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Original article

Thirteenth century wall paintings under the Siena Cathedral (Italy). Mineralogical and petrographic study of materials, painting techniques and state of conservation

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Abstract

The thirteenth century wall paintings (45 scenes) recently discovered under the Siena Cathedral (Italy) constitute an unusually important pictorial cycle within the panorama of European medieval painting. Scientific research was carried out to acquire detailed information to provide technical and philological support to the current restoration. This paper deals with the mineralogical and petrographic characterization of the materials, as well as inferences about the painting techniques (suitable reference specimens were prepared for this purpose) and the state of conservation of the wall paintings. The study is primarily based on analyses of microfragments in thin cross-sections by means of a polarising microscope equipped for observations in transmitted and reflected light; XRD, SEM-EDS and Micro-Raman spectroscopy were also used to confirm and supplement the microscopic data. Plaster joints with a specific horizontal and vertical trend that follows the separation of the different scenes indicates a “pontate” method of execution. The supporting plaster, lying directly on the masonry, is monolayered. Two main types of plasters were observed: lime plaster and lime plaster with cocciopesto. In the first type plant fibres are locally present. The paint film is often multilayered. Thirteen pigments were identified, all of them used in the original paintings or, at most, in repaintings before the middle of the fourteenth century. Two pigments, crocoite and chrysocolla, have never been found before in medieval wall paintings. The finding of crocoite (very probably of natural origin) is of particular historical-scientific importance. The most typical microstratigraphies in the main figurative elements are illustrated. The painting techniques used are fresco (including the variant lime fresco painting), tempera and lime painting, very often combined in the paint film. The distinguishing petrographic features of each technique are described and illustrated. The main results of the study are discussed in regard to their historical and artistic significance, and they are compared with materials and techniques known in other contemporary pictorial cycles. The state of conservation of the wall paintings before the restoration is illustrated and related to the complex history of the room hosting the paintings. Referenced digital mapping of the preservation status was carried out for the major scenes using a Geographic Information System (GIS), which allowed adequate processing of the entire data set.

Keywords: Medieval wall paintings; Pigments; Crocoite; Chrysocolla; Microstratigraphy; Painting techniques; State of conservation; GIS

1. Introduction: history of the paintings and aims of the research

Recent excavations under the floor of the Siena Cathedral revealed wall paintings that remained buried since the middle of the fourteenth century [1]. They constitute an exceptional pictorial cycle going back to the earliest period of Sienese painting (the beginning is dated to about 1270), whose extraordinary aesthetic and historiographic importance has already been pointed out [2].

The room hosting the paintings is under the floor of the Cathedral close to the baptistery. The paintings completely cover the perimeter walls of the room and two octagonal-based pillars; they consist of 45 scenes mainly representing stories from the Old and New Testaments, culminating in the

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three grand scenes of the *Crucifixion*, *Deposition from the cross* and *Deposition in the sepulchre* which occupy the centre of the southern wall. The scenes are accompanied by faux marble dados with various geometric motifs (Figs. 1, 2).

The paintings have been subjected to particular events since their creation, linked to the complex evolution of the Cathedral. Only some basic notes about their history (those pertinent to this work) are given here.

The main function of the room hosting the wall paintings is not very clear: it seems to have served as an atrium of the posterior entrance of the Cathedral [1,3], but also as a space with religious importance. Indeed, some paintings show signs of degradation related to ritual uses, especially the burning of candles. The presence of these signs on fourteenth century repaintings (described in Section 5) suggests that the room was used for such purposes also in the first half of the fourteenth century. Around the middle of the fourteenth century the previous painted vault ceiling, whose remains are still visible in the upper part of the paintings, was removed and the room was filled with rubble (fragments of the ribbed vaults were included) to support the Cathedral floor that was under construction. Only the eastern sector of the original room ("Cripta delle Statue") was not filled.

Thus, most of the paintings remained buried for about six centuries, with the exception of narrow portions of the western wall, where the debris was partially removed at the beginning of the eighteenth century to create some tombs [1].

Removal of the rubble in 2000–2001 revealed the wall paintings. The necessary restructuring works were then undertaken, mainly to support the Cathedral floor, and restoration scaffolding was set up, together with systems to monitor and control the microclimate.

Scientific investigations were necessary to provide adequate background knowledge for the restoration. This paper deals with the mineralogical and petrographic characterization of materials, as well as inferences about the painting techniques and the state of conservation of the wall paintings. The resulting data are compared with the results of similar studies of contemporary European wall paintings, thus contributing to the historical and artistic knowledge of this important thirteenth century pictorial cycle.

2. Experimental methods

About 200 microfragments (mostly smaller than 1 mm) were collected from different scenes and decorative elements. Sampling was conducted in close collaboration with the restoration staff according to a principle of minimum invasiveness, i.e. taking samples from the margins of existing lacunae.

The study is primarily based on analyses of fragments in thin cross-sections by means of a polarizing microscope equipped for observations in transmitted and reflected light. Observations were also carried out with non-conventional devices that increase the diagnostic potential of the method. Light microscopy allowed a preliminary characterization of the materials in the paint film and the supporting plaster, as well as exhaustive identification of the microstratigraphy of the paint film. Light microscopy also played a prominent role in the recognition of painting techniques. For this purpose, we tested the petrographic method (not currently used for such analyses) by preparing suitable test pieces thank to determinant support of the restorers of the wall paintings. The reference specimen were prepared using materials similar to those in use in ancient times, thus reproducing paint films applied with different techniques on an appropriately prepared plaster. Diagnosis of the painting techniques was based on the textural relationships between the various microstratigraphical units and on a preliminary identification of the nature of the binders by optical and microstructural characters.

X-ray diffraction analyses were carried out with a Philips X'Pert PRO PW 3040 diffractometer (Bragg–Brentano geometry) operating at 40 kV and 40 mA, equipped with a post-diffraction monochromator and a PW3015 X'Celerator detector, using CuKα radiation in the 5–70° 2θ range with a scan speed of 1.6° per min. The analyses were usually performed directly on the collected microsamples to allow their re-use for other kinds of analyses. In some cases, the pigment under study was isolated under a stereomicroscope and directly pulverized on a silicon support wich provides a low scattering contribution.

SEM-EDS analyses, using a Philips XL20 electron microscope operating at 20 kV acceleration voltage and equipped with an EDAX DX4 energy dispersive spectrometer, were carried out to confirm and supplement the optical and diffractometric data. SEM analyses were performed directly on thin sections covered by a light carbon film.

Micro-Raman spectroscopy was applied for further diagnostic details of particularly interesting pigments. Raman spectra were recorded using a Renishaw RM2000 instrument, equipped with a CCD Peltier-cooled detector (Department of Chemistry, University of Florence, Italy). The incident laser radiation was provided by an Argon air-cooled laser source with excitation wavelengths at 514.5 nm. A $50\times$ magnification objective was employed to focus the laser beam onto the sample, providing a spatial resolution of about 1–2 µm. The irradiating laser power was about 2 mW. The scattered light was analysed using a grating monochromator with 1200 lines per millimetre. Spectra were recorded with a collection time up to 200 s.

Diagnosis of the state of conservation of the wall paintings was based on direct macroscopic observations, sometimes supported by the aforementioned analytical methods. The conservation status of the three large scenes of the *Crucifixion* and the *Depositions* was mapped with a Geographic Information System (GIS) using ESRI ArcView 3.2 software, which allowed adequate processing of the entire data set.

3. Characterization of materials and microstratigraphies

3.1. The supporting plaster

The supporting plaster consists of a single layer (average thickness about 5 mm) lying directly on the brickwork and subordinately on calcareous stone masonry. Therefore, it

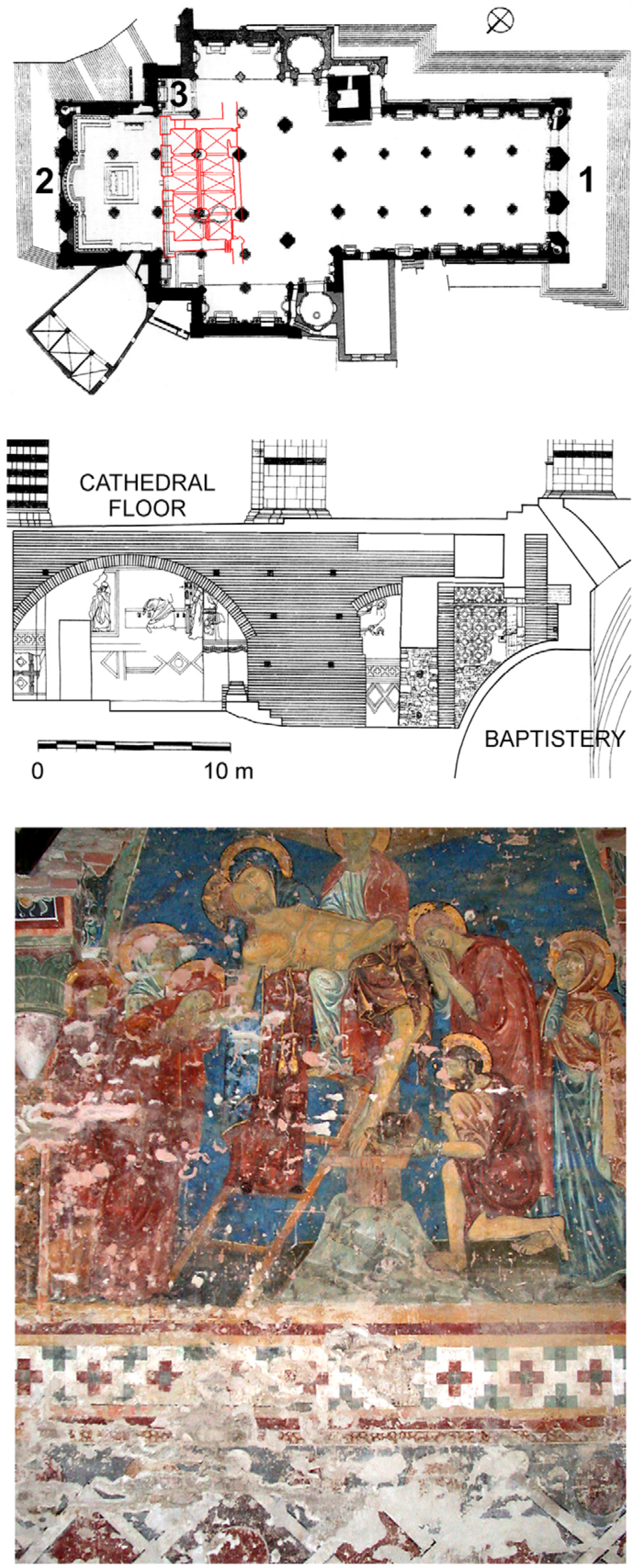

Fig. 1. Upper image: plan of the room (red) hosting the thirteenth century wall paintings recently discovered under the Siena Cathedral (modified after [3]). 1: façade of the Cathedral; 2: entrance to the baptistery of Saint John; 3: present entrance to the room with the wall paintings. Central image: vertical section of the room (modified after [4]). Lower image: a scene of the wall paintings (*Deposition from the cross*, on the southern wall). The faux marble dado with geometric motifs is seen in the lower part. The image shows the appearance of the paintings before the current restoration.

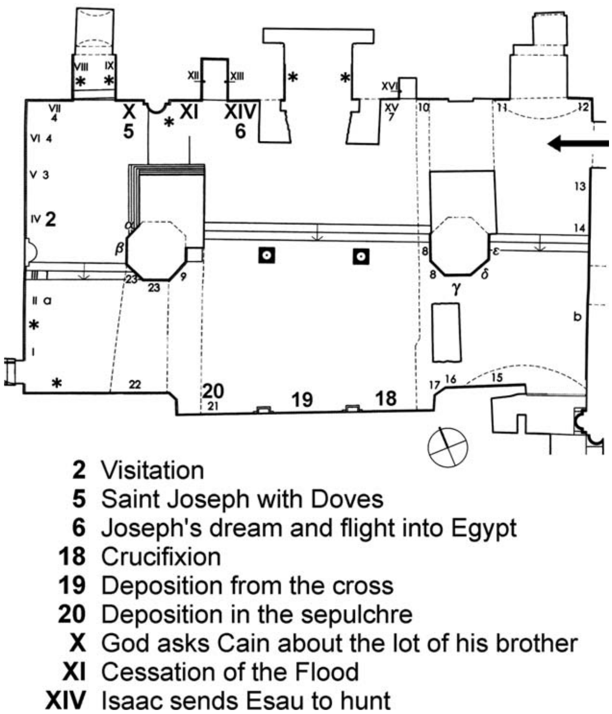

Fig. 2. Map of the room hosting the paintings (arrow indicates the present entrance to the room). The scenes mentioned in this paper are specified. The map and the names of the scenes are taken from [2].

lacks an "arriccio" layer, a technical detail frequent in European wall painting until the end of the thirteenth century [5–7].

Two main types of plaster were recognized: a lime plaster and a lime plaster with cocciopesto.

The plain lime plaster is based on a sandy aggregate, with grain size between 40 and 300 µm, largely consisting of quartz and calcite and, to a lesser degree, lithic fragments with prevailing Pliocene sandstone, which constitutes the geological substratum of the historical centre of Siena [8]. The binder consists of microcrystalline calcite. The binder/aggregate ratio is usually between 1/1.5 and 1/2. In three scenes on the northern wall (*Cessation of the Flood*, *Isaac sends Esau to hunt*, *Joseph's dream and flight into Egypt*), the lime plaster was prepared with variable quantities of thin whitish fibres several millimetres in length, probably of vegetable origin. The use of organic (usually plant) fibres occurs in Italian wall painting from the Early Middle Ages to the early seventeenth century. Cennini (early fifteenth century) does not mention it, but the addition of straw in the arriccio and tow in the plaster is recommended by Dionysius of Furna, a seventeenth century Greek painter who reported on much earlier indications [9–11]. Plant fibres have also been found in paintings of the Holy Sepulchre Chapel in Winchester Cathedral (twelfth century) and in Saint Mark's Cathedral and the Church of San Nicolò dei Mendicoli in Venice (early fourteenth century) [5,12,13]. Moreover, plant materials appear in plasters of the decoration of the Siena Cathedral's baptistery (mid-fifteenth century), bordering on the room under study here [14]. Their function was mainly to keep the plaster wet during the delicate setting phase, and it is not surprising that they were used here in plasters of the wall whose external part corresponded to the original façade.

The lime plaster with cocciopesto consists of a sandy aggregate very similar in composition, quantity and grain size to that of the plain lime plaster. The grains of cocciopesto are present in variable quantities; they show a wide range of grain size, with a prevalence of the fine fraction (a few µm). The use of this type of plaster is limited to the southern wall, i.e. the wall with the three large scenes of the *Crucifixion* and the *Depositions*, and to the octagonal-based pillars. The addition of cocciopesto gives very hydraulic properties to this plaster; thus, it was very probably applied to protect the paintings located on the dampest walls. Cennini recommended cocciopesto to obtain waterproof plasters and Giotto used it in the arriccio of the Scrovegni Chapel [10,15]. Cocciopesto has been rarely founded in the Tuscan medieval paintings. It was used in Siena for the *Maestà* painted on the external wall of the Due Porte (exiting Via Stalloreggi), probably in the final years of the thirteenth century; the artist had strong links to the style of Giotto of the Upper Basilica in Assisi (see for example the *Ascension of Christ*) [16]. Instead, cocciopesto is used more frequently in Latium, for instance in the decoration of the crypt of the Anagni Cathedral (frescos: late twelfth–early thirteenth century) [7,17].

3.2. Pigments

3.2.1. Artists' palette of colours

The identified pigments are reported in Table 1, together with their specific uses in the different pictorial elements of the paintings. Their frequent combination as overlapping layers in the paint film and/or their mixing within the same layer produced a wider range of chromatic tonalities.

All the pigments are well preserved, even lead white, minium and cinnabar which are considered easily subject to alteration [18]. Only azurite presents frequent chromatic alterations to the greenish tonalities due to transformation into paratacamite and sometimes malachite; this phenomenon has been found in many medieval paintings [18–20]. There are also very localized transformations of yellow ochres into red ochres due to the heat of candle flames or oil lamps (see Section 5).

Comparison of the palette of colours of this thirteenth century pictorial cycle with those of other contemporary European wall paintings [5–7,20–25] shows that most of the pigments identified thus far are common to the period. However, crocoite and chrysocolla have never been found in European paintings of the same age. These two pigments are more widely described and discussed in the following sections.

Some remarks concerning green earth and lime white are necessary.

In these wall paintings, green earth is represented by a mineral of the mica group; the first analyses indicate the presence of colacbrite.

The term lime white is used here in its broadest sense, including proper lime white (water-slaked lime) and bianco sangiovanni, a pigment with a substantial proportion of calcium carbonate deriving from the ancient manufacturing pro-

Table 1
Palette of the recognized pigments and their main uses in the wall paintings

	Pigment	Main use in the scenes	Use in decorative elements (socle and frames of the scenes)
RED	*Cinnabar*	Draperies, blood	No
	Red ochre	Draperies, flesh, preparatory drawing, architectural motifs, dark backgrounds, hair	Yes
ORANGE	*Minium*	Orange halos, draperies, missione (ground preparation for gold leaf), flesh, architectural motifs	No
YELLOW	*Yellow ochre*	Flesh, draperies, preparatory drawing, architectural motifs	Yes
	Crocoite	Architectural motifs, flesh and minor figurative elements (with ochres and/or minium), heightenings in reddish drapery, orange halos (with minium), outlines,	Yes
GOLD	*Gold leaf*	Halos, ornaments in draperies	No
GREEN	*Green earth*	Flesh (ground tonality)	Yes
	Verdigris	Probable component in missione	No
BLUE	*Azurite*	Sky, draperies, architectural motifs	Yes
LIGHT BLUE	*Chrysocolla*	Draperies	No
BLACK	*Coal black*	Ground tonality, dark shadings in draperies, outlines, architectural motifs, dark backgrounds	Yes
WHITE	*Lead white*	Missione, heightenings in draperies, architectural motifs	Yes
	Lime white	Draperies, architectural motifs, outlines	Yes

cess described by Cennini [10]. Our experience suggests that the thin-section analysis by light microscopy would allow to distinguish the original carbonate component characterizing bianco sangiovanni. This component is probably represented by the portions in which microcrystalline calcite is darker in transmitted plane polarised light and has greater reflectance than the microcrystalline calcite deriving from direct carbonation in situ (for example, see layer B in Fig. 3b). The differences in optical properties of the carbonate fraction could be due to the different crystallinity of calcite formed during the two distinct moments of carbonation.

3.2.2. Crocoite

Crocoite ($PbCrO_4$, monoclinic), with a brilliant yellow colour, is fairly diffuse, albeit in very small quantities, in several kinds of pictorial elements (Table 1). It is usually used, either as the only pigment forming a more or less continuous thin layer (Fig. 3a–c), or, sometimes, combined with other pigments, e.g. ochres and minium (Fig. 3e, f). Crocoite was well revealed by XRD (Fig. 4 and Table 2) and Raman spectroscopy (Fig. 5), while the SEM-EDS analyses confirmed the significant presence of Cr and Pb in the pigment (Fig. 3c, d).

The peculiar history of the paintings implies that the pigment was applied before the room was filled with rubble, certainly no later than the mid-fourteenth century. The data obtained thus for plant out a diffuseuse of this pigment in repainting interventions (see also section 5). However, this contrasts with current knowledge about the history of the scientific identification of natural crocoite and the production and use of synthetic $PbCrO_4$-based yellow pigments, on the whole known as “chrome yellow”; indeed, these events took place later than the second half of the eighteenth century ([26] and references therein).

Crocoite in these wall paintings has therefore very probably a natural origin. In nature, crocoite is a rather uncommon secondary mineral occurring in the oxidised zones of lead mineralisations; in Europe, small deposits are found in Germany, Scotland and France, in addition to the important deposits in the Urals, where crocoite was first discovered and described in 1766 [27]. The pigment could have been obtained by pulverization of well developed crystals, which show reddish tonalities and whose powder is yellow (Fig. 3g,h), or, perhaps, from micro-cryptocrystalline aggregates, which are naturally yellow.

The rarity of the mineral in nature can explain by itself the extraordinariness of this finding.

3.2.3. Chrysocolla

Chrysocolla, a nearly amorphous hydrated copper silicate, was found in light blue-greenish draperies of two scenes on the northern wall (*God asks Cain about the lot of his brother*, *Saint Joseph with doves*). The pigment was always secco-applied by the lime painting technique.

No single investigation was able to identify the pigment. Instead, the combination of several results obtained from different analytical methods allowed its determination.

In thin section, the grains of the pigment appear almost round, or rarely fibrous or sharp-cornered, with grain size usually between 10 and 50 µm. Under transmitted plane polarized light, the grains show a pale blue colour, sometimes with greenish shades. In reflected light darkfield, the grains show a dark bluish appearance. Under transmitted light with crossed polarizers, the pigment shows isotropic features, or, more frequently, the grains show a faint birefringence with an inhomogeneous, undulating extinction. Sometimes the grains contain irregularly shaped inclusions of azurite. The association between chrysocolla and azurite in the samples can be explained by the fact that the two phases are often associated in natural copper mineralisations. The images in BSE obtained at the scanning electron microscope better underline the microstructural characters of the pigment, while the analyses with EDS microprobe show that it consists mostly of Si and Cu (Fig. 6). The low crystallinity of the compound is confirmed by XRD analyses (Fig. 7).

Fig. 8 shows the Raman spectrum of the pigment, which does not match the spectra of known pigments. A more detailed Raman spectroscopy study is necessary because of

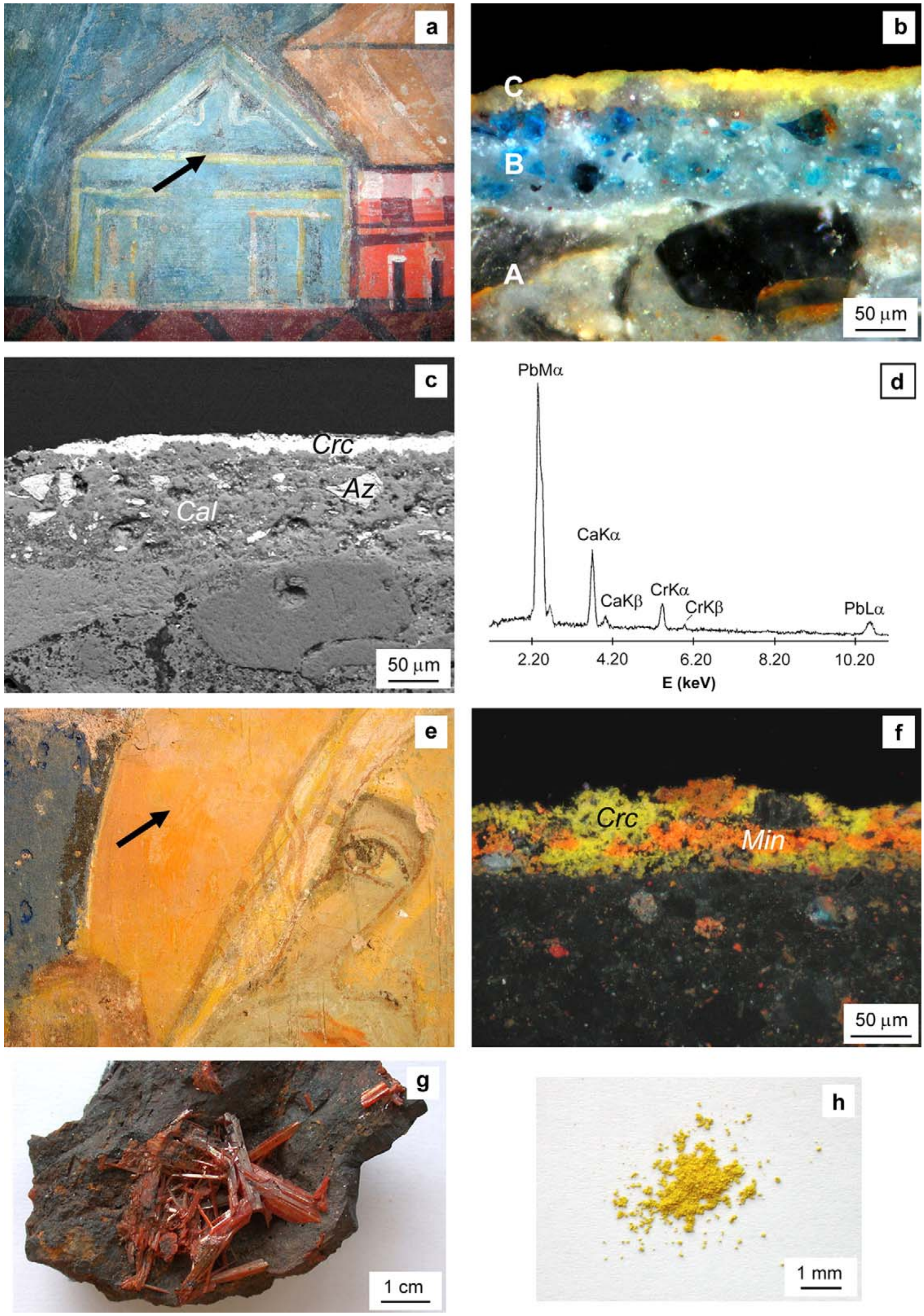

Fig. 3. (a) An example of the use of crocoite in architectural motifs (*Visitation* scene), and (b) relative microstratigraphy (reflected light darkfield). A: lime plaster with sandy aggregate. B: azurite secco-applied in lime binder (probably St. John's white). C: veil of crocoite applied on a thin underlying lime layer. (c) Same image obtained by SEM with BSE (*Crc* = crocoite; *Az* = azurite, *Cal* = calcite). (d) EDS spectrum of crocoite in the previous image (calcium is an expression of the underlying lime layer). (e) Use of crocoite in an orange halo (*Crucifixion* scene), and (f) relative microscopic appearance of the paint film (reflected light darkfield); crocoite (*Crc*) is mixed with minium (*Min*) in the paint film. (g) A sample of natural crocoite from Dundas, Tasmania (with thanks to the Museum of Natural History, Accademia dei Fisiocritici, Siena). The well-developed prismatic crystals have a bright translucent reddish colour. (h) The relative powder, instead, is brilliant yellow.

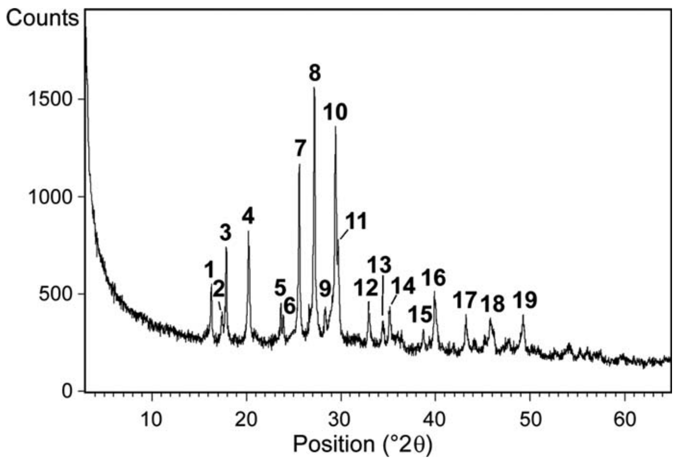

Fig. 4. XRPD spectrum of crocoite separated under the stereomicroscope from the sample shown in Fig. 3a. Data for each of the main peaks indicated with numbers are reported in Table 2.

Table 2
Data relative to XRPD spectrum of crocoite in Fig. 4 XRPD compared to X-ray diffraction data of a natural standard crocoite (PDF 1-74-2304 from ICDD database)

Peak	Sample data		Standard data		
number	*d* (Å)	*I* (%)	*d* (Å)	*I* (%)	*hkl*
1	5.434	21.4	5.42668	19.2	–101
2	5.080	19.2	5.08832	8.8	110
3	4.956	33.3	4.95112	17.9	011
4	4.388	36.0	4.38351	38.9	–111
5	3.761	10.8	3.76297	8.9	111
6	3.721	18.6	3.71800	8.3	020
7	3.480	65.1	3.48889	59.2	200
8	3.27	100.0	3.28127	100.0	120
9	3.15099	9.3	3.15852	12.5	210
10	3.036	82.8	3.03003	56.9	012
11	3.009	36.5	3.00315	29.1	–112
12	2.71	17.0	2.71334	15.7	–202
13	2.60	7.2	2.59905	12.8	112
14	2.548	14.7	2.54895	15.1	–212
15	2.324	7.3	2.32198	10.8	031
16	2.25	25.8	2.25276	15.6	–131
17	2.09	13.7	2.09321	20.0	212
18	1.981	11.9	1.97813	17.8	–132
19	1.849	14.3	1.84831	21.8	–322

the chemical and structural variability of the compound and the lack of standard reference spectra in the literature.

The presence of chrysocolla seems to be exceptional for European medieval wall paintings. Thus far, the pigment has only been reported in ancient wall paintings in Egypt, India and China [28,29].

3.3. Some significant microstratigraphies of the paint film

The paint film can be mono- or, more often, multilayered. In many cases, two or more layers are observed: one acts as preparation or ground tonality, while the overlying layer represents the finished colour; this layer, in turn, can be surmounted by thin and discontinuous glazings (heightenings and shadings). However, even more complex microstratigraphies can

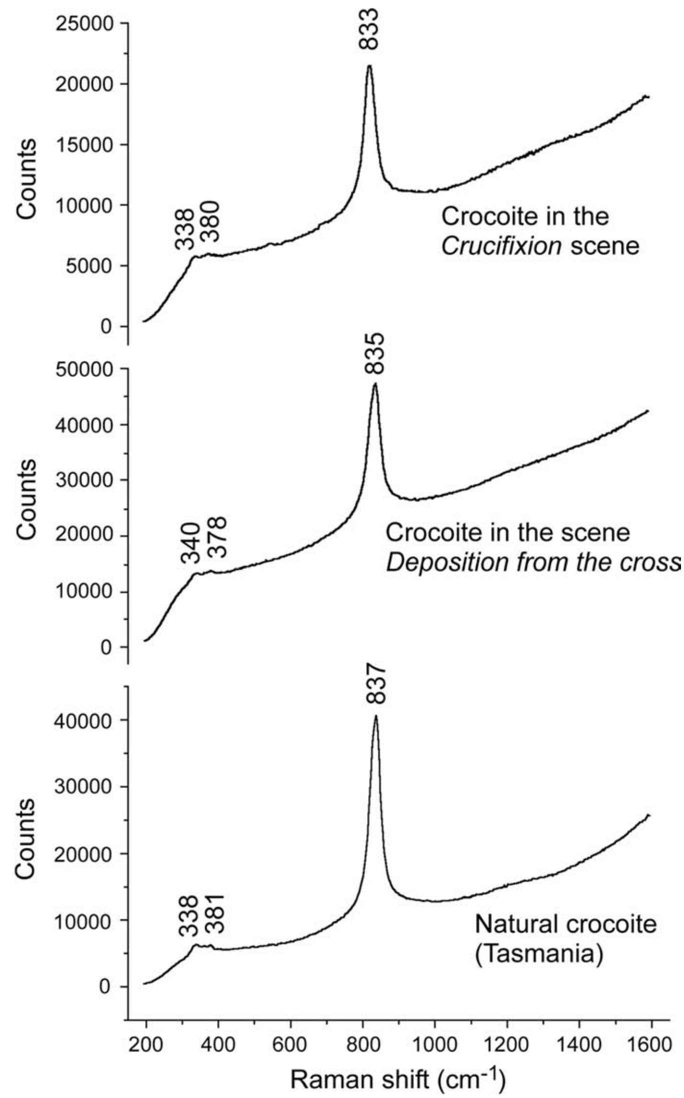

Fig. 5. Raman spectra of two crocoite samples from the wall paintings, compared with Raman spectrum of natural crocoite (sample from Dundas, Tasmania, see Fig. 3g).

be found, for example in repaintings (Fig. 10b) and in zones where contiguous fields of colour overlap.

A preparatory drawing is often present at the base of the paint film, generally represented by a very thin, sometimes discontinuous, fresco-applied layer consisting of yellow and/or red ochres e.g. (Fig. 10a).

Similar pictorial elements of the various scenes may present marked microstratigraphic complexity and variability. Nevertheless, we will describe and illustrate (Figs. 9 and 10) some of the more significant microstratigraphies in the main pictorial elements, also indicating the respective painting techniques (fully discussed in Section 4). The following elements are considered here: sky, red and blue drapery, flesh, golden and orange halos and decorative elements.

3.3.1. Sky

The blue colour of the background representing sky is always due to azurite, present as coarse crystals (up to about

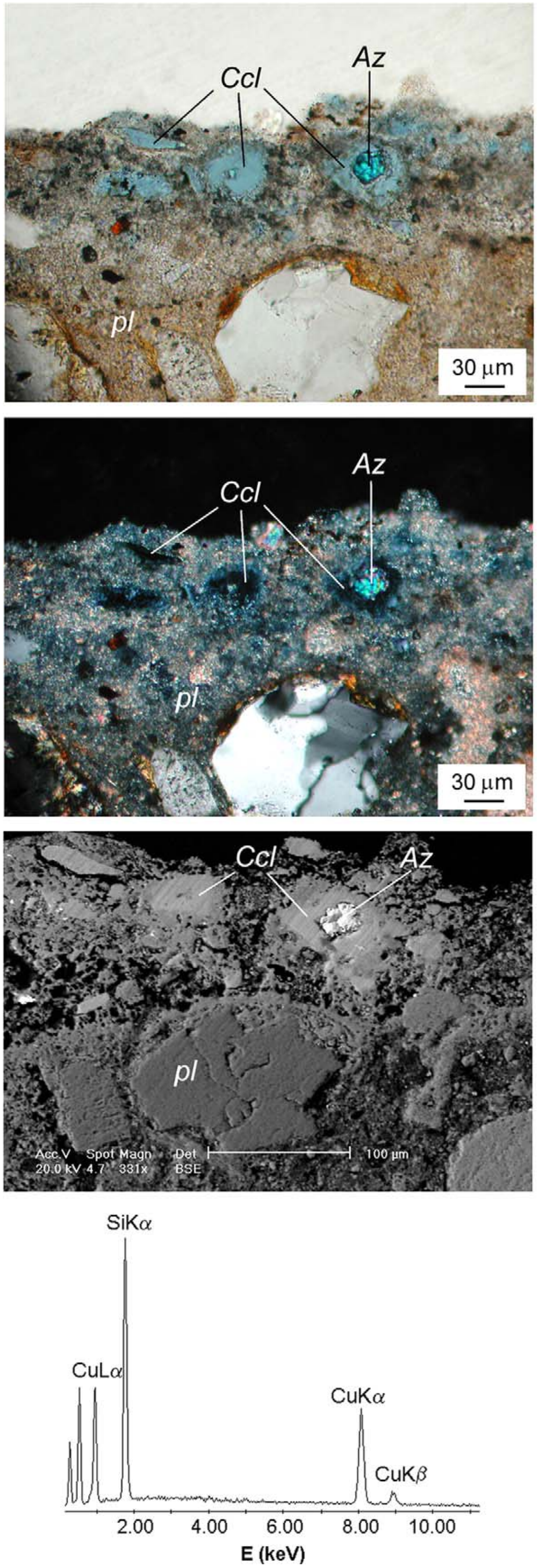

Fig. 6. Use of chrysocolla in light blue draperies. The pigment (*Ccl*) is plunged in lime binder; the layer is secco-applied on the underlying plaster (*pl*). An azurite (*Az*) inclusion is highlighted. From top to bottom: transmitted plane polarized light, crossed polarizers, BSE image obtained at SEM-EDS and compositional spectrum of chrysocolla.

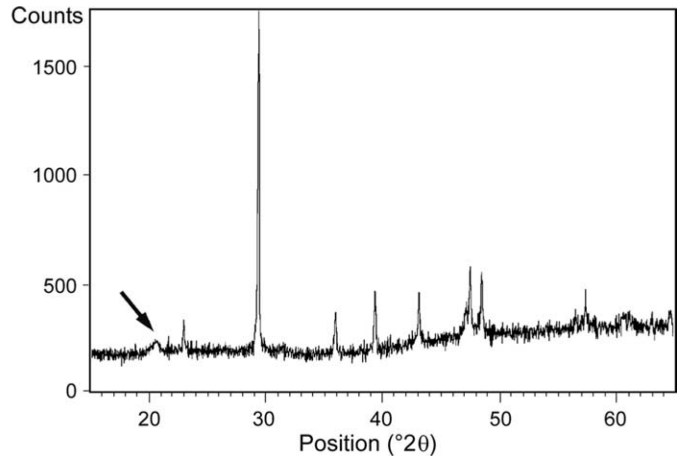

Fig. 7. XRD spectrum of the surface of a microfragment with chrysocolla. The main peaks refer to calcite associated with the pigment as binder; the wide peak indicated by the arrow (d = 4.275 Å) can be referred to the peak of maximum intensity of chrysocolla.

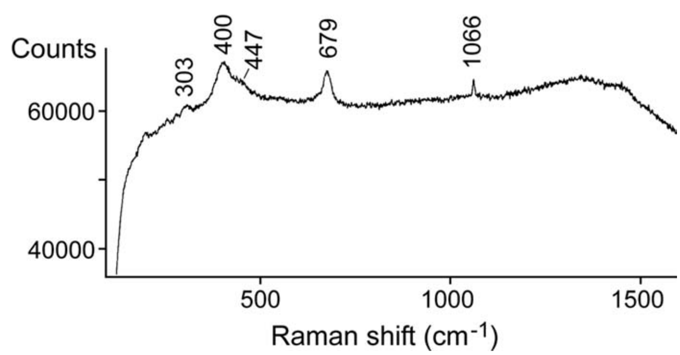

Fig. 8. Raman spectrum of chrysocolla in the wall paintings.

100 μm) applied with the tempera technique (preliminary GS-MS data indicate the use of egg yolk as binder—M.P. Colombini, personal communication). Azurite is often applied in two consecutive layers of considerable thickness (on the whole, up to 300 μm), separated by a thin calcium oxalate level deriving from transformation of the original organic glue. The thin oxalate level is easily distinguished by light microscopy because of its greater durability than the binders of the single layers. The azurite usually lies on a ground layer of coal black in lime binder, mostly secco-applied on the supporting plaster (Fig. 9a).

3.3.2. Drapery

Only draperies with red and blue colours are here considered, since they are the most diffuse types in the paintings.

In the reddish drapery, the red colour is due to red ochres (normally fresco-applied), often surmounted by a level pigmented with cinnabar or minium (Fig. 9b–d). Shadings were usually obtained by mixing the basic colour with more or less abundant coal black.

Bluish drapery is usually characterized by a secco-applied layer of azurite grains in lime binder (Fig. 9e,f). As mentioned above, a lighter blue pigment, chrysocolla, was used in two

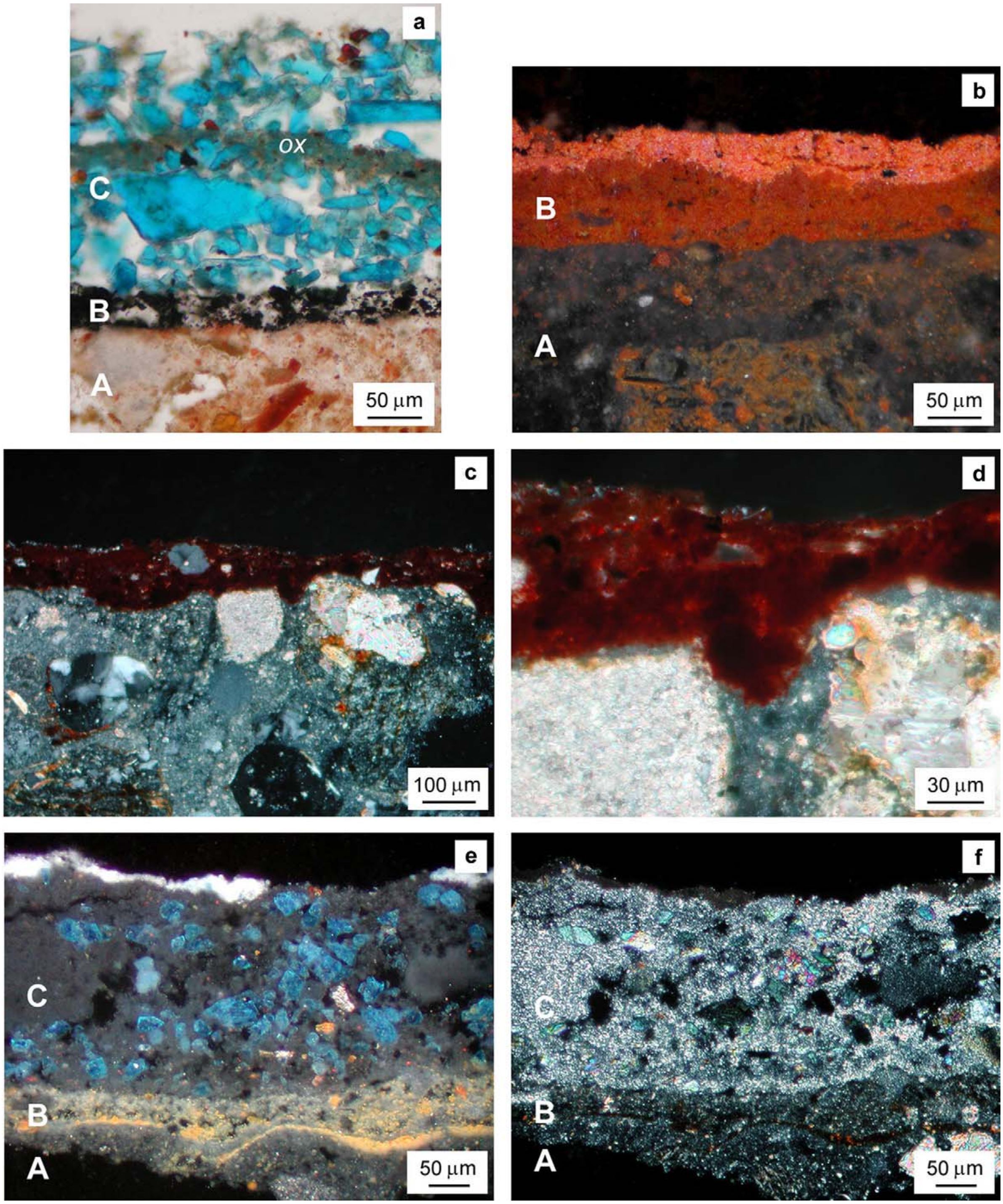

Fig. 9. Some significant microstratigraphies of the main pictorial elements. (a) Microstratigraphy representative of sky (reflected light darkfield with bright background). A: lime plaster with sandy aggregate and cocciopesto. B: coal black in lime binder secco-applied (lime painting). C: azurite tempera-applied in two layers separated by a calcium oxalate layer (*ox*). (b) Microstratigraphy representative of reddish drapery (reflected light darkfield). A: lime plaster with sandy aggregate and cocciopesto. B: red ochres fresco-applied, with overlying cinnabar. (c) Another example of a microstratigraphy relative to reddish draperies (crossed polarizers with converging lens). The fresco application of the red ochres is evident: the paint film adapts itself very well to the texture of the plaster. (d) A detail of the previous image. (e) Microstratigraphy representative of bluish drapery (reflected light darkfield). A: lime plaster with sandy aggregate. B: yellow ochres fresco-applied (preparatory drawing). C: azurite in lime binder secco-applied (lime painting), with overlying heightenings in lead white. (f) Same microstratigraphy as the previous one, transmitted light, crossed polarizers.

scenes in the northern walls, always secco-applied with lime binder (Fig. 6). Heightenings were created by a thin spreading of lead white (rarely lime white), while shadings were usually made with a glazing of azurite.

3.3.3. Flesh

Flesh colours were generally obtained by applying a layer of yellow ochres in lime binder on a ground layer of green earth secco-applied (lime painting) on the underlying plaster. Super-

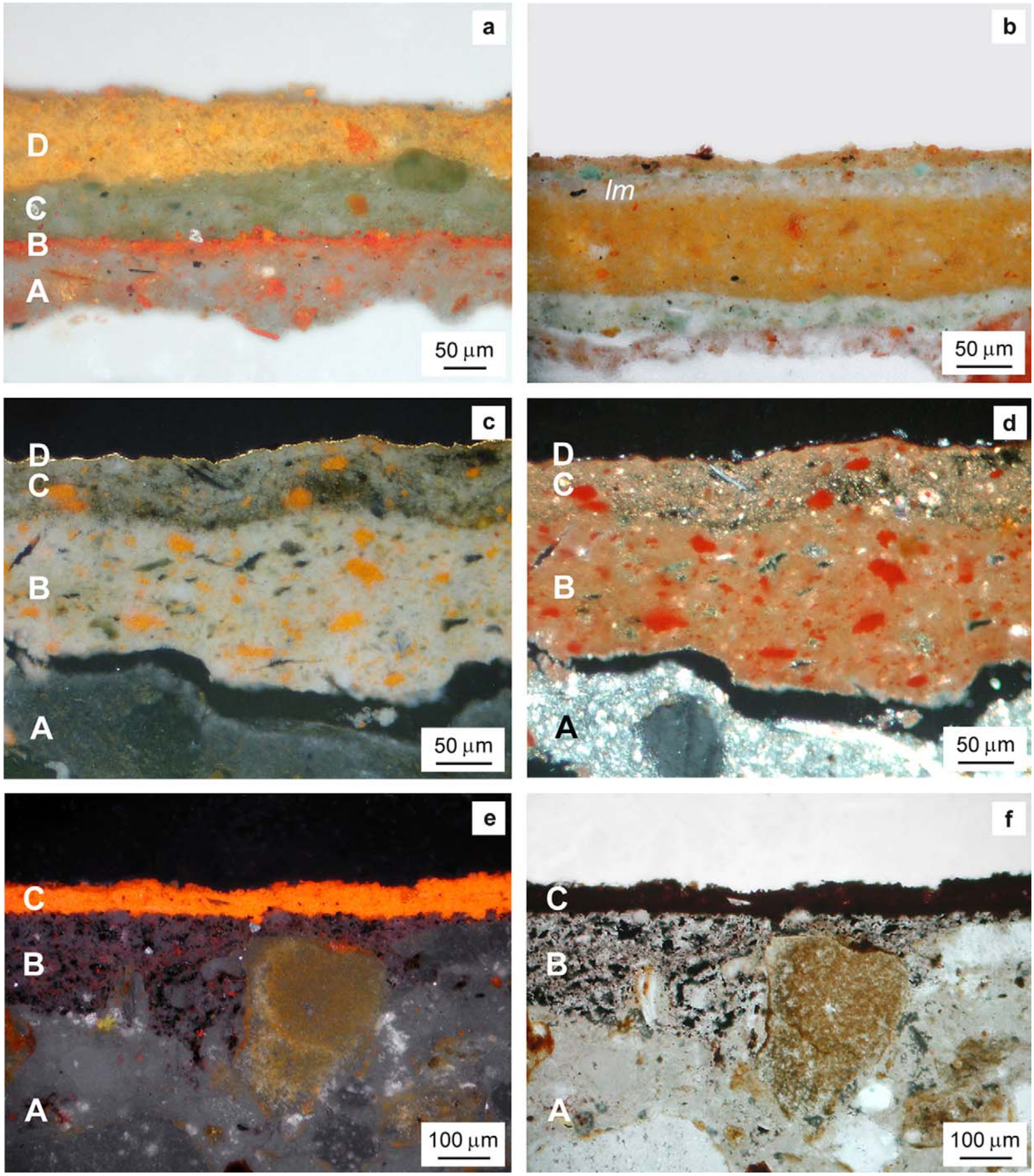

Fig. 10. Other significant microstratigraphies. (a) Microstratigraphy representative of flesh-chest of Christ in the *Crucifixion* scene (reflected light darkfield with bright background). A: lime plaster with sandy aggregate and cocciopesto. B: red ochres fresco-applied (preparatory drawing). C: green earth (lime painting). D: yellow ochres secco-applied with lime binder, with a fresco-applied superficial veil of red ochres and subordinately minium. (b) Repainting of the face of Mary Magdalene in the same scene (reflected light darkfield with bright background). The layers in the repainting are applied over a thin layer of lime –*lm*–, and they are repeated in the same sequence as the underlying layers but are much thinner. (c) Microstratigraphy representative of golden halos (reflected light darkfield). A: lime plaster with sandy aggregate. B: lead white, minium and probably verdigris in organic binder. C: lead white, minium, probably verdigris and unidentified micrograins in oily adhesive (missione). D: gold leaf. The entire paint film is detached from the plaster. (d) Same microstratigraphies as the previous one, transmitted light, crossed polarizers with converging lens. (e) Microstratigraphy representative of an orange frame in the scene *God asks Cain about the lot of his brother* (reflected light darkfield). A: lime plaster with sandy aggregate. B: coal black and rare red ochres in lime binder fresco-applied (fresco lime painting). C: minium fresco-applied on the underlying layer. (f) Same microstratigraphy as the previous one, transmitted plane polarized light.

ficial shades were obtained with yellow ochres, red ochres and, subordinately, minium and crocoite fresco-applied on the underlying layer (Fig. 10a,b).

3.3.4. Halos

In golden halos, the gold leaf (thickness of about 1 μm) is applied on a ground preparation composed of lead white, minium, probably verdigris and unidentified micrograins in an oily adhesive (missione; Fig. 10c,d): these are the materials cited by Cennini (chapters CLI–CLII) to make the mordant gildings, in which the lead-based pigments serve to accelerate the drying of the oil [10].

In orange halos, the paint film mainly consists of a single layer of minium, sometimes accompanied by crocoite (Fig. 3f).

3.3.5. Decorative elements

It is not easy to provide a representative characterization of the decorative elements, since they are very different both from the iconographic point of view and in regard to the materials and painting techniques. As an example, the microstratigraphy of an orange frame is shown in Fig. 10e,f.

4. Painting techniques

The painted walls contain plaster joints with a specific horizontal and vertical trend that usually follows the frames of the different scenes. The sequence of execution of the paintings is inferable from the way the joints overlap: one can observe a series of horizontal bands succeeding each other in the single walls of the room from top to bottom and from left to right, indicating a "pontate" method of execution.

There is no evidence of extensive and detailed sinopias underlying the plaster. Nevertheless, although arriccio is lacking, we cannot state that they are completely absent, since there are cases of medieval frescos (Winchester Cathedral, *Stories of Isaac* and *Stories of the Passion* in the Upper Basilica of Assisi) in which the sinopia was drawn directly on the wall surface [12,20,21,30]. In the paintings under study, the loss of large areas of plaster in the *Nativity of Jesus* revealed sporadic signs on the brickwork that must have served to delineate some essential parts of the composition.

Anyway, the scenes were painted on the thin plaster lying directly on the brickwork, often following the preparatory sketches realized with thin layers of ochres applied directly to the fresh plaster.

The pigments were applied by means of the following basic painting techniques: (a) *fresco* (including the variant *lime fresco painting* as defined in [21]); (b) *tempera*; (c) *lime painting* (a technique performed on dry plaster like the preceding one). As shown by the microstratigraphies, these basic techniques were often combined with each other according to the desired pictorial effects or the specific characteristics of the pigments used.

Recognition of the painting techniques was based on thin section in Figs. 9 and 10 microscopy, which allows direct investigation of the ways the various stratigraphic units of the paint film were applied via the examination of reference specimens. The main characters of the various techniques are discussed below.

The classic fresco technique is characterized by the heavy accumulation of pigments in the paint layer. In transmitted plane polarized light with high magnification, some pigments occasionally betray the microcrystalline structure characteristic of the carbonate binder. It is also possible to observe the adaptation of the pigment layer to the texture of the plaster, i.e. it appears thinner in correspondence to aggregate elements near the surface of the plaster, while it thickens in correspondence to binder (Fig. 9c,d). The latter characteristic is even more evident in the lime fresco, where the pigments mixed in lime milk variably penetrate the plaster until they become an integral part of it (Fig. 10e,f). It should also be mentioned that cocciopesto plaster was a limiting factor in the use of the fresco technique, because of its colouration and hydraulic properties which accelerate the process of carbonation.

In the two secco techniques, tempera and lime painting, the contact between the plaster and overlying paint film is usually clear and is prevalently rectilinear. Identification of the binder is obviously crucial for their recognition. In lime painting, the carbonate binder containing the pigments is easily distinguished with the polarizing microscope; if the paint film lies on the plaster, there is an evident discontinuity at the contact, shown by the different optical properties and microstructural characters of the respective binders (in particular see Fig. 9f). The discontinuity is often highlighted by a very thin line, of dark colour under the polarizer and with high reflectance, present on the carbonate surface of the plaster (Fig. 3b). Preliminary analyses with the transmission electron microscope (Department of Earth Sciences, University of Siena, Italy) revealed a much finer granulometry (average 10–20 nm) than that of the microcrystalline calcite forming the binder of the plaster (average around 0.5–1 µm). In general, the tempera-applied paint film also presents the aforesaid discontinuity with the supporting surface (see for instance Fig. 9a). Organic chemistry is necessary for the precise recognition of this painting technique. In favourable cases, microscopic observations allow at the most the recognition of the presence of microcrystalline calcium oxalate (weddellite), deriving from the transformation of the original organic binder.

Finally, we should mention the relative frequency in the mixed techniques of thin fresco- or secco-applied layers (veils) to complete some pictorial elements, e.g. heightenings in clothing (Fig. 9e).

The petrographic method generally provided important information about the painting techniques (especially those using lime binder), as it is based on the evaluation of several parameters. However, it has two main limitations: the reduced scale of observation and the need of supporting investigations in some circumstances. The first limitation is due to the fact that a thin section of a paint film (especially one spread over a large surface area) might not be sufficient to make a reliable diagnosis that can be extrapolated to the whole surface. Hence, two or more microfragments sampled far apart should be analysed. The second limitation refers to the fact that organic chemistry is sometimes essential to identify the specific nature of the organic binders and also of possible organic substances added to the lime binder. In several cases, pigments considered very incompatible with the alkaline environment and humidity for their alterability, such as lead white, cinnabar, minium and azurite, were found fresco-applied or as lime painting. To overcome this incompatibility, protein or oily organic substances were probably added to protect the pigments, as often found in other contemporary wall paintings [18,21].

5. State of conservation

The main types of alterations that affected the wall paintings before the restoration are listed in Table 3, were they are related to the types of processes that probably caused their formation. Some significant images are shown in Fig. 11, together with an example of GIS mapping of the preservation status.

The alteration processes are closely related to the complex history of the paintings. The following brief discussion is a chronological outline of the main circumstances.

The early use of the room as a religious site, certainly no later than the first half of the fourteenth century, is shown by blackenings due to soot deposits from burning candles or oil lamps, essentially concentrated in proximity to the frame separating the scenes from the faux marbles dados. Chromatic alterations in the form of scattered red haematite stains, due to dehydration of the Fe-oxyhydroxides caused by the heat of the flames acting on the yellow ochres, are associated with the blackenings in the decorative yellow bands. The transformation occurs at about 270–300 °C, depending on various factors [31–33].

In a later phase, the degradation of the paintings led to repainting of the damaged areas during the first half of the fourteenth century. Thus, many of the faux marble dados present a layer of new plaster on which the original geometric motifs were replicated, sometimes with simplified decor; in the scenes of the *Crucifixion*, the *Deposition from the cross* and the *Deposition in the sepulchre*, the repainting was extended to various parts of the figurations, with repainting of the backgrounds, some persons (e.g. Fig. 10b) and some draperies directly on the original layers. The extent of these repaintings will be assessed in the current restoration.

Other human-induced alterations, like marks, drawings and inscriptions improperly engraved on the paintings, belong to an even later period, related to the abandonment of the room as a religious site and the extension of the work on the Cathedral.

The demolition of the painted vaulted ceiling and the gradual filling of the room with rubble, begun in the mid-fourteenth century, certainly caused the main mechanical alterations, due to abrasive and compressive processes responsible for most lacunae in the paint film and the supporting plaster.

The processes that occurred throughout the more than six centuries of burial are not easy to infer; we can assume that physico-chemical and biological processes produced salt crystallisation phenomena (mostly gypsum, visible in Fig. 11b), biological patinas (in zones with greater persistence of humidity) and some chromatic alterations (mainly transformation of the blue of the sky into green shades, due to the azurite–paratacamite or azurite–malachite transition). These processes were certainly related to the variable environmental conditions, e.g. those in the sector adjacent to the burial place starting from the eighteenth century (western wall), to which can be attributed the local abundance of nitrates on the painted surface, and those of the wall underlying the three large scenes of the *Crucifixion*, the *Deposition from the cross* and the *Deposition in the sepulchre*, which was in direct contact with fairly permeable bedrock (partially cemented sands). With regard to that, we should point out that chemical and physical characters of the plaster with cocciopesto used this wall must have favour the development of wide spread detachments of the plaster from the brickwork, which, in this case, show by far a major extent in comparison with those present in the other walls where the plaster does not contain cocciopesto.

Lacunae and detachments of the paint film could also be due to causes intrinsic to the painting techniques: the secco-applied paint films (tempera or lime painting) generally appear less durable than the fresco-applied films. In tempera-applied paint films, the loss of organic binders is very evident in microscopic observations, and is seen macroscopically as pulverization due to loss of cohesion of the pigment. This is particularly evident in the areas of azurite representing the sky and, more specifically, in the three large scenes of the *Crucifixion* and the *Depositions*, where the secco techniques prevail.

Nevertheless, for some aspects and/or some sectors, the burial of the wall paintings likely had a conservative action.

Removal of the debris in 2000–2001 probably caused a change in the thermo-hygrometric conditions and a sudden release of pressure. These factors have further developed the detachments of the paintings from the masonry, especially in the situations already precarious like those of the three large scenes (preventive lime in-fillings were realized to restrict the loss of portions of the paintings).

Table 3
The main types of alterations visible on the paintings before the restoration intervention, related to the processes that probably caused their formation

<table>
<tr><th>Mainly physico-chemical alterations</th><th>Mainly mechanical alterations</th><th>Human-induced alterations</th><th>Biological alterations</th></tr>
<tr><td colspan="2">Lacunae of the paint film (partial or total)</td><td>Superficial opacity due to dust deposits</td><td>Biological patinas</td></tr>
<tr><td colspan="2">Detachment of the paint film from the plaster</td><td>Marks, drawings and inscriptions improperly engraved on the plaster</td><td></td></tr>
<tr><td colspan="2">Detachment of the plaster from the brickwork (sometimes with camberings and cracks)</td><td>Blackening due to soot deposits</td><td></td></tr>
<tr><td>Salt crystallization (efflorescences, blistering, encrustations)</td><td>Lacunae of the supporting plaster, sometimes with underlying brickwork visible</td><td></td><td></td></tr>
<tr><td>Chromatic alteration of the paint film due to mineralogical transitions of the pigments</td><td>Diffuse and irregular abrasions of the paint film and the plaster</td><td></td><td></td></tr>
<tr><td></td><td>More or less deep scratches</td><td></td><td></td></tr>
</table>

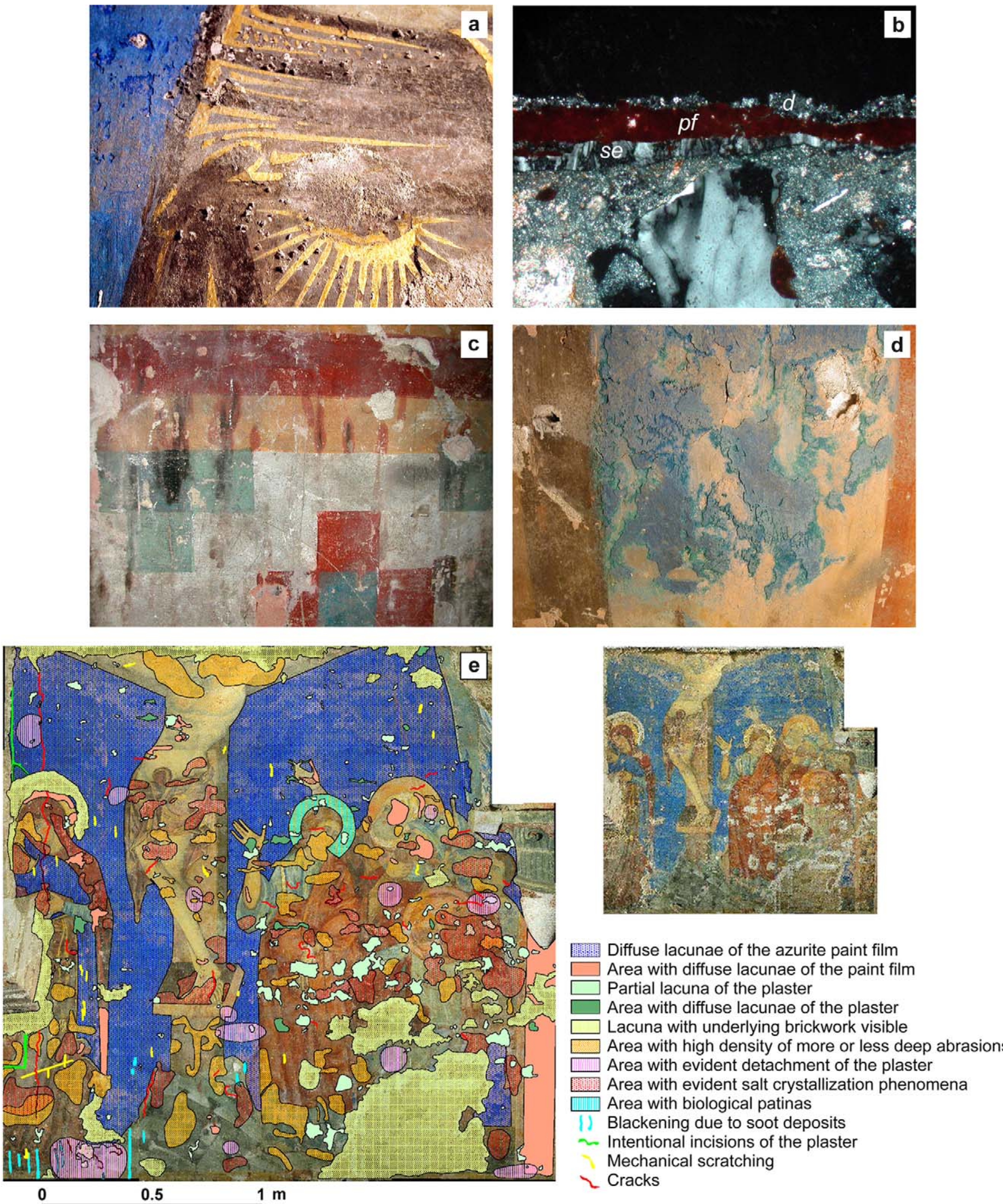

Fig. 11. Images showing the conservation status of the paintings. (a) Macroscopic appearance of salt crystallisation phenomena (blistering and efflorescences). (b) Thin section image of subefflorescences *–se–* with dust deposits *–d–* involving the paint film *–pf–*. (c) Blackening due to candle flames and diffuse red stains due to transformation of Fe-oxyhydroxides in the yellow ochres into haematite. (d) Lacunae in the plaster and diffuse partial or total lacunae in the double-layered azurite film, with evident transformations into paratacamite and sometimes malachite. (e) GIS mapping of the conservation status of the *Crucifixion* scene. The mapping refers to the conservation status before restoration, except for the preventive lime in-fillings performed immediately after the discovery of the paintings. These in-fillings usually coincide with the perimeter of the larger lacunae of the plaster. The opacity of the surface (due to dust deposits) and the diffuse areas of transformation of azurite into paratacamite-malachite were not mapped. The portions of the mapping lacking key symbols have negligible degradation.

The burial and recent restructuring of the room led to a diffuse opacity of the surface of the paintings, due to adhesion of dust deposits.

6. Concluding remarks

The thirteenth century wall paintings found under the Siena Cathedral constitute an unusually important pictorial cycle within the panorama of late medieval painting. The many aspects dealt with in this study of the materials used, the painting techniques and the state of conservation are very useful to provide technical and philological support of the current restoration.

One of the most important results is the discovery of crocoite and chrysocolla, whose use in European medieval paintings was not known until now. The peculiar history of the paintings and the position of the pigments in the paint film make it certain that we are dealing with original colours or, at most, colours used in repainting before the middle of the fourteenth century. The finding of crocoite (very probably of natural origin) is of particular historical-scientific importance, and it opens a new chapter in our knowledge of the use and availability of this pigment in ancient times.

Important from the methodological perspective is the development of a petrographic method for the study of the painting techniques and microstratigraphies, which have been described in detail for the most significant figurative elements.

In future, since the restoration work is only a little more than half completed, the mineralogical-petrographic approach will be further developed and supplemented with other methodologies and also used to resolve specific problems of conservation.

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