CONSERVATION PROBLEMS OF HISTORIC WALL PAINTINGS OF TAXIARHIS CHURCH IN CUNDA, AYVALIK

A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

In Architectural Restoration

By
Kerem ŞERİFAKİ

July 2005
İZMİR

We approve the thesis of **Kerem ŞERİFAKİ**

Date of Signature

…………………………………………………….. **19 July 2005**
Assoc. Prof. Dr. Hasan BÖKE
Supervisor
Department of Architectural Restoration
İzmir Institute of Technology

…………………………………………………….. **19 July 2005**
Assoc. Prof. Dr. Başak İPEKOĞLU
Co-Supervisor
Department of Architectural Restoration
İzmir Institute of Technology

…………………………………………………….. **19 July 2005**
Assoc. Prof. Dr. Funda TIHMINLIOĞLU
Department of Chemical Engineering
İzmir Institute of Technology

…………………………………………………….. **19 July 2005**
Prof. Dr. Ömür BAKIRER
Department of Architecture
Middle East Technical University

…………………………………………………….. **19 July 2005**
Assoc. Prof. Dr. Başak İPEKOĞLU
Head of Department of Architectural Restoration
İzmir Institute of Technology

……………………………........……………………………..
Assoc. Prof. Dr. Semahat ÖZDEMİR
Head of the Graduate School of Engineering and Sciences

ACKNOWLEDGEMENTS

I would like to thank my supervisors Assoc. Prof. Dr. Hasan Böke and Assoc. Prof. Dr. Başak İpekoğlu for their guidance suggestions, contributions and criticisms during the study. I would like to thank Assoc. Prof. Dr. S. Sarp Tunçoku for his helps and morale support during the study.

I would like to express my special thanks to the jury members of Prof. Dr. Ömür Bakırer and Assoc. Prof. Dr. Funda Tıhmınlıoğlu for their attendance to my thesis defence seminar and for their valuable suggestions to this study.

I would like to thank the staff of the Centre for Materials Research of the Institute for the XRD, SEM and, Filiz Özmıhçı for the DSC and TGA and, Res. Assist. Meral Budak and Res. Assist. Özlem Çizer for their helps during the laboratory studies in the Material Conservation Laboratory.

I would like to thank my dear term friends Sevinç Çulcu, Özlem Aslan Özkaya, Işıl Talu and Elif Uğurlu for their endless morale support. I feel fortunate to be in a term like this.

I would like to thank my dear friends, Ufuk Derya Bahçacı, Nuray Benli, Eda Ezgi Bingül, Şebnem Korkmaz and Yunus Tekel for their sincere friendship and endless support.

Finally, I am indebted to my family for their endless support, patience and tolerance.

ABSTRACT

In this study, wall paintings of the Taxiarhis Church were investigated with the purpose of conservation. Wall paintings are documented by photographs and drawings. It was aimed to determine the application technique and material properties of the paintings. Wall paintings of the Taxiarhis Church were executed in two different periods. Hence, samples including all periods were collected. Basic physical properties, raw material compositions, chemical and mineralogical compositions and micro structures of the plaster layers were determined. Chemical and mineralogical compositions and the microstructure of the painting layers and weight loss of the binder due to heat were determined. These studies were carried out by X-Ray diffraction (XRD), scanning electron microscope, thermogravimetric analyzer (TGA), Differential scanning calorimeter (DSC) and infrared spectroscopy (FT-IR).

Wall paintings were executed on fine lime plaster by using vegetable oils (linseed, walnut, poppy seed, etc.) by oil painting technique.

Wall paintings of both periods were executed on fine lime plasters. Vegetable oil mixed with ZnO was used in the preparation of binding media. Priming layer over binding layer is composed of Anglesite ($PbSO_4$) and vegetable oil. Pigments that gave the color to the paintings were executed on the priming layer and may be defined as green earth, lead red and iron oxide.

Vandalism is an important effect in the deterioration of the paintings. Beside this, crack formation on the paint surfaces and disintegration of the fine plaster and paint layers due to the wetting drying cycles are observed. Deteriorations observed on paintings will be prevented by the consolidation of the structure and the control of the dampness.

Keywords: Taxiarhis Church, Wall painting, Linseed oil, Oil painting, Cunda

ÖZET

Duvar resimleri tarihi alanların ve tarihi yapıların ayrılmaz parçaları olarak kabul edilmektedirler. Kültürel mirasın bütünlüğü açısından duvar resimlerinin yerlerinde korunmaları önemlidir. Duvar resimleri tarihi yapıların karşı karşıya kaldıkları bozulma sorunlarından doğrudan etkilenmektedirler. Duvar resimleri aynı zamanda tarihi yapıların vandalizme en fazla hedef olan bölümünü oluşturmaktadırlar. Uygun olmayan yöntemler ve malzemelerle yürütülen restorasyon uygulamaları, duvar resimlerinin bozulmasının en önemli nedenlerinden biridir.

Bu çalışmada, Taxiarhis Kilisesi'nde yer alan duvar resimleri koruma amaçlı incelenmiştir. Kilisede yer alan duvar resimleri fotoğraflar ve çizimler aracılığı ile belgelenmiştir. Duvar resimlerin uygulanma tekniğinin ve kullanılan malzemelerin özelliklerinin belirlenmesi amaçlanmıştır. Resimlerin uygulandığı sıva tabakalarının temel fiziksel özellikleri, hammadde kompozisyonları, kimyasal ve mineralojik kompozisyonları ve mikroyapısal özellikleri belirlenmiştir. Resimleri oluşturan tabakaların kimyasal ve mineralojik kompozisyonları, mikroyapısal özellikleri belirlenmiştir. Bu çalışmalarda X ışınları kırınım cihazı (XRD), taramalı elektron mikroskobu (SEM-EDS), TGA, Diferansiyel Taramalı Kalorimetre (DSC) ve Kızılötesi Spektroskopisi (FT-IR) kullanılmıştır.

Çalışma sonucunda, duvar resimlerinin bazı bitki tohumlarından (keten, ceviz, afyon vb.) elde edilen yağ kullanılarak, yağlı boya tekniği ile kireç sıva üzerine hazırlandığı belirlenmiştir.

Resimler, iki tabakadan oluşan kireç sıva üzerinde yer almaktadırlar. Kireç sıvanın üzerine, çinko içeren bileşikler (ZnO) ile karıştırılarak uygulanan bitkisel yağ bağlayıcı tabakayı oluşturmaktadır. Bağlayıcı tabakanın üzerinde yer alan astar tabakası kurşun sülfat ile karıştırılan bitkisel yağdan oluşmaktadır. Astar tabakasının üzerinde ise pigmentler bulunmaktadır.

Resimlerin bozulmasında vandalizm önemli bir etkendir. Bunun yanı sıra resimlerde ve sıva tabakalarında ıslanma ve kuruma ile oluşan kabarmalar ve ayrılmalar tespit edilmiştir. Yapıda gerçekleştirilecek strüktürel sağlamlaştırmadan sonra duvar resimlerinin korunması çalışmalarının başlatılması uygun görülmektedir.

Anahtar kelimeler: Taxiarhis Kilisesi, Duvar resmi, Beziryağı, Yağlı boya, Cunda

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1. Subject and Aim

Wall paintings have been the cultural expression of human creativity throughout history, they form a very important part of world's cultural heritage, and thus their conservation is very important.

Interventions carried out on historical buildings must intend to uncover their historical, aesthetic, social and cultural values. In Venice Charter wall paintings and decoration were emphasized as the integral parts of the monuments that must be safeguarded (ICOMOS 1999). Principles specialized on the conservation of wall paintings were manifested by ICOMOS (International Council on Monuments and Sites) in 2003 WEB_1 (2005). These principles can be summarized as follows.

Wall paintings have been the integral pieces of historical sites and buildings from cave paintings to present. The essential principle in their conservation is to protect them in situ. To separate the color and figurative decoration will damage the aesthetic unity of the historical building.

The aim of conservation must be to minimize deterioration and to extend the life period of wall paintings and to raise the apprehensibility of the form and the content of wall painting. Interventions must be held at minimum level and their authenticity must be reserved. Layers belonging to different periods must be preserved in situ if possible. Natural aging is a part of authenticity of paintings so they must be respected. All kinds of interventions applied to paintings must be reversible. Transfer of wall paintings is a very dangerous, coercive and irreversible intervention so it must be avoided.

Problems that affect the wall paintings depend on the deficient conditions of the building in which they exist. Wall paintings are exposed to all problems affecting the building. For this reason during the conservation of wall paintings, architectural structure must be regarded as a whole and structural condition, dampness, illumination and environmental control, etc. must be taken into consideration. Inappropriate usage of buildings, maintenance deficiency, frequent repairs and alterations are the main reasons for deterioration of wall paintings. Beside these, unconscious restorations, usage of incompatible materials in restoration and expert deficiency are the important problems affecting wall paintings.

Documentation of wall paintings and required research must be done before all sorts of intervention. Restoration work must be applied by a team of art historians, archaeologists, architects, engineers and material experts specialized on conservation. Present condition, technical and formal characteristics of paintings, all steps of restoration and results must be recorded.

Continuous monitoring of wall paintings and environment is quite important. Permanence of conservation must be provided. Reaction of wall paintings to present conditions after restoration must be observed continuously. Preventive measures and periodical care are indispensable for full conservation.

In Turkey restorations related to wall paintings are generally done without taking authenticity into consideration and carrying out required research about the original technique and deterioration problems. Restorations composed of repainting with new material and integration of lost parts are irreversibly damaging our cultural heritage.

Researches carried on the characterization of wall paintings are limited with the restoration project of the wall paintings of the cut rock Churches of Cappadocia (Schwartzbaum 1986). Therefore this study gains special importance in points of the preservation of the wall paintings in Turkey.

There are many churches in Anatolia decorated with wall paintings. Most of them have serious structural problems due to the effects of earthquake, neglect and inappropriate use. Taxiarhis Church is one of the examples of these buildings. The Church was mentioned in the heritage at risk 2004-2005 report which was published by ICOMOS due to the structural condition of the building and its wall paintings WEB_2 (2005).

In this context, the study aims to determine the original technique and conservation problems of the wall paintings of Taxiarhis Church in Cunda. Before intervening wall paintings, the original technique, properties of materials used in and sources of deteriorations must be determined. This information will guide the choose of the appropriate intervention methods in the conservation works of the wall paintings.

1.2. Limits of the Study

In the scope of this thesis wall paintings of the Taxiarhis Church in Cunda Island were analyzed. The building was constructed in 1873 (Psarros 2004), has lost its function by the exchange of Rum and Turkish populations at 1923 (Arı 1995, İpek 2003) and reached to the present day without any intervention. Taxiarhis Church is an important historical building since it has been preserved with most of its authentic values and wall paintings. Paintings of the church are in danger of demolishing due to the structural condition of the building. Thus documentation of the wall paintings and, determination of their application technique is quite important.

In Taxiarhis Church wall paintings belong to two different periods. Wall paintings from each period were analyzed by the scope of this thesis. Two wall paintings from the apse, and one painting from the north arm of the cross was studied as examples of the first period as they are the most deteriorated ones. Wall painting in the niche on the north of the main apse was studied as the example of the second period, with the same reason.

1.3. Method of the Study

Documentation of wall paintings by photographs, collection of samples from the wall paintings and experimental studies carried on samples constitute the method of the study. Documentation of wall paintings was carried out by photographs, and drawings were prepared by the help of *Photoshop* and *AutoCAD* software programs over these photographs. In experimental studies, layers forming the wall paintings were analyzed in detail, and it is tried to determine the technique used in the application of paintings and properties of materials used in. Physical properties and raw material compositions of plasters, mineralogical and chemical compositions and the microstructural properties of the plasters and painting layers were determined by laboratory studies. Results of the experimental studies were discussed and evaluated.

The first chapter of the study includes the subject and the aim, limits of the study and the method. The second chapter includes general information about the techniques, history of wall paintings, and oil painting technique. The third part architectural characteristics of the Taxiarhis church were explained. In the fourth part, method of the study composed of sampling and experimental study is presented. The fifth chapter includes the results of the experimental study. The sixth part is the conclusions of the study.

CHAPTER 2

GENERAL HISTORICAL AND TECHNICAL INFORMATION ON WALL PAINTINGS

Wall paintings can be classified as *fresco* or *secco* according to their application process. A painting executed on wet renderings and in which pigments were fixed by the carbonization of lime from the rendering is called *fresco*. Paintings in which pigments were executed on dry surfaces and fixed by a media are called *secco*. In *fresco* painting generally pigments were mixed with water. *Secco* paintings can vary according to binding media used. Pigments can be mixed with lime putty or organic binders. If the binder is vegetable gum or animal animal glue such as egg yolk, Arabic gum, etc. it is called *tempera* (Mora et al. 1984), if the binder is vegetable oil it is called *oil painting* (Rona 1997, Mora et al. 1984).

Wall paintings of the Taxiarhis Church were evaluated as oil paintings according to the results of the laboratory studies.

2.1. History of Wall Paintings

The first mural paintings were the positive and negative imprints of hands applied to the surfaces of caves. These paintings are dated to 30.000 B.C., the beginning of Upper Palaeolithic period (Mora et al. 1984). The pigments used in these paintings were natural earths containing iron oxide (Van den berg 2002). Blood was also used in these paintings.

In the Magdalenian period (16.000–10.000 B.C.) Palaeolithic rock painting reached its full development. Paintings at Altamira and Lascaux are the masterpieces of this period (Figure 2.1). The principal pigments used by Palaeolithic artists were natural oxides of iron and manganese, hematite, and limonite. A colour range from brown ochre to yellow was provided by these pigments. Charcoal and bone were used to provide black colour, and clays were used for white colour. Investigations on the paintings of Lascaux show that pigments applied in a dry state to a possibly damp support. Water seeping through the walls of the cave contains dissolved limestone. This solution crystallized on the walls and formed a thin, transparent calcium carbonate layer which holds the pigment on the wall (Mora et al. 1984).

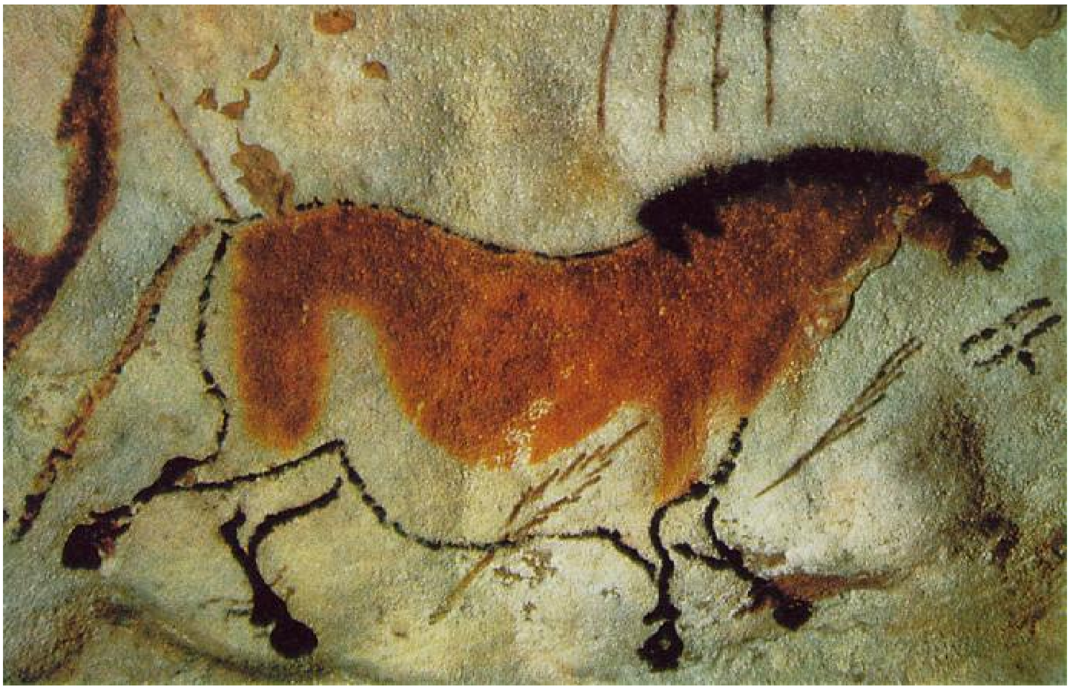


Figure 2.1. Horse figure from Lascaux cave, France, 15.000-10.000 B.C., (Source: Gombrich 1995)

Figure 2.2. Prehistoric wall paintings of Latmos, (Source: Peschlow and Bindokat 1998)

Wall paintings founded in Latmos are the one of the most important samples of Prehistoric art of Anatolia (Figure 2.2). Wall paintings which were dated to the millenniums between the Epipalaeolithic and the Chalkolithic periods (8.000 B.C) were applied directly to wall surfaces, iron oxide containing natural earths were used as pigment (Peschlow and Bindokat 1998).

Artists of Palaeolithic period generally applied paintings directly on the rock surfaces without any plaster. In the Neolithic period wall painting began to be associated with architecture (Mora et al. 1984). Man made walls and clay based plasters took the place of the irregular and rough surfaces of caves.

In Çatalhöyük wall paintings that dated back to the beginning of Neolithic period (6.000 B.C.) were applied on a clay based plaster (Figure 2.3, Figure 2.4). It can not be identified if any binding media is used in these paintings (Mora et al.1984).

Figure 2.3. Wall painting from Çatalhöyük (Source: WEB_3 (2005))

Figure 2.4. Wall painting from Çatalhöyük (Source: WEB_4 (2005))

In Egypt, wall paintings were applied on a one or two layered plaster according to the smoothness of the wall (Figure 2.5). Generally first layer of this plaster was composed of silk and the second layer was composed of gypsum that contains calcium sulphate and calcium carbonate (Mora et al.1984). Arabic gum, gelatine, egg white and beeswax are the defined binding medias used in Egypt (Boxall 1978).

Figure 2.5. Wall painting from Egypt Thebes, Asasif (1400-1390 B.C.) (Source: WEB_5 (2005))

In Mesopotamia a much greater variety of painting techniques were used. While the traditional clay plaster technology was still in use, lime plaster technology developed. A lime kiln dated back to at least 2.500 B.C. was discovered in Baghdad (Forbes 1965, Mora et al.1984).

Figure 2.6. Wall painting from Zimrli-Lim Palace, Mari (Source: Atlaslı büyük uygarlıklar ansiklopedisi

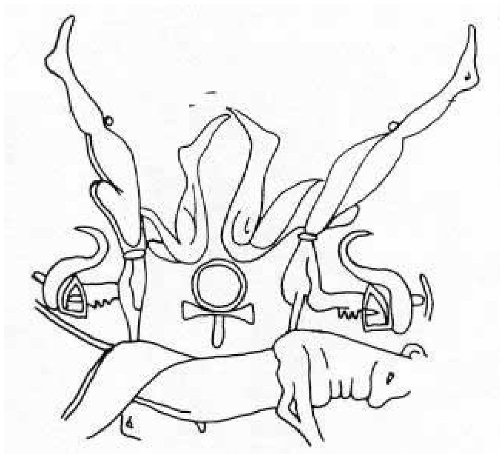


Figure 2.7. Illustration of wall painting in Alalakh, 1700 B.C. (Source: WEB_6 (2005))

Wall paintings of Zimrli-Lim Palace (Figure 2.6) at Mari are dated to the beginning of the second millennium B.C. These paintings had been executed directly on a mud wall surface or mud plaster with straw covered with thin whitewash of plaster. The technique used in these paintings was most probably tempera. (Parrot 1958, Mora et al.1984). Wall paintings of Yarim-Lim palace (Figure 2.7) at Atchana which are roughly contemporary to Zimrli-Lim Palace were applied on a two layered lime rendering. First layer (4-8 mm) was applied directly on brick wall surface or primary rendering of clay and finishing layer on this plaster was 1 mm. thick pure lime (Mora et al. 1984). The main contours of the painting were incised in the fresh plaster and the painting was executed a *fresco* with highlights a *secco* (Wooley 1955, Mora et al. 1984). According to this, paintings of Atchana can be evaluated as first known *frescoes* (Wooley 1955, Mora et al. 1984).

Generally it can be said that renderings in Mesopotamia and Egypt become coarser over time. Traditional procedure of Neolithic period painting was still used in spite of Greek and Roman effects (Mora et al. 1984).

Wall paintings of Cretan and Mycenaean civilizations show properties between Egypt and Mesopotamia and Greece (Mora et al.1984). In Mesopotamia and Crete fresco technique developed in various ways at 2.000 B.C.. Traditional tempera technique was still in use and these two techniques were used together (Mora et al. 1984). Wall paintings of Knossos (Figure 2.8) which is one of the most important site of the era were executed on a support composed of mud and rubble. This support was covered with a thick, two layered (1.2 cm. and 0.6 cm. thickness) calcium carbonate plaster with impurities (Karo 1912, Mora et al. 1984).

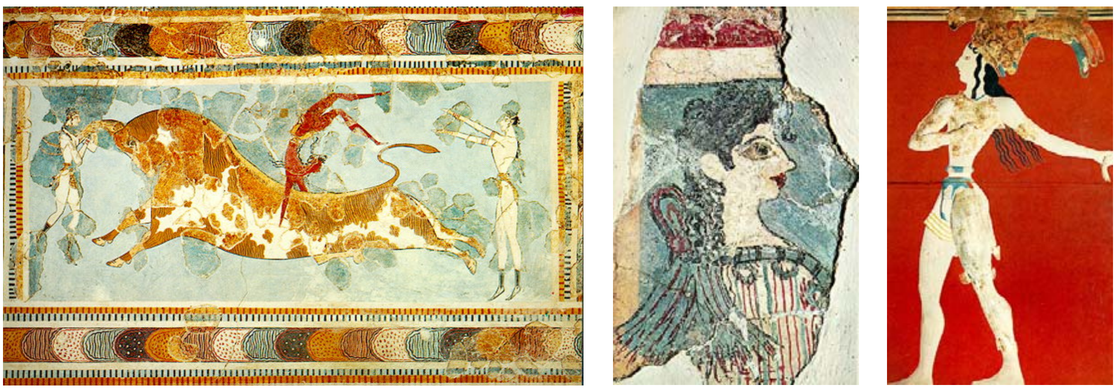


Figure 2.8. Wall paintings of Knossos (Source: WEB_7 (2005))

Four different techniques were determined in a fragment from Knossos. Lime fresco, lime painting (a secco), lime caseinate (tempera) and a technique in which pigments applied on a fresh rendering of lime and gypsum (similar to Egypt) (Mora et al. 1984). Samples taken from Tiryns show a similar structure. The first plaster layer which is thicker was composed of lime and limestone powder, while the second layer was composed of only lime (Mora et al. 1984).

Fresco technique has been known since Mycenaean and Cretan civilizations and it was developed by archaic Greek civilization (Mora et al. 1984). In Greece, secco and fresco techniques were used together also. Wall paintings applied on terracotta supports were able to survive from the archaic period of Greece. In these paintings generally colors are matte and contrarily to small terracotta objects, color was not fixed by firing. Painted panel from Clazomenae and Apollo temple at Thermos dated to 7th century B.C. show similar properties (Mora et al. 1984). Berger identified that many of the paintings of this period were executed on lime plaster as secco and preserved by using punic wax. (Berger 1904, Mora et al. 1984) Wall paintings from the tomb at Paestum were applied on a thin lime plaster and these paintings are accepted as fresco (Mora et al. 1984).

The plasters of Greek wall paintings in the archaic period and 5th century were lime based and did not include gypsum, thus, they could be related with Mycenaean and Cretan civilizations (Eibner 1926, Mora et al. 1984).

In the Roman period fresco technique reached perfection. The most important source reached us about this period is the VII. Book of Vitrivius (Vitrivius 1960). Wall paintings in Rome, Pompei and Herculaneum represent the common and characteristic construction technique of the Roman period (Mora et al. 1984). Usage of the tempera technique in the Republic period was reduced by the rise of fresco technique but it was not abandoned. Binding materials used in secco in this period are animal glues, gums, egg, honey and milk (Winfield 1968, Mora et al. 1984).

According to a text from the beginning of the middle age, wall paintings were applied to wall surfaces as fresco, to timber surfaces by using wax and to parchment by using fish glue in this period (Mora et al. 1984). Plasters used in Byzantine period shows differences from ones used in the Roman period and Western Europe. Basically, this period's plasters were composed of lime, straw, chopped hog bristles, and contain only a small quantity of sand. Thus they are related to traditional clay renderings (Mora et al. 1984). During Byzantine period bricks were used in walls. Brick walls absorbs much moisture from the plaster, because of this the thickness of plasters were increased to provide the moisture needed for frescoes (Mora et al. 1984).

Rock churches of Cappadocia which were dated to a period between 9th and 12th centuries are very important for their mural paintings. Wall paintings in these churches were executed in three different techniques. In many churches pigments were applied directly to cut rock surfaces. Pigments were fixed while the surface of the rock was hardening. The second technique is classical fresco technique. And the third technique is the tempera technique in which the pigments were applied on a gypsum plaster (Mora et al. 1984).

In Western Europe during the Romanesque period painting technique is basically similar to Byzantine technique (Mora et al. 1984). In this period oil started to use on wall paintings. Usage of vegetable oils on mural paintings goes back to the 10th century. Oil was used as white ground for painting rock panels and for making imitation marble columns (Mora et al. 1984). In a French manuscript from 12th A.D. it was specified that tempera and oil was used in mural paintings. (Mora et al. 1984). In this manuscript it was advised to use oil in white and green colors as they are siccitative. (Mora et al. 1984)

In the 13th century important developments on preparation of siccitative oils were obtained. In France and England oil was used in mural paintings in the 13th and 14th centuries (Mora et al. 1984). In England, oil was used in the paintings of Ely Cathedral built in 1325-1358 and St. Stephen's Chapel in West Minster (Mora et al. 1984). In France, oil, glue and egg was used in the decoration of Hesdin Castle, Conflans Castle and Marais Chapel (Mora et al. 1984). Oil painting technique was developed in Northern Europe by the development of Gothic Architecture from the 14th century (Mora et al. 1984). Usage of vegetable oils became widespread after 15th century as oil makes painting more transparent and less opaque. (Van den Berg 2002)

Tempera and oil allowed the use of pigments which cannot be used in fresco paintings. These pigments are; orpiment, cinnabar, azurite, minium, verdigrigs, lac and lead white (Mora et al. 1984). Oil painting was becoming popular in sixteenth century, for it could produce same effects on walls as in panel and canvas paintings. Oil painting was preferred by Leonardo da Vinci, because it gives opportunities to continual reconsiderations and corrections interspersed with long pauses. But at the same period Michelangelo regarded fresco as the epitome of heroic painting (Mora et al. 1984).

In Baroque art oil painting technique was modified according to needs of the period. The smooth, almost polished intonaco was replaced with a rough intonaco to get the vibrating effects of tones (Mora et al. 1984).

In 19^{th} century the great majority of wall paintings were executed a secco either in tempera or in oil in Europe (Mora et al. 1984).

In the Ottoman Empire, in 18^{th} and 19^{th} centuries geometrical decorations were start to be replaced with wall paintings by the westernization. These paintings can be evaluated as the westernization of traditional miniature (Kuyulu 1996). Themes of the paintings were generally composed of natural scenes and urban panoramas.

Wall paintings became to be widespread in the beginning of 18^{th} century in Ottoman Empire. Evolution of wall paintings was continued until 19^{th} century (Renda 1985). Wall paintings formed an important part of the decoration programs of the buildings in this century. First wall paintings were executed by the same technique as in traditional chasings. Natural earth pigments mixed with water or glue were used. Oil paints were started to be used by the second half of the 19^{th} century. Paintings of this period were generally applied on dry plasters or timber (Renda 1985). Four different techniques were used in Ottoman Period. In the first technique, pigments mixed with water or glue were executed on dry plasters. In the second technique, paintings were executed as oil painting on dry plasters. In the third technique, paintings were executed on timber surfaces as oil painting. And in the fourth technique, paintings were executed on canvas or oilcloth which was stretched on wall or ceiling surfaces as oil painting (Renda 1985).

2.2. Oil Painting Technique

Oil paintings are executed on directly dry stone or renderings as secco. Drying oils have been used as binding media for pigments in wall paintings in Western art for centuries. Oils, which can form solid film layers by reacting with air, are called siccitative oils. Oils that acquire this feature were used in mural paintings. The most common vegetable oils used in mural paintings since medieval times are walnut oil, poppy seed oil and linseed oil. (Van den Berg 2002). These vegetable oils contain high percentages of unsaturated fatty acids, mainly consisting of 18 carbon atoms (Surowiec et al. 2004). Main fatty acids giving drying oil character to these oils are linolic, linolenic, oleic, palmitic and stearic acids (Table 2.1). Linolic and linolenic acids have isolated double bonds. Oleic acid is mono-saturated and palmitic and linolenic acids are saturated fatty acids (Surowiec et al. 2004). Drying oils show very similar properties and can be separated by oil acids they contain. Type and the percent of fatty acid can be determined by gas chromatography (Van den Berg, 2002, Gimeno-Adelantado 2001).

Table 2.1. Typical fatty acid compositions of linseed oil, poppyseed oil and walnut oil. (Source: Van den Berg 2002)

Oil	**Fatty Acid (% of total FA)**				
	Palmitic[a]	Stearic	Oleic	Linoleic	Linolenic
Linseed	4-10	2-8	10-24	12-19	48-60
Poppyseed	9-11	1-2	11-18	69-77	3-5
Walnut	3-8	0.5-3	9-30	57-76	2-16

Oils used in wall paintings harden by reacting with the oxygen in the air. This reaction is known as autooxidation (Figure 2.9). Oil, originally composed of unsaturated lipids reacts with oxygen and form lipidhydroperoxide as sub product. Then this sub product forms non-volatile solid products (Van den Berg 2002).

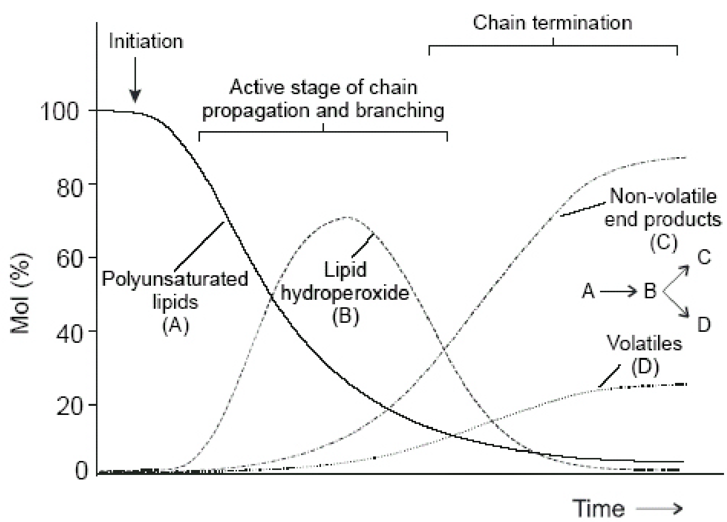


Figure 2.9. Schematic time course of autooxidation of drying oil (Source: Van den Berg 2002)

In Italian painting walnut oil was introduced in the 15th century, but linseed oil became more common from the 16th century on (Mills and White 1994, Surowiec et al. 2003). Linseed oil has been the most widely used vegetable oil in oil paintings. (Van den Berg 2002).

Linseed oil is obtained from flax. Linseed oil has to be purified before use in painting to prevent drying problems. This can be supplied by different ways. The easiest method is washing with water. In this method proteinaceous material and free fatty acids precipitate. Beside this oil becomes lighter in color. A second method is cooling oil by frost. Addition of slightly acidic liquid like vinegar or sulphuric acid also refines the oil (Van den Berg 2002). Refined linseed oil can be processed to obtain different properties. Heating and air blowing were the processes used for increasing the viscosity of oil to shorten the drying time. Blowing air while mildly heating oil between temperatures of 40- 150 ºC will raise the viscosity of it (Van den Berg 2002). If linseed oil is heated to a temperature of 150 ºC with addition of metal oxides, carbonates or acetates it is cold boiled linseed oil. The heating treatment improves drying properties, increases refractive index, reduces light scattering at oil-pigment interface and thereby increases the saturation of the pigment color (Van den Berg 2002). Stand oil is formed if oil is heated to temperatures between 270 and 310 ºC (Van den Berg 2002).

In traditional oil painting the drawing was sketched in charcoal on dry rendering, and then gone over with ink. Then a preparatory layer of glue or whole egg and fig milk diluted with water was applied with a sponge or brush (Mora et al. 1984).

Siccitative pigments such as lead compounds or zinc oxide are used for accelerating drying speed of linseed oil. These two pigments are white and generally used in priming layer in wall paintings (Lang et al. 2003, Van den Berg 2002)

In a book from 16th century, the preparation of dry intonaco “the last layer of the rendering” to paint was defined. Two or three layers of boiled oil were applied on intonaco, this procedure continues while intonaco does not absorb any more. When this layer dries it was covered with priming made of a mixture of siccitative colors. In the second method, arriccio “lower layer of intonaco” was composed of marble powder or crushed brick. This layer was covered with a layer of linseed oil and then a mixture of Greek pitch, resin (mastic) and thin varnish. The mixture is boiled, then brushed on and spread with a hot towel to obtain a uniform surface. When it is dry, priming made of a mixture of siccitative colors is applied on which it is possible to work in oil as on a panel (Vasari 1906, Mora et al. 1984).

Oil paint can be defined as a mixture of organic or inorganic pigments and drying oils. The type and the amount of pigment will influence the properties of the painting. Lead white (basic lead carbonate: $2PbCO_3.Pb(OH)_2$), Naples yellow ($Pb_3(SbO_4)_2$), azurite (basic copper carbonate: $2CuCO_3.Cu(OH)_2$), vermilion (HgS), verdigris (copper acetate: $Cu(OCOCH_3)_2.2Cu(OH)_2$), malachite ($CuCO_3.Cu(OH)_2$), umbers, red and yellow ochres (mainly $Fe_2O_3.H_20$ or Fe_2O_3), zinc oxide (ZnO), cobalt blue ($CoO.Al_2O_3$), or more complex inorganic mixtures lie smalt (cobalt potash glass) or natural zeolite ultramarine are the inorganic pigments used in oil paintings. Organic pigments used in traditional oil paintings are indigo, Indian yellow (Mg or Ca salts of euxantin acid), alizarin, madder, luteolin and quercetin (Van den Berg 2002).

CHAPTER 3

ARCHITECTURAL CHARACTERISTICS OF THE TAXIARHIS CHURCH

In the present day Ayvalık has thirteen historical church buildings. Seven of these churches are located in the city center, and 6 of them are located in the districts of Ayvalık. Three of the churches which are located out of the city center are in Cunda Island. These churches are: Cunda Panagia Church, Cunda Taxiarhis Church and Cunda Hagios Ioannes Church (İpek 2003).

Taxiarhis Church was built in 1873 by Architect Emanuel Kounas as the main Church of Cunda (Psarros 2004). The church was built in neoclassical style and it shows the basic properties of Byzantine church architecture although it was built in late period.

The building was used until 1923. The building has lost its importance and function by the exchange of Rum and Turkish populations at 1923 (Arı 1995, İpek 2003). Taxiarhis church suffered structural failures by the earthquakes occurred in 1942 and 1944 in Dikili and Ayvalık. The damages increased due to the lack of maintenance and today, the building is at the risk of demolishing. At the present day the building is closed to visit but on the courtyard of the building some religious ceremonies are carrying out.

3.1. Location

Taxiarhis Church was situated on Namık Kemal Street, No: 1657 in Cunda (Alibey) Island in Ayvalık. It is located in a high and wide courtyard which is in the middle of a historical district (Figure 3.1). The courtyard was bordered with streets on east, west and south directions and on the north side it is limited with historical houses. Entrance of the courtyard was raised by seven steps and emphasized with a fronton (Figure 3.2). There is a fountain on the west of the fronton.

3.2. Spatial Characteristics

Taxiarhis Church has a closed cross plan composed of three naves and three apses. Side apses and niches lie symmetrically on two sides of main apse. There naves are separated from each other with four circular columns. There was an Iconostasis wall separating the bema from naos which is not present today. Naos of the building lies on east-west direction. On the north and south facades of the building there are the projections of arms of the cross. These projections are semicircular inside and polygonal outside of the building. Narthex situated on the west of the building was circumscribed by staircases on two sides. The narthex is on a high platform raised by stairs and it is rectangular in shape. Entrance of the building is provided through the narthex and staircases. There is a mezzanine floor over the narthex continuing on side aisles to the arms of cross. The staircase on the south reaches the belfry of the church (Figure 3.3).

Figure 3.1. General view of the Taxiarhis Church

Figure 3.2. West Elevation of the Church

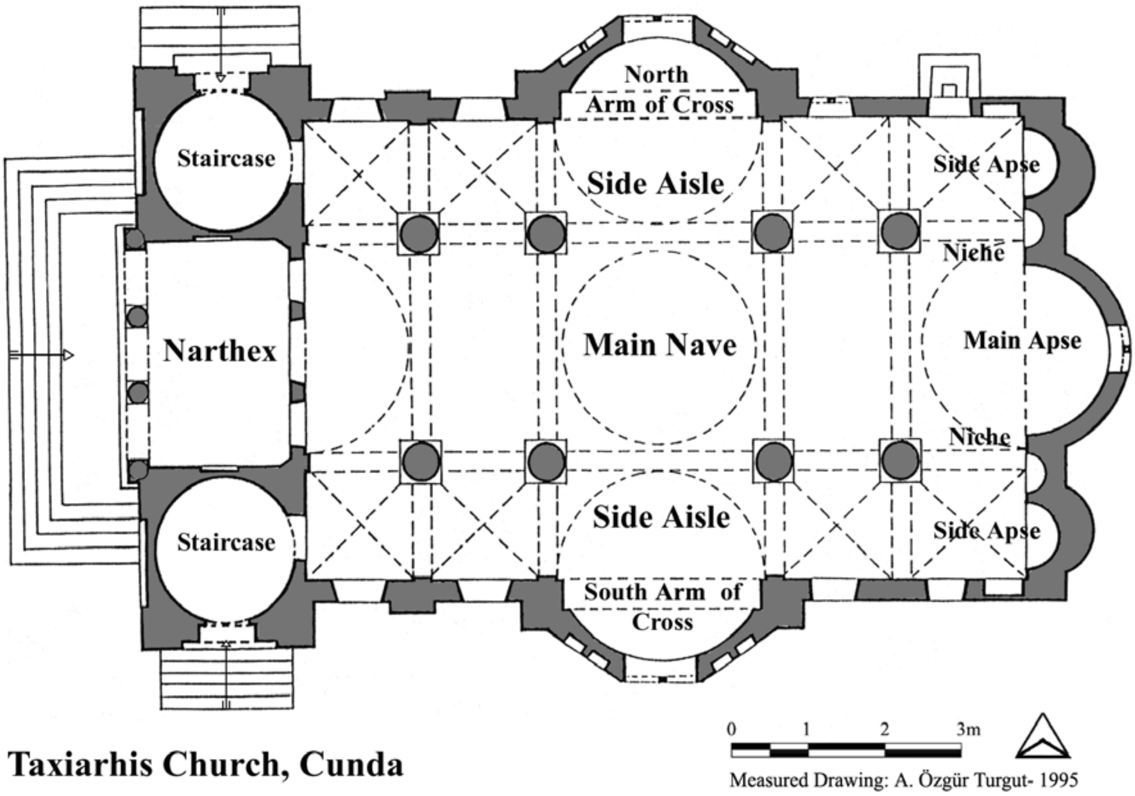


Figure 3.3. Plan of Taxiarhis Church, Source: Turgut 1996)

Figure 3.4. Interior views of the Church

Figure 3.5. Interior view of the Church

3.3. Construction Technique and Materials

Exterior walls of the building were constructed in rubble stone masonry system. On the sides of openings brick was also used. Circular columns bearing the barrel vault covering of naos, and mezzanine floor was constructed by using brick and lime mortar. All of the walls and columns are plastered inside and outside. Superstructures of the main nave and arms of the cross are barrel vault and were constructed with brick. Corners between the arms of the cross are covered with cross vault. End of the arms of the cross and apse were covered with a semi dome. On the center of the arms of cross there is a dome seated on a high drum. Transition element of this dome is a pendentive (Figure 3.4).

Important structural failures appear in Taxiarhis Church. It is thought that structural failures became after the earthquake in 1944. And because of no intervention, these problems gradually increased. Severe vertical cracks in the columns of naos, and cracks (north-south direction) in semi domes of the arms of the cross were determined (Figure 3.5). Beside these, detachments in the barrel vault covering the naos were observed (Figure 3.4). All of these structural problems and demolition of windows make the building open to rain water and caused dampness in the building.

3.4. Wall Paintings and Decoration

Taxiarhis Church is very important in the point of wall paintings it contains. Wall paintings showing the events expressed in the Holy Bible and the Old Testament increase the importance of the church. Wall paintings are located on the main apse, niches near the apse, end of the arms of the cross, over the doors binding stairwells to the naos and drum of the dome. Wall paintings on the apse are bordered with reliefs made of gypsum. Other wall paintings lie in a geometric patterned border.

In apse, paintings belong to four apostles are present. The one on the north is Petrus and the one on the south is Paulos (Figure 3.6). Other two apostles can not be identified. These paintings are surrounded by stuccos made of gypsum.

In the niche on the north of the main apse, the birth of Christ (Figure 3.7) and in the niche on the south of the main apse the baptism of Christ was painted(Figure 3.8). These two paintings show different characteristics from the other paintings on the point of their themes and deteriorations.

On the doorway near two sides of the narthex two circular wall paintings exist, over the south door, landing of Prophet Jonah from the mouth of a fish (Figure 3.9) was painted. The painting over the north door is completely lost (Figure 3.10).

On the north arm of the cross, on the east of the window the figure of Gabriel, and on the west of the window the figure of Mikael was painted (Figure 3.11). On the south arm of the cross Emperor Constantine and Empress Helena were painted (Figure 3.12).

Drum of the dome on the center of the cross was decorated with the paintings of apostles (Figure 3.13). Over the paintings on the main apse, remains of a painting on canvas exists. But it is demolished today and only a small part of it is present.

Figure 3.6. Paintings of four apostles on the wall of the main apse

Figure 3.7. Painting on the niche on the north of the main apse

Figure 3.8. Painting on the niche on the south of the main apse

Figure 3.9. Painting over the doorway on the South of the narthex

Figure 3.10. Traces of the painting over the doorway on the north of the narthex

Figure 3.11. Paintings of the angels (Mikael on the left and Gabriel on the right) on the north arm of the cross

Figure 3.12. Paintings of the Empress Helena and Emperor Constantine on the south arm of the cross

Figure 3.13. Wall paintings on the drum of the dome

All of the wall paintings in the church were damaged because of the dampness developing due to the structural problems of the building and vandalism. General problems observed on the paintings are the loss of paint due to blistering and loss of plaster layers. The paintings do not contain any deposit due to the washing effect of rain water.

Gypsum reliefs and cornices are the other decorational elements used in the church. On the pendentives of the dome and surfaces of the vault gypsum reliefs exist. Cornices between the walls and the vault, and between the pendentives and the drum are coloured and geometric patterned.

CHAPTER 4

EXPERIMENTAL METHODS

In this study, wall paintings of Taxiarhis Church were analyzed in order to determine their application technique, raw material compositions and basic physical, mineralogical, chemical and microstructural properties, and their deterioration problems.

4.1. Sampling

Samples of all layers of wall painting were collected by using lancet and chisel, and stored in polyethylene bags. During sample collection it was cared not to damage the wall paintings.

Depending on observations made in situ, it is thought that, wall paintings of Taxiarhis Church were applied in two different periods. Wall paintings of the first period were executed on fine plaster layers (intonaco), which was applied over a rough plaster layer (Arriccio) (Figure 4.1).

Wall paintings on the niches near the two sides of the main apse are belonging to the second period and these paintings were executed on a fine plaster layer which was applied over the fine plaster of the first period (Figure 4.1). Hence, samples were collected by taking into consideration these two different periods

Rough (arriccio) and fine (intonaco) plaster layers were collected from the apse and arms of cross, from sections near by the paintings, in order to determine their physical properties (Figure 4.2). Intonaco samples of the first periods paintings were collected from the main apse (Figures 4.2 and 4.3). Intonaco samples of the second periods paintings were collected from the niche on the north (Figures 4.2 and 4.4). Plaster layers lying under this layer are thought to be same with those belonging to the first period.

Painted plaster samples were collected from detached parts of the paintings, it was cared to collect samples as small as possible in size.

Each of the samples was labeled with abbreviations considering the section of the church they collected from, and the type of the sample (plaster or paint sample) (Table 4.1).

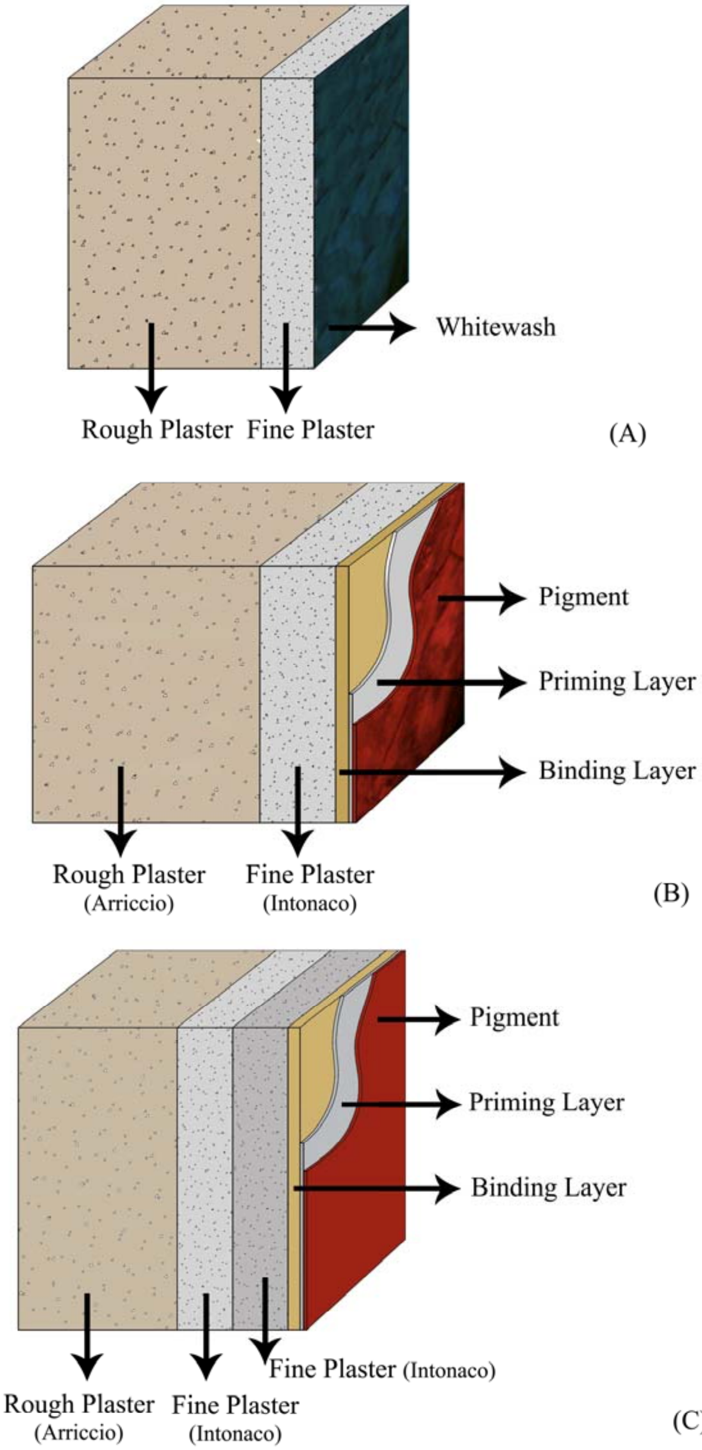


Figure 4.1. Illustrative cross-sections of the plaster layers of Taxiarhis Church A: Wall Plasters of the church, B: Plaster layers of the wall paintings of the first period, C: Plaster layers of the paintings of the second period

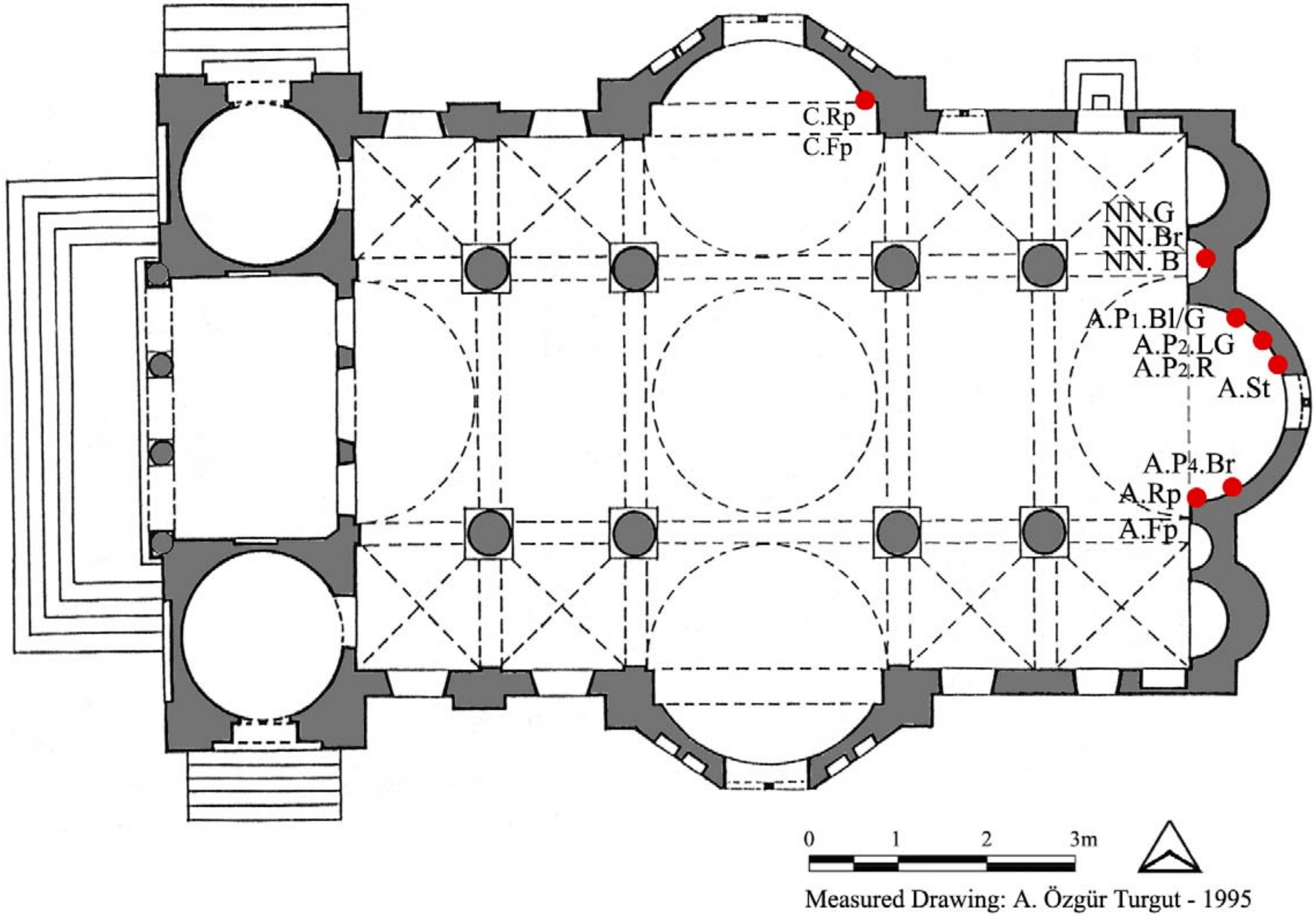


Figure 4.2. Plan of Taxiarhis Church showing the places of samples taken from

Figure 4.3. Painted plaster samples taken from the main Apse

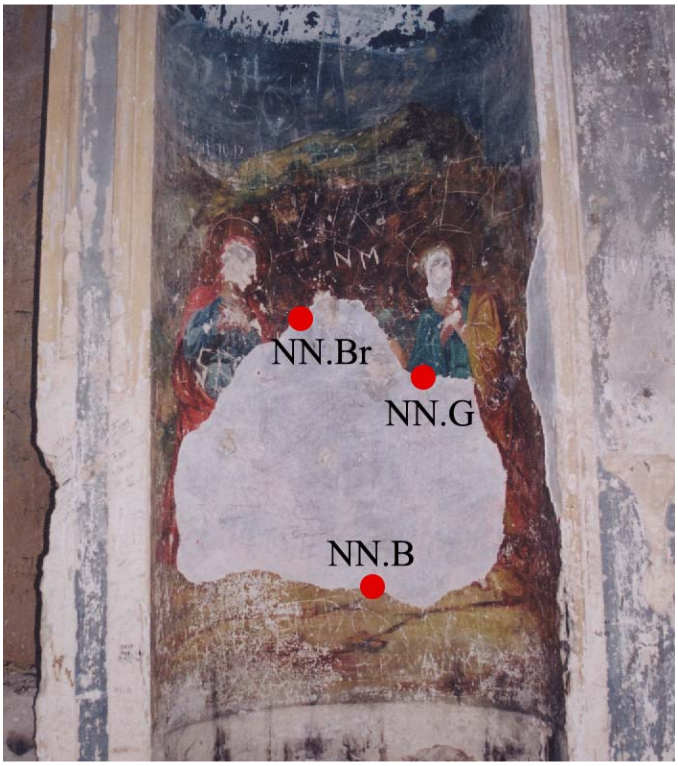
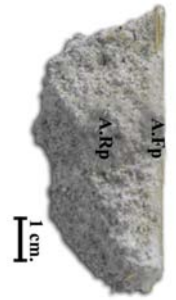
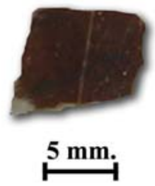
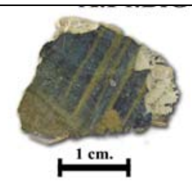
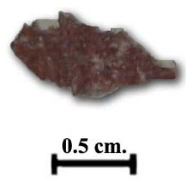
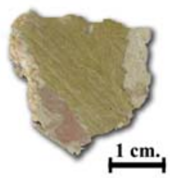


Figure 4.4. Painted plaster samples taken from the painting on the north niche

Table 4.1. Definitions of the collected samples

Plaster Samples	Sample Name	Sample Definition
	A.Rp	Rough plaster layer (arriccio) from the South corner of the main apse.
	C.Rp	Rough plaster layer (arriccio) from the North arm of the cross.
	A.Fp	Fine plaster layer (intonaco) from the South corner of the main apse
	C.Fp	Fine plaster layer (intonaco) from the North arm of the cross.
Painted plaster samples		
	NN.G	Green painted fine plaster (intonaco) from the niche on the north
	NN.Br	Brown painted fine plaster (intonaco) from the niche on the north
	NN. B	Beige painted fine plaster (intonaco) from the niche on the north
	A.P_1.Bl/G	Blue/Green painted fine plaster (intonaco) from the 1st painting in the main apse
	A.P_4.Br	Brown painted fine plaster (intonaco) from the 4th painting in the main apse
	A.P_2.LG	Light green painted fine plaster (intonaco) from the 2nd painting in the main apse
	A.P2.R	Red painted fine plaster (intonaco) from the 2nd painting in the main apse
Stucco Sample	A.St	Stucco decoration from the 2nd painting in the main apse

A: Apse **C**: Arm of the Cross **NN**: North Niche
Rp: Rough Plaster **Fp**: Fine Plaster **St**: Stucco
G: Green **Br**: Brown **B**: Beige **Bl/G**: Blue/Green **LG**: Light Green
R: Red **$P_{1,2,4}$**: Order of the painting

4.2 Experimental Study

Different series of laboratory tests was applied to each layer of painting samples in order to determine their basic characteristics.

In plaster layers, tests are carried out to determine:

- Basic Physical Properties of Plasters
    - Bulk density
    - Porosity
- Raw Material Compositions of Plasters
    - Lime-aggregate ratios of plasters
    - Particle size distribution of aggregates
- Mineralogical and Chemical Compositions and Microstructural Properties of Plasters

In binding media, tests are carried out to determine:

- Mineralogical and Chemical Compositions and Microstructural Properties of Binders by XRD, FT-IR and SEM-EDX
- Melting and Decomposition Points of Binders by DSC and TGA

In paint layer, tests are carried out to determine:

- Mineralogical and Chemical Compositions and Microstructural Properties of Pigments by XRD and SEM-EDX

4.2.1. Determination of Basic Physical Properties of Plasters

Bulk density and porosity of the plaster layers were determined by using standard RILEM test methods (RILEM 1980). Bulk density is the ratio of the mass to its bulk volume. Its unit of measurement is grams per cubic centimeters (gr/cm^3) (Equation 4.1). Porosity which is expressed in percent (%) is the ratio of the pore volume to the bulk volume of the sample (Equation 4.2).

Two samples were used for analysis. All plaster layers were carefully separated from each other and then they were dried in oven at 60°C for at least 24 hours in order to prevent their decomposition. Dry samples (M_{dry}) were weighed by a precision balance (AND HF-3000G) and then immersed in a beaker containing distilled water. Samples immersed in water put in the vacuum oven (Lab-Line 3608-6CE) operated under low pressure to entirely filling the fine pores with water. After being saturated with water, their saturated (Msat) and the hydrostatic weights (March) in distilled water were noted by using the precision balance.

Using the dry, saturated and hydrostatic weights, densities and porosities of the samples were calculated by the following formula:

$$\text{Density (gr/cm)} = M_{dry} / (M_{sat} - M_{arch}) \quad (4.1)$$

$$\text{Porosity (\%)} = [(M_{sat} - M_{dry}) / (M_{sat} - M_{arch})] \times 100 \quad (4.2)$$

In the formula:

M_{dry} : Dry Weight (g)

M_{sat} : Saturated Weight (g)

M_{arch} : Archimedes Weight (g)

$M_{sat} – M_{dry}$: Pore Volume

$M_{sat} – M_{arch}$: Bulk Volume

4.2.2. Determination of Raw Material Compositions

Lime-aggregate ratio and particle size distribution of aggregates used in plasters were determined.

4.2.2.1 Lime-aggregate Ratios of Plasters

Ratio of lime and aggregate used in plaster layers were determined by treatment of plaster samples with dilute hydrochloric (HCl) acid (Jedrzejevska 1981, Middendorf and Knöfel 1990). Two samples from each plaster were dried in oven and weighed ($M_{samp.}$) by a precision balance. Then, these samples were put in diluted hydrochloric acid (%5) until all of the carbonated lime reacts with acid and completely dissolve. Insoluble parts were filtered and washed with distilled water until all chlorine ions removes. Samples were dried in oven and weighed ($M_{agg.}$) by a precision balance. Percents of acid soluble and insoluble parts were calculated with following formula (Equation 4.3, 4.4):

$$\text{Insoluble \%} = [(M_{samp} - M_{agg}) / M_{samp}] \times 100 \quad (4.3)$$

$$\text{Acid Soluble \%} = 100 - \text{Insoluble \%} \quad (4.4)$$

In the formula:

M_{samp} : Weight of the mortar sample

M_{agg} : Weight of the aggregates

Calcareous aggregates such as lime stone or marble powder can easily react with hydrochloric acid and dissolve. So, calculation above, does not give the real ratio of aggregate and lime used in plaster.

Acid soluble ratio does not give the exact lime ratio of the plasters, since it is calculated with the dissolved carbonated lime ($CaCO_3$). The lime ratio must be calculated according to the lime ($Ca(OH)_2$) which had been used during the production process of the plasters. Lime/aggregate ratio was calculated by the formula as follows (Equation 4.5, 4.6):

$$\text{Aggregate \%} = (100 \times \text{Insoluble \%}) / [((\text{Acid Soluble \%} \times M.W._{Ca(OH)_2}) / M.W._{Ca(CO_3)}) + \text{Insoluble \%}] \quad (4.5)$$

$$\text{Lime \%} = 100 - \text{Aggregate \%} \quad (4.6)$$

Where,

$M.W._{Ca(CO_3)}$: Molecular weight of $Ca(CO_3)$ which is 100.

$M.W._{Ca(OH)_2}$: Molecular weight of $Ca(OH)_2$ which is 74.

4.2.2.2 Determination of Particle Size Distribution of Aggregates

Particle size distributions of the aggregates were determined by sieve analyses (Teutonico 1988). Aggregates were separated through a series of sieves (Retsch mark) having the sieve sizes of 53µm, 125µm, 250µm, 500µm, 1180µm by using an analytical sieve shaker (Retsch AS200).

4.2.2.3 Mineralogical and Chemical Compositions and Microstructural Properties of Plasters, Binding Media and Paints

Mineralogical composition of lime plasters and paint layers were determined by X-ray diffraction (XRD) analyses performed by Philips X-Pert Pro X-ray Diffractometer. Analyses of plasters were carried out using powdered samples with particle size less than 53µm. Analyses of paint layers were performed on the surfaces of solid samples.

Chemical compositions and microstructural properties of plasters, binding media and paints were determined by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with X-ray Energy Disperse System (EDS). SEM-EDS were performed on both crushed or polished cross-sections, and paint surfaces.

The chemical composition of the binding media was also determined by using FT-IR. The binder was finely ground on an agate mortar. 0.5 mg of this mixture was then dispersed and further ground in about 70 mg of KBr and pressed into pellets under about 10 tons/cm^2 pressure. Spectral measurements were carried out on a Magna-FT-IR 550 Nicolet spectrometer. Spectra were acquired between 400 -4000 cm^{-1}.

4.2.2.4 Determination of Melting and Decomposition temperatures and weight loss by heating of Binders by DSC and TGA

Binding media used in wall paintings was analyzed by thermogravimetric analysis (TG/DTG) by using Shimadzu TGA-21, and by DSC analysis by using Shimadzu DSC-50, in order to determine its melting and decomposition temperatures and weight loss by heating. The thermogravimetric analysis was carried out in static nitrogen atmosphere at a temperature range of 30-1000 °C with a heating rate of 10°C/min. DSC analyses were carried out in static nitrogen atmosphere at a temperature range of 20-600 °C with a flow rate of 40 ml/min.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter includes the results of experiments carried on plasters and painting layers of collected samples. Densities and porosities of plaster layers, their raw material compositions, microstructural features and mineralogical compositions; chemical compositions, microstructural features and mineralogical compositions of painting layers and weight loss of the binding media by heating were expressed and discussed.

5.1 Basic Physical Properties of Plasters

Plasters in Taxiarhis Church are generally composed of two layers. First (bottom) layer which was applied over the wall structure is rough and second layer (upper) over this layer is finely smooth. Density and porosity values of the first plaster layer are about 1.7g/cm^3 and 33 % by volume respectively. Density and porosity values of the second plaster layers are about 1.1g/cm^3 and 35 % by volume respectively (Figure 5.1)

Density values of plasters on which paintings were applied are greater than other unpainted upper plasters. Porosity values of these layers are also higher than those of others. Their high density and porosity values can be explained by the use of dense aggregates and fibrous materials in their composition.

Plasters of the paintings from the apse have the density value of 1.4 g/cm^3 and porosity value of 41 %. Plasters of the painting on the niche on the north of the main apse have the density value of 1.3g/cm^3 and porosity value of 41 % (Figure 5.1).

These results may show that materials other than lime and oakum were used in these plasters to form a dense structure. Marble powder has been well known fine aggregates used in mural painting plasters for centuries (Mora et al. 1984, Biscontin et al. 1981). Density value of stucco surrounding the wall paintings on the main apse is 1.1g/cm^3 and its porosity value is 48%.

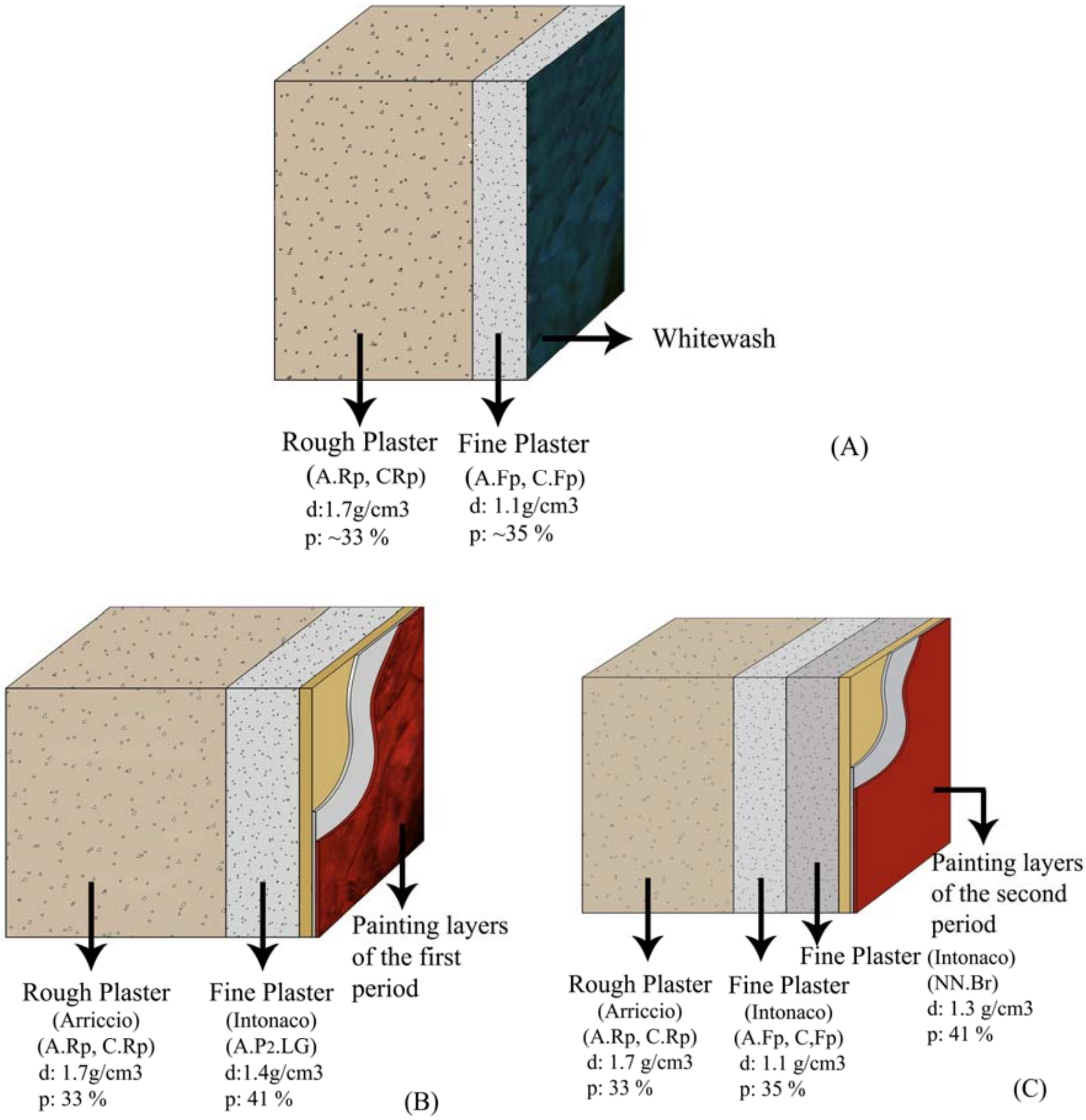


Figure 5.1. Porosity and density values of plasters. A: Wall Plasters of the church, B: Plaster layers of the wall paintings from the first period, C: Plaster layers of the paintings from the second period

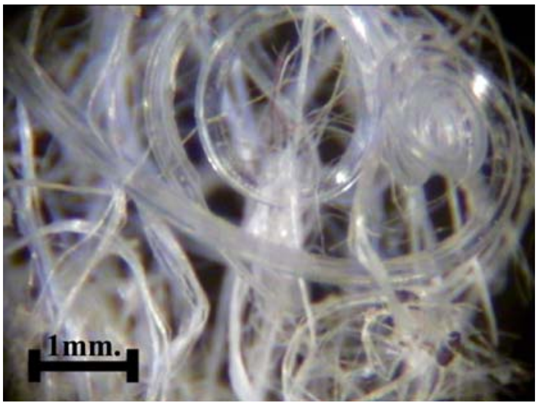
5.2. Raw Material Compositions of Plasters

Binder- aggregate ratios and particle size distributions of the aggregates were determined for plaster samples in order to express the raw material composition.

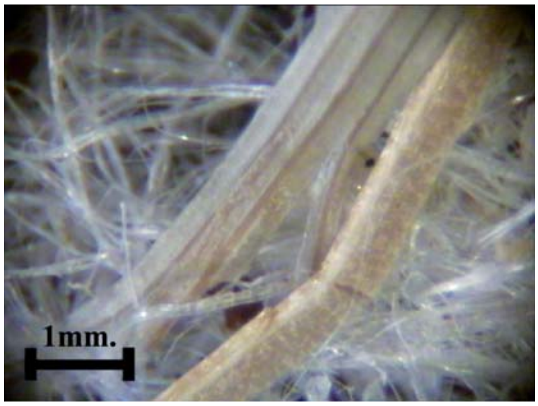
5.2.1. Lime-Aggregate Ratios of Plasters

Bottom plaster layers used in Taxiarhis Church contain little quantities of oakum and straw pieces beside lime and aggregate (Figure 5.2). Lime/Aggregate ratios of bottom plaster layers are between 1/4 and 1/3 by weight (Figure 5.3). Upper plaster layers are basically composed of lime, oakum and straw pieces. Oakum and straw could be used in order to avoid cracks formation during drying and carbonation of the lime (Mora et al. 1984).

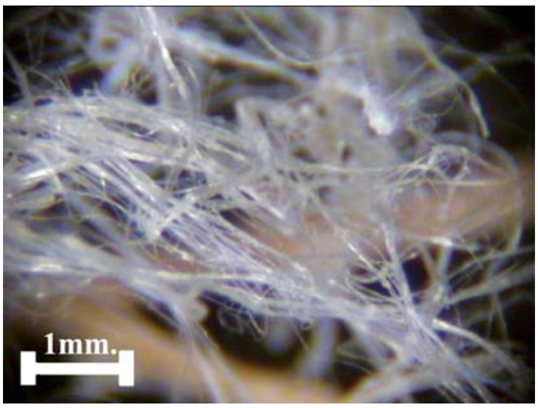
Fine aggregates were observed in plasters on which paintings were applied. These aggregates entirely dissolve in HCl and include some SiO_2 and Fe_2O_3 particles in their composition. Raw material compositions of the Stucco have not been determined due to the presence of gypsum in their composition.



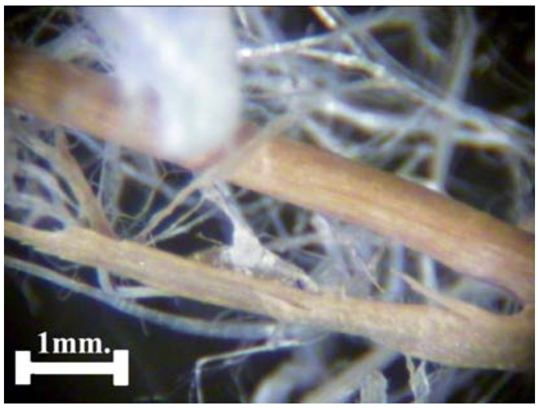
Oakum from rough plaster sample C.Rp



Straw from rough plaster sample C.Rp



Oakum from fine plaster sample C.Fp



Straw from fine plaster sample C.Fp

Figure 5.2. Stereo microscope images of oakum and straw used in plaster samples

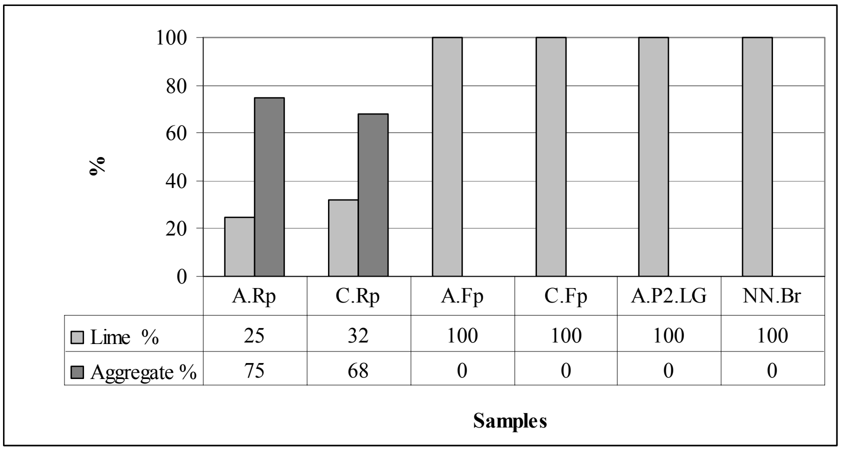


Figure 5.3. Lime/Aggregate ratios of plasters

5.2.2. Particle Size Distribution of Aggregates used in Plasters

The aggregates of rough plasters with particle size between 1180-500µm composed the largest fraction of the total aggregates and varied in the range of 61-73 %. (Figure 5.4). Aggregates bigger than 1180 µm and the smaller than 125 µm are composed the smallest fraction of the total aggregate (Figure 5.4). This shows that mostly fine aggregates between coarse (Greater than 1 mm.) and very fine (less than 0.125 mm) were used in the preparation of the rough plasters.

The aggregates used in the bottom plasters are semi-circular in shape and they are mainly white and semi-opaque. Little quantities of yellow and red aggregates are also present. (Figure 5.5).

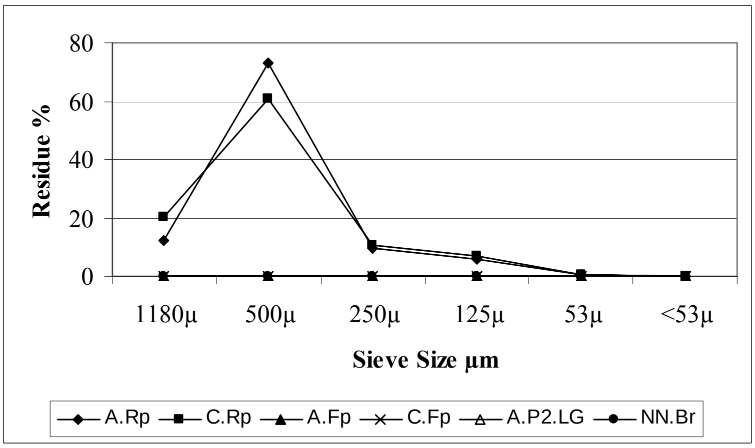
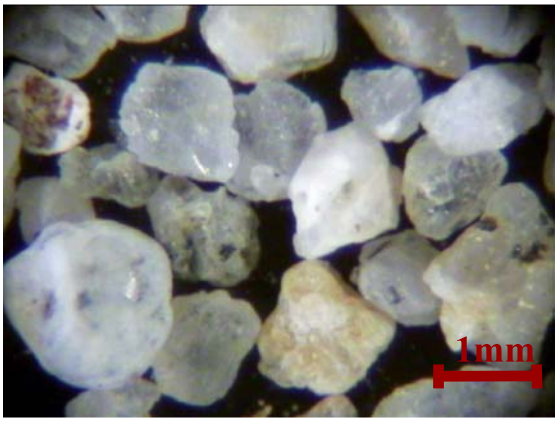
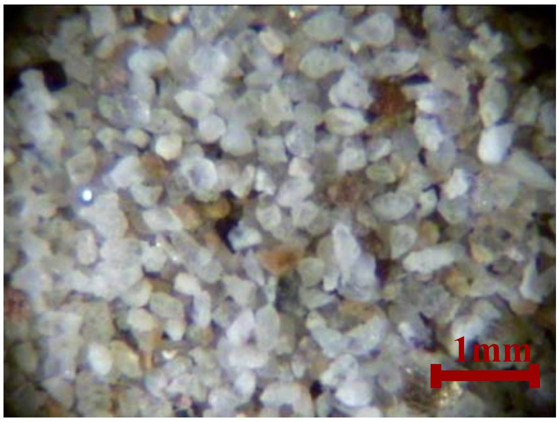


Figure 5.4. Particle size distribution of aggregates used in plasters

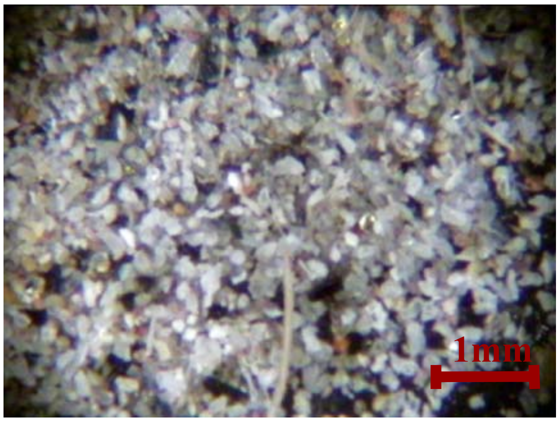


>1180µm

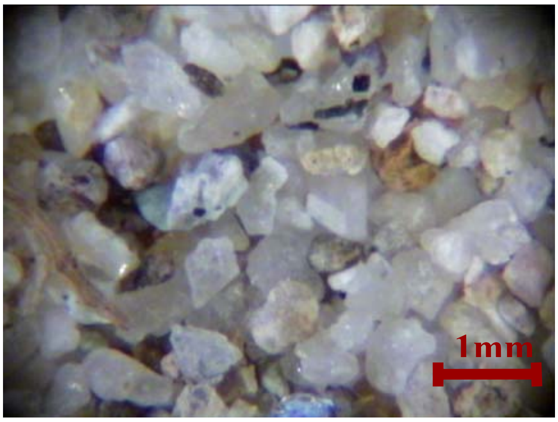


250-125µm

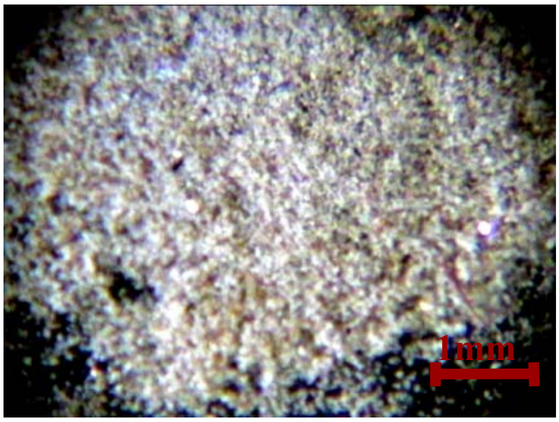
1180-500µm



125-53µm



500-250µm



< 53µm

Figure 5.5. Stereo microscope images of aggregates used in rough plaster samples (A.Rp)

5.3. Mineralogical and Chemical Compositions and Microstructural Properties of Plasters and Paintings

Mineralogical and chemical compositions and microstructural properties of samples collected from the wall paintings were investigated in order to determine characteristics of original materials, their use in the wall paintings and to determine deterioration problems. Supplied information by this work will be able to guide to choose the best methods and used materials in consolidation and cleaning works of the wall paintings.

5.3.1. Mineralogical and Chemical Compositions and Microstructural Properties of Plasters

Mineralogical composition of plaster layers were determined by X-ray diffraction (XRD). XRD patterns of the rough plasters (Figure 5.6) indicated that they were mainly consists of calcite, quartz, albite and feldspar. Calcite is originated from lime and quartz, albite and feldspar from aggregates.

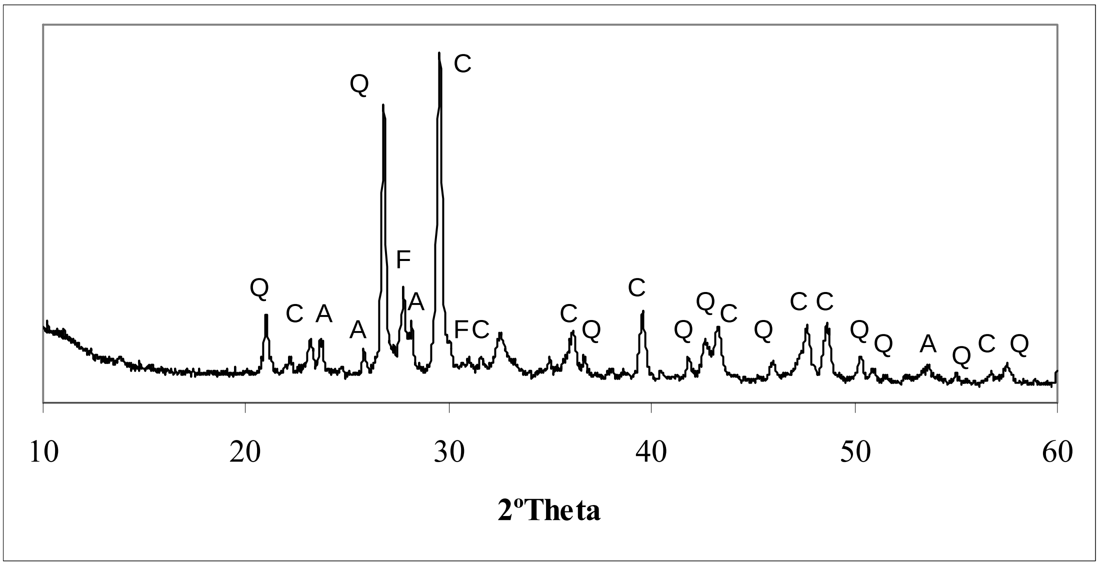
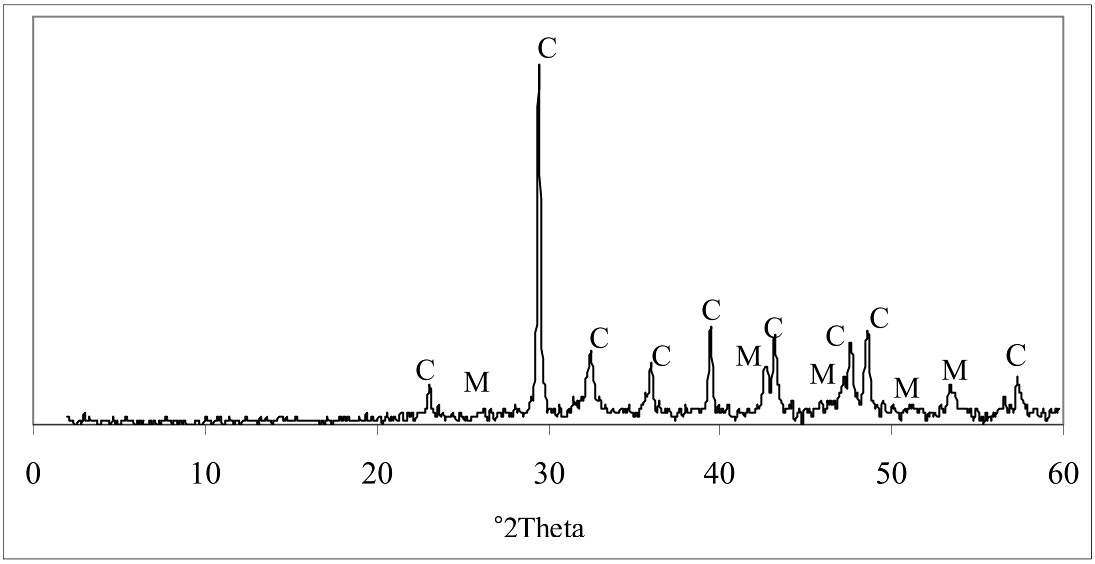
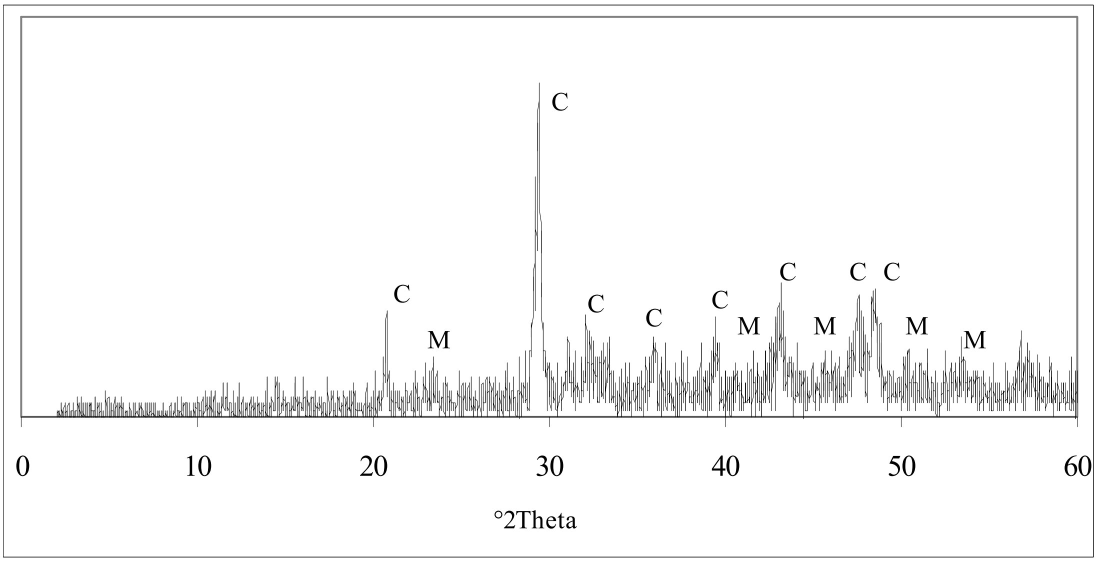


Figure 5.6. XRD pattern of rough plaster layer (C: Calcite, A: Albite, F: Feldspar, Q: Quartz)

Mineralogical compositions of the fine plasters on which paintings were applied in two different periods were similar. Their XRD patterns show that they were mainly composed of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) (Figure 5.7).



(A)

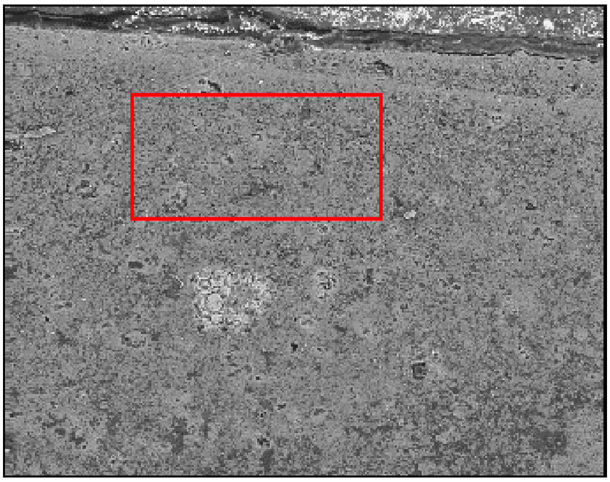


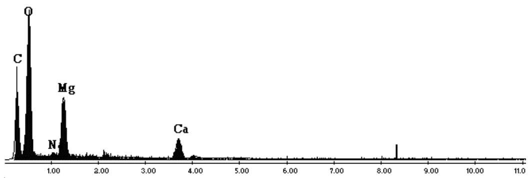
(B)

Figure 5.7. XRD patterns of fine plaster layers A: Intonaco from the first period, B: Intonaco from the second period (C: Calcite, M: $MgCO_3$)

Their elemental composition analysis carried by SEM-EDS revealed that they were consisted of high amounts of calcium (Ca) and magnesium (Mg) (Figures 5.8, 5.9).

Considering the above results, it can be claimed that fine plaster layers were prepared by using lime containing magnesium hydroxide as binder. The use of lime with magnesium hydroxide as binder in the paintings has also been found in some works (Alfano 2005, Manzano et al. 2000).



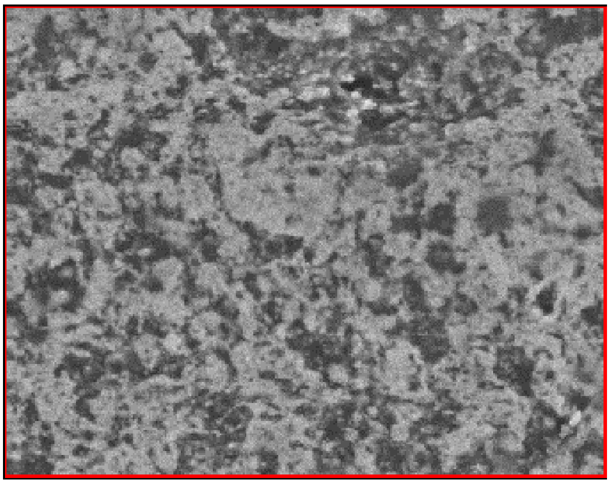


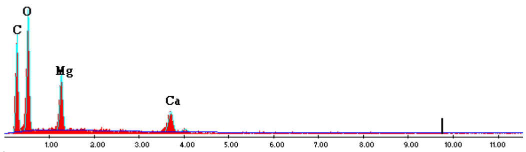
(B)

(C)	**Oxide**	**%**
	Na_2O	3.42
	MgO	61.75
	CaO	34.83
	Total	100.00

(A)

Figure 5.8. SE image (A), EDX spectrum (B) and chemical composition (C) of the intonaco from the first period, A.P_4.Br





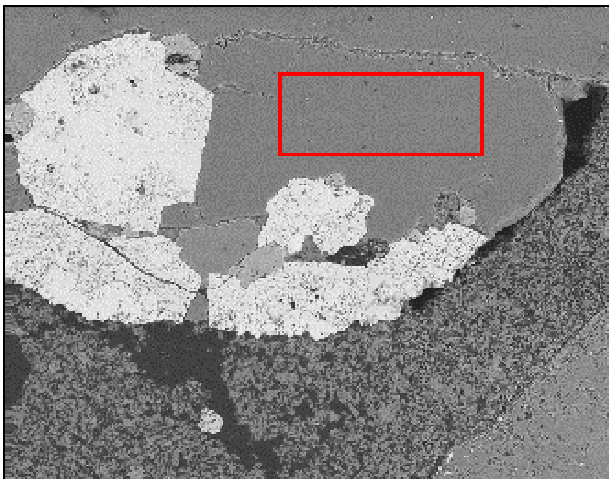
(B)

(C)	**Oxide**	**%**
	MgO	59.46
	CaO	40.54
	Total	100.00

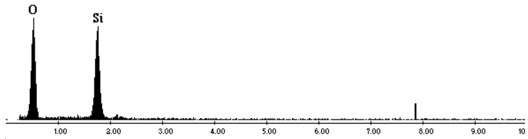
(A)

Figure 5.9. SE image (A), EDX spectrum (B) and chemical composition (C) of the intonaco from the second period, NN.G

Aggregates in the plaster found in small quantities in the matrices of fine plasters with fibrous materials contain mainly silica and iron oxides (Figures 5.10, 5.11).



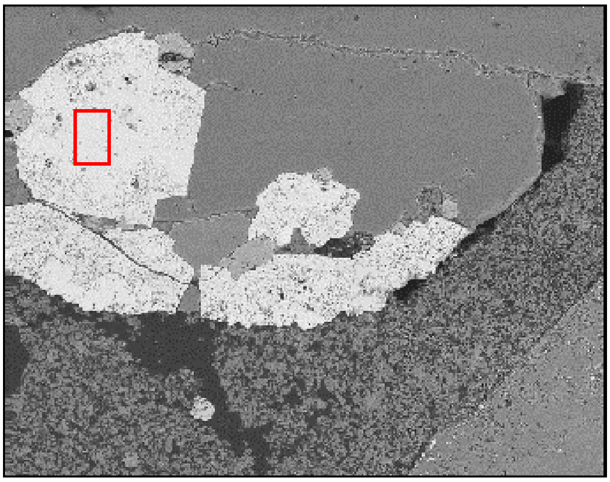
(A)



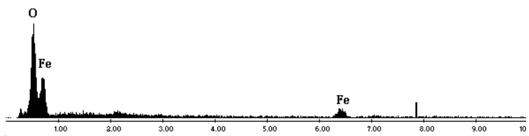
(B)

(C)	Oxide	%
	SiO_2	100.0
	Total	100.0

Figure 5.10. SE image (A), EDX spectrum (B) and chemical composition (C) of the aggregates observed in the intonaco from the first period, A.P_4.Br



(A)



(B)

(C)	Oxide	%
	Fe_2O_3	100.0
	Total	100.0

Figure 5.11. SE image (A), EDX spectrum (B) and chemical composition (C) of the aggregates observed in the intonaco from the first period, A.P_4.Br

5.3.2. Mineralogical and Chemical Compositions and Microstructural Properties of Paintings

5.3.2.1. Composition of the Binder

The composition of the binding media of the paintings were determined by SEM-EDS, FT-IR, DSC and TGA analysis in this study. These analyses are not always sufficient to determine the exact composition of the used binding media. Binding media should also be characterized using chromatographic, spectroscopic and mass spectroscopic techniques (Sutherland 2003, Gimeno-Adelantado et al. 2001, Surowiec 2004).

In this study, both paintings applied in different time are composed of binding, priming and pigment layers determined by SEM analysis (Figures 5.12, 5.13).

In DSC analyses of the binding media, phase changes was observed at the temperature of 130.5 ºC due to melting, and 335 ºC due to decomposition of the materials (Figure 5.14). This may indicate the presence of polymeric substances in the binding media. Similar results have been obtained by using standart painting layers made of vegetable oil (linseed, walnut, etc.) by DSC analysis (Prati et al. 2001).

TGA analyses of the binding media also support these results. Weight losses are observed in the range of 30-200°C, 200-600 °C and 600-900°C which are mainly due to adsorbed water, decomposition of organic matter and due to the CO_2 respectively.

The weight losses of the samples for both periods are similar to each other. The weight losses of the first and second period samples within a temperature range from 30°C to 200°C are 3.01 and 3.40 % respectively.

Their weight losses within a range from 200°C to 600°C and 600-900 °C are varied between 27.05-32.63 % and 2.11-1.52 % respectively (Figures 5.15, 5.16). The observation of high amounts of percent loss at 200-600 °C shows the presence of high amount of organic matter in the binder.

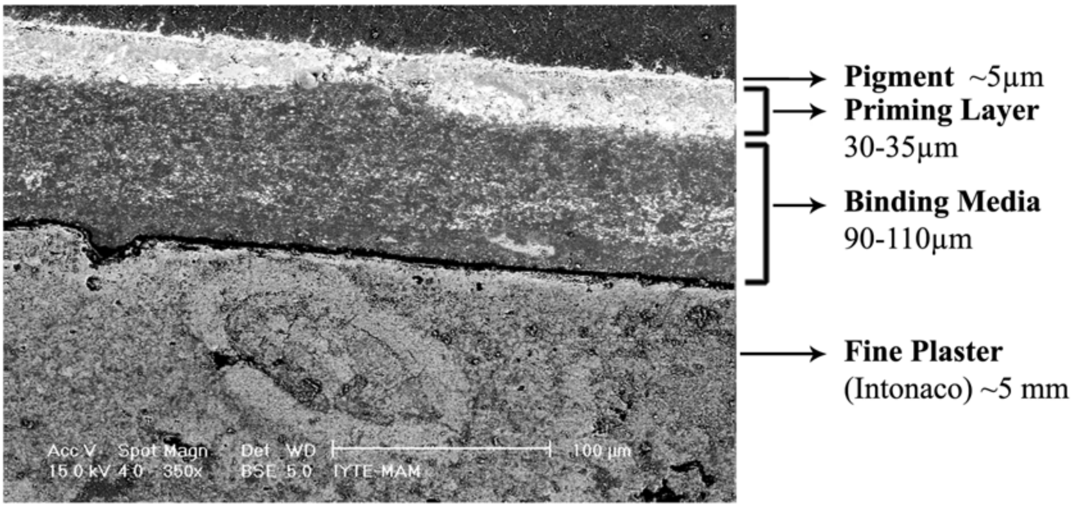


Figure 5.12. BSE image showing the layers of the first period painting (A.P_4.Br)

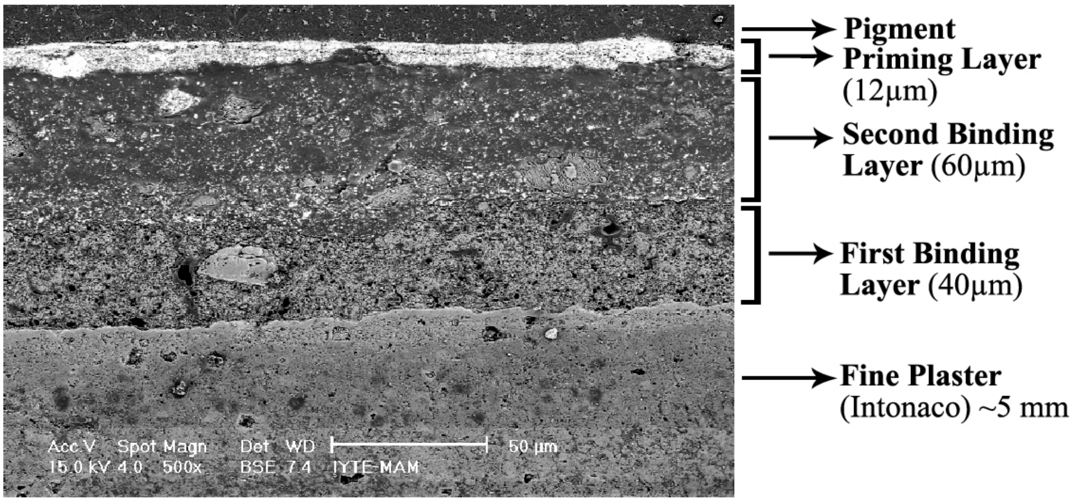


Figure 5.13. BSE image showing the layers of the second period painting (NN.G)

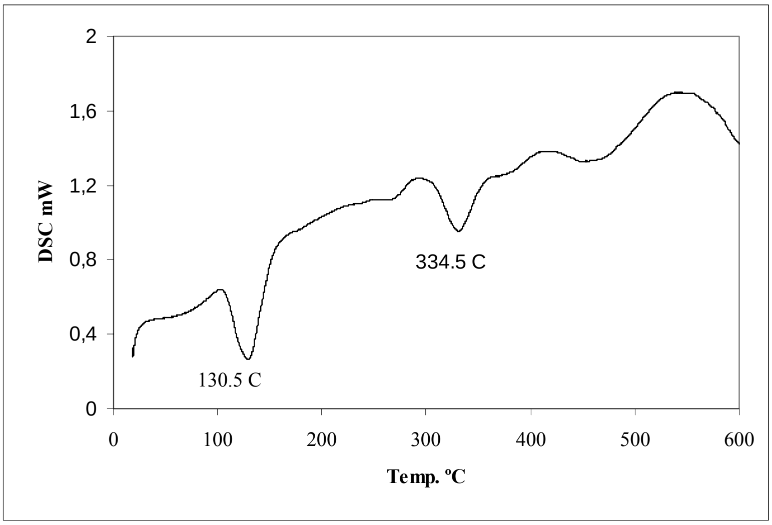


Figure 5.14. DSC graph of binding media used in the second period paintings (NN.Br)

Chemical composition of the binder was determined by FT-IR analyses. In the IR spectrum of the binding media, vibrations bands due to the hydroksil (O-H) at 3410 cm^{-1}, fatty acids (CH_2) at 2924 and 2854 cm^{-1}, esters (C=O) 1743 cm^{-1}, oxalate ($C_2O_4^{-2}$) at 1620 cm^{-1}, carbonate (CO_3^{-2}) at 1419 and 875 cm^{-1} and sulphate (SO_4^{-2}) at 1118 cm^{-1} were observed (Figures 5.17).

The FT-IR spectrum of the binding media was similar with the ones of made with linseed oil (Van der Weerd 2002). Hence, the observed fatty acids and esters bands in FT-IR spectrum may be explained due to the use of drying oils in the preparation of the binder. The oxalate was observed similarly in another recent study by Van der Weerd 2002 but its source or formation was not known. Carbonate bands may show the existence of calcium carbonate in the samples as impurity originated from fine plaster layer.

As a result of IR, DSC and TGA analyses of the binding media, it is concluded that wall paintings of Taxiarhis Church could be prepared by using drying oils such as linseed or nut oil.

The actual vegetable oil used in the wall paintings has been determined by using gas chramotography calculating the ratios of the fatty acids (palmitic[a,] stearic, oleic, linoleic, linolenic) in the oils (Van den Berg, 2002). In this study the actual type of oil could not been determined.

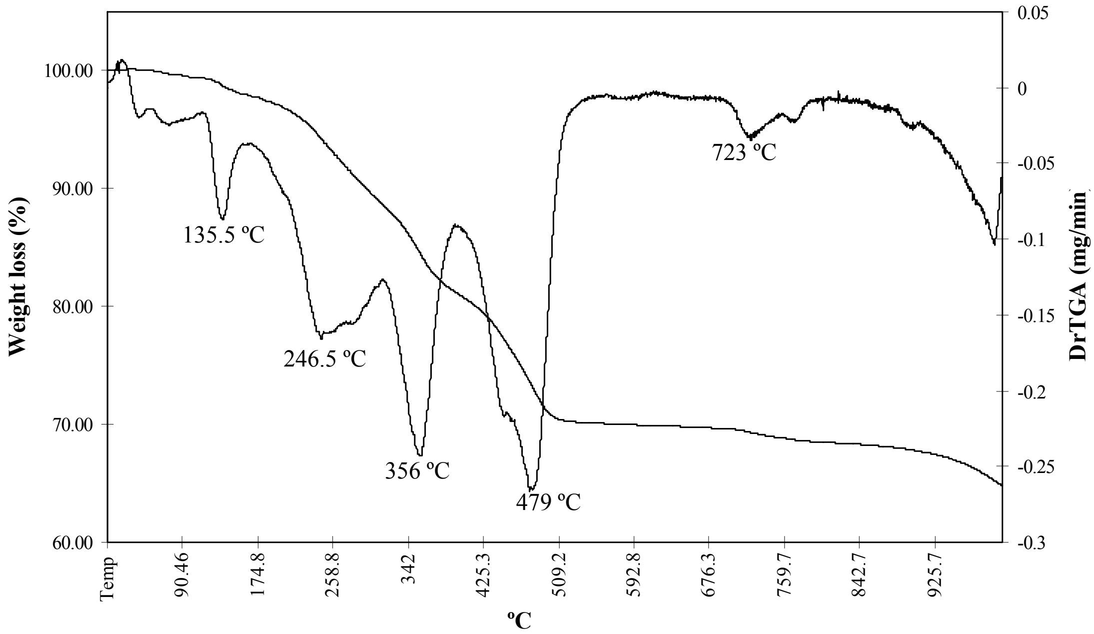


Figure 5.15. TGA graph of the binding media used in the first period

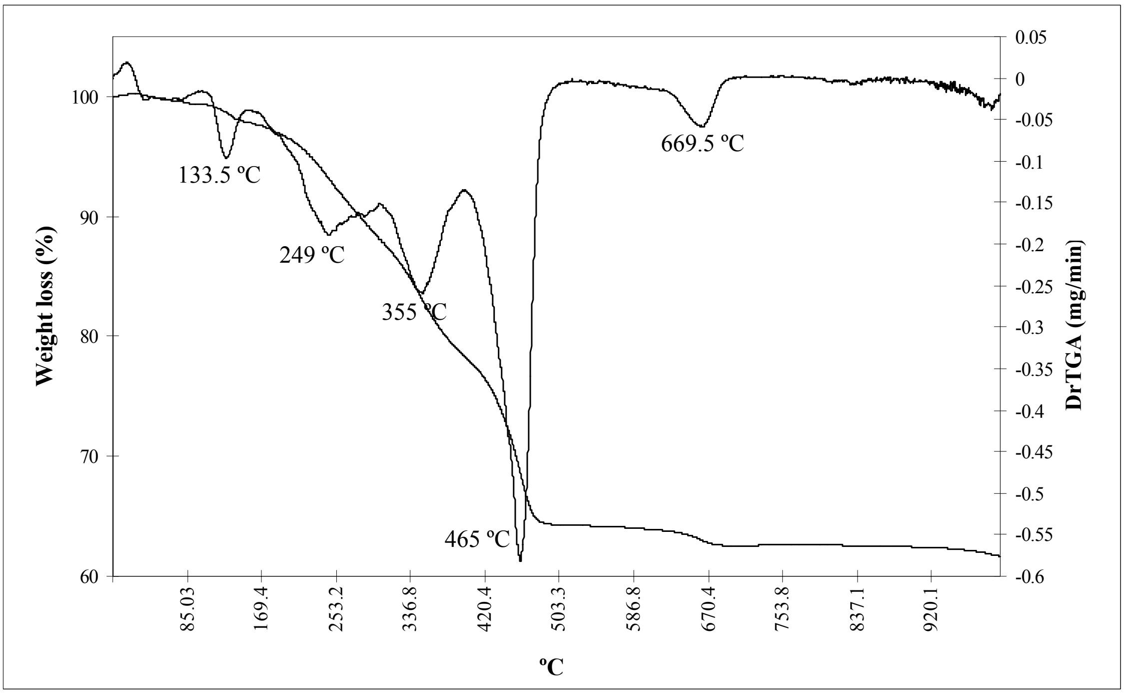


Figure 5.16. TGA graph of the binding media used in the second period

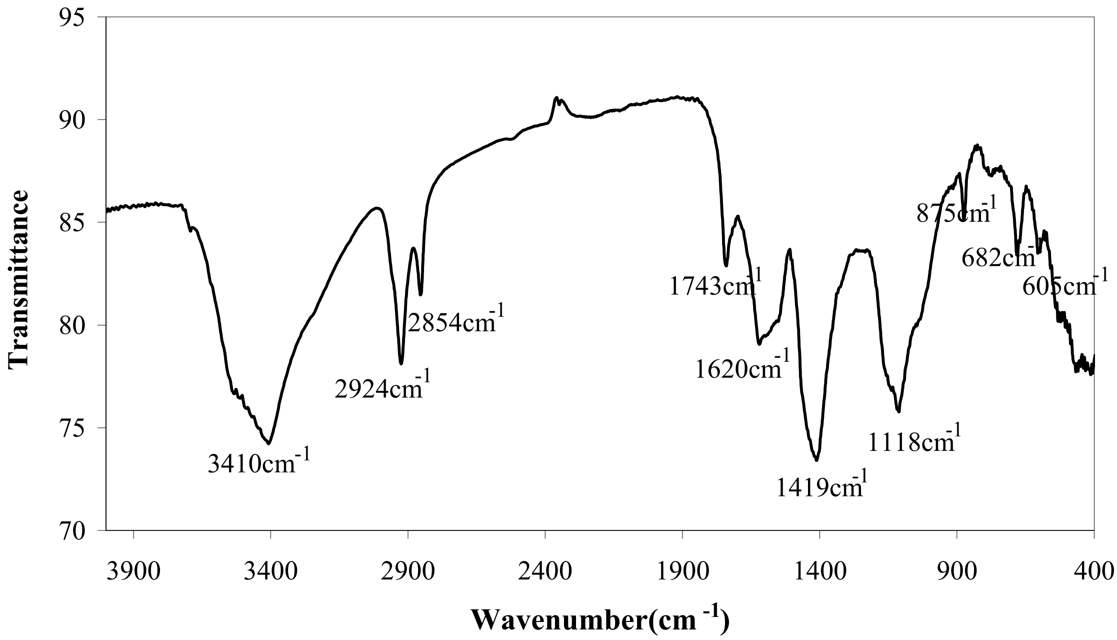


Figure 5.17. FT-IR Spectrum of the binding media, NN.Br

5.3.2.1.Mineralogical and Chemical Compositions and Microstructural Properties of Paintings from the First Period

Mineralogical, chemical and microstructural properties of the paint layers have been determined by XRD, Optic microscope and SEM- EDS analysis. Paintings are formed by three successive layers (Figure 5.18). The first layer over the fine plaster layer is the binding media. Binding media is mainly composed of C, O and Zn determined by SEM-EDS analysis (Figure5.19). Carbon and Oxygen are mainly originated by the use of vegetable oil.

Zinc compounds has been a well known additive used for bleaching and brightening binding media of the paintings (Van der Weerd, 2002; Lang et al., 2003). Zinc Oxide also accelerates polymerization process of vegetable oils (Van der Weerd, 2002). Hence, the presence of zinc in binding media may be explained by their catalytic effect for the polymerization of the vegetable oil.

The second layer is the priming layer which is composed of mainly C, O, Pb and S (Figure 5.20). Lead sulphate is a siccitative element used for bleaching the binding media (Clark 2002) and accelerating polymerization of the vegetable oil (Van Den Berg

2002). Hence, lead sulphate may be added as bleaching materials for the paint and accelerator for the polymerization of the linseed oil.

Pigments applied over the priming layer are classified according to their color and functional properties as white, colored, black, etc.

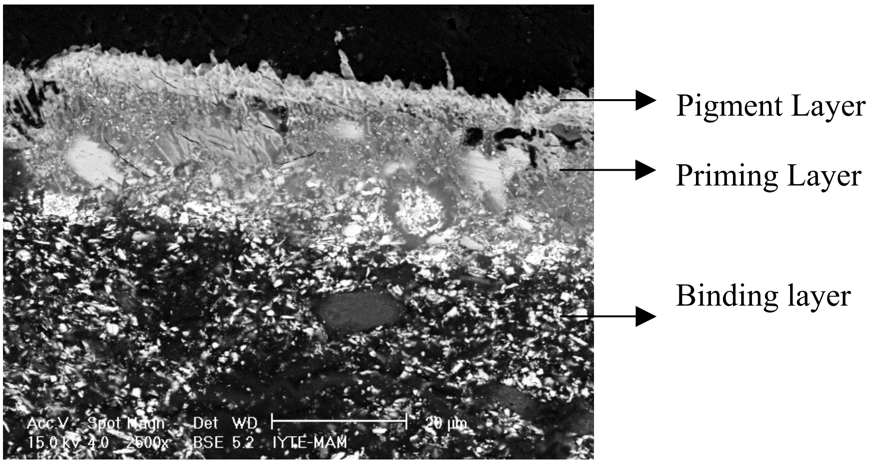
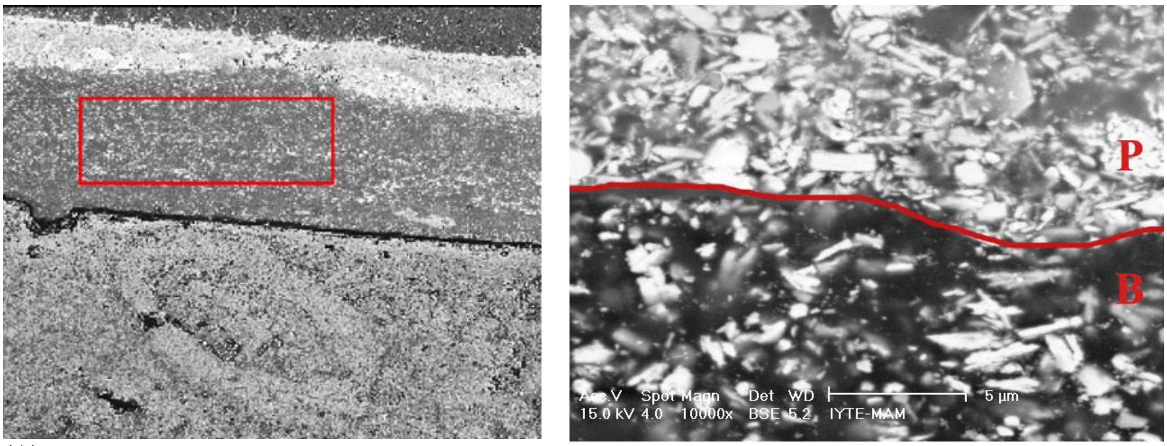
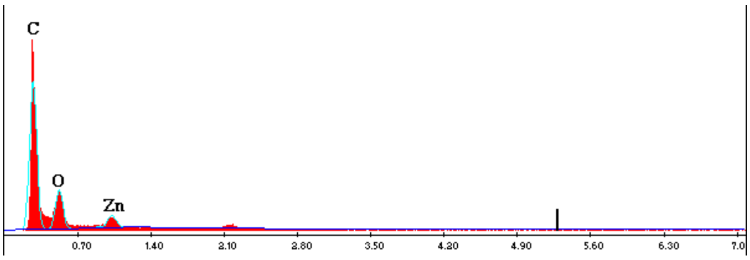


Figure 5.18. BSE images of the cross-section of painting from the first period



(A) P:Priming Layer, B: Binding Layer (B)

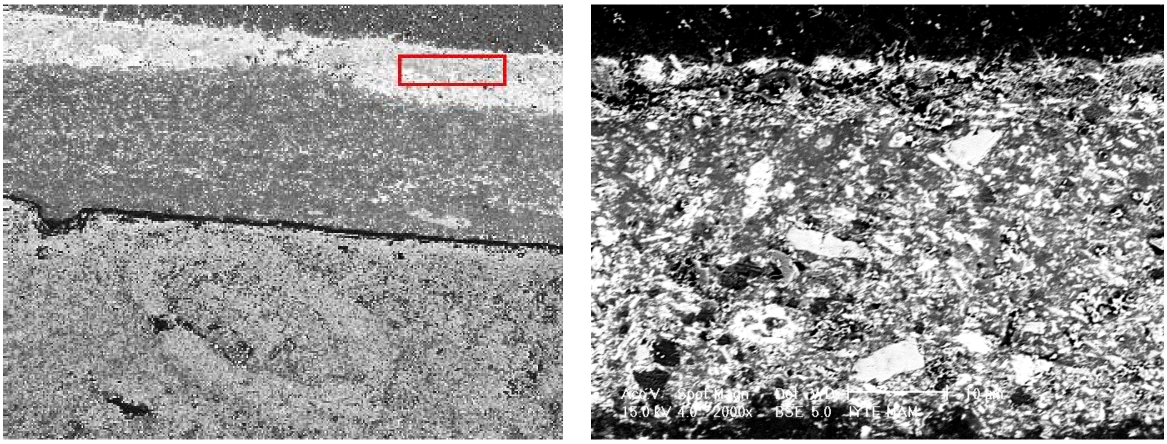


(C)

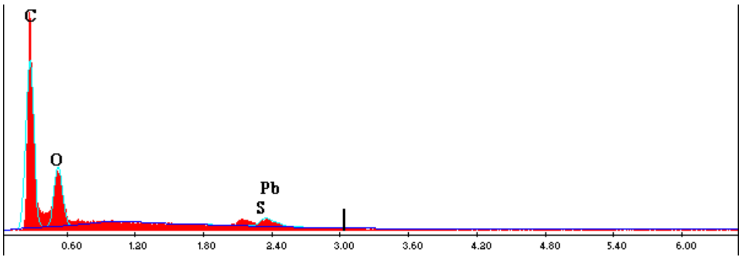
(D)

Oxide	%
C	69.22
O	25.43
Zn	5.35
Total	100.00

Figure 5.19. SE image (A), BSE image (B), EDX spectrum (C) and chemical composition (D) of the binding layer from the first period, A.P_4.Br



(A) (B)



(C)

(D)

Oxide	%
C	64.87
O	30.67
S	0.68
Pb	3.78
Total	100.00

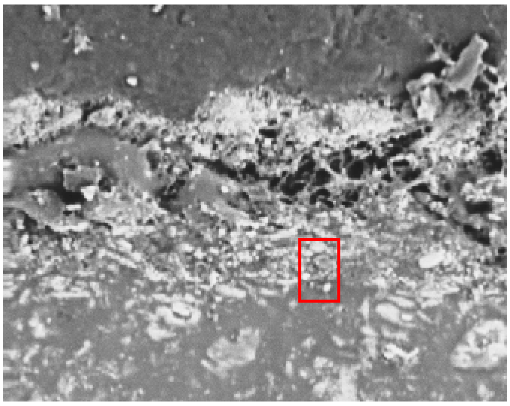
Figure 5.20. SE image (A), BSE image (B), EDX spectrum (C) and chemical composition (D) of the priming layer from the first period, A.P_4.Br

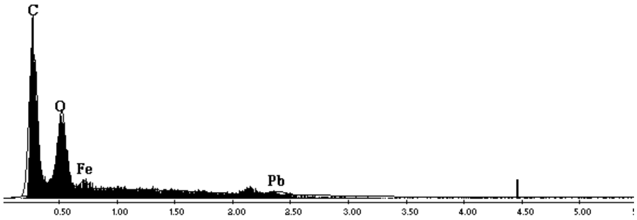
The mineralogical composition of the pigments was not determined by XRD due to their low concentration in the thin films over priming layers. Hence, SEM-EDS analysis were carried out to find the elements which was present in the painting layers.

The elemental composition analysis of the brown painting surfaces indicate that they are mainly composed of iron (Fe), lead (Pb) and aluminum (Al) (Figures 5.21, 5.22). The presence of lead may be explained due to the presence of lead sulphate in the priming layer. The less amounts of iron may show the use of iron containing pigments such as iron oxide (Clark 2002, Harley 2001). The observation of aluminum in the paint layer can be explained as impurity found in the iron compounds.

In the EDS analyses of the red colored paintings surfaces the lead content found is fairly high from the other colors (Figure 5.23). Hence, red color could be prepared by the use of lead red (minium, Pb_3O_4) (Bell et al. 1997).

In the EDS analyses of the blue painting any trace of inorganic pigment that is known to be used in blue color can not be determined. This can be explained either by the use of some blue organic substances as pigments (Clark 2002, Bell et al. 1997) or the low concentration of inorganic pigment used in painting.





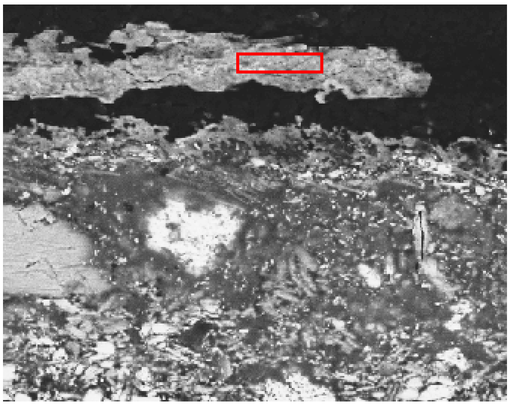
(B)

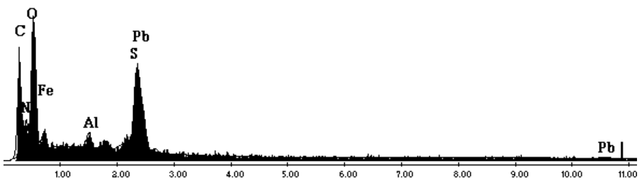
(C)

Oxide	%
C	54.62
O	30.25
Fe	13.47
Pb	1.67
Total	100.00

(A)

Figure 5.21. SE image (A), EDX spectrum (B) and chemical composition (C) of the brown painted fine plaster from the first period, A.P_4.Br





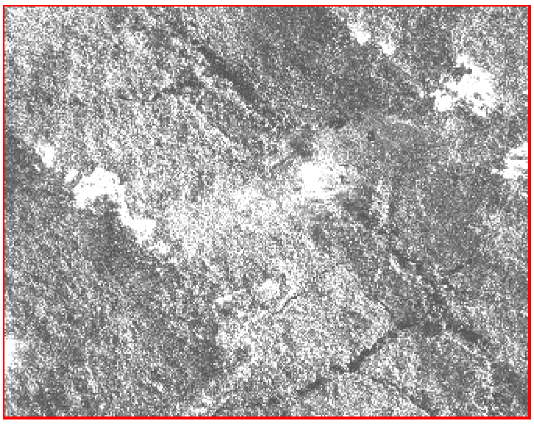
(B)

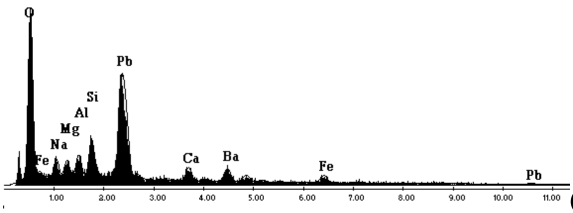
(C)

Oxide	%
CO_2	35.29
N_2O_5	15.03
Fe_2O_3	8.36
Al_2O_3	0.73
SO_3	2.23
PbO_2	38.36
Total	100.00

(A)

Figure 5.22. SE image (A), EDX spectrum (B) and chemical composition (C) of the brown painted fine plaster from the first period, A.P_4.Br





(B)

(C)

Element	%		
O	29.50	Si	3.17
Na	2.11	Ca	2.00
Mg	1.55	Ba	7.88
Al	1.83	Fe	3.47
		Pb	48.50

(A)

Figure 5.23. SE image (A), EDX spectrum (B) and chemical composition (C) of the red painted fine plaster from the first period, A.P_2.R

Thicknesses of the paint layers were measured by SEM. Binding media (vegetable oil) mixed with zinc oxide was applied as a 90-110 µm thick layer over the fine lime plaster (Figure 5.12). Priming layer, composed of vegetable oil and compounds containing lead and sulfur, was applied with a thickness of 30-35µm over the binding layer (Figure 5.12). Pigment containing layer was applied as a very thin strata (5µ) on the priming layer (Figure 5.12).

Adhesion of pigments with priming layer and priming layer with binding media are quite well (Figure 5.24). But a clear detachment between binding media and the fine plaster is observed (Figure 5.24). This detachment is the main deterioration problem of the wall paintings of the first period.

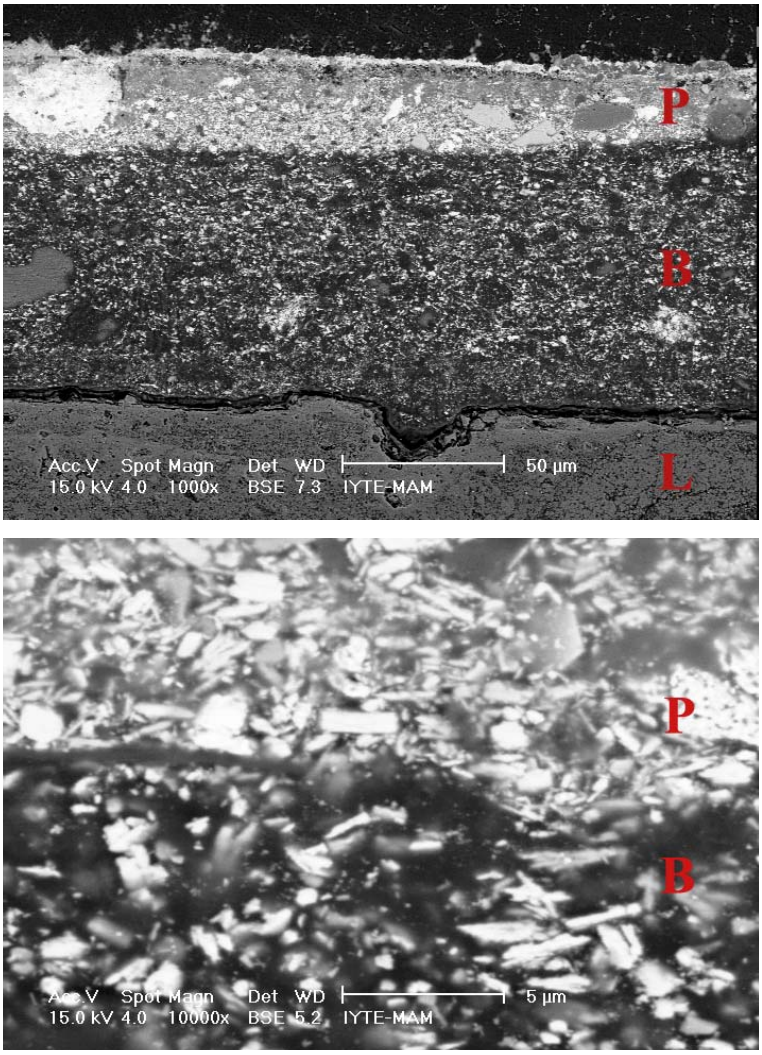
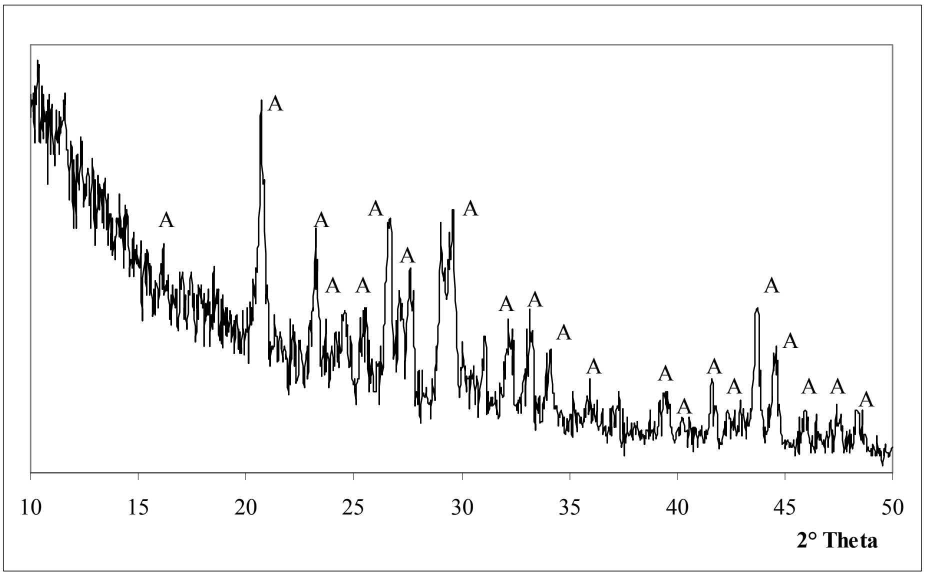


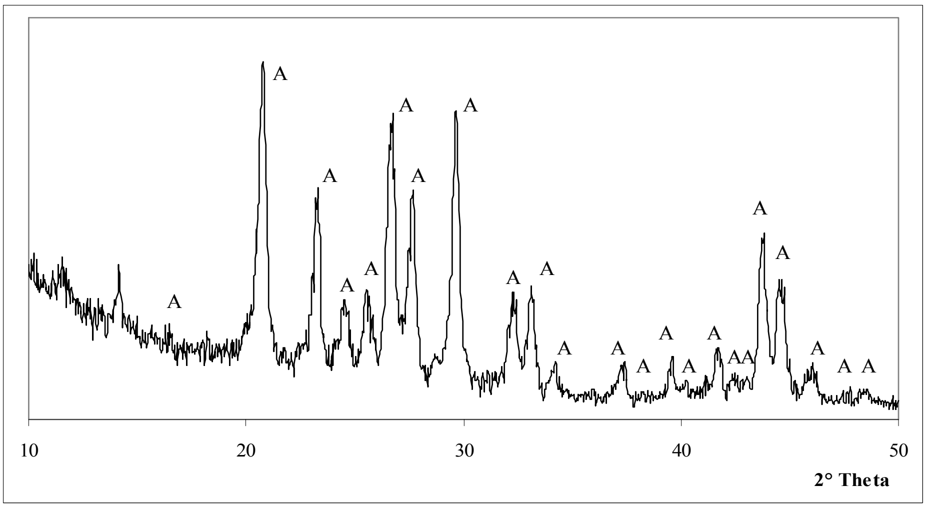
Figure 5.24. BSE image of the cross-section of the painting from the first period, A.P$_4$.Br (P: Priming layer, B: Binding Layer, L: Lime Plaster)

In the mineralogical analyses of the all paint layers by XRD, anglesite ($PbSO_4$) was mainly observed in the XRD spectrum (Figures 5.25 and 5.26). Anglesite is known to be used as bleaching substances in oil paintings (Clark 2002). Thus, anglesite may have been used in the making of priming layer of the paintings. Determination of Pb and S in the EDS analyses of the priming layer also supports such a finding.



(A: Anglesite $PbSO_4$)

Figure 5.25. XRD pattern of Blue/Green painted fine plaster from the first period, A.P_1.Bl/G



(A: Anglesite $PbSO_4$)

Figure 5.26. XRD pattern of light green painted fine plaster from the first period, A.P_2.LG

5.3.2.2. Mineralogical and Chemical Compositions and Micro-structural Properties of the Paintings from the Second Period

The paintings of the second period are characterized by XRD and SEM-EDS analysis. Second period paintings are also multi-layered systems. But, they have two successive binding layers differently than the paintings applied in the first period.

The first binding layer containing calcium and vegetable oil was applied over the fine lime plaster (Figure 5.27). The thickness and porosity of this layer determined by SEM analysis are about 35µm and 28.19 % respectively.

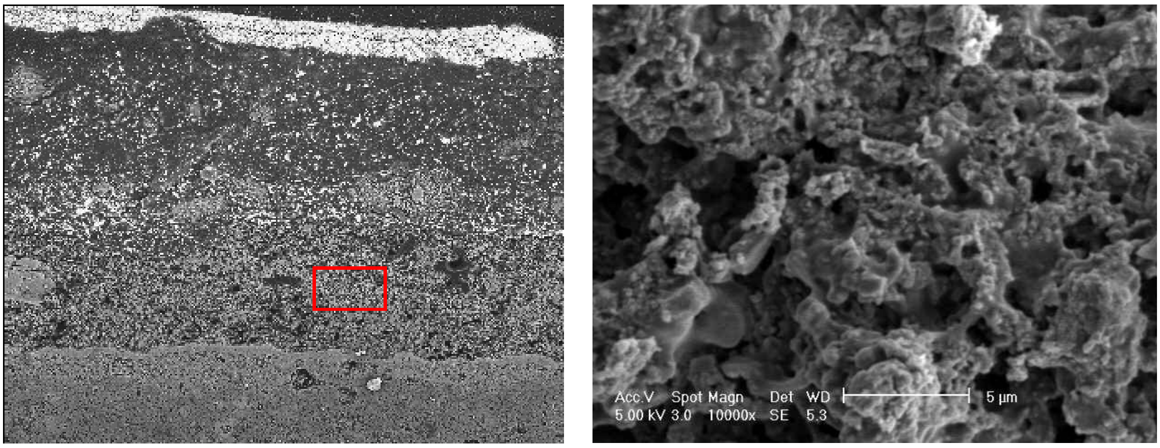
Second binding layer over the first one is composed of basically vegetable oil with zinc, sodium and lead containing compounds (Figure 5.28). The average thickness of this layer is about 60 µm. This layer is nonporous and has a jelly like appearance (Figure 5.28).

Priming layer applied over second binding layer is composed of vegetable oil with lead containing compounds (Figure 5.29). Its average thickness is about 12 µm.

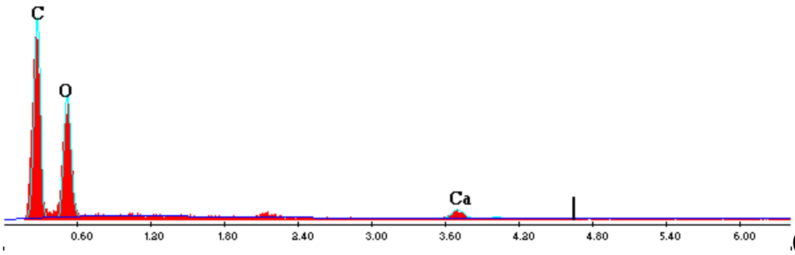
Mapping of elemental compositions of the paintings by SEM-EDS can be used to distinguish the paint layers. The marker elements used to distinguish paint layers were calcium, magnesium, lead, zinc and sodium in this study (Figure.5.31). As it is seen from mapping them in Figure 5.31, adhesion between the lime plaster, binding layer, priming layer and pigments are quite well (Figure 5.32).

Pigments applied on the paint surfaces were mixed with vegetable oil and they were well combined with the binding medium (Figure 5.30). XRD was used for the determination of the mineralogical composition of the pigments. But, mainly anglesite peaks ($PbSO_4$) were observed due to its use in priming layer (Figures 5.33, 5.34). Hence, XRD was not a tool for determining the mineralogical composition of the used pigments. Raman Spectroscopy may be a suitable tool to determine the mineralogical compositions of the pigments (Clark 2002, Edwards et al. 1997, Perardi 2003).

In this study, SEM-EDS analysis was carried out to find the elements which was present in the painting layers.



(A) (B)

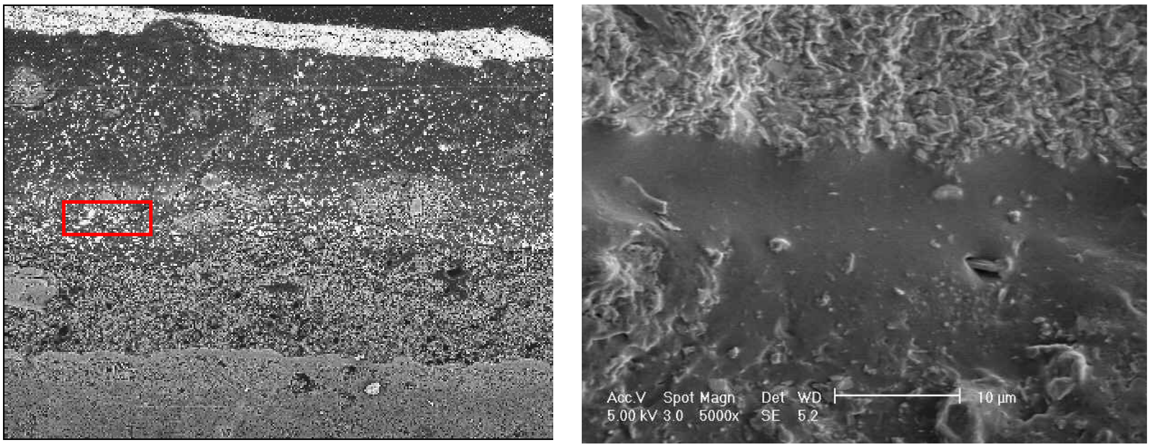


(C)

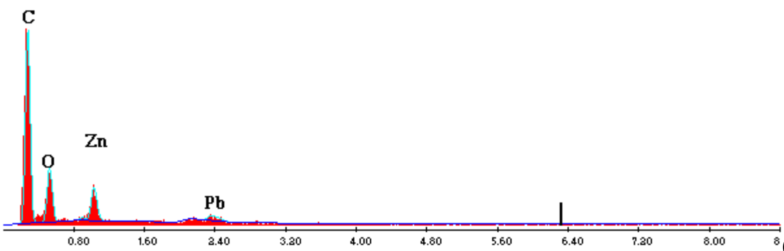
element	**%**
C	54.17
O	43.44
Ca	2.39
Total	100

(D)

Figure 5.27. SE image (A, B), EDX spectrum (C) and chemical composition (D) of the porous first binding layer



(A) (B)

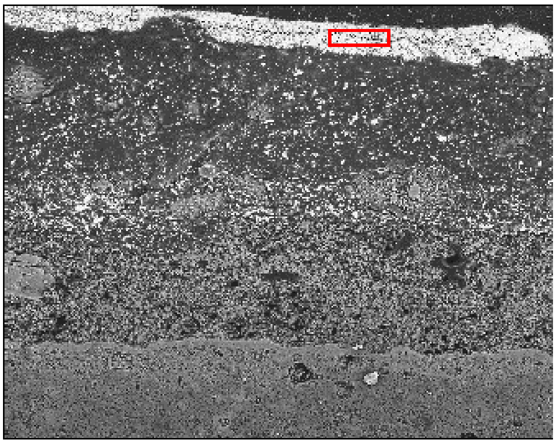


(C)

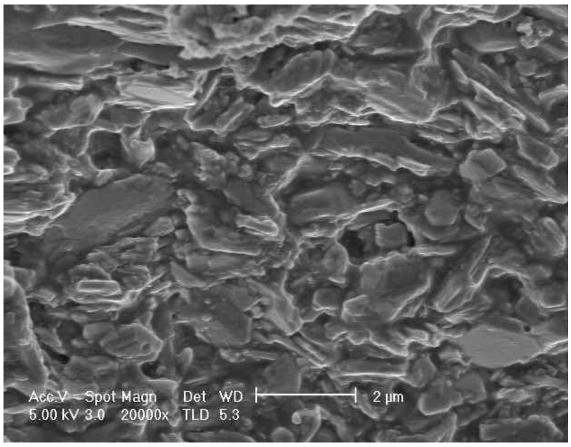
Oxide	**%**
ZnO	80.15
PbO_2	19.85
Total	100

(D)

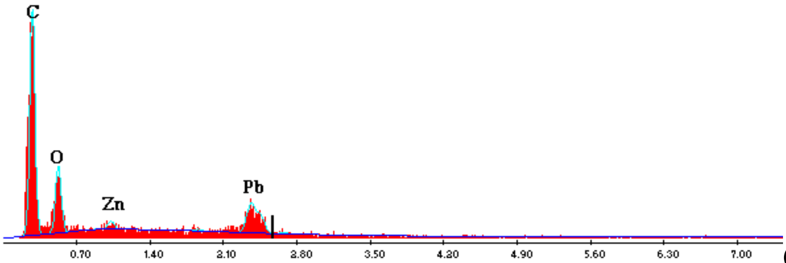
Figure 5.28. SE image (A, B), EDX spectrum (C) and chemical composition (D) of the second binding layer



(A)



(B)

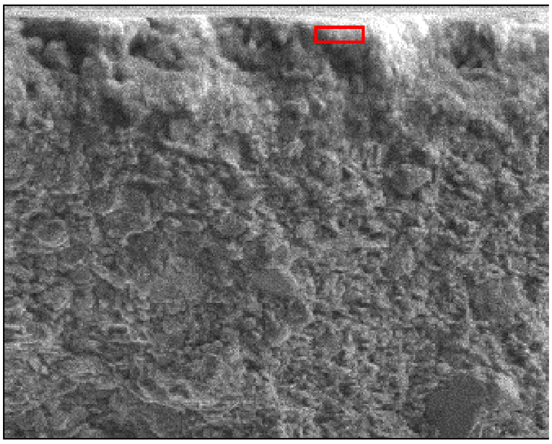


(C)

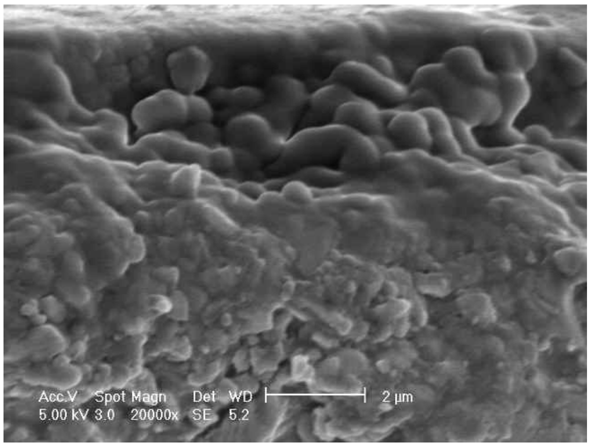
(D)

Oxide	**%**
ZnO	16.07
PbO_2	83.93
Total	100.00

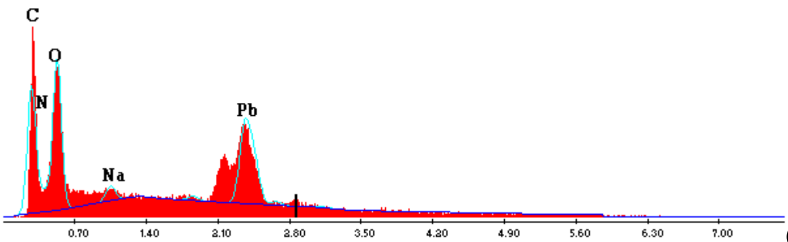
Figure 5.29. SE image (A, B), EDX spectrum (C) and chemical composition (D) of the priming layer



(A)



(B)



(C)

(D)

Element	**%**
C	21.20
N	4.68
O	18.08
Na	1.39
Pb	54.66
Total	100

Figure 5.30. SE image (A, B), EDX spectrum (C) and chemical composition (D) of the pigment layer

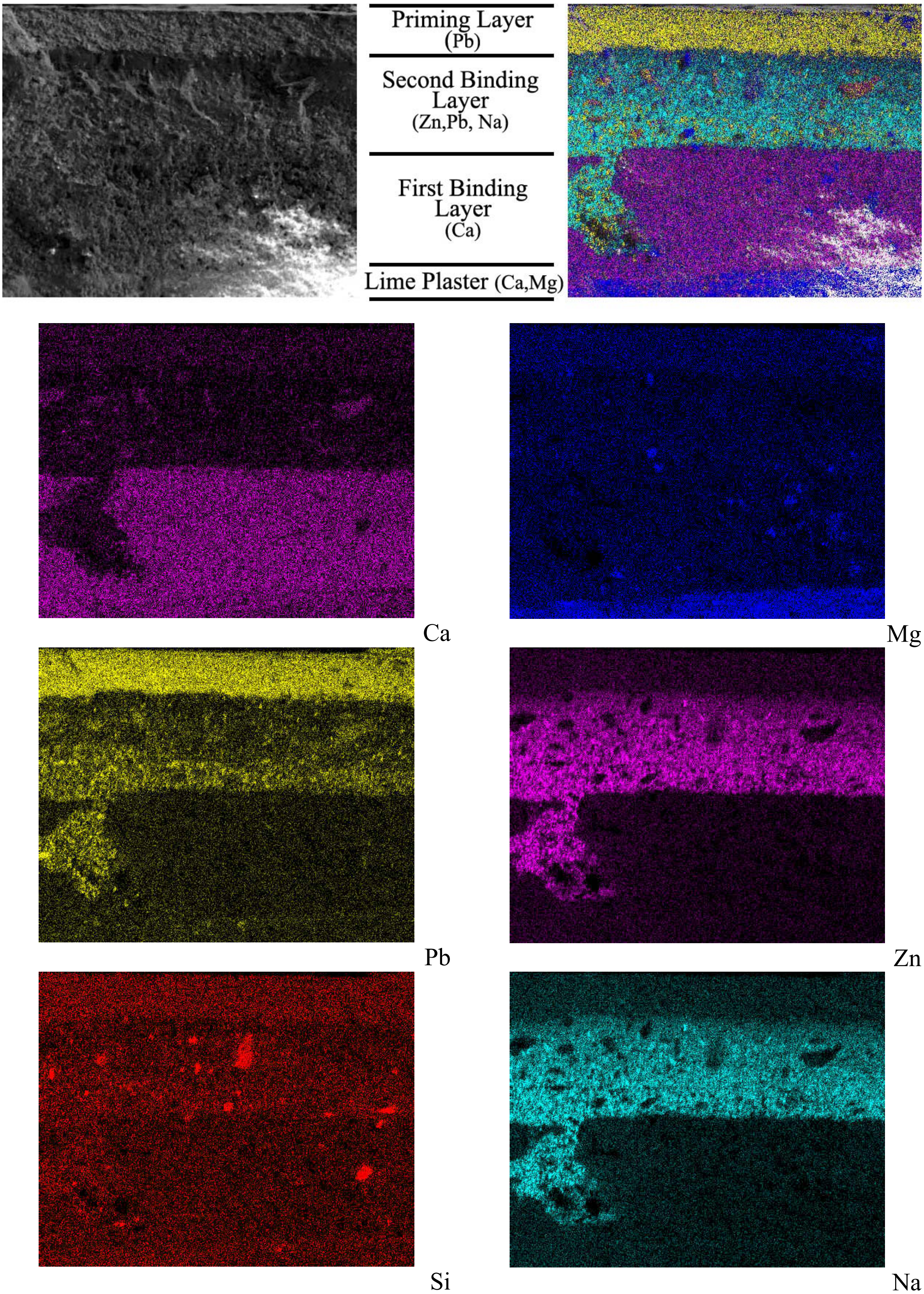


Figure 5.31. Mapping based on the chemical compositions of layers forming wall painting

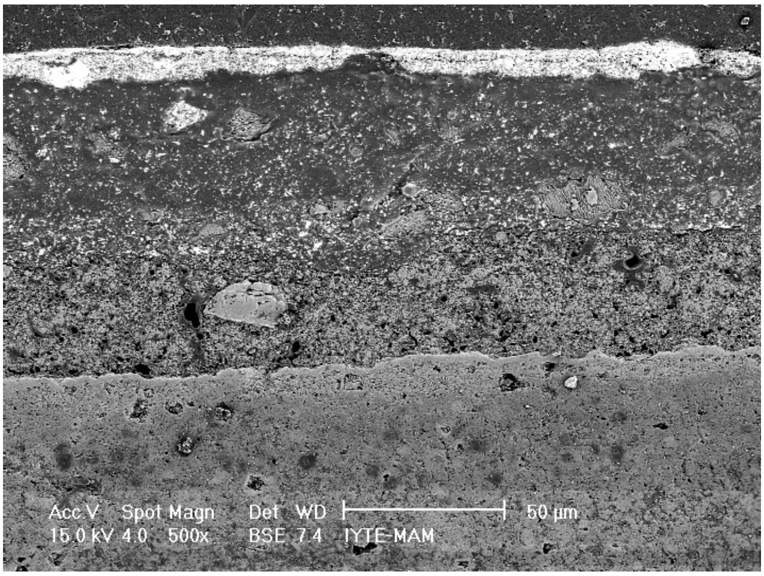
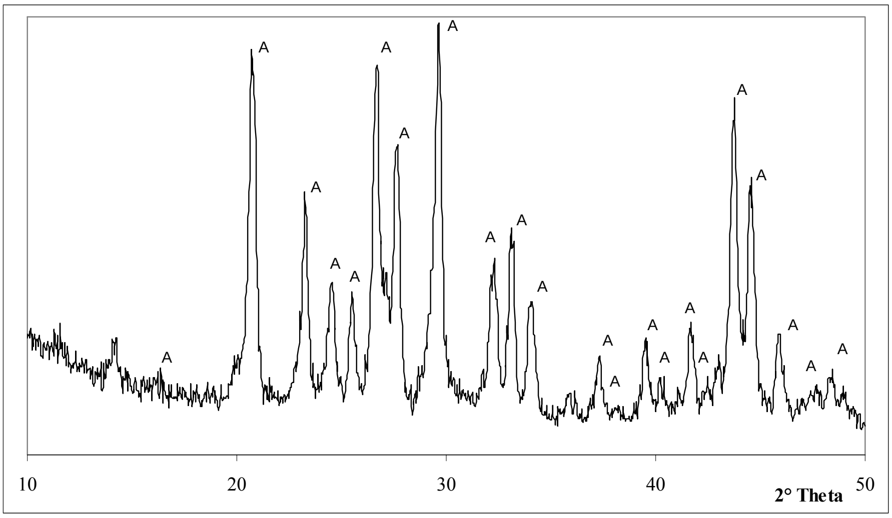


Figure 5.32. BSE image showing the adhesion between the layers of the painting from the second period

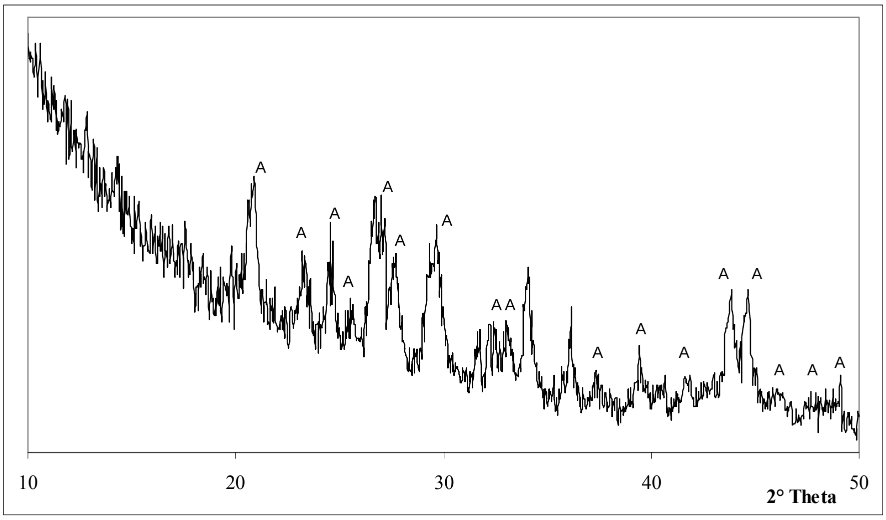
In the SEM-EDS analyses of the green painting samples, sodium (Na), magnesium (Mg), aluminum (Al), and iron (Fe) was detected (Figure 5.35). A mixture of celadonite and glauconite called “green earth” (Fe, Mg, Al, K, hydrosilicate) had been used in wall paintings as green pigment (Clark 2002, Harley 2001, Hradil et al. 2003). The observation of similar elements found in the composition of green earth may indicate the use of green earth as green pigment in the second period painting.

EDS analyses of the brown paintings from the second period are very similar to the brown paintings from the first period (Figure 5.36). Lead (Pb), iron (Fe) and Aluminum (Al) was determined.

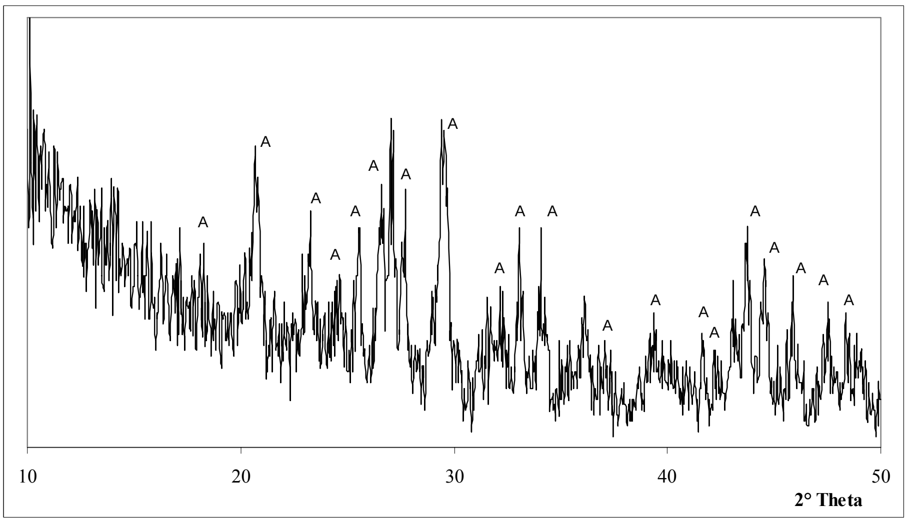
In the EDX analyses of the beige color much amounts of calcium (Ca), magnesium (Mg), aluminum (Al) and silicon (Si) was observed (Figure 5.37). Beige color may be produced by a pigment containing these elements.



NN.B



NN.G



NN.Br

Figure 5.33. XRD pattern of painting samples from the second period in mirror modeA: Anglesite ($PbSO_4$)

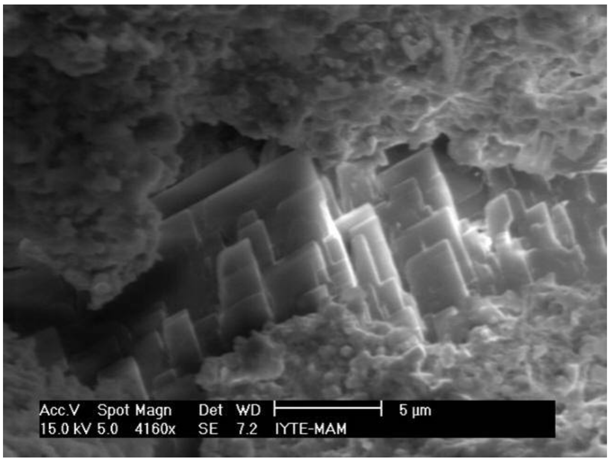
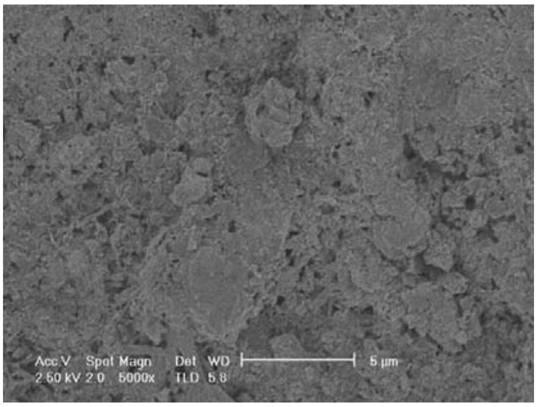
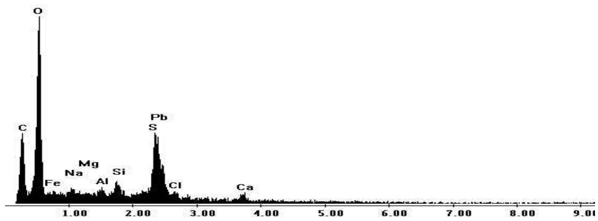


Figure 5.34. SE image of the lead sulphate crystal used in the priming layer



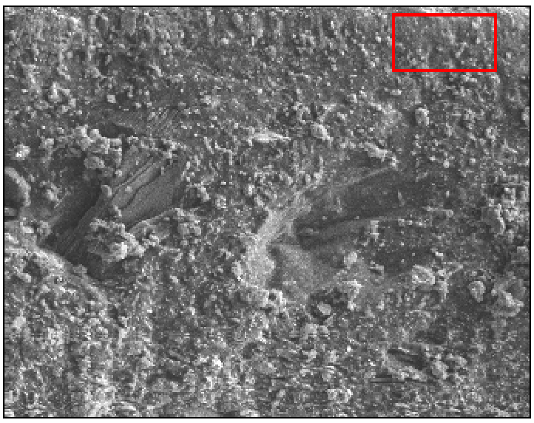
(A)



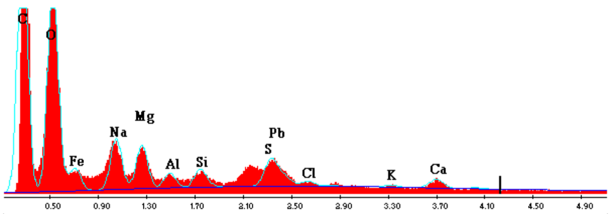
(B) (C)

Oxide	%		
Fe_2O_3	23.62	SO_3	7.32
Na_2O	5.22	PbO_2	45.16
MgO	3.32	Cl2O	1.69
Al_2O_3	4.60	CaO	2.98
SiO_2	6.10	Total	100.00

Figure 5.35. SE image (A), EDX spectrum (B) and chemical composition (C) of the green painted plaster from the second period, NN.G



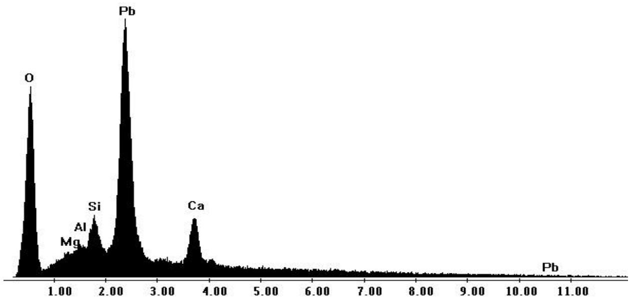
(A)



(B) (C)

Element	%	Element	%
C	43.18	Si	1.85
O	22.84	S	2.33
Fe	9.67	Pb	6.38
Na	3.91	Cl	1.19
Mg	3.38	K	1.06
Al	1.37	Ca	2.84
		Total	100

Figure 5.36. SE image (A), EDX spectrum (B) and chemical composition (C) of the brown painted plaster from the second period, NN.Br



(A)

Oxide	%
MgO	4.40
Al_2O_3	6.62
SiO_2	15.16
CaO	23.47
PbO_2	50.35
Total	100.00

(B)

Figure 5.37. EDX spectrum (A) and chemical composition (B) of the beige painted plaster from the second period, NN.B

5.4. Deteriorations of the Wall Paintings

Deterioration problems observed on the wall paintings of the Taxiarhis Church are, loss of plaster layers, disintegration of plaster layers, loss of paint layers (blistering and peeling) and discoloration (Figures 5.38, 5.39).

Those deteriorations were shown on the measured drawings of the paintings (Figures 5.40, 5.41, 5.42, 5.43, 5.44). Main source of the deteriorations is the dampness (Nicolaus 1999) occurring due to the rain penetration through the cracks or holes in the walls and ceiling and the broken windows.

Vandalism is also one of the main problems that destroy the integrity of the paintings (Figure 5.39).

Figure 5.38. Loss of plaster and painting layer due to dampness in the painting no:4 on the main apse of the church

2003

2004

Figure 5.39. Loss of the paints due to the vandalism. Region bordered with red color was destroyed by human beings between 2003-2004 in order to discover the underlying cross figure

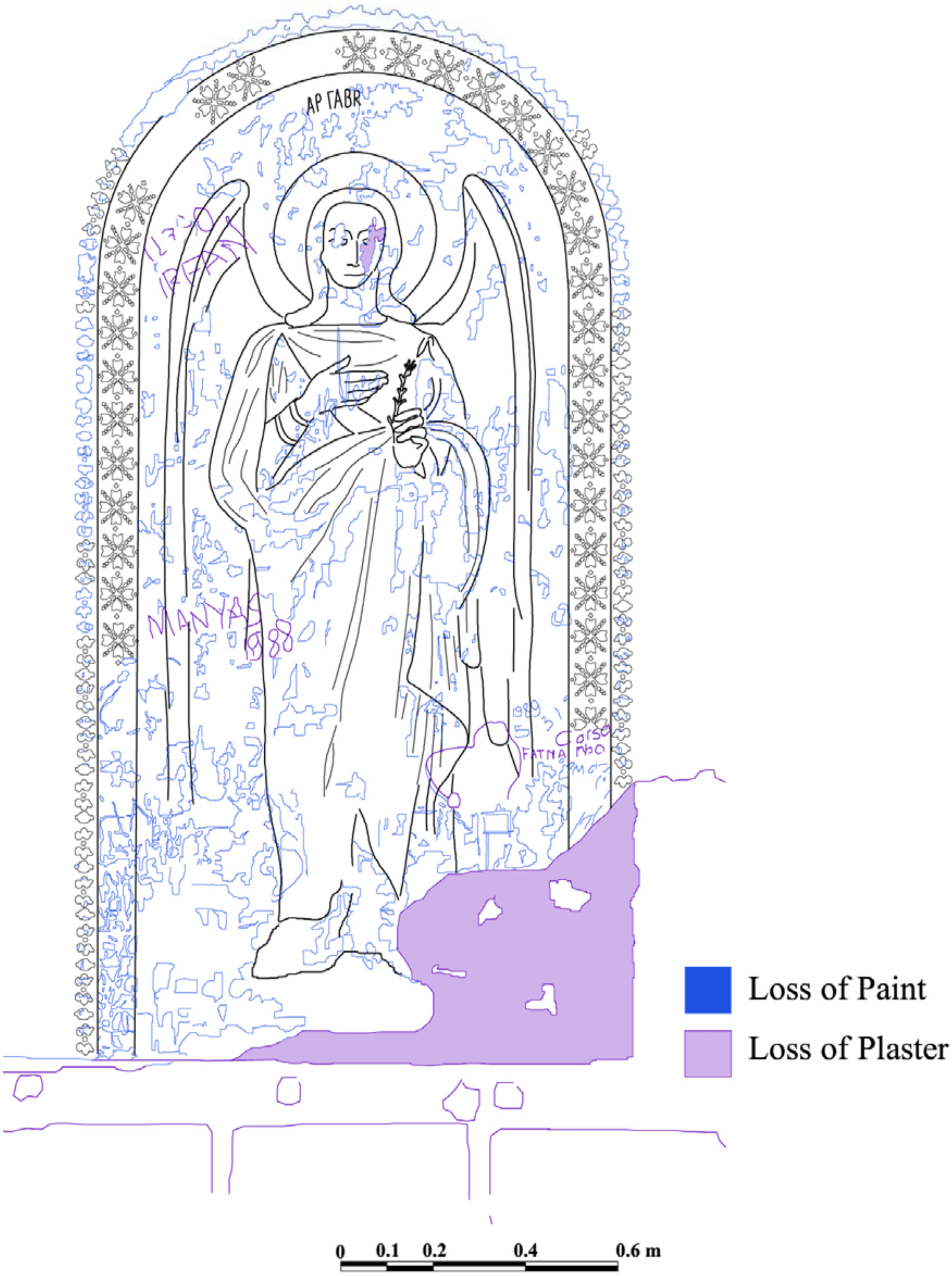


Figure 5.40. Measured drawing of the Gabriel painting on the north arm of the cross

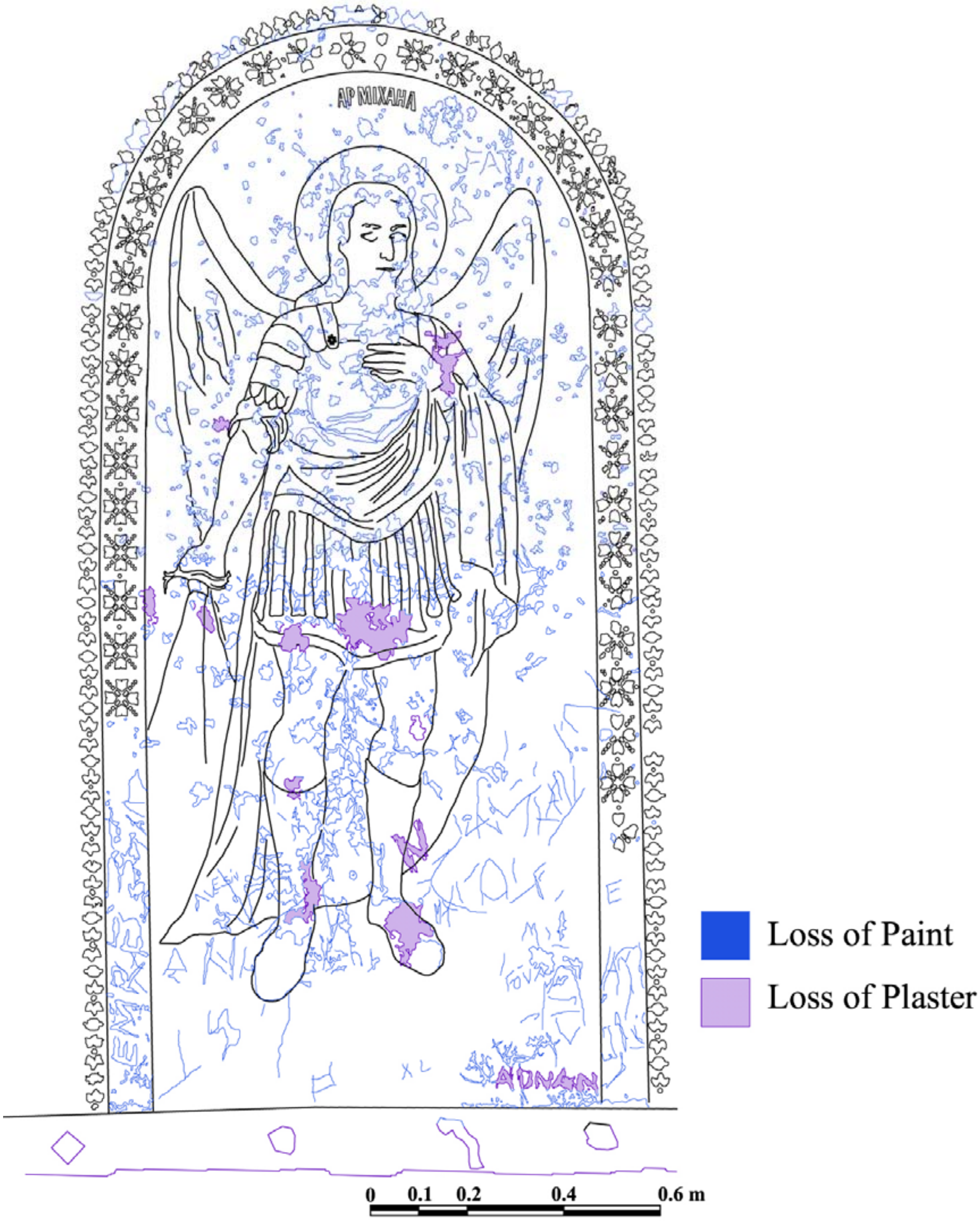


Figure 5.41. Measured drawing of the Mikael painting on the north arm of the cross

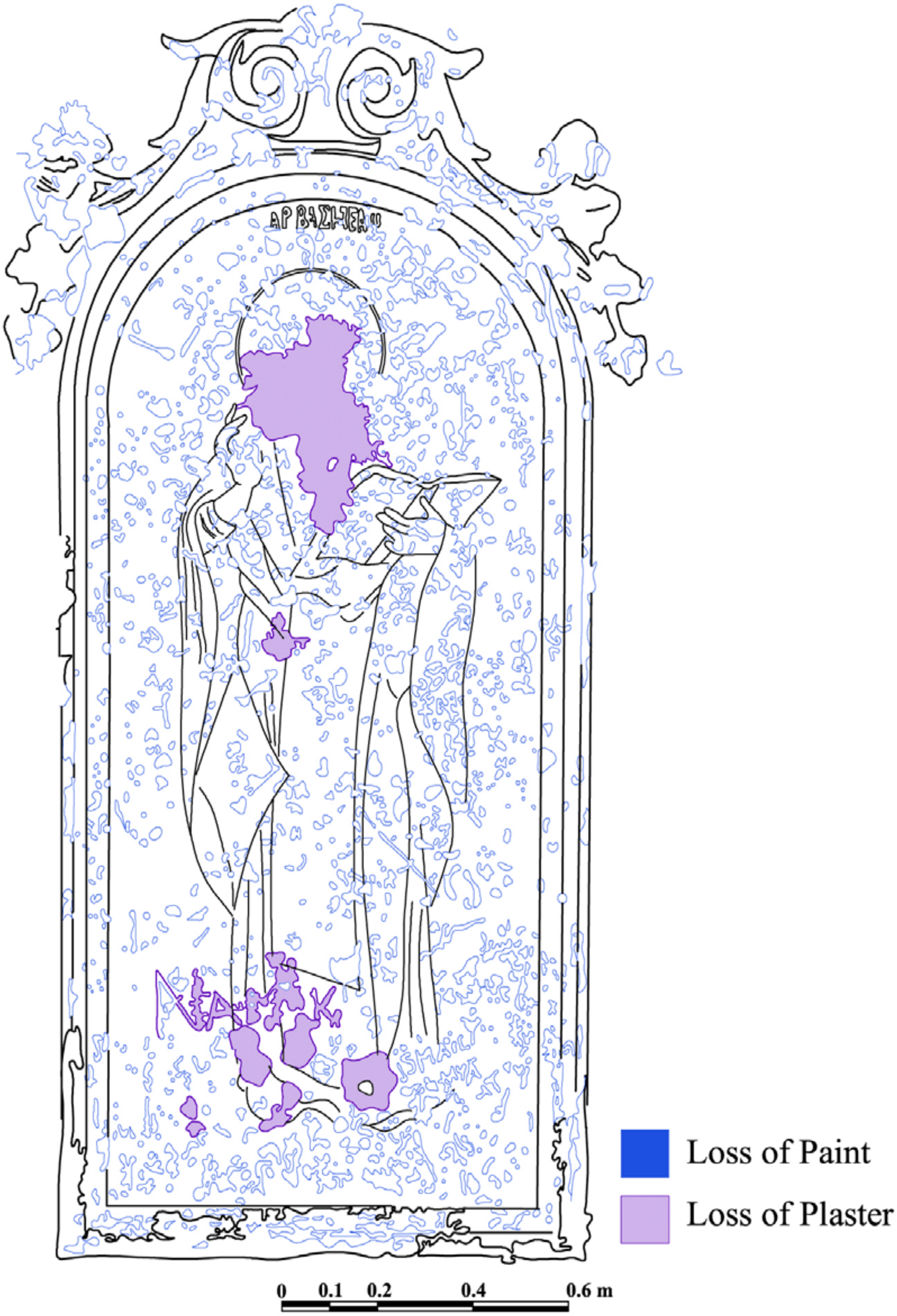


Figure 5.42. Measured drawing of the Apostle (no:1) painting on the main apse

Figure 5.43. Measured drawing of the Apostle (no:4) painting on the main apse

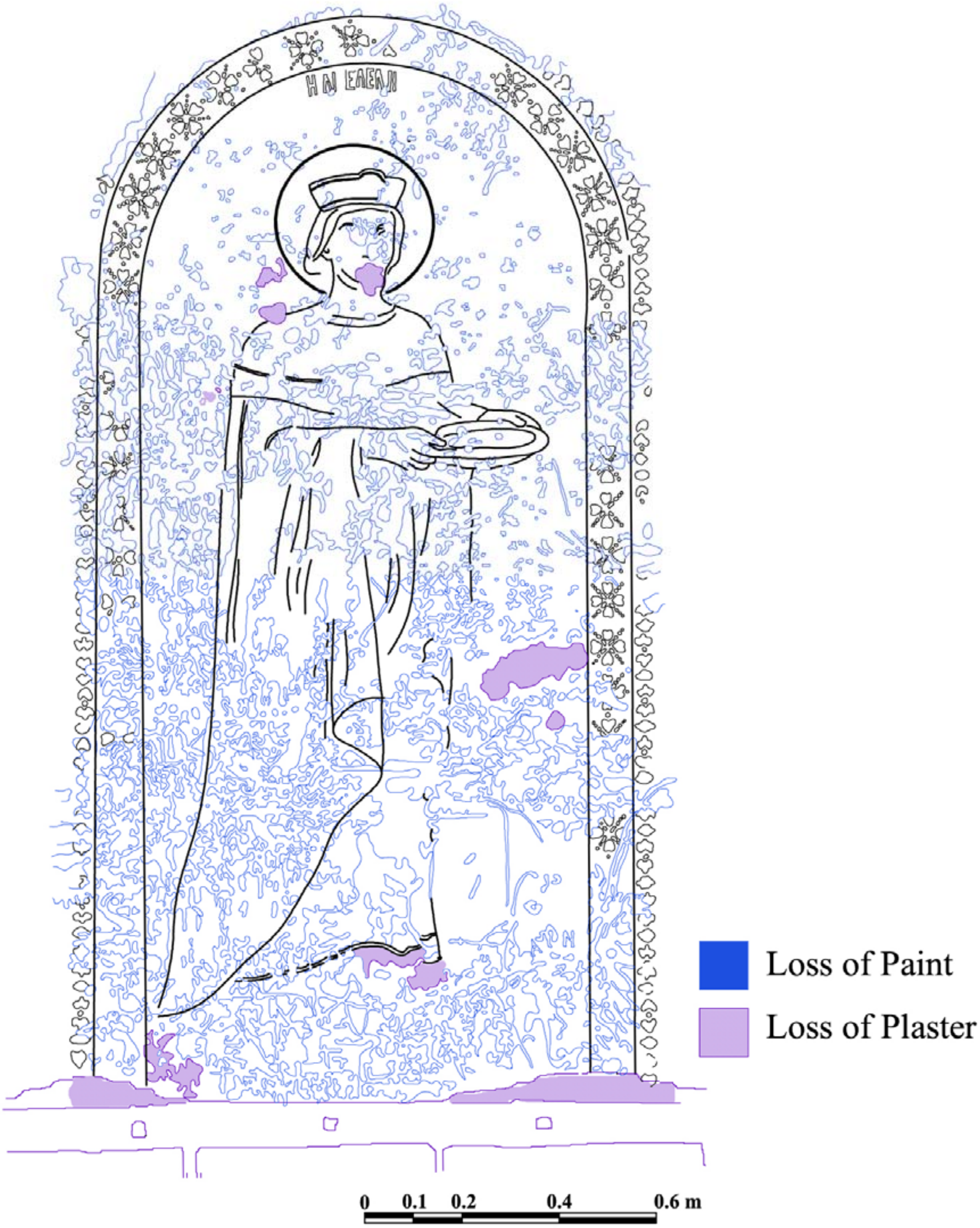


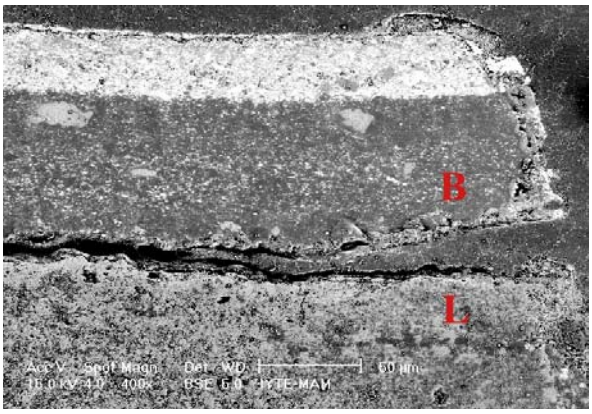
Figure 5.44. Measured drawing of the Helena painting on the south arm of the cross

SEM was used for detailed investigation of the present conditions of the paintings. One of the main problems observed to the first period paintings is the formation of micro-cracks and blistering (Figures 5.45, 5.46) Adhesion of the pigment, priming layer and the binding media is good, but a clear disintegration between the binding media and the fine lime plaster was observed (Figure 5.45).

In the wall paintings of the second period, adhesion of the binding media and the fine plaster is quite good. The first binding layer obtained by mixing the vegetable oil and lime may acquire the well adhesion to the fine plaster and second layer binding layer via its porous structure. Its physical property may also be similar with the fine plaster and second binding layers due to the linseed oil and lime in its composition. It may be the reasons of the good adhesion of the binding media and the fine plaster.

The main problem of the second period paintings are the detachment of fine plaster with paint layer from the first period fine plasters. The dampness in the building must be one of the main source of this deterioration. Beside loss of fine plaster layer with paintings, blistering and micro crack formations on the surfaces of the paintings were observed (Figure 5.47).

(A)



(B)

Figure 5.45. Stereo microscope image (A) and BSE image (B) showing the detachment of painting layers from the lime plaster, A.P_4.Br (B: Binding Layer, L: Lime plaster)

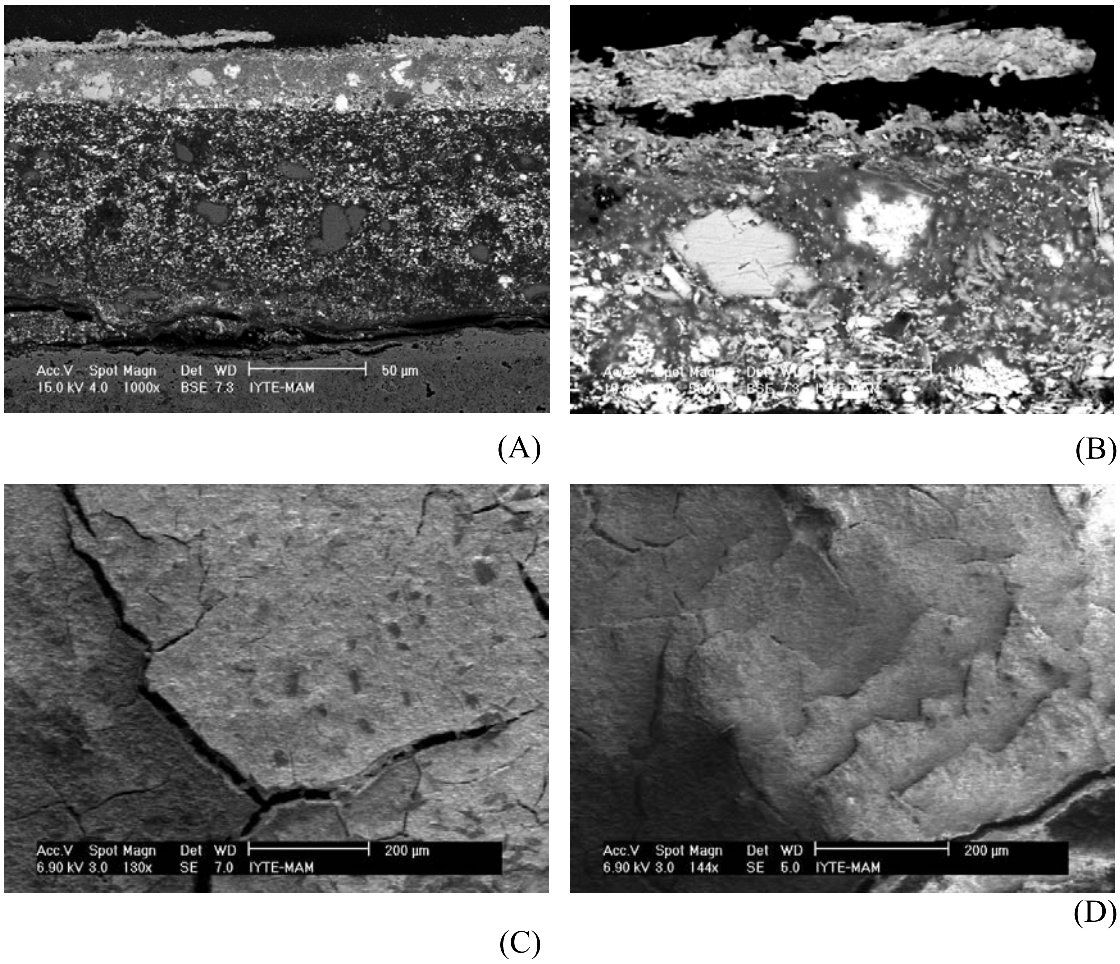
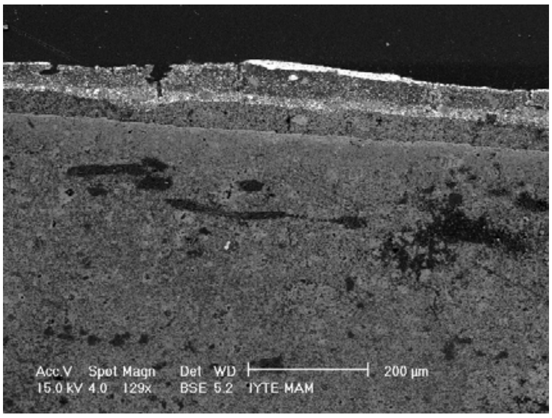
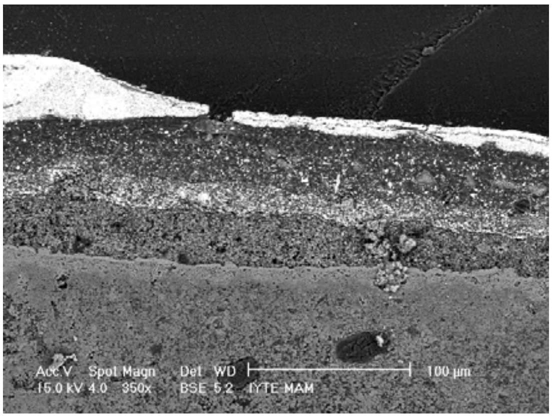


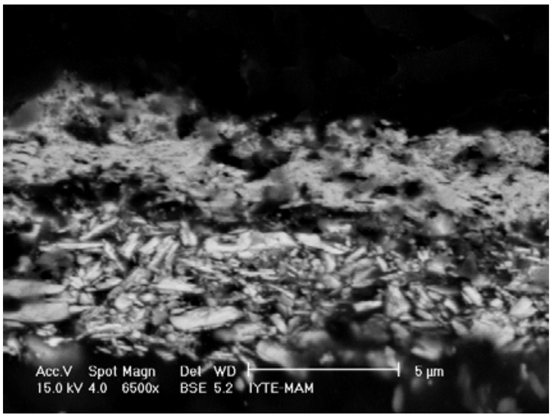
Figure 5.46. SE and BSE images of deteriorations observed on the paintings of the first period. A,B: Blistering, C,D: Micro crack formation



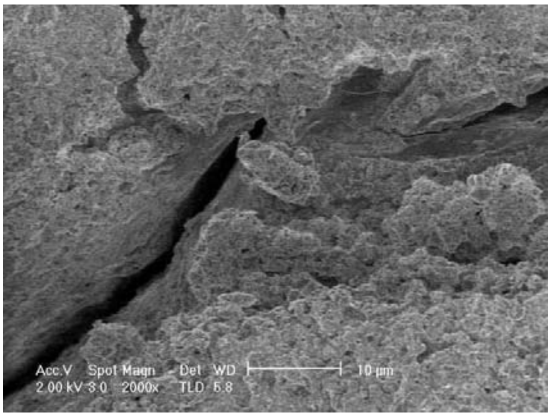
(A)



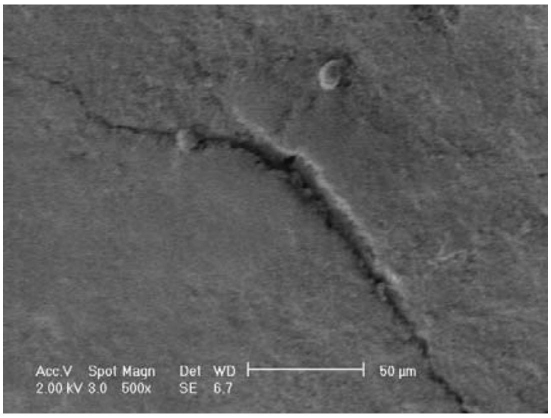
(B)



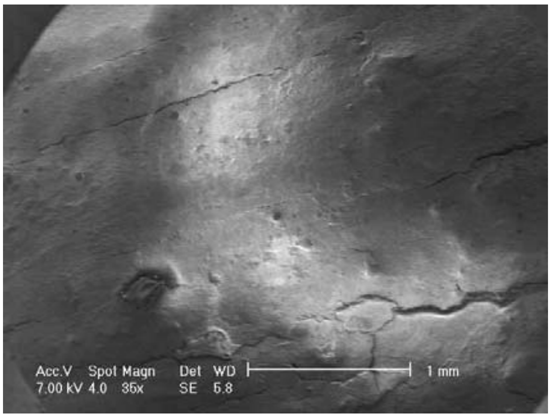
(C)



(D)



(E)



(F)

Figure 5.47. SE and BSE images of deteriorations observed on the paintings of the second period. A B,C: Blistering, D,E,F: Micro crack formation

CHAPTER 6

CONCLUSION

This study was carried out in order to form a database of the application technique, material properties and deterioration problems of the wall paintings of the Taxiarhis Church with the purpose of conservation.

Wall paintings in the Taxiarhis Church were applied in two different periods. Wall paintings from both periods were executed by oil painting technique over lime plasters by using vegetable oil.

Plasters of the Taxiarhis Church are lime plasters. Lime/Aggregate ratio of the rough plasters which are composed of lime, aggregate, straw and oakum range between 1:4 and 1:3. Fine plaster layers do not contain aggregate. Rough plaster layers have a denser structure than fine plaster layers. Intonacoes have higher density and porosity values than other fine plasters.

The wall paintings of the first period are composed of binding layer, priming layer and pigment. Vegetable oil mixed with ZnO was used in the preparation of binding media. ZnO was used as accelerator of the polymerization of the vegetable oil. Anglesite ($PbSO_4$) was used in the priming layer in order to bleach the vegetable oil. Pigments used in wall paintings of the first period may be defined as green earth, lead red and iron oxide.

The wall paintings from the second period are composed of a two layered binding layer, priming layer and pigment. The first binding layer is composed of calcium and vegetable oil, Vegetable oil mixed with siccitative pigments, such as ZnO and $PbSO_4$ were used in the preparation of the second binding media. The priming layer was composed of $PbSO_4$ and vegetable oil.

The wall paintings are affected by the problems of the structure in which they exist. The building and the decoration must be accepted as a whole and interventions related to the consolidation of wall paintings must be discussed together with the consolidation of structural failures that cause dampness and threats the physical unity of the building. The main problem in the wall paintings of the first period is the loss of paint layers due to the loss of adhesion between the binding layer and the lime plaster. In the wall paintings of the second period there is a clear detachment between the intonaco layer and the building. Deteriorations observed on the wall paintings are formed by the dampness in the building. Water must be removed from the building. Detaching layers of the paintings must be consolidated with appropriate materials and methods. Paintings do not require cleaning due to the fewness of deposits over them.

In this study the application technique of the paintings was determined. A detailed study must be carried out in order determine the exact type of the vegetable oil and the pigments.

Restoration of the paintings must be performed after the consolidation of the building. Paintings must be covered with suitable methods in order to avoid any damage that can occur during the restoration of the building. Intervention decisions (consolidation, integration, etc.) for paintings must be specified by an interdisciplinary specialist team.

After restoration, illumination, environmental control and control of the dampness sources are very important for the sustainability of the conservation. Continuous monitoring of wall paintings and environment and permanence of conservation must be provided. Reaction of wall paintings to present conditions after restoration must be observed continuously.

REFERENCES

Alfano, D., Scarabino, C., Inverso,D., Proto, A. 2005. “Chemical and Spectroscopic Investigation on the Plaster of a Byzantine Church,” *Annali di Chimica*, 95, 3-4, 125-132.

Arı, K., 1995. *Büyük Mübadele ve Türkiye’de Zorunlu Göç* (1923-25), (Tarih Vakfı Yurt Yayınları, Ankara)

Atlaslı Büyük Uygarlıklar Ansiklopedisi – Mezopotamya ve Eski Yakındoğu, 1996. (İletişim, İstanbul)

Bell, I. M., Clark, R. J. H., Gibbs, P. J. 1997. “ Raman Spectroscopic Library of Natural and Synthetic Pigments (Pre-~1850 AD),” *Spectrochimica Acta Part A.* Vol. 53, p. 2159-2179.

Berger, F. 1904. *Die Maltechnik des Altertums*, (Callwey, Munich)

Biscontin G., Piana M. and Riva G. 1981. "Research on Limes and Intonacoes of the Historical Venetian Architecture. Characterization of Some 'Marmorino' Intonacoes From the 16th to the 17th century." Proceedings of the Symposium of Mortars, Cements and Grouts Used in the Conservation of Historic Buildings, Rome, (3-6 november 1981), pp. 359-373.

Boxall, J. A., 1978. “History of Paint Technology. Part 1 - Pre-18th century,” *Paint manufacture*. p.18-22.

Clark, R. J.H. 2002. “Pigment Identification by Spectroscopic Means: an Arts/Science Interface,” *Academie des Sciences*, Vol. 5, No.1, p.7-20.

Edwards, H. G. M., Brooke, C. J., Tait, J. F. K. 1997. “ Fourier Transform Raman Spectroscopic Study of Pigments from English Mediavel Wall Paintings,” *Journal of Raman Spectroscopy*. Vol. 28, p. 95-98.

Eibner, A. 1926. *Entwicklung und Werkstoffe der Wandmalereii vom Altertum bis zur Neuzeit*, (B.Heller, Munich)

Forbes, R. J. 1965. *Studies in the Ancient Technology*, 3. E.J.Brill, Leyden p.213

Gimeno-Adelantado, J. V., Mateo-Castro, R., Doménech-Carbó, M. T., Bosch-Reig, F., Doménech-Carbó, A., Casas-Catalán, M. J., Osete-Cortina, L. 2001. "Identification of Lipid Binders in Paintings by Gas Chromatography Influence of the Pigments," *Journal of Chromatography A*. p. 385-390.

Gombrich, E. H., 1995. *The Story of Art*, (Phaidon, London)

Harley, R. D., 2001. *Artists' Pigments* c. 1600-1835, (Archetype Publications, London)

Hradil, D., Grygar, T., Hradilová, J., Bezdićka, P. 2003. " Clay and Iron Oxide Pigments in the History of Painting," *Applied Clay Science*. Vol. 22, p. 223-236.

Icomos, 1999. "Venice Charter, The International Charter for the Conservation and Restoration of Monuments and Sites", in *International Documents Regarding the Preservation of Cultural and Natural Heritage,* edited by E. Madran and N. Özgönül (METU-Faculty of Architecture Press, Ankara), pp. 31-34.

İpek, G. G., 2003. Ayvalık Tarihi Kent Merkezindeki Kiliselerin İncelenmesi, (M.Sc. Thesis, Dokuz Eylül University, İzmir)

Jedrzejevska, H. 1981. "Ancient Mortars as Criterion in Analysis of Old Architecture", Proceedings of Symposium on Mortars, Cements and Grouts Used in the Conservation of Historic Buildings, Rome, pp. 311-329.

Karo, G. 1912. Tiryns, Die Ergebnisse der Ausgrabungen des Kaiserlichen Archäologischen Instituts in Athens.

Kuyulu, İ. 1996. "Anatolian Wall Paintings and Cultural Traditions", *EJOS: Electronic Journal of Oriental Studies*. Vol. 3, no. 2, p. 1-27

Lang, P. L., Keefer, C.D., Juenemann, J.C., Tran, K.V., Peters, S.M., Huth, N.M., Joyaux, A.G. 2003. "The Infrared Mikrospectroscopic and Energy Dispersive X-Ray Analysis of Paints Removed From a Painted, Medieval Sculpture of Saint Wolfgang," *Microchemical Journal*. Vol.74, no.1, 33-46.

Manzano, E., Bueno, A.G., Gonzalez-Casado, A., Olmo, M. 2000. "Mortars, Pigments and Binding Media of Wall Paintings in the 'Carrera del Darro' in Granada, Spain," *Journal of Cultural Heritage*. Vol.1, p.19-28.

Middendorf B., Knöfel D. 1990. "Use of Old and Modern Analytical Methods for the Determination of Ancient Mortars in Northern Germany", Proceedings of the 3rd Expert Meeting, Hamburg, NATO-CCMS Pilot Study on Conservation of Historic Brick Structures, Berlin, Germany, pp. 75-92.

Mills, J. S., White, R. 1994. *The organic chemistry of museum objects*, (Butterworth-Heinemann, Oxford)

Mora, P., Mora, L., Philippot, P., 1984. *Conservation of Wall Paintings*, (Butterworths, London)

Nicolaus, K., 1999. *The Restoration of Paintings*, (Könemann, Cologne)

Parrot, A. 1958. "Mission Archeologique de Mari," *Le Palais: Peintures Murales*. Vol. 11, p. 53-65

Perardi, A., Appolonia, L., Mirti, P. 2003. " Non-destructive in Situ Determination of Pigments in 15th Century Wall Paintings by Raman Microscopy," *Analytica Chimica Acta*. Vol. 480, p. 317-325.

Peschlow and Bindokat 1998. "The prehistoric rockpaintings of the Latmos (Besparmak)," *Stonewatch magazine*. Vol. 3, p. 27-29

Prati, S., Chiavari, G., Cam, D. 2001. "DSC Application in the Conservation Field," *Journal of Thermal Analysis and Calorimetry*. Vol. 66, p. 315-327.

Psarros, D., 2004. “Ayvalık/ Kydonies’ın Kentsel Tarihi”, Proceedings of the Ege’nin İki Yakası-I, Ayvalık Kent Tarihi Çalışmaları Conference, Ayvalık, (28-30 October 2004)

Renda, G., 1985. “19. yy’da Kalemişi Nakış-Duvar Resmi”, in Tanzimat’tan Cumhuriyet’e Türkiye Ansiklopedisi, (İletişim, İstanbul), pp. 1530-1534

RILEM, 1980. “Tests Defining the Structure,” *Materials and Construction.,* Vol. 13, p. 73.

Rona, Z. 1997. “Yağlıboya”, in Eczacıbaşı Sanat Ansiklopedisi, (YEM, İstanbul), pp.1911

Schwartzbaum, P. M. 1986. “Conservation of the Mural Paintings in the Rock-Cut Churches of Göreme” appendix in Tokali Kilise: Tenth-century Metropolitan Art in Byzantine Cappadocia by Eibstein, A. W. (Dumbarton Oaks, Washington)

Surowiec, I., Kaml, I., Kenndler, E. 2004. “Analysis of Drying Oils Used as Binding Media for Objects of Art by Capillary Electrophoresis With Indirect UV and Conductivity Detection,” *Journal of Chromatography A.* p.245-254.

Sutherland, K. 2003. “Solvent-Extractable Components of Linseed Oil Paint Films,” *Studies in Conservation*. Vol. 48, no. 2, p. 111.

Teutonico J.M. 1988. “Porous Building Materials,” in *A Laboratory Manual for Architectural Conservators*, (ICCROM Publishing, Rome), pp. 35-68.

Turgut, A. Ö., 1996. A*yvalık Kilise ve Manastırları,* (B.A. Thesis, Ege University, İzmir)

Van den Berg, J.D.J. 2002. Analytical Chemical Studies on Traditional Linseed Oil Paints, (PhD Thesis, Institute for Atomic and Molecular Physics (AMOLF), Amsterdam)

Van der Weerd, J. 2002. Microspectroscopic Analysis of Traditional Oil Paint, (PhD Thesis, Institute for Atomic and Molecular Physics (AMOLF), Amsterdam)

Vasari, 1906. Introduzione, Appendix 6 in The Conservation of Wall pantings. Mora, P., Mora, L., Philippot, P., 1984. (Butterworths, London)

Vitrivius, 1960. *The Ten Book on Architecture*, (Dover, Newyork)

WEB_1, 2005. Icomos Principles for the Preservation and Conservation/ Restoration of Wall Paintings, 01/07/2005. http://www.international.icomos.org/charters/wallpaintings_e.htm

WEB_2, 2005. Heritage at Risk Reports, 01/07/2005. http://www.international.icomos.org/risk/2004/turkey2004.pdf

WEB_3, 2005. Çatalhöyük, 01/07/2005. www.ucl.ac.uk/ ~tcrneas/catalhoyuk.htm

WEB_4, 2005. Çatalhöyük, 01/07/2005. http://catal.arch.cam.ac.uk/visit/historyEN.html

WEB_5, 2005. Egypt wall painting, 01/07/2005. http://www.metmuseum.org/explore/newegypt/htm/wk_frame.htm

WEB_6, 2005. Mesopotamia, Alalakh, 01/07/2005. http://www.lectio.unibe.ch/04_2/ HTML/guillaume_blockman.htm#_edn8

WEB_7, 2005. Knossos, 01/07/2005. http://www.culture.gr/2/21/211/21123n/00

Winfield D. C. 1968, Middle and Later Byzantine Wall Painting Methods. A Comperative Studies, *Dumbarton Oak Papers*, Vol.22, p. 61-140

Wooley, L. 1955. *Alalakh*, (Oxford)