Multi-technique diagnostic analysis and 3D surveying prior the restoration of *St. Michael defeating Evil* painting by Mattia Preti

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Abstract

In this study, a multi-methodological analysis involving optical and physical/chemical diagnostic techniques and 3D photogrammetric survey was successfully applied, for the first time, on the large *St. Michael defeating Evil* painting by Mattia Preti, located inside the Church of the Immaculate Conception of Sarria (Floriana) in Malta. Pigmenting agents, binder media and raw materials were first characterized, both at elemental and molecular scales, through X-ray fluorescence spectroscopy (XRF), optical stereo microscopy (SM), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), Fourier transform infrared spectroscopy (FT-IR) and gas chromatography coupled with mass spectrometry (GC-MS). The main goal was to properly identify the execution technique of this famous painter, the pigment's palette and possible non-documented interventions. The 3D photogrammetric survey, on the other side, allowed us to non-invasively evaluate the extension of the areas that experienced restorations, and to properly map the domains of the different canvases observed. The joints between canvases suggested that the painting was folded and rolled up. In addition, the employment of a thermal camera gave evidence of the different consolidating material injection points used during the restoration to strengthen the painting. The obtained results offer useful information for the development of optimized restoration and conservation strategies to be applied and provide, at the same time, answers to open questions related to provenance and dating of the investigated artwork.

Keywords

Conservation, Lunette, Mattia Preti, Pigment's identification, Globigerina limestone, Multi-technique analysis, 3D photogrammetric survey

1. Introduction

The *St. Michael defeating Evil* painting is a masterpiece of the painter Mattia Preti, a renowned Italian artist active in Malta between 1661 and 1699, the year of his death. It is one of the seven paintings that Mattia Preti executed inside the Church of the Immaculate Conception of Sarria (Fig. 1a-c) in Floriana (Malta), in occasion of its reconstruction in 1677 as *ex voto* for the end of the plague in 1676. The Church, commissioned by the Grand Master of the Knights of Malta, friar Nicolas Cottoner, is characterized by a central plan almost totally designed by Mattia Preti himself. The pictorial cycle includes five paintings depicting *Mary Immaculate and the Saints protectors from the plague* and, painted on two large Lunettes, two examples of the *struggle of Good against Evil* in relation to the plague disease interpreted as divine punishment. These "oil on canvas" paintings were all executed between 1677 and 1679, and are essentially inspired by subjects that Mattia Preti had depicted almost twenty years earlier in seven frescoes, on as many gates of the city of Naples, as *ex voto* for the end of the plague epidemic of 1656.

The *St. Michael defeating Evil* painting, under investigation in the present study, is one of the two Lunettes of the arches (see Fig. 1d), together with the *Allegory of the Order of St. John the Baptist* painting (Fig. 1e). This large-sized (235 cm × 475 cm) work depicts the exterminating Archangel dressed as a Knight of the Order of Malta, with armor and bright red cloak, as he bursts from above holding his sword at the head of a host of executioner angels armed with foils and lightning bolts, ready to punish demons, offenders and sinners depicted in a tangle of lifeless bodies or dismayed and subjugated by terror.

At the beginning of the restoration process, the painting appeared seriously damaged, being the canvas heavily compromised and the pictorial surface severely re-painted and darkened by oils and waxes applied over the years. Therefore, it was necessary to study the dramatic state of conservation of the painting thanks to archival research, in order to understand the problems of the work and to plan the most appropriate scientific investigations to be executed.

In particular, it was understood that over the centuries the Lunette had undergone several conservation interventions, two of which documented by archival sources.

In the 30s of the twentieth century, considering the poor conservation conditions (the painting must already have been very incomplete) it was reupholstered on a new canvas.

The work was the subject of a very bad lining operation which involved the almost complete detachment of the original canvas and the application of only the preparation and the pictorial film on a new canvas. The gluing was performed with animal glue, not very elastic, which in a few years, due to a polymerization process, stiffened the painting to completion. During this operation, the numerous gaps created were filled with plaster and glue colored with iron oxide, in order to match them chromatically with the original brown-colored preparation by Mattia Preti. By means of oil colors, the gaps created with the detachment of large portions were completely repainted, and many of the original figures that were lost were re-proposed.

Concerning the second documented intervention, it took place after the Second World War. At that time, the most important paintings in churches throughout the island of Malta were protected at the outbreak of the conflict by collecting and hiding them in bunkers in uninhabited areas. In particular, in the case of the *St. Michael defeating Evil* painting, the artwork was removed from the frame and rolled up. The latter operation caused very serious damages, due to the stiffening of the glue employed in the 30s, which caused the tearing of the artwork into overlapping bands. In the 50s, a new conservative intervention was carried out, during which, since the re-sheathed canvas could not be removed, a new canvas was applied over the previous one, this time with paste, unfortunately free of bactericide. In addition, new gaps were plastered and some new re-paintings were carried out.

In the framework of restoration interventions, the possibility to create digital models and 3D replicates of objects/artworks of historical and artistic value has gained, in recent years, considerable attention (Yilmaz et al. 2007; Arias et al. 2007; Armesto et al. 2008; Remondino et al. 2009; Remondino 2011; Fiorillo et al. 2015; Balletti et al. 2016; Aicardi et al. 2018; D'Amico et al. 2020). As a matter of fact, digitization of artifacts by triangulation procedures allows the assembly of digital archives which can be used to plan and support the different restoration phases. In addition, 3D reconstructions are quite simple to be accomplished, providing at the same time reliable information about the spatial/geometrical properties of objects and environments, basically without any direct contact. To further support the definition of optimized restoration and conservation strategies to be applied to artifacts, the multi-technique characterization, through complementary, non- or at least micro-destructive methodologies, of the constituent materials such as pigmenting agents, binding media and preparatory materials, represents an extremely valuable source of information (Edwards et al. 2004; Castro et al. 2008; Bersani et al. 2008, 2014; Rosi et al. 2009; Tschegg et al. 2009; Ruffolo et al. 2010; Barbera et al. 2012; La Russa et al. 2014; Comite and Ricca 2016; Crupi et al. 2018; Ricca et al. 2019; Venuti et al. 2020; Zuena et al. 2020; Fermo et al. 2020) in order to give answers concerning open problems such as execution technique, dating and provenance.

In this work, a preliminary *in-situ* investigation through portable X-ray fluorescence spectroscopy (XRF) allowed for the identification, at the elemental scale, of the composition of some representative areas, in terms of major and minor constituents. Then, a sampling procedure was performed in order to assess the samples stratigraphy, and to better understand the pigment's palette and the raw materials used by the artist for the preparatory layer and for the painting, by applying optical stereo microscopy (SM) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). In addition, Fourier transform infrared spectroscopy (FT-IR) was adopted to primarily identify inorganic compounds although the technique, in the field of Cultural Heritage, is mainly used for the identification of the organic ones. In the specific case, investigations were carried out to characterize the superficial and painted layers of the samples and to further support the investigations conducted by XRF and SEM-EDX. Moreover, gas chromatography coupled with mass spectrometry (GC-MS) was used for a preliminary investigation of the used binders.

Along with a detailed diagnostic investigation of the materials composition, the 3D digitalization of the masterpiece allowed us to highlight, for the first time on a painting by Mattia Preti, the unevenness of the original surfaces as well as the presence of layers subsequently applied during the various restoration interventions.

It is worth underlying that the knowledge of all the aforementioned aspects does not simply constitute a fundamental pre-requisite in view of the development of proper restoration strategies to be applied. As a matter of fact, being the composition of the grounds of Italian painters of the 17th century, such as Mattia Preti, connected to the place where the artwork was realized (Hradil et al. 2020), the identification of the source materials represents the groundwork for dating and locating the *St. Michael defeating Evil* painting to a specific period of the artist's productive life, i.e. in Italy or in Malta. This is, at present, an ongoing controversy among the scientific community, also considering the close relation between these two regions.

Fig. 1 a) Map of Malta, with the town of Floriana indicated. **b**) External and **c**) internal view of the Church of the Immaculate Conception of Sarria in Floriana, Malta. **d**) *St. Michael defeating Evil* and **e**) the *Allegory of the Order of St. John the Baptist* paintings

2. Materials and methods

Overall, 12 points were investigated, *in situ* and in the laboratory (see Fig. 2).

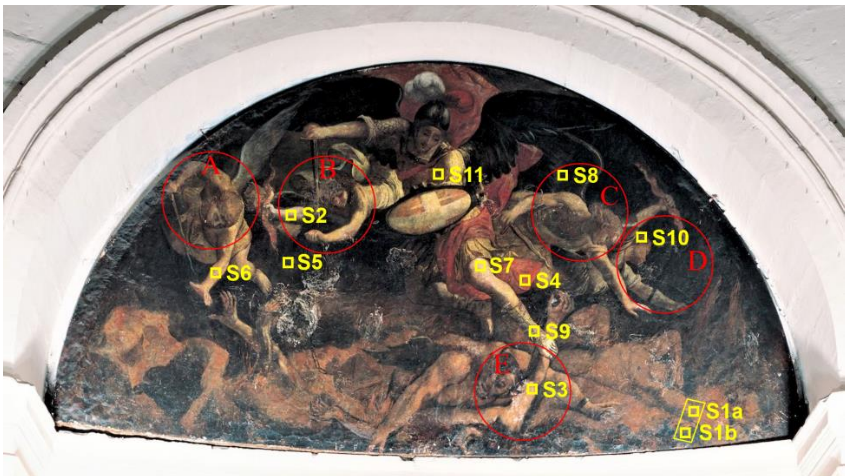

Fig. 2 Analyzed points from the *St. Michael defeating Evil* painting. Red circles account for the position of the four angels (A-D) and the devil (E)

In particular, as far as laboratory analyses are concerned, 11 micro-fragments of the pictorial surface (size smaller than ~ 5 mm^2) were sampled from the edge of already-existing lacunae, in proximity of ageing-induced surface cracks, during the latest restoration intervention in 2019. This allows the characterization of the pictorial technique as well as of overlapping layers on the painting. Details about sampling are described in Table 1, together with all the analytical techniques employed.

Table 1 Investigated samples, description and techniques employed

Sample ID	Description	Techniques employed
S1a[a]	Bottom, right-side of the canvas*, Light area*	XRF
S1b	Bottom, right-side of the canvas*, Dark area*	XRF, SM, SEM-EDX, FT-IR
S2	Right arm of the angel on the left (B), *Brown-gray*	SM, SEM-EDX, FT-IR
S3	Right arm of the devil (E), *Uncertain color tending to brownish-bluish*	SM, SEM-EDX, FT-IR, CG-MS
S4	Cloak of *St. Michael*, *Red*	XRF, SM, SEM-EDX, FT-IR
S5	Angel wing on the left (A), *Black*	XRF, SM, SEM-EDX, FT-IR
S6	Incarnate of the angel on the left (A), *Beige*	SM, SEM-EDX, FT-IR
S7	Incarnate of *St. Michael*, *Uncertain color tending to beige-grayish*	SM, SEM-EDX, FT-IR, CG-MS
S8	Angel wing on the right (C), *Blackish-brownish*	XRF, SM, SEM-EDX, FT-IR
S9	Sandalwood of *St. Michael*, *Green-yellowish*	XRF, SM, SEM-EDX, FT-IR
S10	Hair of the angel on the right (D), *Uncertain color tending to brownish*	SM, SEM-EDX, FT-IR
S11	*St. Michael*'s armor, *Uncertain color tending to beige-grayish*	SM, SEM-EDX, FT-IR

[a]Unfortunately, due to practical difficulties, the sampling of micro-fragment S1a was not possible. Accordingly, only *in-situ* XRF spectroscopy was carried out.

It is worth underlying that the sampling procedure was conducted following minimal invasiveness principles, and taking into account that the painting under investigation was, at the time, in an advanced state of deterioration. In this sense, the identification of colors by visual inspection turned out to be a very challenging task.

XRF spectra were collected through a portable XRF “Alpha 4000” (Innov-X system) analyzer, which allowed the detection of chemical elements having an atomic number (Z) between phosphorus and lead. The instrument was equipped with a Ta anode X-ray tube excitation source, and a Si PIN diode detector with an active area of 170 mm^2. The apparatus operated using a Compton Normalization algorithm (“soil” mode), designed for achieving the lowest Limit of Detection (LOD) possible (trace concentrations, from levels of ppm) for soil and bulk samples. The “soil” mode was here adopted together with the “Environmental” elements suite. For the used “soil” mode, the following element list was used: P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, I, Ba, Au, Hg, Pb. For each analysed area, two sequential tests were carried out. In particular, the working conditions were 40 kV and 7 µA for the first one and, 15 kV and 5 µA for the second one, for a total collection time of 120 s (60 s per run). A Hewlett-Packard iPAQ Pocket PC was used to manage the instrument and as data storage. The calibration was carried out by soil LEAP (Light Element Analysis Program) II and was verified using alloy certified reference materials produced by Analytical Reference Materials International. Lines detected at ~ 8.15 keV and ~ 9.34 keV, observed for all the investigated samples, were attributed to the L_α and L_β energy transition of Ta anode.

Stereomicroscopic investigations were conducted to closely examine the cross sections of the samples and were carried with a Zeiss Axiolab microscope equipped with a digital camera to capture images. Observations allowed to highlight the different structure of samples, i.e. the stratigraphy and the overlapping of the various and subsequent layers.

SEM-EDX analyses were performed on the surface of the samples (both on the back and on the front of the fragments) to obtain information about the micromorphology and chemical composition (in term of major elements). Analyses were performed with a scanning electron microscope Hitachi TM4000, equipped with a detector STEM. Microanalysis was performed using an energy dispersive spectrometry EDX Oxsford -AztecOne. Analyses were carried out with an acceleration voltage of 5 kV, 10 kV e 15 kV and under high vacuum conditions.

As FT-IR is concerned, the spectrophotometer used was a Perkin Elmer Spectrum 100, equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode, in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. Due to the complexity of the FT-IR absorbance profiles, the samples' spectra were also compared with those of standard minerals and/or pigments from databases (Vahur et al. 2016) and literature (Derrick et al. 2000) for a reliable assignment of the bands.

The determination of the organic binding media was carried out by means of gas chromatography/mass (GC-MS) technique using a GC-MS_TQ8040NX instrument (Shimadzu); He was the carrier gas (1mL/min) and separation was achieved by a capillary column VF-5ms (26 m x 0.25 mm i.d. x 0.25 µm). The sample (1µL) was introduced into the column by splittess injection with the following temperature program: 100°C for 2 minutes, 6°C/min up to 280°C, and finally 280°C for 10 minutes. Mass spectra were recorded in full-scan mode with the m/z range 50-1000 amu. Sample preparation was achieved following a consolidated procedure reported in the literature (Colombini et al. 1999); briefly the micro-fragment was submitted to a previous clean-up procedure by NH_3 and to an acid hydrolysis by HCl 6M and a subsequent derivatization by BSTFA.

Concerning the 3D survey, the final 3D model was obtained (Fig. 3) by applying the processing and workflow described in (Colica et al. 2018) and (D’Amico et al. 2017), and after the fine mesh geometry generation and reconstruction, the model was textured and used also for orthomosaic generation. Finally, a Digital Elevation Model (DEM) of the surface was generated. The same process was applied also to images acquired using ultra-violet (UV) light and a different digital model of the painting was generated (Fig. 3a). An accurate 3D model of the frame was also obtained (Fig. 3b).

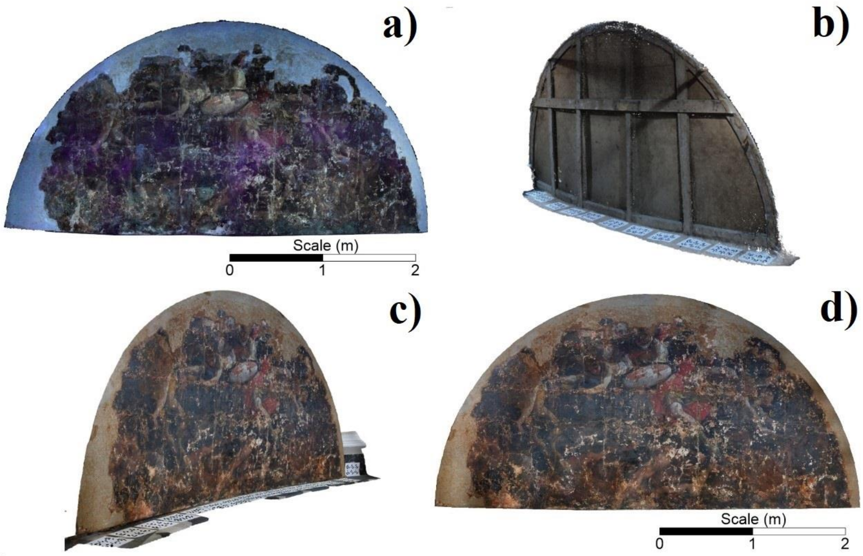

Fig. 3 3D photogrammetric reconstruction of the *St. Michael defeating Evil* painting. **a**) Model reconstructed using the UV light, **b**) 3D model of the painting frame, **c**) and **d**) show the 3D model and the orthophoto obtained using the RGB pictures

Both 3D digital Red-Green-Blue (RGB) (Fig. 3c-d) and UV (Fig. 3a) models were inspected for a first visual analysis and different filters were applied in order to improve the contrast between the different areas and parts of the painting. In particular, the use of the UV orthophoto, coupled with some information gathered during the physical survey, allowed to discriminate regions potentially covered by the original painting or subsequent restorations. To the referenced and measurable 3D RGB model a 3x3 filter was firstly applied, in order to smooth the DEM with the main goal of eliminating noisy points that generate a false rugose texture. After this step, we applied a typical set of procedures that are usually used in topographical analysis. In this context, the high-resolution of the 3D model and the accurate measurements allowed us to use technique not quite often used in archaeometry and mainly used for large scale objects, such as topographic profiles at different scales, contour maps, hill shading visualization and 3D visualization. This approach allowed us to obtain a very good representation of the topographic variations spanning from the millimetric to the metric scale and gave us the possibility to identify topographic alignments as well as mapping other morphologic features. An ad-hoc Geographic Information System (GIS) environment was generated and the DEM, the RGB and UV orthophotos were imported. Through the use of this tool, mainly using the DEM and the UV orthophotos as a further digital support, we generated polygons delimitating the different canvas and the restored parts on the RGB orthophoto. We also were able to map the principal alignments generated by topographic variations, color variations or a combination of both.

3. Results and discussion

3.1 XRF analysis

XRF measurements on six different areas of the Lunette were carried out (Fig. 2, Table 1) in order to identify the elemental composition of superficial layer. Specifically, spectra were collected from points S1a and S1b, respectively associated to a light and a dark area of the canvas (the surface paint layer was, in these points, locally damaged), and from points S4, S5, S8 and S9, corresponding to red (S4), black (S5 and S8) and green-yellowish (S9) pigmented areas. The obtained elemental composition of the aforementioned areas is summarized in Table 2, whereas the obtained spectra, with the exception of spectrum of sample S8, that almost completely matched the spectrum of sample S5, are reported in Fig. 4.

Table 2 Elemental composition, as obtained by XRF data, of the analyzed points. The key elements for pigment identification are marked in bold. The minor or trace elements are presented between brackets

Point of analysis	XRF elemental composition
S1a	Ca, S, Pb, (Cl, Fe, K, Zn, Sr, Ba)
S1b	S, Ca, Pb, Cl, Fe, (As, K, Ba, Zn)
S4	S, Pb, Cl, As, **Fe**, Ca, K, **Hg**, (Sn, Cd)
S5	**Ca**, S, As, Fe, Pb, (Sr, Sb, Mn)
S8	S, **Ca**, Pb, As, Fe, (Sb, Mn, Sr)
S9	S, Ca, Pb, K, (**Fe**, As, Sb, Ba, Zn, Mn)

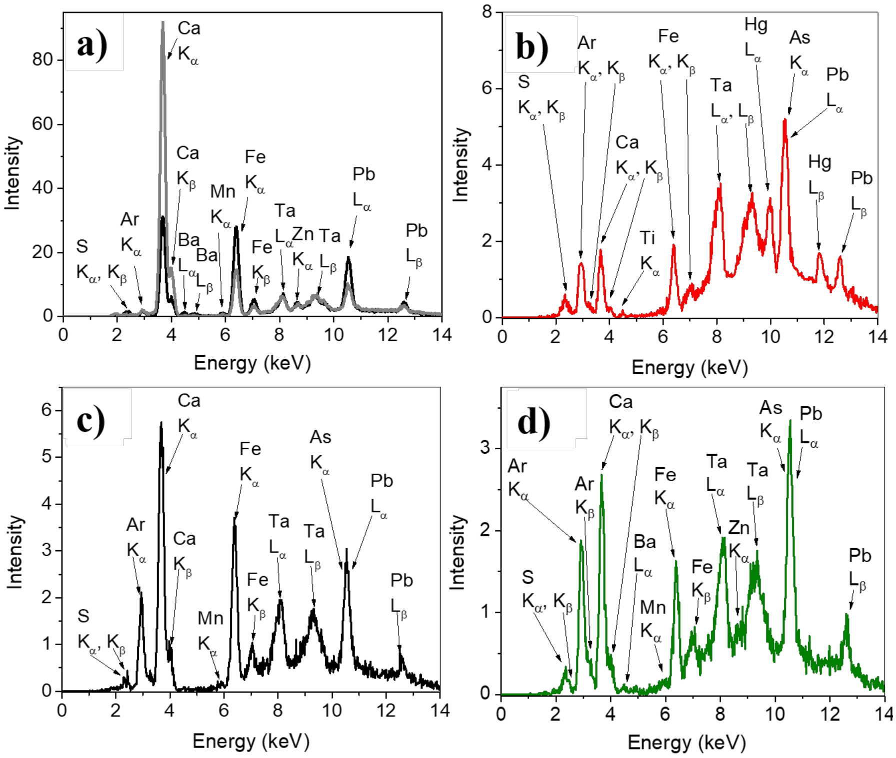

Fig. 4 XRF spectra, in the 0-14 keV range, collected on **a)** the light (point S1a, grey line) and dark (point S1b, black line) area on the right-side of the canvas, **b)** the red cloak of *St. Michael* (point S4, red line), **c)** the black wing of the angel on the left side of the painting (point S5, black line), and **d)** the green-yellowish sandalwood of *St. Michael* (point S9, green line)

A first inspection of Fig. 4a reveals, for both S1a and S1b points, the detection of S (K_α and K_β transition lines at ~ 2.31 keV and ~ 2.46 keV, respectively), Ca (K_α and K_β transition lines at ~ 3.68 keV and ~ 3.99 keV, respectively), Pb (L_α and L_β transition lines at ~ 10.55 keV and ~ 12.61 keV, respectively) and Fe (K_α and K_β at ~ 6.40 keV and ~ 7.05 keV, respectively). Their simultaneous presence suggests that the investigated surface can be attributed to a Ca-based and S-based preparatory layer, probably made of calcium carbonate ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$), mixed with a Fe-based compound, probably ochre (Fe_2O_3), lightened by a Pb-based compound, that could be lead white ($2PbCO_3 \cdot Pb(OH)_2$), according to what reported in literature regarding Mattia Preti's execution technique (Hradil et al. 2020).

Moreover, being "oil on canvas" the painting technique used by Mattia Preti for the realization of the panel, the use of a Pb-based compound as dryer for the binder could be also reasonably hypothesized (Venuti et al. 2020). It is worth underlying that although sample S1b appeared, during the measurement acquisition, of an intense darkish-brownish coloration, the XRF spectrum collected on this area did not reveal any components attributable to pigmenting agents capable to offer dark shades/tonalities. The brownish color clearly visible to the naked eye could therefore be due to a natural oxidation of the investigated portion of the canvas, also considering that measurement was performed on a deteriorated area and taking into account the high amount of Pb detected.

In the case of the red area (Fig. 4b), the detected chemical elements suggested the use of Hg-/Fe-based compounds, indicating that a mixture of cinnabar (HgS) and red ochre was probably employed. In addition, the detection of Pb allows us to reasonably hypothesize the use of a Pb-based red (such as minium, Pb_3O_4) and/or white (such as lead white) pigment, in order to obtain red/reddish tonalities, as those found in the bottom part of the analysed cloak (see Fig. 2).

For what concerns the investigated black areas (S5 and S8), a comparable elemental composition can be observed (see Table 2), suggesting the employment by Mattia Preti of a similar receipt for the blackish-brownish tonalities. More in detail, the observation of high intensity peaks (Fig. 4c) at ~ 3.68 keV and ~ 3.99 keV, respectively ascribed to the K_α and K_β transition lines of Ca, indicates the use of a typical Ca-based blackish pigment of organic nature. It is reasonable to assume that the aforementioned pigmenting agent was also applied as color background for other dark areas of the Lunette, including the entire upper-section of the painting, the *St. Michael*'s helmet and the wings of the angels. In this case, however, no further information can be obtained by means of XRF spectroscopy, since the characteristic elements of such compound have a low Z number. Nevertheless, the simultaneous detection of traces of Fe and Mn suggests that the organic black pigment was probably mixed with natural umber (Fe_2O_3 + MnO_2 + nH_2O + Si + Al_2O_3), a common Fe/Mn-based dark-brownish pigment.

As far as the XRF spectrum of the green-yellowish area is concerned (Fig. 4d), the detection of the characteristic XRF transition lines of Fe and Pb indicates the application of a common Fe-based green pigment, mixed, even in this case, with a Pb-based white compound (possibly lead white) in order to obtain different shades/nuances. Going on, the observation of trace of Sb (see Table 2), in conjunction with Pb, suggests the possible addition in the mixture of a Pb/Sb compound, probably Naples yellow, in order to obtain the observed yellowish nuance. Worth of note, the experimental XRF spectrum of the green-yellowish area did not reveal any contribution related to Cu, which leads us to exclude the use of a Cu-based green pigmenting agent in the painting, although frequently applied at that time.

For all the investigated areas, the presence of Ba and Zn, when detected, indicates the possible application of modern synthetic compounds, probably ascribed to previous restoration interventions (Feller 1986).

Finally, the presence of a significant amount of Ca in all the investigated areas deserves clarifications. In fact, this occurrence supports the hypothesis regarding the presence of the typical globigerina limestone in the preparatory layer of the painting (Hradil et al. 2020), whose observation appears crucial in order to ascribe the investigated painting to the Maltese period of the artist. However, confirmation of this statement needs the endorsement of complementary methodologies, being the distinction among different chemical compounds by XRF analysis not possible.

3.2 Stereomicroscopic analysis

Stereomicroscopic investigations were conducted to closely examine the cross sections of the sampled micro-fragments (see Fig. 5).

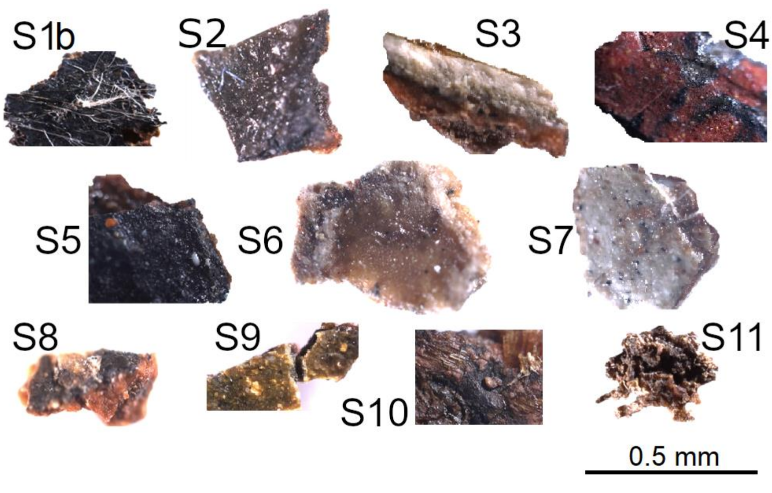

Fig. 5 Images by stereomicroscope of the sampled micro-fragments

Sample S1b is completely impregnated, which makes the stratigraphy unclear with the exception of the most superficial layer that appears of brownish color. Nevertheless, given the strong sample impregnation and translucent appearance probably due to the use of different compounds (e.g. glues) in previous restoration interventions, it is not clear whether the latter dark layer can be related to an alteration or to a superficial pictorial film. Sample S2 is also impregnated, but shows three overlapping layers that. from the surface to the inside. Appear brownish, blackish and reddish in color, respectively. Sample S3 is the only one with clearer stratigraphy and four visible layers. From the surface inwards, it is possible to distinguish a layer with blue pigments, followed by a whitish layer, a blackish layer and a reddish one. Sample S4 shows three clearly visible layers, which from the surface inwards range from a red layer, to a blackish layer and a reddish one in the lower portion. Samples S5-S9 are all strongly impregnated samples with unclear stratigraphy, where only the superficial pictorial layer is clearly visible. Specifically, S5 shows a pictorial blackish layer, S6 beige, S7 whitish-beige, S8 brownish-blackish, and S9 green-yellowish. Regarding samples S10 and S11, they are also heavily impregnated, the stratigraphy is not delineated and, furthermore, the painted surface layer is not visible.

3.3 SEM-EDX analysis

SEM-EDX investigations were conducted on 11 micro-fragments (see Table 1), investigating both the pictorial layer and the underlying stratifications. A summary of the data is reported in Table 3, where the elemental composition is shown for each sample analyzed.

EDX analyses, although semi-quantitative, can provide information on the artist's technique for the creation of the canvas as well as identifying the presence of elements that could be associated to restorations carried out in the past.

As for the composition of the layers under the painting film, for almost all the samples the presence of Ca, Pb and Fe prevails (Table 3). Such composition clearly suggests that the preparatory layer could contain species linked to these elements, such as calcium carbonate, lead white and red ochre (Fig. 6a-c). These data are in agreement with the findings of the XRF survey.

It is worth to note that several studies report the use of such compounds during the Maltese period of Mattia Preti (Lalli et al. 2014; Pelosi et al. 2018; D'Amico et al. 2019; Ridolfi 2019).

For some fragments, as in the case of sample S1b, it was possible to investigate the stratigraphy (Fig. 6d-i), acquiring EDX maps in false colors. The maps better highlighted the artist's execution technique and the application of the preparation layer on the canvas. The data acquired suggested that: a) the layer in contact with the canvas, has a composition mainly based on Ca and Fe; b) the layer below the pictorial film shows the presence of Pb and S. The use of pigments such as lead white, ochre and calcium carbonate could be hypothesized. Furthermore, the presence, even if in low concentration, of Al, K, and Si (Table 3) is detected. These elements are compatible with the presence of alunite ($KAl_3(SO_4)2(OH)_6$) and silicates, commonly used by the artist for the preparatory layers of his paintings on canvas (Hradil et al. 2020). Further morphological observations by SEM, carried out in more detail on the layer in contact with the canvas, highlighted the presence of foraminifera and in particular of the genus globigerina (Fig. 6l-n), with typical calcitic composition (Fig. 6o). The foraminifera represents the fingerprint of the artist's Maltese production, deriving from the use of the local globigerina limestone that Mattia Preti used to accentuate the red color for the preparation layer of his paintings. According to the literature (Pelosi et al. 2018; D'Amico et al. 2019), Mattia Preti preferred the red color of the soil made by microfossiliferous limestones, adding gypsum, alunite, opal, silicates, hematite and lead white.

Table 3. Summary of EDX elemental (weight %) analyses for all the samples

		O	Ca	Si	S	Na	Mg	Al	Pb	Fe	Ba	Zn	Cl	P	K	Hg	Sb	Mn
layer underneath the paint film	**Sample S1b**	29.79	52.55	0.97	2.03	0.44	0.30		10.29	1.40			0.83	0.40	1.00			
	Sample S2	33.65	45.19	8.16	3.69	1.79	1.18	1.92	31. 99	2.16				0.27	1.99			
	Sample S4	33.24	34.01	5.64	4.06	2.60		5.21	11.64	1.00				1.10	1.50			
	Sample S6	33.32	48.58	5.19	2.77	2.60	0.52	1.39	2.44	1.80			0.37	0.42	0.60			
	Sample S8	35.30	29.86	12.92	1.43	1.20	0.82	2.29	6.44	7.50			0.47	0.47	1.30			
	Sample S10	30.68	34.64	3.00	4.16	3.77	0.53	1.47	5.59	5.55	5.65	1.96	0.73	0.58	1.69			
	Sample S11	30.20	30.32	3.18	4.64	3.68	0.96	1.62	6.57	3.97	8.37	2.00	1.64	0.68	2.17			
pictorial film	**Sample S1**	27.20	24.37	2.96	4.36	1.10	0.31	1.45	23.28	5.67	4.21	2.92	1.04	0.76	0.37			
	Sample S2	31.90	18.03	2.99	6.21	0.63	3.08	1.44	22.07	3.09	3.92	3.92	1.44	0.71	0.57			
	Sample S3	29.99	34.15	0.93		0.48	0.61	0.85	22.99	10.00								
	Sample S4	19.88	8.54	1.23	15.72	1.31	0.22	0.95	20.90	0.79		0.43	0.53		2.14	27.36		
	Sample S5	36.15	34.73	3.04	4.05		0.72	1.01	18.20						2.11			
	Sample S6	20.55	22.30	5.84	3.85	0.86	0.34	3.04	33.91	3.54	2.66	1.14	0.63	0.28	1.06			
	Sample S7	20.70	24.01	5.73	5.72	0.58	1.00	3.24	33.88	3.81			0.50		0.83			
	Sample S8	18.57	11.25	3.49	1.54	1.01	0.34	1.25	57.58	2.65	0.75			0.47	1.10			
	Sample S9	24.64	13.55	3.82	5.54	1.52	0.99	0.61	38.93	2.66	2.91		1.12		3.71			
	Sample S10	28.21	29.83	6.30	3.46	2.12	0.60	2.43	10.13	7.32	3.15	1.48	0.91	0.69	1.98			1.39
	Sample S11	29.51	27.08	7.16	2.45	2.25	0.89	3.45	11.25	8.04	1.94	1.16	0.69	0.89	1.75			1.49

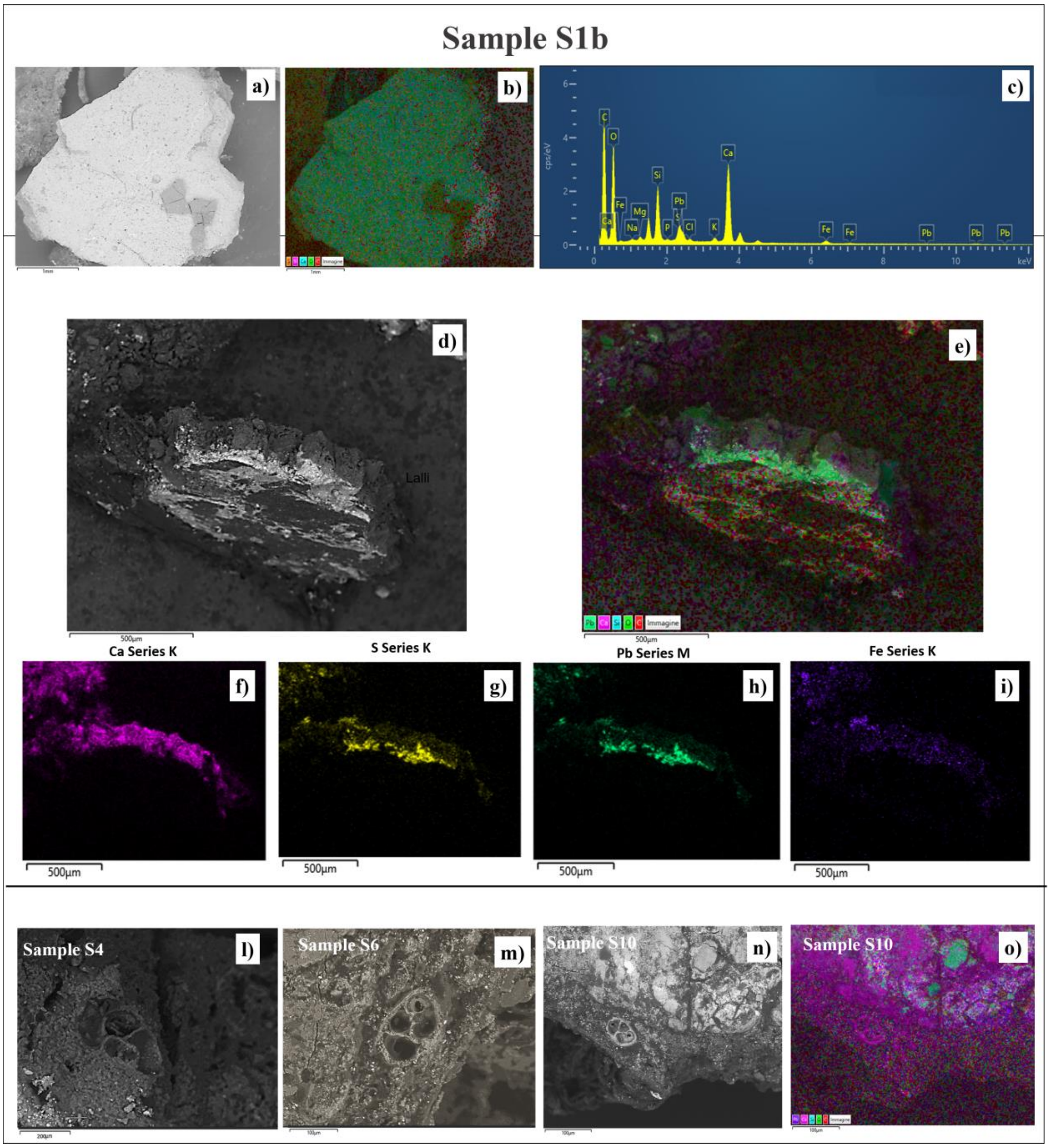

Fig. 6 SEM images showing the layers below the pictorial film of some samples. **a**) Back-Scattered Electrons (BSE) image of sample S1b; **b**) SEM-EDX false-color map obtained from the analysis of the surface of sample S1b; **c**) EDX spectrum obtained from the analyzed surface of sample S1b, **d**) BSE image of sample S1b placed vertically to the painting surface; **e**) false-color map obtained from the analysis of the surface of sample S1b placed vertically to the sampled surface; **f**) SEM-EDX false color map of Ca; **g**) SEM-EDX false color map of S; **h**) SEM-EDX false color map of Pb; **i**) SEM-EDX false color map of fe; **l**) BSE image of globigerina observed in sample S4; **m**) BSE image of globigerina observed in sample S6; **n**) BSE image of globigerina observed in sample S10; **o**) SEM-EDX false color map of sample S10 where globigerina was observed

As regards sample S2, the EDX investigations on the pictorial layer showed a high Pb content, thus allowing us to hypothesize the use of a lead white also as a pigmenting agent and not only for the preparatory layer of the canvas.

For samples S3, S5 and S8 it was not possible to hypothesize specific pigments, in agreement with what was already observed, in the case of sample S5 and S8, by XRF analysis. In fact, in line with the first observations performed by stereomicroscope, the pictorial surfaces showed a blue color for the sample S3, while for S5 and S8 a brown-blackish and black color respectively. It is known that Mattia Preti used pigments such as carbon black, vine black, black bone (Chiavari et al. 2007; Lalli et al. 2014; Pelosi et al. 2018; Hradil et al. 2020) for the black color, while blue glaze, indigo or lapis (Chiavari et al. 2007; Pelosi et al. 2018; Ridolfi 2019) for blue pigments. Nevertheless, the elements indicative of the presence of these pigments were not highlighted.

As for the S4 sample, that appeared red by the stereomicroscope observations, the EDX analyses showed high concentrations of S, Hg, Pb and Ca (Table 3, Fig. 7), which suggest the use of cinnabar, as also hypothesized by XRF analysis, and of minium, both pigments used together in the palette of Mattia Preti to paint red surfaces (Chiavari et al. 2007; Pelosi et al. 2018). On sample S4, EDX maps were acquired in false colors (Fig. 7a-f), confirming that the entire surface is composed of the aforementioned elements. Further investigations, by performing an EDX analysis following a linear trajectory along the sample surface (Fig. 7g), revealed similar profiles of Hg (series M) and S (series K), confirming the presence of HgS. On the contrary, those of Ca (K series) and Pb (M series) appear different, suggesting that lead is present on the surface as a pigment different from lead white (probably minium).

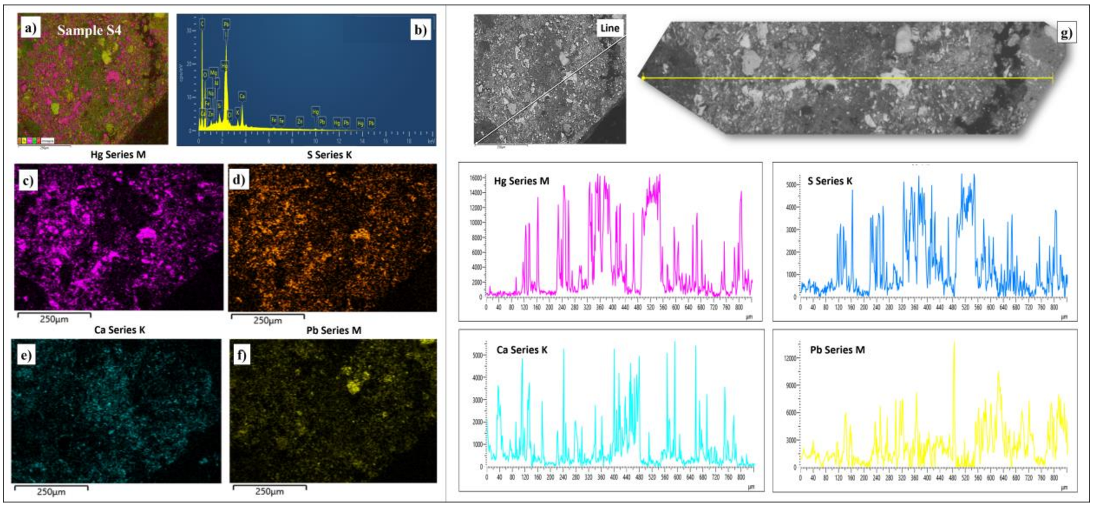

Fig. 7 SEM- EDX images showing the analysis of sample S4. **a**) SEM-EDX false-color map obtained from the analysis of the surface of sample S4, **b**) EDX spectrum obtained from the analyzed surface of sample S4, **c**) SEM-EDX false-color map of Hg, **d**) SEM-EDX false-color map of S, **e**) SEM-EDX false-color map of Ca, **f**) SEM-EDX false-color map of Pb, **g**) EDX analysis following a linear trajectory performed on the surface of sample S4, with associated profilometry spectra of Hg, S, Ca and Pb

Samples S6 and S7, taken from two different areas of the incarnates, respectively those of the angel on the left of the canvas (S6) and from St. Michael (S7), show an almost similar chemical composition of the pictorial layer with high concentrations of Pb and Ca and lower quantities of Si, Al and Fe. The chemical composition detected by EDX suggests, on the basis of the elements characteristic of the corresponding pigments, the use of a mixture composed of lead white added to red lead and green earth, pigments used by Mattia Preti to reproduce a skin color (Lalli et al. 2014). The only difference in the chemical composition of S6 and S7 (Fig. 8) is the presence of low concentrations of Ba and Zn (Table 3), the latter found only in S6 (and also in other samples as reported in Table 3).

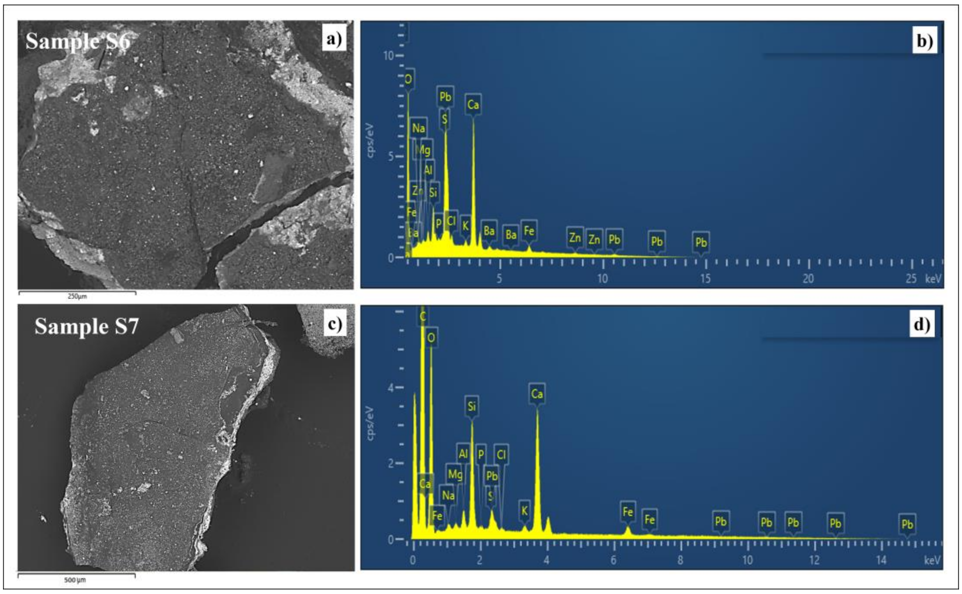

Fig. 8 SEM- EDX images showing the analysis of sample S6 and S7. **a**) BSE image of sample S6, **b**) EDX spectrum obtained from the analysed surface of sample S6, **c**) BSE image of sample S7, **d**) EDX spectrum obtained from the analysed surface of sample S7

The presence of Ba and Zn on the pictorial surface in some specific points confirms that the canvas has undergone restoration work in the past. In fact, these two elements can be due to the use of zinc white (ZnO) and barium white ($BaSO_4$) or to the use of lithopone, i.e. a white composed of barium sulfate and zinc sulphide ($BaSO_4 + ZnS$), pigments produced since the end of the 19th century.

As for the EDX analysis performed on the S9 sample, it allowed us to support the use of Naples yellow pigment, also known as "Giallo d'Antimonio", among the most used yellow pigments in Mattia Preti's palette (Ridolfi 2019; Hradil et al. 2020), as already suggested by the XRF composition collected on the same point. In this regard, Pb and Sb were, in particular, detected (Table 3, Fig. 9a,b) on single particles, such as that shown in Fig. 9c, whose EDX spectrum is reported in Fig. 9d. Interestingly, low amount of Fe can be recognized, in agreement with XRF results, indicating the possible addition of a Fe-based pigment in order to obtain different green-yellowish shades/nuances.

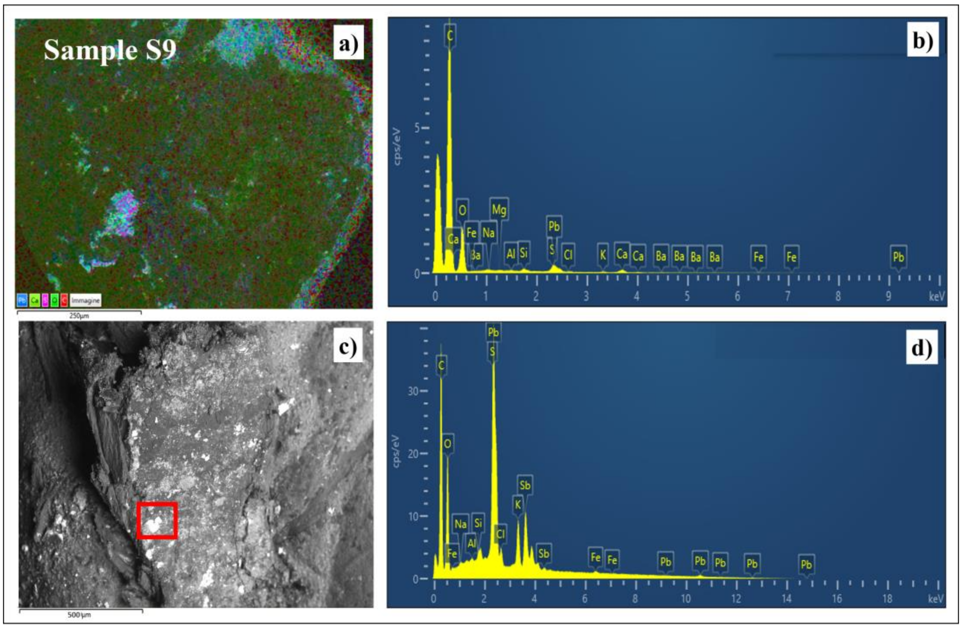

Fig. 9 SEM- EDX images showing the analysis of sample S9. **a**) SEM-EDX false color map obtained from the analysis of the surface of sample, **b**) EDX spectrum obtained from the analyzed surface, **c**) BSE image of an area of sample S9 (the red rectangle indicates the analyzed area), **d**) EDX spectrum obtained from the analyzed area

Lastly, the brownish colored samples S10 and S11, as evidenced by the observations by stereomicroscopy, show a similar chemical composition, which is typical of the use of Sienna, a color composed of iron oxides, clay silicates and small amount of manganese dioxide, probably mixed with lead white (the presence of all these species is suggested by the elemental composition highlighted). In fact, high concentrations of Ca and Pb (Table 3) were detected, followed by Al, Si and Fe, and low concentrations of Mn.

3.4 FT-IR analysis

Infrared spectroscopy was essentially addressed at characterizing the main inorganic materials (i.e. mineralogical phases) within the samples. All the analyses are referred to the whole sample, since it was not possible to isolate the surface from the bulk and the various layers, nor much less the sample was ground, given its very small size, fragility and the risk of completely losing material. Some representative spectra are reported in Fig. 10.

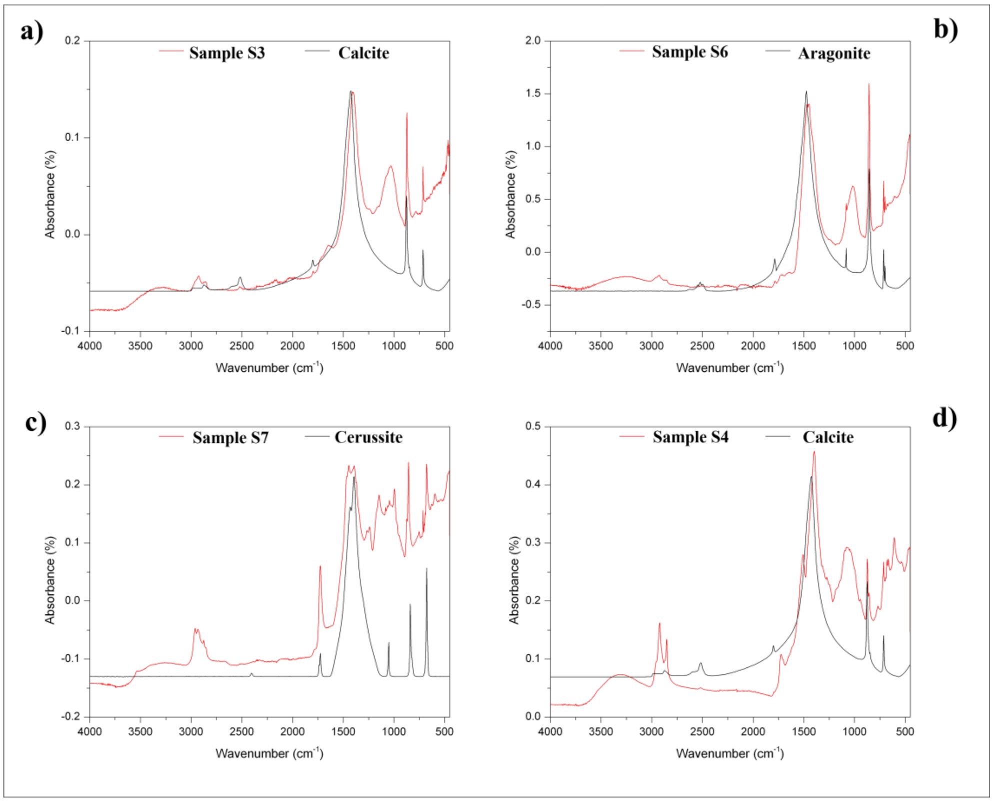

Fig. 10 Representative FT-IR absorbance spectra of the **a**) S3, **b**) S6, **c**) S7 and **d**) S4 samples

In all analysed samples, the stretching vibrations of calcite, peaked at ~ 1409, ~ 875 and ~ 711 cm^{-1} were identified (Derrick et al. 2000; Vahur et al. 2016), supporting the thesis that the artist used the globigerina limestone, the typical oligo-Miocene limestone of Malta, in the preparatory layers. This thesis can be further confirmed as in some samples (i.e. samples S6 and S9) aragonite (i.e. a polymorph of calcium carbonate) has been identified (peaks respectively at ~ 1788, ~ 1473, ~ 1082, ~ 906, ~ 854, ~ 712 and ~ 699 cm^{-1}) (Linga Raju et al. 2002), as a consequence of the dissolution of calcium carbonate skeletal fragments and typical of the skeletal structures of organisms such as foraminifera (globigerina). Overall, calcite and aragonite have to be considered as binder phases, because the majority of the matrix is composed by calcium carbonates as also suggested by the SEM-EDX analysis. Of course, both phases may have also been used as white pigments; based on the fact that aragonite was often used in association with cinnabar in order to “dilute” the red color, or with other pigments to tone down the color and to dose the shade, or to prepare a white base (Angelini et al. 2019).

The absorbance band, which is strong in all the samples, peaked at ~ 1020 cm^{-1} is ascribable to the stretching of Si-O bond, indicating silicate compounds, probably deriving from sandy raw materials used as inert in the preparatory layers or as pigmenting agent.

The presence of cerussite (i.e. lead carbonate, $PbCO_3$) was also detected in samples S7, with typical peaks at, ~ 1432, ~ 1394, ~ 1051, ~ 838, ~ 677 cm^{-1}. It is indicative of the probable use of lead white, one of the most widely used white pigments in the past, mainly because of its high opacity and hiding power (Learner 2007; de Viguerie et al. 2018; Gonzalez et al. 2019).

Finally, taking into account the hypothesis deduced from the XRF and SEM-EDX investigations, related to S6, S7 and S9, no bands attributable to green earth have been identified.

In addition to inorganic compounds, samples showed the stretching bands of the carboxylic (-COOH) group peaked at ~ 1700 cm^{-1}, particularly evident in sample S7, and those of the stretching of C-H group at ~ 2852 and ~ 2922 cm^{-1}, suggesting the presence of an organic matter which is probably highly related with the binder. In the case of sample S4 the band at ~ 1700 cm^{-1} is present together with a band at about 1530 cm^{-1} that could be due to the amide group (Fermo et al. 2020) (the third typical amide band is at about 1440 cm^{-1}, but it is below the carbonate signal); these signals are therefore due to amino acids present confirming the presence of a protein-type ligand.

3.5 GC-MS analysis

GC-MS analyses were carried out only on samples S3 and S7. Both fatty acids and amino acids were detected in both samples. Thanks to the comparison with references values reported in the literature (Casoli et al. 1996; Colombini et al. 1998, 1999), the presence of linseed oil and an animal glue were disclosed. The animal glue was probably present in the preparatory layer underneath the painting film, while the siccative oil was employed as binder. This is in accordance with what already found for other paintings by Mattia Preti (Chiavari et al. 2007). This preliminary study deserves further investigation by expanding the number of samples.

3.6 3D photogrammetric survey

Three different canvases as well as the areas that experienced previous restorations were identified and mapped. Each of these areas have characteristic features, as "geographic" distribution, topographic position, texture, RGB range of colors and response to the UV light (Fig. 11a). Canvas 1 represents the canvas where the original paint is located. It has a central position in the painting and, clearly, presents restored parts. The restored part represents the restoration stucco, used to complete the missing parts of the Canvas 1 (Fig. 11b, c). It is interesting to see how this restored parts (which represent parts were the original paint were damaged) have got lineal patrons. Canvas 2 is a canvas under the Canvas 1 and used in a previous and old restoration phase. Presumably, the actual total size of this canvas is bigger than the Canvas 1, but it is covered by it, so the exposed area is relatively small. Canvas 3 lays under Canvas 1 and Canvas 2, in contact with the latter. As Canvas 2, the majority of its area is covered, and it is well exposed in the borders of the painting. Table 4 shows the size of the total and the visible areas of the different canvases, extracted from the GIS analysis.

Table 4 Results extracted from GIS analysis

	Total Area (sq m)	**Total Area (%)**	**Visible Area (sq m)**	**Visible Area (%)**
Canvas 3	8.39	100	1.38	16.47
Canvas 2	7.01	83.53	2.35	28.01
Canvas 1	4.66	55.52	2.85	33.99
Restored	1.81	21.53	1.81	21.53
Restored area in relation with Canvas 1 (%)	38.78			

During the analysis of the reconstructed 3D digital model, it was possible to recognize on the painting different kinds of alignments (Fig. 11d). Those parts are different in color, texture and topographical features. In light blue we marked a horizontal line approximately in the middle of the painting. This line is pointing an alignment affecting just the Canvas 1. It is interpreted as a merging feature within the Canvas 1. The upper light blue dashed line (inferred position) is located parallel to the first one and separated of about 1.20 m. In this region, Canvas 1 is not visible, thus we located the potential position of the merged canvases taking into account the position of the main join as well as the size of the typical canvas at the time of Mattia Preti available in Malta and southern Italy. The green line is interpreted as an internal union of the Canvas 2. This union is very evident and directly visible, and it affects neither Canvas 1 nor Canvas 3. The lines in red are placed where the original painting was damaged, and we interpreted them as a weakness line. They are distributed both in the horizontal and vertical directions. We interpret those features as sign of folding of the painting. In fact, historical fonts report that the painting has been folded a couple of times, the latter during the Second World War, when the painting was stored away and kept in a secure place. The folding was done probably first in the horizontal direction, and then the painting was rolled, causing the damage in the vertical direction.

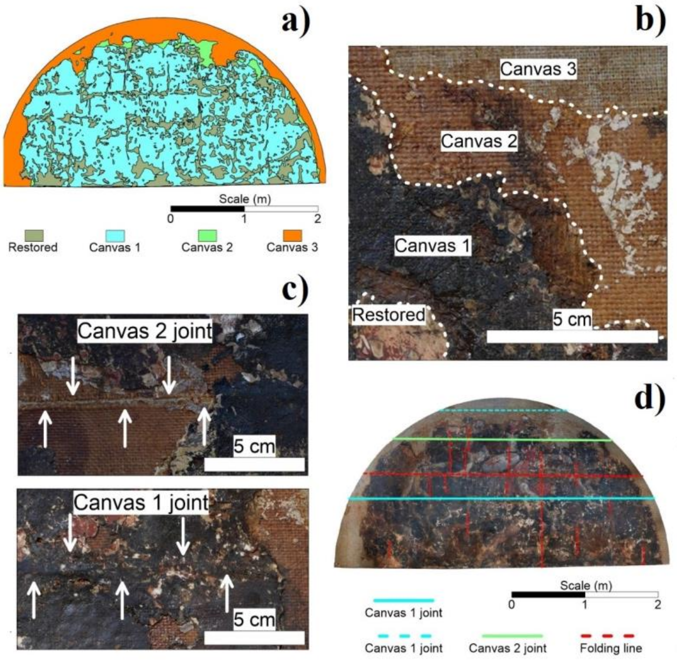

Fig. 11 Results of the interpretation obtained using the digital 3D model. **a**) Mapping of the three different canvases and restored areas. Panels **b)-d**) show details of the painting highlighting the different types of canvas as well as the joints between them

The topographical/morphological analysis (Fig. 12) revealed the external "U" shape of the Lunette, being flatted on the boarder. This "U" shape is less evident near to the top of the painting. The difference between the highest part on the edges and lowest part on the low center of the painting turned out to be 28 cm. The construction of the frame following this shape was necessary in order to accommodate the painting in its present location. This analysis, together with the 3D model (Fig. 3), will allow to print the frame with exactly the same features and measurements in case of any damage to the structure. The high resolution DEM also allowed us to do observations at more detailed scale. At millimetric scale, it was possible to discriminate among the three different canvas and to determinate the thickness of the Canvas 1 (between 1 and 1.5 mm), with a relatively thick paint layer, and of the Canvas 2 (1 mm), without any paint.

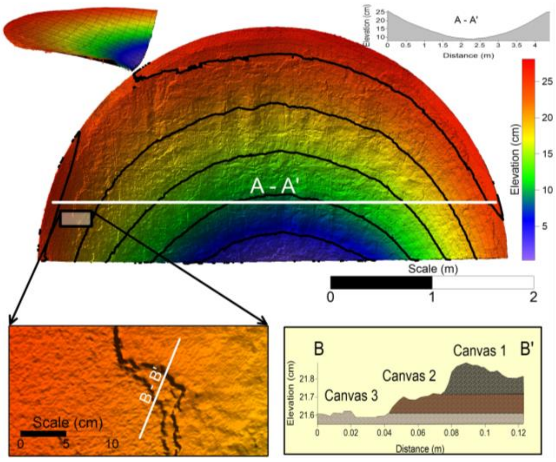

Fig. 12 Reconstructed DEM of the painting. The top panel shows the high precision model of the entire artefact as well as its curvature. Bottom panel shows a detail of the model where the 3 different canvases can be identified; the sketch on the right reports a schematic reconstruction

Finally, during the restoration a thermal camera was used to monitor the application of consolidation material (Fig. 13) used to strengthen the painting. In particular, different injection points of such consolidating media were revealed, identified as the dark spots/areas in thermal images. In the future, such kind of approach can be used in real-time to monitor each phase of the restoration works with the aim of optimizing the timing of the different phases.

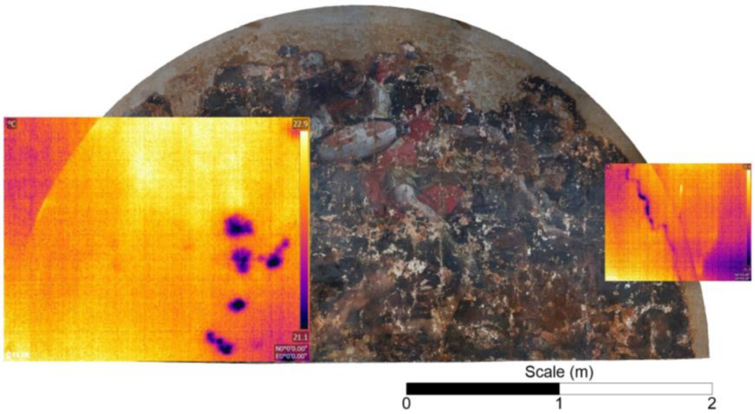

Fig. 13 Thermal image of the painting during the restoration

4. Concluding remarks

In the present work, a combined approach involving non-invasive optical and physical/chemical analysis, ranging from elemental to molecular scale, and 3D digital survey, was successfully applied on the large *St. Michael defeating Evil* painting by Mattia Preti, located inside the Church of the Immaculate Conception of Sarria (Floriana) in Malta. In particular, the combined use of XRF, SEM-EDX, FT-IR and GC-MS techniques allowed us to identify, starting from the evaluation of elemental/molecular compositions, the pigmenting agents, preparatory and organic binding materials used by the artist, so providing a better understanding of the execution technique, the pigment's palette and the occurrence of non-documented restoration treatments. In this context, random interventions were testified by the detection of elements generally associated to modern/synthetic media. In addition, measurements allowed us to confirm, among other aspects, the use by Mattia Preti of the typical Maltese globigerina limestone as main component for the painting ground, furnishing an experimental evidence of the Maltese origin of the investigated painting. This also contributes to temporally locate the investigated Lunette to the Maltese period of the artist, which was, up to now, still unverified. On the other side, the obtained 3D digital models of the painting allowed us to quantify the extension of damaged parts, to map the domains of the different canvases employed, to derive its state of conservation and to highlight possible additions made during previous non-documented restorations. These aspects, along with the characterization of the materials through complementary methodologies, contribute to support/plan future restoration and intervention strategies to be applied.

Declarations

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

S. D'Amico, S. Guido, G. Mantella, V. Venuti performed sampling. S. D'Amico, E. Colica and L. Galone carried out the 3D photogrammetric survey. V. Comite, P. Fermo carried out SEM-EDX and GC-MS investigation. G. Paladini, V. Crupi, D. Majolino, V. Venuti carried out XRF investigation. M. Ricca, M. F. La Russa, L. Randazzo carried out stereomicroscopic analysis and FT-IR investigation. S. Guido, G. Mantella provided all information regarding the historic-artistic context. S. D'Amico, V. Comite, G. Paladini, M. Ricca, V. Venuti wrote the manuscript. All authors read and approved the final manuscript.

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