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Analyses of Saint George (Kirk Dam Alti) Church Paint Layers Using ESEM-EDX&FTIR Methods

Saint George (Kırk Dam Altı) Kilisesi ESEM-EDX ve FTIR Metodu ile Boya Tabakası Analizleri

Hande Günözü Ulusoy*

Öz

Bu çalışmada; Kapadokya Bölgesi, Ihlara Vadisi, Bizans Dönemi, Saint George (Kırk Dam Altı) Kilisesi duvar resimlerinden alınan boya örnekleri, kesit ve toz haline getirilerek ESEM-EDX (Philips-FET XL 3D-ESEM-FEG OXFORD X MAX 80 mm2 Xray Detector/ INCA software) ve FTIR (Fourier Transform Infrared Spectroscopy) aletli analiz metotları kullanılarak, boya tabakalarının stratigrafisi ve karakterizasyonu açığa çıkartılmıştır. Marcell Restle'nin yapıda görsel incelemeye dayanarak yaptığı boya tanımlamaları ile analiz sonuçları tutarlılık göstermiştir. ESEM-EDX ve FTIR sonuçları, kullanılan pigmentlerin ağırlıklı olarak kırmızı, yeşil ve sarı okra tonları olduğunu göstermektedir. Gri-mavi boya örneğinin; karbon siyahı, smalt ve ultramarin ile caput mortuum'un karıştırılmasıyla oluşturulduğu, lacivert renk elde etmek için karbon siyahının, gypsum ile karıştırılarak kullanıldığı ve beyaz renk için saf gypsum kullanıldığı ortaya çıkarılmıştır, örneklerde saptanan fosfor (P) kazein kullanımını düşündürmekle birlikte kazeinin tempera olarak kullanımına dair ileri analiz metotları ile araştırılması gerekmektedir. İlaveten, ESEM-EDX ve FTIR yöntemlerinin boya katmanlarının stratigrafisinin açığa çıkartılmasında kullanılmasının, avantaj ve dezavantajları üzerine değinilmiştir.

Anahtar Kelimeler: *Ihlara Vadisi, Saint George Kilisesi, Kırk Dam Altı Kilisesi, Boya Tabakası Karaterizasyonu, Kapadokya Bizans Sanatı.*

Abstract

This study investigates the characterization of the wall paint layers of Saint George (Kirk Dam Alti) Church, a Byzantine-period rock-cut structure located in the Peristrema area of Ihlara Valley, Cappadocia. To identify the paint layers, the stratigraphy and composition of cross-sections and powdered samples were analyzed using ESEM-EDX (Philips-FET XL 3D-ESEM-FEG OXFORD X MAX 80 mm² X-ray Detector/INCA software) and Fourier Transform Infrared Spectroscopy (FTIR). The paint analyses result roughly align with Marcell Restle's visual predictions. The ESEM-EDX and FTIR results indicate that the pigments used are predominantly shades of red, green, and yellow ochre. The analysis of the dark blue paint sample shows that carbon black was mixed with gypsum. A detailed examination of the blue paint sample reveals a gray-blue tone achieved by mixing carbon black, smalt, ultramarine, and caput mortuum. Pure gypsum was used for the achieve white, while the presence of phosphorus (P) across the samples indicates the use of casein, as identified in FTIR and ESEM-EDX analyses. A future analysis is needed to clarify the presence of casein used as tempera. Additionally, the advantages and disadvantages of using ESEM-EDX and FTIR methods for characterizing the stratigraphy of paint layers are discussed.

Keywords: *Ihlara Valley, Saint George Church, Kirk Dam Alti Church, Characterization of Paint Layer, Byzantium Art in Cappadocia.*

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This study focuses on the stratigraphy and chemical composition of fifteen paint layer samples from the architectural painted surfaces of Saint George Church by using ESEM-EDX and FTIR methods. All analyses were conducted in 2012 at the laboratories of the Science Department of the Getty Conservation Institute (GCI) in Los Angeles, United States. The selection of samples and methods was supervised by Prof. Dr. Giacomo Chiari, who was the Head of the GCI Science Department in 2012. The ESEM-EDX analyses were carried out with Dr. David Carson, General Director of the GCI Science Department, and the FTIR analyses were performed with Dr. Lee Lym, Assistant Scientist at the GCI Science Department.

Saint George Church, also known as, Church of the Forty Roofs (Kirk Dam Alti) is located in the Ihlara Valley "Peristrema" at Cappadocia Turkey. According the Marcell Restle's architectural descriptions; the rock-cut church is of the one aisled-basilica plan type and additionally *"a completely irregular chamber with arcosolium niches on all sides and burial chambers lower down, at the bottom of the cave. The apse has come away from the main chamber to a very considerable extent. A vaulted roof"*[1] . The interior architectural surfaces of the church are adorned with wall paintings, depicting scenes such as the Ascension of Christ, the Crucifixion, and the Transfiguration, Saint George, and donor portraits. The church's inscription provides information about its dedication to Saint George and its donors. According to the inscription, the church was constructed during the reigns of Emperor Andronikos II and Sultan Mesud II, with estimates suggesting it was built between 1282-1304 or 1283-1295[2] (Figs. 1-6).

To determine the stratigraphy and characterization of the wall painting support, plaster, and paint layers of the Church of Saint George in Ihlara Valley, various instrumental analysis methods were employed. These included ESEM-EDX (Philips-FET XL 3D-ESEM-FEG OXFORD X MAX 80 mm^2 X-ray Detector/INCA software) and FTIR (Fourier-Transform Infrared Spectroscopy). As the characterization analyses of the plaster and support layers of Saint George Church in Ihlara Valley have been previously published in detail, this study does not delve into the results of these analyses[3]. The primary aim of this study was to map and identify the stratigraphy of the paint layers and their chemical composition. Cross-sections were prepared by including both the intonaco layer and the paint layer, and general stratigraphic mapping was first performed using a polarizing microscope image transfer system. Subsequently, the samples were scanned using ESEM-EDX to reveal their stratigraphy, and point spectra were extracted from necessary areas. Samples with complex and multi-layered compositions were separated into individual layers, powdered, and examined using the FTIR method. This study, however, will focus solely on the stratigraphy and chemical composition of the paint layers. The paint samples collected from Saint George Church were labeled as SNG, short for "Saint George" followed by the sample number and "P" for "paint." The locations and descriptions of the samples are provided in the table (Figs.25-27).

Analysis Methods

For to identification the paint layers, stratigraphy and the composition of the cross sections are analyzed by ESEM-EDX (Philips-FET XL 3D-ESEM-FEG OXFORD X MAX 80 mm2 X-ray Detector/ INCA software), Fourier Transform Infrared Spectroscopy (FTIR) instrumental methods. Cross-sections were prepared by including both the thin plaster layer and the paint layer, and general stratigraphic mapping was first performed using a polarizing microscope imaging system. Samples

[1] Restle1967, I: 176
[2] Restle 1967 I: 66, 176-177; Restle 1967 III: fig. LX, 510-516, Kostof 1989: 275
[3] Ulusoy-Günözü 2021: 152-153; Ulusoy-Günözü 2017: 271, 294; Günözü 2014: 32, 44; Günözü 2016: 25,46;

were scanned using ESEM-EDX to identify their stratigraphy, and point spectra mostly were extracted from pigments. Samples with multi-layered and complex compositions were separated into individual layers, powdered, and examined using the FTIR and ESEM-EDX methods.

Although the ESEM-EDX method for mapping and point spectrum scanning does not provide detailed data on the sub-elements of the pigments, it is frequently utilized due to its capability to provide general elemental data and the stratigraphy of the paint layers. This method is particularly valuable in cases where it is not possible to take thin sections and powdered sample to understand the stratigraphy of wall painting support, plaster, and paint layers, as well as deterioration processes. By transforming the entire plaster and paint layers into a cross-section without wasting samples, it illuminates the overall matrix in broad terms. In historical paint analyses, when the sample quantity is sufficient, this method not only allows for the preservation of the sample as a whole but also serves as a reference for future analyses. Additionally, with ESEM-EDX, it is possible to gain general insights into the painting techniques of the period and to obtain comparative data on the statement of the paint without causing damage to the sample[4].

Results and Discussion

Initial visual examinations of the paint samples revealed that the paint layer was very thin, ranging from a minimum of 0.1 mm to a maximum of 0.4 mm. The colors generally appeared not vibrant, Marcel Restle describe the paint layers "muddy"[5]. Due to the large hall in the apse, which currently serves as the church's entrance, the paint layers has been severely deteriorated by exposure to atmospheric conditions which are initially water damages, salt efflorescence and the various kinds of atmospheric dust. Unfortunately, due to active water damage in Ascension of Jesus scene some paint and plaster layers deteriorated in recent years. It would be appropriate to evaluate the vibrancy of the paint layers following the completion of future conservation efforts, particularly during the cleaning phase. Future research will aim to reveal the full palette on a structure-by-structure basis through comparative analysis of materials during the conservation processes. Therefore, this study provides individual explanations for the paint layer mapping, stratigraphy, and general content of the paint samples.

ESEM-EDX and FTIR Analysis: Cross-Section Paint Layer Results

The mapping and spectrum scanning data obtained from the cross-sectional analysis of paint layers using ESEM-EDX are detailed below for each sample. In the sample labeled SNG 9P, due to complexity of the element map of the paint layer, advanced analytical methods were required and FTIR analysis conducted.

SNG-1P: Upon integrating the ESEM-EDX mapping and point spectrum scanning data, the presence of aluminum silicate (Al_2SiO_5) indicates the use of an earth-based pigment. Additionally, significant peaks of potassium (K), magnesium (Mg), iron (Fe), and arsenic (As) are observed. Although arsenic is rare, it is known to occur in earth-based green pigments. These findings suggest that the green paint layer may consist of a complex mineral pigment, potentially Green Earth $K[(Al,Fe^{3+}),(Fe^{2+},Mg)](AlSi_3,Si_4)O_{10}(OH)_2$ (Fig. 7-8).

SNG-2P: Iron (Fe) and aluminum silicate (Al_2SiO_5) were detected, suggesting that this yellow paint sample may consist of the earth-based pigment, Yellow Ochre **(**Fig. 9).

SNG-3P: Carbon black was detected in the paint layer. It appears that carbon black was applied in combination with gypsum (Fig. 10).

[4] Cheilakou et al 2014: 545-553; Sbroscia et al 2020: 98-103, Pelosi et al 2013: 104-106; Hein A. et al 2009: 2069-2070

[5] Restle 1967, I: 176

SNG-4P: Iron (Fe) was detected in the paint layer, suggesting that this red paint sample may be Red Ochre (∝-Fe_2O_3). A layer of gypsum is present over the red paint layer (Fig. 11).
SNG-5P: This sample comprises five layers: 1 plaster - 2 paint - 3 plaster - 5 paint - 6 gypsum. Both plaster layers share a similar composition, and iron (Fe), aluminum (Al), and silicon (Si) were detected in both paint layers. In the 2nd paint layer, iron (Fe) is less concentrated than in the 1st layer. The presence of iron (Fe) in these two layers suggests that the red paint layers may be Red Ochre (∝-Fe_2O_3). Arsenic (As) is present across the entire sample (Fig. 12).
SNG-6: The analysis for this sample was canceled due to overheating during cross section preparation.
SNG-7P: The analysis for this sample was canceled due to sample amount is insufficient for obtaining a cross- section.
SNG-8P: Iron (Fe) was detected, indicating that this red paint layer may be Red Ochre(∝-Fe_2O_3) (Fig. 13).
SNG-9P: According to ESEM-EDX results, carbon black and gypsum layers are clearly visible in the dark blue sample (Fig.14). FTIR analysis, which involved separating, and powdering the paint layer along with its overlying deposit, identified gypsum and caput mortuum in the top gray layer, as well as manganese blue and smalt in the middle black layer (Fig.15 -16).
SNG-11P: These sample shares similar characteristics with Sample 7P, where iron (Fe) and aluminum silicate (Al_2SiO_5) were detected, suggesting that the paint may be Yellow Ochre (Fig. 17).
SNG-12P: Based on ESEM-EDX mapping results, iron (Fe) is observed as a distinct layer, implying that the green layer may consist of Green Earth pigment (Fig. 18).
SNG-13P: This sample contains two red paint layers, both of which show the presence of iron (Fe). This suggests that the paint layers may be Red Ochre (∝-Fe_2O_3) (Fig. 19-20).
SNG-14AP: A lime wash layer is observed beneath the paint layer, with large amounts of $CaCO_3$ and aluminum silicate (Al_2SiO_5), indicating the presence of lime wash. Iron (Fe) is present in a powdered form and is visible in small amounts (Fig. 21).
SNG-15P: Both gypsum and lime are present in this paint layer, with a high calcium content (Fig. 22).
SNG-16P: This paint layer consists entirely of pure gypsum, with possible casein mixtures observed across the entire plaster layer. Phosphorus (P) is widely present. A future analysis is needed to clarify the presence of casein used as tempera (Fig. 23-24).

Conclusion

While the ESEM-EDX method of mapping and point spectrum scanning does not provide detailed data on the sub-elemental groups, it is frequently employed to provide stratigraphy and general elemental data of paint layers. This method is particularly useful in understanding the support, plaster, and paint layers of wall paintings, as well as the processes of deterioration. It allows for cross-sectional analysis of the entire plaster and paint layers without sample waste, shedding light on the general matrix, especially when thin-sectioning is not feasible. When sufficient sample quantities are available, this method allows for the preservation and storage of the sample as a reference for future analyses.

Marcell Restle describes the Wall Painting technique as follows;[6]
"The colours (green, red, ochre, grey-blue) are muddy and, except for the white, have probably darkened owing to use of a glue-type binding medium. Composition, technique and drawing are based on old models, but are clumsy and schematic. Superimposed

[6] Restle 1967, I: 176

on the local colors - quite unsystematically - we find internal details drawn in with a broad brush in a darker tone in one place and light drawn in in white in another. This has mostly been applied with a pointed brush, often as a transparent wash and occasionally in pure white. The faces are set out in a muddy-looking light ochre glykasmos moulded with reddish brown ochre drawing. White lights hardly occur at all, but there are sometimes thin, transparent green shadows"

We can say that the paint analyses result roughly align with his visual predictions. The combined results indicate that the pigments used are predominantly in shades of red, green, and yellow ochre. The black paint sample demonstrates that carbon black was used in combination with gypsum. The detailed analysis of the blue paint sample reveals a gray-blue tone obtained by mixing carbon black, smalt, and ultramarine with caput mortuum. Pure gypsum was used to achieve white, while the presence of phosphorus (P) across the samples indicates the use of casein, as identified in FTIR and ESEM-EDX analyses.

The Saint George paint samples present a challenging group for analysis due to the thinness (0.1 mm to a maximum of 0.4 mm) of the paint layer and the active deterioration such as mainly powdering. Therefore, it is recommended that future paint analysis studies employ in situ analytical methods to fully reveal the entire paint palette. To date, no conservation efforts have been undertaken on the wall paintings of the Ihlara Valley's Saint George Church, which is in a state of active deterioration due to partial exposure to atmospheric conditions. Consequently, it is imperative that conservation efforts be initiated in an immediate manner for the Ihlara Valley, Saint George Church Wall Paintings.

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Fig. 1. Ihlara Valley, *Peristrema*, (H. Günözü Ulusoy)

Fig. 2. Saint George, (*Kirk Dam Alti)* Church, Northern Entrance (H.Günözü Ulusoy)

Fig. 3. Saint George Church, North West Wall (H. Günözü Ulusoy)

Fig. 4. Saint George Church, Ascension of Christ Scene (H. Günözü Ulusoy)

Fig. 5. Saint George Church, South West Wall (H.Günözü Ulusoy)

Fig. 6. Saint George Church South West Wall (H.Günözü Ulusoy)

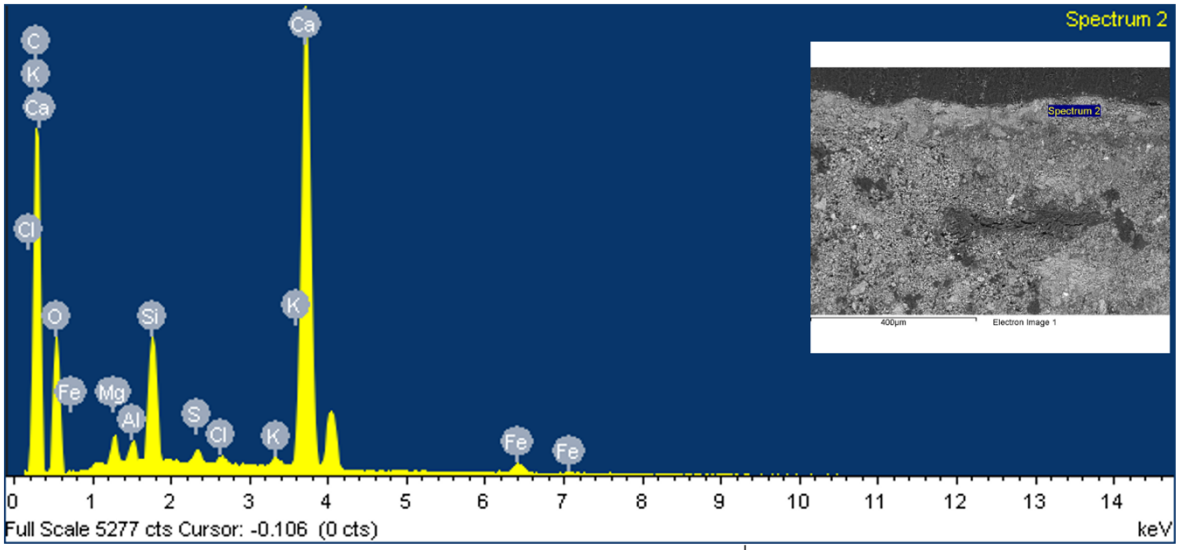


Fig. 7. SNG 1P/ESEM-EDX

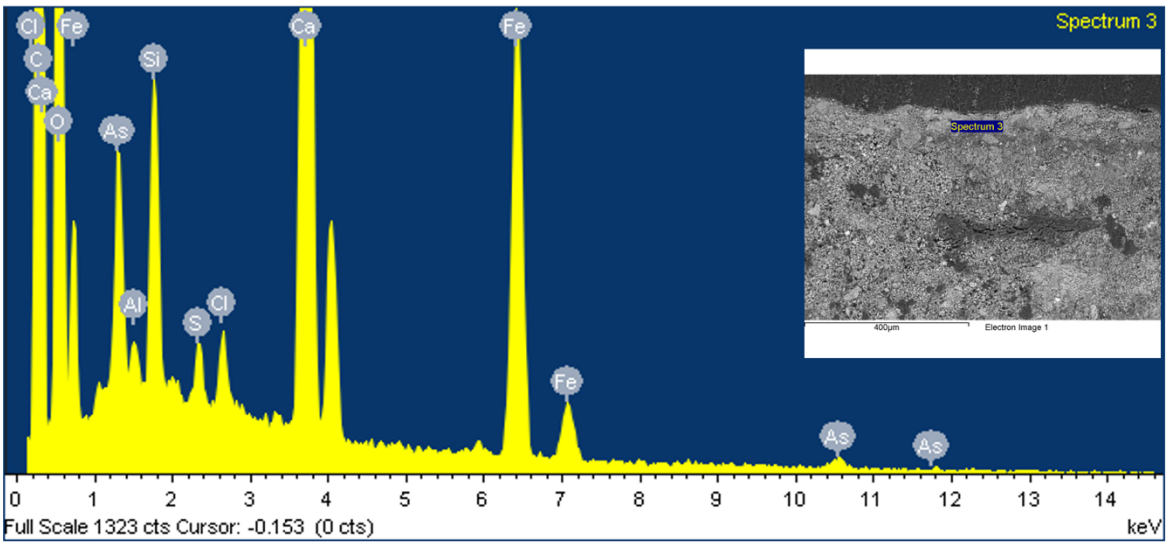


Fig. 8. SNG 1P/ESEM-EDX

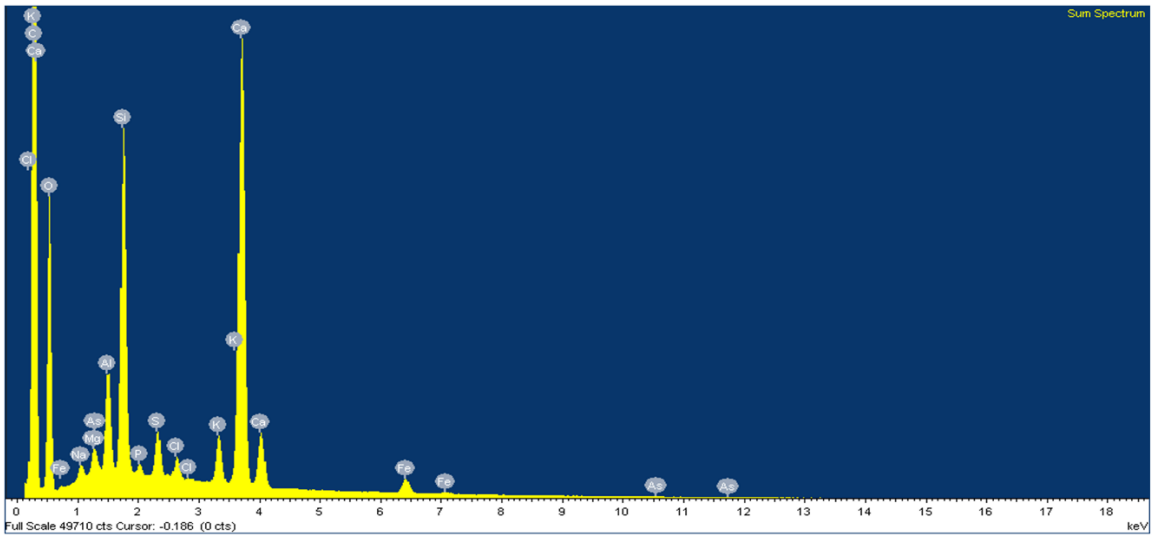


Fig. 9. SNG-2P/ESEM-EDX

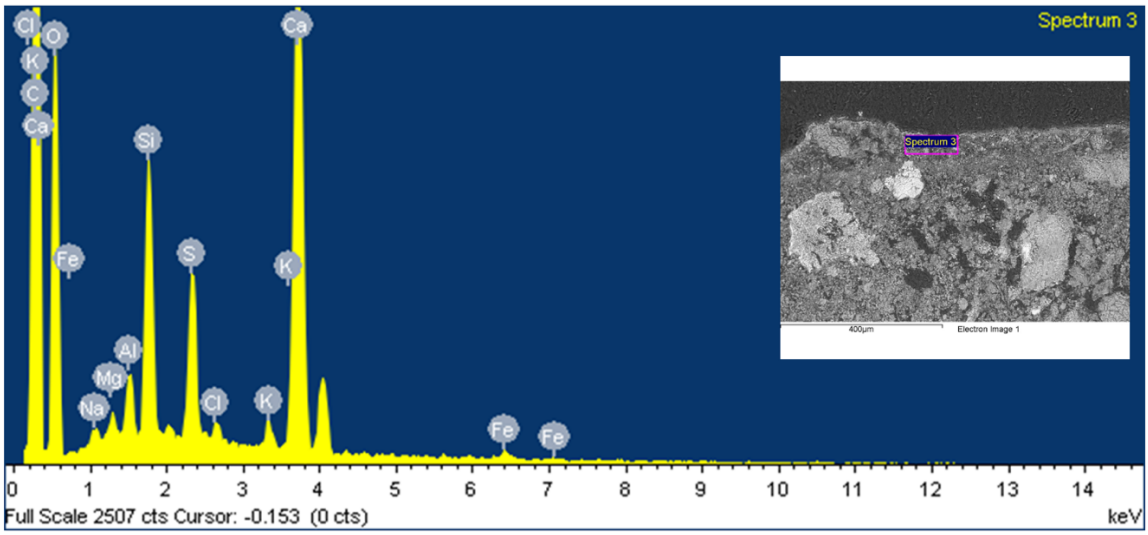


Fig .10. SNG-3P/ESEM-EDX

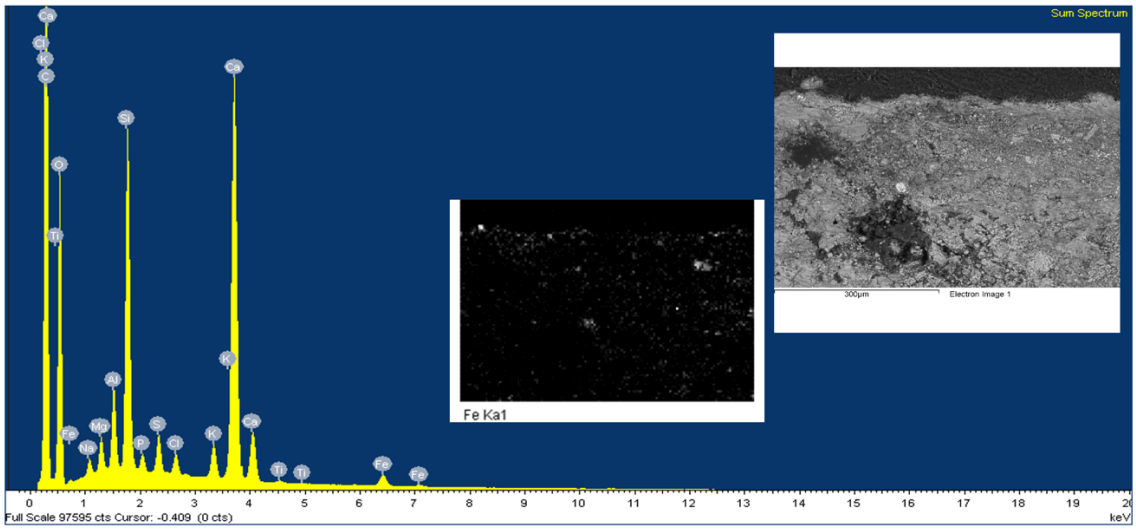


Fig. 11. SNG-4P/ESEM-EDX

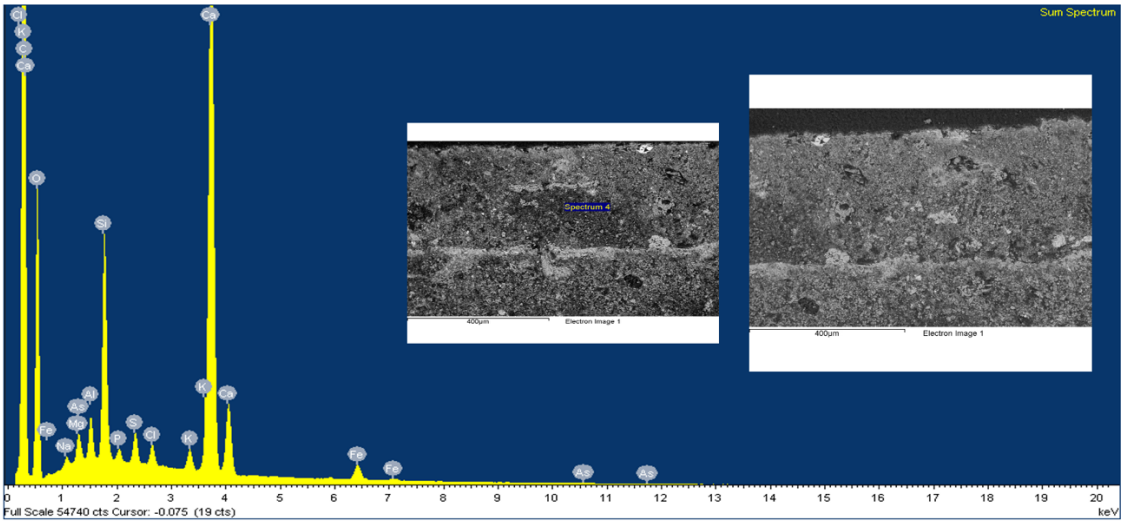


Fig. 12. SNG-5P/ESEM-EDX

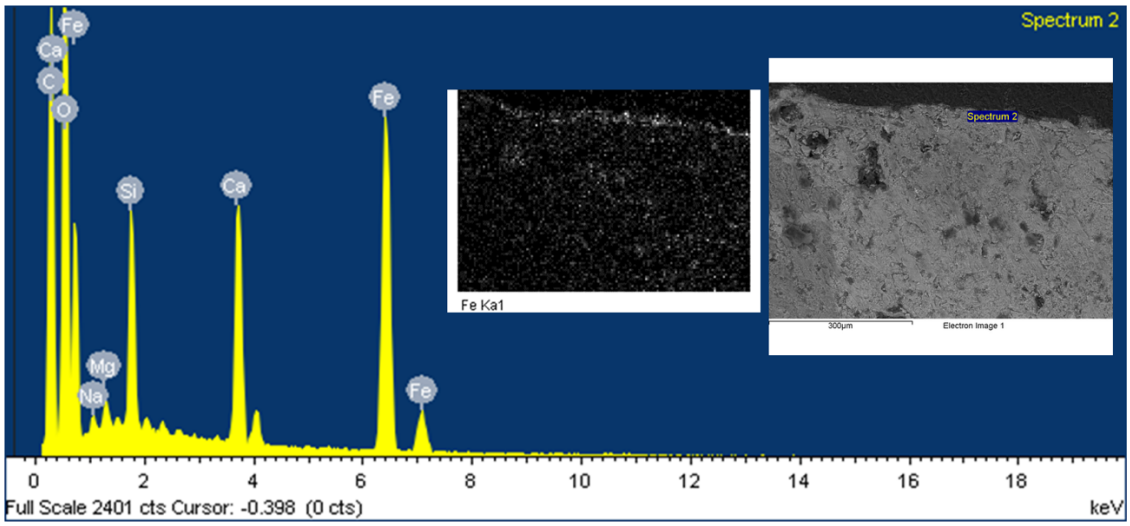


Fig. 13. SNG-8P/ESEM-EDX

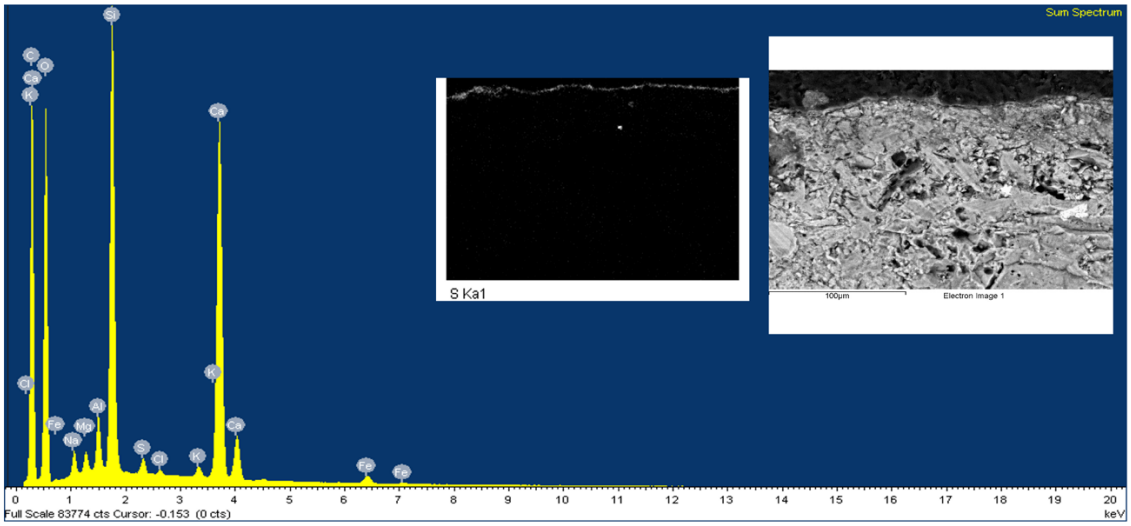


Fig. 14. SNG-9P/ESEM-EDX

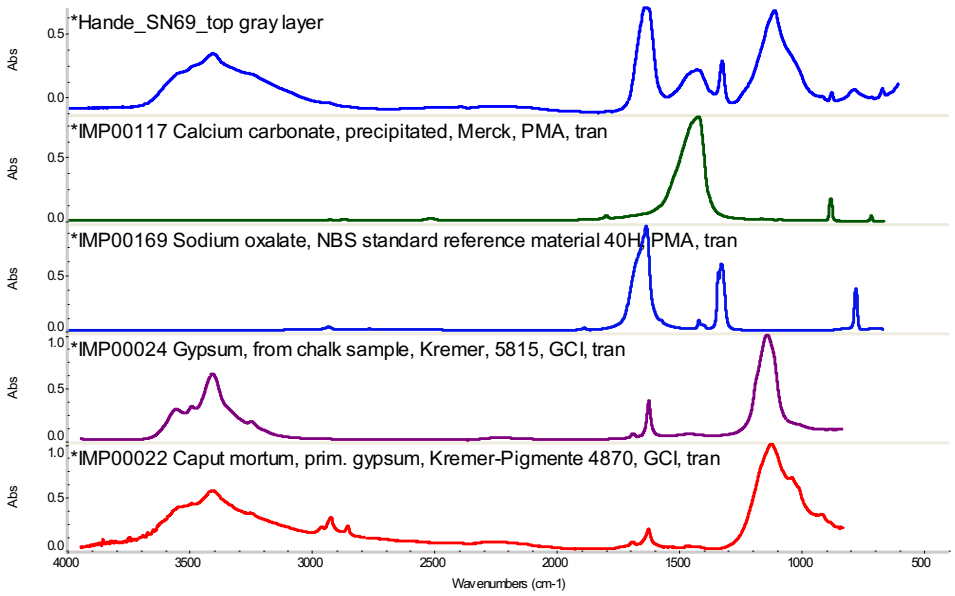


Fig. 15. SNG-9P 1st. paint layer, FTIR.

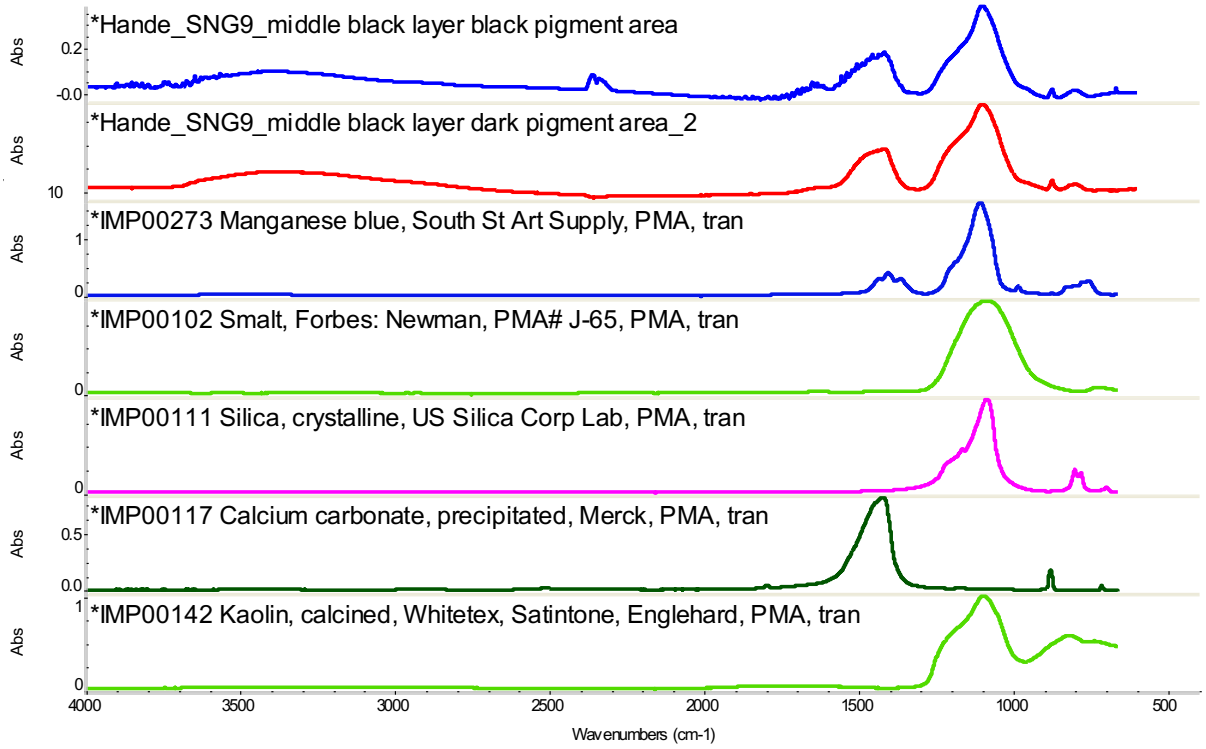


Fig.16. SNG-10P 2nd layer, FTIR.

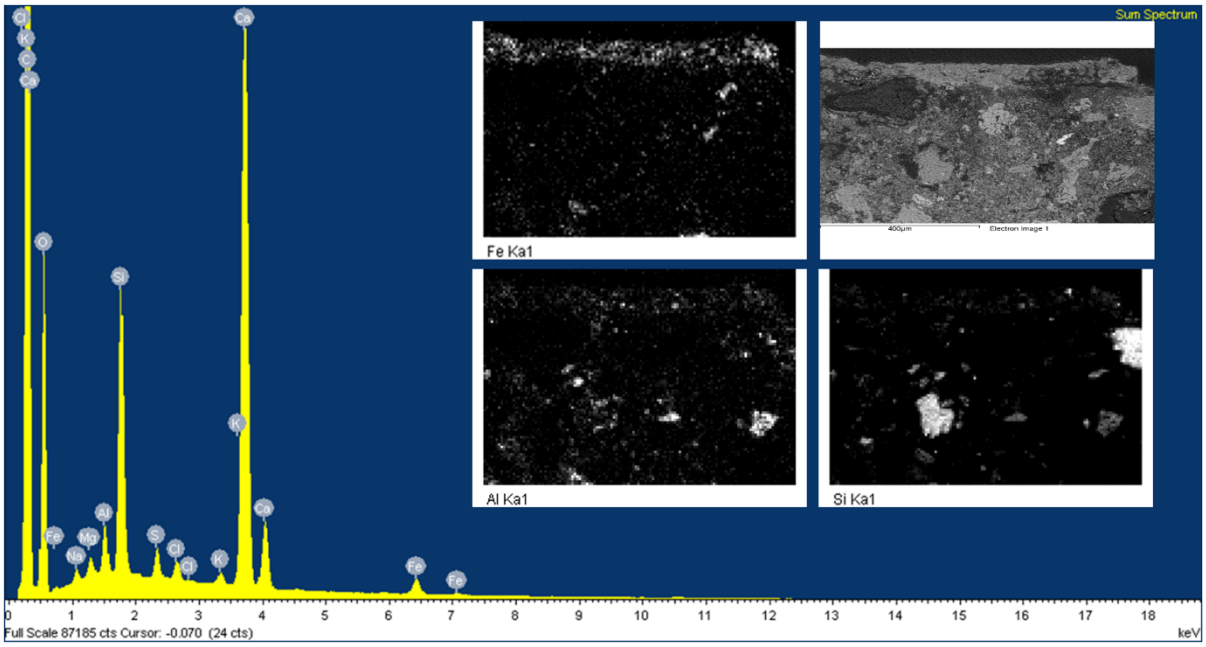


Fig. 17. SNG-11P/ ESEM-EDX

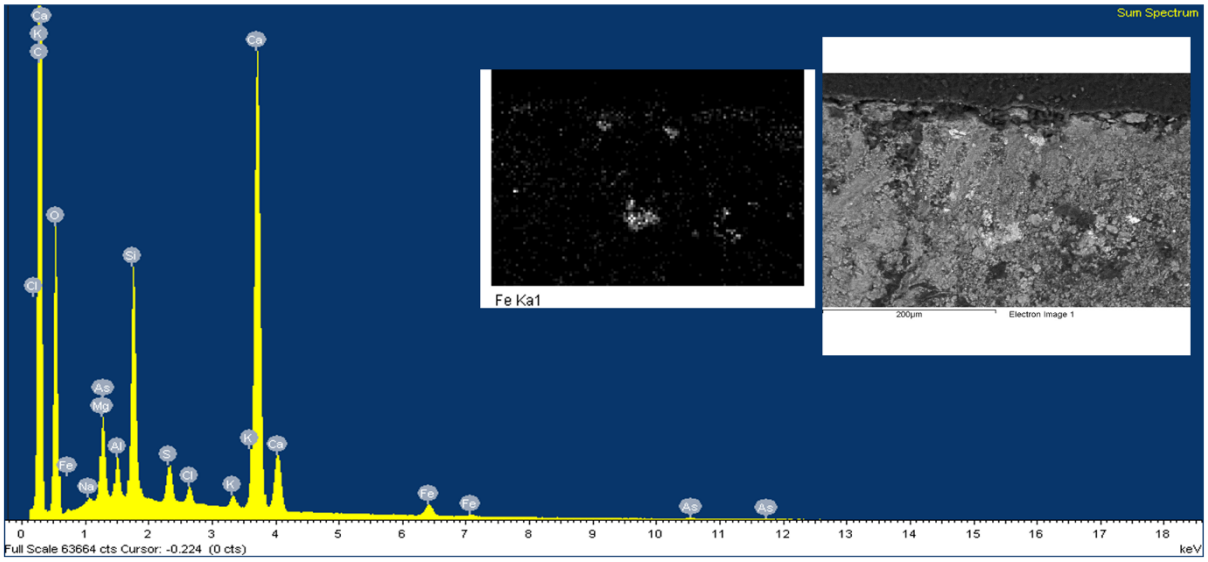


Fig. 18. SNG-12P/ESEM-EDX

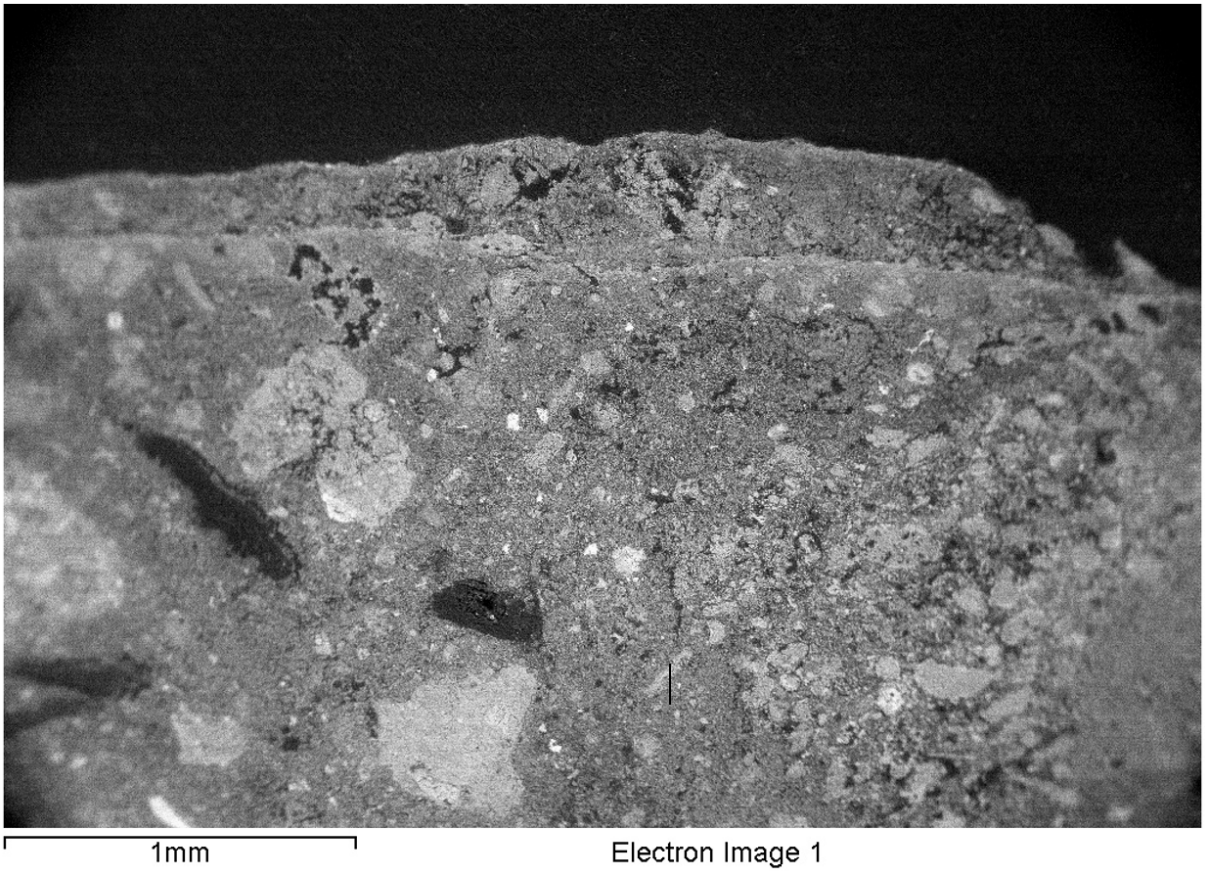


Fig. 19. SNG-13P E-Image

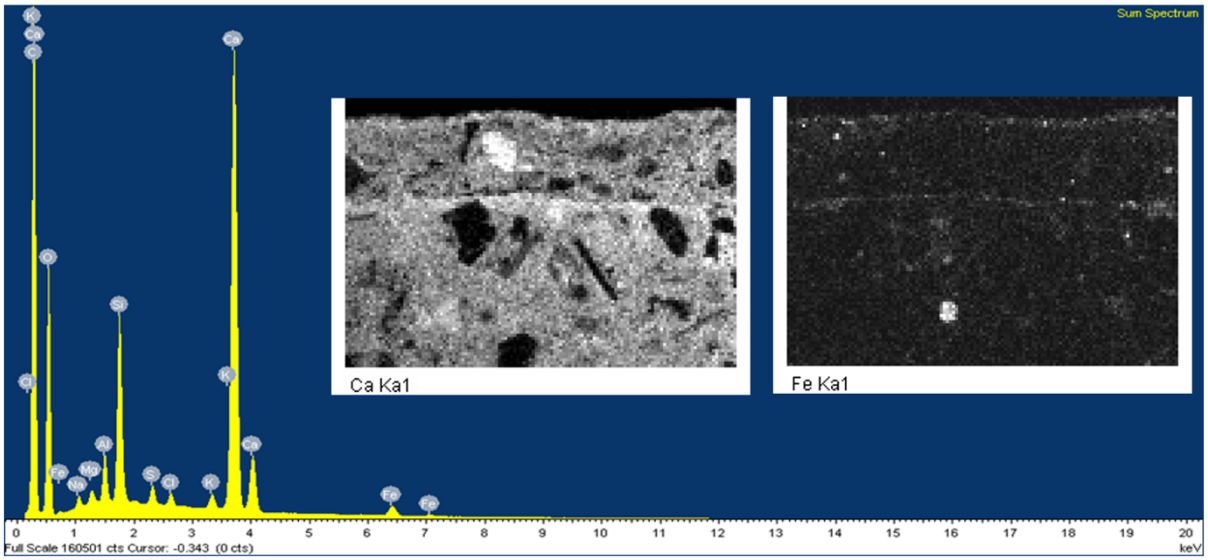


Fig. 20. SNG-13P ESEM-EDX

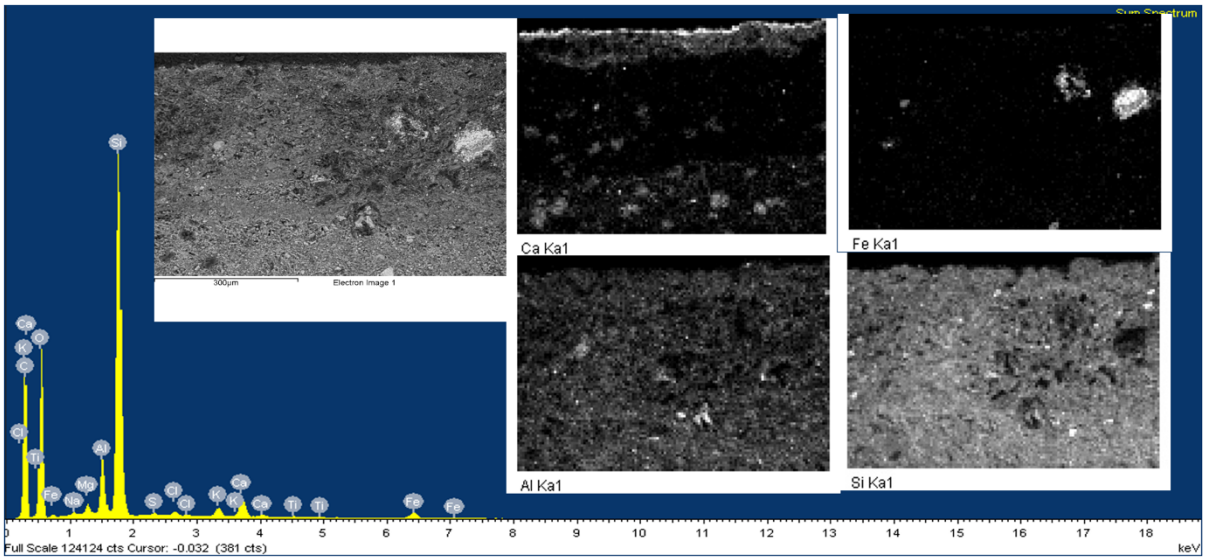


Fig. 21. SNG 14-AP/ESEM-EDX

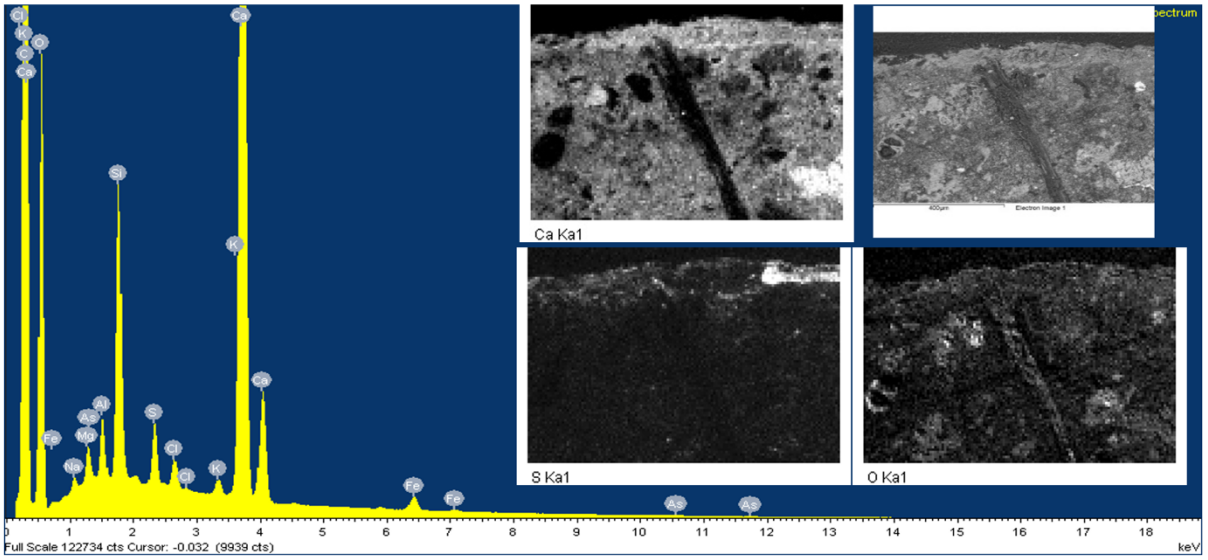


Fig. 22. SNG-15P/ESEM-EDX

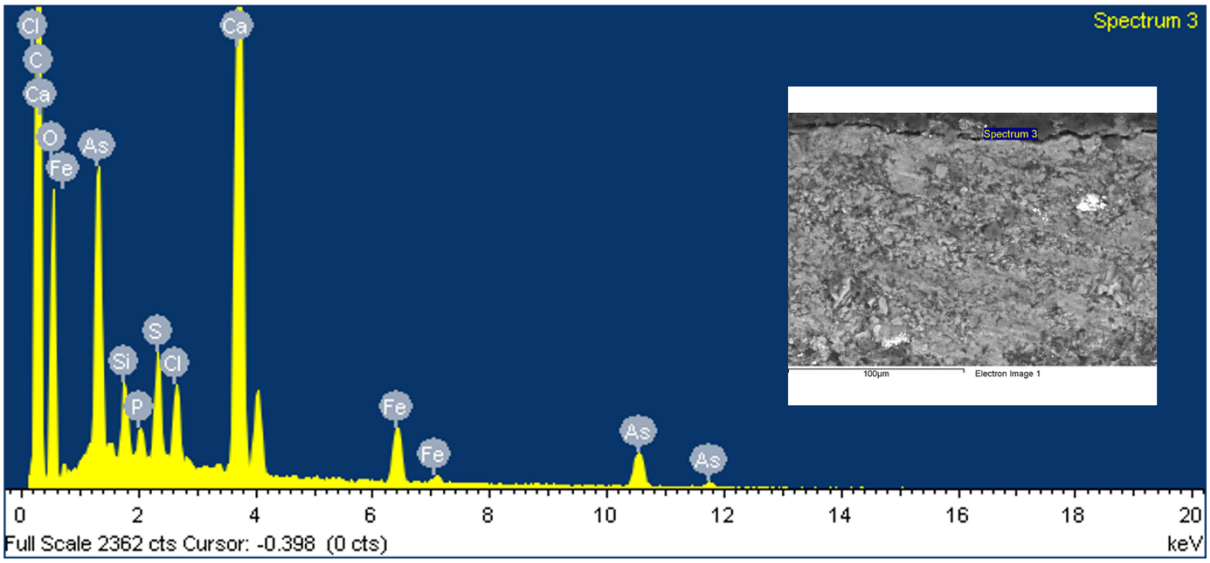


Fig. 23. SNG-16P/ESEM-EDX

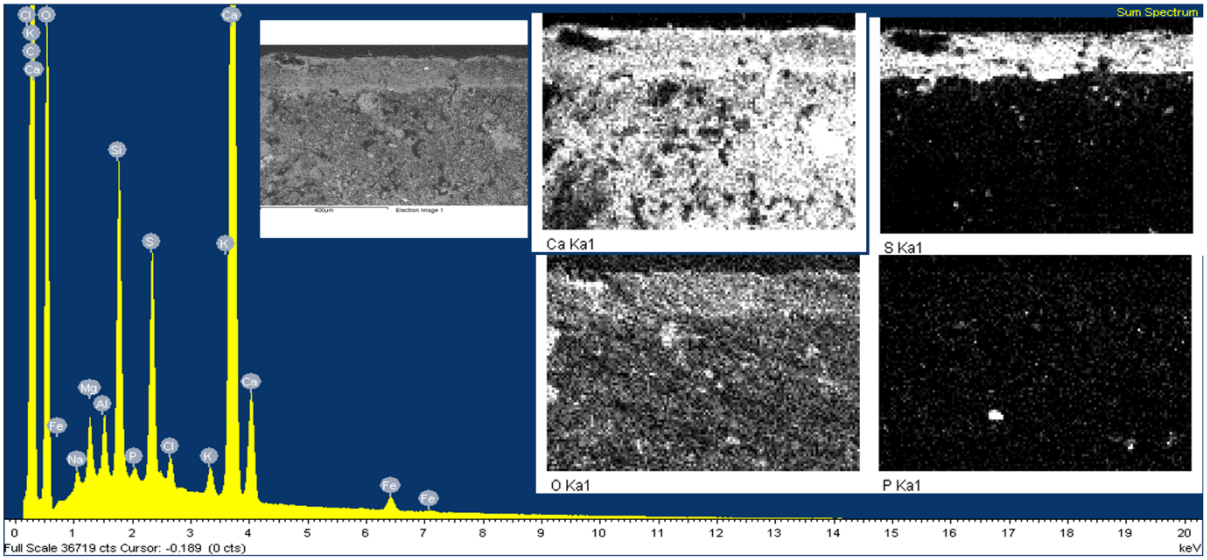
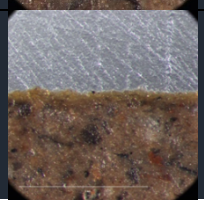


Fig. 24. SNG-16P/ESEM-EDX

Sample	Color	Statement	Cross Section	IDENTIFICATION OF PAINT LAYERS			
				1st Layer	2nd Layer	3rd Layer	4th Layer
SNG 1P	Green	Apse		Green Earth	-	-	-
SNG 2P	Yellow	Apse.		Yellow Earth	-	-	-

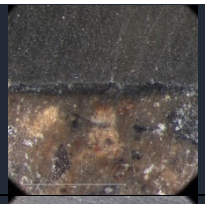
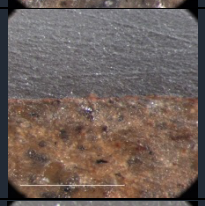
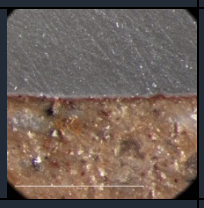
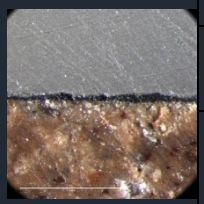
SNG 3P	Dark Blue	Apse		Carbon Black Gypsum	-	-	-
SNG 4P	Red	Apse		Red Ochre	-	-	-
SNG 5P	Red	Apse		Red Ochre	Lime Based Plaster	Red Ochre Density is lesser than the 1st Layer.	Gypsum

Fig. 25: Saint George (Kırk Dam Altı) Church Statigraphy of the Samples I

Sample	Color	Statement	Cross Section	IDENTIFICATION OF PAINT LAYERS			
				1st Layer	2nd Layer	3rd Layer	4th Layer
SNG 6P	Grey	Apse	Canceled Epoxy resin is over heated and damaged the paint layer.	-	-	-	-
SNG 7P	- Black - Beige	North entrance	Sample amount is insufficient for obtaining a cross- section.	-	-	--	-
SNG 8P	-Red - Whit e	North wall.		Red Ochre	-	-	-
SNG 9P	Dark Blue	North wall		ESEM/EDX Carbon Black FTIR Middle Black Layer Kaolin Manganese Blue Smalt Silica Calcium Carbonate	ESEM EDX Gypsum FTIR Top Grey Layer Gypsum Caput Mortuum Calcium Carbonate Sodium Oxalate	-	-
SNG 10P	Dark Blue	West wall	Canceled The sample amount is insufficient for obtaining a cross- section.	-	-	-	-

SNG 11P	Yellow	West wall		Yellow Earth	Gypsum	-	-

Fig. 26: Saint George (Kırk Dam Altı) Church Statigraphy of the Samples II

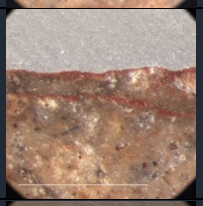
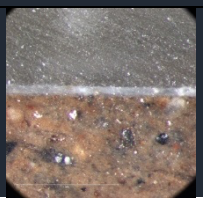
Sample	Color	Statement	Cross Section	IDENTIFICATION OF PAINT LAYERS			
				1st Layer	2nd Layer	3rd Layer	4th Layer
SNG 12P	Green	West wall		Green Earth	-	-	-
SNG 13 P	Red	West wall		Red Ochre	Lime Crushed Lime	Red Ochre	Gypsum
SNG 14AP	Red	North wall		Lime Wash Ca_2CO_3 and Al_2SiO_5 big amount	Red Ochre Fe is in small amount because of powdered hematite	-	-
SNG 15P	Beige	South wall		Gypsum and Calcium Carbonate together. Calcium Carbonate is dominant over Gypsum	-	-	-
SNG 16P	White	North wall		Gypsum Phosphorus (P)	-	-	-

Fig. 27. Saint George (Kırk Dam Altı) Church Statigraphy of the Samples III