Microanalytical investigations on a Byzantine fresco of the *Dormitio Virginis* from Sicily

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Abstract. This paper represents an interdisciplinary research focused on the microscopic and mineralogical investigations of the original fragments of a precious medieval painting, a rare byzantine Dormition of the Virgin in Italy. The painting has discovered in the rural monastery of Santa Maria del Rogato (Sicily), thanks to a recent restoration work. In order to obtain an exhaustive description of both the original mortars and pigments, several investigation methods are employed, from optical, polarization-fluorescence and electron microscopies, elemental analyses and X-ray diffraction as well. The experimental analyses, useful as a guideline in the restoration, allowed to the knowledge of the original materials as well as of the techniques used to realize the artwork. The paintings are realized by *a fresco* technique, by using lime and a simple color palette, based on natural earth, as typical of the Byzantine pictorial tradition.

Keywords: Historic mortars; Preparatory layers; Pigments; Thin section observations; Optical microscopy; X-ray diffraction; Scanning electron microscopy

1. Introduction

The Byzantine monks, who settled in eastern Sicily after the conquest of Emperor Justinian (518 – 527 A.D.), brought figurative languages and architecture affecting many artistic features of the island [1, 2, 3]. A rare and beautiful pictorial artwork represents an extraordinary example of Byzantine culture in Sicily, discovered by a recent restoration work and placed inside the monastery of Santa Maria del Rogato in Alcara Li Fusi, Messina. This artwork represents the only fresco of the Dormition of the Virgin in Sicily and it could be considered an extraordinary example in Italy. In particular, the pictorial figures are part of a theological program focused on the Virgin Mary. The main scene is focused on the dormitory of the Virgin, while other portions of the painted wall describe Orthodox Saints and the Virgin nursing the Child Jesus. The artwork presented, however, severe conditions of decay, related to a cohesion loss of the preparatory layers and of the paintings as well, and it was necessary to carry out a restoration intervention. During this intervention, the study of the early mortars have been of utmost importance in order to support and to guarantee the conservation of such early artwork, giving valuable information about its history and past interventions too [4-10]. In addition, if we consider that, during the Middle Ages, colors were seen as a part of symbolic expression [11], the analytical investigations of the painted layers constitute another great contribution in the historical report of the artwork and in the original painting techniques as well [12, 13]. Actually, it is known that written sources offer only ambiguous information about painting techniques, and they generally focus on metropolitan monuments [14, 15].

In this sense, the present work represents an exceptional study finalized to the knowledge both of the original materials and of the wall painting procedures in a rural Byzantine monument, in relation to

technical and historical peculiarity of this Dormition of the Virgin. Moreover, this study allowed to plan a correct conservative intervention, providing, at the same time, precious elements for historians to trace the authorship of the work of art [4, 16].
Actually, after a preliminary artistic and historic description of the paintings, the paper is focused: 1) to perform the petrographic, chemical, mineralogical and microstructural characterization of the internal renders; 2) to provide noticeable information about the chemical analysis and the texture of the pictorial layers. The characterization analyses, consisting in a sensitive stage due to the scarcity of available fragments, are performed by means of several techniques such as X-ray fluorescence (XRF) and X-ray diffraction (XRD), polarization-fluorescence and optical microscopic (OM) analyses, polarization-fluorescence microscopy (PFM) and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX). These investigations are crucial to identify the employed materials and the adopted techniques, putting them in relation to the different age of realization of the artwork itself.

Research aim. This paper is focused on the study of the rural byzantine fresco of Dormition of the Virgin, unique example in the South of Italy. For its unicity, the characterization of this mural painting allows to give a noticeable contribution for the knowledge of the materials composing the fresco, so giving valuable information about its history and supporting the conservation procedures of such early artworks. This work, moreover, points to provide for the scarcity of information about the development of wall painting procedures in the Byzantine era.

2. Historical and artistic description

The church of Santa Maria del Rogato, located in Alcara Li Fusi (Sicily, Italy), Fig. S1, was probably founded before 1105, as reported in the testament of Gregorio. He was the one who reorganized the Basilean monastic spirituality in the Valdemone, in the northeast Sicily, during the Norman period [17]. Moreover, starting from 1137, the church was documented in the hagiographic sources in relation to the visits of the hermit San Nicolò Politi. Despite the heavy tampering during time, the church can be considered a rare artistic and historical documentary example, both in terms of the architectural features and of the pictorial documenst, related to the Italian-Greek monastic culture of the Valdemone [18]. The main relevance of the church can be associated to the striking wall painting representing the Dormition of the Virgin, recently restored (Fig.1). During the restoration intervention, the restorers recovered a large wall painting, located along the same wall of the Dormition and datable of the same historical period, as confirmed by the experimental characterization reported below. The 3D rendering (Fig.S2) shows the place where the two main wall paintings are located. The discovered wall painting reveals four front figures, aligned within double frames: two saints, in a standing position, are clearly attributable to Saint John the Baptist and Saint Anthony the Hermit, founder of Eastern Christian monasticism (Fig. S3*a)*) [19]. Saint Anthony can be probably associated to Athanasius of Alexandria (296 – 373 A.D.) too, defender of Orthodoxy, friend and disciple of Saint Anthony, often characterized by the same clothing. A nimbate character, not easily identifiable, appears into a smaller rectangular frame. The youthful appearance, the swollen hair and the presence of the crouching dog, refer to the iconography of Saint Vitus, which was incorporated into the group of Fourteen Holy Helpers during the Middle Ages (Fig.S3*b)*). The central figure of the panel presents a suggestive haloed face having an incomplete wimple, probably attributed to a female figure that can be associated to Saint Agata or Saint Margherita (Fig.S3*c)*).
Regarding the major wall painting, dedicated to the Dormition of the Virgin, it does not deviate from the canonical schemes of analogous subjects, elaborated in the eastern and western area between the X and the XII centuries. Actually, the passing of the Virgin Mary was widely found in a great number

of influential writings and pictorial artworks. Details varied, but the core story was the same. According to the first Byzantine icons of the Dormition, (X century), the Virgin was lying horizontally on the bed, and whose head was generally facing right side. Two groups of apostles surrounded the rich bed of Mary. The first one was placed around Peter, at the head of the bed; the other group was gathered in the opposite side, guided by Paul always embracing the Mary's feet. At the center of the composition, Jesus took in his arms the soul of Mary, represented as a newborn. Two flying angels were disposed to receive in their hands the Mary's soul [20, 21].

The setting of the Dormition in the Sicilian monastery is comparable to the passages of the apocryphal Gospels, to the Homily on the Dormition of John the Theologian, as well as to the Homilies on the Blessed Virgin of John Damascene. As concerns the iconographic description, the composition shows a rigorous horizontal division, represented by the Virgin's bier, in contrast with the longitudinal axis with the figure of Christ, holding in his arms a newborn, the soul of Mary. The Christ wears a red *pallium* on a blue tunic and around him there is a dark *mandorla*, similar to a cave. The *mandorla* is enlivened by small pearls and star decorations, and it is supported by two angelic figures, slightly curved. In particular, the two angels maintain a compositional correspondence with the epigraphic Greek inscriptions, written in capital letter "H KOIMHCIC THC Θ(EOTO)KOY / IC XC" (whose translation is "the Dormition of the Virgin / Jesus Christ"). The Virgin is laying on her rich deathbed, covered by a brown-red drape with racemes of Byzantine taste. She has a big nimbus that isolates and emphasizes the oval face. Large dark lines mark the reed folds of her mantle and tunic, inserted into a solid geometric structure, giving to the figure a rigid and schematic setting. The bed is placed on two little pillars of grey stone, partially visible, adorned with a dotted rhombus grid, similar to other early examples [22]. The Virgin is horizontally delimited by the figures of Saint Peter, dressed similar to Christ and swinging the chain censer, and Saint Paul, bent at the foot of the bed. At the center of the coffin, and under the figure of Christ, Saint John, curved and seeing the face of the Virgin, is represented as well. On the right of the Christ, it is possible to identify the apostles Matthew, having a white beard, and Mark. In the foreground and in a standing position facing the viewer, two figures, presumably related to Saint Philip and the apostle Simone, are recognizable; a third character, not clearly defined, is represented too. On the left of Christ, Luca the young and James are recognizable too, perfectly aligned behind Peter and Andrew. Definitively, all the twelve apostles are represented [23].

In addition, we can observe two Saints Bishops, both disciples of Saint Paul, marked by the nimbus and with the omophorion adorned with crosses; they have a specular position respect to Christ and are placed behind the Virgin. As the inscription clearly indicates, they are Dionysius the Areopagite and the blessed Hierotheus, bishops of Athens. In the upper part of the fresco, two imposing building dominate the picture, connected with the big angel's wings. On the background, we can see a building with a double-arched window and twisted column, together with castellated towers. The two women into the window, that probably suggest a *matroneum*, are connected with the subject of "the three virgins" cited by John the Theologian. In this painting the women into doubled-arched window present a folksy connotation, differently from the reserved behavior of the original mournful female figures. The educational intent, focused on the importance of the Crusades and of the rebuilding of Holy Places, clearly appears in the fortified building on the left side of Christ. This building looks like the Holy Sepulcher and probably represents the Church of Saint Mary between the Mount of Olives and Mount Sion, believed by Eastern Christians to be the burial place of Mary. The middle floor of the building is similar to the Holy Sepulcher, but smaller [24]; a very interesting detail is the elegant doubled-arched window, showing a Cross potent in the ogival arch. In the upper part, a little building with three pointed-arch windows is located, characterized by the presence of open shutters and marked by battlements. These aspects underline the relation with the Holy Places, which the

pilgrims, the knights and the member of Order of Hospitallers used for votive intentions, when they come back from Holy Land.
After restoration, the apocryphal episode with the Archangel Michael chopping the jew Iephonias's hands off clearly appears. The Archangel has the wings outstretched, and he dresses many pearls both on the stole and on the nimbus. He owes the victory not only to his sword but mainly to the thin Red Cross near the Jew, connected with his conversion too.
Regarding the Dormition of Alcara Li Fusi, the unknown painter probably reworked the early stereotypes from icons or illuminated manuscript of the so-called "macedonian renaissance" (867 – 1056 A.D.). An example could be represented by the Dormition in the Saint Catherine's Monastery (Mount Sinai) (Fig.S1, S4), dated between 11th and 12th Century [25, 26]. Actually, in the Dormition of Alcara traditional iconographic byzantine canons are clearly recognizable. There is a very close connection of the figure of Christ, holding the Mother's soul, characterized by the presence of the "clavo" on the tunic. In addition, as found in the early Byzantine icons of the Dormition, the head of the Virgin rests on the right side [21]. Moreover, both the Greek inscriptions as well as the position of the newborn in regards to the Virgin, are similar to what found in the Byzantine fresco of the Dormition in the church of St. Nikolas Kasnitzes in Kastoria (Macedonia, Greece), dated at the end of the 12th century (c. 1191), Fig. S1 [21]. Definitely, the frontality of the characters, the linear solutions of some figures, the physiognomic characteristics, the geometric shapes of the young faces, but also the rigid configuration of Virgin's body, the direction of deathbed and the color range, have a very interesting connection with several Byzantine early fresco of the Dormition [27]. The byzantine iconographic program is the same, especially for the construction of the figures of Saint John and Saint Paul, having the same position in relation to the Virgin's bier that is decorated with the same phytomorphic adornment with racemes. The unknown painter used the same reference for the monumental figure of the young Philippe, dressed a big pink cloak with old-fashioned drapery. The painter pays also attention to draw, for this figure, the same physiognomic characteristics, just like the Saint Mark's head and especially the hagiographic characteristic of the Blessed Hierotheus on the left.
Nevertheless, a typical western element, that is the presence of the *mandorla*, referred to iconographic and stylistic solutions recalling the schemes of the Dormition of the early 14th century, is recognizable. Indeed, in such schemes, Christ is closed into a "*mandorla*" rounded by angels [28].
After a careful analysis of the stylistic figures and of the technical aspects of execution, the painting seems to refer to an artist of eclectic culture, able to combine expressions of western stylistic elements strongly affected by the Byzantine iconographic traditions. These characteristics are already found, after the fall of Acre (1291 A.D.), along the main maritime routes of Levant, due to the flow of icons, artists and itinerant workers throughout the Mediterranean, escaping from the Mamluk advance [29].

3. Characterization analyses

3.1 Sampling

The sampling is a crucial step that can influence the success of the characterization methodology and results [13]. In order to reduce or to limit the damages due to the sample selection, we collected fragments or very small samples from the highly degraded areas (e.g., fractures and lack of adhesion) by using a small chisel. The zones have been documented before and after removal of the samples. The samples are collected from the following pictorial scenes: 1) the main composition, that is the Dormition of the Virgin (**DV**, Fig. S5*a)*), 2) the painting of St. John the Baptist and other Orthodox Saints (**S**, Figs S5*b)-c)*) and 3) the picture representing the Virgin with Child Jesus (**VJ**, Fig. S5*d)*).
From each pictorial scene, we collected few samples from several sampling areas and the original materials consisted of two groups: i) micro-fragments of paint and preparatory layers; ii) fragments

of rough plaster layer (*arriccio*), that is the under layer of plaster on which the drawing of the fresco is done.

3.2 Analysis of characterization of mortars and pigments

The collected samples are analyzed either as they are, in form of micro-fragments, or prepared in cross-sections, depending on the scope and on the instrumental techniques, according to literature recommendations [6, 8, 30, 31]. The micro-fragments allow the mineralogical and microstructural analysis of the mortars but also the observation of the painted surface composition, texture, and state of conservation. From the cross-sections, it is possible to gather data about the number and paint layers stratigraphic succession, mortars and paint layers thickness and composition, pictorial technique, pigments physical and optical properties and, finally, its state of conservation.

Once in laboratory, we carried out a first careful observation of the collected mortars samples by using a stereo-zoom optical microscope (Leika S8 APO, with Leica EC3 digital camera), in order to identify particular details such as lime lumps or additives (fibers, inclusions, clays, charcoal, etc.) and, if necessary, to analyze the different stratigraphic layers.

The components constituting the preparatory layers and the *arriccio* samples are analyzed by means of several techniques such as optical microscopy (OM), thin section analyses with polarization-fluorescence microscopy (PFM), X-ray diffraction (XRD), and scanning electron microscopy equipped with energy dispersive x-ray spectrometer (SEM-EDX). In particular, the general examination of the structure and the texture of the samples is performed on thin-sections, by means of polarization-fluorescence microscopy (PFM, AXIO Scope A1-Zeiss). Unfortunately, due to the the small dimensions of the available pictorial fragments, we carried out the thin sections obsterv ations only for the plaster layers (*arriccio*).

Qualitative and quantitative composition of the crystalline phases are determined with a PANalytical XPert PRO diffractometer, equipped with XCelerator detector and Cu X-ray source. The diffraction pattern is registered in the range of 5-70° 2Theta and 0.026° steps. The experimental diffraction patterns are elaborated by a Profile Fit Software (HighScore Plus software package, PANalytical), and crystalline phases were attributed by ICDD and ICSD reference databases. Quantitative analyses are carried out by means of the Rietveld refinement: X-ray data are fitted using the pseudo-Voigt profile function. Specimen displacement, polynomial coefficients for the background function, lattice parameters, profile parameters, and Gaussian and Lorentzian profile coefficients are refined [32].

SEM observations are performed on a Philips XL30CP with a X-ray spectrometer Oxford INCA Energy 250, allowing a further insight on the composition and the morphology of the constituents of the mortar samples. Particularly, it can be used to examine the textural interrelation of those constituents that are too small to observe by optical microscopy, like salts, or organic/biological constituent. The EDX spectra, registered in parallel to the morphological image, allow the elemental analysis of specific mortar components, and hence, it can complement the XRD analysis. Prior to SEM analysis, the samples are coated with a thin film of gold in a vacuum evaporation system.

As concerns painted samples, the investigation is focused to identify and to characterize their constituents and some features like, for example, the number and thickness of each layer, the type of pigments and their proportion. The micro-fragments of paint and preparatory layers are prepared as polished sections, mainly examined by OM and SEM-EDX. The preparation of the polished cross-sections is conducted by impregnating the sample with an epoxy resin and cutting it perpendicularly to the layer. The polished surfaces are observed by means of the stereo-zoom optical microscope and by a fluorescence microscope *Zeiss Imager A2* with a *Leica DFC 350 FX* digital camera. The optical observations of cross-sections enable the study of their layered structure together with the measurement of the thickness of each layer of paint, color, texture, and pigment particle size. The fluorescent microscope can be useful either to put in evidence the concentration of fluorescent

minerals (such as calcite) and/or to assess the presence of biological autofluorescent material, a naturally occurring phenomenon that is observed in many plant and animal tissues. Afterwards, the cross-sections are analyzed by SEM-EDX, used for the chemical analyses of the pigments.

3. Results and discussion

From the stereo-zoom optical microscope, (Figs 2*a-d)*), all the *arriccio* samples present similar appearances, so giving rise to the hypothesis that the application of the plaster was draft in at the same time.

In particular, from the polished section of the fragment from **DV**, reported in Fig. S6, we can observe that the *arriccio* is characterized by a matrix of brown-yellowish color, presenting voids of average values of 0.14 mm, and aggregates of dimensions generally ranging from 0.025 mm up to 0.150 mm. Some larger aggregates of about 5 mm are observed too. The presence of charcoal inclusions, which are most probably a remnant of the burning process (Fig. S6*a)*), is revealed as well. In addition, some shrinkage fissuring, related to a lime obtained by burning too marly limestone, therefore lacking sufficient binding properties, or to the low binder/aggregate ratio is evidenced too. Finally, as typical of historic lime mortars, all samples show the presence of white nodules, also called *lime lumps*. The lime lumps present quite homogeneous and floury features, as shown in Fig. 2*b)*, and they vary in size from about 0.25 mm up to 5 mm.

The origin of lime lumps is not agreed upon yet, but their investigation can be very useful to indicate the original methods of production and mixing of the mortars. Actually, it is known that the older manufacturing process of lime mixtures started when the pieces of burned limestone (calcium oxide, or quicklime) were removed from the furnaces, and they were immersed in pools containing water where the slaking process took place forming lime putty (i.e. calcium hydroxide). A continuous manual mixing, carried out with traditional tools, assisted the slaking process. Once the quicklime was completely dissolved, the lime putty was filtered and stored in pits dug in the ground. Usually, after a proper aging time the lime putties were mixed with sand and other aggregates to produce mixtures such as mortars, plasters and renders [33-35]. Lime lumps, originated in any case from the binder material, can be derived from several causes depending on the quality of the binder and on the adopted technique:

- hard carbonate crust that forms on top and around the edges of lime putty as it matures in the pit or in other container [36];
- a difficult workability, due to a poor mixing process or to hot mixing methods of fresh quicklime directly with sand and water, as well as to a low water/lime ratio, resulting in an inhomogeneous and course distribution of the binder between the aggregates [37];
- under-burned fragments but also over-burned fragments as well [38].

As concerns thin section observations, we reported in the Figures 3 and S7 the analysis of sampling areas from **S**, **DV** and **VJ** respectively. In particular, the specific sampling areas are shown in Fig. S5. The thin section of the **S** pictorial scene (**P17** sampling area) shows the presence of large, sub-angular, polycrystalline rock fragment (about 6 mm in length) with hypidiotopic texture, composed of sub-euhedral dolomite crystals (Fig. 3). The crystals have cloudy cores and limpid rims indicating replacement of carbonate clasts [39]. These clasts are of sedimentary origin. Smaller dolomite clast fragments and single crystals are scattered in the enclosing dark matrix. The latter is composed by aggregation of rounded or elongate, dense amorphous material. The irregular vugs in the matrix are linen with carbonate microcrystals. Rare, small and sub-rounded quartz crystals occur in the matrix.

Similar results are observed in **DV** and **VJ** samples (**P18** and **P25** sampling area, respectively), as reported in Figs S7. Actually, as concerns the **DV** sample, two sub-angular, hypidiotopic dolomite rock fragment in contact with a dense matrix composed of rounded or elongate, plastically moulded

amorphous material, are recognized. Along the edge of the thin section is present a rounded fine-grained quartz arenite clast (Fig. S7*a)*). In the matrix, rare sub-angular quartz crystals of igneous origin and heterometric dolomite rock fragments and crystals, as well as calcite microcrysts, are present (Fig. S7*b)*). The thin section of the **VJ** sample shows that it is composed of dolomite clast (about 2.2 cm long) having sub-angular outline and hypidiotopic texture (like **P17**). Along one edge, it is in contact with dense amorphous material composed of moulded rounded or elongate fragments outlined by very fine-grained calcite crystals. Micrometric oxides of black and rusty red colour are scattered within the matrix.

The phase composition and the relative quantitative analyses of the *arriccio* samples (as well as the analysis of the separated lime lump), are evaluated by means of XRD investigation and reported in Table 1. We observed that the samples are crystalline, denoted by well-defined Bragg peaks and a flat background in the X-ray diffraction patterns; moreover, the mineralogical analyses confirm the similarity between the different *arriccio* samples, characterized by a magnesium calcite in the binder fraction and with aggregates essentially composed of dolomite and some aggregates of other natures, such as quartz. The mineralogical analyses of the lime lumps samples, isolated from the surrounding matrix, indicate that they are composed only by completely carbonated lime. This result, together with the powdering and inhomogeneous features, leads us to assume that the lumps arise from the absence of suitable working of the mortar, so as not to enable complete mixing of lime and inert and to the use of technologies based on the non-aging of the lime, producing in this way mixtures with low plasticity [37, 39, 40].

The optical images related to most representative preparatory layers are reported in Figs. 2*e-h)* and S8*e-i)*, respectively. From the visual investigations, **DV** (Figs 2*f-f)*, S8*e-h)*) and **S** samples (Figs 2*g)*, S8*i)*) are characterized by a whitish color matrix, with a quite homogeneous texture; aggregates of dimensions up to 1mm are observed as well. Moreover, all the fragments show the presence of pure lime lumps but also of some strands of straw distributed inside the mortar (as remarked in the higher magnification image in Fig. S8*h)*). On the contrary, the sample from the **VJ** zone, (Fig. 2*h)*), has a quite inhomogeneous matrix and we never observed traces of straws, used as a reinforcing agent; in addition, some dark and sharp-cornered inclusions are distributed inside the volume of the fragments.

From the mineralogical analyses, in the preparatory layers we measured a clear prevalence of calcite respect to dolomite and quartz, due to the highest binder content in the preparatory layers respect to the *arriccio*. In particular, the **DV** and **S** samples appear composed of similar amounts of calcite, (with small variations in quantity due to sampling), while the **VJ** samples revealed a higher amount of the aggregates. Moreover, in **VJ** samples the XRD analyses confirm the presence of other phases, related to the dark inclusions that, separately analyzed, result composed by clay minerals. Actually, the Rietveld analyses carried out on isolated dark inclusions allow to establish the following composition: 66.5% muscovite (ICSD # 98-001-7049), 14% calcite (ICSD # 98-016-6364), 7.6% of quartz (ICSD # 98-003-9830), 6.6% gypsum ((ICSD # 98-000-2057), 5.3% vermiculite (ICSD # 98-003-4812).

The analysis of the mortars of the preparatory layers is followed by the investigations of the pictorial layers as well. Because of the higher amount of the collected fragments, we mainly focused our analyses on the pigments referred to the pictorial scene of the Dormition of the Virgin. The following colors are present: three different tone of red (from dark to light red), yellow ochre, white and black. The most representative fragments, as observed by means of the stereo-microscope, are reported in Figs. S8.

When we analyzed in detail such fragments, we observed that the dark red pigment, (**P3** sampling), is composed by a mixture of red pigment with black particles inside, conferring the dark tone (Fig. S9*a)*). The sample shows that the painted layer is well adherent to the preparatory layer and it has a

thickness of about 20 µm reaching values of 40 µm in presence of the black particles (Fig. 4*a)*). In addition, under the pictorial film, a white and denser layer of the plaster is observed, particularly marked when observed by the fluorescent microscope (Fig. 4*b)*), thus confirming the composition carried out by means of the mineralogical analyses. SEM-EDX analysis allows to reveal that, in addition to the presence of Ca, O, Mg and Si, (related to the mortar composition), in the pigment layer different areas are characterized by specific elements such as Fe O, and C. These elements can be related to the presence of hematite (Fe_2O_3) and C, associated to the use of natural red earth and to finely ground charcoal from vine pruning (black carbon inclusions).
Similar considerations can be ascribed to the other red fragment (**P21** sample). The red pigment characterizes the pictorial layer, with a variable thickness from 10 to about 50 µm. As before, in the stratigraphic section, under the painted film, a compact and dense layer of the mortar, consisting of a high lime content is clearly visible (Figs 4*c-d)*).
This high binder content confirms that the preparatory layer, after been painted, was polished using the technique inherited from the Roman tradition, called "polisage" or "politiones" [41-43]. This technique consists in the realization of a smooth plaster surface; this surface improves the painted frescoes so approximately reproducing the appearance of a precious marble. Actually, in the Byzantine method, such use of plastering had also the purpose to have an excess of lime on the surface and lengthen the time of plaster carbonation, allowing more time to paint the fresco. In this regard, it can be useful to cite the archaeologist and scholar of medieval Christian art, Didron. About the execution of a Byzantine site of frescoes in the monastery of Esphigmenou,(Mount Athos, Greece), Didron wrote "*Avant de dessiner, maître peitreunit chauxavec a spatule*", that is, "*before drawing, the painter's master crushes the lime with a spatula*", [44]. This practice was possible thanks to the use of natural agents for the retention of water, such as straw and coal, which finely chopped were mixed in mortar to reduce the drying time.
The **P15** sample presents different chromatic layers: red, white and yellow, characterized by similar thickness observed before (Figs 4*e-f)*). Moreover, SEM-EDX analysis carried out on the red pigment confirm the presence of Fe and O, while on the white color, the absence of Ti, Zn or Pb, allows establishing that the white pigment can be attributed to lime white. As concerns the yellow pigment, the presence of Fe reveals that it is a yellow ochre, typically composed by hydrated iron hydroxide.
The connection with the Eastern tradition finds further evidence in the analysis of **P6** fragment, taken from the black background behind the figure of Jesus Christ (Figs 4*g-h)*). In the Byzantine or Medieval pictorial cycles, black scenery has a shade that the human eye apparently sees as dark blue, also called *blue optic* or *Veneda*, an optical illusion originated by the combination of the charcoal of the plant fibers with the lime used as a binder [18, 45]. The SEM observation of the stratigraphic section on **P6** sample supports the vegetal origin of the carbon black, since it visualizes the walls of the parenchymal cells of a fragment of vegetal fiber, (Fig.S10), confirming the particular Byzantine pictorial technique in the use of black.
Finally, in all the samples, the adherence of the paint layers to the preparatory layer, presenting a mixing between lime and pigments having an inorganic origin, indicated that they were applied when the plaster was “fresco” (wet) [12, 15].
In Fig. 5 we finally reported the polished section from the fragment related to **VJ** zone. If compared with the preparatory layers observed in the **DV** samples, we note the presence of a larger amount of aggregates, also related to clay minerals, that is, the darker inclusions, presenting a green color at high magnifications, Fig. 5*b)*. Moreover, no effect referred to the "politiones" technique can be observed, confirming the different procedure adopted in the realization of the frescos.
In conclusion, these analytical evidences support the hypothesis that the difference between the preparatory layers of **DV** respect to **VJ** can be due to different times of realization; in particular, the

VJ fresco was realized in a following time, probably almost two centuries later, with the introducing of different materials in the mortar composition.

Conclusions

The investigations of the technical aspects and of the original materials, characterizing the frescoes of Santa Maria del Rogato, revealed the peculiarities of the Eastern methodological tradition, such as the smooth plaster surface obtained by the "politiones" technique, and the use of pigments based on natural earth and carbon black. From chemical and mineralogical characterization, the *arriccio* layer results mainly composed by lime and dolomitic aggregates, together with several lime lumps dispersed inside. Differently, the preparatory layers appear constituted by a very high binder content, confirming the "politiones" technique. In addition, the adhesion of the paint to the preparatory layer indicates that the *'a fresco'* technique was used for the realization of the wall paintings. The obtained results are consistent with the hypothesis that the frescoes were realized by Byzantine monks, dwelling in the Sicilian Monastery, and coming from the Latin Orient to the eastern Sicily during the beginning of the Aragonese period. These monks were able to combine expressions of western stylistic elements strongly inflicted by the Byzantine iconographic traditions.

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Figures

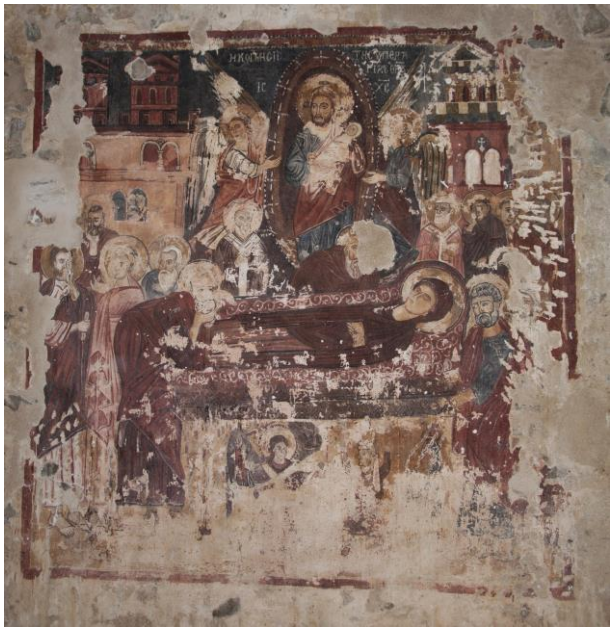

Figure 1. The fresco of the Dormition of the Virgin, **DV**, after the restoration intervention.

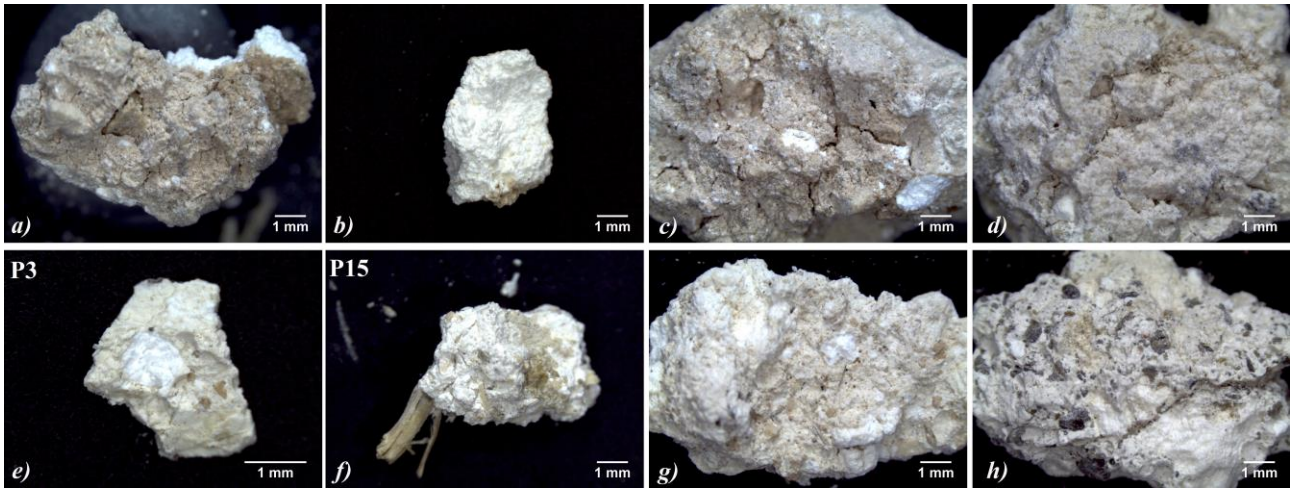

Figure 2. Stereomicroscope images of the *arriccio* samples taken from the following pictorial scenes: *a-b)* the Dormition of the Virgin (from **P18** sampling area), **DV**; *c)* the Saints, **S** (from **P17** sampling area); *d)* the Virgin with Child Jesus, **VJ** (from **P25** sampling area). In *b)* an isolated lime lump from **DV** is shown. Stereomicroscope images of the fragments of the preparatory layers taken from the following pictorial scenes: *e-f)* the Dormition of the Virgin, **DV**; *g)* the Saints, **S**; *h)* the Virgin with Child Jesus (**VJ**).

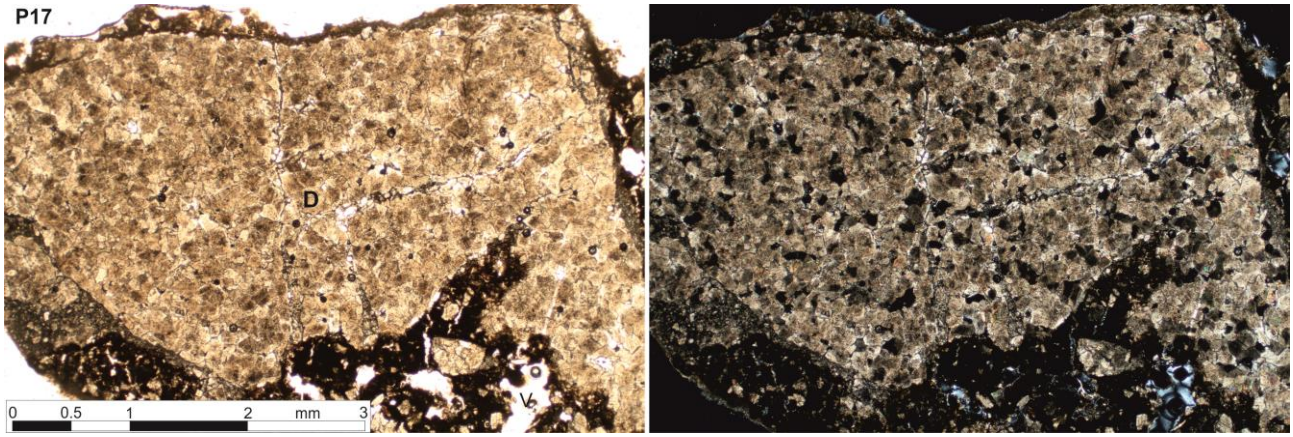

Figure 3. Thin section images of the Saints **S** pictorial scenes (from **P17** sampling area). Magnification 2.5X: left image 1 nicol, right image 2 nicols. Legend: D=dolomite, V=vugs.

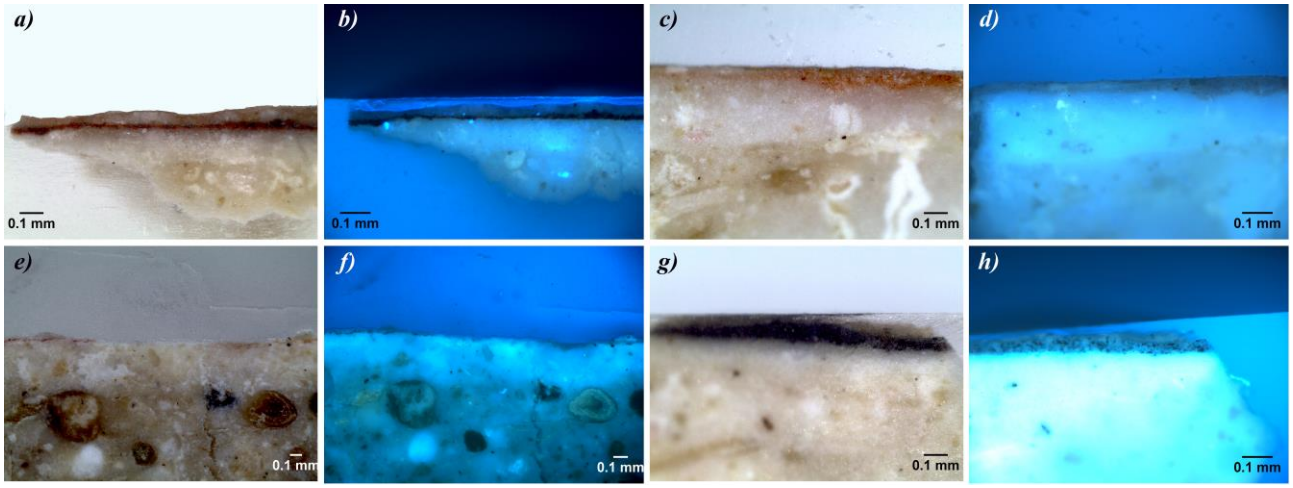

Figure 4. Optical and fluorescent images from polished cross section of the pictorial layers in **DV** scene: *a-b)* the dark red pigment (**P3** sampling); *c-d)* the light red pigment (**P21** sampling); *e-f)* the sequence of red, white and yellow pigments (**P15** sampling); *g-h)* the black pigment (**P6** sampling).

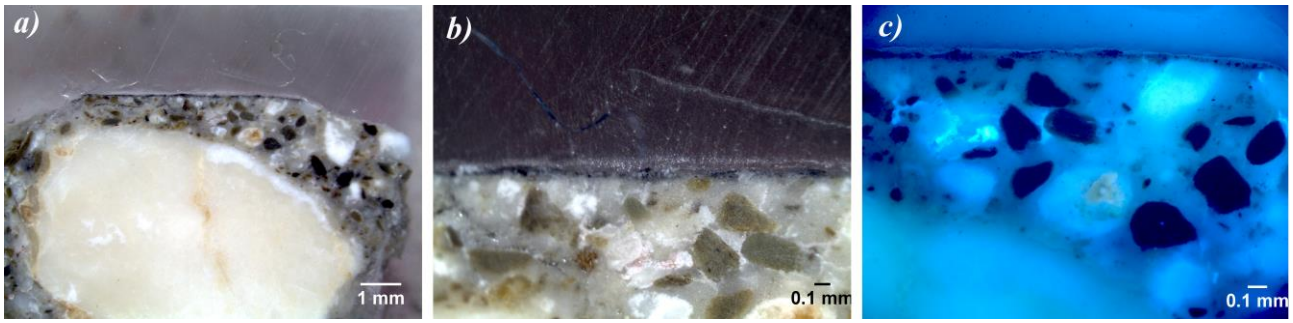

Figure 5. Images of the **P24** sampling (**VJ** zone), as seen by the polished section: *a-b)* from stereomicroscope; *c)* from the fluorescent optical microscope

Supplementary materials

Figure S1. Geographical map including all the places mentioned in the paper; **1)** Church of Santa Maria del Rogato, Alcara Li Fusi (Sicily, Italy); **2)** Saint Catherine's Monastery (Mount Sinai, Egypt); **3)** Church of St. Nikolas Kasnitzes in Kastoria (Macedonia, Greece).

Figure S2. 3D reconstruction of the location of the small recess.

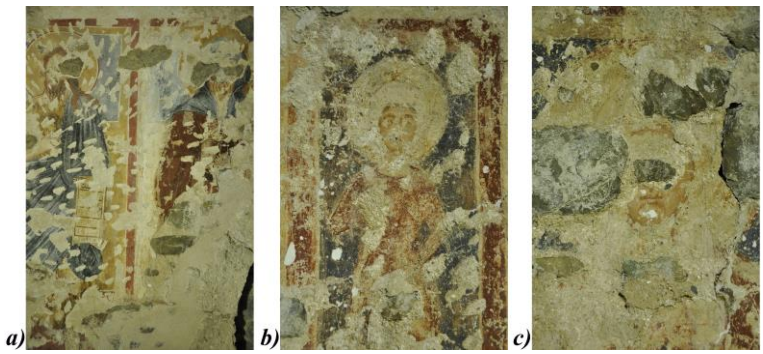

Figure S3. The main pictorial scenes in the rural Byzantine church; *a)* the picture representing St. John the Baptist and other Orthodox Saints, **S**; *b-c)* pictures representing Saint Vitus and Saint Agata, respectively.

Figure S4. Paintings referred to the Dormition of the Virgin in Saint Catherine's Monastery (Mount Sinai).

Figure S5. The pictorial scenes and the samplings areas: *a)* the Dormition of the Virgin, **DV**; *b)* the picture representing St. John the Baptist and other Orthodox Saints, **S**; *c)* detail related to St. John the Baptist; *d)* the Virgin with Jesus, **VJ**

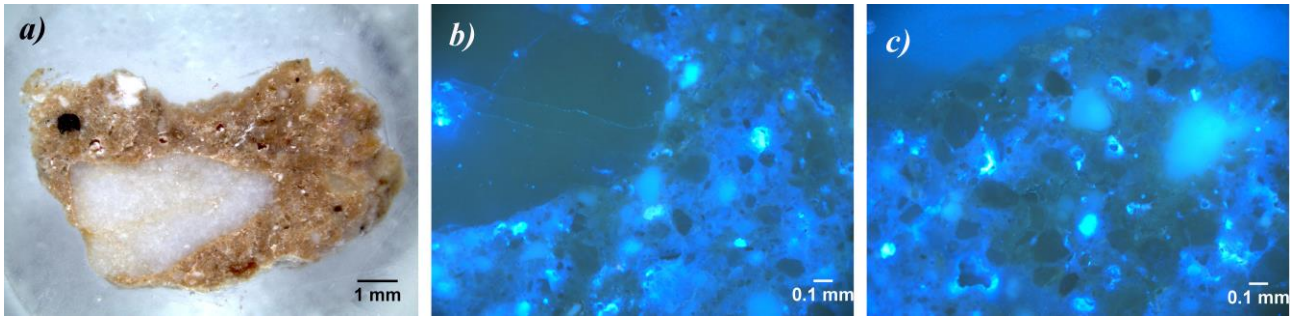

Figure S6. Polished section of the arriccio from **DV**, observed by: *a)* stereomicroscope, *b-c)* fluorescent microscope.

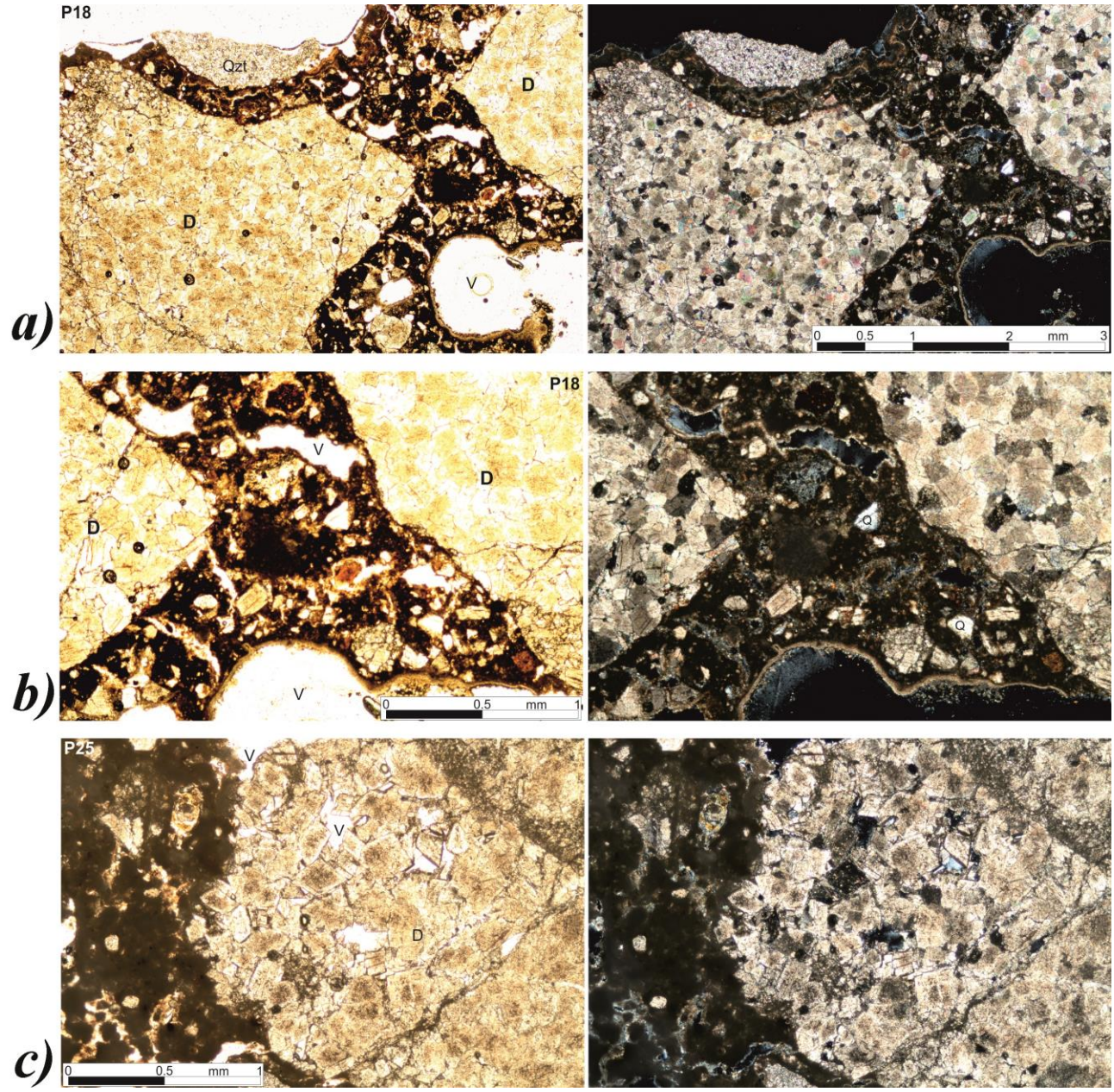

Figure S7. Thin section images of the Dormition of the Virgin **DV** and of the Virgin with Child Jesus

VJ pictorial scenes (**P18** and **P25** sampling area, respectively). *a)* Magnification 2.5X: left image 1 nicol, right image 2 nicols; *b)* Magnification 5X: left image 1 nicol, right image 2 nicols. Legend: D=dolomite, V=vugs, Qzt=quartz arenite, Q=quartz; *c)* Magnification 2.5X: left image 1 nicol, right image 2 nicols. Legend: D=dolomite, V=vugs.

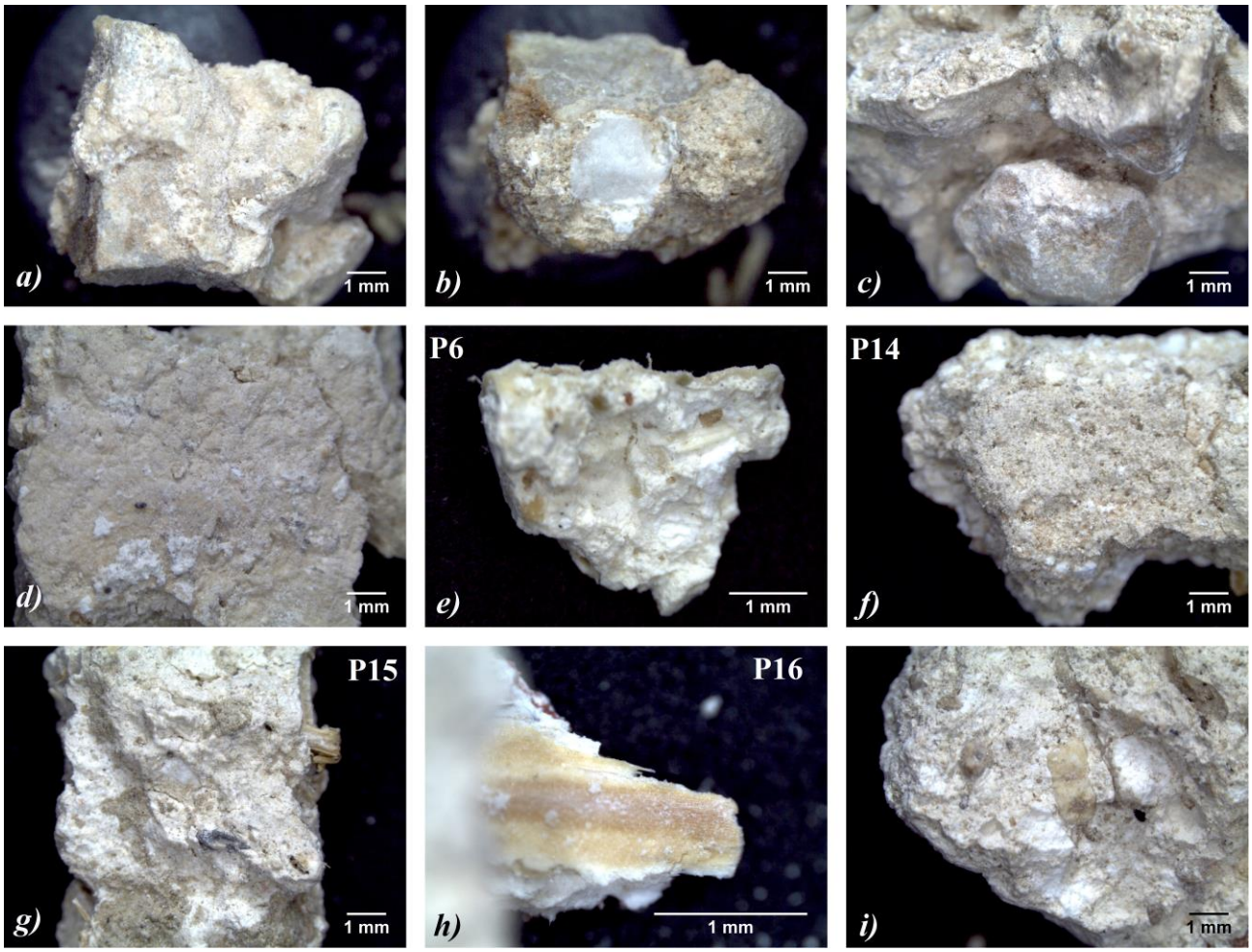

Figure S8. Stereomicroscope images of the *arriccio* samples taken from the following pictorial scenes: *a-b)* the Dormition of the Virgin (from **P18** sampling area), **DV**; *c)* the Saints, **S** (from **P17** sampling area); *d)* the Virgin with Child Jesus, **VJ** (from **P25** sampling area).
Stereomicroscope images of the fragments of the preparatory layers taken from the following pictorial scenes: *e-h)* the Dormition of the Virgin, **DV**; *i)* the Saints, **S**.

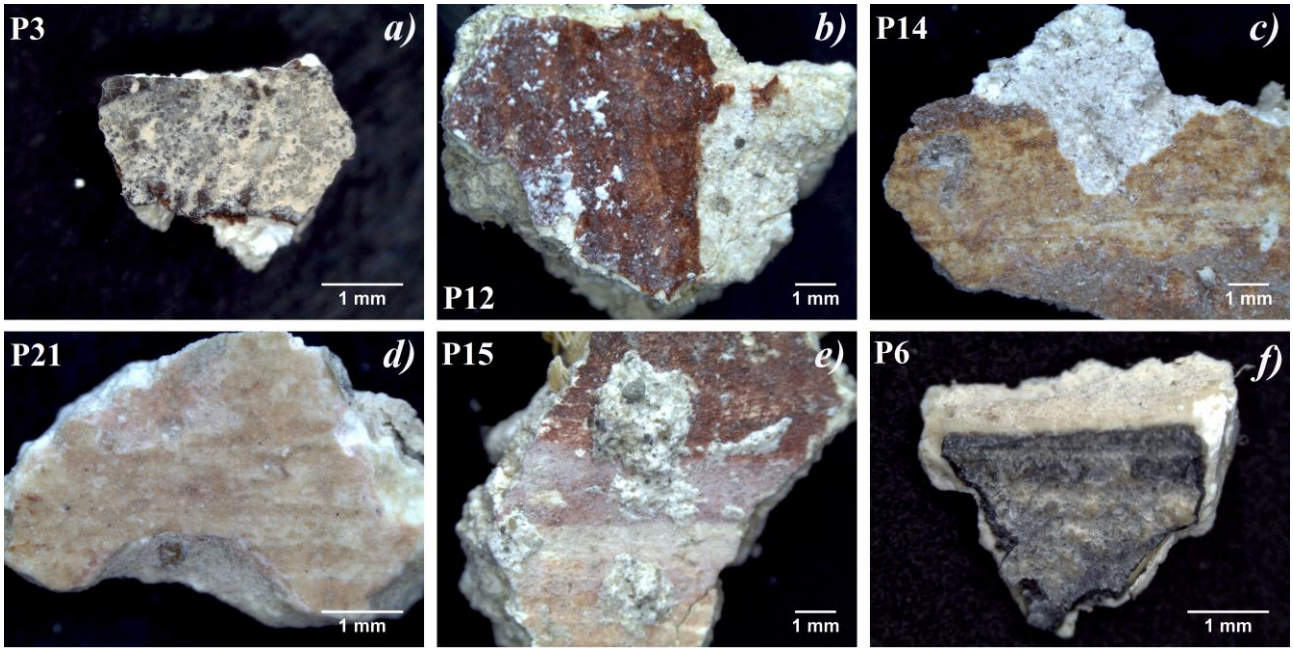

Figure S9. Pictorial fragments from Dormition of the Virgin, as observed by means of the stereomicroscope: *a)* dark red (affected from the successive render on the surface); *b)* red; *c-d)* yellow ochre; *e)* a sequence of colors from red, light red, white (marked by the arrow) and yellow ochre; *f)* black.

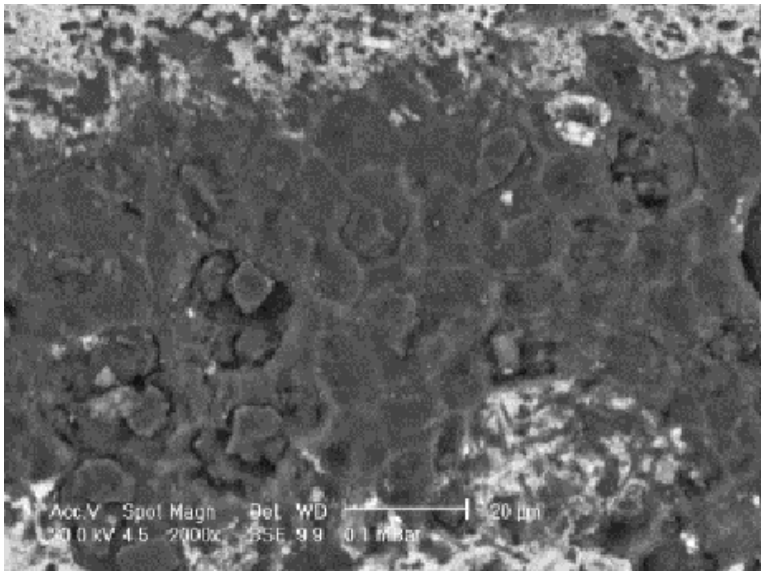

Figure S10. Detail from SEM image of the polished section in **P6** sampling: the shape of the cell walls is typical of the parenchymatic cells constituting the axial parenchyma of the hardwoods, within which the largest holes are the remains of resinous vessels.

Tables

Table 1. Mineralogical composition and quantitative analyses (Rietveld method) carried out on the arriccio and preparatory layers samples taken from the pictorial scenes of the Dormition of the Virgin (***DV***), the Saints (***S***) and the Virgin that nurses Child Jesus (***VJ***).

	Zones	**Magnesium Calcite** $Ca_{0.97}Mg_{0.03}CO_3$ **ICSD 98-008-6161**	**Calcite** $CaCO_3$ **ICSD 98-016-6364**	**Dolomite** $CaMg(CO_3)_2$ **ICSD 98-003-1209**	**α-quartz** $\alpha\ SiO_2$ **ICSD 98-003-9830**	**Muscovite** $(KAl_2((AlSi_3)O_{10})(OH)_2$ **ICSD98-008-6161**
Arriccio	**DV**	29.3%	-	70.0%	0.7%	-
	S	24.1%	-	75.0%	0.9%	-
	VJ	27.6%	-	72.2%	0.2%	-
Preparatory layers	**DV**	-	78.1%	18.8%	3.1%	-
	S	-	75.2%	22.1%	2.7%	-
	VJ	-	66.0%	30.4%	2.1%	1.5%