chemical and morphological features with indication of the painting technique.

SEM-EDX analysis		Sample 1			Sample 2	Sample 3		Sample 4	Sample 5	Sample 6
Ground layer composition		Mg-lime Siliceous sands			Mg-lime Siliceous sands	Mg-lime Siliceous sands		Mg-lime Siliceous sands	Mg-lime Siliceous / carbonate sands	Mg-lime Siliceous / carbonate sands
Painting layer(s)		**1**	**2**	**3**	**1**	**1**	**2**	**1**	**1**	**1**
Painting layer(s) composition		**Fe** Ca $\underline{Mg}$	**Ca** Fe $\underline{Mg}$ $\underline{K}$ $\underline{Si}$ $\underline{Al}$	**Ca** Fe $\underline{Mg}$ $\underline{K}$ $\underline{Si}$	**Ca** Mg $\underline{Fe}$	**Ca** Si $\underline{Mg}$ $\underline{Fe}$ $\underline{Al}$ $\underline{K}$	**Ca** Si $\underline{Mg}$ $\underline{Fe}$ $\underline{Al}$ $\underline{K}$	**Fe** Ca $\underline{Mg}$	**Fe** Mg $\underline{Ca}$ $\underline{Si}$	**Ca** Mg $\underline{Fe}$ $\underline{S}$ $\underline{Hg}$
Thickness painting layer (µm)		20–40	50–150	10	20–50	50	30	80	50–100	100
Ca-rich interface ground and first painted layer	**BSE image**	YES	–	–	NO	YES	–	NO	NO	NO
	CaKα X-ray map	YES	–	–	NO	NO	–	NO	YES	NO
Ca-rich veil on the painted layer	**CaKα X-ray map**	?	–	–	NO	YES	–	NO	NO	NO
Painting technique		*A secco* or *a fresco* on *intonaco stanco*			*A* fresco	*A secco* or *a fresco* on *intonaco stanco*		*A* fresco	*A secco* or *a fresco* on *intonaco stanco*	*A* fresco

Note: **Z** principal chemical element Z subordinate $\underline{Z}$ accessory.

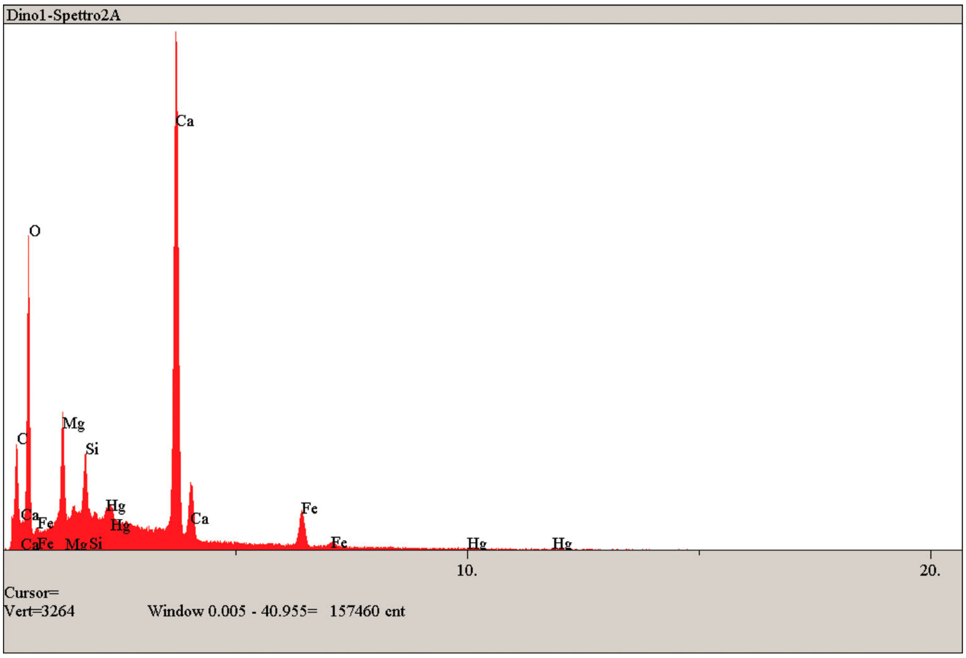

Figure 4. Sample 6: micro-analysis of the red pictorial layer (small area).

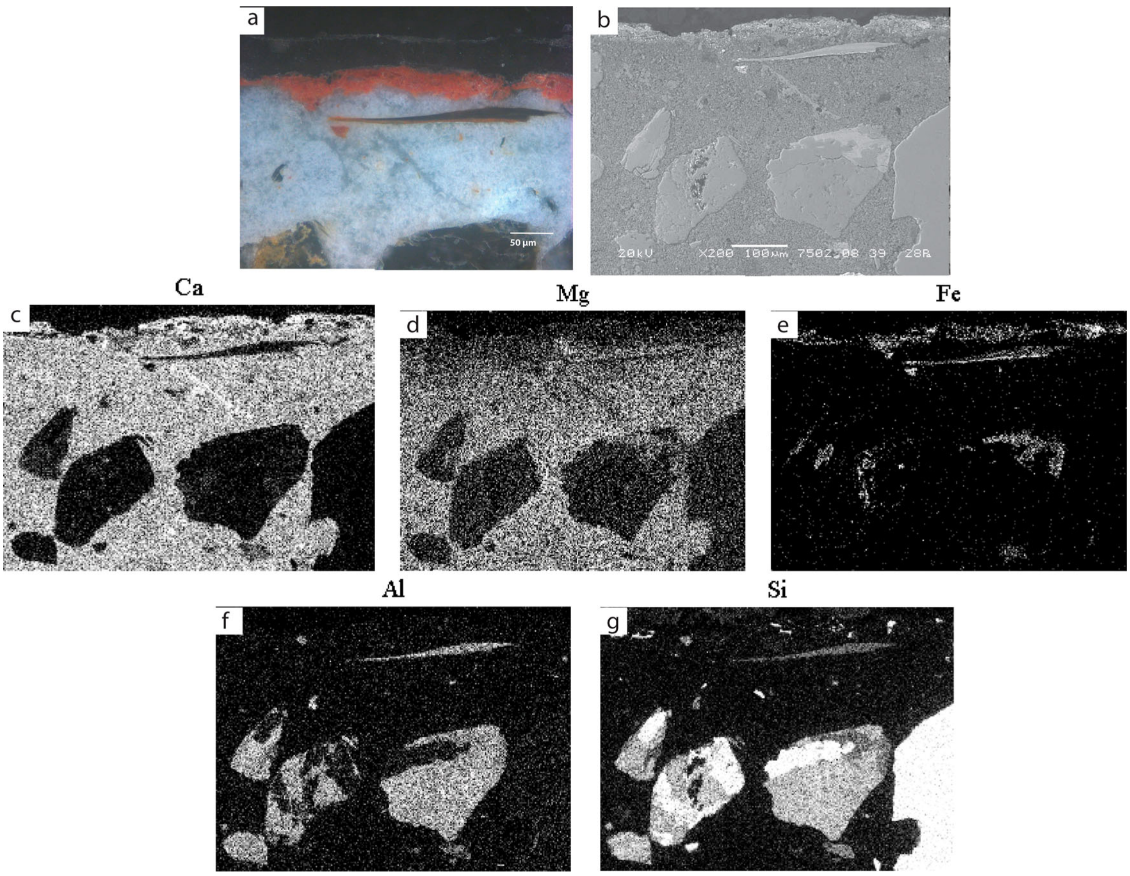

Figure 5. Sample no. 2. (a) micrograph in reflected light (PLM); (b) BSE image; (c–g) X-ray maps.

with pure water or dolomitic lime water and dolomitic slaked lime applied on a wet or humid *intonaco*.

The painted fragment in St. Giovanni church at Cevio (sample 1, Figure 8) exhibits the presence of a Ca-rich interface between the ground and the first red paint layer. This feature could be interpreted as either *a secco* painting or a preparatory drawing applied on an *intonaco stanco* (plaster in the early stage of the carbonation process) The relative amount of the pigment compared with the medium is indicative of the use of pure or lime water as a pictorial medium being Fe>>Ca+Mg. The execution of the

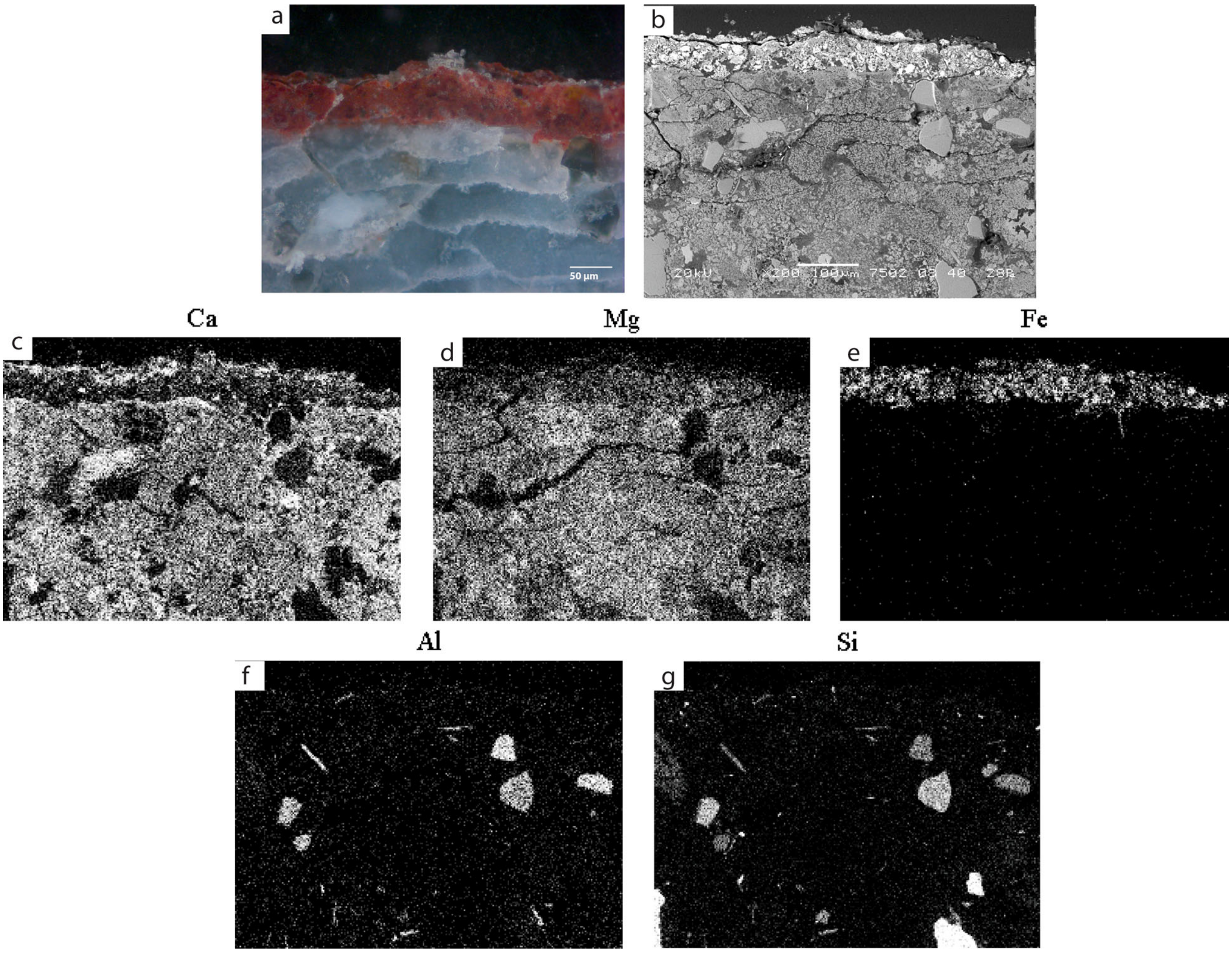

Figure 6. Sample no. 4. (a) micrograph in reflected light (PLM); (b) BSE image; (c–g) X-ray maps.

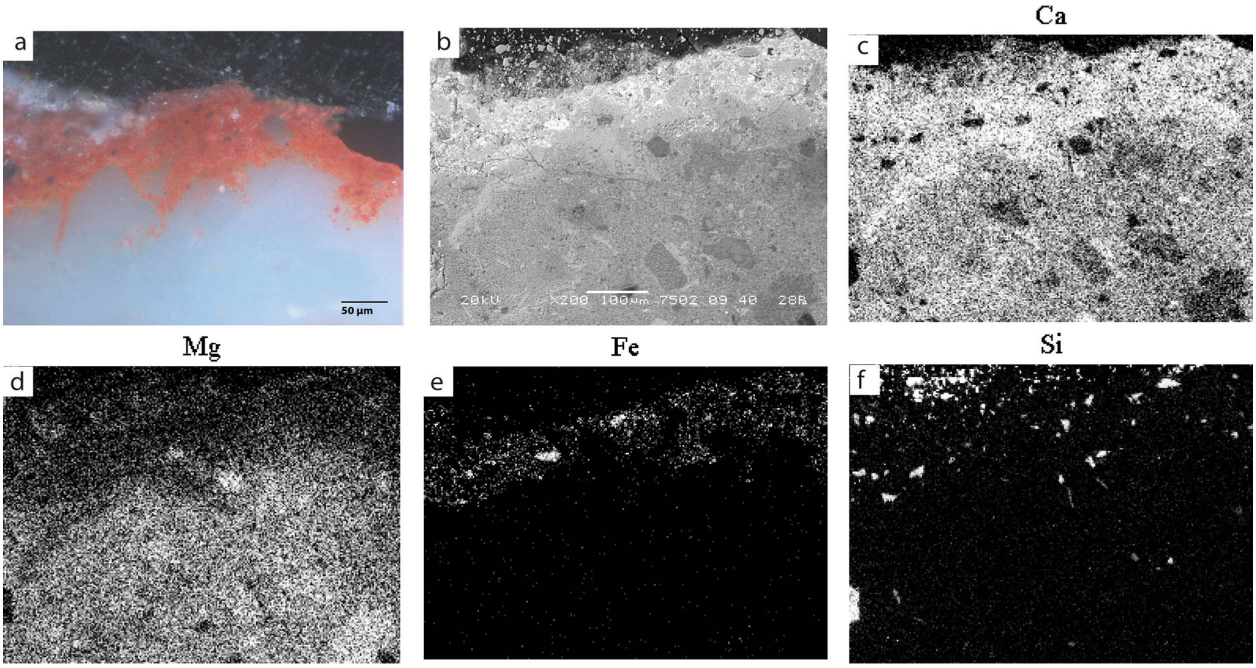

Figure 7. Sample no. 6. (a) micrograph in reflected light (PLM); (b) BSE image; (c–f) X-ray maps.

skin color was obtained by mixing a yellow–orange Fe-based pigment with dolomitic slaked lime (Ca +Mg>>Fe) applied *a secco* over the first layer. According to traditional Romanesque painting technique, the volume of the flesh tones was executed applying a green colour to the yellow paint layer. The

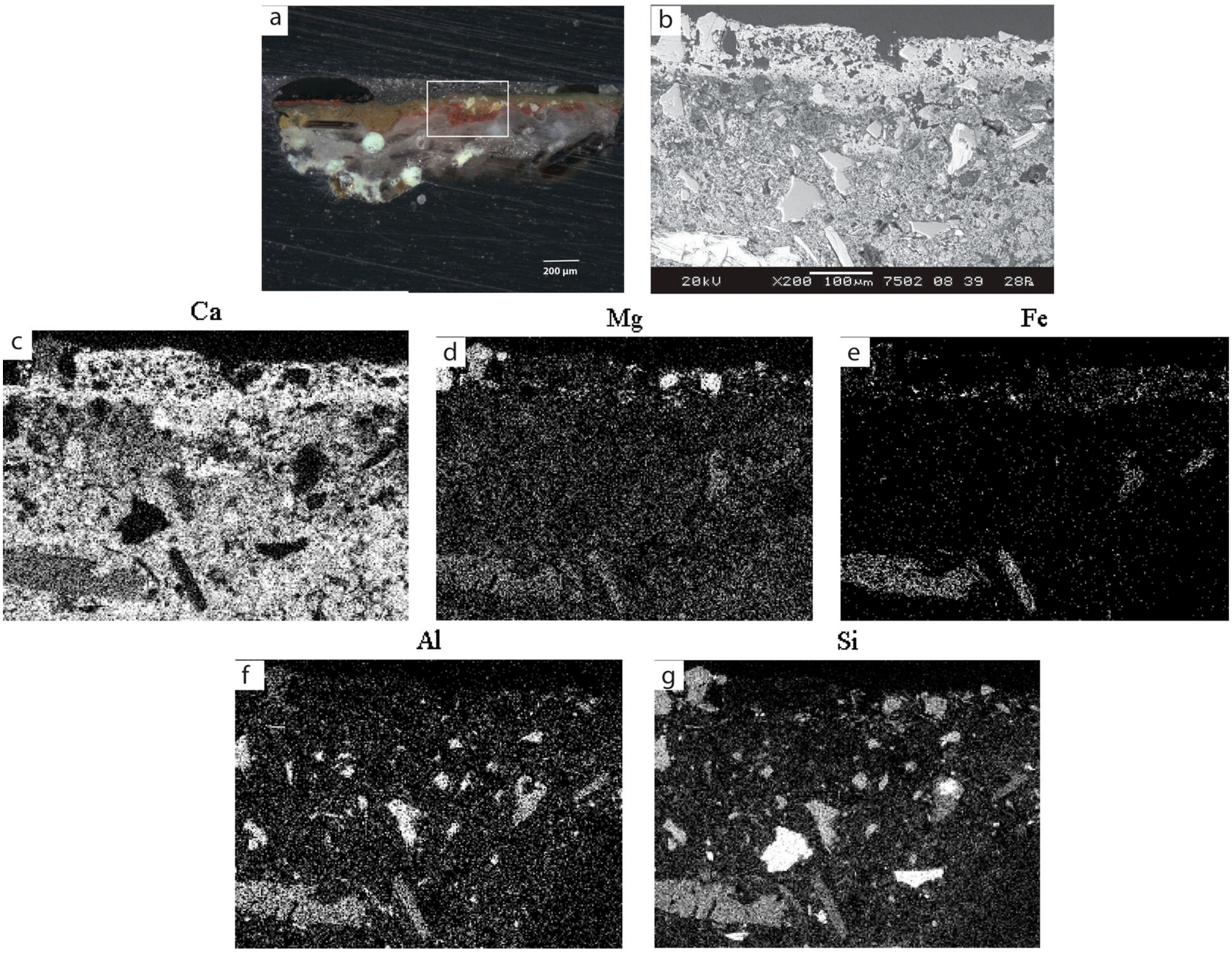

Figure 8. Sample no. 1. (a) micrograph in reflected light (PLM); (b) BSE image; (c–g) X-ray maps.

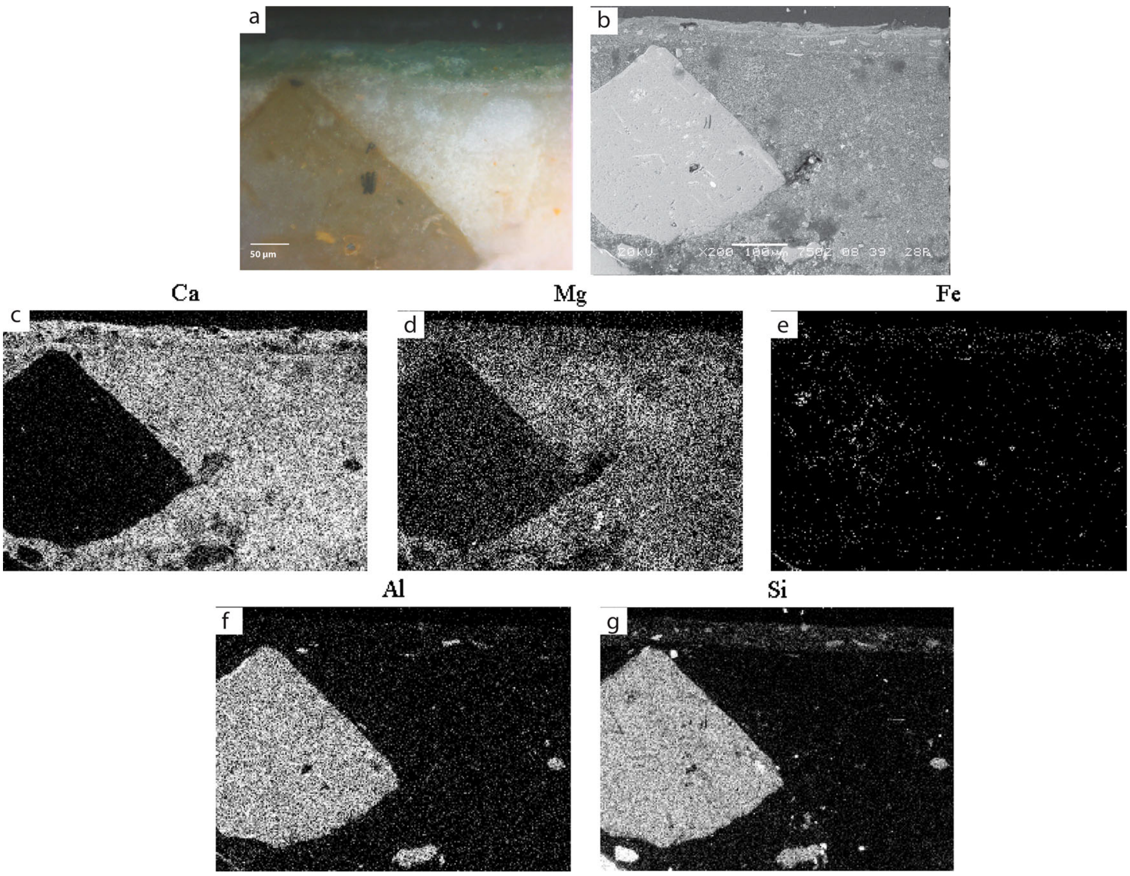

Figure 9. Sample no. 3. (a) micrograph in reflected light (PLM); (b) BSE image; (c–g) X-ray maps.

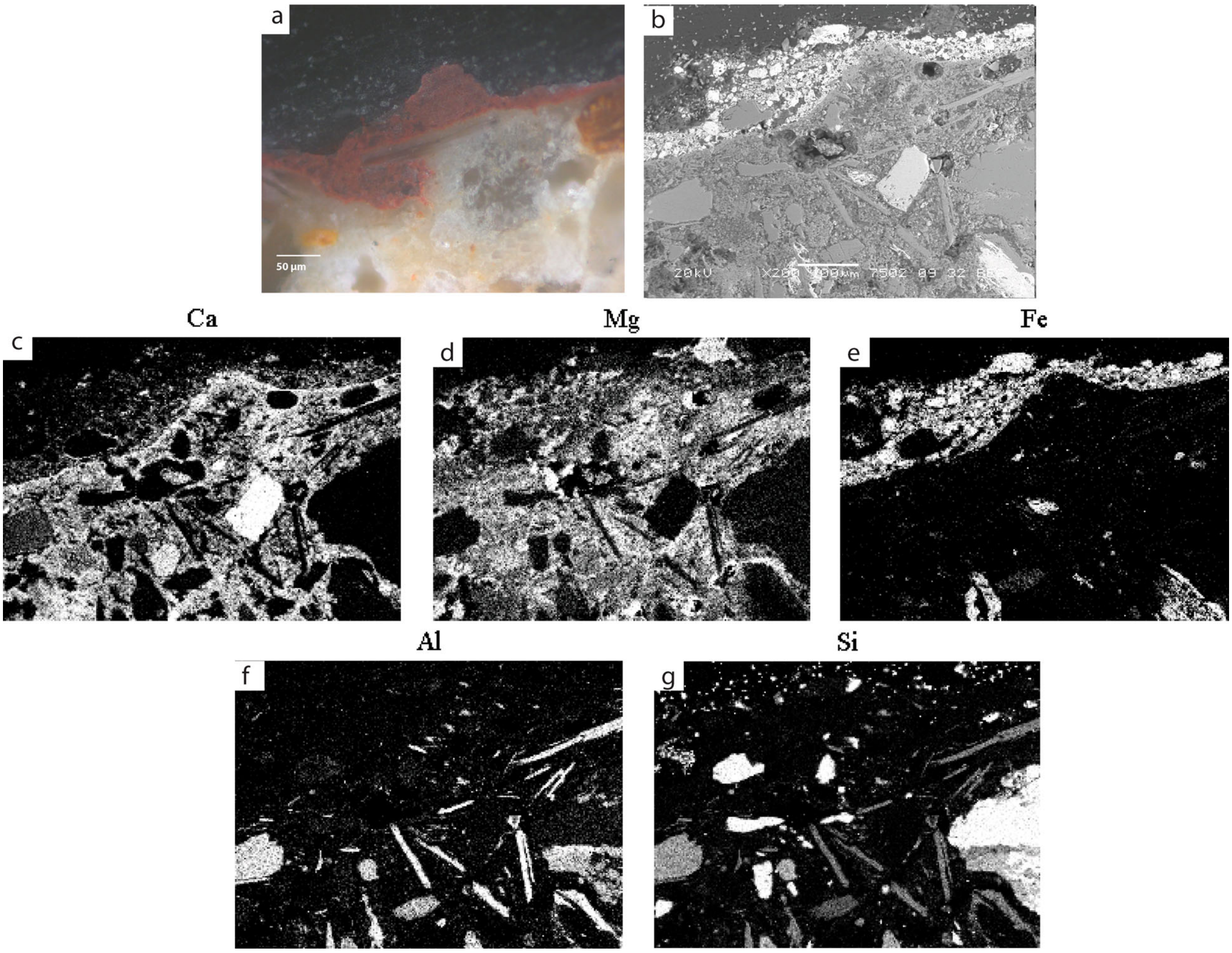

Figure 10. Sample no. 5. (a) micrograph in reflected light (PLM); (b) BSE image; (c–g) X-ray maps.

finishing green brushstrokes are obtained dispersing the green earth in dolomitic slaked lime.

The green paint layers of the archaeological painted fragment coming from Cademario church (sample 3) shows green earth applied on a ground layer exhibiting the presence of a Ca-rich interface recognizable both in the BSE image and in the CaKα X-ray map (Figure 9). In addition, this thin layer is clearly visible at the interface between the first and second green earth layer. In both cases, the interface is very linear indicating an accurate preparation of the ground layer. The interpretation of the painting technique is doubtful also in this case (dry *intonaco* or *intonaco stanco*). Finally, the relative amount of the pigment (Fe+Al+Si) is comparatively less than the binder (Ca+Mg) suggesting the use of dolomitic lime as pigment medium.

Samples 2 from Cademario church (Figure 5), 4 from St. Carlo church at Negrentino (Figure 6), and 6 from St. Nazario church at Dino (Figure 7) clearly display the same *a fresco* pictorial technique: no interface was observed between the ground and the paint layer. However, they differ in the relative ratio between pigment and binder. In the sample 3 Fe>>Ca+Mg indicating the use of pure or lime water; in the sample 6 Ca+Mg>>Fe suggesting the use of dolomitic lime as binder; in the sample 2 the relative ratio is not so clear (*a fresco* lime technique? *A fresco* painting technique?). Noteworthy is the presence of cinnabar mixed with Fe-based pigment in the sample 6; this finding is important for the understanding of Tessin Canton art because it is not common to find cinnabar in Romanesque wall paintings, even if an important medieval treatise (Teofilo 2000) mentions it for making flesh tones.

According to the micro analytical evidence, the painting technique in St. Lorenzo Cathedral in Lugano (Sample 5) is rather doubtful because the BSE image does not show the Ca-interface which is visible in the CaKα X-ray map.

Conclusions

The proposed methodology can be used as a valid approach for the characterization of wall painting technique in general, and Romanesque in particular.

Replicas of wall painting techniques clearly allow for the discrimination of the *a fresco* technique which features well the physical continuity between the ground and first painted layer. On the other hand, the presence of the Ca-rich interface between the ground and painted layer cannot always be used as general criterion for discriminating between *a fresco* and *a secco* painting techniques because it was noted in replicas executed in *a fresco* conditions (*intonaco stanco*, plaster in the early stage of carbonation). This anomaly was very import for the interpretation of the painting techniques of real case studies.

The analysis of the Romanesque painted samples allowed for clearly understanding the painting technique and also for discriminating between *buon fresco* and *a fresco* lime on the basis of the relative amount of pigment and its binder.

It is important to point out that the CaKα X-ray maps should be analyzed in combination with BSE images because sometimes the correlation is not so evident. In addition, in dolomitic lime Mg does not contribute to the formation of the interface; hence the behavior of dolomitic lime is comparable with calcic lime.

Finally, the thickness of the paint layers in Romanesque wall painting is not an objective criterion for determining painting technique as it can vary over a wide range (10–150 μm).

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