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DECAY OF RED PIGMENTS ON A WALL PAINTING ADORNING THE CHURCH OF 'SAN FRANCESCO DEI CAPUCCINI' IN RACCONIGI (ITALY): ARCHAEOMETRIC SURVEY AND RESTORATION INTERVENTION

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ABSTRACT

An archaeometric survey allowed to understand the causes of an atypical ongoing decay, manifested by a 19th century fresco of an unknown artist titled 'The divine adoration of King St. Louis IX', held in the Church of 'San Francesco dei Cappuccini', in Racconigi (Northwestern Italy). The wall painting suffered of a diffuse darkening, principally affecting the red garments and flesh of some of the portrayed religious characters. The adopted multi-analytical approach (consisting of X-ray powder diffraction, micro-Raman and FT-IR spectroscopies) pointed out that the causes of the manifest darkening were represented by multiple, strictly intertwined factors. In particular, a partial but progressive blackening of the red pigments had occurred, due to an incipient conversion of hematite (Fe_2O_3) into magnetite (Fe_3O_4). Such a transformation, possibly confined in a very thin, superficial and discontinuous film on the pigmented layers, had been favoured by an ongoing sulfation - and consequent alteration of calcite into gypsum due to exposure to gaseous sulfur compounds (SO_2 and SO_3), produced after the burning of oil in votive lamps, candles and incense positioned directly below the artwork. In addition, these combustions caused a significant amount of particulate (soot and powders) to cumulate on the fresco surface, thus contributing to generally enhance the dimming of the whole painting. These results gave way to a restoration intervention, which removed most of the gypseous efflorescences and particulate from the artwork surface, thus rendering at best its original chromatic aspect and brilliance. While performing these operations, the signature of the presumed artist - identified as Dionigi Faconti, a renowned Italian painter of the 19th century - and the date of realization of the artwork (1852) were recovered.

KEYWORDS: wall painting, pigment, hematite, magnetite, sulfation, particulate.

1. INTRODUCTION

It is well known that polluted atmosphere may affect the state of conservation of artworks and historical buildings, causing mineralogical changes (Maguregui *et al.*, 2009; Aramendia *et al.*, 2012). The alteration of pigments in wall paintings can be caused by environmental factors, such as light, humidity, pH, and microbial activity, often assisted by the consequent action of specific stressors, such as soluble salts deriving as either impurities from the constituent materials (wall, plaster and paint) or external contaminants. A chemical and biological deterioration, therefore, may contribute – acting alone or together – to damage these important works of art (Ciferri, 1999; Mugnaini *et al.*, 2006; Kotulanová *et al.*, 2009).

Some pigments, in particular, may undergo specific deterioration processes, according to their peculiar physical-chemical properties and the environmental conditions in which the artworks are conserved. Frescoes, in particular, due to their wide surface area, are subjected to the direct exposure of numerous local factors, such as heat (Rickerby, 1991), aggressive gaseous agents (e.g., SO₂ and SO₃; Maguregui *et al.*, 2014), dust, intense light sources and smoke (e.g., due to the burning of candles, in religious buildings). The role of sulfur (brought by water infiltrations and/or atmospheric pollutants, causing formation of gypsum crusts as well as other decaying processes) and saline efflorescences (favoured

by moisture or wall dampness) is essential in favouring phase transformation and diversification, often coupled to mechanical weathering (i.e., cracking and spalling, due to salt crystallization, icing/deicing cycles or sulfation) (Steiger, 2002; Camuffo, 2014). All these factors may contribute in causing a sensibly enhanced alteration of the painted layers, commonly coupled to a loss of the original chromatism. Some earlier archaeometric work on the wall painting has been made (Salama *et al.*, 2016; Helmi *et al.*, 2016; Gutman *et al.*, 2016).

This study describes an atypical colour alteration and decay of pigments undergone by a fresco held in the Church of ‘San Francesco dei Cappuccini’, in Racconigi (Italy). A detailed scientific survey was performed with a multi-analytical archaeometric approach, in order to thoroughly understand the related causes and mechanisms. These results played a fundamental role in choosing the most adequate procedures for an effective restoration intervention.

2. MATERIALS AND METHODS

2.1. Case study and materials

The Church of ‘San Francesco dei Cappuccini’ (*‘St. Francis of the Capuchins’*) (Fig. 1) is located in Racconigi, near Cuneo, in the Piedmont region, Northwestern Italy.



Figure 1. The Church of ‘San Francesco dei Cappuccini’ (*‘St. Francis of the Capuchins’*), located in Racconigi, near Cuneo, Piedmont region (Northwestern Italy).

The edifice was built in 1625 and soon hosted the local order of the Capuchin monks, who significantly helped the population during the black plague in 1630. The monastery housed an important seminary school, supplied with an important library. After the suppression of religious orders dictated by Napoleon (1802-1805), the building was sold to private citizens. In 1827, however, it was partly given back to the monks and only two years later, the prince Carlo Alberto di Carignano financed the purchase of the residual portion. In 1846 it was enlarged, a new façade was built and in 1872 the education of the novices was re-established there. The Church is composed of a single central nave surrounded by six chapels. The 'Immacolata' chapel is the most important one, with an altar surrounded by elegant columns in walnut wood. In the presbytery, two religious wall paintings (approximately 3.80 m wide and 2.90 m tall) of an unknown artist adorn both sides of the altar, at a height of about 5 m from the floor. The one on the right, almost facing the altar, is named the 'Glory of the Immaculate among celestial choirs' – with no sign of alteration. The one on the left is titled the 'The divine adoration of King St. Louis IX' and portrays several characters (Fig. 2a): in the back row, St. Louis IX, King of France (who participated in the crusade promoted by Innocent IV and died in Tunis in 1270) stands on the left, with an adoring posture. In front of him, on the right, is St. Elizabeth of Hungary (widow of Louis IV, duke of Turingia) wearing a mourning red tunic – affected by severe darkening. At the extreme right, kneeling, the blessed Caterina De Mattei from Racconigi ap-

pears (a Dominican nun); on her left, also in front and kneeling, is St. Ludovic (Bishop and Franciscan Friar). In front, kneeling on the left, is the blessed Ludovic from Savoy (a Clarisse). Of the two cherubs in the centre, the one on the back holds a shield with a cross, sided by a helmet (the weapons of Louis IX). The cherub in front holds in his left hand a book with the insignia: 'FACITE JUDICIUM ET IUSTITIAM ET DILIGITE PAUPERES' ('hold judgement and justice and love poor people'). This fresco, unlike the other one, was affected by quite a disturbing decay. Besides being widely dimmed by the heavy deposition of fine particles on the whole artwork surface (incoherent deposits from smoke and powders, such as soot, ashes and mineral dust), an additional, peculiar darkening selectively affected some specific areas painted in red and/or pinkish hues, presumably symptomatic of an ongoing degradation of the related pigments. In particular, this dusky effect – apparently permeating the pigmented layers and sensibly stifling the brightness of the original colours – was especially marked on the grieving red tunic and skin (face, neck and hands) of St. Elizabeth of Hungary. In addition, a severe depletion affected some parts of her visage (e.g., below the chin and ear) and hair, due to a drastic pigment loss (see magnification in Fig. 2b). Such a situation brought the Capuchin Monks, financially supported by the local authorities, to request the help of both Conservation Scientists and Restorers, in order to possibly understand the causes of such a phenomenon and plan an effective restoration intervention.



Figure 2. 'The divine adoration of King St. Louis IX' fresco, as it appeared before restoration. a) global view: a general dimming is observed on the whole artwork surface, presumably due to the deposit of soot, ashes and dust. b) magnification of St. Elizabeth of Hungary, in which the specific blackening of the red pigments on the tunic and flesh, as well as the severe pigment loss on the visage (under the chin and ear) and hair, can be better appreciated. Areas subjected to sampling are contoured by dashed lines (numbering detailed in the text).

2.2. Sampling procedure and Methods

A multidisciplinary archaeometric protocol was used, which includes the combined application of multiple analytical methods, in order to thoroughly characterize all constituent materials and decay products. Such an approach involves the sequential application of diffraction and spectroscopic techniques (X-ray powder diffraction and vibrational spectroscopies, such as Raman and FT-Infra Red); these methods – despite their micro-destructivity, as related to the extraction of micro-fragments from the works of art (a procedure adopted in the current work) – provided an adequate diagnostic of the investigated case study.

A preliminary examination showed that most of the painting had been realized with the ‘*a fresco*’ technique – the different ‘*giornate*’ being at times distinguishable. However, some areas are clearly visible in which later ‘*a secco*’ interventions were performed – consequent to retouches after second thoughts of the artist (once the artwork was finished) or restoration attempts.

Pictures of the wall painting were taken by mounting a TL-D/08 ‘Blacklight Blue’ filter and UV lamp on a Nikon D3200 AF-S DX 18-55 mm digital camera, in order to test the fluorescence response from the painted surface.

Specimens for analyses were collected, whenever possible, by following the Italian legislation (DL Normal 3/1980), using sterile bistoury, tweezers and glass-fibre brush directly on the fresco surface. Strict limitations, however, were imposed, as the upholders recommended that sampling collection could be performed only by ensuring that such an operation implied no visible damage – not even negligible – to the artwork. Therefore, only tiny fragments from the very superficial layers of the fresco – i.e., those subjected to the impending decay – were collected (thus including superficial particulate and carbonate layer, pigment particles and related degradation products). Conversely, no sample for complete stratigraphic analyses (comprehending all painted layers and underlying preparatory substrate) could be extracted – so not to create detectable “holes”, albeit tiny, on the artwork surface.

Representative, submillimetric fragments (few mg each) were extracted from the superficial coatings of some red and red-to-pinkish areas, undergoing an evident darkening apparently due to presence of a sort of dimmer, surface patina – especially on the tunic (yellow dashed areas, labelled ‘1’ and ‘2’ in Fig. 2.b) and skin (yellow dashed areas, labelled ‘3’, ‘4’ and ‘5’ in Fig. 2.b) of St. Elisabeth of Hungary. Particular care was adopted in order to check presence of red pigment particles in each of the collected

samples. For comparative purposes, specimens from clean portions of the same areas were also collected (white dashed areas, labelled ‘6’ and ‘7’ in Fig. 2.b), adopting the same precautionary methods described above. Moreover, samples from some ‘*a secco*’ retouches were also extracted (green dashed areas, labelled ‘8’ and ‘9’ in Fig. 2.a), so to compare their pigment distribution with that of the rest of the painting. All specimens were placed in sterile tubes before analyses, in order to avoid possible contamination.

X-ray powder diffraction (XRPD) data were collected in the 3-70° 2 θ range (angular increment: 0.02° 2 θ ; dwell-time: 5 s) on powdered samples, obtained by finely crushing in an agate mortar a fraction of the collected tiny fragments. An automated Siemens D-5000 diffractometer with $\theta/2\theta$ setup in Bragg-Brentano geometry was used, with graphite monochromatized Cu-K α radiation and a zero-background flat sample holder; experimental conditions were maintained constant during data collection for all specimens. Data were processed with the Diffrac Plus (2005) software (EVA 11, 0 0, 3).

Raman spectra were recorded with two different instruments: a) Horiba Jobin Yvon Labram HRVIS spectrometer (filter: edge; integration time: 10 spectra/5 seconds), by exciting with a 633 nm laser, and b) inVia Raman Microscope (Renishaw; filter: edge; integration time: 10 spectra/5 seconds), with an excitation line of 532 nm. Data were collected directly on the extracted fragments, by using a confocal Olympus BX41 microscope with a magnification of 100 X with the Labram HRVIS instrument, and an objective of 50 X, with a numerical aperture of 0.75 with inVia Raman instrument. A laser power of 0.01-0.1 mW was adopted, in order to avoid any possible transformation in Fe oxides induced by the laser energy (Hanesh, 2009).

Fourier-Transform Infra-Red data were acquired with a Bruker Vertex 70 spectrophotometer coupled with a Hyperion 3000 microscope, in Attenuated Total Reflectance (ATR) mode. For any sample, 64 spectra were recorded with a resolution of 2 cm⁻¹.

3. RESULTS

A preliminary survey, performed prior to the archaeometric approach, proved that by softly wiping the fresco surface with a dry ‘wishab’ sponge, a faint blackish residue was released – especially from the darkened areas. This superficial, incoherent deposit has to be related to the presence of ash, soot and mineral dust on the surface of the wall painting, unequivocally contributing to the global darkening and loss of colour brilliance of the artwork. In addition to this general dimming effect, a further contribution was represented by a specific decay particularly af-

fecting the red pigment(s), for the understanding of which apt scientific analyses had to be performed. Moreover, by illuminating the wall painting with a UV radiation lamp, a certain fluorescence was observed in some areas, suggesting that a fixative material might have been spread (e.g., above the cherub holding the red-crossed shield, where 'a secco' retouches had been made).

3.1. X-ray powder diffraction (XRPD)

XRPD allowed a detailed characterization of all mineral phases representing the colourizing agents and constituent materials in the extracted specimens (Table 1). Besides, such an approach was also capable of diagnosing the feasible causes of the decay affecting the investigated fresco.

As far as the tunic of St. Elizabeth of Hungary is concerned, the diffraction patterns of those samples extracted from the clean area (labelled '6' in Fig. 2b), marked by a vivid red colour and lack of darkening (thus apparently not subjected to decay), show an indisputable presence of predominant hematite (Fe_2O_3). Traces of cinnabar (HgS) were also possibly detected, thus contributing to enhance the brilliancy of the red hue on the garment. Marked reflections of another reddish-to-yellowish agent were also observed – namely 'Naples Yellow' (or lead antimonate),

an artificial pigment used extensively by the Old Masters and well into the 20th century, akin to the mineral bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_7$). Presence of talc, often used as a filler or inert in works of art, may be related either to the pigmented or to the preparatory layers. Calcite was obviously detected, together with traces of gypsum and anhydrite – likely to be related to an incipient sulfate attack. Patterns of slightly worse quality were recorded in the darkened areas of the tunic (labelled '1' and '2' in Fig. 2b), in which the same phases cited above can be distinguished – and others testified by fainter reflections (Fig. 3). Among these, the feasible presence of small amounts of magnetite (Fe_3O_4) is worth mentioning – ascertained by the detection of two shoulders corresponding to the (220) and (311) strong reflections at $2\theta \approx 29.94^\circ$ and 35.40° respectively, siding the (100) and (110) peaks of bindheimite and hematite respectively (see Fig. 3, magnification in the upper right corner). Moreover, a presumed slightly higher amount of gypsum might characterize the darkened areas, rather than the clean ones, as apparently suggested by the mutual intensities of the related reflections in the different XRPD patterns. Presence of anglesite (PbSO_4) is dubious, as its reflections (if any) would be overlapped to those of other phases.

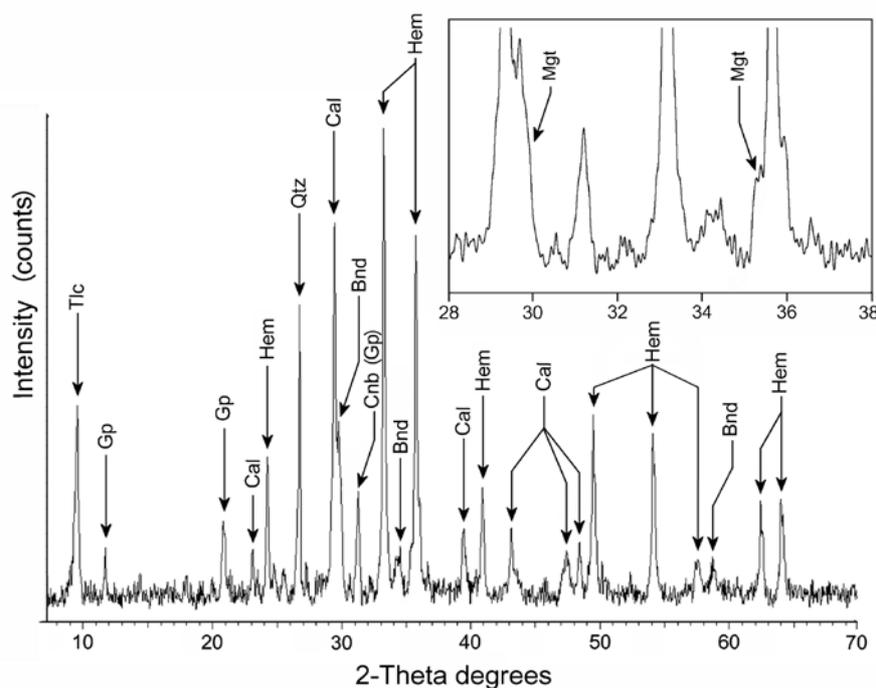


Figure 3. XRPD pattern collected on a specimen extracted from the darkened areas of St. Elizabeth's red tunic [mineral abbreviations reported, whenever possible, according to Siivola and Schmid (2007) as follows: Tlc = talc; Gp = gypsum; Cal = calcite; Hem = hematite; Qtz = quartz; Bnd = bindheimite ('Naples Yellow'); Cnb = cinnabar]. Presence of slight amounts of magnetite (Mgt: Fe_3O_4) is highlighted in the pattern magnification reported in the upper right corner.

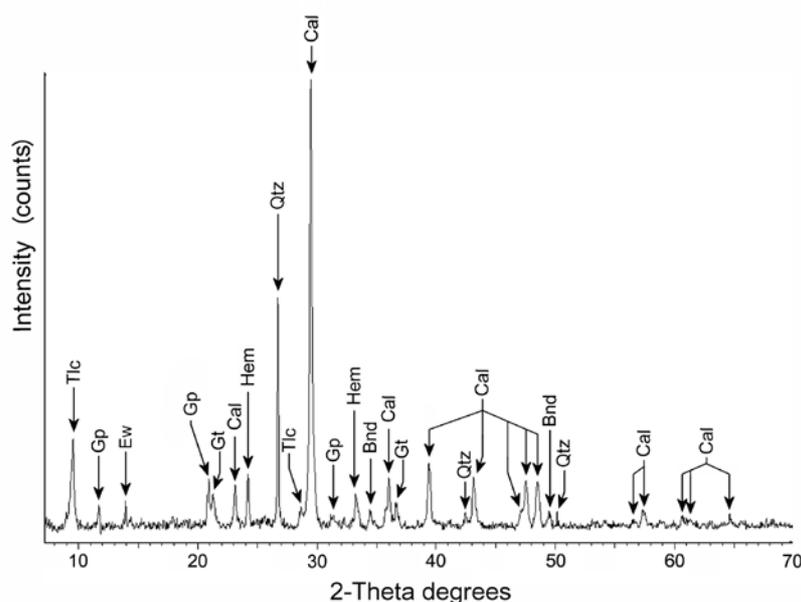


Figure 4. XRPD pattern collected on a specimen extracted from the clean areas of St. Elizabeth's flesh [mineral abbreviations reported, whenever possible, according to Siivola and Schmid (2007) as follows: Tlc = talc; Gp = gypsum; Cal = calcite; Hem = hematite; Qtz = quartz; Bnd = bindheimite ('Naples Yellow'); Ew = ewaldite; Gt = goethite].

The exam of the flesh-coloured areas of the fresco, unaffected by evident darkening (labelled '7' in Fig. 2b), proved that by diluting the predominant hematite (possibly mixed to the other red-to-yellowish pigments) with CaCO_3 a pink colour was obtained, used to render the hue of the skin (Mazzocchin *et al.*, 2003). The degree of this dilution is marked by a systematic decrease in the intensity of those reflections related to hematite (if compared to the XRPD patterns of the tunic), accompanied by an enhancement

in those of calcite (Fig. 4). Again, presence of 'Naples Yellow' is evident whereas that of cinnabar dubious – as is that of goethite [$\text{FeO}(\text{OH})$]. Use of talc as a filler is confirmed. The XRPD patterns of the darkened rose-pink areas on the flesh (labelled '3', '4' and '5' in Fig. 2b) show no evident difference from the clean ones: the same minerals are detected, together with modest amounts of gypsum and anhydrite, which account for an incipient sulfate attack (Table 1).

Table 1. List of mineral phases, as resulting by XRPD, of crushed specimens extracted from the red and red-to-pinkish painted areas of the tunic and flesh of St. Elizabeth of Hungary, and from areas in which 'a secco' retouches had been made (legend for reflections intensity: VS = very strong; S = strong; M = medium; W = weak; VW = very weak; ??? = dubious).

Mineral phase/Chemical compound (crystal-chemical formula)	Red tunic of St. Elizabeth of Hungary		Flesh and skin of St. Elizabeth of Hungary		'A secco' re- touches
	clean areas (not darkened)	dar- kened areas	clean areas (not darkened)	dar- kened areas	
calcite (CaCO_3)	S	S	VS	VS	VS
gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	W	M	W	W	M
anhydrite (CaSO_4)	VW	VW	VW	???	W
quartz (SiO_2)	M	M	W	M	M
hematite (Fe_2O_3)	VS	VS	W	W	M
cinnabar (HgS)	VW	M	???	???	VW
bindheimite ('Naples yellow'; $\text{Pb}_2\text{Sb}_2\text{O}_7$)	M	M	M	W	=
talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$]	M	M	VW	M	M
magnetite (Fe_3O_4)	VW(?)	W	???	???	=
anglesite (PbSO_4)	???	???	=	=	=
metacinnabar (HgS)	=	???	=	=	=
graphite (C)	=	???	=	???	=
goethite [$\text{FeO}(\text{OH})$]	=	=	=	=	M
muscovite [$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$]	=	=	=	=	W
ewaldite [$\text{BaCa}(\text{CO}_3)_2$]	=	=	=	W	W
weddellite ($\text{C}_2\text{CaO}_4 \cdot 2\text{H}_2\text{O}$)	=	=	=	=	W

Samples extracted from the 'a secco' areas (labelled '8' and '9' in Fig. 2a) evidenced presence of hematite as above – and possibly also cinnabar. However, no 'Naples Yellow' was detected, but rather a significant amount of goethite [FeO(OH)]. In addition, weddel-

lite ($\text{C}_2\text{CaO}_4 \cdot 2\text{H}_2\text{O}$) was found in some samples, perhaps related to an oxalate patina. Calcite and talc were observed, together with moderate amounts of gypsum. No traces of fixative materials were found.

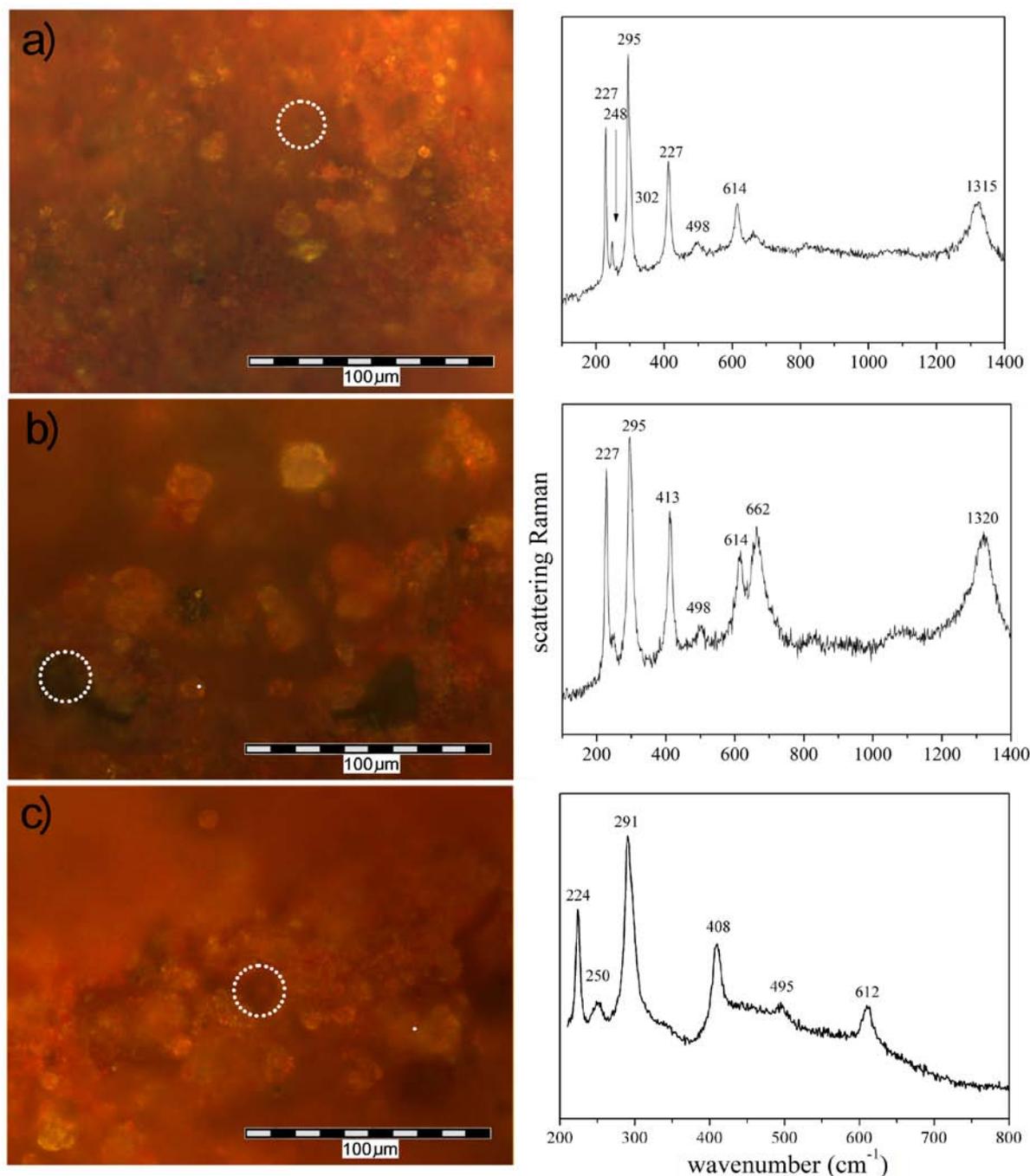


Figure 5. Microphotographs of red pigment grains sampled from the artwork surface, coupled to the related μ -Raman patterns (spot analyses contoured by dashed circles): a) a homogeneous red coat, showing most of the typical phonon signals and magnon band of hematite (Fe_2O_3); b) in those areas where distinct brown-to-blackish grains are visible, an additional band at 662 cm^{-1} appears amidst the modes of hematite, which has to be related to presence of magnetite (Fe_3O_4); c) at times, a broad signal at 250 cm^{-1} is detected on the surface of some red pigment grains, related to presence of cinnabar (HgS).

3.2. Vibrational Spectroscopies

Several small fragments, extracted from the surface of the 'a fresco' painted layers in both the clean and darkened areas of St. Elizabeth's tunic and flesh, together with others from the 'a secco' retouched areas, were analysed with vibrational spectroscopies (Micro-Raman and FT-IR). All detected constituent materials and degradation products are listed in Table 2, together with the wavenumbers of the related vibrational modes.

3.2.1 Micro Raman

By disposing of a μ -Raman, several spot analyses were collected for each specimen, basing on the colour of the pigments; particular care was taken in analysing those grains marked by red or black-to-brownish colours (Fig. 5). For what concerns the red garment of St. Elizabeth, the clean red-coloured grains sampled from area '6' (Fig. 2b) show the Raman signals typical of α -Fe₂O₃ (de Faira *et al.*, 1997; Bouchard and Smith., 2003; Legodi and deWaal, 2007; Cheilakou *et al.*, 2014). In particular, the most intensely coloured ones show all seven phonon signals (namely two Ag: 227 and 498 cm⁻¹; five Eg bands: 248, 295, 302, 413 and 614 cm⁻¹), together with the magnon band at 1315 cm⁻¹ (Fig. 5a). All red grains, however, show the typical magnon bands (around 1305-1320 cm⁻¹) as well as the three strongest features at lower wavenumbers, though slightly red-shifted (i.e., Ag mode at 227, 221 and 217 cm⁻¹; Eg modes at 295, 285, 281, 413 and 401 cm⁻¹) – thus being unequivocally recognized as pure hematite.

As for the black-to-brownish grains, sampled from areas '1' and '2' of the tunic (Fig. 2b), the attribution is more problematic due to an overlapping of the Raman signals. Sporadically, however, some of

these 'darker' grains showed, together with features related to α -Fe₂O₃, signals indicative of magnetite, Fe₃O₄ – namely an intense band at 662 cm⁻¹ (de Faira *et al.*, 1997; Legodi and De Waal, 2007; Maguregui *et al.*, 2012; 2014; Fig. 5b). Small amounts of cinnabar are indeed present in some red pigment grains, though its detection is not always straightforward. In some cases, however, the most intense Raman-active mode of cinnabar is visible at 250 cm⁻¹ (Fig. 5c), undisturbed by other hematite signals. The weaker cinnabar band expected at 290 cm⁻¹, on the other hand, is systematically covered by the stronger signal of hematite located at around 291 cm⁻¹.

Some reddish grains were isolated from the pink-coloured areas (with darkened portions: '3', '4' and '5' in Fig. 2b) of St. Elizabeth's flesh, whose spectra contain six main features (231, 252, 299, 418, 500 and 618 cm⁻¹) attributable to α -Fe₂O₃. In addition, some grains also show a clear band at 396 and a weaker one at 305 cm⁻¹, possibly related to presence of α -FeO(OH) – goethite (de Faira *et al.*, 1997; Edwards and Chalmers, 2005; Cheilakou *et al.*, 2014). As far as the 'a secco' areas are concerned ('8' and '9' in Fig. 2a), some samples show signals (strong band at 543-555 cm⁻¹; weaker features at 261, 819 and 1097 cm⁻¹) related to presence of the oxalate ion (Bordignon *et al.*, 2008). In a single case, a complex spectral pattern was detected – possibly attributable to an (unidentified) organic medium (Table 2). All other samples bring features typical of α -Fe₂O₃ (bands at 229, 250, 295, 414 and 617 cm⁻¹), together with the occasional presence of talc (strong band at 677 and weak one at 381 cm⁻¹; Blaha and Rosasco, 1978).

Most samples, both in the 'a fresco' and 'a secco' areas, show typical bands at around 1330 and 1590 cm⁻¹, related to presence of carbon.

Table 2. List of mineral phases, as resulting by vibrational spectroscopies (micro-Raman and FT-IR) of tiny fragments extracted from the red and red-to-pinkish painted areas of the tunic and flesh of St. Elizabeth of Hungary, and from areas in which 'a secco' retouches had been made.

Mineral phase/Chemical compound (crystal-chemical formula)	Vibrational modes (cm ⁻¹)	Red tunic of St. Elizabeth of Hungary		Flesh and skin of St. Elizabeth of Hungary		'A secco' retouches
		clean areas	darkened areas	clean areas	darkened areas	
Micro-Raman						
hematite (Fe ₂ O ₃)	227, 248, 295, 302, 413, 498, 614, 1315	X	X	X	X	X
cinnabar (HgS)	250, 290(?)	X	X	=	=	=
talc [Mg ₃ Si ₄ O ₁₀ (OH) ₂]	381, 677	X	X	X	X	X
magnetite (Fe ₃ O ₄)	662	=	X	=	X	=
goethite [FeO(OH)]	305, 396	=	=	X	X	X
carbon	1330, 1590	X	X	X	X	X
organic medium (unidentif.)	1543, 1450, 1340, 1287, 1215, 1087, 985, 824, 782, 745, 690	=	=	=	=	X
ATR FT-IR						
gypsum	672, 1115, 1625	X	X	X	X	X
calcite	712, 875, 1430	X	X	X	X	X
quartz	780, 798, 1038	X	X	X	X	X
oxalate(s)	516, 1325, 1649	X	X	X	X	X

3.2.2 Fourier Transform Infra-Red

ATR FT-IR spectra were collected on the same grains analysed with μ -Raman, so to infer further information about the constituent materials and degradation products on the artwork surface (Table 2).

All recorded spectra show quite a homogeneous and repetitive pattern (Fig. 6). In particular, strong signals attributable to a carbonate (namely calcite, CaCO_3) are clearly detected. Besides, evident pres-

ence of Ca-sulfate, in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is testified by the systematic detection of the related modes at 1115 (very strong band), 1625 and 672 cm^{-1} (medium-strong signals).

In addition to signals related to quartz [1038 (very strong), 798 and 780 cm^{-1} (medium)], such an approach confirmed presence of oxalates (probably weddellite: $\text{C}_2\text{CaO}_4 \cdot 2\text{H}_2\text{O}$) on the artwork surface – an occurrence already hypothesized by XRPD.

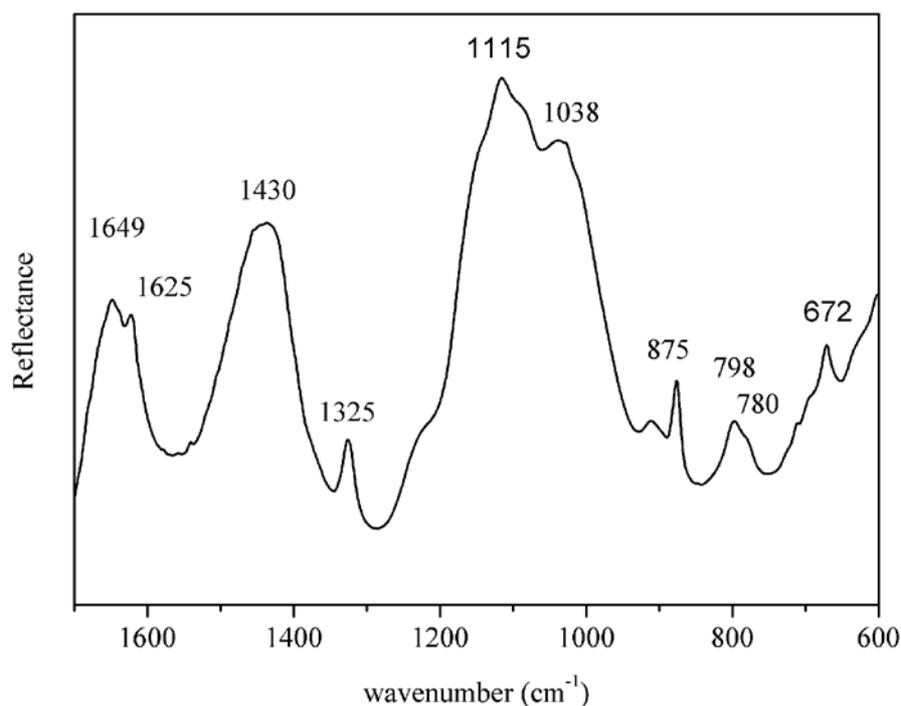


Figure 6. ATR FT-IR pattern collected on a grain sampled from the artwork surface, showing the signals typical of gypsum (672, 1115 and 1625 cm^{-1}), calcite (875, 1430 cm^{-1}), quartz (780 and 798 cm^{-1}) and oxalates (1325 and 1649 cm^{-1}).

4. DISCUSSION

The archaeometric study performed on the 'The divine adoration of King St. Louis IX' fresco identified two causes as the main responsible for the darkening and loss of brilliance observed on its surface: a) a partial but progressive alteration of the red pigments, accountable for a specific blackening of the red areas; b) the presence of a surface particulate layer (i.e., soot, ashes and powder), coupled to an incipient sulfation, responsible for a general and diffuse dimming of the whole artwork.

4.1. Alteration of the red pigments

In the studied wall painting, the red hue had been rendered by a mixture of pigments, namely hematite (predominant) and cinnabar (subordinate, sometimes even absent), at times accompanied by 'Naples yellow', perhaps used to confer an orange hue to the painted coating. The simultaneous use of hematite and cinnabar – as well as other red pigments – is known in literature; since the Romans, a thinner cin-

nabar layer could be spread over an existing coating of hematite, so to reinforce the colour brilliance (Béarat, 1996; Daniele, 1999; Edreira et al., 2003; Clark and Mirabaud, 2006).

The darkening of red pigments in frescoes is a well-known phenomenon: cinnabar (Da Pieve et al., 2013; Kegelman Neiman et al., 2015), hematite (Maguregui et al., 2014) and also red lead (Aze et al., 2007; 2008) can be transformed into black chemical species by the effect of photo-decomposition or due to interaction with reactive species. The analytical results indicate that, in the studied case, the observed darkening might be originated – at least in part – by an incipient but progressive transformation of the surface hematite coating (the most abundant, if not sole, red pigment) to magnetite, a composite Fe oxide with a typical black colour. Hematite is quite a stable iron oxide that, once exposed to humid air, can modify its hydration state thus reducing the symmetry around the Fe^{3+} ions and modifying its colour from red to orange (Cristini et al., 2010). Its

conversion to a black phase, namely magnetite Fe_3O_4 , is not spontaneous in environmental condition, but may occur thanks to the interaction with a reducing agent, such as SO_2 . This pollutant, commonly present in the air, is known to interact with the plaster surface in a very specific way, acting as a catalyser and favouring a degradation process that causes the coupled transformation of calcite into gypsum and of Fe_2O_3 into Fe_3O_4 . A detailed study of the interaction of SO_2 with mural paintings and its effect on the darkening of the red pigment due to hematite-to-magnetite reduction was reported by Maguregui et al. (2010; 2011; 2012), who studied and justified, through thermodynamic modelling, an analogous phenomenon in Pompeii. In the current study, the widespread presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on the surface of the 'Divine adoration' fresco – unequivocally detected by both XRPD and FT-IR – confirms that an intervened interaction of the wall surface with sulfur oxides indeed occurred. Such an evolution – and the consequent hematite-to-magnetite transformation – probably involved a very thin and discontinuous micro-layer on the surface of the wall painting, after exposure to a source of sulfurous compounds polluting the specific micro-environment of the 'San Francesco dei Cappuccini' Church. As per the nature of this source, presence of SO_2 as a common pollutant in the churches atmosphere is known to be related to combustion of oil in votive lamps, candles and incense (Kontozova et al., 2014). This is further confirmed by the significant layer of soot and ashes found on the whole fresco surface, responsible for a general dimming of the artwork (see Fig. 2a) and deposited after the burning of large candles, probably positioned directly under the painting. All these evidences suggest that a prolonged interaction occurred between the fresco surface and the produced sulfurous gases and smokes, thus triggering the further phenomena responsible for the widespread darkening (see Section 4.2).

Weak reflections related to magnetite are visible in the XRPD pattern of the darkened areas of St. Elizabeth's tunic (Fig. 3). Analogous signals – though markedly weaker – apparently appear also in those regions not yet affected by darkening (Table 1), testifying that probably such an incipient decay was spreading on the whole tunic of St. Elizabeth. In the seemingly clean areas, the amount of magnetite is almost unnoticeable to the naked eye – though probably close to the technique detection threshold. As far as Raman is concerned, the signals of magnetite were detected on some brown-to-blackish pigment grains, located close to other reddish ones that clearly showed also the Raman bands of hematite (Fig. 5b). Such a coexistence confirms that the presence of magnetite has to be interpreted as the result

of a partial but progressive reduction of an original hematite. Actually, some authors (Shebanova and Lazor, 2003; Cheilakou et al., 2014) hypothesize that in a Raman experience the conversion of hematite into magnetite could be artificially induced by the exposure to the Laser beam. In our analyses, however, particular care was adopted during sample analysis, in order to exclude such an eventuality. In particular, an exciting laser with low power (no more than 1-2 mW on the sample) was employed and a choice was made about acquiring more spectra with a short integration time, so to avoid any possible degradation/alteration of the samples. All measures repeated on different grains gave reproducible spectra, thus supporting the reliability of the obtained results. Use of these precautions allow us to state, with some confidence, that the detection of magnetite in our specimens has indeed to be related to an intervened, partial conversion of Fe_2O_3 into Fe_3O_4 caused by the SO_2 -rich atmosphere reaching the fresco surface in the church – rather than an analytical artifact. Neither coquimbite nor paracoquimbite – Fe^{3+} sulfate nanohydrates, at times observed in similar circumstances (Maguregui et al., 2010; 2011; 2012; 2014) – could be clearly identified. However, the detection of soot and metal oxalate (by μ -Raman and XRPD/FT-IR, respectively) in some of the examined grains further supports the fact that this hematite-to-magnetite reduction, induced by sulfur-polluted atmosphere, has to be considered one of the causes responsible for the red pigment darkening in the 'Divine adoration' fresco.

For what concerns a possible contribution to the dimming of the artwork offered by the blackening of cinnabar, caution must be invoked. The transformations and colour changes undergone by cinnabar/vermillion, or other lead-containing paint layers, known to cause discoloration and turn to dark grey/black, have been widely studied – though not yet completely understood (Cotte et al., 2006; Keune and Boon, 2005; Nöller, 2015; Kegelmann Neiman et al., 2015). Traditionally, Scholars have attributed cinnabar alteration to a light- (and/or other factors) induced conformational change from α -cinnabar (HgS ; trigonal red) to β (or meta)-cinnabar (HgS ; cubic, black) (Feller, 1967; Gettens et al., 1972; Daniels, 1987; Spring and Grout, 2002; Grout and Burnstock, 2000; Béarat et al., 2004). Although such a process cannot be excluded, the analytical protocol employed here hardly has the sensibility requested to identify this degradation agent and related by-products. Assuming that reflections of meta-cinnabar appear in the XRPD data, these would be extremely weak – certainly preventing an indisputable attribution. The experimental identification of meta-cinnabar within altered cinnabar on a Cultural

Heritage object was hardly reported (e.g., by Istudor et al., 2007, on wall paintings in a 16th century monastery). Not even recent analyses performed with highly sensitive micro-analytical approaches (i.e., Raman spectroscopy and synchrotron-based methods, such as μ XRD and μ XANES) have achieved a thorough recognition of this decaying phase, supporting such a prudent behaviour (Cotte et al., 2006; Radepont et al., 2011; Radepont, 2013). The detection of rather low amounts of cinnabar, if compared to hematite, even on the unaltered areas of the 'Divine adoration' fresco, further contribute to raise doubts about acknowledging the relevance of such a contribution (if any).

An alteration of 'Naples yellow', detected by XRPD, might also have occurred. This pigment is lightfast and chemically stable, but is known to darken with high temperatures, exposure to iron compounds or sulfur fumes (e.g., presence of atmospheric H_2S). Its mixing with hematite (or magnetite), however, should not trigger such a process, as Fe in the form of oxides, hydrates or complex combinations (e.g., in Prussian blue) should not exert any effect (Church, 1901). Some authors, however, state that 'Naples yellow' may be liable to changes when in composition with ochres (Field, 1835). No plattnerite (PbO_2), however, was found, although local presence of sulfur compounds in the atmosphere (promoting hematite-to-magnetite conversion as well as incipient sulfation) might have implied partial transformation of 'Naples yellow' into anglesite ($PbSO_4$) – a black sulfate whose XRPD detection on the studied fresco cannot be completely ruled out (Table 1).

The fact that those agents presumed responsible for the dimming of the fresco could not be detected in the flesh-coloured areas should not be surprising. In these areas, in fact, the red pigments (main responsible for the darkening) are subordinated and mixed to white compounds (i.e., calcite and talc), their signals consequently becoming weaker. Accordingly, those bands/reflections related to the degradation products (i.e., magnetite) become extremely difficult (if not impossible) to perceive. In the 'a secco' areas, the distribution of the pigments is similar – though not identical – to that of the 'a fresco' portions. In particular, while in the latter 'Naples yellow' was systematically used to confer an orange hue to the red-to-pinkish portions, goethite was adopted instead in the others. This might suggest that the 'a secco' portions might have been applied well after completion of the artwork, resulting from inconsistent later restorations – rather than retouches of the original artist.

4.2. Incipient sulfation and presence of particulate

Diffuse presence, on the fresco surface, of sulfates (i.e., gypsum and anhydrite), both on the clean and on the selectively darkened areas (judging from the mutual intensities of the related XRPD reflections, more abundant on the latter; Tables 1 and 2), account for an intervened, incipient sulfation of the calcareous substrate. This process is commonly due to the combined action of H_2O (reaching the fresco surface as condensate or moisture) and sulfur compounds (SO_2 and SO_3 , common pollutants in the air), with formation of diluted H_2SO_4 aqueous solutions that cause partial but progressive transformation of calcite ($CaCO_3$) into gypsum ($CaSO_4 \cdot 2H_2O$). Such a development is detrimental for the fresco survival (Mora et al., 2001), causing both aesthetical damages and mechanical disrupting. In those areas where 'a secco' retouches had been made, presence of sulfates was also detected by both XRPD and FT-IR. Assuming that these areas – as hypothesized – should be related to later restorations rather than interventions of the original artist, this sulfate attack should therefore be considered quite a recent phenomenon. Presence of this homogeneous – albeit thin – 'gypseous film' on the whole fresco surface might concur to the darkening process, due to the embedding of ash, soot, mineral dust, organic pollutants and microorganisms (thus forming a 'slimmer' equivalent of the so called 'black crusts': Del Monte et al., 1981; Saiz Jimenez, 1993; Whalley et al., 1992). In the studied case, however, presence of a surface carbonaceous film (probably soot) was also detected by merely wiping the fresco surface with a dry sponge – upon which a blackish residue was left. Such carbonaceous residues therefore, resulting (as stated above) by fumes given off by large candles lit on the altar below and beside the fresco, apparently were not even incorporated by the sulfate layer. These residues could not be identified by XRPD, due to the overlapping of the main reflection of graphite (the C surrogate crystal phase mainly related to soot; Buseck et al., 2012) with that of quartz, preventing a clear attribution. However, diffuse presence of carbon (the main constituent of soot) on the artwork surface was unequivocally confirmed by μ -Raman.

For what concerns the possible presence of a fixative material, possibly spread due to previous conservation attempts and resulting from a certain fluorescence to the UV light of selected areas of the wall painting, no evidence was found from XRPD. Raman, on the other hand, detected an unidentified organic medium near the retouched, 'a secco' areas (Table 2). Such a treatment, therefore, cannot be completely ruled out.

5. RESTORATION INTERVENTION

Once the archaeometric survey exploring the possible causes of the darkening of the wall painting surface was completed, a feasible restoration intervention was planned, consistently with the diagnostic results.

Preliminary tests for a cleaning procedure were performed on selected panels of the artwork, operating at first in dry conditions and using a soft 'wishab' sponge, in order to remove the incoherent superficial particulate (i.e., soot and powders) cumulated on the surface. A second step consisted in applying (for 5-10 minutes) sheets of tissue paper imbibed with distilled H₂O on the fresco surface; the solute was then removed by using a cotton wool

swab embedded in distilled H₂O, gently rotated on the painted surface. Once the effectiveness of these preliminary tests was acknowledged, a global cleaning was undertaken on the whole artwork surface, following the above mentioned procedure; such an operation rendered at best the brightness of the original colours (Fig. 7a). In addition, some 'undertone' retouches were performed in those areas where the original pigments had inevitably been lost (i.e., on the visage, under the chin/ear, and on the hair of St. Elizabeth of Hungary; Fig. 2b), so to improve the global appearance of the artwork with an eye towards respecting the artist's rendition (Fig. 7b).



Figure 7. 'The divine adoration of King St. Louis IX' fresco, as it appears after restoration: a) global view of the artwork; b) magnification of St. Elizabeth of Hungary; a significant reduction of the 'blackening effect' on the tunic and flesh is observed, as well as the presence of 'undertone' retouches in those areas where severe pigment loss had occurred (e.g., on the visage - under the chin and ear - and hair).

Obviously, such a plain intervention - basically aimed at removing this surface incoherent particulate while preserving the underlying pigments - was ineffective about removing the superficial discontinuous film of magnetite, selectively distributed on the tunic of St. Elizabeth. Besides, the transformation from hematite to magnetite is known not to be reversible in the conditions under which the artwork is conserved. The reverse process (oxidation from Fe₃O₄ to Fe₂O₃), in fact, occurs only by annealing in air at T ≥ 400 °C - the exact value depending on the system composition and O₂ partial pressure (Mozanam *et al.*, 2014). As a result, these darker, black-to-brownish areas - due to presence of a surface thin layer of magnetite - are still visible even after restoration (see the brownish portions in Fig. 7b). Despite this, the adopted protocol was able to mechanically

clean the dirt (not yet consolidated) and the gypsum deposits (highly soluble in H₂O) from the fresco surface, thus rendering to the artwork (at the best, at least) its original chromatic aspect. The principle of the best obtainable result with the minimum less invasive effort was therefore adopted, and the effectiveness of such a treatment has been acknowledged by no further decay having been reported so far, more than three years after completion of the intervention.

During these operations, the signature of the presumed artist and the year of the supposed realization were recovered in the lower right area of the artwork, brought to light by surface cleaning from dust and particulate - quoting the name 'Faconti 1852'. A rather notorious Italian artist, by the name of Dionigi Faconti (Bergamo, 09.10.1826 - Turin, 22.04.1865), was active in Turin mainly in the period

following the church enlargement and renovation (1846). Faconti acquired a certain fame, mostly as a painter of canvas focused on historical, religious or mythological subjects. In 1860, once the King of Italy – Vittorio Emanuele – purchased one of his painting, he was named 'Assistant Master to the Chair of Painting' under G. Ferri and E. Gamba, a role he maintained until his death (Camerana, 1869; Lambertini, 1980; Maggio Serra, 1990).

6. CONCLUSIONS

An archaeometric survey was performed on a wall painting titled '*The divine adoration of King St. Louis IX*', in the 'San Francesco dei Cappuccini' Church, in Racconigi (Italy). The painting, realized mainly with the '*a fresco*' technique, had been suffering lately of an incipient darkening, generally involving the whole artwork surface but particularly affecting those areas painted in red and pink (in particular, the garment and flesh of St Elizabeth of Hungary). The performed scientific analyses proved that the investigated global decay and its peculiar selectivity on the red-to-pinkish areas had to be related to two coexisting and intertwined factors,

namely the presence of a diffuse particulate pellicle (i.e., soot and powder) and an unusual degradation specifically affecting the red pigments – in particular hematite and its partial transformation to magnetite. Such a phenomenon, though uncommon, may happen in particular circumstances, such as abundance of polluting sulfur oxides in volatile form in a confined environment. Besides, an incipient sulfation of the calcareous substrate was also detected, which is consistent with the supposed environmental conditions. Other causes, such as the degradation of cinnabar and '*Naples Yellow*', might also have contributed – although in a minor way – to enhance the observed darkening effect.

These experimental outcomes led the way to a restoration intervention, which rendered to the wall painting (at least at the best) its original aspect and colours. Furthermore, such a procedure led to discover the signature of the artist – possibly identified as the Italian painter Dionigi Faconti – as well as the year (1852) in which the artwork had been made. More than three years later, no further decay has been reported.

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