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An Archaeometric Investigation on the Pigments Used in the Wall Paintings of Post-Byzantine (XIX. century) Churches in Cappadocia

Kapadokya'daki Post-Bizans (XIX. yüzyıl) Kilisesindeki Duvar Resimlerindeki Pigmentlerin Arkeometrik Teknikler ile Araştırılması

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Abstract

Cappadocia region, rock churches, monasteries, houses, underground settlements, valleys and historical and geological formations have unique beauty. The region, which is rich with its cultural assets belongs to Christian culture in Anatolia, is generally known with its rock churches, and is a subject to researches. The purpose of this study is; to understand the wall painting technology of the 19th century church, and to make a comparison with the wall painting materials of the rock churches. The study material is composed of pigments in the wall paintings of the Church of St. Theodoros Trion, which is from the 19th century, and located in Nevşehir. Scanning Electron Microscope and Energy Dispersive Spectrometer (SEM-EDX), X-Ray Diffraction Spectrometry (XRD) and Fourier Transformed Infrared Spectrophotometer (FTIR) are used to determine material characterization of pigments. X-Ray Fluorescence Spectrometer (XRF) analysis method was used in the analysis of the soil structure. As a result of analysis of the wall painting, it has been found that the ultramarine pigment is obtained from the lapis lazuli mineral and the covellite mineral of the covellite blue. In red, the red ochre and the caput mortuum pigment in purple color has been found. In the mineral of different pigment species, bauxite mineral belongs to the region have been detected. Green color, it has been determined that it is obtained from the glauconite and celadonite mineral in the region. According to the research carried out in the region in green color, it has been detected that only this pigment species has been used from the 6th century to the 19th century.

Keywords: *Cappadocia, Pigments, Wall Painting, Post-Byzantine Church, Archaeometry.*

Öz

Kapadokya bölgesi, kaya kiliseleri, manastırları, evleri, yeraltı yerleşimleri, vadileri ve tarihi ve jeolojik oluşumları eşsiz güzelliklere sahiptir. Anadolu'da Hristiyan kültürüne ait kültürel varlıkları ile zengin olan bölge, genellikle kaya kiliseleri ile tanınmakta ve araştırmalara konu olmaktadır. Bu çalışmanın amacı; 19. yy kilisesinin duvar resim teknolojisini anlamak ve kaya kiliselerinin duvar resimlerinde kullanılan malzemeler ile karşılaştırma yapmaktır. Çalışma materyalini Nevşehir'de bulunan 19. yüzyıldan kalma St. Theodoros Trion Kilisesi'nin duvar resimlerinde bulunan pigmentler oluşturmaktadır. Pigmentlerin malzeme karakterizasyonunu belirlemek için Taramalı Elektron Mikroskobu ve Enerji Dağıtılmış Spektrometre (SEM-EDX), X-Işını Kırınım Spektrometresi (XRD) ve Fourier Dönüşümlü Kızılötesi Spektrofotometre (FTIR) kullanılmıştır. Bölge toprağının analizinde X-Ray Floresans Spektrometresi (XRF) yöntemi kullanılmıştır. Duvar resminin analizi sonucunda lacivert pigmentinin lapis lazuli mineralinden ve kovellit mavisinin kovellit mineralinden elde edildiği tespit edilmiştir. Kırmızıda, kırmızı aşı boyası ve mor renkte kaput mortuum pigmenti bulunmuştur. Farklı pigment türlerinin mineralinde bölgeye ait boksit minerali tespit edilmiştir. Yeşil rengin yörede bulunan glokonit ve seladonit mineralinden elde edildiği belirlenmiştir. Yeşil renkte bölgede yapılan araştırmalara göre 6. yüzyıldan 19. yüzyıla kadar sadece bu pigment türünün kullanıldığı tespit edilmiştir

Anahtar Kelimeler: *Kapadokya, Pigment, Duvar Resmi, Post-Bizans Kilisesi, Arkeometri.*

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Introduction

Wall paintings have been the expression and cultural statement of human creativity in the period from the earliest period rock paintings to present-day wall paintings. Wall paintings are significant immovable cultural and natural assets that gives information about the history, art, faith, and social life of the period. The examination of the materials in these paintings, which are subjects to artistic style (religious-church etc.) in terms of the function of the buildings, has a great importance in understanding the technology of the period. Understanding the term technology in period is essential for proper protection and repairment. Archaeometry, which is an efficient science on investigation of the archaeological material, is intertwined with the conservation and restoration science. Multiple methods are used to define the physical and chemical structure of the pigment. Particle size distribution of the pigment, average particle size, particle shape, determination of the aggregate; sedimentation analysis, granulometric, light scattering methods, sieve analysis, optical microscope, scanning and transmission electron microscopy (SEM and TEM) methods are used. The composition of the inorganic pigment is determined by XRD (X-ray diffraction), Raman, IR (Infraed Spectroscopy), UV and VIS techniques spectrum. XRD is also used in the analysis of the crystal structure and size of the pigment. Qualitative and quantitative elemental composition; Determined by X-ray fluorescence analysis (XRF), wet chemical analysis, atomic absorption spectroscopy (AAS), EDX (Energy Dispersive Spectrometer), EPMA (Electron Probe Micro Analysis), OES (Optical Emission Spectrometry), MS (Mass Spectrometry), and LIBS (Laser Induced Plasma Spectroscopy)[1].

Most of the wall painting in Anatolia is found in Cappadocia. The reason for this is Byzantine art. Undoubtfully, the most important factor in Byzantine art is Christianity. The reason why the Cappadocia is a significant place to analyze is that it embraces every phase of Byzantine art. While the apostles who migrated from Palestine to Anatolia were living in caves, fairy chimneys, and valleys, they experienced the first stages of Christianity. The cross, geometric and animal motifs in the rock churches show that art has been interrupted during the Iconoclasm period. Due to the Macedonian dynasty, the new churches were built in the Göreme, Ihlara and Soğanlı valleys through the release of the Icon[2]. The wall paintings in these churches have been the subjects of the researchers recently. When we look at the work done to understand the material technology of the wall paintings in Nevşehir, it appears that there is a study between the 6th and 13th centuries[3]. However, Byzantine art in Cappadocia continued during the Seljuk and Ottoman periods[4].

While most of the information about the early period is elicited from ancient period writers and historical sources, it is seen that there are limited resources there is not enough information about the wall paintings of later periods. In particular, this information limit is valid for 18-19th century. While the determination of the pigments in the wall paintings in the region and the wall painting technique is confirmed by experimental studies and ancient and historical sources, there is no data and information about the wall paintings of the 19th century in the region.–In this study of the 19th century wall painting technology, and the comparison of

[1] Artioli 2012, 266-278; Toschi et al. 2016, 114-122; Pfaff 2017, 16.
[2] Akyürek 2000, 229.
[3] Pelosi et al. 2013, 99-108.
[4] Pekak 2009, 250.

periodical differences and similarities with the pigments found in the churches in Nevşehir will contribute to the art history.

2 Experimental

2.1. Samples

The materials of the Church of St. Theodoros Trion, from this period, constitute the study material. St. Theodoros Trion Church is located on Nevşehir-Niğde highway in the Bayramlı neighborhood of Derinkuyu district of Nevşehir. This church was dedicated to Saint Theodoros Trion on May 15, 1858 during the reign of Sultan Abdülmecid. The samples were taken from the wall painting with a scalpel. In addition, painted plaster fragments falling from dome, vault and column were also examined. Samples taken from the church are shown in Figure 1. The cross sections of the painted plaster pieces were examined in SEM. To examine the chemical and mineralogical structure of the pigments, samples were subjected to 5% HCl process. In the process, 37% HCl acid was diluted with distilled water and turned into 5%.

It was applied to destroy the calcite found in the lime plaster (CaCO3) in the plastered samples, and the calcite in the powder samples from the sampling or the matrix residue on the back surface of the pigment. This method, which was used for SEM-EDX, XRD method, was not used for the FTIR method. Some of the plastered samples were acid treated, and the other part was reserved for organic material determination (FTIR). The structure of the soil taken from the Monastery Valley was examined with XRF. The soil was not pre-treated for analysis.

2.2. Instrumentation

Analyzes were made at Pamukkale University Advanced Technology Research Center (ILTAM). SEM-EDX and FTIR were used to determine the wall painting technique at the beginning of the study. The Scanning Electron Microscope and Energy Dispersive Spectrometer (SEM-EDX) used is the SUPPRA ZEISS 40 VP. BSE (ASB) detector was used to examine the samples. In the cross-sectioned plaster pieces were coated with Au-Pd (gold-palladium) to ensure SEM image of good quality. The image consists of 100x, 200x, 500x magnification.

For the binder analysis, surface of the plaster pieces had engraved with a scalpel. Samples were turned into small particles in agate mortar. The powdered samples were placed in the sample chamber of the FTIR-ATR. The chamber was purged with alcohol in the placement of each sample. The measurements of the pressed samples were made in the range of 4400−400 cm^{-1} in Fourier Transform Infrared Spectrophotometer (FTIR-ATR Spectrum-II, Perkin-Elmer).

After the investigation of the wall painting technique, it was examined the elemental and mineralogical structure of pigment and EDX and XRD were used in the samples subjected to HCl treatment. The samples to be determined in EDX had coated with C (carbon). Elemental analysis was made regionally and appropriately. The density of the main elements in the pigment was examined method by mapping. The pigment type was determined with the elements identification in EDX and the mineral source was investigated with XRD. The X-Ray Diffraction Spectrometer (XRD) device used in the study was GNR APD Pro 2000. X-ray CuK radiation was used to investigate the mineralogical structure of the samples. X-ray wavelength is 1,54059 A0 (angstron). The screening range for the experiments is between 2theta = 50 - 80. In X-Ray

Fluorescence Spectroscopy (XRF) used in the investigation of soil in the Monastery Valley for the production of pigment, the device is Spectro XEPOS-II. The in-device method was used to examine the samples.

Fig. 1. a) Image of St. Theodoros Trion church, Nevşehir; b) view of apse; c) gallery floor; d) dome of St. Theodoros Trion church

SAMPLE	**ATTK1**	**ATTK2**	**ATTK3**	**ATTK4**	**ATTK5**	**ATTK6**	**ATTK7**	**ATTK8**
COLOR	Blue	Blue	Blue	Red	Red	Purple	Green	Green

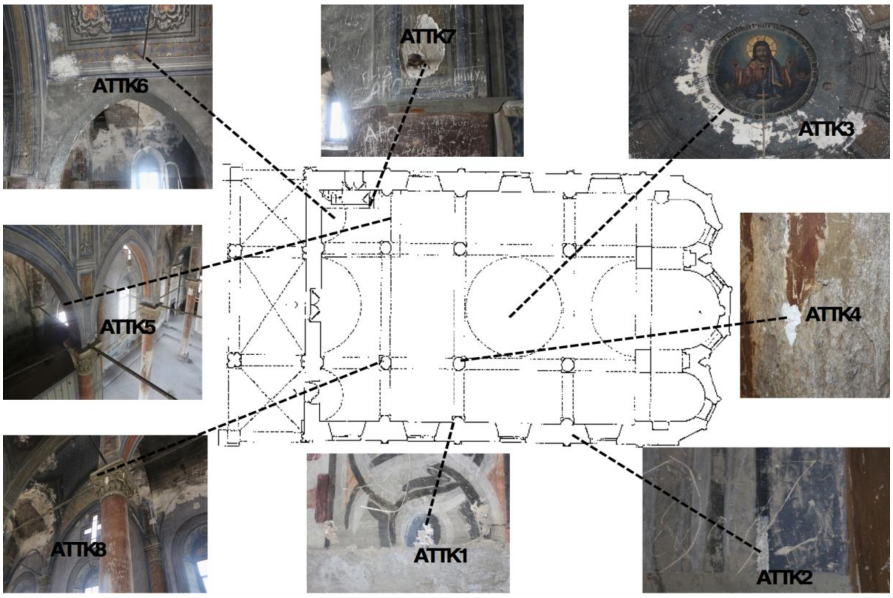

Fig. 2. Code and color property of samples

3 Results and Discussion

3.1. Technique of Wall Painting

ATTK7 and ATTK8 samples were used for the wall painting technique. The SEM image of the sample with ATTK7 and ATTK8 codes is shown in Figure 3. The results of the analysis of the samples in EDX are given in Table 1.

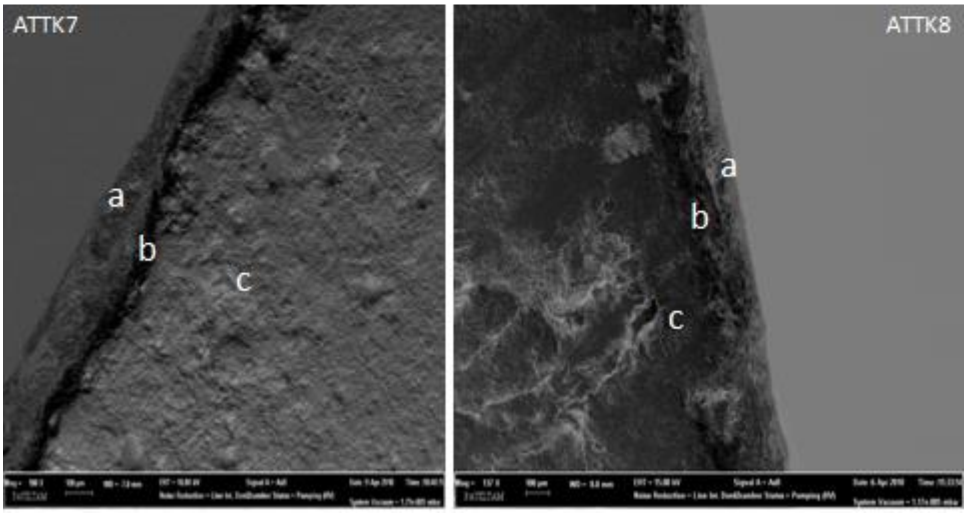

Fig. 3. Right and left image; a) paint layer; b) binding layer; c) plaster layer

Samples Code	O	Ca	Au	C	S	Pd
ATTK7	43.96	29.22	11.64	8.27	4.83	2.09
ATTK8	46.71	27.91	11.14	7.10	5.47	1.66

Table 1. The binding EDX result

As a result of EDX made with ATTK7 and ATTK8 coded example; O, Ca, Au, C, S and Pd elements were founded. Au and Pd are elements belong to the coating material used for imaging and element analysis. Ca, O and C elements indicate the use of CaCO3 as binders. Element S does not belong to gypsum. Because the result of the FTIR analysis shows that the plaster consists of CaCO3[5]. S is the element belongs to the soil of the region where the density of tuff is intense. Because stucco has aggregates made of sand. CaO and CO2 gas is released by heat treatment in quicklime. When H2O is added to CaO, slaked lime is obtained. CaO in EDX is thought to be belong to extinguished lime. EDX, H forbidden element is not visible in the analysis results. As a result of analysis, the ratio of O is much higher than other elements. Because it is bonding with Ca and C. The CO_2 are required for carbonation on the wall surface. It is thought that this gas will belong to the lime milk that is applied to the wall surface. In Fresco technique, the wall surface is moistened with lime milk or water. With the drying of lime milk, carbonation occurs with CO_2 on the surface and the pigment is fixed on the wall surface. In the EDX found elements provide information about inorganic compounds.

FTIR method is required for the determination of organic compounds. The FTIR spectrum of the ATTK7 and ATTK8 coded samples is shown in Figure 4.

[5] Vornicu et. al. 2013, 385; Pelosi et. al. 2013, 104.

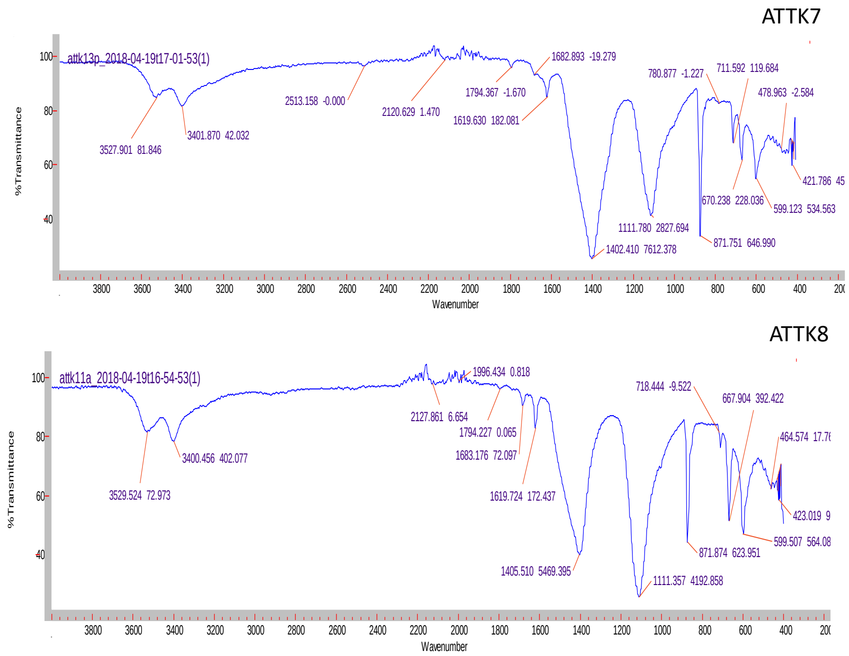

Fig. 4. FTIR spectrum of ATTK7 and ATTK8

According to the research conducted in the literature, strong vibrations of calcium carbonate in the infrared frequency band are observed at 1400 cm^{-1}, and the frequency band of CO3 anions is observed at 0-C-0 (bending-band/tension band) 873 cm^{-1} and 872 cm^{-1}. Similar vibrations are observed in the ATTK7 and ATTK8 coded sample. The strongest band is 1402 cm^{-1} in ATTK7 and 1405 cm^{-1} in ATTK8. In this case, it shows that CaCO3 is used as a material in the plaster. Although the strong vibrations in the frequency band indicate that the painting can be made in the fresco technique, there are also bands belonging to organic materials in the data. The band of the protein is 3529 cm^{-1} in ATTK7 and 3527 cm^{-1} in ATTK8. According to the literature, asymmetric vibration bands belong to the N-H group and represent egg protein (3238 cm^{-1} etc.). Flaxseed oil is seen in the carbonyl group (C=O) at 1122 cm^{-1} in the FTIR band. In ATTK7 and ATTK8, flaxseed oil is seen as 1111 cm^{-1}[6]. When the analysis results based on the wall painting technique are evaluated, it is seen that the painting started with the fresco technique but was completed as secco. Therefore, it can be said that the wall painting has the technique of mezzo fresco (chalky dry fresco technique).

3.2. Analysis of Pigments on Wall Paintings

Pigments of wall paintings were identified by methods EDX and XRD. While SEM-EDX yielded data of the elemental composition of the samples from different points or areas, mineral structure information was obtained from XRD. Table 2 shows the SEM-EDX result of pigments.

[6] Vornicu et. al. 2013, 385; Pelosi et. al. 2013, 104; Schönemann-Edwards 2011,1173-1180; Margaretha et all. 2012, 3-33; Cristache et all. 2013, 71-82; Khachani et all. 2014, 615-624; Pelosi et al. 2009, 548.

Samples	Na	Ca	Si	O	S	Al	Fe	Mg	K	Cl	Ti	Cu	Pb	As
ATTK 1	0.76	0.76	22.61	52.80	0.80	7.66	6.57	6.39	1.66	-	-	-	-	-
ATTK 2	4.43	2.66	31.44	47.22	0.55	8.84	3.66	-	1.20	-	-	-	-	-
ATTK 3	2.16	1.85	27.49	55.35	-	7.55	2.49	1.14	1.97	-	-	-	-	-
ATTK 4	-	-	56.69	39.07	-	0.57	2.22	0.68	-	0.78	-	-	-	-
ATTK 5	0.63		16.86	52.74	-	4.75	18.00	6.44	0.59	-	-	-	-	-
ATTK 6	-	1.37	23.62	47.94	-	3.70	15.33	8.03	-	-	-	-	-	-
ATTK 7	1.07	0.62	16.51	54.07	-	8.23	16.86	1.23	0.80	-	0.61	-	-	-
ATTK 8	1.55	0.59	9.09	50.12	-	3.66	1.52	0.80	1.15	12.00	1.83	1.16	13.29	3.21

Table 2. SEM-EDX results of pigments

3.2.1 Blue Pigments

The EDX analysis of ATTK1, ATTK2 and ATTK3 samples revealed the elemental structure of ultramarine pigment ($Na_3CaAl_3Si_3O_{12}S_n$). XRD method on samples was used to determine the mineral group of this pigment obtained from lapis lazuli and lazurite mineral. The result of XRD analysis is given in Figure 5. In the XRD analysis, lazurite, pyrite, calcite and feldspar alkaline group belong to were found to contain albite and quartz mineral. It was thought that Na, Ca, Al, Si, O and S elements obtained in the EDX results belong to lazurite $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$ and albite ($NaAlSi_3O_8$). It shows that Fe element will belong to pyrite (FeS), Mg element ($MgCO_3$) calcitic dolomite, K element's deterioration (salt) on wall painting surface or other elements in the structure of lapis lazuli. In addition, new mineral was found in XRD. Elements of this mineral were not found in EDX. Covellite mineral found in ATTK3 about there is not much information in the literature. It is thought that blue pigment is produced from this mineral which is a feature of 19th century. The XRD results of blue colored samples are given in Figure 6-7-8. Literature in the interpretation of analysis of blue colors, ICDD library data source is referenced[7].

[7] Nel et al. 2006, 490; Salvado et al. 2014, 3613; Manso et al. 2010, 326; Ganio et al. 2017, 8.

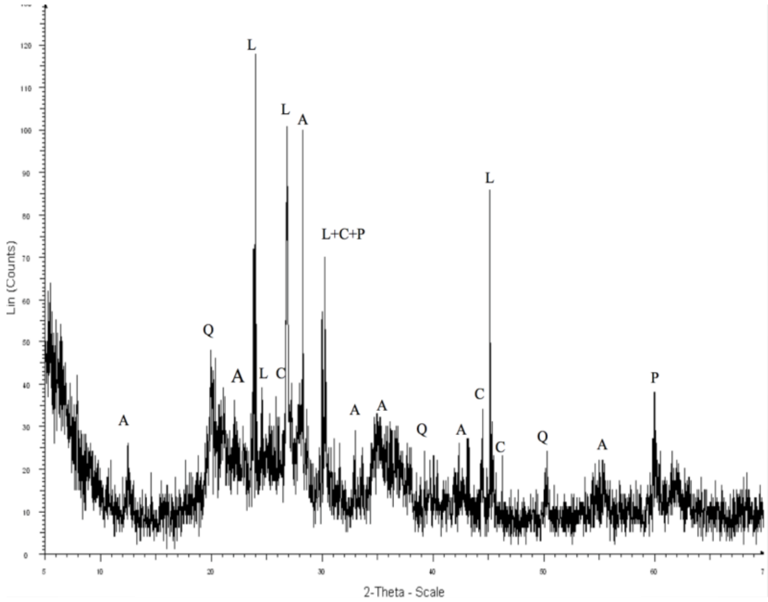

Fig. 6. ATT K1 coded sample XRD spectrum;
A: albite, Q: quartz, L: lazurite, C: calcite, P: pyrite

The ATTK1 code sample corresponds to the highest peak lazurite in the X-axis with 2 theta values. Lazurite along the X axis: 24, 25, 27, 30, 45; quartz: 19,38, 50; calcite: 25, 26, 30, 44, 46; albite: 13, 22, 29, 32 35, 42-43, 55; pyrite: gives peak at 30 and 60.

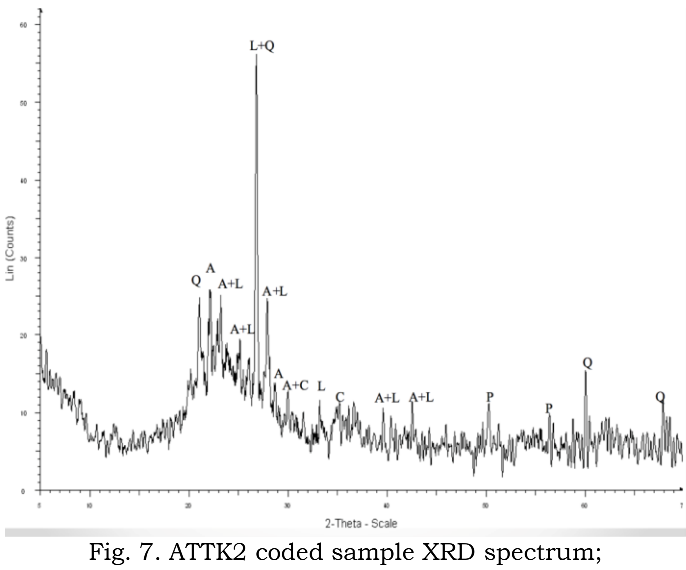

Fig. 7. ATTK2 coded sample XRD spectrum;
A: albite, Q: quartz, L: lazurite, C: calcite, P: pyrite

The ATTK2 code sample corresponds to the highest peak lazurite and quartz in the X-axis with 2 theta values. Lazurite along the X axis: 23, 25, 26-27, 33, 40, 42; quartz: 21, 26-27, 60, 68; calcite: 30, 35; albite: 22, 23, 25, 28, 29, 40, 42; pyrite: gives peak at 50 and 56.

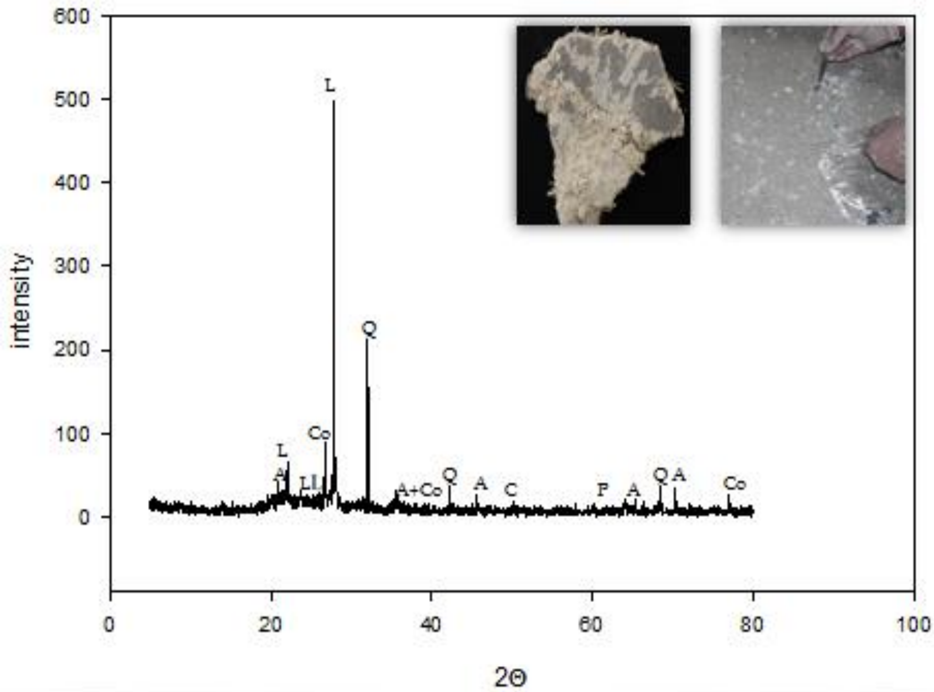

Fig. 8. ATTK3 coded sample XRD spectrum;
A:albite, Q: quartz, L: lazurite, C: calcite, P: pyrite, Co: covellite

In ATTK3 the sample was obtained in two ways. The first of these is the plaster falling from the dome. The second is the pigment of the paint layer pouring from the dome. When the dark color layer of the surface of the plaster was excavated, a lighter paint layer was found in the lower layer. The dark colored paint layer has the same visual characteristic as the pigments poured from the dome.

As a result of the analysis, covellite mineral was found in the dark layer. Light-colored paint is lazurite. For example, minerals in the XRD spectrum are as follows. The ATTK3 code sample corresponds to the highest peak lazurite in the X-axis with 2 theta values. Lazurite along the X axis: 23-26, 33; quartz: 37, 41-42, 6; calcite: 50; albite: 20, 28-29, 37, 45, 65, 74; pyrite At 50 and 60; covellite: 29, 93, 31, 5, 37 gives peak.

3.2.2. Red and Purple Pigments

The red pigments consist of ATTK4 and ATTK5 and the purple pigment is ATTK6. In the SEM-EDX results of the ATTK4 and ATTK5 coded samples, Fe, Si, O elements of the red ochre (hematite + quartz + clay) were observed. Other elements in the data other than Ochre consist of Na, K, Mg, Al and Cl.

In ATTK6 coded purple sample, elements of Caput Mortuum (Fe, Al) pigment were found. Other than Caput Mortuum, Mg, Ca, O and Si elements are included in the spectrum. It is thought that the Si, O element in the ATTK4 coded sample belongs to the quartz (SiO_2) mineral in the bauxite or the clay type formed by the SiO_2 and Al_2O_3 tetrahedrons and octahedron layers of due to the Al element. The Fe, O elements in EDX belong to hematite (Fe_2O_3) mineral in bauxite. Mg and Cl elements were probably found to belong to the $MgCl_2$ salt derived from degradation of the wall painting surface.

The EDX data XRD results obtained in the ATTK5 code sample are similar to ATTK4. The only difference separating ATTK5 from ATTK4 is the elements Na and K. Na and Al were considered to belong to albite ($NaAlSi_3O_8$) and K was related to again salt based on degradation. The findings obtained in the ATTK6 coded sample are not different from ATTK4 and ATTK5. It is thought that the Fe element of the EDX is the hematite (Fe_2O_3), Si and O element of the bauxite mineral belongs to the quartz (SiO2) or Si, Ca and Al source clay group. The Mg element belongs to the MgO compound in the bauxite mineral. It is thought that Mg does not have salt origin since Cl is not encountered in EDX data. The XRD spectrum of the red pigments is given in Figure 9 and Figure 10. The spectrum of the purple colored ATTK6 coded sample is shown in Figure 11. Literature in the interpretation of bauxite mineral, ICDD library data source reference was taken[8].

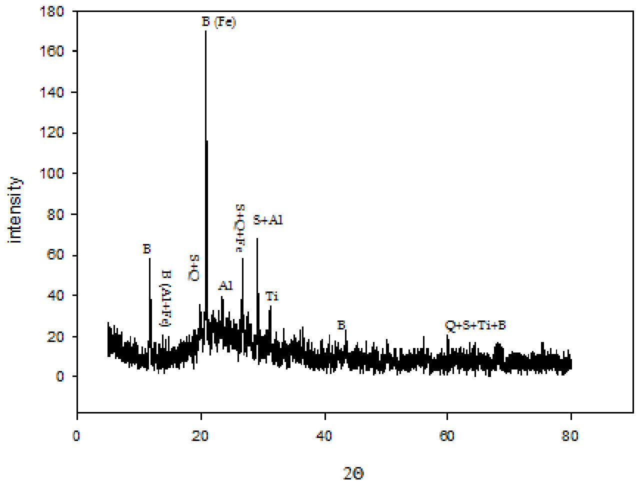

Fig. 9. ATTK4 coded sample XRD spectrum;
B: bauxite, Al: AlO_2, Q: quartz, Fe: Fe_2O_3, Ti: TiO_2, S:SO_2

The ATTK4 coded sample, the highest peak at the 2theta angle value corresponds to Fe2O3 in the bauxite mineral. Along the X axis Fe_2O_3: 19.91, 22.09, 26.78; S_2O_3: 20.92, 26.78, 29.25, 68.33; Al_2O_3: 19.91,20.92, 23.57, 29.25; SiO_2: 20.92, 26.78, 68.33; TiO_2: 31.24, 68.33; Bauxite: 11.80, 22.09, 44, 68.33 gives at peaks.

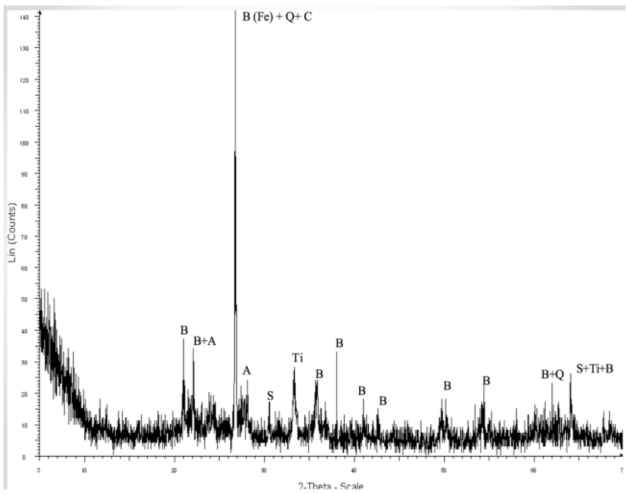

Fig. 10. ATTK5 coded sample XRD spectrum;
B: bauxite, A: albite, Q: quartz, Fe:Fe_2O_3, Ti: TiO_2, S:SO_2 C: calcite

[8] Reedy et al. 2014, 116; Oliveira et al. 2002, 537; Zhang- Lv 2016, 812; Yang et al. 2015, 240; Tsamo et al. 2017, 5-6; Ribeiro et al. 2012, 128.

The ATTK5 coded sample, the highest peak at the 2theta angle value corresponds to Fe_2O_3, quartz and calcite in the bauxite mineral. Bauxite along the X axis: 21, 22, 27, 35.80, 41, 42,5, 50, 54, 63; albite: 22, 28; quartz: 27, 63; calcite: 27; S2O3: 30.80, 64; TiO_2: 33.82, 63 gives at peaks.

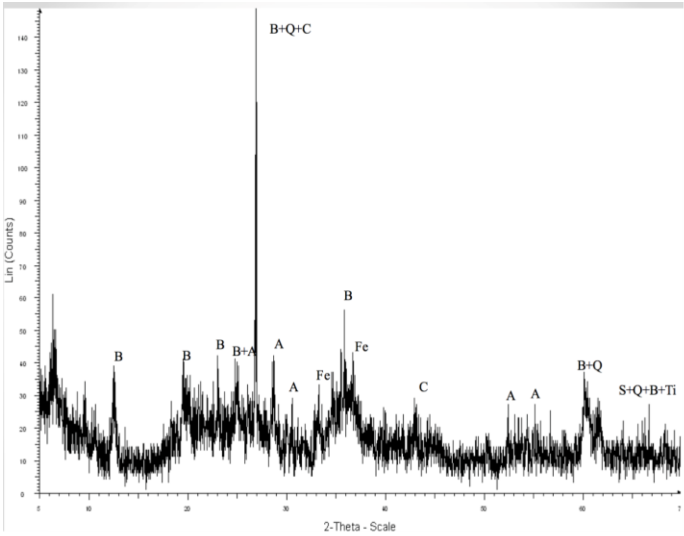

Fig. 11. ATTK6 coded sample XRD spectrum;
B: bauxite, A: albite, Q: quartz, Fe:Fe_2O_3, Ti: TiO_2, S:SO_2 C:calcite

The ATTK6 coded purple sample, the highest peak at the 2theta angle value corresponds to Fe2O3, quartz and calcite in the bauxite mineral. Bauxite along the X-axis: 11.70, 20, 23, 25, 27, 36, 60, 67; albite: 23, 28, 30, 52.80, 55; quartz: 27, 60, 67; calcite: 27; S_2O_3: 67; TiO_2: 67 gives peak at Fe_2O_3: 32 and 37.

3.2.3. Green Pigments

Mineralogical and chemical structure of ATTK7 and ATTK8 green pigments were investigated by SEM-EDX method. The structure of the T1 coded soil in the monastery valley investigated in the production of pigment was investigated by XRF method. The XRF result of T1 is given in Table 3. In the T1 coded sample taken from the monastery valley, glauconite and celadonite minerals were detected. The results of the EDX analysis in ATTK7 consist of O, Fe, Si, Al, Mg, Na, Ca, K and Ti. Green soil pigment consists of Fe^{+2}, Fe^{+3} elements and green clay minerals (celadonite, glauconite), quartz and feldspar group. According to the EDX result of ATTK7, it is green earth pigment because it has elements of celadonite $(K(Mg,Fe_2+)(Fe_3+,Al)(Si_4O_{10})(OH)$ and glauconite ((K,Na)(Fe,Al,Mg)2(Si,Al)4O10(OH)2) mineral. Due to the Fe, Al, Mg, Si, K elements in the EDX, this pigment is thought to produce from the glauconite mineral.

The results of the EDX analysis in ATTK8 consist of Ca, Si, Al, Cu, O, Ti, As and Pb. Based on the data obtained, it is thought that the pigment may be termed parrot green because of its Cu, As, Pb content. This pigment emerged by the discovery of the emerald green. According to the information in the dictionary called Pigment Compendium, lead turns into blue color in cold sugary solution and contains a little yellow color in it. This solution is mixed with emerald green (Cu, Acetate, As) and parrot green is formed[9]. Due to the Cu and Cl elements, it may also be possible that the pigment is atacamite (Cu_2Cl (OH) $_2$) But there is not as in the structure of the atacamite. The presence of the Ti element in the results of the analysis indicates that

[9] Eastaugh et al. 2004, 298.

TiO_2 (white) is used to obtain the light green tone. Figure 12 shows the density distribution of the elements in the EDX map made of green colored samples. The transmitted signals form maps of the element distribution, with higher image brightness corresponding to areas of high element concentration in this method.

Atomic Number	**Compendium**	**Component**	**% Concentration**
11	Na2O	Sodium	2.26 %
12	MgO	Magnesium	1.166 %
13	Al2O3	Aluminium	13.64 %
14	SiO2	Silicium	70.96 %
15	P2O5	Phosphor	0.24 %
19	K2O	Potassium	3.51 %
20	CaO	Calcium	1.76 %
22	TiO2	Titanium	0.40 %
25	Mn	Mangan	0.07 %
26	Fe2O3	İron	5.90 %
	Total		99.91

Table 3. XRF result of T1

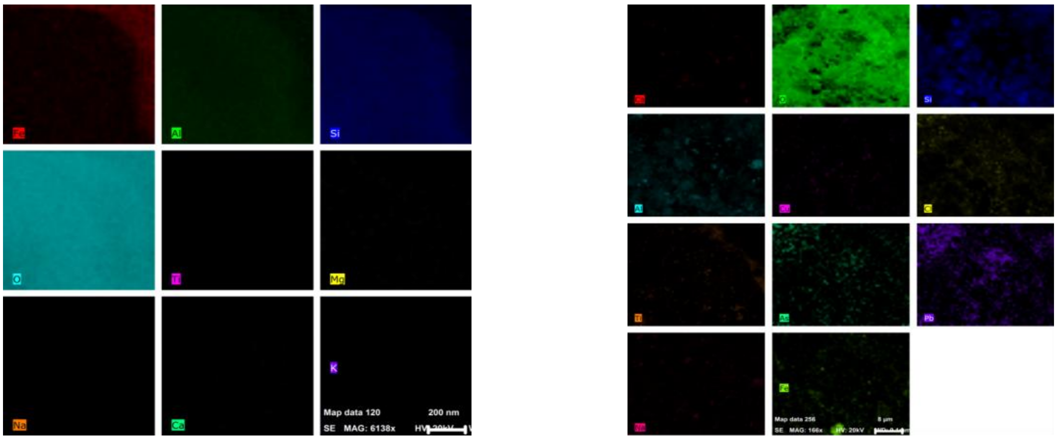

Fig. 12. a) EDX mapping of ATTK7, b) EDX mapping of ATTK8.

The mass-sensitivity of EDX analysis substantially depends on the ratio of peak signal to emission background. Obtaining maps of the element distribution is possible only for concentrations of over 1% because peaks from trace elements are extremely difficult to separate from the background. For concentrations below few tenths of a percent, peak intensity is higher than the background intensity only about 30–50%. Errors in the cut-off of a background level may result from the different background intensity on the left and on the right side of the peak. Therefore, for measurements of the background level, the dependency of the intensity of the continuous spectrum from the atomic number is usually applied[10]. Figure 12 contains a sample mapping of the distribution of chemical elements on the scanned surface. This map shows the distribution of elements in the pigment. This distribution is directly proportional to the EDX elemental analysis.

[10] Wassilkowska et al. 2014, 143-145.

4. Conclusions

The data obtained from the analysis of wall paintings are summarized in Table 5. The results of the analysis show that the same minerals are used in red and purple pigments. While the same pigment and mineral usage was observed in case blue color, it was determined that another mineral group was used in ATTK3 coded sample. As shown in Table 4 different pigments and mineral are used in green color.

Color	Sample Code	Pigment	Chemical Formul	Mineral
Blue	ATTK1	Ultramarine	$Na_3CaAl_3Si_3O_{12}S_n$	Lapis Lazuli
Blue	ATTK2	Ultramarine	$Na_3CaAl_3Si_3O_{12}S_n$	Lapis Lazuli
Blue	ATTK3	Ultramarine	$Na_3CaAl_3Si_3O_{12}S_n$	Lapis Lazuli
Blue	ATTK3	Covellite	CuS	Covellite
Red	ATTK4	Red ochre	Fe_2O_3+clay+quartz	Bauxite
Red	ATTK5	Red Ochre	Fe_2O_3+clay+quartz	Bauxite
Purple	ATTK6	Caput Mortuum	Iron Oxide	Bauxite
Green	ATTK7	Green Earth	Fe-Silicate	Glokonite
Green	ATTK8	Parrot Green	$3Cu(AsO_2)_2.$ $Cu(C_2H_3O_2)_2$	Coppera cetoarsenite

Table 4. The analysis results of wall paintings

The presence of different mineral groups and pigment species in the same colors in the analysis of the Church with no historical documents suggests that the Church had been under repair in particular historical periods. Since the parrot green pigment was produced in 1906, it shows that the church had been under repair after the period in which it was built[11]. In the experimental studies conducted in the region, it was demonstrated that ultramarin, indaco (lazy), lazurit, lapis lazuli and azurite are in blue color; hematite, ocher, litharge, filth, alizarin and cinnabar (vermillion) are in red color. For the green color, green earth what found. For yellow color, jarosit and giallorino were found. For white color, biacca (lead white and Bianco S. In black color, C has been identified. In the chronological study conducted by Pelosi for some churches in the region, in red pigments show the use of hematite, red lead (litharge) and goethite in the 6th, 7th, 8th, 9th, 10th and 13th centuries churches (23, 24)[12]. The use of green and blue colors does not change according to centuries, since green earth and ultramarine pigment have been found so far in the analysis of wall paintings.

The reason why the scientists who work in the region have found various pigment species in the same color in the wall paintings is that the structure is depend on the founder of the building. Construction of the building and the paints of the wall paintings are related to the cost. The presence of different pigments shows that different art workshops work in this region. In the T1 sample taken from the valley of monasteries, glauconite and celadonite minerals were identified, and this data belonged to the minerals from which ATTK7 coded green earth pigment was obtained. The bauxite mineral, which is red and purple is also observed in Kayseri and Adana according to MTA data. There is a diasporite mineral in Nevşehir province map. Since bauxite is a mixture of diasporite, gibbsite and carbohydrate minerals, it can be thought that bauxite mineral may also exist in this region. In his book, the ancient period writer, Plinius, describes Cappadocia as the area where the red color is mostly produced. Hematite (bauxite mineral content) was found in the analysis of wall paintings at that time. This data shows that the local red pigment production

[11] Eastaugh et al. 2004, 298.
[12] Pelosi et al. 2013, 108; Pelosi et al. 2009, 548.

continued until the 19th century. The covellite mineral found in the sample with ATTK3 code was found in Kayseri in recent researches. As a result of the data, since the church was built with non-Muslim people’s own means in the Ottoman period, it is thought that the artists in the region worked in this church, and painted in wall paintings by using local materials.

In addition, in the experimental studies conducted in the region, the presence of the same pigment and mineral in red, green and blue color shows that there is an art workshop in this area. Research on the subject is continuing.

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