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TECHNICAL PAPER

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THE ROCK HEWN WALL PAINTINGS IN CAPPADOCIA (TURKEY). CHARACTERIZATION OF THE CONSTITUENT MATERIALS AND A CHRONOLOGICAL OVERVIEW

Claudia Pelosi[1], Giorgia Agresti[1], Maria Andaloro[1], Pietro Baraldi[2], Paola Pogliani[1], Ulderico Santamaria[1]

This paper presents the results of the analysis on the rock hewn wall paintings of eleven churches in Cappadocia, Turkey. A large group of churches in the region of Nevşehir were analysed in order to increase the database of materials and techniques of medieval wall paintings in Asia Minor and to support the restoration, conservation and valorisation project of the Forty Martyrs Church in Şahinefendi, and of the New Tokalı church in the Göreme Open Air Museum.

The research concerns a group of churches dating back to a period between the sixth and ninth century. The New Tokalı church shows pictorial evidence of 10th-Century and some 13th-Century churches. Micro samples were examined by means of polarized microscopy, Fourier-transform infrared spectrometry and micro-Raman spectroscopy. The study of wall painting materials puts in evidence changes in pigments and plaster typology. In the older churches painting was applied using the *secco* technique over a thin gypsum layer directly spread on the rock. In the 8th and 9th Centuries, both gypsum and lime mortars were used with the addition of rock fragments and plant fibres. In the New Tokalı church a white lime mortar with plant fibres was employed and the painting was applied on a finishing gypsum layer. In 13th-Century churches, paint was applied on lime mortar, sometimes with a final gypsum layer. Hematite, goethite, carbon black, green earth, jarosite, lead oxides, lead white, ultramarine blue and indigo were identified. Some pigment deterioration phenomena were observed (i.e. blackening) associated with lead-based pigments.

1 Introduction

The focus of this research is the study of the historical, artistic and technical aspects of the medieval rock paintings in Capadoccia through the analysis of a large group of churches (6th –13th century) in the Region of Nevşehir, in order to enhance the database on the materials and techniques used for the wall paintings.[1-5] It is worth stressing that the rock hewn wall paintings are the result and the peculiar expression of Cappadocia's scenic context where the permanent union between a stunning landscape and the painted churches constitutes the identity of this area.[6] The landscape was shaped by natural geological-structural evolution, together with the erosive effects due to precipitation, corrosion and more generally due to thermoclastic processes.[7-8] The result is a unique landscape characterized by extraordinary morphology moulded in the ignimbrites, i.e. the well-known pinnacles, 'mushrooms' or 'fairy chimneys'.[8] The human activity strongly affected the entire area with the use of these pinnacles since their soft rock was carved out to create hundreds of rock hewn churches and monasteries that are the object of the present study.

Between 2006 and 2012, 50 churches were analysed and they were divided into three separate groups according to the stylistic and technical characteristics. The first group includes 30 churches with wall paintings from an extremely controversial period. Their dating was discussed by various authors and it is still doubtful, ranging from the 6th [9-11] to the 9th Century.[12]

Figure 1: The rock hewn wall paintings of the Hagios Basilios Kilisesi at Mustafapaşa.

Figure 2: The rock hewn wall paintings of the Kapılı Vadısı Kilisesi at Karacöeren.

Within this group of churches, it was possible to sort out the paintings dating back to the 6th and 7th Centuries: Hagios Stefanos Kilisesi, Keşlik Monastir at Cemil; Hagios Basilios Kilisesi at Mustafapaşa (Fig. 1); Joachim ve Anna Kilisesi at Kizil Çukur; Üzümlü Kilisesi at Kizil Çukur; Karşibecak Kilise at Avcilar/Göreme, and the churches dating from the iconoclastic period (8th – 9th Century)[6,13]: Güllü Dere nr. 5 (Süslü Kilise) and Kapılı Vadısı Kilisesi at Karacöeren (Fig. 2), which are characterized by an exclusively aniconic decoration.

The wall paintings in these churches are generally characterized by the presence of superimposed or adjacent layers ascribable to different historical periods. The correct interpretation of these phases is far from straightforward because they are not characterized by pure painted mortars but instead can be assumed as *a secco* layers applied over thin white washing, sometimes without any decoration at all. The reading of the layers is complicated by the poor state of preservation and by the fragmentary character of the paintings.

As an example of the pictorial evidence of the 10th Century in Cappadocia, the New Tokalı church was studied. This church is the most important monument of the Open Air Museum in Göreme (Fig. 3).[14-16] Since 2011, the first step forward the process concerning the analysis and restoration of the wall paintings has been taken, in collaboration with the Archaeological Museum of Nevşehir.

The preliminary investigation concentrated on the north wall paintings. The *in situ* observation and documentation of the painted surfaces revealed the use of the *a secco* technique for the wall paintings probably by a proteinaceous binder, as described by other authors.[17] In fact, the typical craquelure, likely due to *a tempera* painting can be observed on the surface (Fig. 4). A peculiarity of the New Tokalı is the extraordinary use of ultramarine blue that strikes visitors on entering, and gilding still surviving on the haloes.[18]

Figure 3: A partial view of the interior of the New Tokalı church with extraordinary wall paintings.

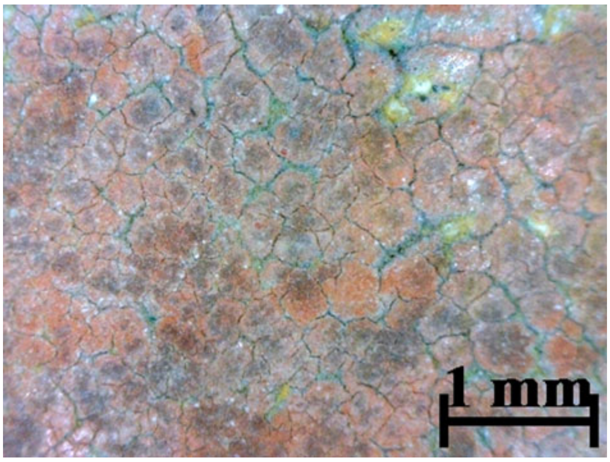

Figure 4: A micrograph of a detail of a wall painting of the New Tokalı church.

In order to study the chronology and changes in the technique used in Cappadocia churches, a group of 13th-Century churches was investigated: the Forty Martyrs' church at Şahinefendi,[6] the Arcangelos Kilisesi in the Keslik Manastir at Cemil[19], the Sarica Kilise nr. 1 at Ürgüp.[6,11]

The 13th-Century churches are characterized by wall paintings applied on pink-white mortars sometimes containing fibres. The plaster was generally spread by means of large horizontal bands relating to scaffolding lifts (*pontata*). In the Forty Martyrs' church, conservation work was performed in order to unveil the wall paintings covered by a thick sooty layer due to fires lit in the past. The cleaning intervention revealed a figurative cycle developed throughout the two naves of the church (Fig. 5).

To understand the evolution of the materials and techniques of the wall paintings in Cappadocia from its origin to the 13th Century, various aspects of the research were supported by scientific analyses carried out according to a methodology tested during years of surveys in Turkey.[20] For this reason, during the surveys conducted in Cappadocia, a great deal of images was

Figure 5: The Forty Martyrs' scene at Şahinefendi before and after the cleaning intervention.

recorded with a portable video microscope in order to study the painted surfaces in detail and to choose the best sampling points for laboratory analysis. In particular, micro samples were examined by means of polarized microscopy, Fourier-transform infrared spectrometry and micro-Raman spectrometry. These techniques were chosen to provide information about the micro stratigraphy of the painting samples, about the binding media and the pigment composition, respectively.

The scientific analysis supported historical and artistic studies to clarify some aspects of the wall painting not yet solved. In particular, the scientific investigation contributed to clear identification of the various superimposed layers, and to the characterization of the painting materials and of their degradation products. Furthermore, the study of the extraordinary pictorial complex of Cappadocia is required to carry out its conservation and restoration.

2 Experimental

2.1 In Situ Investigation

Preliminary *in situ* investigations were performed using a portable video microscope, Dino Lite AM 413 (AnMo Electronics, New Taipei City) in order to study the surfaces and identify sampling points.

2.2 Laboratory Analysis

The *in situ* investigations, carried out between 2006 and 2011, allowed us to collect several micro samples from the wall paintings. They were analysed by different and complementary analytical techniques in order to obtain as much information as possible about the materials and the technique. Microscopic investigation of cross and thin sections, infrared spectrometry and micro-Raman spectroscopy were performed.

To obtain the cross sections, a small quantity of the selected samples was mounted in transparent polyester resin. The sample cross sections were observed and photographed using a Zeiss Axioskop (Carl Zeiss Italia, Milano) polarising microscope equipped with a Zeiss AxioCam digital camera. The cross-sections were also studied using UV radiation using a mercury-vapour lamp directly connected to the microscope in order to observe fluorescence. A filter with the following characteristics: excitation BP 365/12, beamsplitter FT 395, and emission LP 397, was placed between the mercury lamp and the sample.

Infrared spectra were obtained using a Nicolet Avatar 360 Fourier-transform spectrometer (Thermo Fisher Scientific, Waltham MA). For each sample, 128 scans were recorded in the 4000 to 400 cm^{-1} spectral range in diffuse reflection mode (DRIFT) with a resolution of 4 cm^{-1}, using OMNIC 8.0 software. Samples were ground with spectrophotometric grade KBr (1% sample in KBr) in an agate mortar. The spectrum of the KBr powder was used as the background.

The micro-Raman spectrometer used in this case was a Labram Model from Jobin Yvon-Horiba (Edison NJ) with a spatial resolution of 1 μm and with quick detection ability as a result of the CCD detector 1024x256 pixels cooled to -70 °C by a Peltier element. The spectral resolution was 5 cm^{-1}. The excitation wavelength was the 632.8 nm red line of a He-Ne laser. Integration times varied between 10 and 20 s with 5 accumulations. The maximum laser power was 5 mW.

3 Results and Discussion

3.1 Analysis on the Micro Stratigraphy

3.1.1 6^{th}-7^{th}-Century Churches

In this group the following churches have been included: Hagios Basilios, Üzümlü, Joachim ve Anna, Karşibecak and Hagios Stefanos. *In situ* investigations revealed the presence of different pictorial phases, in particular: a single phase in the churches of Üzümlü and Karşibecak, two phases in the churches of Hagios Basilios and Joachim ve Anna and three phases in that of Hagios Stefanos.

The study of the cross sections of the micro samples taken during the various campaigns in Cappadocia was very useful to better understand the technique and the materials of the wall paintings and to find analogies and differences between the pictorial phases. Concerning the five churches dated back to the 6^{th} and 7^{th} Century, micro stratigraphic investigation identified similar techniques and materials as well as some superposition of the painted layers (Fig. 6).

In particular, the cross sections of the micro samples from Hagios Basilios Kilisesi, Üzümlü Kilisesi, Joachim ve Anna Kilisesi, and Karşibecak Kilisesi, exhibit similar characteristics of the plaster. In the churches of Üzümlü and Karşibecak, where a single phase is visible, the paint is applied over a thick transparent layer (about 100 μm, nr. 2 in Figs. 6a, b, c, d) made of gypsum, as revealed by micro-Raman (main band at 1008 cm^{-1}) performed on the cross section and FTIR analysis (Fig. 7, bands at 3544 cm^{-1}, 3402 cm^{-1}, 3231 cm^{-1}, 2237 cm^{-1}, 2103 cm^{-1}, 1684 cm^{-1}, 1620 cm^{-1}, 1141 cm^{-1}, 1120 cm^{-1}, 668 cm^{-1}, 603 cm^{-1}). The white plaster visible in the cross sections (nr. 1 in Figs. 6a, b, c, d) is also made of gypsum. Traces of organic materials were found due to the presence of the C-H stretching bands (very weak) at about 2927 cm^{-1} and 2844 cm^{-1}. The bands of calcium oxalate (1320 cm^{-1} and 781 cm^{-1}) were also observed in the FTIR spectra.

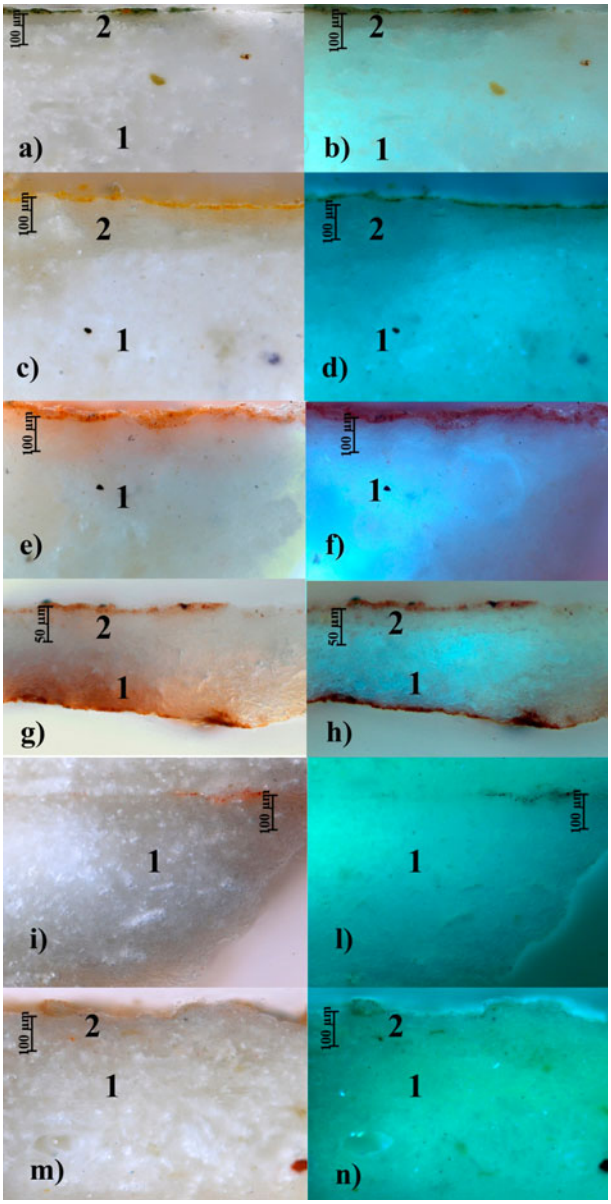

Figure 6: Photomicrographs of the cross sections of the micro samples from Üzümlü Kilisesi (a, b); Karşibecak Kilisesi (c, d); Hagios Basilios Kilisesi first layer (e, f) and second layer, (g, h); Joachim ve Anna Kilisesi first layer (i, l) and second layer (m,n). Reflected light (a, c, e, g, i, m), UV fluorescence (b, d, f, h, l, n).

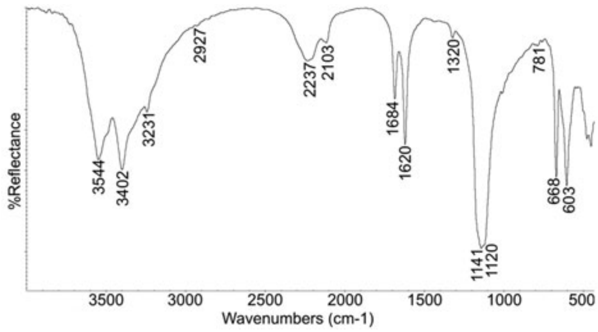

Figure 7: Diffuse reflectance FTIR spectrum of a sample from the church of Üzümlü.

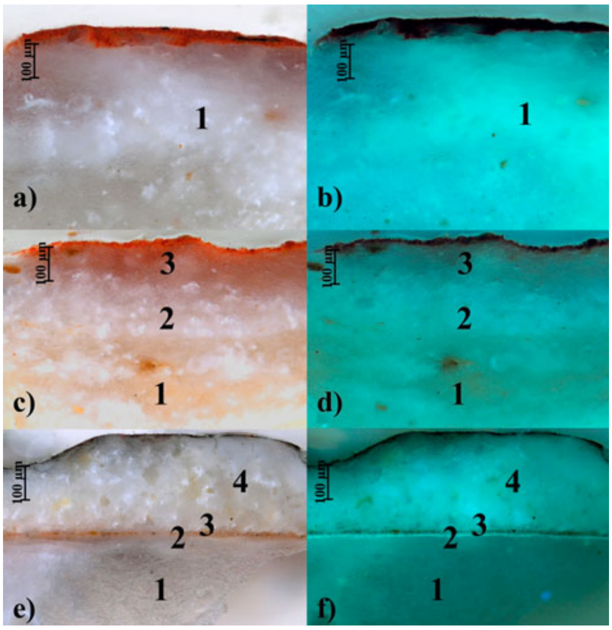

Figure 8: Photomicrographs of the cross sections of the micro samples from Hagios Stefanos Kilisesi. First phase (a, b); second phase (c, d), third phase (e, f). Reflected light (a, c, e), UV fluorescence (b, d, f).

Art historians have detected two pictorial phases in the churches of Hagios Basilios and Joachim ve Anna. The cross section seems to confirm this assumption. Since both layers (Figs. 6e, f, g, h and 6i, l, m, n) show very homogeneous features for thickness, composition (gypsum white plaster), traces of a thin flimsy fragmentary red paintings, it is rather difficult to chronologically discriminate them, except for the presence of a transparent setting layer in the second layer (nr. 2 in Figs. 6g, h and 6m, n).

In spite of difficulties with the complex and fragmentary stratigraphy of the 6^{th} and 7^{th} Century churches, some hypotheses can be derived from the comparison of the cross sections. The analogy of the plasters allows to propose homogeneous phases that were created in the same historical period, or with a short time interval between them.

The wall paintings of the Hagios Stefanos Kilisesi show a more complex stratigraphy. Three phases were observed during *in situ* investigation. The examination of cross sections confirmed this, based on mapping with the aid of photographic and graphical documentation. The first pictorial phase (Figs. 8a, b) is made of a white plaster from gypsum. The second phase (Figs. 8c, d) is made of three layers, all constituted mainly by gypsum: a pink layer (nr. 1 in Figs. 8c, d), a white one and a thin transparent layer. In this second phase the painting is applied over the thick transparent layer (nr. 3 in Figs. 8c, d).

The third phase (Figs. 8e, f) shows a white transparent plaster over which a very thin fluorescent layer (nr. 2 in Fig. 8f) is applied. Over this fluorescent layer a thin and discontinuous red painting is visible (nr. 3 in Fig. 8e). At last, a white layer was applied in some areas of the wall paintings (nr. 4 in Figs. 8e, f) probably during the 20^{th} century to cover decorations.[6] This layer contains gypsum, calcium carbonate (bands at 2511 cm^{-1}, 1794 cm^{-1}, 1440 cm^{-1}, 875 cm^{-1} and 710 cm^{-1}, see FTIR spectrum in Fig. 9) and organic materials. The presence of organic materials can be proposed due to UV-induced fluorescence and to some bands in the infrared spectra (Fig. 9, bands at 2923 cm^{-1}, 2854 cm^{-1} and 1654 cm^{-1}). This white layer is covered by a homogeneous black layer due to the habit of lighting fires in the church.

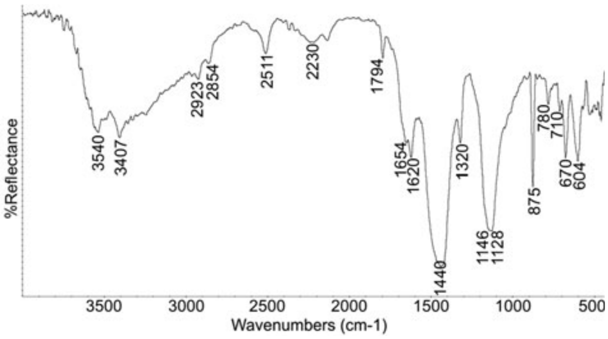

Figure 9: Diffuse reflectance FTIR spectrum of a sample from the third phase of the church of Hagios Stefanos Kilisesi.

3.1.2 8 th-9 th Century Churches

Concerning the two 8th-9th Century churches, the cross sections are shown in Fig. 10. The micro stratigraphy of the sample from the Kapılı Vadısı Kilisesi at Karacöeren (Fig. 10a, b) shows that a thin white plaster (nr. 2) is applied over a lime mortar (nr. 1), characterised by the presence of plant fibres, not visible in the cross section, part of Fig. 10. The FTIR spectrum of a micro sample from the mortar is shown in Fig. 11: the main compound is calcium carbonate with silicates (bands at 1110 cm^{-1}, 795 cm^{-1} and 473 cm^{-1}), traces of gypsum (bands at 3546 cm^{-1}, 3405 cm^{-1}, 1622 cm^{-1} and 670 cm^{-1}), oxalates (1320 cm^{-1}) and organic materials (2923 cm^{-1}, 2868 cm^{-1} and 1650 cm^{-1}).

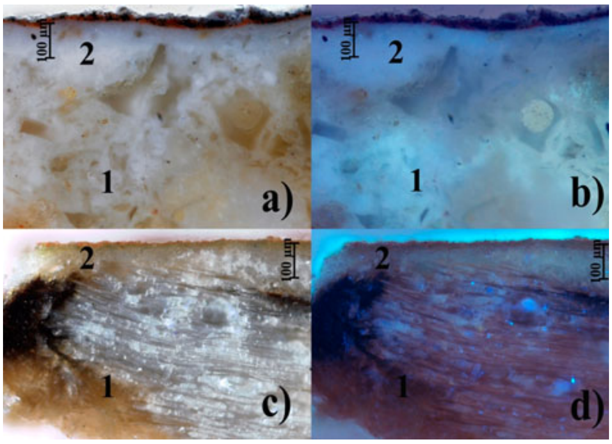

Figure 10: Photomicrographs of the cross sections of the micro samples from Kapılı Vadısı Kilisesi at Karacöeren (a, b) and Güllü Dere nr. 5 (Süslü Kilise; c, d). Reflected light (a, c), UV fluorescence (b, d).

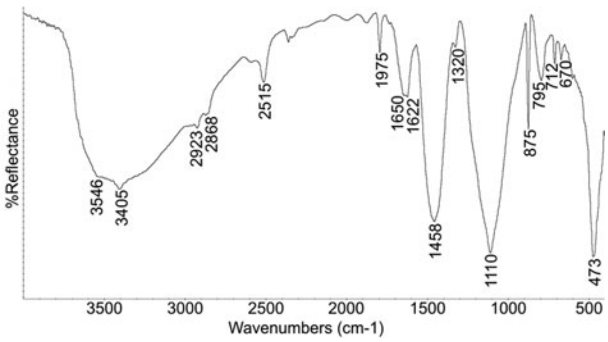

Figure 11: Diffuse reflectance FTIR spectrum of a sample from the mortar of the church of Karacöeren.

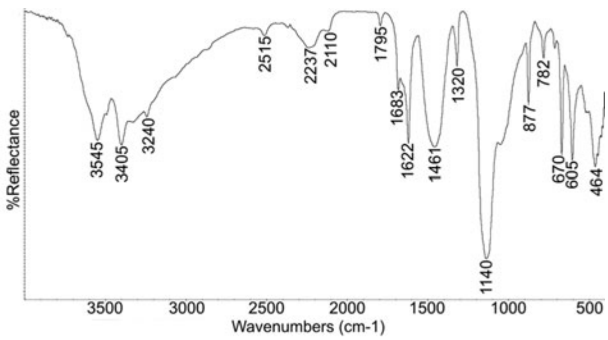

Figure 12: Diffuse reflectance FTIR spectrum of a sample from the painted layer of the Süslü Kilise.

The sample from Güllü Dere nr. 5 (Süslü Kilise) exhibits a thin white layer (nr. 2 in Figs. 9c, d), made of gypsum (see FTIR spectrum in Fig. 12), applied over a lime plaster containing schistose rock fragments (visible in the cross section, Fig. 10c, d, nr. 1). The micro-Raman analysis carried out on layer nr. 2 of the cross section revealed only the presence of gypsum.

3.1.3 10 th Century Church

The study of the 10th century church, the New Tokalı, was studied in 2011 with the aim to perform conservation on this most important monument of the Open Air Museum of Göreme. In the New Tokalı church the plaster is made of calcite and plant fibres (not visible in Fig. 13). Over the plaster layer a thin gypsum setting was spread. At last the pigments were applied by an organic binder, probably a proteinaceous compound (Fig. 14, bands at 3303 cm^{-1}, 1657 cm^{-1} amide band I, 1543 cm^{-1} amide band II, 1450 cm^{-1} C-H deformation). Some bands in the spectrum of Fig. 12 (2960 cm^{-1}, 2920 cm^{-1}, 2856 cm^{-1}, 1730 cm^{-1}, 1250 cm^{-1}, 1140 cm^{-1}, 1048 cm^{-1}) can be attributed to the presence of an acrylic resin used during the conservation work performed in the 1970s.[17]

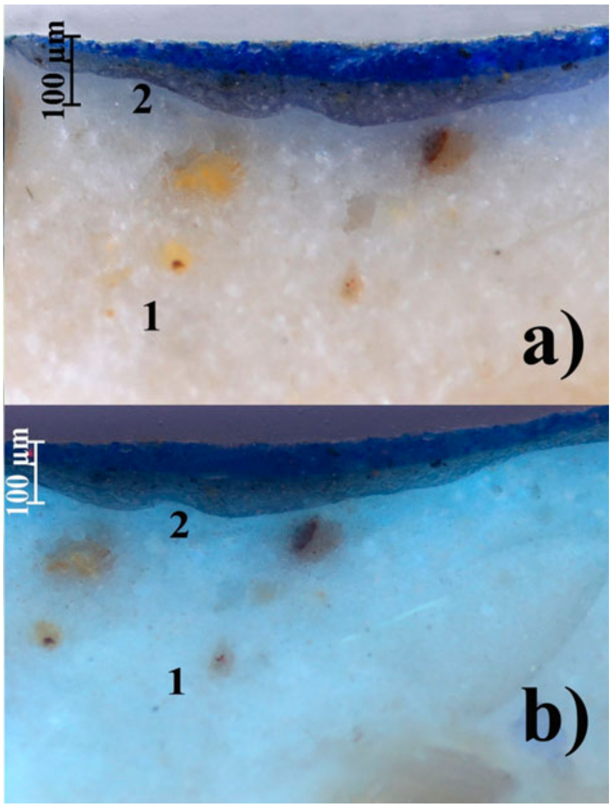

Figure 13: Photomicrographs of the cross section of a micro sample from the New Tokalı church: a) reflected light ; b) UV fluorescence.

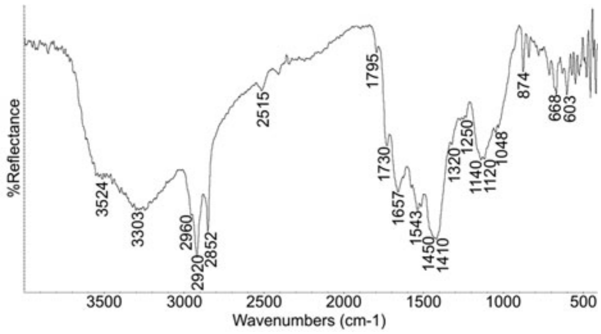

Figure 14: Diffuse reflectance FTIR spectrum of a sample from the New Tokalı church.

3.1.4 13 th Century Churches

The churches in this group are: the Forty Martyrs' church at Şahinefendi; the Arcangelos Kilisesi in the Keslik Manastir at Cemil; the Sarica Kilise nr. 1 at Ürgüp. The wall paintings of the Arcangelos Kilisesi are almost completely covered by a soot layer, making interpretation difficult. The cross section of a sample from the 13th century phase of this church is shown in Fig. 15a, b. The plaster is made of calcite with traces of gypsum and organic materials (Fig. 16).

The Sarica Kilise nr. 1 at Ürgüp is characterized by two very fragmentary pictorial phases: in the first one, showing aniconic paintings, gypsum with traces of organic compounds is used. The second phase (Fig. 15c, d) that may be dated back to the 13th century is characterized by a plaster made of calcium carbonate, gypsum and organic compounds with traces of calcium oxalate (Fig. 17).

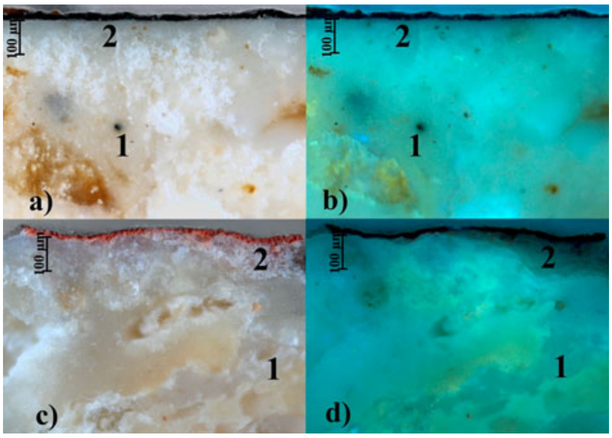

Figure 15: Photomicrographs of the cross section of the micro samples from the Arcangelos Kilisesi (a, b) and Sarica Kilise (c, d). Reflected light (a, c), UV fluorescence (b, d).

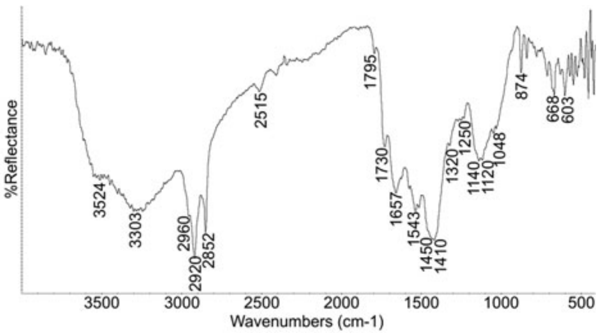

Figure 16: Diffuse reflectance FTIR spectrum of a sample from the 13 th century phase of the Arcangelos Kilisesi.

The Forty Martyrs church at Şahinefendi is characterized by different painted phases whose interpretation is not completely clear yet. The careful investigation carried out during the conservation work allowed to reveal the presence of at least four pictorial phases and of thin whitewash layers applied over the pre-existing

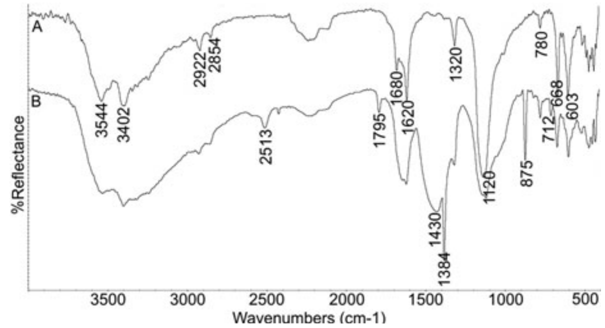

Figure 17: Diffuse reflectance FTIR spectrum of two samples from the church of Sarica nr.1. A is the spectrum of a sample from the first pictorial phase, B is the spectrum of a sample from the second pictorial phase.

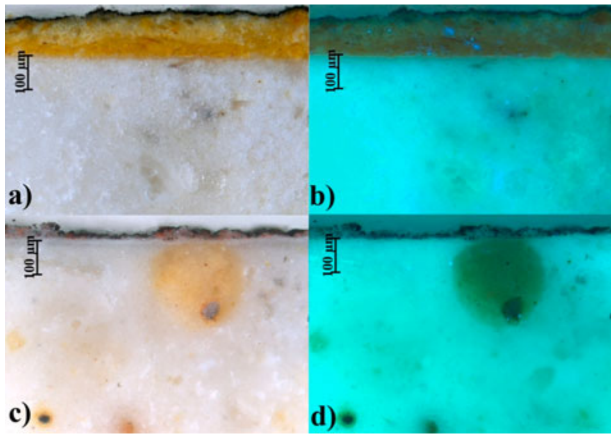

Figure 18: Photomicrographs of the cross sections of two micro samples from the Forty Martyrs Church. Reflected light (a,c); UV fluorescence (b,d).

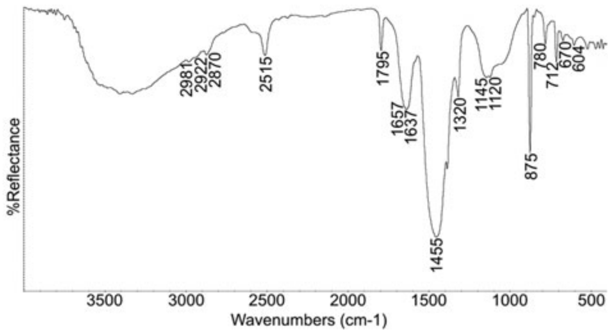

Figure 19: Diffuse reflectance FTIR spectrum of a sample from the Forty Martyrs Church. Calcium carbonate is the main component.

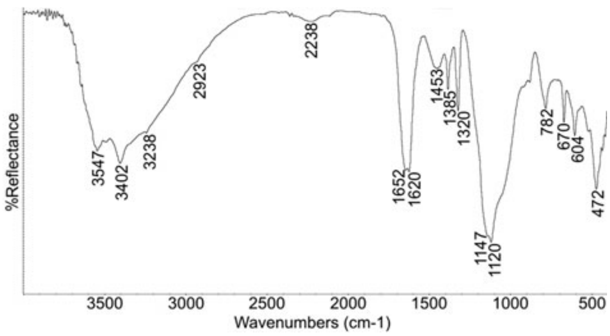

Figure 20: Diffuse reflectance FTIR spectrum of a sample from the Forty Martyrs Church. Gypsum is the main component.

paintings in order to change the wall decoration. The analysis of the wall paintings of the Forty Martyrs church is still in progress. At present, after the removal of the sooty layer that covered up the paintings, the Forty Martyrs scene is clearly visible and it was possible to date it back to the 11th Century A.D. The fourth layer was dated back to 1216-1217 A.D. thanks to the presence of an inscription, clearly visible after the cleaning work. The micro stratigraphic analysis of the samples taken from the Forty Martyrs layer showed a white, sometimes pinkish, plaster (Fig. 18).

FTIR analysis revealed the presence of calcium carbonate, traces of gypsum, oxalates and organic materials (Fig. 19). Micro-Raman analysis, performed both on the cross-sections and on the powders, allowed to detect the presence of calcite, gypsum, anhydrite (Raman band at 1020 cm^{-1}) and calcium oxalate. Gypsum is present in all the mortar with a greater concentration in the area under the painting layers: probably it was used as a setting layer 20 (Fig. 20).

3.2 Pigments

The pigments were identified by micro-Raman spectroscopy by comparing the obtained spectra to literature data and spectral databases.[21-27] The main red pigment in all the examined churches is highly crystalline hematite (Fe_2O_3, Fig. 21) often associated to magnetite (Fe_3O_4). The presence of magnetite, whose Raman spectrum is characterized by a broad band at 660-670 cm^{-1} could also be due to thermic processes that the wall paintings often underwent because of the fires lit inside the churches[26].

Lead red (Pb_3O_4) was also widely used in the wall paintings in Cappadocia. Raman spectrum of this pigment is characterized by the following bands: 116(vs) cm^{-1} (deformation of the angle O-P^{IV}-O), 149(m) cm^{-1}, 220(w) cm^{-1}, 311(w) cm^{-1}, 389(m) cm^{-1}, 479(w) cm^{-1}, 544(s) cm^{-1} (vibrations of elongation of P^{IV}-O bond).[26-27]

Lead red was found in the following churches: Üzümlü Kilisesi, Karşibecak Kilise, and in the II phase of the Hagios Stefanos Kilisesi. The areas painted with lead red show evident surface blackening due to the presence of plattnerite (PbO_2) whose Raman spectrum is characterized by a medium broad band at 515 cm^{-1} and two very weak bands at 653 cm^{-1} and 424 cm^{-1}. Raman analysis revealed also the presence of anglesite often associated to lead red ($PbSO_4$). Raman spectrum of anglesite is characterized by a sharp band at 975 cm^{-1} (Fig. 22). The spectra of Fig. 22 correspond to two different points of the sample.

In a red frame with white pearls of the New Tokali church an organic dye was found whose Raman spectrum is shown in Fig. 23. The spectrum exhibits some analogies with the Raman pattern of alizarin.[25] This dye should be related to restoration in 1970s because it is usually used as water colour for pictorial retouching.

The yellow decorations were created especially with ochre containing goethite. Often goethite was mixed with lead oxide. Raman spectrum of goethite is characterized by the following bands: 245(w) cm^{-1}, 299(m) cm^{-1}, 387(s) cm^{-1}, 480(w) cm^{-1} and 549(w) cm^{-1}. The Raman spectrum of lead oxide is characterized by a

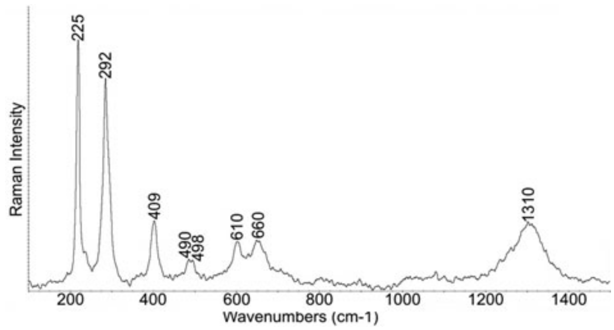

Figure 21: Raman spectra of a red grain in the sample from Arcangelos Kilisesi.

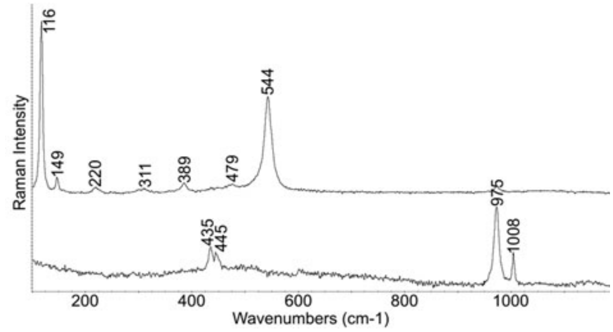

Figure 22: Raman spectra of a sample from Karşibecak Kilise. Lead red, anglesite and gypsum are visible.

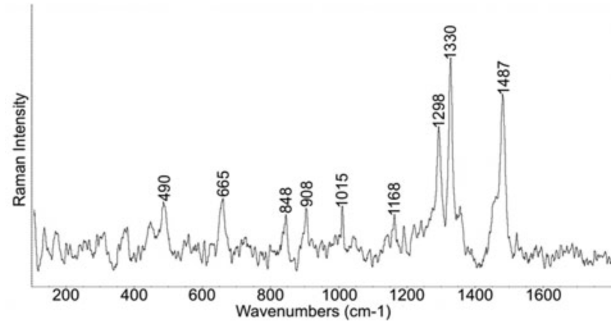

Figure 23: Raman spectrum of a red brilliant grain in a sample from the New Tokalı church.

very strong peak at 144 cm^{-1} due to the lattice Pb-O stretching and two other weak bands at 296 cm^{-1} and 383 cm^{-1}.[25,27] In the Forty Martyrs church also jarosite was found, a natural iron sulphate [$KFe_3(SO_4)_2(OH)_6$] rarely used as pigment.[28] Raman spectrum of jarosite is shown in Fig. 24.

Green colour was obtained, in all the examined samples, with green earth. Various siliceous minerals of dull greyish green colour are found known generally as green earth.[29] The main minerals of green earth are celadonite, approximately $K[(Al^{III}, Fe^{III})(Fe^{II}, Mg^{II})]$, $(AlSi_3,Si_4)O_{10}(OH)_2$ and glauconite, $(K, Na)(Fe^{III}, Al^{III}, Mg^{II})_2(Si,Al)_4O_{10}(OH)_2$. Both minerals belong to the mica group.[29] Raman spectra of green earth vary according to the provenance of the material and they can exhibit different bands. The experimental spectrum (Fig. 25), compared with the literature data, shows clear analogies with that of celadonite.[30]

Ultramarine blue was found in the Güllü Dere nr. 5, New Tokali church, Forty Martyrs church and Arcangelos Kilisesi. Raman spectrum of ultramarine blue has a well-defined Raman pattern with the following bands: 256(w) cm^{-1}, 548(vs) cm^{-1}, 1095(m) cm-

1 (Fig. 26). In the New Tokalı the ultramarine blue was widely used to paint the backgrounds, the Virgin and Christ's garments. Traces of indigo were also detected, main bands at 140(w) cm^{-1}, 256(m) cm^{-1}, 548(m) cm^{-1}, 603(w) cm^{-1}, 1251(w) cm^{-1} and 1577(vs) cm^{-1}, mixed with ultramarine blue (Fig. 26).

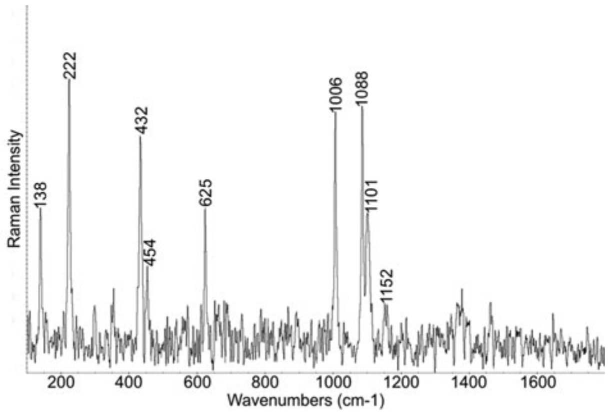

Figure 24: Raman spectrum of a yellow grain in a sample from the Forty Martyrs church. Calcite is also visible (main band at 1088 cm^{-1}).

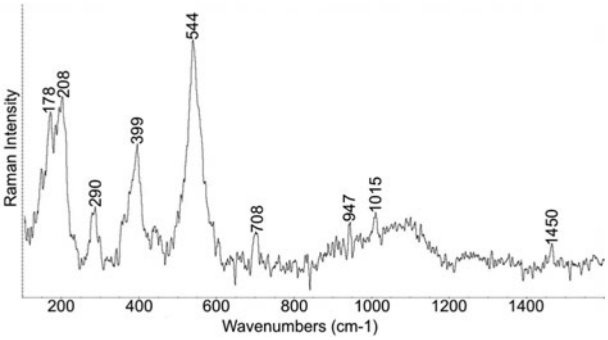

Figure 25: Raman spectrum of a green area in a sample from the New Tokalı church.

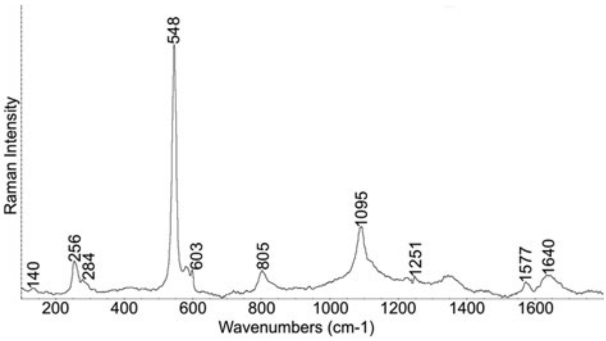

Figure 26: Raman spectrum of a blue grain in a sample from the New Tokalı.

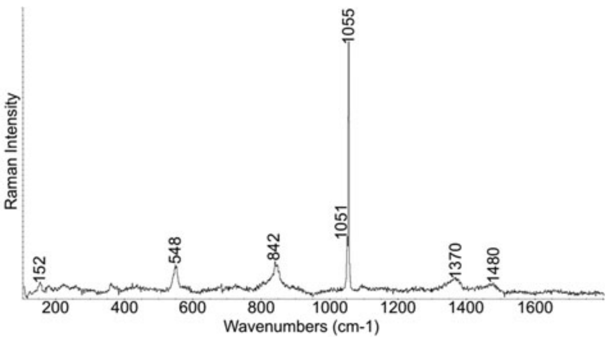

Figure 27: Raman spectrum of a white grain in a sample from the Arcangelos Kilisesi. Traces of ultramarine blue are also visible in the Raman spectrum of Fig. 27 (band at 548 cm^{-1}).

Traces of indigo were found also in the Forty Martyrs church at Şahinefendi. In the Güllü Dere nr. 5 church ultramarine blue was found in a bluish green decoration mixed with green earth. Finally, in the Arcangelos Kilisesi ultramarine blue, mixed with lead white and yellow lead oxide, was found in a light blue background, covered with soot. Lead white was found also in the church of Joachim ve Anna at Kizil Çukur in a floral element of the first layer decoration. A mixture of cerussite ($PbCO_3$) and hydrocerrusite $Pb_3(CO_3)_2(OH)_2$ can be detected, due to the presence of a doublet at 1051-1055 cm^{-1} in the Raman spectrum (Fig. 27).[26]

Black colour is made out of carbon based black sometimes characterized by fine chip-shaped grains under polarizing microscope. This pigment is characterized by a typical Raman spectrum with two broad bands at about 1340 cm^{-1} and 1580 cm^{-1}. Table 1 summarizes the results of the analysis discussed above. Concerning other materials, found in the samples by micro-Raman and FTIR spectroscopy, it is worth noting the presence of different kind of sulphates whose origin needs to be further investigated.

4 Conclusions

In this paper the results of a first survey of eleven Cappadocian churches are reported and discussed. It must be stressed that these results will need further integration and research in order to characterize the organic binders of the paintings and also to include other churches, which are at present still under investigation. The scientific analysis was performed in order to support art historians and restorers work to define the chronology of the investigated churches and to study the materials and techniques. In fact, the interpretation of wall paintings in the rock hewn churches is difficult due to the presence of various superimposed layers and to their bad state of preservation.

The study of the internal micro stratigraphy and of the pigments allowed to define analogies and differences between the examined churches, sometimes unraveling complex chronological issues.

The churches from the 6^{th} and 7^{th} Century are generally characterized by the use of a gypsum plaster directly applied on rock. A widespread use of lead-based pigments has been found in these churches, often associated with blackening due to pigment degradation. Blue colour was not found in the decoration of these churches.

The two churches from the 8^{th} and 9^{th} Century are characterized by decorative elements painted over a thin finishing white layer applied on a lime mortar containing schistose minerals in the Güllü Dere nr. 5, and plant fibres in the Kapılı Vadısı Kilisesi at Karacöeren. In the Güllü Dere nr. 5 there is evidence of ultramarine blue mixed with green earth.

The New Tokalı church was dated back to the 10^{th} century. The plaster was made of lime with plant fibres and organic materials. The pigments were applied by means of an organic binder. Ultramarine blue was widely used to paint the backgrounds, the Virgin and Christ's garments.

Church	Century	Plaster	Pigments	Other materials
Hagios Stefanos Kilisesi, Kislik Monastir Cemil	6th-7th	Gypsum with traces of organic material	Hematite, red lead, goethite, carbon black	Calcite in the third pictorial phase. Calcium oxalate, magnetite, anglesite
Hagios Basilios Kilisesi, Mustafapaşa	6th-7th	Gypsum with traces of organic material	Hematite, red lead, lead oxide, goethite, green earth, carbon black	Calcium oxalate, iron sulphate, traces of calcite
Joachim ve Anna Kilisesi, Kizil Çukur	6th-7th	Gypsum with traces of organic material	Hematite, goethite, green earth, carbon black, lead white	Calcium oxalate, magnetite, anhydrite
Üzümlü Kilisesi, Kizil Çukur	6th-7th	Gypsum with traces of organic material	Hematite, read lead, goethite, lead oxide, green earth	Calcium oxalate, anglesite and other probable sulphates, magnetite
Karşibecak Kilise, Avcilar/ Göreme	6th-7th	Gypsum with traces of organic material	Hematite, goethite, red lead, green earth	Calcium oxalate, anglesite, plattnerite, potassium sulphate
Kapılı Vadısı Kilisesi, Karacöeren	8th-9th	Thin white plaster on a lime mortar with plant fibres and silicates	Hematite, lead oxide, carbon black	Traces of calcium oxalate, magnetite, plattnerite, sulphates and nitrates in a salt efflorescence
Güllü Dere nr. 5, Süslü Kilise	8th-9th	Thin gypsum plaster on a lime mortar with schistose minerals	Hematite, goethite, lead oxide, green earth, ultramarine blue	Silicates and silica
New Tokali	10th	Lime with plant fibres	Hematite, goethite, ultramarine blue, green earth, carbon black, lead oxide, indigo	Traces of gypsum, organic materials, alizarin, magnetite, silicates
Forty Martyrs, Şahinfendi	13th	Lime with traces of organic material. Thin setting layer made of gypsum	Hematite, red lead, goethite, lead oxide, jarosite, carbon black, green earth, indigo	Organic materials, silicates, anhydrite, magnetite, calcium oxalate, quartz
Arcangelos Kilisesi, Keslik Manastir Cemil	13th	Lime with traces of gypsum	Hematite, goethite, carbon black, ultramarine blue, lead oxide, lead white	Calcium oxalate, magnetite, anhydrite
Sarica Kilise Ürgüp	13th	First phase: gypsum. Second phase: lime	Hematite, goethite, carbon black	Traces of organic materials in both phases

Table 1: Summary of the internal micro stratigraphic, FT-IR and micro-Raman analysis.

Finally, the 13th-Century churches exhibit a different internal micro stratigraphy. The mortar was made of lime and the painted layers were applied over a thin layer made of gypsum using the *a secco* or lime technique. The main pigments are natural earths and ochres, lead based compounds, ultramarine blue and indigo.

Further analysis is necessary to better characterize the plasters and especially the organic binders that could not be accurately determined by micro-stratigraphic and FTIR analyses.

5 Acknowledgments

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