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Characterization of Wall Painting Fragments from the West Courtyard Passage at St. Nicholas Church in Demre

Demre Aziz Nikolaos Kilisesi Batı Avlu Geçiş Mekanında Bulunan Duvar Resmi Parçalarının Karakterizasyonu

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Abstract

This paper presents archaeometric analyses of representative wall painting fragments (dated to middle Byzantine period) from the West Courtyard Passage at Demre St. Nicholas Church (in ancient Myra), which is located in Antalya province today. Wall painting fragments were analyzed by a multi analytical methods which includes physical and chromametric determinations, optical microscopy, X-ray diffraction (XRD), Raman spectrometry and X-ray fluorescence spectrometry (μ-XRF and PED-XRF), in order to identify the characteristics of the materials, painting technique and the pigments used. Microscopic examinations showed that the samples were two-layered (intonaco and arriccio) wall paintings that executed using the secco technique. The elemental compositions of the plasters are quite similar. The pigments used in the wall paintings is similar to others in the literature, including red and yellow ochre, calcite, green earth (celadonite) and carbon black. Archaeometric studies for the identification of archaeological pigments are carried out with micro-Raman spectroscopy and multiple analytical techniques. The same methodology was applied in this study. The results obtained will also contribute to the conservation/restoration studies of wall paintings.

Keywords
Archaeometry, wall paintings, Demre St. Nicholas Church, material characterization, Raman spectroscopy

Öz

Bu çalışmada, Antalya'nın Demre ilçesinde bulunan St. Nicholas Kilisesi'nin (antik Myra kentinde yer alan) Batı Avlu geçiş mekânından ele geçen duvar resmi parçalarının arkeometrik analizleri sunulmaktadır. Duvar resmi parçaları; malzeme özellikleri, boyama teknikleri ve kullanılan pigmentler açısından fiziksel ve kromametrik belgelemeler, optik mikroskopi, X-ışını difraktometresi (XRD), Raman spektroskopisi ve X-ışını floresan spektroskopisi (μ-XRF ve PED-XRF) içeren çoklu analitik metotlar ile analiz edilmiştir. Mikroskobik incelemeler, duvar resimlerinin iki katmanlı (intonaco ve arriccio) olduğunu göstermiştir. Secco tekniği kullanılarak uygulandığı tespit edilen duvar resmi parçalarına ait sıva tabakalarının kimyasal bileşimleri oldukça benzerdir. Duvar resimlerinin pigment paleti literatür ile uyumlu olup, kırmızı ve sarı aşı boyası, kalsit, yeşil toprak (seladonit) ve karbon siyahından oluşmaktadır. Arkeolojik pigmentlerin tanımlanmasına yönelik arkeometrik çalışmalar mikro-Raman spektroskopisi ile beraber çoklu analitik tekniklerle gerçekleştirilmektedir. Bu çalışmada da aynı metodoloji uygulanmıştır. Elde edilen sonuçlar duvar resimlerinin konservasyon/restorasyon çalışmalarına da katkı sağlayacaktır.

Anahtar Kelimeler
Arkeometri, duvar resimleri, Demre Aziz Nikolaos Kilisesi, malzeme karakterizasyonu, Raman spektroskopisi

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Genişletilmiş Özet

Aziz Nikolaos Kilisesi'nin bulunduğu Myra kenti, günümüzde Antalya ilinin Demre ilçesinde yer almaktadır. Myra, Teke Yarımadası'nın güneyinde yer alan; kaya mezarlarından edinilen verilere göre tarihi İÖ 5. yüzyıla kadar uzanan bir antik kenttir. Myra, liman kenti Andriake'nin Akdeniz'in önemli limanlarından birisi olmasının da etkisiyle Roma Dönemi'nde ticaretle zenginleşmiş ve İmparator II. Theodosius (408-450) tarafından Likya bölgesinin başkenti ilan edilmiştir. Bizans döneminde de Likya bölgesinin metropolitliğini 5-15. yüzyıllar arasında sürdüren kent, dinî bir merkez olmuştur.

4. yüzyılda Patara'da doğduğu bilinen Nikolaos'un, Myra'da piskoposluk yaptığı, ölümünden sonra da Myra'da gömüldüğü bilinmektedir. Aziz'in adına burada bir kilise veya şapel yapılmışsa da 529 yılındaki depremde yıkıldığı ve daha sonra aynı yerde bazilikal bir yapı inşa edildiği düşünülmektedir. 12. yüzyılda yapıya ekler yapıldığı, 13. yüzyılda da yapının büyük bir onarım gördüğü bilinmektedir. 13. yüzyılın ikinci yarısında veya sonrasında da Myra kentinin kuzeyinde yer alan Myros Çayı'nın taşması sonucu kilise galeri seviyesine kadar alüvyonla dolmuştur.

Bu çalışmada, Aziz Nikolaos Kilisesi'nin Batı Avlusu'na geçiş mekânında bulunan, tonoz ya da kemerin iç kısmında olduğu düşünülen duvar resmi parçalarına ait boya ve sıva tabakalarının malzeme analizleri gerçekleştirilerek, kullanılan hammaddelerin karakterizasyonu ve yapım tekniklerinin belirlenmesi amaçlanmıştır. Önümüzdeki dönemlerde yürütülecek konservasyon ve restorasyon çalışmaları ile toprak içinden kırık ve dağınık bir biçimde açığa çıkarılan söz konusu duvar resmi parçaları birleştirilerek sahneye ait süsleme programının anlaşılması planlanmaktadır. Dolayısıyla bu makale kapsamında gerçekleştirilen çalışmalar, konservasyon ve restorasyon uygulamalarına temel oluşturmaya yönelik bilgiler de içermektedir.

Çalışma kapsamında, Aziz Nikolaos Kilisesi'nin yukarıda belirtilen kısmından açığa çıkarılan duvar resimleri arasından seçilen 3 boyalı sıva ve sıva üzerinde bulunan 7 pigment örneği, fiziksel ve kromametrik belgelemeler, petrografik ince kesit optik mikroskop (stereo ve polarizan ışık altında), X-ışını difraktometresi (XRD), Raman spektrometresi ve X-ışını floresan spektrometresi (μ-XRF ve PED-XRF) ile incelenmiştir.

Örneklerin renk analizleri el tipi spektrofotometre cihazı ile yapılmıştır. Elde edilen sonuçlar CIE L'a'b' sistemine göre verilmiş olup, gözlemci açısı 10° ve ışık kaynağı D65'tir.

Petrografik analizler kapsamında sıvaların ince kesitleri (reçine ile sertleştirme yapılarak) hazırlanmış, stereo ve polarizan mikroskop altında, farklı sıva tabakalarının sayısı, bağlayıcı/agrega oranları, agrega türleri ve dağılımları ile mineral/kayaç içerikleri belirlenmiştir.

Duvar resimlerinin sıva tabakalarının faz analizleri, X-ışını difraktometresi ile 2θ:10-80° arasında, 2°/dk tarama hızında Cu-Kα radyasyonu kullanılarak gerçekleştirilmiştir. Duvar resimlerinde kullanılan pigmentlerin kimyasal içeriği ve olası bozulma ürünlerinin karakterizasyonu için Raman spektrometresi analizi uygulanmıştır. Analiz, dispersif Raman mikroskop ile 785 nm dalga boylu lazer ve 20x objektif lens kullanılarak gerçekleştirilmiştir. Çalışma süresince uygulanan lazer gücü, en iyi spektrumu elde edecek şekilde 10-25 mW aralığında değiştirilmiştir.

Raman spektrometresi ile sonuç alınamayan sarı renkli boya örneğinin kimyasal analizi için μ-X-ışını floresan spektrometresi cihazı kullanılmıştır. Analizler, μ-XRF spektrometresi ile molibden X-ışını tüpü kullanarak, 60 kV voltaj ve 400 μA akım şartlarında gerçekleştirilmiştir. Analiz üç farklı noktadan, 45 saniyelik ölçümler ile gerçekleştirilmiş ve ortalamaları alınmıştır.

Duvar resimlerinin sıva tabakaları PED-XRF analizi için yetersiz olduğundan, yalnızca bir sıva örneğine ait katmanların kimyasal bileşimi belirlenebilmiştir. Agat havanda toz hâline getirilen sıva tabakaları, 32 mm’lik diskler oluşturularak X-Lab 2000 PED-XRF spektrometresi ile analiz edilmiştir. Temel ve az elementler oksit yüzdeleri hâlinde, iz elementler ise milyonda bir (ppm) derişimle verilmiştir. Birleşik Devletler Jeolojik Araştırma (USGS) standartları ve referans olarak GEOL, GBW-7109 ve GBW-7309 kullanılmıştır. Sıva tabakalarının hidroliklik özelliği Cementation Index (CI) verileri yardımı ile değerlendirilmiştir.

Boyaların sıva tabakalarıyla olan etkileşimi duvar resimlerinde kullanılan tekniği göstermektedir. Boyama tekniği stereo mikroskop kullanılarak belirlenmiş ve tek katmanlı olduğu anlaşılmıştır. Sıva ile boya tabakası arasındaki sınırın oldukça keskin olması duvar resmi örneklerinde *secco* tekniğinin kullanıldığını, boyaların kuru sıva üzerine uygulandığını düşündürmektedir. Kuru sıva üzerine boyama yapılmasının bir gereği olarak pigmentin sıvaya tutunabilmesi için kullanılan organik veya inorganik bağlayıcı ortamının tespit edilmesi ise ilerleyen dönemlerde yapılması planlanan başka bir çalışmanın kapsamı içinde tutulmuştur.

Antik çağ kaynaklarında duvar resimlerinin üç katmandan oluştuğu belirtilmektedir: *Arriccio, intonaco* ve boya tabakası. *Arriccio* olarak adlandırılan en alttaki katman, doğrudan duvara uygulanmaktaır. *Arriccio*, duvardaki düzensizlikleri gidermek ve *intonaco* adı verilen ikinci katın yapışmasını da kolaylaştırmak ve yüzey alanını artırmak için genellikle kireç ve kaba agrega karışımından oluşmaktadır. *Intonaco* tabakası ise boyama için çok pürüzsüz bir yüzey elde etmek için daha ince parçacıklar içermektedir. Bu çalışmada incelenen tüm örnekler, bağlayıcı alanları ve agrega türleri bakımından benzer olup iki tabakalı sıvalardır. Sıvaların kireçtaşı, çört, kuvars, opak mineraller ile kayaç parçalarından oluşan, çok düşük oranda (<%10) agrega içerdiği tespit edilmiştir. Sıvalar üzerinde gerçekleştirilen

XRD analizlerinde kuvars ve kalsite ait karakteristik piklerin tespit edilmesi de bu sonucu desteklemektedir.

Boya örneklerinin analizlerinden elde edilen veriler şu şekilde özetlenebilir:

Yeşil renkli boya örneğinin Raman spektrumunda tespit edilen pikler, yeşil toprak pigmentinin varlığını göstermiştir. Kaynakları, killerin de eşlik ettiği glokonit, seladonit ve klorit gibi mineraller olan yeşil toprak boyaların spektroskopik yöntemlerle ayırt edilmesi zor olmakla birlikte, Raman spektrumundaki bazı farklılıklar bu çalışmada incelenen yeşil rengin seladonit kaynaklı olduğuna işaret etmektedir.

Siyah renkli boya örneğinin Raman analizleri ile, duvar resimlerinde karbon siyahı kullanıldığı belirlenmiştir. Eski çağlardan beri kullanılan karbon siyahının elde edilmesinde bitkisel kaynakların yanı sıra, kalsine kemik veya fildişi kullanımı da görülmektedir. Bu çalışmada siyah boyaların Raman analizlerinden elde edilen sonuçlar, karbonun bitkisel kökenli kaynaklardan elde edildiğini göstermiştir.

Duvar resimlerinde kullanılan kırmızı renkli boyaların Raman analizleri, kullanılan mineralin kırmızı toprak pigmentinin/okra (Hematite / α-Fe2O3) olduğunu göstermektedir. Aynı spektrumlarda, kalsit minerali renk tonunu açmak için kirecin kullanıldığını, kuvars ise pigmentin öğütülmesi sırasında kumun katılmış olabileceğini düşündürmektedir.

Sarı renkli boyanın Raman spektrumlarından sonuç alınamamış olup, XRF analizlerinde yüksek demir içeriğinin tespit edilmesi, sarı okranın varlığını işaret etmektedir.

Duvar resimlerinde kullanılan beyaz rengin elde edilmesinde kireç (kalsit) kullanılmıştır.

Introduction

The ancient city of Myra, where the St. Nicholas Church is placed, is located in the Demre district of Antalya province today. Myra is an ancient city located in the south of the Teke Peninsula and dates back to the 5th century BC according to the data obtained from rock tombs. Myra was enriched with trade during the Roman period with the effect of its port city Andriake being one of the important ports of the Mediterranean and was declared the capital of the Lycian region by Emperor Theodosius II (408-450). During the Byzantine Period, the city continued to be the metropolitan of the Lycian region between the 5th and 15th centuries and became a religious center[1].

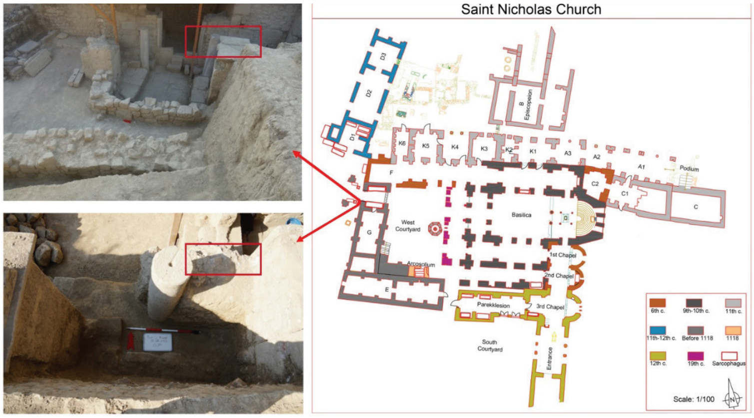
Born in the 4th century in Patara, Nikolaos is known to have served as a bishop in Myra and was buried in Myra after his death. Although a church or chapel was built here in the name of the saint, it is thought that it was destroyed in the earthquake in 529. It is thought that a basilical structure was probably built in the same place later. In the 12th century, additions were made to the building, and it is known that it underwent a major repair in the 13th century. In the second half of the 13th century or later, it is known that the church was filled with alluvium up to the gallery level as a result of the flooding of the Myros Stream, which is located north of the city of Myra[2].

During the 2016 archaeological excavations, fragments of painted plaster, which are thought to be located in an arch or vault of passageway to the West Courtyard **(F. 1)**, were recovered from the earth. The presence of a large number of bricks in the soil where the painted plaster fragments were found suggests that there was an arch or vault here. As a result of the conservation and restoration works to be carried out in the coming periods, these painted plaster fragments will be tried to be combined and the ornamentation in this area will be tried to be understood. Archaeometric investigations, which are the subject of this article, should be seen as a part of this work. This study was carried out in order to understand the layers of the plaster, the construction technique and to identify the pigments used. Samples of all color types were taken from all available fragments and all colors of the ornamentation in that section were tried to be identified[3].

1 Nevzat Çevik and Süleyman Bulut, "İkinci Kazı Sezonunda Myra ve Limanı Andriake," *Arkeolojisinden Doğasına Myra/Demre ve Çevresi* (Ankara: T.C. Kültür ve Turizm Bakanlığı Yayınları, 2010), 25-115; Sema Doğan, Nilay Çorağan, Vera Bulgurlu, Çiğdem Alas, Ebru Fındık and Emre Apaydın, *Demre – Myra Aziz Nikolaos Kilisesi* (İstanbul: Arkeoloji ve Sanat Yayınları, 2014), 9-10.

2 Urs Peschlow, "Die Architektur der Nikolaoskirche in Myra," *Myra* (Berlin: Gebr. Mann Verlag, 1975), 303-424.

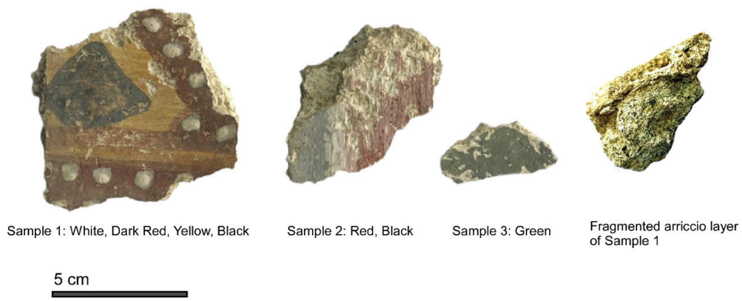
3 Archaeological excavation and conservation works were carried out by Prof. Dr. Sema Doğan between 2014-2021 with the permission of the Ministry of Culture and Tourism, General Directorate of Cultural Heritage and Museums and Project Number BK0l0708. The Demre Museum Directorate granted the permission for the archaeometric examination of the wall painting samples from St. Nicholas Church in a document dated February 18, 2023 with the identification code E-70793822-155.01-2218489.



F. 1: Plan of St. Nicholas Church Excavation and pictures showing the location of the area where samples were found (St. Nicholas Church Excavation Project Archive).

1. Materials and Method

7 paints from 3 wall painting fragments were selected for the analyses as shown in Figure 2. It was understood that the plaster layers of wall painting samples had two layers. In Sample 1, it was determined clearly that the intonaco layer of this wall painting sample was 6.31 mm and the arriccio layer was 35.12 mm.



F. 2: The pictures, codes, and the colors of the wall painting fragments studied in this work (Kayser, Ormancı, Akyol, 2023)

The color coordinates of the wall painting samples were recorded in the CIE (**C**ommission **I**nternationale de l´**E**clairage / The International Commission on Illumination) L’a’b’ color system using the standard illuminant D65 and the 10° observer, by a Konica Minolta CM-700d/600d spectrophotometer. Each color was measured at five points on the surface and the average of the measurements were calculated **(Table 1 and F. 2)**.

The paint samples have been cross-sectioned, and the sections have been observed in reflected light using a Nikon SMZ 1000 stereomicroscope (1–8×), equipped with a digital camera to define colours, thickness and painting technique **(F. 3)**. Phase analyses of the plasters was performed by a Rigaku Miniflex X-ray diffractometer with CuKα radiation at 30 kV and 15 mA over a 2θ range of 20–80° with 0.02° steps **(F. 4)**.

Raman microscopy measurements were performed directly on the samples using a Bruker SENTERRA Dispersive Raman spectrometer, which is equipped with a TE-cooled CCD detector. Spectra were recorded with a spectral resolution of 4 cm^{-1} and 20x magnification objectives were employed. Red laser (785 nm) was used, with changing irradiating laser power and the exposure time, avoiding any damage to the samples. The Raman spectra were processed with the OPUS 7.5 Senterra software and compared with those from various databases.

Only one sample (Sample 1-Yellow) failed to produce an identifiable Raman spectrum, thus, X-Ray Fluorescence (XRF) spectrometry was employed for this sample. XRF measurements were performed with a Bruker ARTAX 800 XRF spectrometer, provided with a molybdenum X-ray tube and a silicon drift detector, with an energy resolution of 150 eV. The working parameters were set at 400 µA current intensity and 50 kV tube voltage, no filtering, air atmosphere, and 60 s analysis time. Elements' identification was conducted in ARTAX software.

The chemical composition of the plaster of wall painting fragment (Sample 1) was determined by using the X-ray Fluorescence Analysis Method (PED-XRF) **(Table 2)**. After the analysis samples were powdered in agate mortar, 32 mm discs were formed, each disc was mixed with a chemical (wacks) used in XRF analysis, placed in the sample area of the instrument and analyzed. In this study, X-LAB 2000 model PED-XRF (Polarized Energy Dispersive-XRF) spectrometer was used. In the analysis, major and minor elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn and Fe) were given as oxide percentages (%), while trace elements (Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Hf, Ta, W, Hg, Tl, Pb, Bi, Th and U) were given at a concentration of parts of per million (ppm or µg/g). USGS (United States Geological Survey) CNRM standards and reference materials GEOL, GBW-07109 (Ijoiitse Syenite), and GBW-07309 (stream sediment GSD-9) were used for calibration. The binder category (hydraulic feature) of the plaster of wall painting fragment (Sample 1) were evaluated with the help of the Cementation Index (CI) data obtained with the chemical composition properties by PED-XRF analysis of the sample.[4] Cementation Index is the ratio of the soluble part in acid to the soluble part in bases. Lime-containing mortars are classified as fat lime (slaked or air lime) mortar (FL) and hydraulic lime mortar (WHL: Feebly hydraulic lime (NHL 2); MHL: Moderately hydraulic lime (NHL 3.5); HL: Eminently hydraulic lime (NHL 5)) depending on the amount (content) and type of active clay in lime.

4 Robert, S. Boynton, *Chemistry and Technology of Lime and Limestone* (New York: John Wiley & Sons, 1980).

2. Results and Discussion

2.1. Colorimetric Analysis

Colorimetric analyses of the painting surfaces were carried out by using a reflectance spectrophotometer and evaluating CIE Lab Color Sytem parameters. A summary of the obtained values is given in Table 1.

Table 1: Sample codes, and the measurements of the colors in the CIELab system (Kayser, Ormancı, Akyol, 2023)

Sample code	**Observed colors**	**CIE Lab Values**		
		L	**a**	**b**
Sample 1	White	85.41	0.79	2.62
	Dark Red	47.25	32.53	14.32
	Yellow	59.12	12.59	36.41
	Black	33.54	-0.13	-2.11
Sample 2	Red	-	-	-
	Black	62.01	0.09	-0.2
Sample 3	Green	60.72	-9.26	7.79

2.2. Painting Technique

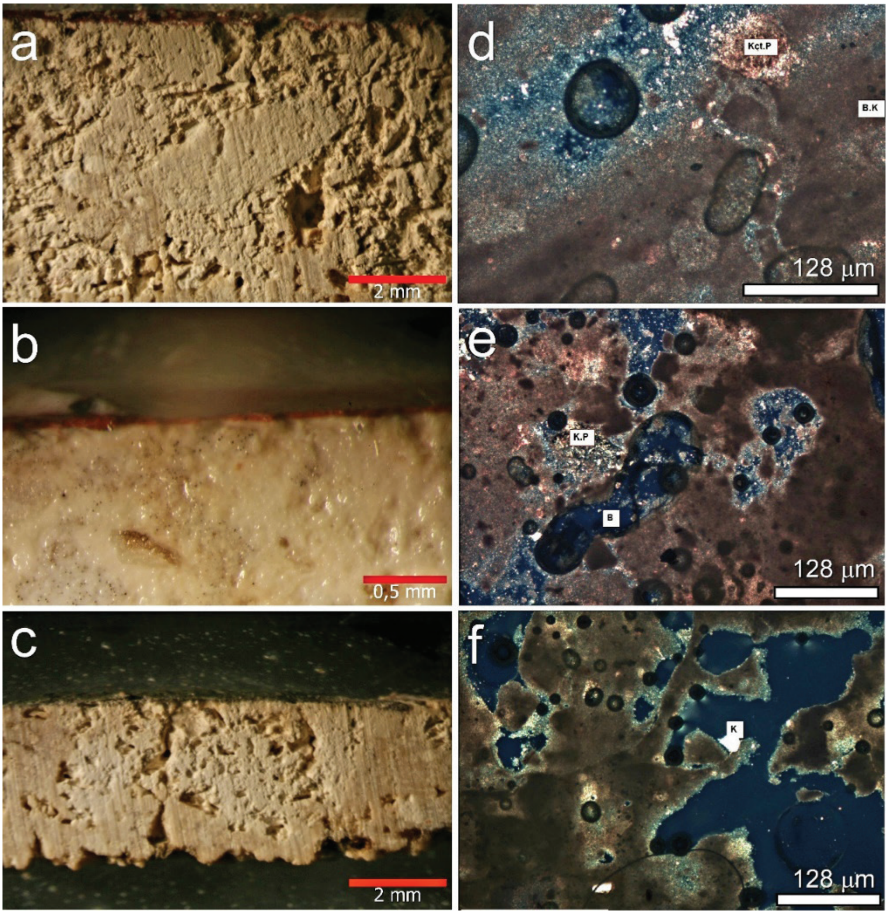
Painting fragments were viewed under an optical microscope for stratigraphic analysis and the paint layer of the samples were found to be single-layered **(F. 3 a-c)**.

As recognised under the optical microscope, the wall paintings were executed using the *secco* technique. The boundary between the plaster and the paint layer is always sharp enough to conclude the secco application.

The term *secco* indicates the technique of painting on dry plaster and it meant that painters could work at a slower pace and use a wider range of pigments than *fresco* artists who paint on wet plaster.[5] As a necessity of painting on dry plaster, secco technique requires a binding medium, which can be either organic or inorganic, in order to attach to the pigments to the plaster.[6]

5 Roger Rosewell, *Medieval Wall Paintings* (Bloomsbury Publishing, 2014).

6 Maria Amadori, Sara Barcelli, Gianluca Poldi, Fabiano Ferrucci, Alessia Andreotti, Pietro Baraldi and Maria



F. 3: a-c) The stereomicroscope images of Sample 1, Sample 2 and Sample 3 respectively, d-f) The polarizing microscope images of the thin sections of Sample 1, Sample 2 and Sample 3 respectively, under crossed polars (Kayser, Ormancı, Akyol, 2023)

2.3. Plaster Layers

Typically, a wall painting consists of three layers: *Arriccio, intonaco*, painting. The most inner layer is called *arriccio* and laid directly on the wall. The arriccio is usually consist of a mixture of lime and coarse aggregates to increase the surface area and thus, the adhesion of the second layer, called *intonaco*, is improved. The intonaco

Perla Colombini, "Invasive and Non-invasive Analyses for Knowledge and Conservation of Roman Wall Paintings of the Villa of the Papyri in Herculaneum," *Microchemical Journal* 118 (2015), 183-192; Emilio J. Emilio Cerrato, Daniel Cosano, Dolores Esquivel, Cesar Jiménez-Sanchidrián and Rafael Ruiz, "A Multi-Analytical Study of Funerary Wall Paintings in the Roman Necropolis of Camino Viejo de Almodóvar (Córdoba, Spain)," *The European Physical Journal Plus* 135 (2020), 1-20; Maja Gutman, Katharina Zanier, Judita Lux and Sabina Kramar, "Pigment Analysis of Roman Wall Paintings from Two Villae Rusticae In Slovenia," *Mediterranean Archaeology & Archaeometry* 16(3), (2016), 193-206; Chryssa Apostolaki, Vassilis Perdikatsis, Efttychia Repuskou, Hariclia Brecoulaki and Sarah Lepinski, "Analysis of Roman Wall Paintings from Ancient Corinth/Greece," (Proceedings of the 2nd International Conference on Advances in Mineral Resources Management Environmental Geotechnology, Hania, 25-27 September 2006).

layer, on the other hand, contains finer particles to obtain a very smooth surface for painting.[7]

The plasters investigated in this study are consist of two layers: arriccio and intonaco. However, the arriccio layer is disaggregated because of the dispersive nature of the plasters and could not be viewed under microscope.

According to the petrographical analyses, all the samples are based on lime and they were found to be similar on the basis of their binder areas and aggregate types. **(F. 3 d-f)**. It has been determined that the plasters contain very low ratio (<10%) aggregates consisting of limestone, chert, quartz, opaque minerals and rock fragments. Detection of characteristic peaks of quartz and calcite in XRD analyzes performed on plasters also supports this result. The binder composition of the plasters is similar and is in mixture of fired clay (20%, dusted brick/pottery) and lime (80%). Similarly, organic fiber (chaff) content is also present in the plasters (10% of the total aggregate). **(F. 3 d-f)**.

The chemical composition of Sample 1 (intonaco and arriccio layers separately) were determined by PED-XRF analysis. The composition of the intonaco/arriccio layers of the samples (in descending order); LOI (total carbonate, 38.6% / 38.9%), CaO (56.5% / 56.5%), SiO_2 (3.7% / 3.5%) **(Table 2)**.

Cementation Index (CI) data was obtained from the chemical contents of the layers of the Sample 1 obtained by PED-XRF analysis **(Table 2)**. These data, which give an idea about the lime types, showed that the samples were in same lime type (Slaked Air/Fat Lime - FL). The CI values of the plaster samples were 0.21 and 0.19.[8]

Table 2. Results of PED-XRF analysis of the plaster layers of the Sample 1 (Kayser, Ormancı, Akyol, 2023)

Element	Main Element Composition (%)		Element	Trace Element Composition (ppm)	
	Sample 1-intonaco	Sample 1-arriccio		Sample 1-intonaco	Sample 1-arriccio
Na_2O	0.05	0.05	Co	19.3	17.2
MgO	0.50	0.25	Ni	64.8	43.7
Al_2O_3	0.63	0.35	Cu	3.8	2.1
SiO_2	3.7	3.5	Zn	8.5	6.6
P_2O_5	0.07	0.08	Ga	2.4	2.7
SO_3	0.90	0.10	Ge	0.4	0.5
Cl	0.07	0.03	As	2.6	0.9
K_2O	0.22	0.14	Se	0.3	0.3

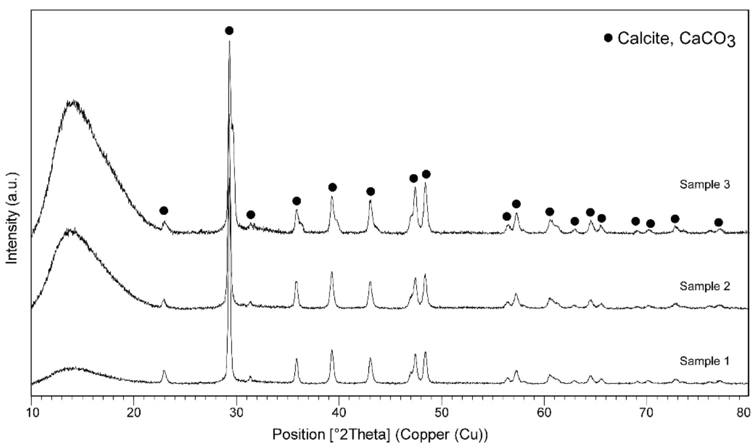
7 Paolo Mora, Laura Mora and Paul Philippot, *Conservation of Wall Paintings* (Glasgow: Butterworths, 1984), 494.

8 Fat Lime (FL): <0.30, Weakly Hydraulic Lime (WHL): 0.30 – 0.50, Moderately Hydraulic Lime (MHL): 0.51 – 0.70, Eminently Hydraulic Lime (EHL): 0.71 – 1.10, Natural Cements (NC): 1.11-1.70, Natural Cements / Cements (NC/C): 1.70<

Table 2. Continue

Element	Main Element Composition (%)		Element	Trace Element Composition (ppm)	
	Sample 1-intonaco	Sample 1-arriccio		Sample 1-intonaco	Sample 1-arriccio
CaO	56.5	56.5	Br	6.1	6.7
TiO_2	0.06	0.03	Rb	4.7	2.8
V_2O_5	0.004	0.003	Sr	263.4	355
Cr_2O_3	0.03	0.01	Y	1.5	1.8
MnO	0.02	0.02	Zr	16.9	9.8
Fe_2O_3	0.78	0.46	Nb	3.6	3.2
LOI*	38.55	38.92	Mo	3.4	3.0
			Cd	0.9	1.0
			In	0.8	1.0
			Sn	1.1	1.0
			Sb	1.1	1.1
			Te	1.3	1.4
			I	3.2	2.1
			Cs	3.8	4.2
			Ba	49.9	32.7
			La	27.5	24.6
			Ce	11.0	16.2
			Hf	2.8	2.8
			Ta	2.9	2.8
			W	3.0	2.7
			Hg	0.8	0.8
			Tl	0.8	0.9
			Pb	15.9	5.3
			Bi	1.0	0.7
			Th	0.6	0.6
			U	14.3	8.5

Figure 4 displays the XRD patterns of plasters of the wall painting fragments. The characteristic peaks of calcite were obtained for all samples and no additional phases were detected.

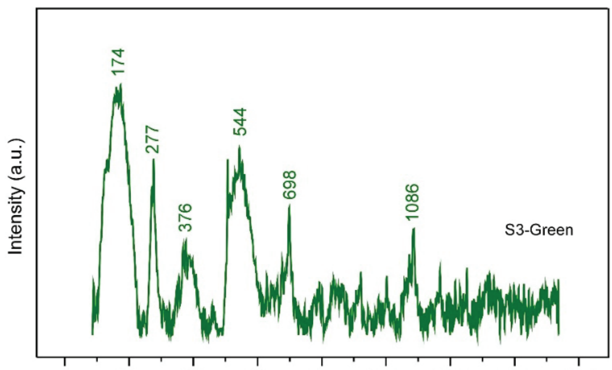


F. 4: XRD patterns of plasters of the wall painting fragments (Kayser, Ormancı, Akyol, 2023)

2. 4. Pigments

Green

The Raman peaks found at 174, 277, 376, 544, 698 cm^{-1} in the green paint suggest the presence of green earth pigments **(F. 5)**.[9] Green earths, glauconite, celadonite and chlorite, are formed from iron silicates accompanied by clays.[10] These are illite clay minerals based on celadonite, K $(Mg,Fe,Al)_2(Si,Al)_4O_{10}(OH)_2$, and glauconite, K $(Fe,Al)_2(Si,Al)_4O_{10}(OH)_2$ and chlorite. Because of having such a similar and complex chemical formula, their identification is also difficult by Raman spectroscopy.[11] However, some spectral differences are helpful in distinguishing between the two species. Moretto et. al reported a study which aims to exploit different spectroscopic techniques for the identification of celadonite and glauconite present in the green pigments of some wall paintings, and the strong peaks at about 260-280 cm^{-1} were reported as a marker for differentiating celadonite (~279 cm^{-1}) and glauconite (~264 cm^{-1}). In another study, by Ospitali et. al, concerning vibrational and elemental characterization of green earth pigments, it is reported that, in glauconite the 170 cm^{-1} band is not present and only a band between 188 and 200 cm^{-1} is observable and, the medium-strong intensity peak at about 265 cm^{-1} has a lower wavenumber in glauconite (264 cm^{-1}) than in celadonite (270 cm^{-1}). The presence of Raman peak at 174 and 277 cm^{-1} in this study, may be an evidence for the identification of celadonite.



F. 5: The Raman spectrum of the green paint layer of Sample 3 (Kayser, Ormancı, Akyol, 2023)

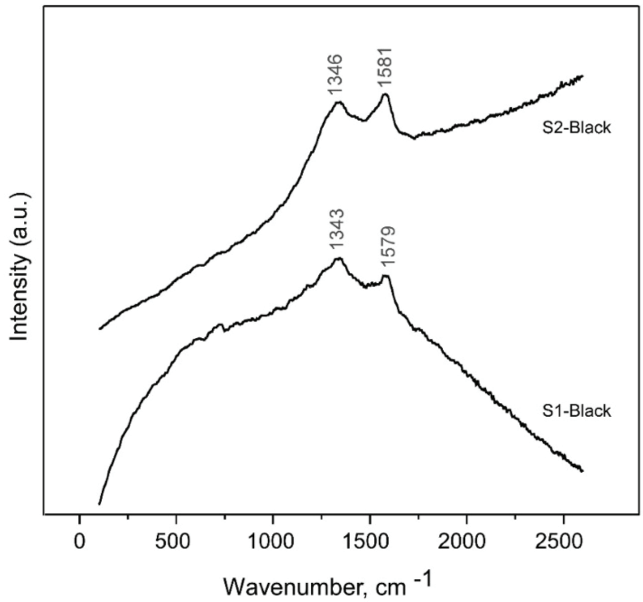
9 Francesca Ospitali, Danilo Bersani, Gianfranco Di Lonardo and Pier Paolo Lottici, "'Green Earths': Vibrational and Elemental Characterization of Glauconites, Celadonites and Historical Pigments," *Journal of Raman Spectroscopy* 39(8) (2008), 1066-1073.; Ligia Maria Moretto, Emilio Francesco Orsega and Gian Antonio Mazzocchin, "Spectroscopic Methods for the Analysis of Celadonite and Glauconite in Roman Green Wall Paintings," *Journal of Cultural Heritage* 12(4) (2011), 384-391.

10 *Analytical Archaeometry: Selected Topics,* eds. Edwards Howell and Peter Vandenabeele (United Kingdom: Royal Society of Chemistry, 2016), 219.

11 Susana Jorge-Villar and Howell Edwards, "Green and Blue Pigments in Roman Wall Paintings: A Challenge for Raman Spectroscopy," *Journal of Raman Spectroscopy* 52(12), (2021), 2190-2203.

Black

The black paints in both Sample 1 and Sample 2 showed similar Raman spectra **(F. 6)**, which proved their amorphous carbon nature with the bands in the range 1300-1600 cm^{-1} that can be assigned to the ν(C–C) stretching vibrations. In this case, the absence of any signature of phosphate bands at 960 cm^{-1} could be attributed to usage of vegetable carbon source rather than a calcined bone or ivory source. [12]



F. 6: The Raman spectra of the black paint layer of Sample 1 and Sample 2 (Kayser, Ormancı, Akyol, 2023)

Red

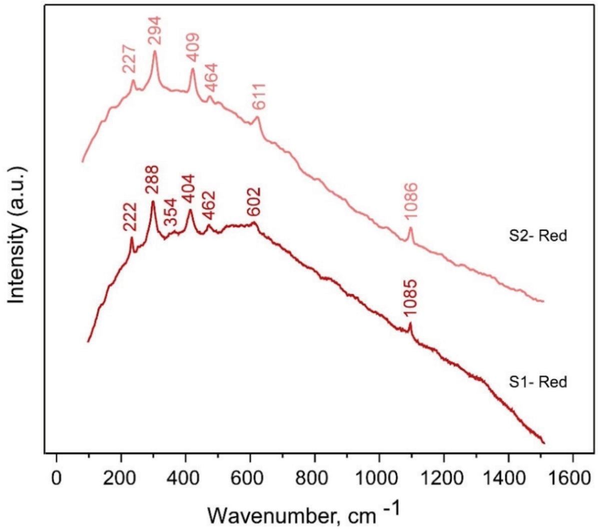
Hematite (α-Fe_2O_3) was recognized by the presence of bands at 222-227, 288-294, 404-409, 602-611 cm^{-1}, together with features attributable to calcite at 1085-1086 cm^{-1} due to the ν1 symmetric stretching mode of the CO_3^{2-} anion[13] **(F. 7)**. However, the other characteristic Raman bands of calcite is overlapped with that for hematite. The name hematite is derived from haima, referring to blood and is a common choice for coloring because of displaying quite an intense color and being the commonest

12 Antonio Hernanz, Jose Gavira-Vallejo, Juan Ruiz-López and Howell Edwards, "A Comprehensive Micro-Raman Spectroscopic Study of Prehistoric Rock Paintings from the Sierra de las Cuerdas, Cuenca, Spain," *Journal of Raman Spectroscopy* 39(8), (2008), 972-984; Claudio Frausto-Reyes, Martin Ortiz-Morales, Juan Bujdud-Pérez, Gloria Magaña-Cota and Ricardo Mejía-Falcón, "Raman Spectroscopy for the Identification of Pigments and Color Measurement in Dugès Watercolors," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 74(5) (2009), 1275-1279.

13 Mercedes Iriarte, Antonio Hernanz, Jose Gavira-Vallejo, Jose Alcolea-González, and Rodrigo de Balbín-Behrmann, "μ-Raman Spectroscopy of Prehistoric Paintings from the El Reno Cave (Valdesotos, Guadalajara, Spain)," *Journal of Archaeological Science: Reports* 14 (2017), 454-460.

occurring ore of iron.[14] It is reported that the addition of powdered calcite enhances the appearance of pigment[15] but in this case, calcite may be used to lighten the color tone.

The presence of the peak at 462/464 cm^{-1} in both spectra is assigned to asymmetric bending of O-Si-O bond inside the SiO_4 tetrahedron[16], and an indicative of quartz probably from admixture with sand.



F. 7: The Raman spectra of the red paint layers of Sample 1 and Sample 2 (Kayser, Ormancı, Akyol, 2023)

Yellow

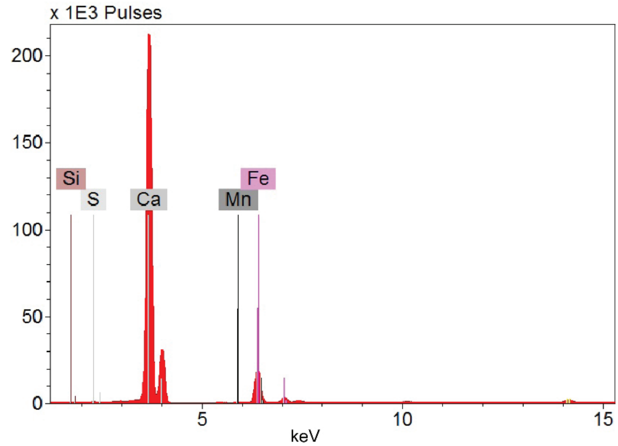
Unfortunately, the yellow paint in the Sample 1 could not be identified by μ-Raman microscopy because of a highly fluorescent background. Thus, XRF spectrometry was employed for this sample and high content of iron indicated the presence of yellow ochre **(F. 8)**. Besides Fe, XRF analyses also revealed the presence of Ca, Si, Mn. Natural iron oxides-hydroxides used as pigments are usually mixed with clay minerals

14 Nicholas Eastaugh, Valentine Walsh, Tracey Chaplin and Ruth Siddall, *Pigment Compendium: A Dictionary of Historical Pigments* (Routledge, 2007), 320. Zhaojun Liu, Rui Yang, Weihao Wang, Wenzhong Xu and Mengzhu Zhang, "Multi-analytical Approach to the Mural Painting from an Ancient Tomb of Ming Dynasty in Jiyuan, China: Characterization of Materials and Techniques," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 279 (2022), 121419, 1-8; Pierluigi Rosina, Hugo Gomes, Hipolito Collado, Maria Nicoli, Lisa Volpe and Carmela Vaccaro, "Micro-Raman Spectroscopy for the Characterization of Rock-art Pigments from Abrigo del Águila (Badajoz–Spain)," *Optics & Laser Technology* 102 (2018), 274-281.

15 Daniel Damiani, Elisabetta Gliozzo, I. Memmi Turbanti, and Jorge Spangenberg, "Pigments and Plasters Discovered in the House of Diana (Cosa, Grosseto, Italy): An Integrated Study Between Art History, Archaeology and Scientific Analyses," *Archaeometry* 45(2) (2003), 341-354.

16 Hongshen Liu, Hüseyin Kaya, Yen Ting Lin, Andrew Ogrinc and Seong Kim, "Vibrational Spectroscopy Analysis of Silica and Silicate Glass Networks," *Journal of the American Ceramic Society* 105(4) (2022), 2355-2384.

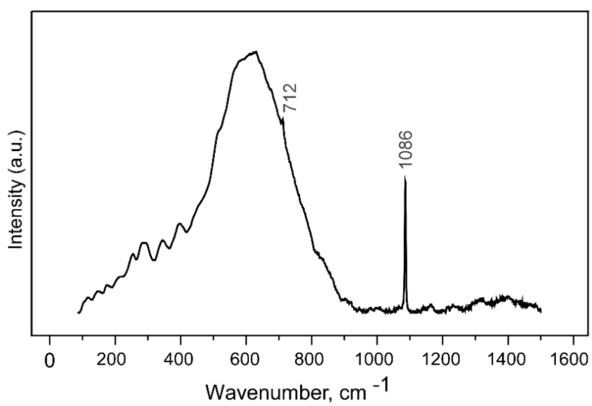
forming ochre pigments and the presence of the mentioned elements in the spectrum confirmed the pigment was yellow ochre which have been used since the Palaeolithic.[17]



F. 8: XRF spectrum of the yellow paint layer of Sample 1 (Kayser, Ormancı, Akyol, 2023)

White

Figure 9 shows the Raman spectrum of the white paint of Sample 1. The Raman bands at 712 and 1086 cm^{-1} suggest the presence of calcite, which is thermodynamically the most stable phase of calcium carbonate mineral ($CaCO_3$) and widely distributed in the Earth's crust.[18]



F. 9: The Raman spectrum of the white paint layer of Sample 1 (Kayser, Ormancı, Akyol, 2023)

17 Isabel Garofano, Antonio Duran, Jose Perez-Rodriguez Maria Dolores Robador, "Natural Earth Pigments from Roman and Arabic Wall Paintings Revealed by Spectroscopic Techniques," *Spectroscopy Letters* 44(7-8) (2011), 560-565; David Hradil, Tomas Grygar, Janka Hradilová and Petr Bezdička, "Clay and Iron Oxide Pigments in the History of Painting," *Applied Clay Science* 22(5) (2003), 223-236.

18 Sethu Gunasekaran, Gopalakrishnan Anbalagan and S. Pandi. "Raman and Infrared Spectra of Carbonates of Calcite Structure," *Journal of Raman Spectroscopy* 37(9) (2006), 892-899.

Conclusion

Considering the limited number of wall paintings in Anatolia as of the period, the importance of the mural paintings of the Church of St. Nicholas in Demre emerges.

In this study, the wall painting fragments recovered from the West Courtyard transition area of the St Nicholas Church (located in the ancient city of Myra) in Demre district of Antalya are discussed from the archaeometric point of view. 3 wall painting fragments were analyzed to achieve some preliminary results on chemical and mineralogical composition of the plaster and paint samples of Demre St. Nicholas Church. The characterization studies were performed using different analytical techniques such as spectrophotometer, optical microscopy, μ-Raman spectroscopy, PED-XRF, μ-XRF, XRD.

Results from the petrographical analyses suggested that the wall paintings were executed using the *secco* technique, and the plasters incorporate two layers based on lime. Detection of characteristic peaks of calcite as the main phase in XRD also supports this result. Moreover, Cementation Index obtained from the PED-XRF results of the representative plaster sample (Sample 1) showed the lime type as slaked air/fat lime.

The composition of the pigments was consistent with those of belong to Byzantine period, but with a limited palette which includes lime, carbon black, yellow ochre, red ochre (hematite), and green earth most probably celadonite.

It is hoped that the present study will be applied to the analysis for much larger numbers of wall-painting samples in order to shed light on the material characteristics and conservation studies of the Byzantine wall paintings in the context of the Mediterranean Region.

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