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HISTORICAL OVERVIEW OF KALENDERHANE MOSQUE (4^{th}-CENTURY CHURCH): CHARACTERIZATION OF ITS FRESCOES USING A MULTI-ANALYTICAL APPROACH

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Abstract

This study aims to characterize the frescoes located in the basement of a historically significant building that was originally constructed as a church (Theotokos Kyriotissa) and is now functioning as a mosque (Kalenderhane). The research employs multiple analytical methods, including X-Ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDS), to investigate the material composition and preservation state of the frescoes. The results indicate significant interactions between environmental factors and the preservation state of the frescoes, highlighting the importance of ongoing conservation efforts. This study contributes to a deeper understanding of the frescoes' historical context and their significance in the architectural heritage of the site. Additionally, it provides recommendations for future research and restoration practices aimed at preserving this invaluable cultural artifact.

***Keywords**: Byzantine frescoes; Pigments; Conservation; Architectural heritage; FTIR; Raman*

Introduction

Historical buildings possess significant cultural value, not only through their architectural aesthetics but also through the artistic elements they contain. Following the transformation of a structure originally built as a church during the Byzantine period into a mosque during the Ottoman era, efforts were made to preserve the frescoes and mosaics located in the building's basement. Such structures are typically adorned with frescoes, mosaics, and other artistic works, which reflect the societal and religious beliefs of their respective eras through the symbols and colors they encompass. Frescoes hold particular importance within religious buildings, serving as a rich source for scholars and art historians seeking to reconstruct the past. The preservation of these works is crucial for understanding them in both historical and cultural contexts. From this perspective, the characterization of the pigments, binders, and other materials used in frescoes forms the foundation for informed restoration and conservation processes. The existing literature on fresco analysis provides insights into the histories of art pieces and contributes to the development of scientific approaches for their preservation. Various studies have offered information about the nature, origins, and long-term alterations of the materials used in frescoes. For instance, research into the chemical compositions of pigments used in ancient frescoes has revealed important clues regarding the techniques and periods of their creation.

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For instance, the multi-analytical characterization of the chemical composition of different parts of frescoes (pigments, mortars, and binders) in the interior and exterior sections of a temple provides valuable insights into their construction techniques and technological practices [1]. Some studies have focused on a detailed investigation of the iron content detected in pigments such as red, yellow, and green, not only through analytical identification but also via physicochemical classification [2]. In another study, microscopic observations and chemical-mineralogical characterization were conducted on pigments found in rock paintings dated to the 5th–6th millennium BC on granite surfaces. The study, which employed multiple analytical techniques, identified hematite and gypsum as the predominant components. Stratigraphically, hematite was determined to be the earliest layer [3]. Additionally, frescoes on the apse wall of Scotterra Church in Italy, now located six meters below the current ground level, were analyzed using various approaches and analytical techniques. These frescoes, which employed natural pigments, were found to contain two lime-based plaster layers [4]. Similarly, as part of an archaeological study in Rome, wall paintings containing red and white fragments were examined using various spectroscopic methods, revealing information about the pigments used to produce the colors and the origins of the materials [5]. A different perspective on fresco characterization was explored in a study investigating how meteoric water infiltration and environmental factors contribute to the degradation of frescoes in a cave church [6].

In conclusion, the characterization of frescoes within a structure converted from a church to a mosque is not merely an artistic examination but also carries critical importance for the preservation of cultural heritage. This process necessitates the development of scientific approaches aimed at tracing the past and ensuring that these historical buildings are passed down to future generations.

Historical and Architectural Background

Kalenderhane Mosque is located within the Fatih district of Istanbul, in the Vezneciler neighborhood, facing the Marmara Sea side of the Valens Aqueduct (Fig. 1). The mosque holds a significant place in Istanbul's historical fabric.

Fig. 1. (A-B) Map of the place of the Kalenderhane Mosque [8]; (C-D) The Present Appearance of the Mosque

The site was originally home to a Roman-era bathhouse and was repurposed throughout the Byzantine, Latin, and Ottoman periods for various functions. The structure was originally built as a Byzantine church (the Church of Theotokos Kyriotissa). Following the conquest of Istanbul by Sultan Mehmed the Conqueror, certain privileges were granted to dervish groups who had participated in the conquest and rendered significant services. With these privileges, the

Kalenderi order, which had settled in the city, repurposed the Byzantine church of Kalenderhane as an imaret (public soup kitchen) [7]. Over time, the building functioned both as a dervish lodge (zaviye) and as a venue for Mevlevi ceremonies held on Fridays, making it the first Mevlevi lodge established after the conquest.

Excavations conducted in and around Kalenderhane Mosque have uncovered numerous Byzantine-era remains. The discovery of the foundations of a small bathhouse, dated to the 4th and 5th centuries, suggests that the structure was built on top of a Late Roman bathhouse dating to around 400 CE. Albrecht Berger proposes that this bathhouse was a private facility operated commercially by its owners for public use.

According to excavation findings, the site was later repurposed as part of a church complex. Following the conquest of Istanbul, it was converted into a mosque, with minor architectural modifications made to accommodate its new function (Fig. 2).

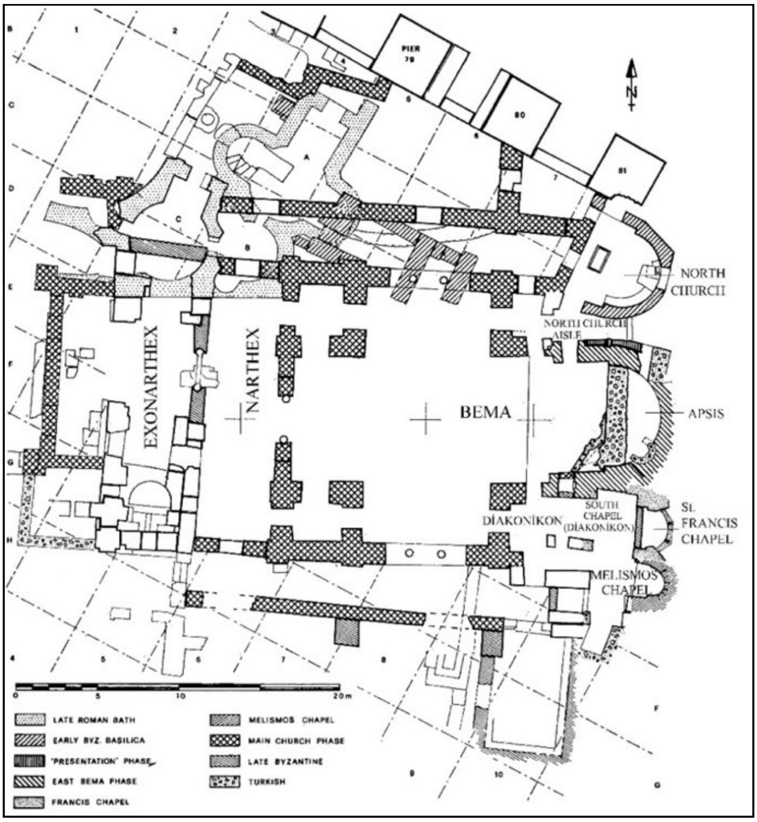

Fig. 2. The Restoration History and Construction Plan of Kalenderhane Mosque (1972) [9]

The site's earliest phase began as a bathhouse, which was later replaced by a church known as the North Church. Lime-based mortars with additions of clay minerals or gypsum are consistent with Roman and Byzantine construction techniques [10]. Following the construction of the North Church, the Bema Church was added in the late 7th century. The Bema Church remained intact until the 12th century, and in 1200, a new main church was built. The substantial size of the Main Church suggests the patronage of a wealthy benefactor, and it remains the only surviving Byzantine structure among the buildings once present on the site. During the Fourth Crusade in 1204, the church fell under Latin occupation and was repurposed as a Catholic church, adorned with Latin influences such as a fresco cycle depicting the life of Saint Francis of Assisi.

In 1261, when the Byzantines reclaimed the city, the structure was decorated with new embellishments during the Palaeologan period, the final artistic phase of the Byzantine Empire.

Following the Ottoman conquest of Istanbul in 1453, the church was converted into a mosque. The most significant architectural modification was the addition of a mihrab, aligned with the qibla direction. In the 18th century, the mosque was restored by Beşir Ağa, and in the 19th century, it underwent further renovation by Hacı Kadri. However, in 1928 or 1929, a lightning strike destroyed its minaret, leaving the mosque temporarily abandoned (Fig. 3).

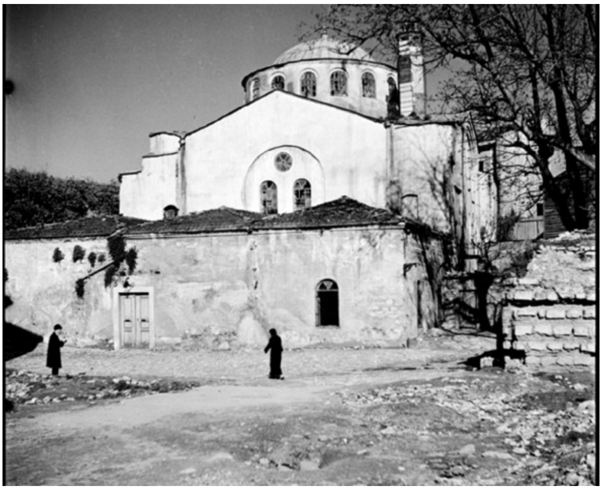

Fig. 3. General View of the Eastern Façade of Kalenderhane Mosque (June 1935) [11]

Kalenderhane Mosque boasts a remarkable artistic heritage, particularly its frescoes and mosaics. Among these, the fresco cycle depicting the life of Saint Francis of Assisi stands out as a significant example of late Byzantine-Latin interaction in religious art. During the Ottoman period, the frescoes were covered with plaster but were rediscovered during restoration efforts. The building's main space follows the closed Greek-cross plan, a common feature in Byzantine religious architecture. The four arms of the cross are covered with barrel vaults, while the central area is topped with a domed drum pierced with windows. Among the modifications made during the Palaeologan period were the closure of the Saint Francis Chapel and the reorganization of the exonarthex. As an important part of Istanbul's historical and cultural heritage, Kalenderhane Mosque embodies traces of both the Byzantine and Ottoman periods. Following extensive excavation and restoration work, it was reopened for worship. With its historical and artistic significance, the structure makes a valuable contribution to the preservation of cultural heritage, reflecting architectural richness spanning centuries. To further understand and preserve its frescoes, spectroscopic analyses were conducted on the three primary pigments used in the paintings, allowing for the characterization of the frescoes through advanced analytical techniques.

Materials and Methods

For this study, samples were collected from various locations in the basement level of the structure to represent all distinct colors observed in the fresco fragments. Sample selection considered visible color variations, signs of deterioration, and differing levels of exposure to environmental factors, allowing for a comprehensive comparison of pigment and binder compositions (Fig. 4).

The sampling was performed in accordance with conservation protocols to ensure the preservation of the original frescoes. Samples were obtained by carefully scraping the colored sections from naturally detached fragments and gently grinding them into a fine powder (Fig. 5).

To avoid contamination, each sample was immediately placed in a separate sealed sample bag following collection. The bags were labeled with detailed information regarding the sampling location, layer depth, and observed characteristics. These meticulous records facilitated the accurate correlation of the analytical data with the physical condition of each sampled area.

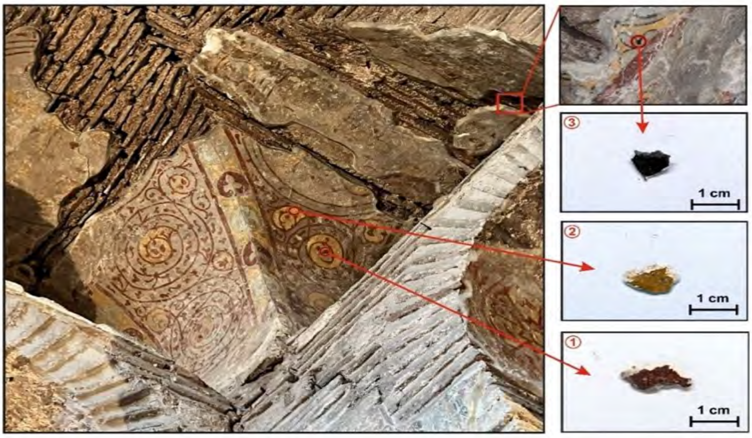

Fig. 4. Locations of the analyzed samples K1, K2, and K3 (the red circle indicates the exact point where the sample was taken)

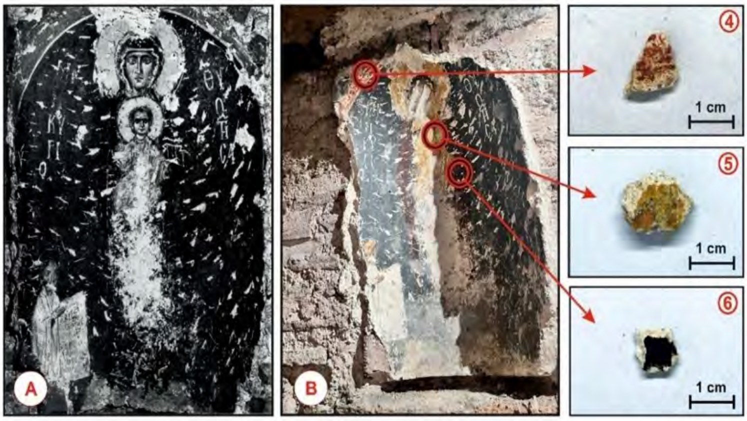

Fig. 5. The fresco containing the analyzed samples K4, K5, and K6 as documented in Striker and Kuban's 1968 study [12] (left) and its present condition (right)

Analytical Techniques

X-ray diffraction (XRD) was employed to determine the mineralogical composition of the fresco samples, including both the pigments and the underlying plaster. This technique provides insights into the crystalline phases associated with the materials used in the fresco application. The samples were finely ground to ensure homogeneity and placed on a low-background sample holder to minimize interference. X-ray diffraction patterns were collected at room temperature using a Malvern PANalytical Empyrean Series 3 X-ray diffractometer at the Aluminum Testing, Training, and Research Center of Fatih Sultan Mehmet Vakif University. The instrument operated with a goniometer speed of 1°/min (2θ) and utilized CuKα radiation ($\lambda = 1.5418$Å, 45kV, 40mA). The data collection covered a 2θ scan range from 5° to 70°, with a step size of 0.02°, a divergence slit of 0.5mm, and a receiving slit of 0.3mm. The analysis and phase identification of the XRD patterns were performed using the Philips X'Pert HighScore Plus software package (PDF-4

Release 2003) in conjunction with the JCPDS (Joint Committee on Powder Diffraction Standards) database.

FTIR analysis was performed on samples collected from fallen fresco fragments, which were ground and packaged prior to the measurements. Due to its ability to identify both organic and inorganic components, as well as pigments and binders, FTIR is one of the most suitable methods for characterizing different colors and underlying plaster compositions in frescoes. The effectiveness of ATR-FTIR for identifying both inorganic and organic components in wall paintings is well-established, particularly for distinguishing calcite, gypsum, clay minerals, and degradation products. Before the analysis, the samples were further ground to ensure optimal contact with the ATR crystal. Approximately 5 mg of the sample was used for the measurement. The IR spectra were obtained in ATR mode using a Jasco-6800 FTIR spectrometer equipped with a diamond single-bounce ATR accessory and Spectra Manager software at the Research Center for the Conservation of Cultural Property, Fatih Sultan Mehmet Vakif University. Spectra were collected with a resolution of 4 cm^{-1}, using 64 scans per sample to improve the signal-to-noise ratio. The spectrum of air was used as the background during the measurements. The spectral range was set from 4000 cm^{-1} to 400 cm^{-1}, covering the mid-infrared region necessary for identifying key functional groups. Background correction was performed before each measurement, and the obtained spectra were processed using specialized software for baseline correction and peak identification. The analysis aimed to identify chemical components such as pigments, binders, and possible degradation products present in the frescoes.

Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDS) was employed to investigate the microstructure and elemental composition of the fresco samples. Small fragments (approximately 2-3mm in size) were carefully collected from areas of the church frescoes where material had naturally fallen or detached, ensuring no intentional damage was caused to the original artwork. Prior to analysis, the samples were mounted on aluminum stubs using carbon adhesive tape to ensure good conductivity and to prevent charging effects. Elemental mapping and spot analysis were conducted to determine the distribution and concentration of elements in the pigments and plasters. The elemental compositions were analyzed using a Hitachi SU3500 SEM equipped with an Oxford X-ACT EDX micro-analytical system at the Aluminum Testing, Training, and Research Center of Fatih Sultan Mehmet Vakif University. To avoid charging, the samples were examined without any coating. The EDX analyses were performed on seven representative samples displaying different colors, with elemental compositions obtained under low vacuum conditions using a 30 kV accelerating voltage and an electron beam. The results provided valuable insights into the materials used in the frescoes and potential degradation processes.

Results

First, the elemental composition of the samples was determined using SEM (Scanning Electron Microscopy) analysis (Table 1). The results of the SEM analysis are crucial for conducting comparative studies with other analytical methods. This technique is particularly essential for understanding the relationship between the elemental composition of minerals or pigments and their role in coloration.

Table 1. The compositions of wall paintings obtained by SEM-EDS, given as a weight percentage of element oxides

Sample code	SiO_2	CaO	SO_3	FeO	Al_2O_3	MgO	Na_2O	K_2O
K1	3.84	62.91	27.49	2.87	1.48	0.80	0.61	-
K2	16.0	57.50	2.46	10.75	7.36	2.44	1.17	1.35
K3	1.79	58.28	38.34	-	0.55	0.58	0.46	-
K4	15.83	56.65	13.80	4.58	7.12	-	0.43	1.59
K5	29.67	35.05	0.91	13.95	17.57	1.15	0.48	0.87
K6	18.88	47.70	0.78	18.34	11.57	1.10	0.46	0.51

The XRD (X-ray Diffraction) analysis of the samples identified their mineral phases. The detected minerals include calcite, kaolinite, gypsum, hematite, and goethite, with their XRD patterns presented in Fig. 6. Calcite is interpreted as the primary component of the mortar used in the fresco's plaster layers. Lime-based mortar, commonly used as a substrate for frescoes, is produced by heating limestone to obtain quicklime, which then reacts with water to form slaked lime. The presence of kaolinite is associated with clay minerals and suggests its use as an additive in both mortar and pigments. Kaolinite may have been included to enhance the plasticity and consistency of the mortar.

Similarly, the presence of gypsum indicates the possible use of gypsum-based layers in addition to lime plaster during fresco construction. Gypsum is often found in preparatory layers and fine decorative coatings, suggesting that it might also have been introduced during later restoration processes. The identification of hematite suggests that it was the source of the red pigment. As an iron oxide mineral, hematite is known for its natural durability, which contributes to the long-term color stability of frescoes. Its presence indicates that a mineral-based red pigment was used, likely sourced from natural deposits. Another detected mineral was goethite, which, as part of the iron oxide group, was commonly used to achieve brownish-yellow hues in frescoes.

The presence of natural mineral-based pigments such as hematite and goethite provides valuable insight into the artistic and technological materials used during the period, shedding light on historical pigment sourcing and application techniques.

In the K1 sample, the detected minerals include gypsum, kaolinite, calcite, and goethite. The mineral responsible for the red coloration in this sample is believed to be goethite. Similarly, in the K2 sample, calcite, kaolinite, and goethite were identified (Fig. 6).

Goethite can produce various hues, ranging from yellowish to reddish-brown, depending on the degree of oxidation. In the K3 sample, only gypsum and calcite were detected. The XRD pattern exhibited an increased amorphous-like background, which may be attributed to oxidation and degradation. The K4 sample contained gypsum, calcite, kaolinite, quartz, and hematite phases. In this case, hematite is the primary mineral defining the color characteristics of the sample. Finally, in the K6 sample, calcite, kaolinite, and goethite were identified (Fig. 6). As observed in the K2 sample, goethite plays a crucial role in enhancing the dominance of yellow hues.

The FTIR analysis of the K1 sample identified bands at 418.8 and 712cm^{-1}, corresponding to the low-energy modes of goethite, an iron oxide phase. The bands at 456.9, 599 and 1110cm^{-1} represent the internal vibrational modes of calcite, while the 872.6cm^{-1} band corresponds to the C-O stretching vibration mode of calcite (Fig. 7). Additionally, a sulfate-specific vibration mode of gypsum was observed at 668.7cm^{-1}.

Similar vibrational modes were identified in the K2 sample, with bands at 872.3 and 1100cm^{-1} corresponding to calcite, a 670.2cm^{-1} band attributed to gypsum, and bands at 530.6 and 795.9 cm^{-1} indicating the presence of goethite (Fig. 7). The observed vibrational bands for calcite (872–1405cm^{-1}) and gypsum (~670cm^{-1}) are fully consistent with previously reported FTIR spectra of fresco materials [13]. In the K3 sample, which exhibits a black coloration, only gypsum and calcite were detected. The findings from SEM analysis were consistent with the results obtained through XRD and FTIR analyses.

In the K4 sample, which exhibits a red coloration, the identified characteristic bands include 670.2cm^{-1} (gypsum), 710.8 and 873cm^{-1} (calcite), 795.6cm^{-1} (kaolinite), and 467.1 and 527.6cm^{-1} (hematite). In the K5 sample, which has a yellow hue, the bands at 790.3cm^{-1} and 533.4cm^{-1} were identified as characteristic bands of goethite (Fig. 8). Additionally, the bands at 872.2 and 1405cm^{-1} correspond to calcite, while the 1032cm^{-1} band is attributed to kaolinite. Finally, in the K6 sample, which exhibits a dark red coloration, the characteristic bands at 464.7 and 534.1cm^{-1} confirm the presence of hematite. The characteristic bands of kaolinite, gypsum, and calcite are also presented in Figure 8.

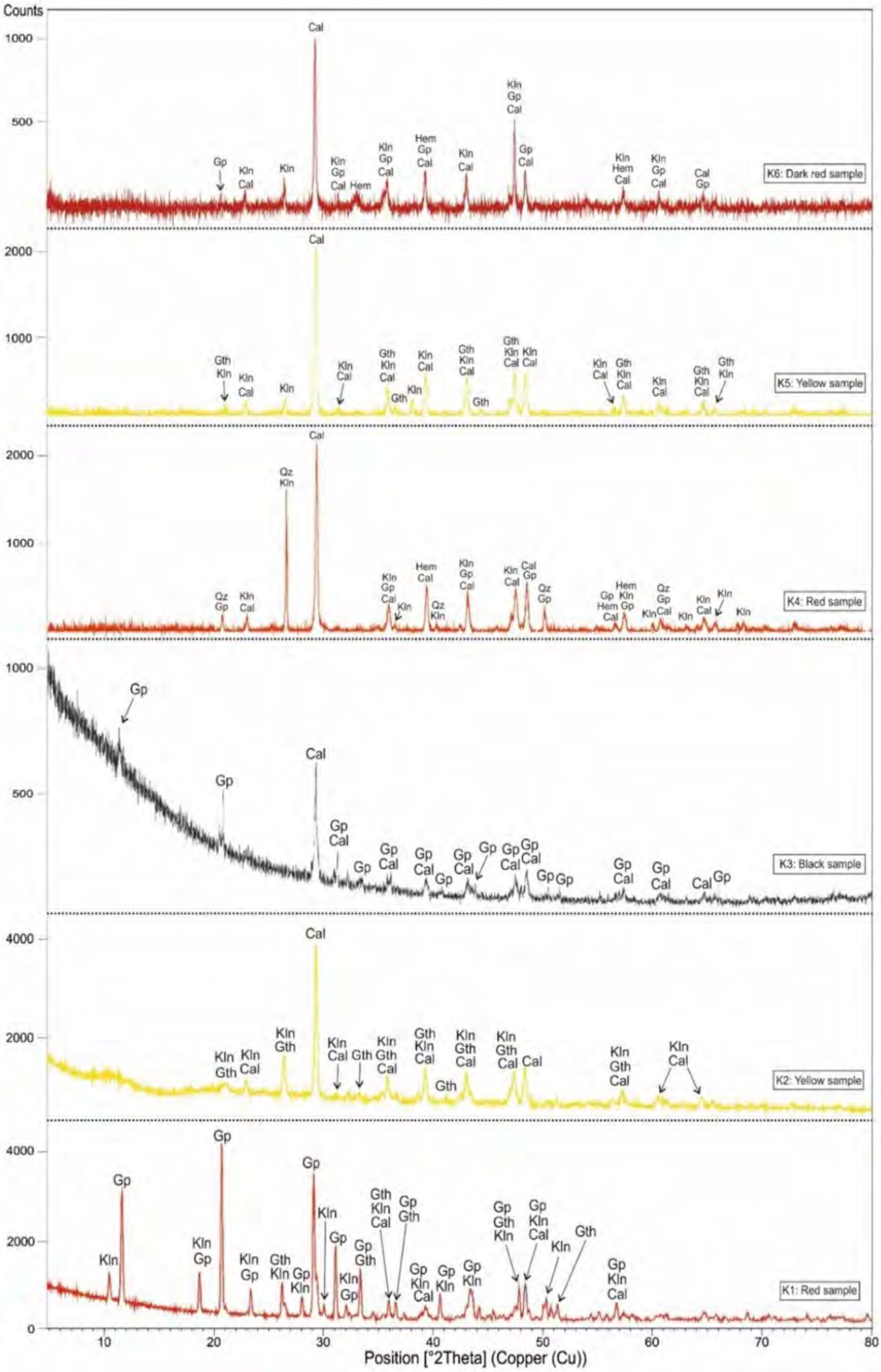

Fig. 6. X-ray diffraction pattern of the bulk samples. Identified minerals: calcite (Cal), gypsum (Gp), hematite (Hem), goethite (Gth), quartz (Qz), Kaolinite (Kln)

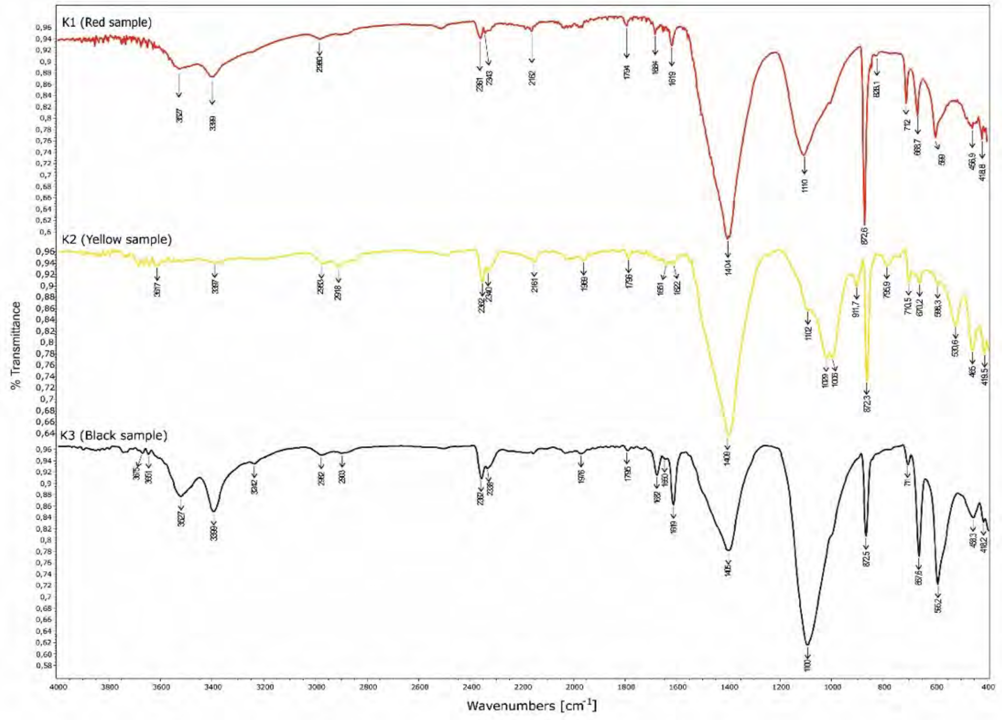

Fig. 7. FTIR spectra collected from samples (K1, K2 and K3)

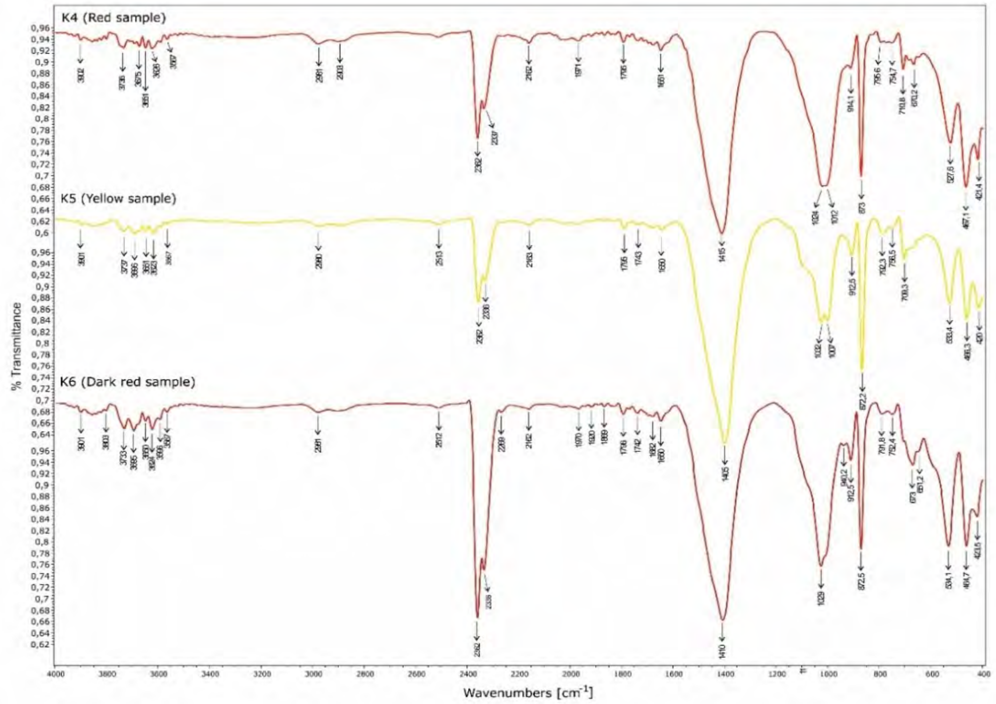

Fig. 8. FTIR spectra collected from samples (K4, K5 and K6)

The Raman analysis identified characteristic bands corresponding to different minerals in the samples. In the K1 sample, which exhibits a red coloration, the Raman spectrum revealed characteristic bands at 1010 and 1087cm^{-1}, corresponding to gypsum and calcite, respectively (Fig. 9).

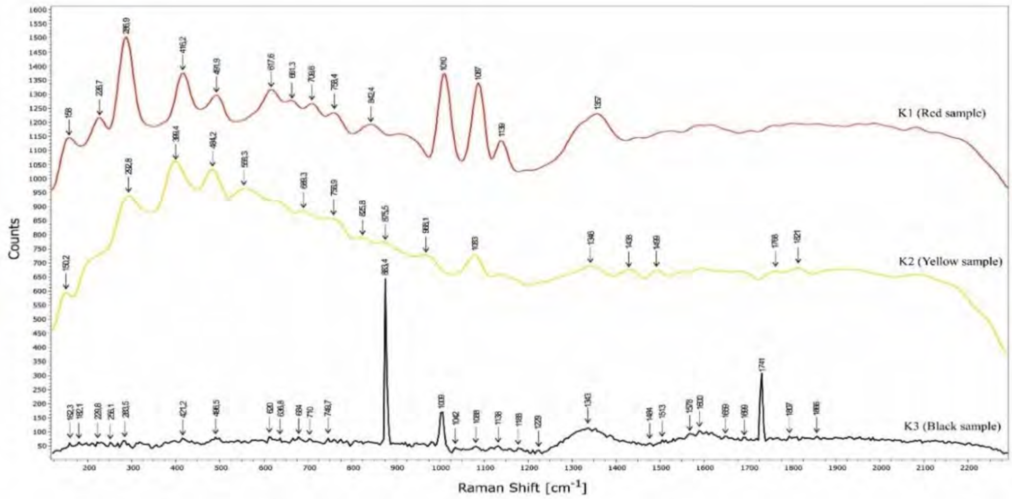

Fig. 9. Raman spectra collected from samples (K1, K2 and K3)

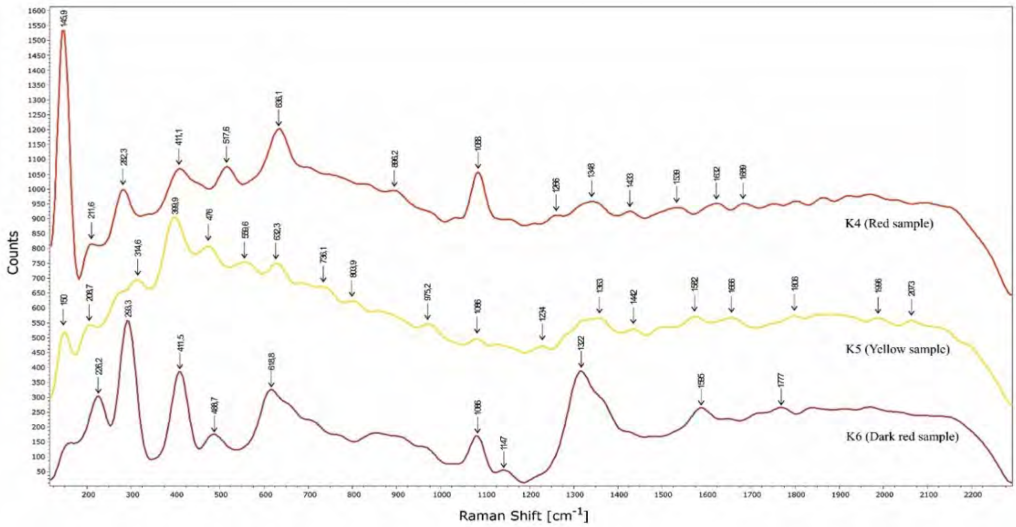

Fig. 10. Raman spectra collected from samples (K4, K5 and K6)

Additionally, the 491.9cm^{-1} band is attributed to hematite, which is likely responsible for the sample's color characteristics. In the K2 sample, the presence of goethite was confirmed by bands at 399.4 and 484.2cm^{-1}, while the 1083cm^{-1} band indicated the presence of calcite. In the K3 sample, weak peaks observed at 283.5, 710 and 1088cm^{-1} are attributed to calcite bands, while the strong peak at 1343cm^{-1} and the weak peak at 1578cm^{-1} are believed to be associated with carbon content. Additionally, the 1009cm^{-1} band is identified as a characteristic band of gypsum, and the strong peak at 883.4cm^{-1} is thought to be linked to an organic component (Fig. 9). For the K4 sample, which exhibits a red coloration, Raman analysis identified the 1088cm^{-1} band as calcite, while the 411.1 and 282.3cm^{-1} bands were attributed to hematite. The characteristic bands observed for hematite and goethite align with reference Raman spectra widely used in archaeological pigment identification [14]. No distinct bands corresponding to other minerals were observed (Fig. 10).

In the K5 sample, most of the detected bands were weak, with the most distinct bands being 399.9cm^{-1}, identified as goethite, and 1086cm^{-1}, attributed to calcite. The bands at ~399 and 482cm^{-1} match the diagnostic features of goethite reported under low-laser conditions [15]. Finally, in the K6 sample, which has a dark red coloration, Raman analysis confirmed the presence of hematite with clear peaks at 226.2, 293.3, 411.5, and 618.8cm^{-1}. Additionally, the 1086cm^{-1} band verified the presence of calcite (Fig. 10).

Discussion

The spectroscopic analysis methods used in this study identified the pigments and minerals responsible for the coloration of some of the frescoes in the structure. The results suggest that the minerals used were either produced in a manner consistent with those found in contemporary buildings of the period or were directly incorporated into the fresco-making process. The use of lime in the plaster composition has led to deterioration of the frescoes over time, influenced by ambient temperature and humidity levels. Humidity-driven deterioration processes affecting fresco plasters, such as salt migration and microcracking, are well-established in wall painting conservation literature [15]. For instance, in frescoes where hematite was used to create a red hue, prolonged exposure to moisture has increased oxidation, causing the transformation of hematite into goethite and resulting in a shift from red to yellowish tones. The hematite-to-goethite transformation under moisture and oxidative stress is well documented in iron oxide systems and may explain the observed color shift. The collected data provides significant insights into the architectural history of the structure and the restorations it has undergone. Notably, modern interventions were observed in previously undisturbed areas of the frescoes, indicating recent modifications. During past restoration processes, efforts were made to renew pigments and minerals using lime, often leading to deviations from the original compositions. Despite evidence of various restoration phases and human-induced damage over time, no specialized conservation efforts are currently in place to protect the frescoed sections of the building. A comparison of archival photographs with the frescoes' present condition clearly reveals the rapid deterioration and degradation of these artworks. As a significant part of cultural heritage, the frescoes require detailed examination and careful preservation efforts. It is hoped that scientific studies such as this will raise awareness and encourage the necessary protective measures to safeguard these invaluable artworks for future generations.

Conclusions

The analysis results obtained in this study have enabled the characterization of the minerals used in the construction of the frescoes within the structure. As a result, a chemical data set has been established, which will be valuable for future restoration and conservation efforts involving the frescoes. Given the rapid deterioration of the frescoes due to environmental factors, modern analytical techniques used in this and similar characterization studies play a crucial role in ensuring their preservation and safe transmission to future generations as part of cultural heritage conservation. For a more comprehensive study, additional samples could be collected from all existing frescoes, and on-site measurements could be conducted using a portable XRF device, particularly to examine damaged paint layers. This would allow for a more detailed analysis of past restoration interventions carried out on the frescoes from their original construction to the present. Furthermore, conducting a detailed study of the mosaics alongside the frescoes would provide valuable insights into the paints, pigments, minerals, and decorative stones used in artistic applications of that period.

Acknowledgments

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