CHARACTERIZATION OF PIGMENTS USED IN THE EXECUTION OF WALL PAINTINGS IN KADIKALESİ

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ABSTRACT

CHARACTERIZATION OF PIGMENTS USED IN THE EXECUTION OF WALL PAINTINGS IN KADIKALESİ

Since prehistoric times wall paintings have been remarkable symbols of existences, identities, cultures and life-styles of human beings and societies and considerable integral parts of art and architecture. In this context, determination of painting techniques and materials employed and deterioration problems of the wall paintings, as of being part of built cultural heritage, have been crucial in terms of conservation. In this study, wall paintings existing in the Byzantine church-monastery edifice which have been uncovered in Kadıkalesi (Anaia) archaeological site were investigated for the purpose of identification of the original materials and painting technique. Mineralogical, chemical and micro-structural characteristic of the pigments and binding mediums employed in the fabrication of paintings; and basic physical properties, raw material compositions, mineralogical, chemical and micro-structural features of surface renderings underlying the painting layers were established. In the analyses, X-Ray diffraction (XRD), scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), optical microscope, Fourier transform infra-red (FT-IR) spectroscopy and thermo-gravimetric analyzer (TGA) were used.

On the basis of analyses results, it was determined that *lime-secco* technique was used in the fabrication of the investigated wall painting fragments; pigments were applied after mixed with lime (generally dolomitic lime) as binder on the surface of dry fine plaster. The density and porosity values of the fine plasters which paintings were executed are 1.20 g/cm^3 and 40 % by volume respectively. The fine plasters were constructed with pure lime with small amount of soil material. Iron oxide-based pigments in red, yellow and purple paintings and aluminosilicate-based pigments; such as celadonite, glauconite in green paintings, lazurite and glaucophane in blue and dark blue paintings were employed.

ÖZET

KADIKALESİ’NDE BULUNAN DUVAR RESİMLERİ UYGULAMALARINDA KULLANILAN BOYALARIN KARAKTERİZASYONU

Tarih öncesi çağlardan beri insanların ve toplumların varlıklarının, kimliklerinin, kültürlerinin, yaşam biçimlerinin önemli sembollerinden biri olan duvar resimlerinin yapım tekniklerinin, kullanılan malzemelerin ve bozulma sorunlarının bilinmesi onların korunması açısından önemlidir. Bu çalışmada Kuşadası, Kadıkalesi (Anaia) arkeolojik alanında ortaya çıkarılmakta olan Bizans kilisesinde bulunan duvar resimlerinin yapımında kullanılan bağlayıcı malzeme ve boyaların mineralojik ve kimyasal kompozisyonları, resimlerin bulunduğu sıva tabakalarının temel fiziksel özellikleri, ham madde oranları, mineralojik ve kimyasal kompozisyonları incelenmiştir. Analizlerde X ışınları kırınım cihazı (XRD), SEM taramalı elektron mikroskobu (SEM-EDS), polarize mikroskop, Fourier dönüşümlü kızılötesi spektroskopisi (FT-IR) ve termogravimetrik (TGA) analiz cihazı kullanılmıştır.

Çalışma sonucunda, resimlerin *kireç-secco* tekniği kullanılarak yapıldığı belirlenmiştir. Bu teknikte pigmentler genellikle dolomitik kireç ile karıştırıldıktan sonra kurumuş ince sıva yüzeyine uygulanmıştır. Kırmızı, sarı ve mor pigmentlerde temel olarak demir oksitler, yeşil, mavi ve lacivert boyalarda ise celadonit, lazurit ve glokofan gibi pigmentler kullanılmıştır. İnce sıva tabakaları sadece kireç bağlayıcı kullanılarak yapılmıştır. Duvar resimlerinin uygulandığı ince sıva tabakalarının yoğunluğu yaklaşık 1.20 gr/cm^3 dir, gözenekliliği ise yaklaşık % 40dır.

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CHAPTER 1

INTRODUCTION

Mural paintings have been a remarkable way of expressions of existence, identity, culture, creativity and life-style of human beings and societies from the earliest beginnings. They have been important parts of the world’s cultural heritage, as well as of the buildings they belong. Therefore, they have to be conserved by providing the fundamental circumstances.

ICOMOS (International Council on Monuments and Sites) manifested a document compromised of several principles on conservation of wall paintings in 2003. In this document, fundamental and universally feasible principles and implementations have been prescribed. These principles could be abstracted generally as follows (ICOMOS Charter 2009).

As the initial access for the conservation of wall paintings, the list of historic buildings, monuments and sites which have mural paintings, even if they could not be apparent, should be made. Law and regulations relevant to conservation of wall paintings should incorporate providing sources for investigation, professional approaches of treatment and controlling, in addition to prohibition of demolition, deformation and alterations.

Conservation program on wall paintings has to be taken up with comprehensive scientific investigations, aimed at determining the constitution of the structure and the stratigraphy of the layers in collaboration with their historic, aesthetic and technical knowledge. The investigations should be carried out in an interdisciplinary manner. Prior requirements in this procedure have been determined as the scholar research on the material analysis, deterioration process, and the identification of environmental conditions. The investigation procedure should not damage the wall paintings.

Conservation-restoration of wall paintings has to be carried out with accurate program of documentation. Each phase of the conservation-restoration materials, methods, and the procedure should be documented in an analytical and overall report, depicted with photographs, mapping, drawings, copies, etc. The report is suggested to be involved in the archives of the public institutions and also be enabled to public interest. Moreover, the outcome of the study should be published.

Conservation program of wall paintings aims at setting up convenient condition in order for minimization of decays, and preventing redundant interventions. Environmental conditions around wall paintings and deterioration processes of the paintings and the supporting structure should be monitored and controlled. Preventive measures and periodical care are required for full conservation. Hence, further deteriorations could be prevented and the life span of mural paintings could be extended.

In case the monuments and sites with wall paintings are assigned to unsuitable and uncontrolled public utility, this causes damage of wall paintings and monuments. Site management should plan strategies of use, access and safety of the monuments and sites thoroughly, even in case they are positioned in isolated locations. Moreover, it is significant to preserve the authentic tangible and intangible values of the monuments and sites and to provide the public esteeming these values.

Wall paintings have been an integral part of the monuments; because of that they should be preserved primarily *in situ*. Conservation program of wall paintings have to be carried out by taking into consideration the architectural entity and unity. Feasible interventions, in such a manner that cleaning, consolidation, reintegration, should be implemented at minimal level in order to prevent reducing of material and authenticity.

The traces of time depending on natural aging process, preceding restorations, and over-painting have been considered as part of the history of wall paintings, they are recommended to be respected and preserved. Cleaning of irreversible chemical and physical interventions and transformations could damage the wall paintings; in that case they should also be preserved.

Materials and methods used in conservation and restoration works of wall paintings should be opted for by considering further behaviours. They have to be executed after thorough scholarly investigations and positive results of tests both in laboratories and *in situ*. The application of traditional materials and methods which are compatible with the painting should be promoted, as new materials and methods could make irreversible and harmful effects in the long term.

Conservation and restoration works are carried out in order to advance the intelligibility of composition of the wall paintings by abiding the authenticity and history of them. In this respect, reintegration and reconstruction of wall paintings have to be distinguishable; additions must be removable, and over-painting must be avoided.

Non-visible or hidden wall paintings should be uncovered after determination its historic and authentic values, estimation on possible losses, and initial investigations on the environmental conditions; without exposing damages.

Conservation and restoration projects should be implemented by the approval of the relevant authorities. A team of professionals who have proper knowledge and skills should be charged.

In cases that wall paintings need to be intervened urgently, the materials and methods used should allow later treatments. The operations of detachment and transferring of wall paintings lead to severe and irreversible problems; such as deformation of unity of the physical and aesthetic composition and deterioration of material structure. It is significant to carry out such severe operations with a team-work of professionals. These operations should be applied just in extreme cases when treatments *in situ* are inefficient; furthermore wall paintings subjected to these operations have to be repositioned in their original location at any time.

In order to implement maintainability of preservation policy on wall paintings research projects and correspondingly investigations within conservation and restoration program have to be developed. The researches based on related disciplines of arts and sciences provide the determination of materials and techniques of original execution and subsequent restoration practices of wall paintings. It is significant that the investigations are carried out without damaging the fabric of the material structure and deforming the unity of the composition and as far as possible limited number of samples should be obtained during the research.

Knowledge acquired from research within the conservation and restoration projects should be disseminated at every level. Therefore, public awareness about the necessity of preservation of wall paintings could be developed. Moreover, conservators-restorers in this field are recommended to exchange knowledge of their research and work in the interdisciplinary manner and to collaborate with their colleagues and specialists around the world.

Conservators and restorers of wall paintings are required to be professionally educated and trained; as they have to gain the necessary knowledge, skills, experience and responsibility.

The traditions of authentic painting techniques of artists and craftsmen in different regions of the world should be encouraged and maintained; on the other hand, conservation treatments must not be implemented by artists and craftsmen.

1.1. Historical Information on Wall Painting Techniques

The first examples of wall paintings are positive or negative (stencilled) hand imprints of human beings on the walls of caves at the beginning of Upper Palaeolithic Era (about 30,000 years B.C.) (Figure 1). The mostly used pigments are derived from red earth, blood, and charcoal black (Mora et al. 1984).

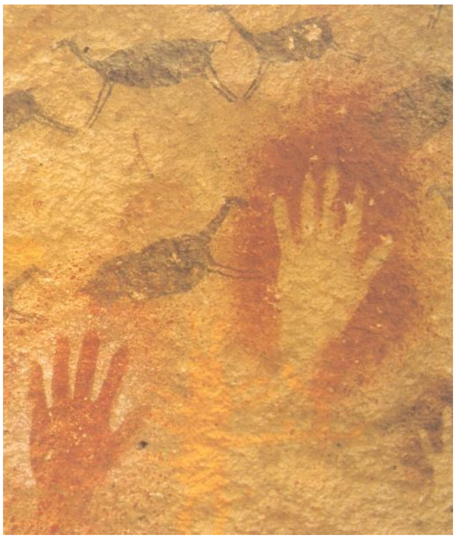


Figure 1. Hand stencils and paintings of guanacos (wild lamas) at Cueva de las Manos, Patagonia (Argentina), date unknown (Source: Bahn 1998).

The most developed examples of Palaeolithic cave paintings appeared at the caves in Altamira and Lascaux in the Magdalenian Period (16,000-8,000 B.C.). The primarily used pigments were natural iron oxides and manganese, hematite, and limonite. These earthen pigments provided various colours from brown ochre to yellow, by adding also black (from charcoal and bones) and white (from certain clays). According to the studies on cave paintings from Lascaux, the pigments in dry state were executed on damp surface (Figure 2). The cave consists of the rocks which have calcareous structure. The exudation of the dissolved calcium carbonate in water through the rocks and crystallization on the surface provided fixation of the pigments. This process lasted over centuries dependent upon the climatic conditions in the cave (Rieth 1970, Mora et al. 1984).

Figure 2. Cave paintings from Lascaux cave, Dordogne (France), 18.000-10.000 B.C. (Source: Janson and Janson 2006).

The prehistoric rock paintings, which have been found at the faces of little caves and overhangs of the Latmos (Beşparmak) near Kuşadası, were dated back to about in the millenniums between the Epipalaeolithic and the Chalcolithic periods. The rock paintings have been considered as one of the most remarkable examples of Prehistoric art in Anatolia. These paintings were executed directly on rock surfaces using materials that contained only red iron oxide as pigment (Figure 3) (Peschlow and Bindokat 1998).

Figure 3. Prehistoric rock paintings of Latmos (Beşparmak), Aydın (Turkey) (Source: Peschlow and Bindokat 1998)

In the Neolithic Era people began to make paintings on the wall surfaces which they had constructed and coated with clay renderings rather than irregular rock surfaces, hence the paintings had become part of the architecture. The most considerable foundlings of paintings from the beginning of the Neolithic period (*c*. 6000 B.C.) were found by James Mellaert at Çatal Höyük in Anatolia (Mellaart 2001) (Figure 4). The paintings were executed on a rendering made of mud or fine clay. The binding, even if used, is not detectable now. The chiefly used pigments are ochres, hematite, azurite and charcoal (Mellaart 2001, Mora et al. 1984).

Figure 4. Gigantic bull figure from Çatalhöyük, Konya (Turkey), *c*. 6000 B.C.
(Source: Mellaart 2001)

Egyptian mural paintings were applied on the one or two-layered plasters related to the supports (Figure 5). If the support was constructed with smooth cut stone, the surface was covered with a layer of gypsum which was composed of calcium sulphate and calcium carbonate, called *alabaste*r in ancient Egypt. On the other hand, when the surface of the support was irregular, it was covered first with a layer of silt and chopped straw and then a layer of gypsum (Lucas 1962). The pigments were executed on a tempera layer; such as Arabic gum, gelatine, egg white and beeswax (Boxall 1978, Lucas 1962). The mostly employed pigments in Egyptian mural paintings were ochres, smoke black, carbon black, and lime white, gypsum, and, for blue a copper-based frit (Egyptian blue), azurite, for green malachite (Lucas 1962).

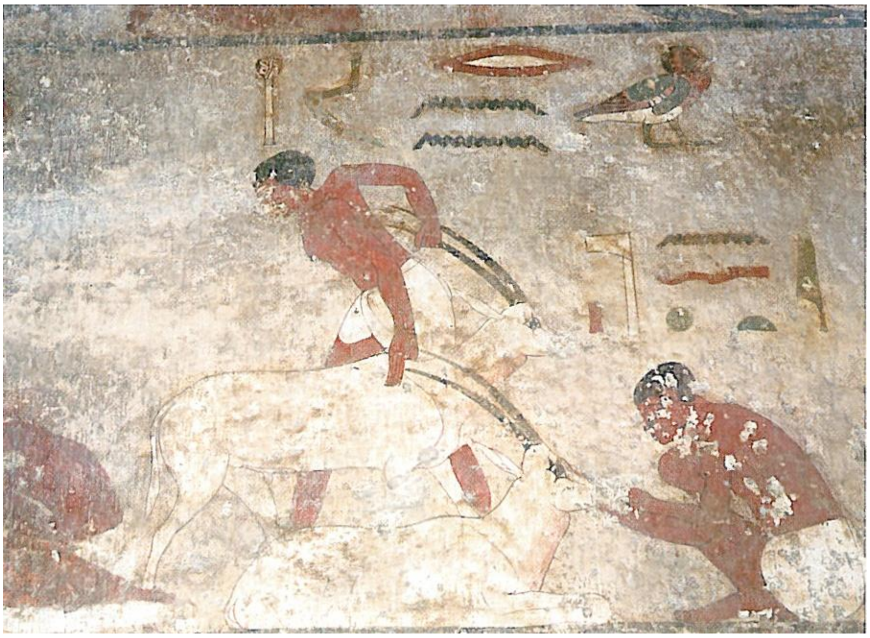


Figure 5. Detail of a wall painting at the Tomb of Khnumhotep, Beni Hasan (Egypt), *c.* 1890 B.C. (Source: Janson and Janson 2006)

In Mesopotamia, whilst the usage of clay as a traditional technology had been lasted from the Neolithic period, lime-based mortars and plaster appeared in earlier times, according to the discovery of a lime kiln that is dated to about 2,500 B.C. in Baghdad (Forbes 1965). The mural paintings in the Zimrli-Lim Palace at Mari, dated back to the beginning of the second millennium B.C., were determined to have been applied on the mud rendering and on a surface rendering of mud and chopped straw, then covered with a thin whitewash of plaster. The latter method was a traditional technique of Neolithic paintings of Çatal Höyük. The painting technique could not have been stated exactly, but tempera had been considered to be used most apparently (Parrot 1958). However, mural paintings of the Yarim-Lim Palace at Atchana (Alalakh) which are considered to have been almost concurrent were executed on a lime surface rendering. The rendering was composed of a layer of *arriccio* (rough plaster) in 4-8 mm thickness. The *arriccio* was applied directly onto the brick wall or onto a primary layer of clay rendering as to the case of the wall. Then the rendering was coated with a layer of pure lime (max. 1mm). In some cases earth or straw and even marble powder were added to the *arriccio* layer. The preliminary drawing of the painting was incised on the fresh plaster and the painting was applied in *fresco* technique. As to this, the mural paintings of the Yarim-Lim Palace are considered as the first known *fresco* paintings (Wooley 1955, Mora et al. 1984).

Mural paintings of Cretan and Mycenaean civilizations were influenced both aesthetically and technically from those of Egyptian, Mesopotamian and mostly Greek paintings because of the geographical adjacency in Mediterranean and Middle East. According to the studies on the samples from Knossos, there existed a layer of clay mixed with mud and rubble, a very thick surface rendering, executed in two layers of calcium carbonate with impurities (Figure 6). The analyses on the fragments taken from Tiryns demonstrated that these fragments have the same structure with the samples of Knossos. However, the first layer of rendering composed of carbonated lime, powdered sandstone was thicker; additionally the painting ground included only calcium carbonate. The painting technique was stated as *fresco* because of the presence of the guiding lines incised in the rendering, and horizontal joins on intonaco layer and non-existence of medium (Mora et al. 1984).

According to the study on the wall paintings in Knossos, four different techniques were stated: lime *fresco*, lime painting (a *secco*), lime caseinate (tempera) and a technique in which the pigments were executed on a fresh rendering of lime and gypsum (Eibner 1926). The pigments defined in Cretan mural paintings are carbonaceous schist (earth) for black, iron oxides (earth) for red and yellow, Egyptian frit (copper silicate and calcium), glaucophane, indigo and riebeckite for blue and malachite green (Filippakis et al. 1976, Mora et al. 1984, Brysbaert 2008).

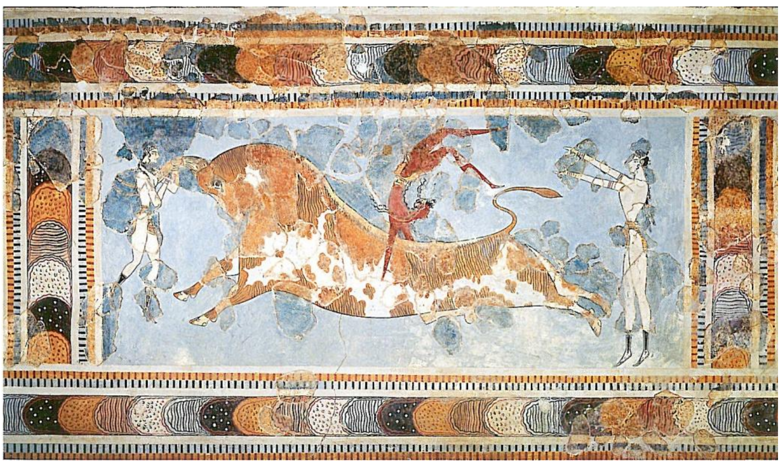


Figure 6. “*The Toreador Fresco”*, from the palace complex, Knossos (Crete), *c.* 1500 B.C. (Source: Janson and Janson 2006)

Greek paintings of the archaic period (800-480 B.C.) were developed from the *fresco* and *secco* paintings of Mycenaean and Cretan cultures. According to analyses on the mural paintings of Clazomenae, the pigments were applied on the lime plaster as *secco* and also Punic wax was executed for protection (Berger 1904, Mora et al. 1984). On the other hand, the wall paintings of a Greek fossa tomb at Paestum at the beginning of the fifth century B.C. were considered as *fresco* due to observations on the structure of the murals; they were executed on lime-based rendering and a thin lime-wash (Figure 7) (Mora et al. 1984).

The mural paintings of a tomb, dated to late fourth or early third century B.C, at Kazanlak in Bulgaria are important in terms of development towards the Roman technique. The *fresco* executed on the damp rendering on the base of the tomb had been exposed to polishing, preceding Hellenistic and Roman imitation marble (Mora et al. 1984).

Figure 7. "*Symposium"* scene in the Tomb of the Diver at Paestum, c. 480 B.C. (Source: Wikipedia 2010).

Certain imitations of marble of the First Style in the Hellenistic period by final polishing were replaced by the development of illusionism in the Second Style in the Roman period. Giving the wall a mirror-like quality, prescribed by Vitruvius as a new aesthetic approach, was achieved by the general use and systematic refinement of polishing technique in Roman *fresco*es. The rise of this *fresco* technique in the Roman paintings of the later Republic led to diminishing the use of the tempera technique; however, it was not totally given up (Mora et al. 1984). Wall painting techniques in

Roman period were defined by Vitruvius in his Book VII of *De Architectura* and also by Pliny in his book of *Historia Naturalis* in that era.

Rigorous studies on the art works at Rome, Pompeii and Herculaneum determined the procedure of the Roman painting (Figure 8). The wall surface was covered with the rough rendering layer, *arriccio* of lime and sand or of lime and pozzolana, and then the *sinopia* or a full-size sketch is drawn on the *arriccio*, if the painting is applied on the fresh *intonaco.* The finer lime-based rendering layer, *intonaco*, can be executed in two or three layers. After the pigments of ground tones were brushed on the damp rendering, first polishing was carried out. Afterwards the superposed decoration was executed in *fresco*, with the pigments mixed with water or lime-milk and a clay such as kaolin. Another polishing can be carried out; besides this, the superposed decorations can only be polished afterwards (Mora et al. 1984).

The mostly used binding mediums in Roman mural paintings were beeswax, egg, gum, resin, and vegetable and animal oils (Laurie 1910). The widely used pigments were yellow and red ochres, *terre verte* (green earth), sienna and umber, chalk, gypsum, lime, blue and green copper ores, cinnabar, orpiment, white lead, charcoal black, bone black, purple dye of murex, indigo, ultramarine from lapis lazuli (Laurie 1910, Vitruvius 1960).

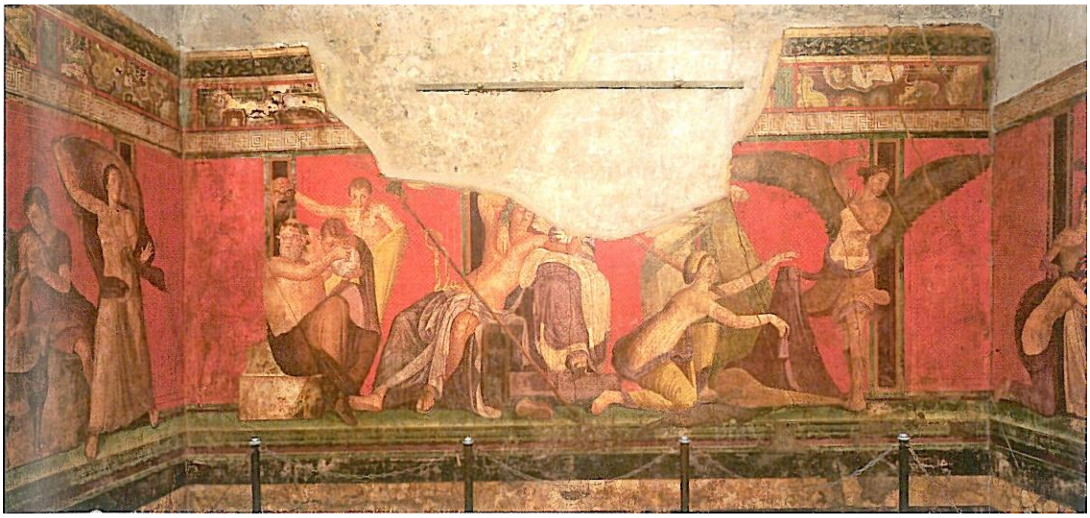


Figure 8. "*Scenes of a Dionysiac Mystery Cult"*, Mural Frieze, *c.* 50 B.C., Villa of the Mysteries, Pompeii (Italy) (Source: Janson and Janson 2006).

The classical Roman painting technique was simplified during the Late Empire. The four- layered rendering structure of Roman wall paintings was reduced to two layers. A new aesthetic value appeared in this period; thus, polishing technique also abandoned in *fresco*es of the Middle Ages (Mora et al. 1984). According to a text in the manuscript of Lucca, dated to eighth century A.D., colours were executed without any binding medium and on this wise in *fresco* in walls, with wax on wood, and with fish glue on parchment (Winfield 1968).

According to the examinations of the works and the texts from that era, renderings of Byzantine wall paintings (Figure 9) consisted of two layers, *arriccio* (rough plaster) and *intonaco* (fine plaster). The main constituent of the renderings was lime that was mixed with sand or marble dust or sometimes broken-up brick fragments. Byzantine renderings differ from Roman and western renderings in that they also contain straw, chaff, or chopped hog bristles, succeeding the oriental tradition of clay renderings (Winfield 1968, Mora et al. 1984). The *arriccio* on a characteristic brick wall of Byzantine period was applied much thicker as brick walls absorb more moisture. In Byzantine mural painting technique, after the *intonaco* layer was laid in horizontal registers, *pontates*, the Byzantine zographs (painters) did the sketch, the *sinopia*. And then the illuminations were executed with different pigments generally mixed with lime milk on the fresh plaster. However, the faces and the flesh parts of the figures were executed in *al secco* (Jeffrey 2008).

The pigments used were mostly natural substances and minerals; so that lime was used for white, charcoal and carbon black for black, azurite and rarely lapis lazuli for blue, terre-verte or malachite for green, iron oxides, caput mortuum, cinnabar, minium, and umber for reddish brown. Gilding of the haloes and nimbuses were made with gold leaf on incised lines of them (Jeffrey 2008). According to the traditional Byzantine technique of wall painting, colours were stratified one above the other. *Proplasmos*, the ground paint layer, was the base for overlaying gradations; over the *proplasmos*, outlines (*grapsimata*) and highlights (*fotismata*) were painted. And then drawing and sense of depth were processed through shadings (outlines and tinnings). Highlights and gradations were rendered by mixing white pigment (commonly lime white) with the other pigment, which was the principle component of the ground colour (Daniilia et al. 2000).

In Byzantine period, mural painting techniques varied with respect to different regions of the empire. Coptic wall paintings of Nubia, the region at the south of Egypt, were applied by Christian artists following the ancient Egyptian traditional tempera technique on a clay-straw based plaster coated with a thin kaolin wash. In Ethiopia, another periphery region of the empire, analogous tempera technique to the wall paintings of Coptic Nubia was executed by using local materials. On the other hand, three different painting techniques were executed in the wall paintings of the rock-hewn churches of Cappadocia region. The first technique was applying the pigments directly to the cut-rock surface. In the second method, a more popular method, the pigments were executed on two-layered lime-based renderings (*arriccio* and *intonaco*) in according to the classic Byzantine fresco painting. The third method was fabricating the painting in tempera on a gypsum rendering (Mora et al. 1984).

Moldavian painters provided reinforcement of pigments by admixing the pigments with both lime and milk or casein together. In Russia, mural paintings were refined stylistically. Since, fresco technique did not supply the needs of new sophisticated paintings, execution of completing a *secco* was improved (Mora et al. 1984).

Figure 9. "*The Anastasis*" fresco in the parekklesion of the Chora Church (Kariye Camii), İstanbul (Turkey), *c.* 1310-1320 .(Source: Janson and Janson 2006).

Wall painting technique in Romanesque period in Western Europe was originated from the Byzantine technique. *Fresco* painting was mostly used technique almost everywhere (Figure 10). Generally lime and also rarely tempera was used for finishing on the *fresco*es, as in the Middle Ages and in the Byzantine world (Mora et al. 1984). Whereas incised drawings were frequent in Byzantine works, they disappeared in Romanesque mural paintings. Besides this, an intermediary phase was developed between the phase of construction lines attesting to the registers and the axes of symmetry and the preparatory drawing in the mid-twelfth century. In this phase geometric diagrams of the figures were drawn (Mora et al. 1984). Pierre de Saint Audemar, a French author, stated that oil could be used with white and green, and gum could be used for minium in the twelfth century (Eastlake 1960).

Romanesque mural paintings, in contrast to Byzantine paintings, were frequently embellished with reliefs in different techniques. These reliefs have been one of the typical features of the late Romanesque, especially in German Zackenstil. In this period a technique of pure *fresco* painting where the modelling of form was accomplished by applying colours in gradations was developed (Bentchev 1980). The inorganic binders of *secco* paintings revealed a translucent effect, unlike lime. The general use and improvement of these techniques at the end of the thirteenth century and at the beginning of fourteenth century is identified with the Gothic rise (Mora et al. 1984).

Figure 10. Detail of painting on the nave vault in St.-Savin-sur-Gartempe, France, early twelfth century (Source: Janson and Janson 2006).

The aesthetic problems of the Gothic art brought about the new techniques in mural paintings and the rise of painting in oils through thirteenth century. According to texts from the 13th century onwards, the most remarkable development was the increasing importance in oil use in mural paintings. Whereas the oil was an important content in paintings in northern Europe, painting in oils was an unusual technique in southern Europe in the fourteenth century. By the establishment of stained glass in Gothic architecture in northern Europe, the solid walls of Romanesque style were replaced with a translucent membrane. Translucence became also a basic principle for paintings; therefore a technique of using glazes developed. However, in Italy the new concept of forming perspectival and formal structure in architecture had promoted the wall plane a function of relating architectural space to pictorial space (Figure 11) (Mora et al. 1984).

Several manuscripts from Gothic Europe mention the preparation of colours, the variety of binders such as parchment glue, oil, and the techniques of gilding and varnishing of the paintings (Mora et al. 1984).

According to the studies on the mural paintings of the church of St. Cecilia, the ground tones were applied on the preparatory drawing in *fresco* technique as to Romanesque tradition. However, there occurred a second layer executed in *secco*- with an undetermined binder- in which modelling was acquired by the gradations in the glazes (Bentchev 1980, Mora et al. 1984).

The renderings of the wall paintings of St. Stephen Chapel in Westminster Palace, dated to 1350, are composed of lime carbonate (or chalk with an undetermined binder). Over this mixture, there is a double priming layer that consisted of a layer of red-orange minium and a layer of lead white. The pigments, excluding reds, were executed in oil (Van Geersdaele and Goldworthy 1978, Mora et al. 1984).

Figure 11. "*The Lamentation"*, fresco by Giotto in the Arena (Scrovegni) Chapel, Padua (Italy), 1305-1306 (Source: Janson and Janson 2006).

Trecento mural paintings, rooted in traditional Byzantine technique, had been developed to the new demands of artistic creation and style at the beginning of the Renaissance art in the fourteenth century. Complex and elaborate compositions of the new style had involved the development of the *sinopia* as the first monumental sketch drawn *in situ* on the *arriccio*, or directly on the wall (Mora et al. 1984). Besides this, modelling and excessive individualization in Renaissance paintings entailed more time and remarkably restricted surface that would be applied a *fresco*. Because the artists demanded a smooth, luminous and transparent surface, as in tempera on a panel, for modelling, they generally opted for pure *fresco* technique, rather than traditional lime painting technique. In the case of necessity of completing the painting a *secco*, egg tempera was used as a binder. Henceforth, the surface carried out a *fresco* each day reduced and the *sinopia* became significant. This process became popular in Trecento art (Mora et al. 1984).

The artists of the Trecento occasionally used tempera and oil on a dry wall. According to Cennini, the mostly used binders were egg-white and yolk, sometimes mixed with 'cuttings of fig sprouts' for a *secco*, and a tempera *verdaccio* for oil painting. Tempera and oil enabled the application of several pigments, which cannot be used in *fresco* painting, such as orpiment, cinnabar, azurite, minium, verdigris, lac and lead white, instead of *bianco di San Giovanni* (powdered lime carbonate) (Cennini 1960, Mora et al. 1984).

Complex and elaborate compositions of the Ouattrocento art (Renaissance) during fifteenth century were improved by the principles of perspective and proportion. These compositions entailed the practice of drawing small-scale preliminary sketch on paper. Transposing of this sketch to full-scale cartoons on the fresh *intonaco* with a pointed instrument or pressing the lines on paper, was achieved by using a square grid to make enlarging. Henceforth, the *sinopia* became to have been replaced by these methods of drawing in this century, since the cartoon encompassed the whole composition (Mora et al. 1984).

Leonardo da Vinci, one of the most important pioneers of the Renaissance art in the sixteenth century, used oil in his famous paintings; the Battle of Anghari in the Palazzo Vecchio and Last Supper at Sta Maria delle Grazie (Figure 12) (Mora et al. 1984). As he considered that oil painting provided the achievement of the execution of the soft modelling to *sfurnato*, the technique explored by him, and the rich range of densities and transparencies he demanded (Mora et al. 1984). Oil painting technique was the most adequate technique for his manner of working, because Vinci demanded for continual revisions and corrections with long pauses. However, Michelangelo stayed loyal to the pure *fresco* technique of Ouattrocento (Figure 13). Therefore, Michelangelo delimited his palette to pigments which were appropriate for using in *fresco*, such as iron oxides, clayey silicates, iron silicates, aluminium silicates, and carbonated calcium hydroxide. Besides this, he occasionally used pigments applied *a secco*, and he preferred mixing with an organic binder instead of water as in *fresco* painting (Gabrielli 1987, Colalucci 1987). On the other hand, Raphael perfected the *fresco* technique in the manner of satisfying the new aesthetic requirements at that era (Mora et al. 1984).

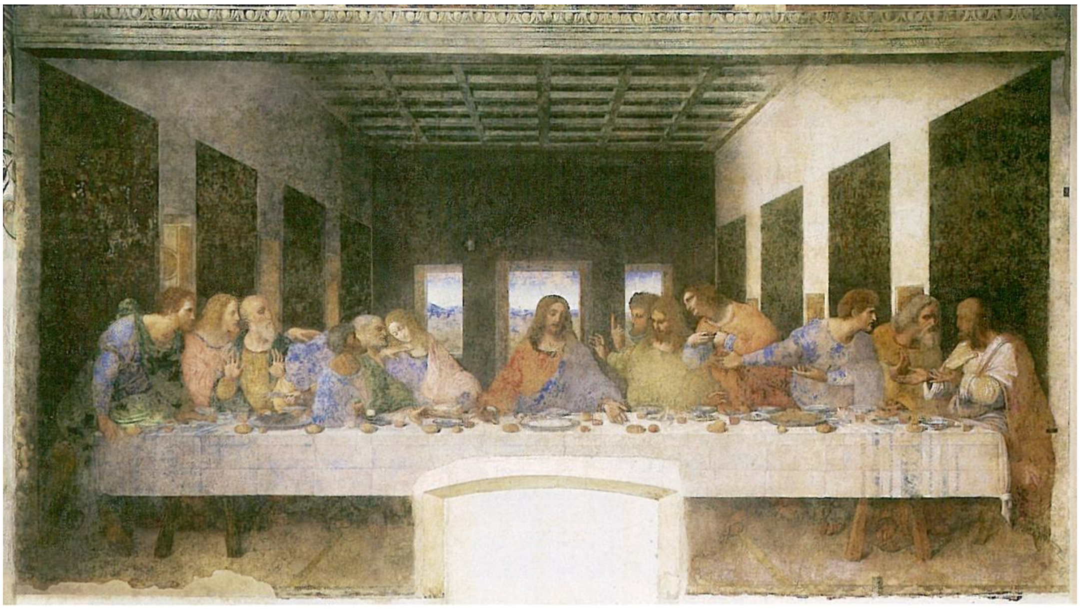


Figure 12. "*The Last Supper"*, Convent of Sta. Maria delle Grazie, Milan (Italy), 1498 (Source: Hartt and Wilkins 2006).

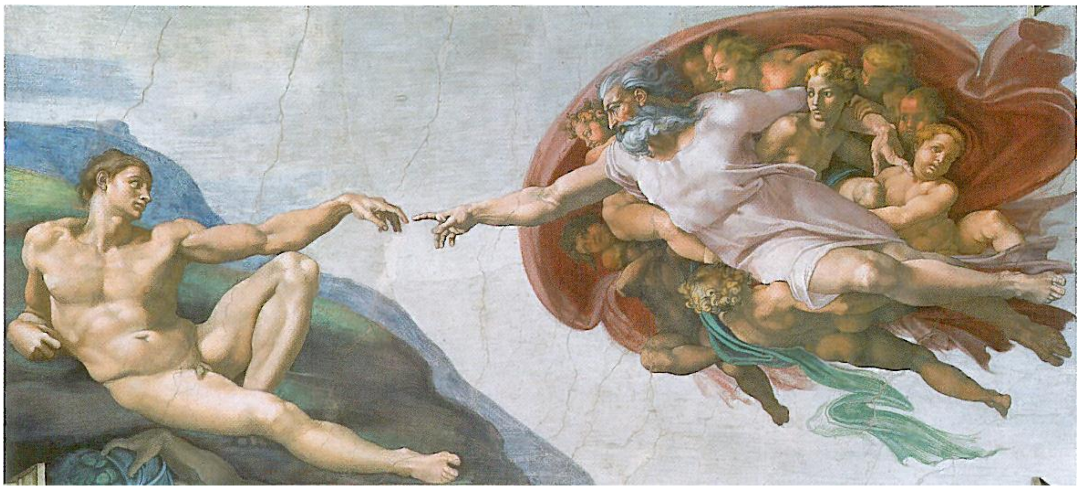


Figure 13. Detail of fresco "*The Creation of Adam*" by Michelangelo on the ceiling of Sistine Chapel, Vatican City, 1508-1512 (Source: Janson and Janson 2006).

Venetian *fresco* technique was promoted in order to make the same effects of popular canvas painting by the use of a special rougher rendering, called *pastellone,* (constituted of crushed brick) and a freer brushing technique (Muraro 1960). Oil painting was becoming prevalent simultaneously, owing to the ability of creating the analogous effects with canvas and panel paintings on walls. Thus, Mannerist and Roman *fresco*s, attaining the dense texture feature of oil paintings by covering with impastos, declined to be reduced as they had none brilliance nor chromatic richness, like in oil paintings (Mora et al. 1984).

The Mannerists artists uniformed the features of both the Michelangelesque concept of the *fresco* and the new pictorial possibilities of oil in the same composition in a sophisticated manner. Thus, two different levels of reality or presence in the image were achieved. Sebastiano del Piambo carried out the Flagellation in the chapel of S. Peitro in Montorio in this method; he applied the altar image in oil as a painting on canvas on paler *fresco* decoration to emphasize the figure (Mora et al. 1984).

Vasari depicted elaborately the different procedures of painting in oil on a dry wall. However, he rapidly outlined a tempera technique; as to this the dry *intonaco* is covered with two layers of hot glue, and then the painting mixed with the same glue is executed. Although Vasari considered *fresco* as the most popular style, the execution of *secco* techniques became increasingly widespread by the artists from the middle of the sixteenth century onwards (Vasari 1906, Mora et al. 1984).

The advance of perspective yielded the prevalent use of cartoons. The detailed cartoons, made of square sheets of paper glued together and then glued to the wall along the edges *in situ*, supplanted the *sinopia* during the sixteenth century (Mora et al. 1984).

The techniques of dots and hatching were carried out by several artists in order to prosper the texture of *fresco* painting, in comparison with painting on panel or canvas towards the end of the sixteenth century.

Baroque mural paintings were depicted in several texts by Andrea Pozzo, Martin Knoller, and G.H. Werner in the seventeenth and eighteenth centuries. In these texts, preparation of the renderings for *fresco*, execution of the preparatory drawing, priming layers, and paint layers were illustrated in detail. The cartoons, as in the sixteenth century, were used for the transfer of the composition, constituted of complex Baroque forms to the fresh plaster (Mora et al. 1984).

Baroque painters used rough surface rendering in *fresco* paintings in order to implement varying densities of paint and vibrating effect of tones, as in the Venetian oil paintings (Figure 14). Baroque *fresco* differentiated by means of the surface texture of the rendering, the method of applying pigments, and the occasional addition of lime. Pigments were brushed as an opaque mass and allowed impastos of extremely diverse thickness, as in oil paintings (Pozzo 1758, Mora et al. 1984).

Figure 14. "*Aurora"*, ceiling fresco by Guercino in the Villa Rudovisi, Rome (Italy), 1621-1623 (Source: Janson and Janson 2006).

Lime-fresco technique was in use in the late sixteenth century in Italy, as a revival of a Romanesque and Gothic technique, and this technique was also popular in eighteenth century in Europe. On the other hand, Pozzo claimed that painting a *secco* was common in Rome in his time. According to him, during the application, the paint was executed on a glue and gesso rendering on a fresh *intonaco* (Pozzo 1758, Mora et al. 1984).

Caravaggio, a Baroque painter, tented to oil painting on dry *intonaco*, instead of *fresco* painting, owing to inadequacy in the terms of improving depth and density in the composition (Zandri 1969, Mora et al. 1984).

Fresco painting in Italian manner was widespread in central Europe in the seventeenth century. However, at that time, Baroque artists in France renounced totally the *fresco*; rather than that, they developed the technique of painting in oil on a canvas, and then they glued the painting to the wall with an adhesive, called *maroufle*. In the seventeenth century and at the beginning of the nineteenth century, the adhesives which had the features of rapid-drying and resistant to humidity developed (Mora et al. 1984).

At the second half of the eighteenth century, the new concept of 'representative illusionism' replaced perspective as the structural principle of the form, and interior converted into a make-believe exterior (Mora et al. 1984). As *fresco* could not provided the aesthetic requirements of the new concept, it was replaced by tempera and painting on cloth in the last third of the eighteenth century. On the other hand, several painters of the *Kirchenmaler* of central Europe and the Orthodox painters of the Balkans lasted the tradition of *fresco* in the nineteenth century. The monumental art came into prominence again with Neo-classism, therefore wall paintings executed vastly in various experimental and individual techniques, instead of Baroque *fresco* technique. The basic binders used were glue, casein, oil and wax (Mora et al. 1984).

In contrast to the attempts for revival of *fresco* tradition, a vast production of nineteenth century mural paintings were carried out a *secco*, either in tempera (usually glue or casein) or in oil. Furthermore, the technique of *marouflage* from Baroque painting tradition in France was used by Delacroix at Bibliothéque du Sénat (Vibert and Serullaz 1963, Mora et al. 1984).

At the beginning of the twentieth century, in Europe, the decorative style of *Liberty* or *Art nouveau* demanded techniques from canvas painting and the applied arts that revived gilding, mosaic and ceramic. However, traditional techniques could not be carried out properly owing to vanishing of required artistic skill and use of new-unknown- synthetic commercial products (Mora et al. 1984).

The artists of the New Mexican School provided 'a last renaissance of *fresco* painting' in 1920s. Whereas Diego Rivera followed the technique described by Cennino Cennini, the younger Mexican muralists gave up the tradition by using synthetic resins, acrylic or vinyl, on various supports: canvas, masonite, aluminium, celotex or even metal relief (Rodriguez 1967, Mora et al. 1984).

1.2. Wall Painting Techniques: *Lime-secco* Painting Technique

Mural paintings are examined as to application techniques in two groups: *Fresco* and *Secco*.

In *fresco* technique, painting is executed on wet plaster. The pigment, after being mixed with pure water is executed on the surface of the rendering or on whitewash with a lime base. This technique is described as *fresco puro* by Cennino Cennini (Cennini 1960). The lime [calcium hydroxide-$Ca(OH)_2$] included in the plaster ground moves towards the surface of the painting, and then it reacts with carbon dioxide (CO_2) in the air as water (H_2O) evaporates. Hence calcium carbonate ($CaCO_3$) is formed on the painting surface and the pigment is fixed by this carbonization process. Chiefly earthen and mineral pigments are used in *fresco* technique (Daniilia et al. 2007).

The pigment can be also applied after mixing with lime water or milk of lime. This technique is called as *lime-fresco* painting. Moreover, the painting can be executed with the addition of tempera medium, like casein on the fresh plaster (Mora et al. 1984).

Vitruvius and Pliny stated that *fresco* paintings had been fabricated using pigments mixed only with water or lime milk; additionally, certain pigments necessitated the use of organic media, such as glue, gum, egg, honey and milk for binding purposes (Pliny 1977, Vitruvius 1960).

Mural paintings made in *secco* technique are the paintings executed on dry plaster or whitewash. The pigment is brushed after being mixed with a medium which enables fixation of pigment. Painting with lime is a prevalent technique a *secco*. The pigment mixed with milk of lime is implemented onto the surface of dry rendering, previously wetted to increase adherence. The lime works as a binder in this technique (Mora et al. 1984).

Besides painting with lime milk, the other main types of *secco* are tempera and oil. In tempera technique, the pigment is brushed by being blended with a medium; such as egg, casein, animal glue, resin, wax and certain vegetable gums. The binder promotes fixation of the pigment as it dries. Oils, such as linseed oil and poppy-seed oil, are also used as binders in mural paintings, besides in paintings on panels and canvases (Mora et al. 1984).

In some cases, two or more different techniques were combined in order to assure certain effects and to provide for the act of certain pigments. For instance, a *fresco* painting in which preparatory drawing, the basic tones, and the finishing of the certain parts was worked up; thus it could be terminated in *secco*, especially for blues or green and certain shades, highlights, and corrections (Mora et al. 1984).

Theophilus highlighted the use of lime as a binding medium in wall painting techniques in any case in Byzantine art (Theophilus 1979). At the same time, Dionysios of Fourna advocated white lime as a binding medium for painting on Byzantine *fresco*. However, as to dry plaster painting, he offered different binders, such as gum, whole egg, egg white, egg yolk, glue, honey, garlic juice, resin, and wax (Dionysios of Fourna 1996).

In Byzantine mural paintings, addition of lime to the pigments for completion of *pure fresco* painting provides extension of the drying time and allows more time for execution. Besides this, in *lime-fresco* technique lime milk, which is mixed with the pigments as a binding medium is executed on the damp rendering, provides a greasy transparency and an unctuous character, which remains after drying. However, when pigments, mixed with lime milk are applied on a nearly dry rendering, lime milk provides an opaque, whitish tonality, like in gouache. Lime use in paintings implements also a play of densities and impastos. The pigments could be lightened by adding lime, which promotes their covering power and also provides different hues. Thus, use of lime generally achieved a more opaque quality in the fourteenth century paintings of the Paleologue era. In this era, the formal complexity of the paintings required more time for execution of more detailed and more sophisticated compositions; so incised preparatory drawing improved. This method was established in the early Middle Ages, and it became much more sophisticated in medieval Byzantine painting due to developing of the complexity of the image (Mora et al. 1984).

Recent scholar investigations on wall paintings have revealed that lime use (or calcite) as a white pigment and a binder in the paint layers provided resistance and stability for the paint layers of the wall paintings (Daniilia et al. 2007).

Besides this, Theophilus stated in his book explicitly the aesthetic reason for addition of lime in *fresco* technique; as advance of the lustre of the ochre (Theophilus 1979). *Fresco* technique was the basic principle almost everywhere; and it was generally completed in *lime-secco* technique, as in the early Christian and Byzantine art or occasionally with tempera (Mora et al. 1984).

Cennini stated the lime to be the most suitable binding medium for *fresco* paintings at the beginning of Renaissance period, and he also identified terminating on dry plaster by using different binders, such as whole egg, egg yolk, and glue (Cennini 1960).

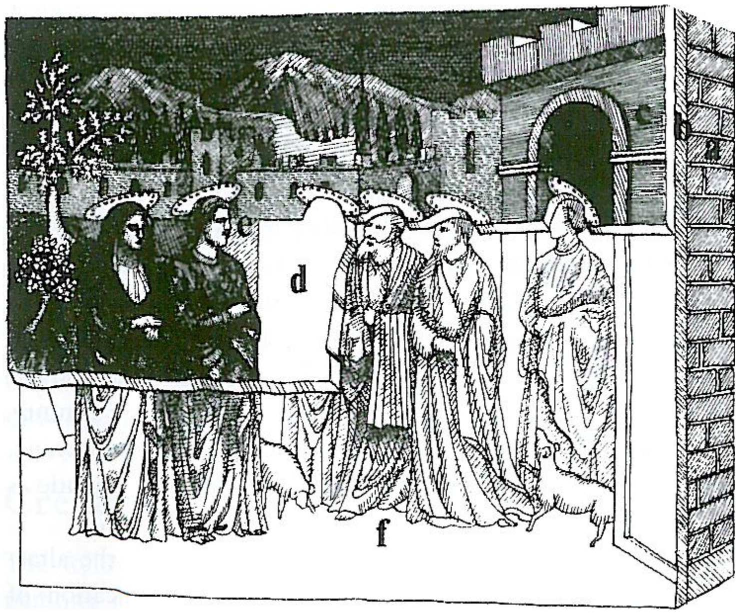


Figure 15. Execution process of fresco painting; a: masonry wall support, b: *arriccio* (rough plaster), c: painted *intonaco* (fine plaster), d: *giornata* of new *intonaco* ready for colour, e: previous day's *giornata*, f: underdrawing in *sinopia* on *arriccio* layer (Source: Hartt et al. 2006).

1.3. Identification of Painting Techniques

Contemporary scientific studies on mural paintings have revealed the suitable methods and technologies for identification of used materials and painting techniques. In this context, macroscopic and microscopic examinations on paint layers have been carried out. Knowledge acquired from observations *in situ* and mineralogical and microchemical analyses on cross-sections for a stratigraphic examination in collaboration with surface of paintings have been evaluated in the case of comparative studies on former investigations on analogous mural paintings (Mora et al. 1984).

Within the scholar studies of technical knowledge about the mural paintings, macroscopic study, as a non-destructive way of investigating the material and the painting technique on the painted surfaces have revealed several features; such as the rough surface texture, marks of trowelling and floating the rendering surface with a stone or other tool, characteristic joins of *pontate* and *giornate* identified under raking light source shining over the surface, string and incision lines of preliminary drawings of compositions, the modelling of the brushstrokes, the presence of very thick *impasto* and fingernail and fingertip impressions. As a preliminary general diagnosis, these features have been deciphered as indications of technique of *fresco* employed (Daniilia

2008a, Daniilia 2008b, Brysbaert 2008). However, as revealed by macroscopic investigations on certain mural paintings, development of fine cracks on the surface of paintings and formation of cupped flakes that is stemmed from shrinkage of a binding medium on drying have been considered as an indication of execution a *secco*. Besides, lime-use in wall paintings could be discerned as to granulated fabric of the surface and by its lustreless, gouache-like appearance that is more obvious when the plaster dried too quickly during application (Mora et al. 1984).

In order to verify this preliminary knowledge and to make a precise determination of the pictorial technique and materials, microscopic investigations have been carried out in most scientific studies on mural paintings. According to micro-stratigraphic examinations on polished cross-sections by polarize microscope, thick accumulation of pigments in the painting layer, diffusion of the paint penetrating into the underlying plaster have been betrayed as signifying painting on wet plaster (Mugnani et al. 2006, Daniilia et al. 2008a, Daniilia et al. 2007). Elsewhere, Mora asserted that penetration of pigments should not be evaluated always as an indication of *al fresco* technique; since this phenomenon may have resulted from inaccurate execution of owing over pressure or use of too soft rendering during execution. Besides this, he claimed that in fresco paintings, generally a conspicuous boundary of carbonated base existed between the plaster and painting layer (Mora et al 1984). However, in certain studies, the presence of the separation line developed from crystals of calcium carbonate between the plaster and the overlying paint layers has been documented as the execution of painting on dry plaster (Daniilia et al. 2007, Weber et al. 2009, Mugnani et al. 2006).

Microscopic examinations carried out by polarize microscope and electron microscope have been essential also in the phase of characterization of employed materials in mural paintings. In this context, pigments, binding mediums, their granule sizes and distribution could have been observed through polarize microscope examination. Moreover, by means of establishment of electron microprobe on paint layer and plaster, elemental composition of pigments and lime as binder and distribution of elements in depth from surface to rendering have been determined within many scholar studies (Hein et al. 2009, Ajò et al. 2004, Brysbaert 2008). In this method, heavy elements such as iron, magnesium could be identified; however, carbon and proteinaceous components indicating of a binding medium cannot be determined (Mora et al. 1984).

In the circumstances of being unsatisfactory of microscopic investigations, in order to achieve more reliable identification, pigments, binders, such as tempera, oil, egg/animal glue, resin, and other materials in painted plasters have been determined by means of microchemical analyses, of mineralogical examination with μFT-IR spectrometer, X-ray diffraction device (Daniilia et al. 2007, Ajò et al. 2004), energy dispersive X-ray fluorescence spectrometer (Hein et al. 2009), μRaman spectroscopy (Zucchiatti et al. 2004), gas chromatography-ion trap mass spectrometry (GC/MS), of principal component analysis (PCA) (Mugnani et al. 2006, Daniilia et al. 2007, Bianchin et al. 2008, Fiorin and Vigato 2007).

Contemporary analytical methods have facilitated identifying the techniques and materials employed in mural paintings. Empirically based scholar study have established rigorously the lost traditions of painting techniques and also continuity into the future.

1.4. Aim of the study

As mentioned before, wall paintings have been integral parts of the monuments and sites. Moreover, they have improved the historic, cultural, aesthetic, and architectural values of the monuments and sites they belong. Aesthetic, cultural, technical and material characteristics of the wall paintings should be revealed through scholar researches in an interdisciplinary approach.

In this respect, investigation for identification of material characteristics and painting techniques of wall paintings is an essential stage of conservation work.

This study has aimed at determining the material constituents and painting techniques of mural paintings in a Byzantine church uncovered in archaeological site of Kadıkalesi (Anaia). The study will guide the conservation works of the wall paintings in the case of evaluation of the course of preservation policy and opting for the most appropriate materials and methods if any intervention is needed. In the further phases of conservation works, other essential studies should be carried out thoroughly for the conservation of wall paintings of the church.

CHAPTER 2

GENERAL AND HISTORICAL INFORMATION ABOUT ANAIA AND THE CHURCH

2.1. Location

Kadıkalesi is an upstate castle situated at the northwest of Davutlar Village, a summerhouse development, in Kuşadası, Aydın. It is approximately 8 km from Kuşadası in Karaova plain (Akdeniz 2006) (Figure 16). Before Ottoman Empire period, Kadıkalesi had been named as Anaia, the name of which was originated from an Amazon who had died in this area (Cramer 1832).

The Citadel of Anaia was located opposite Samos Island (Cramer 1832). The harbour of Anaia, which is today under sea, was approximately 150m away from the coastline to the south-west of Kadıkalesi Mound (Akdeniz 2006). The fortress was erected on a 24-25 meter-high mount from the sea-level and, 250 meter from the sea for the purpose of defending the city and the harbour and controlling sea crossing in the twelfth century on a settlement of 11th-12th centuries of Byzantine era (Mercangöz and Doğer 2009) (Figure 17).

Figure 16. Location of Anaia (Kadıkalesi) (Source: Roma Tre University 2010).

Figure 17. Aerial photograph of Kadıkalesi Mound in 2005
(Source: The archives of Anaia Excavation 2010).

2.2. Historical Information about Kadıkalesi-Anaia

Scientific excavations and surface investigations which have been carried out from 2001 onwards and in historical site of Kadıkalesi-Anaia have demonstrated that the site had been settled before the construction date of the fortress and the site had been identified with the colonization of Samos in some ancient sources. The archaeological finds in the tumulus during the excavations have demonstrated that first settlement dated to Late Chalcolithic Age (4,000 B.C.) (or Neolihtic Age) (Akdeniz 2007). According to the excavations and drilling explorations, six archaeological strata have been determined in the Kadıkalesi tumulus (Figure 18) (Akdeniz 2007):

Stratum I- Islam-Byzantine (Anaia)

Stratum II- Ancient Greece-Roman Empire

Stratum III- Late Bronze Age (three phases)

Stratum IV- Middle Bronze Age

Stratum Va- Early Bronze Age III

Stratum Vb- Early Bronze Age II

Stratum Vc- Early Bronze Age I

Stratum VI- Late Chalcolithic Age

Majority of Mycenaean findings from the Late Bronze Age has indicated the existence of Mycenaean Civilization in the site in that era (Akdeniz 2007). Anaia City has been considered to have been an important destination for Hellenistic colonization, started in 1050 B.C. Furthermore, gravestones pointed out the existence of a temple of Hera in Anaia in Roman period (2nd-3rd centuries A.D.).

Christianity was accepted as official religion in Anaia in 4th century A.D., thus Anaia had been an episcopacy centre all through the Byzantine period (Mercangöz 2007).

During the drilling studies in 2006 excavation term, remnants of walls of a bastion were uncovered. These walls have been considered to have been erected before the existing Byzantine castle, by Comnenian Dynasty of Byzantine Empire in 12th century in order to defend this strategic coastal city and the harbour against Turk invasion (Mercangöz 2007). Anaia was promoted to archbishop centre in 13th century and became also a customs station of Byzantine Empire (Lascarids period) in Western Anatolia (Akdeniz 2006).

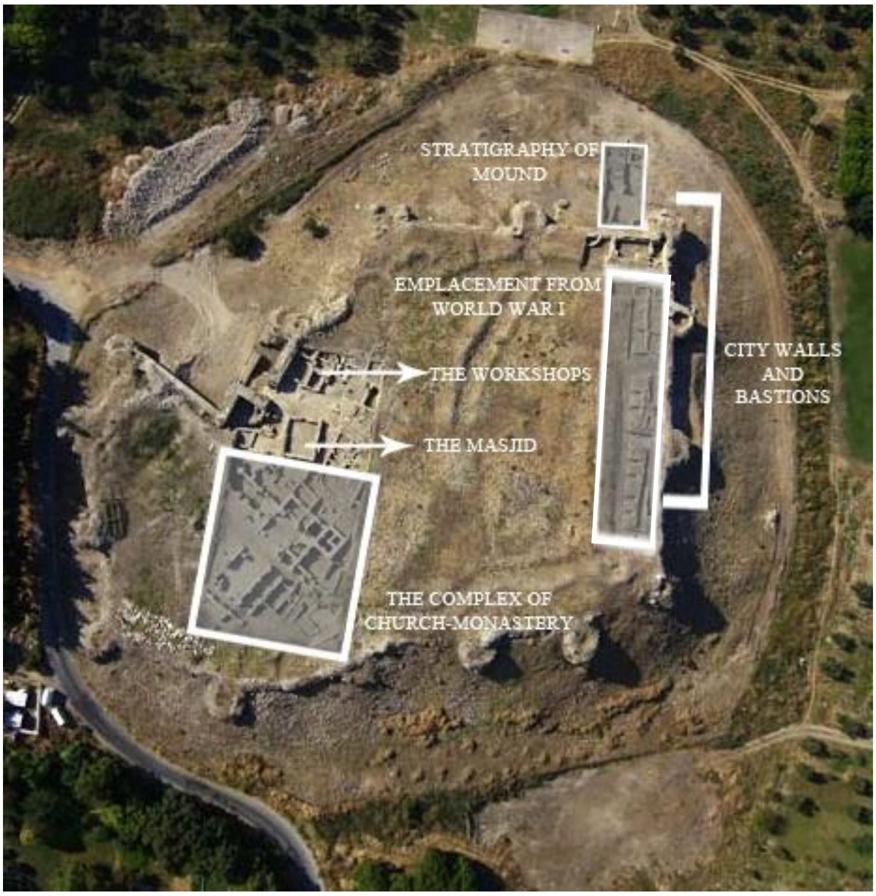


Figure 18. The structures which have been uncovered hitherto
(Source: The archives of Anaia Excavation 2010).

A monumental church-monastery complex was uncovered first in 2005 excavations; this edifice is considered to have been a foundation donated by Konstantinos IX Monomachos, the emperor (1042-1055), in 11th century. The complex is a magnificent edifice, competing with the huge buildings of Constantinapolis, with its monumental stone artworks and mural paintings (Mercangöz 2009) (Figure 19). However, the edifice could not be uncovered utterly due to detaching of mural paintings according as the unfavourable conditions under soil and over the earth. Thus, knowledge about the architectural characteristics of the church-monastery edifice has not been established yet.

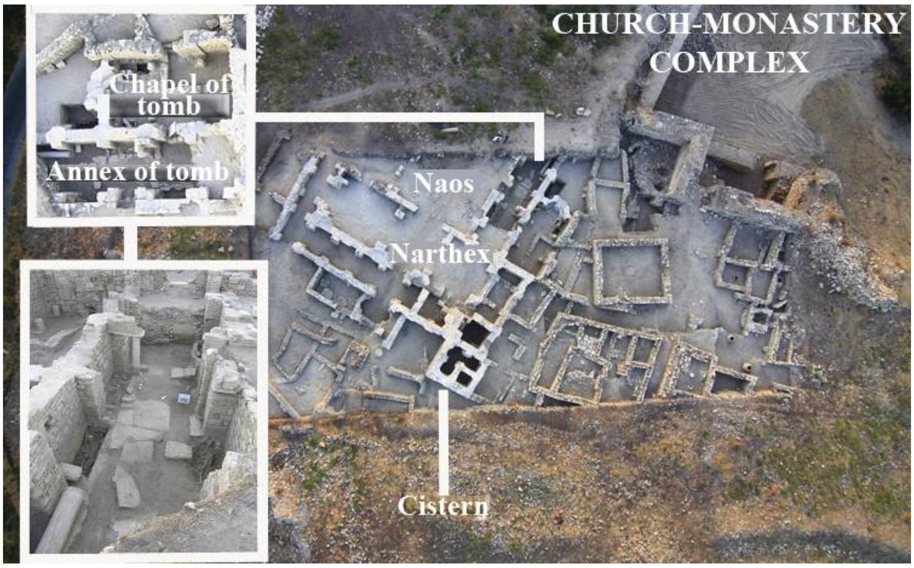


Figure 19. Location of the complex of church-monastery
(Source: The archives of Anai Excavation 2010).

The Byzantines left Anaia to Venetian and Genoese merchants for commercial purposes succeeding two treaties signed in 1261 (Heyd 1923). The Turks probably dominated the city after 1304. Anaia stayed under the government of Aydınoğulları Emirate through 14th century and passed to the governing of Ottoman Empire at the beginning of the 15th century. A masjid was uncovered at the south of the church, belonging to that period (Mercangöz 2009).

Inhabitants of Anaia are considered to have migrated further east to the ridges of the village of Soğucak (Anya) in an unknown date for various reasons, such as the rising of sea water, malaria, pirate attacks or security (Foss 1979).

CHAPTER 3

EXPERIMENTAL STUDY

In this work, wall paintings executed in the Byzantine church-monastery complex in Anaia were characterized in order to understand their application technique, basic physical, mineralogical, chemical and micro-structural properties.

3.1. Sampling

Fragments-in different sizes- of wall paintings that were found under earth during the excavations in Kadıkalesi were taken from the excavation depot of Ege University Art History Department with the permission of Zeynep Mercangöz, Prof. Dr., the head of Anaia excavation team (Figure 20, Figure 22). The samples were stored in polyethylene bags and labelled with abbreviations as to their pigments (Table 1).

The samples, which are mostly fragments of painted fine plasters (*intonaco*) layers, are thought to belong to wall paintings of ruined walls and vaults of the church.

There are also mural paintings in unfavourable environmental conditions on the surfaces of walls, arches, and apses. All of them have been detaching from the surfaces, and paints of some have been wiped away owing to the clays and moisture in earth (Figure 21).

Figure 20. General view of the church and the area that painted plaster samples were found.

a b

Figure 21. Photographs showing the present situations of wall paintings *in situ* (a: Painted plaster that has detached from the surface of the arch, b: Painted plaster that is stuck behind an additional wall).

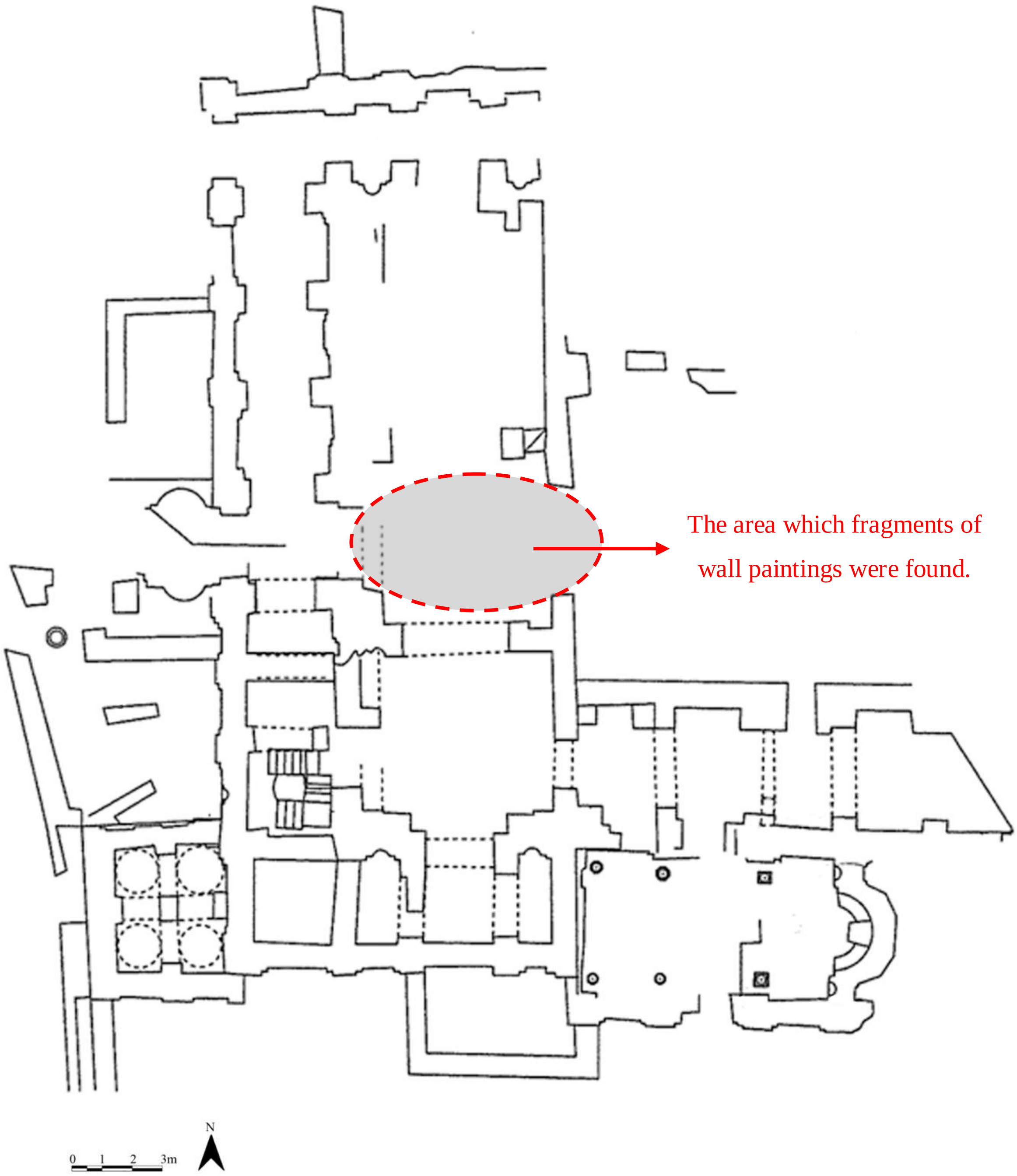
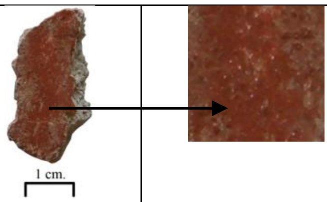
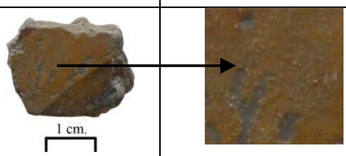


Figure 22. Plan drawing of the complex of church-monastery in 2006 excavations (Source: The archives of Anaia Excavation, 2009, Measured drawing by Seray AKIN and Elif GÜNGÖR KARABACAK).

Table 1. Definitions of the collected samples.

Plaster Samples	Sample Name	Sample Definition
	U-Fp	Unpainted fine plaster layer
Painted Plaster Samples		
	R-Fp	Red painted fine plaster
	B-Fp	Blue painted fine plaster
	Y-Fp	Yellow painted fine plaster
	G-Fp	Green painted fine plaster
	P-Fp	Purple painted fine plaster
	DB-Fp	Dark blue painted fine plaster

3.2. Experimental Methods

Samples were characterized in different laboratory tests in order to establish their basic characteristics.

In fine plaster (*intonaco*) layers, tests were applied to state basic physical properties – bulk density, porosity, raw material compositions and lime-aggregate ratios and particle size distribution of aggregates; and also mineralogical and chemical compositions and micro-structural properties by XRD, FT-IR SEM-EDS and TGA.

In paint layers, tests were carried out to determine mineralogical and chemical compositions and micro-structural properties of paints by XRD, FT-IR SEM-EDS, and Optical Microscopy.

3.2.1. Determination of Basic Physical Properties of Fine Plasters

The standard RILEM test methods were carried out in order to determine the bulk density and porosity of the plaster layers (RILEM 1980). Bulk density (gr/cm^3) is the ratio of the mass to its bulk volume. Porosity (%) is the ratio of the pore volume to the bulk volume of the sample.

All plaster samples were divided into two pieces and then they were dried in oven at 60°C for at least 24 hours in order to prevent their decomposition. The dried samples (M_{dry}) were weighed by a precision balance (AND HF-3000G) and then immersed in distilled water in beakers. The samples were put in the vacuum oven (Lab-Line 3608-6CE) and operated under low pressure in order to truly fill the fine pores with water. The plaster samples after being saturated with water, their saturated (Msat) and the hydrostatic weights (March) in distilled water were weighed by using the precision balance.

Densities and porosities of the samples were calculated by using the dry, saturated and hydrostatic weights in the following formula (RILEM 1980, Teutonico 1988).

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

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

(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)

3.2.2. Determination of Raw Material Compositions of Fine Plasters

Lime-aggregate ratio and particle size distribution of aggregates used in fine plasters were stated. In this procedure, two same plaster samples were dried in an oven at 60°C and weighed ($M_{samp.}$) by a precision balance (AND HF-3000G). Then, these samples were treated with dilute (5%) hydrochloric acid (HCl) (Jedrzejevska 1981, Middendorf and Knöfel 1990). Thus, all of the carbonated lime was implemented to have been dissolved by reacting with acid. Insoluble parts were filtered and washed with distilled water until all chlorine ions removed. Thus, the *intonaco* samples were provided for the purpose of the sieve analysis, the process of sieving through a series of sieves having the sieve sizes of 125 µm, 250 µm, 500 µm, 1180 µm by using an Retsch AS200 analytical sieve shaker.

3.2.3. Mineralogical and Chemical Compositions and Microstructural Properties of Fine Plasters

Mineralogical composition of lime plasters were determined by X-ray diffraction (XRD) analyses performed by Philips X-Pert Pro X-ray Diffractometer operating at 40 kV and 40 mA, using CuKα radiation in the 5-70º range with a scan speed of 1.6º per min. Powdered plaster samples with particle size less than 53µm were analyzed. The Fourier Transform Infra-Red (FT-IR) device was also employed in fine plaster samples to determine the mineralogical compositions of the plasters. The powdered plaster samples with particle size less than 53µm were then dispersed and further ground in some amount of KBr and pressed into pellets under about 10 tons/cm^2 pressure. Spectral measurements were carried out on a Perkin-Elmer System FT-IR Spectrum BX. Spectra were acquired between (4000-400) cm^{-1} and with 4 cm^{-1} resolution. All spectra were collected in absorbance mode. As background, the spectrum of the KBr pellet was used.

Chemical compositions and microstructural properties of painted plasters were stated by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The painted plaster samples were moulded in epoxy resin, ground and polished, in order to produce cross sections for examination under polarizing and scanning electron microscope. The *intonaco* layers and the paint layers could be examined at the same time in the course of analyses on the polished cross-sections.

The thermo gravimetric analysis (TGA) were carried out by Perkin Elmer Diamond TG/DTA in static nitrogen atmosphere in order to determine the amount of lime used in the production of fine plasters by observing the weight loss at the temperature range of 25-1000ºC with a heating rate of 10°C/min.

3.2.4. Mineralogical and Chemical Compositions and Microstructural Properties of Paints

Mineralogical compositions of the surfaces of painted plasters were analyzed by XRD device and FT-IR device. XRD analyses were carried out with X-ray diffraction (XRD) analyses performed by Philips X-Pert Pro X-ray Diffractometer operating at 40 kV and 40 mA, using CuKα radiation in the 5-70º range with a scan speed of 1.6º per min. In order to carry out FT-IR analyses the paint layers over fine plasters were scraped and these powdered samples with particle size less than 53 μm was then dispersed and further ground in some amount of KBr and pressed into pellets under about 10 tons/cm^2 pressure. Spectral measurements were carried out on a Perkin-Elmer System FT-IR Spectrum BX. Spectra were acquired between (4000-400)cm^{-1} with 4cm^{-1} resolution. All spectra were collected in absorbance mode. As background, the spectrum of the KBr pellet was used.

Chemical compositions and microstructural properties of paints were stated by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with X-ray Energy Disperse System (EDS). SEM-EDS were implemented on polished cross-sections, and paint surfaces. Additionally, powdered paint samples were treated with dilute (1%) hydrochloric acid (HCl) and washed with distilled water and injected to the filter paper in order to investigate the elemental composition of the pigments by SEM-EDS device.

The polished sections were also examined under the Leica DMI3000B Optical Microscope. This examination was mainly focused on the painting technique, micro-stratigraphy and thickness of paint layers and preparatory layers.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, basic physical properties, microstructural features, mineralogical and chemical compositions of painted plasters, painting layers and pigments used in the mural paintings of the church are demonstrated and evaluated; aiming to provide an important background for future studies. A series of standard analytical techniques was applied in the sense of extensive chemical and mineralogical examination. The analyses were focused on the identification of painting techniques and materials and the investigation of the micro-stratigraphy of the wall paintings.

4.1. Characteristics of the Painting Layers Applied on Fine Plaster

The wall supports of the church edifice were constructed with alternating series of brick and stone- mostly cut-stone work. The arches and the vaults were erected with brick work and mortars between them that are thicker than bricks in accordance with Byzantine traditions.

The painting layers were studied under the optic microscope and SEM in order to understand their painting techniques. Optic microscope and SEM studies indicated that painted plasters on the walls of the church are composed of a fine plaster layer and painting layer. SEM analysis indicated that the paintings were composed of lime as binding medium and pigments. The thickness of the painting layers varies approximately in the range of 10-70 µm (Figure 23).

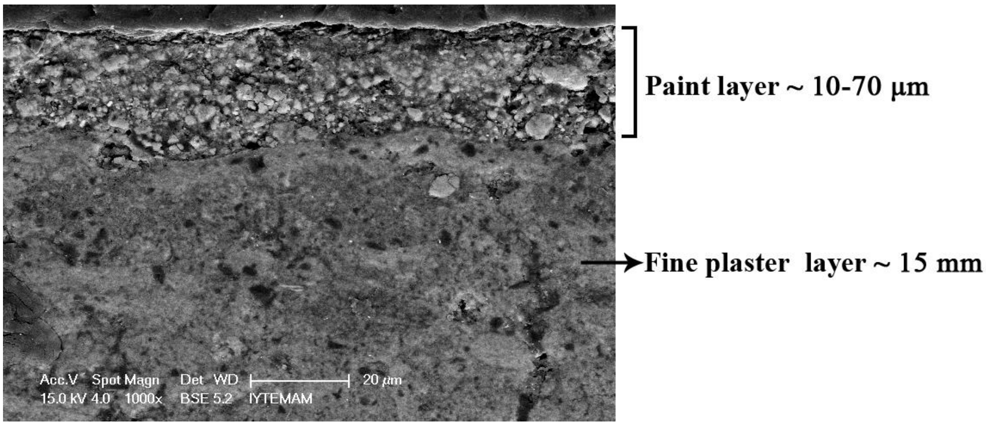


Figure 23. SE image of the painted plaster (yellow-coloured).

According to the test, lime is the principal and most probably the only binder used to fix the pigments. Most of the pigments chiefly contain iron oxides, as they are earth-based pigments with main components as sodium, magnesium, aluminium and silicon. Moreover, dolomite was identified due to use of dolomitic lime as binder in yellow, green, and purple paintings. In one of recent studies, it was determined that since shrinkage of dolomitic (magnesian) lime mortars is slow and uniform, it does not cause cracking (Chever et al. 2010). In the light of this knowledge, use of dolomitic lime as binder prevented crazing on the surface of the paintings (Figure 24) Moreover, the solubility of dolomitic lime is less than fat lime. Hence, it provided resistance and stability for the paint layers of the wall paintings.

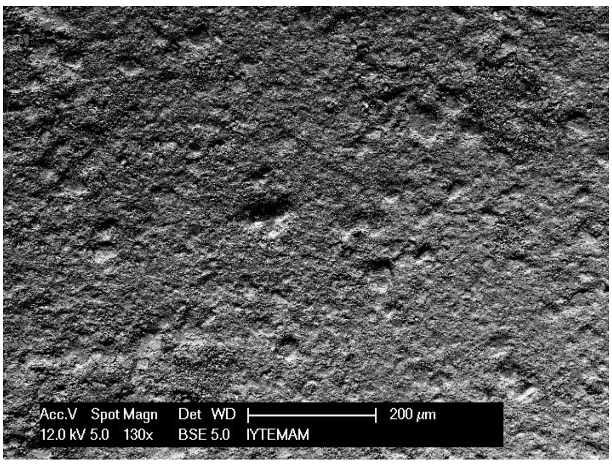


Figure 24. BSE image of surface of red painted plaster.

A collaborative analysis of SEM-EDS and optical microscope on samples' stratigraphy led to the conclusion that *lime-secco* technique of applying the colour layers was used (Figure 25). The boundary of carbonated lime between the paint layers and the fine plaster layers indicated that the *lime-secco* technique was applied for the construction of the investigated wall paintings fragments. Since *lime-secco* was executed properly, no formation of crazing and blistering were determined.

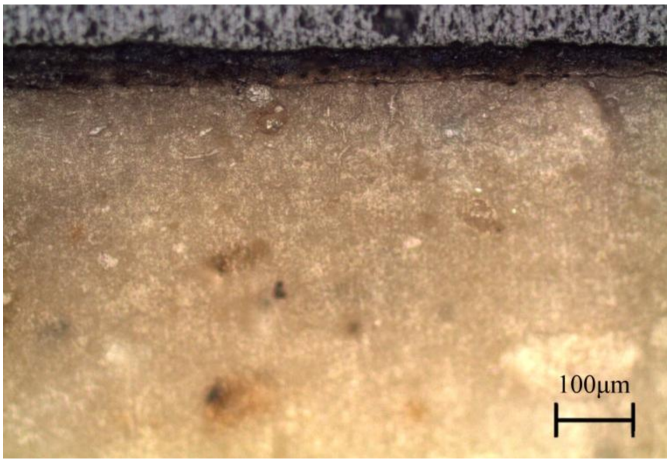


Figure 25. Optical microscope image of painted plaster (blue-coloured) executed in *lime-secco* technique.

The *fresco* technique is used for painting on damp lime-based plaster and the pigments are mixed with plain water or lime water, calcium hydroxide super-saturated solution. However, in the *lime-secco* technique, the pigments are mixed with lime water, as binder and then they are applied on dry lime-based plaster. Recent detailed studies of mural paintings in many early Christian and Byzantine monuments have attested the use of lime as binding medium (Mugnaini et al. 2006, Daniilia et al. 2007, Hein et al. 2009).

4.2. Basic Physical Properties of Fine Plasters

Macroscopic investigation of the wall paintings *in situ* in the case of excessive damage and detachment confirmed that the painted plasters existing still on the wall and the arch surfaces are consisted of two layers: rough plaster (arriccio) and fine plaster (intonaco). The thickness of the rough plaster which was applied over the wall structure is 2.5 cm in average.

Analyses of fragments of painted fine plasters (*intonaco*) have indicated that the thickness of the plasters ranges from 0.5 cm to 2 cm. The density values of the analyzed plasters vary between 1.06 g/cm^3 and 1.36 g/cm^3. Porosity values of the same samples are in the range of 27-61 % by volume. They can be defined as porous and low dense materials. These values were nearly similar to plasters and mortars which had been used in several Byzantine, Roman and Ottoman period buildings (Şerifaki et al. 2009, Aslan and Böke 2009).

4.3. Raw Material Compositions of Fine Plasters

Raw material compositions of the painted plasters were stated after several tests implementing binder-aggregate ratios and particle size distribution. According to these tests, the plaster samples are almost composed of pure lime with small amount of soil material. Similar raw material compositions were also used in production of renderings of many historic mural painting (Daniilia et al. 2007, Brysbaert 2008, Hein et al. 2009). Additionally, lime lumps were detected within the fine plasters, thus this revealed local and pressing production of the lime (Hein et al. 2009).

4.4. Mineralogical and Chemical Compositions and Microstructural Properties of Fine Plasters and Paints

Mineralogical and chemical compositions and microstructural properties of painted plaster (*intonaco*) samples were examined to state the painting technique, characteristics of original materials. This study will provide the required information in order to apply the most appropriate methods and materials for consolidation and cleaning works of the wall paintings.

4.4.1. Mineralogical and Chemical Compositions and Microstructural Properties of Fine Plasters

Mineralogical composition of fine plaster layers were determined by X-ray diffraction (XRD) and FT-IR. XRD patterns show that the plasters are basically composed of calcite and quartz (Figure 26). Calcite is stemmed from lime, and quartz from aggregates. FT-IR results supported the XRD results. The FT-IR spectrum of the plaster has shown CO_3□ bands due to calcite [2($CaCO_3$)] at 2513, 1795, 1442, 874, 713 cm^{-1} and Si-O bands due to quartz [3[SiO_2)] at 1079 cm^{-1} (Figure 27).

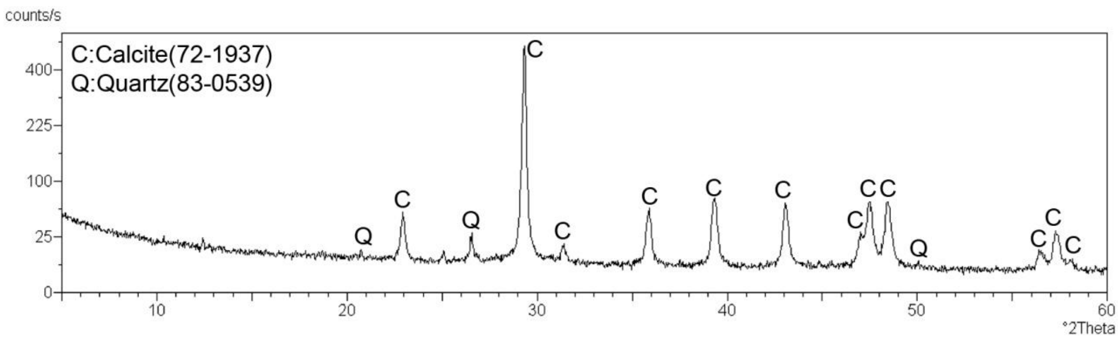


Figure 26. XRD pattern of fine plaster layer (*intonaco*).

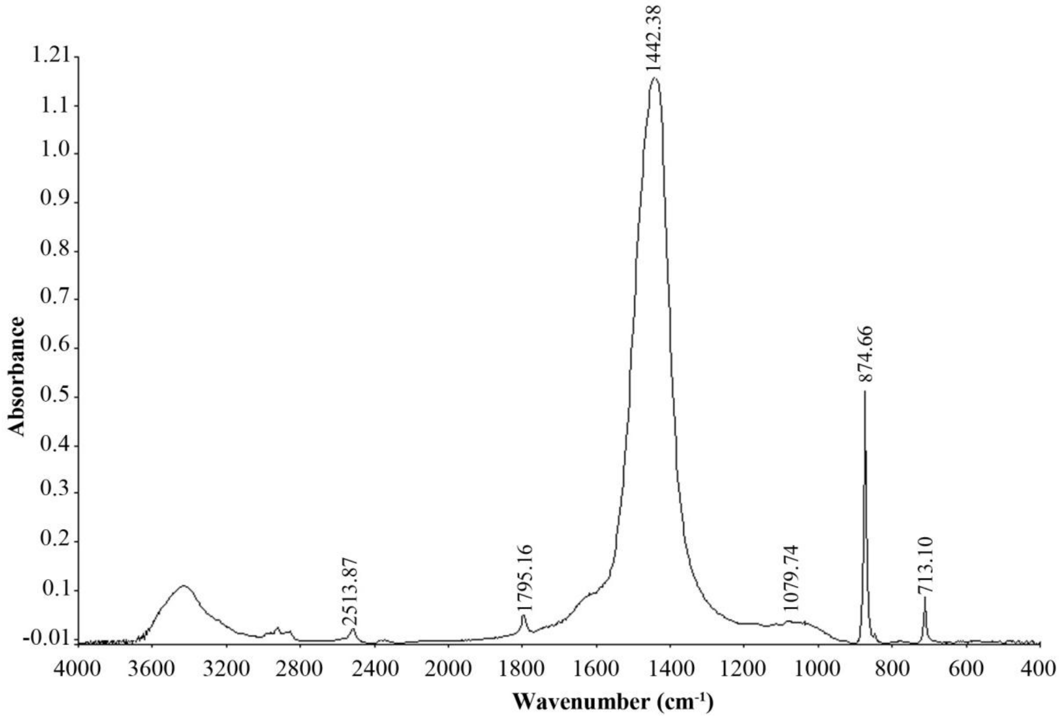
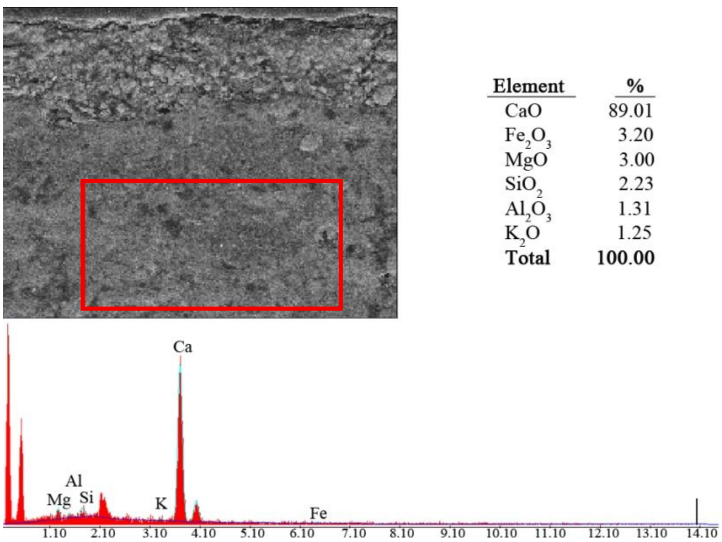


Figure 27. FT-IR spectrum of fine plaster layer (*intonaco*).

Chemical composition of the plaster layers was determined by SEM-EDS analyses. The SEM-EDS analyses for chemical composition revealed that the fine plaster layers consist of high amounts of calcium (Ca) due to use of pure lime (Figure 28).



Element	%
CaO	89.01
Fe_2O_3	3.20
MgO	3.00
SiO_2	2.23
Al_2O_3	1.31
K_2O	1.25
Total	**100.00**

Figure 28. SE image and EDX spectrum of the fine plaster (*intonaco*) of yellow painting.

Amount of lime used in the production of plasters was also determined by TGA by stating the weight loss observed in the range of 550-1000ºC. The percentage of weight loss was around 40% due to loss of CO_2 (Figure 29). According to this result, the lime used in fine plasters (*intonaco*) could be assessed to have been consisted of nearly 90% pure lime (Reaction 4.1).

$$CaCO_3\ (100)\ \text{-----------}\ CaO\ (56) + CO_2\ (44) \qquad (4.1)$$

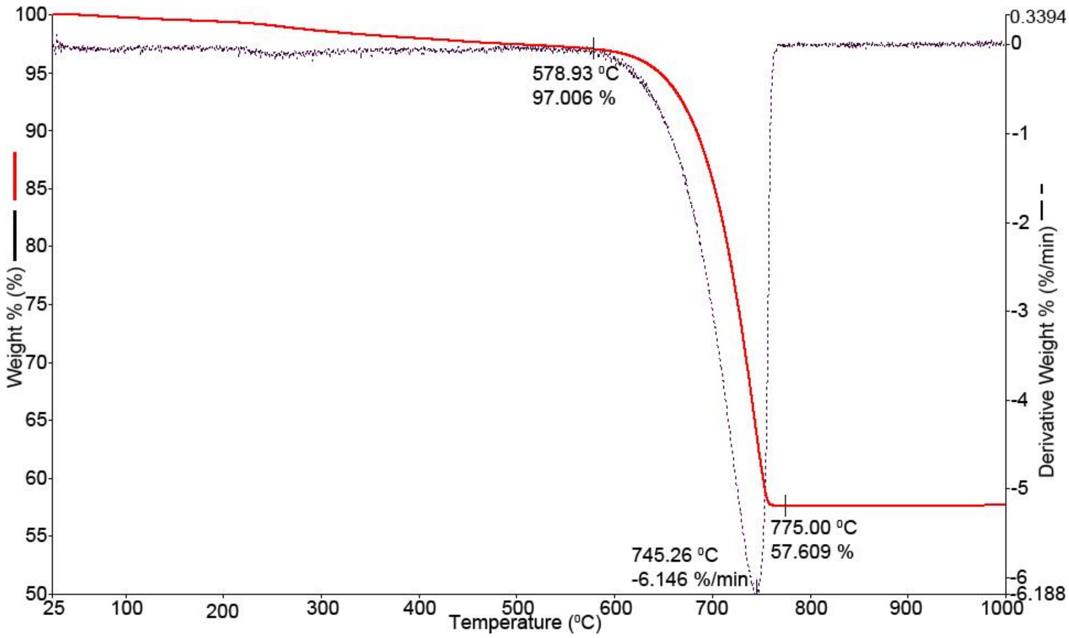


Figure 29. TGA graph of fine plaster sample less than 53 µm.

4.4.2. Mineralogical and Chemical Compositions and Microstructural Properties of Paints

Mineralogical and chemical compositions and microstructural properties of the paint layers were determined by XRD, FT-IR, SEM-EDS, TGA and optic microscope analyses. These analyses have indicated that most of paint layers include high amount of calcium (Ca) and magnesium (Mg) due to use of dolomitic lime used as binder and also iron (Fe) due to commonly used earthen pigments in mural paintings.

a) Red painting layers

Optical microscope and SEM-EDS analyses demonstrated that red painting was fabricated on dry plaster, and the thickness is approximately 70 μm (Figure 30).

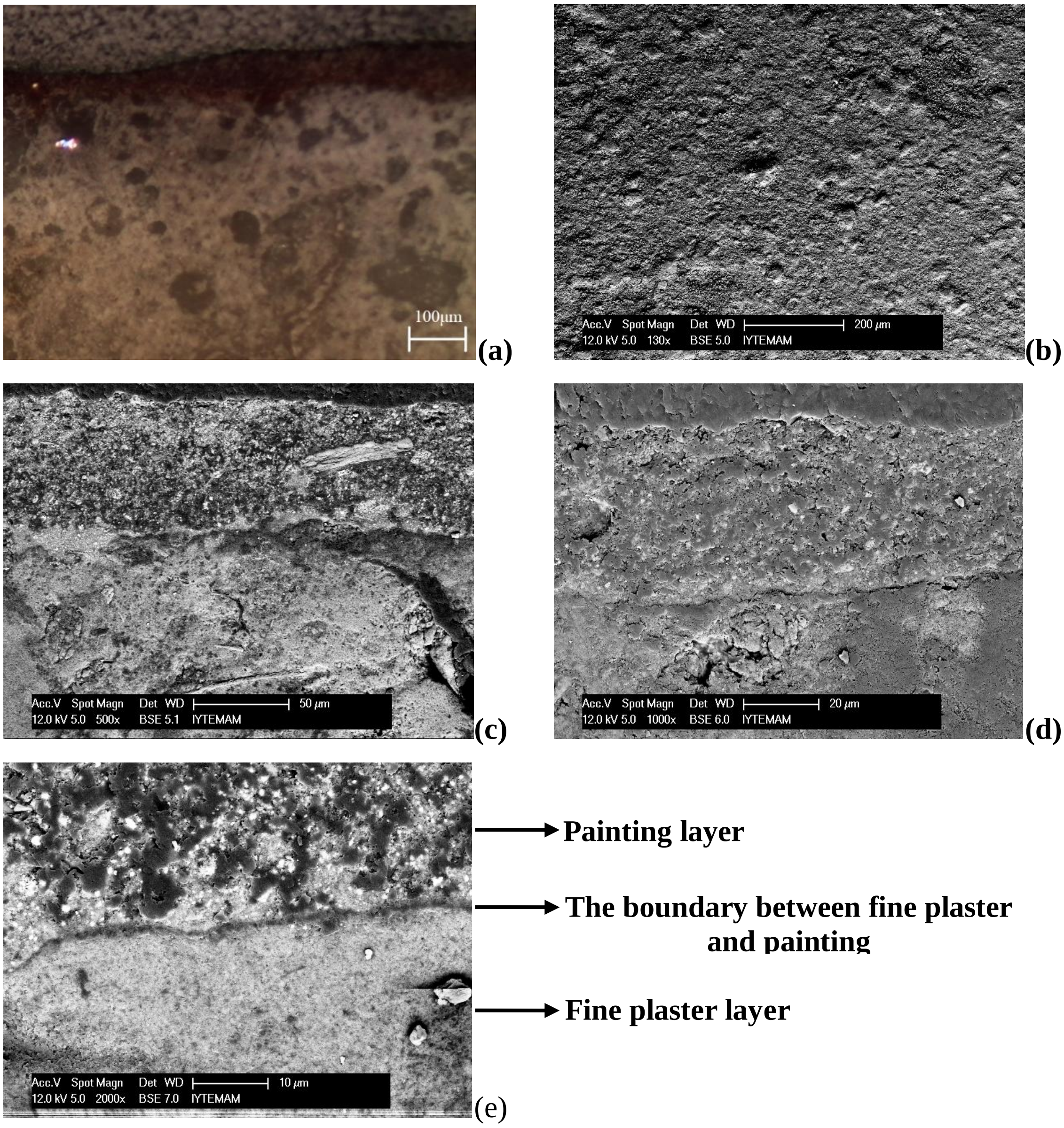


Figure 30. Optical microscope image (a), BSE images of surface in 130x magnification (b), in 500x magnification (c), in 1000x magnification (d), and in 2000x magnification (e) of polished section of red painted plaster.

Mineralogical compositions of the red painting layers were investigated by XRD and FT-IR analysis. In the XRD spectrum of red paint, calcite ($CaCO_3$), hematite (Fe_2O_3) and quartz (SiO_2) were determined (Figure 31).

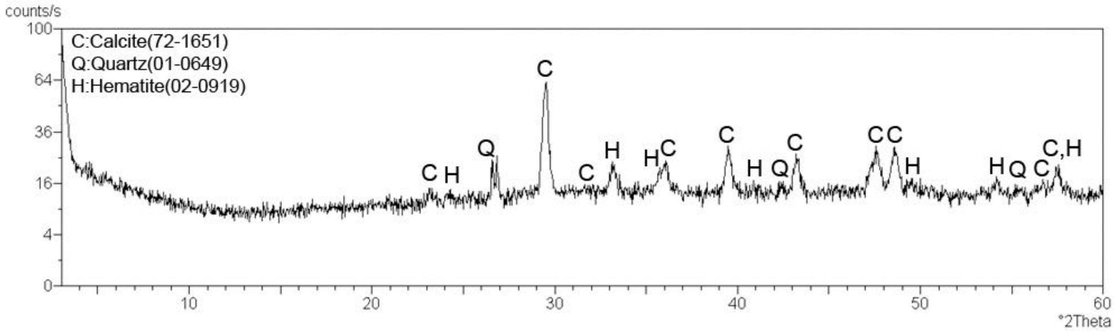


Figure 31. XRD pattern of red painting layer.

The FT-IR spectrum of the red paint indicates CO_3□ bands at 2515, 1797, 1627, 1430, 875, and 713 cm^{-1} due to calcite [2($CaCO_3$)]. The infrared absorption bands at 1154, 1095, 1029 cm^{-1} are observed possibly due to silica. The peaks at 1154, 1095, 914, 799, 546, 471 cm^{-1} are attributed to iron oxide (hematite) [2(Fe_2O_3)] (Bikiaris et al. 1999, Hein et al. 2009, Gadsden 1975), a weak peak at 914 cm^{-1}, the double peaks at 799 and 775 cm^{-1}, and the single peak at 667 cm^{-1} are indicative for the presence of α-quartz [3[SiO_2)] (Figure 32) (Gadsden 1975). The main peaks for both hematite and quartz are in the range of 1080 and 1100 cm^{-1}.

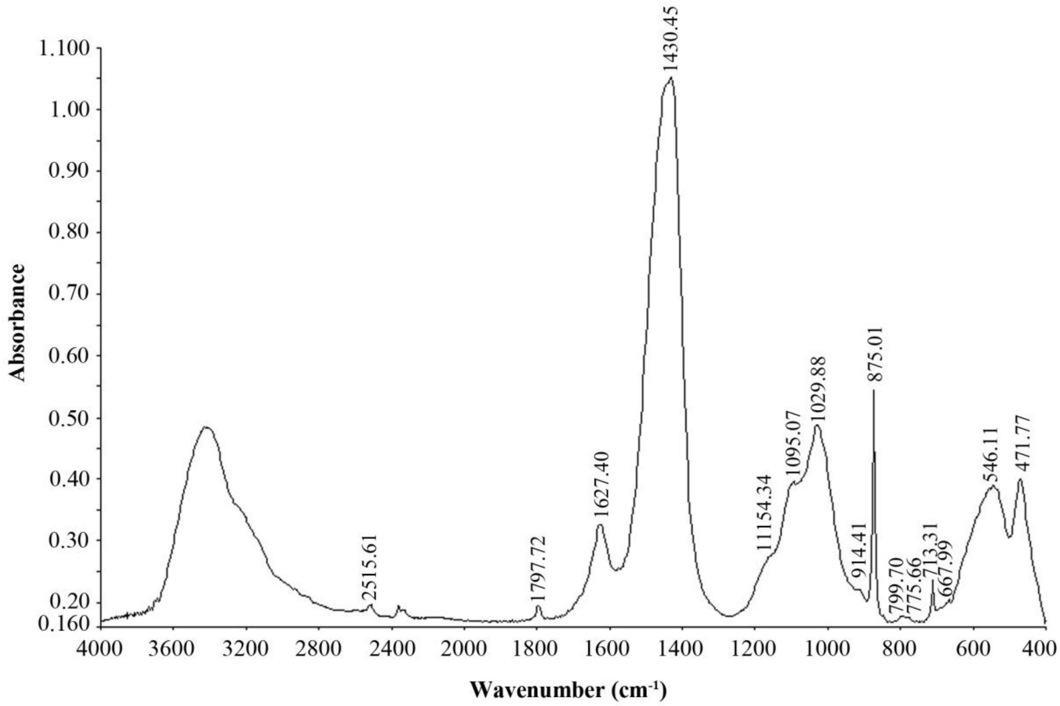
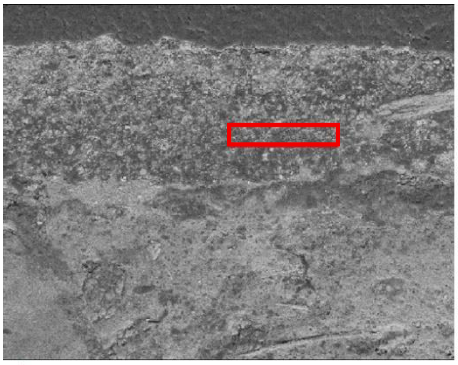


Figure 32. FT-IR spectrum recorded on a sample of the red painting layer.

The EDS and mapping analyses in order to determine the chemical composition on polished cross section of the red-coloured painting have shown that the painting layer includes highly iron (Fe) and calcium (Ca) (Figure 33, Figure 35).

Moreover, the elemental composition of the red pigment was determined by the EDS analysis on the powdered paint samples after treated with dilute HCl. According to this, red pigment could have been prepared by the use of iron oxide (Figure 34).



Element	%
FeK	45.01
CaK	39.80
SiK	7.41
AlK	3.18
NaK	2.32
MgK	2.29
Total	**100.00**

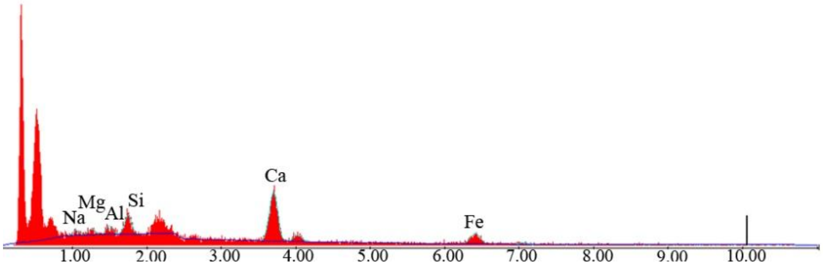
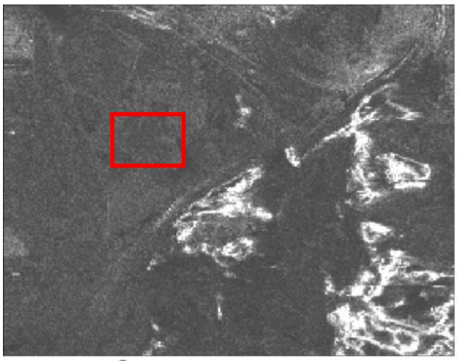


Figure 33. SE image and EDX spectrum of the red painting layer.



Element	%
O	61.56
Fe	18.17
Si	12.38
Al	5.78
Mg	1.28
K	0.83
Total	**100.00**

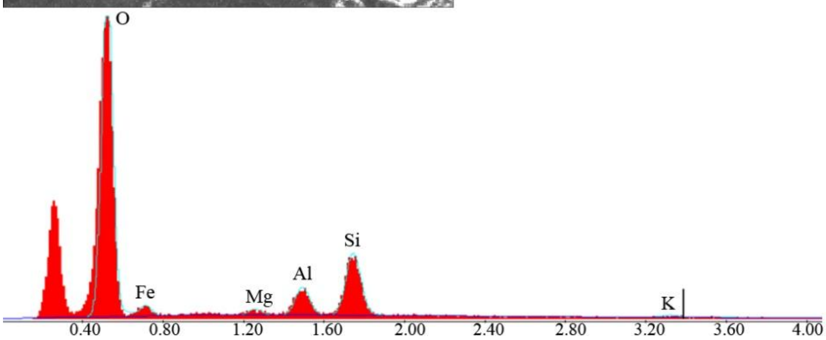


Figure 34. SE image and EDX spectrum of the red pigment.

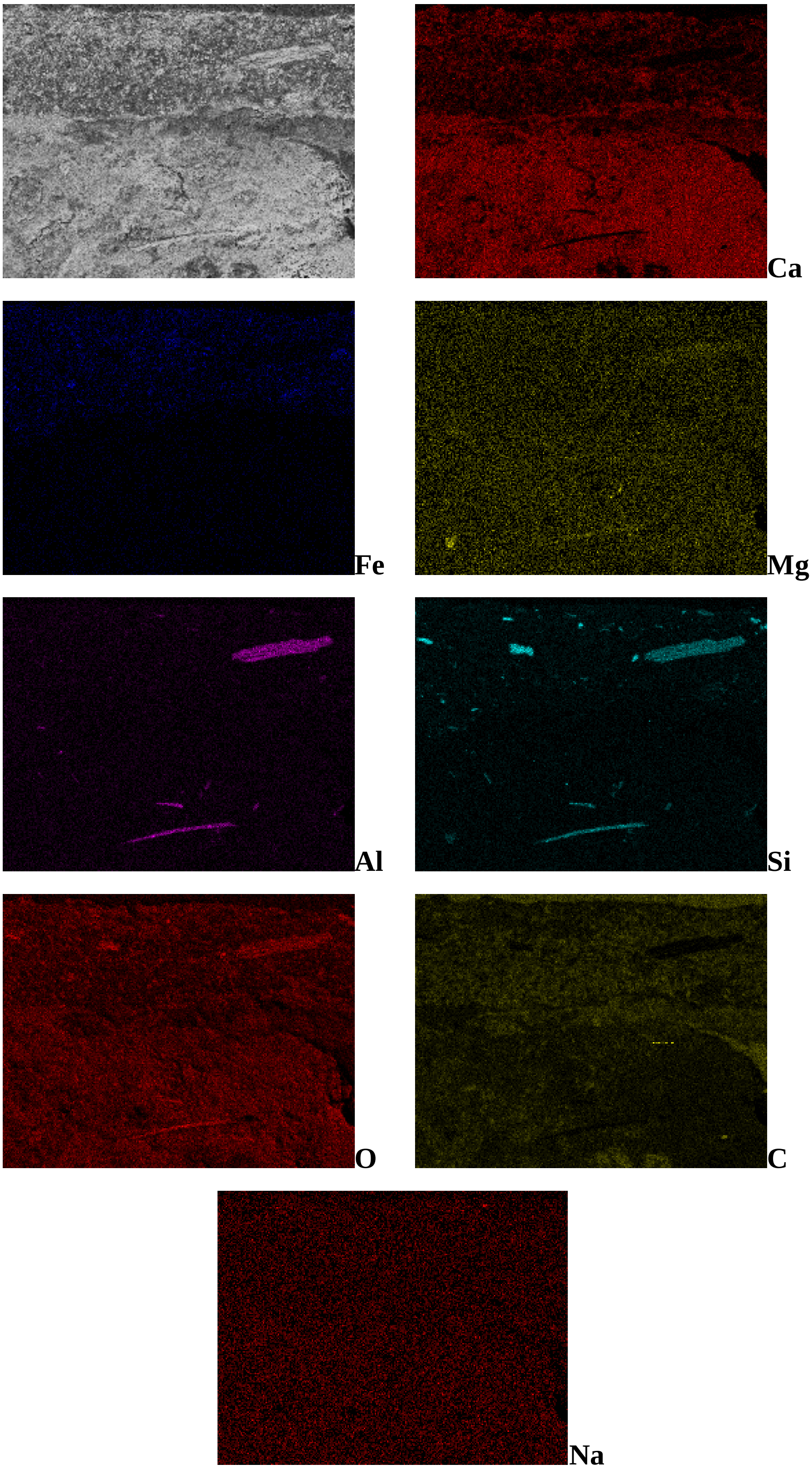


Figure 35. Mapping based on the chemical compositions of layers forming red wall painting.

XRD, FT-IR and SEM-EDX analysis indicated that red pigments used in the execution of red paintings were hematite; additionally, the presence of calcite has demonstrated that lime was used as binder. Hematite (Fe_2O_3), an iron ore, was widely used as red pigment in mural paintings of historic buildings (Hein et al. 2009, Daniilia et al. 2007, Daniilia et al. 2000). The presence of quartz in painting layer could have been arisen from the clays in earth.

b) Yellow Painting Layer

Yellow painting was determined to have been executed on dry plaster surface in about 25 μm in optical microscope and SEM-EDS analyses (Figure 36).

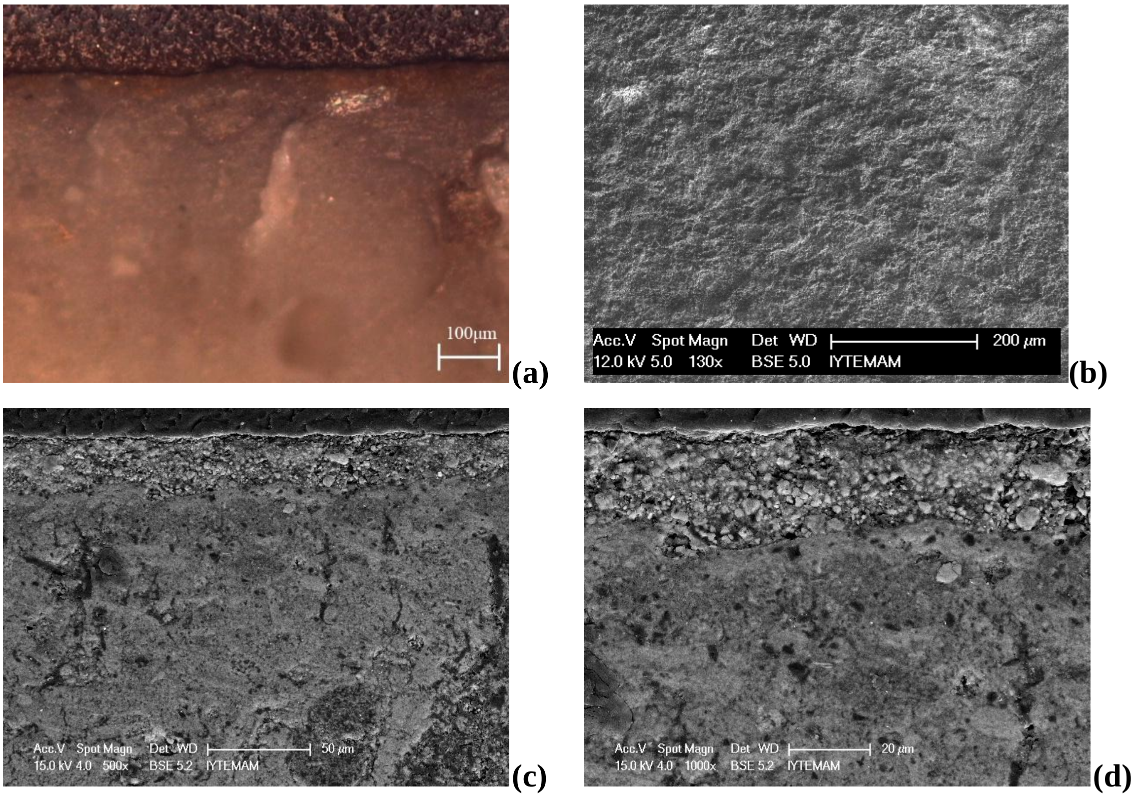


Figure 36. Optical microscope image (a), BSE images of surface in 130x magnification (b), in 500x magnification (c), and in 1000x magnification (d) of polished section of yellow painted plaster.

In the XRD spectrum of the surface of yellow paint has indicated that yellow paint involves mainly calcite ($CaCO_3$), dolomite and quartz (SiO2) (Figure 37). Observation of calcite and dolomite show the use of dolomitic lime as binder in the painting layer. Dolomitic lime was widely used in the mortars and plasters of many historic buildings due to slow and uniform shrinkage that does not cause to cracking (Hein et al. 2009, Weber et al. 2008, Moussa et al. 2009, Chever et al. 2010).

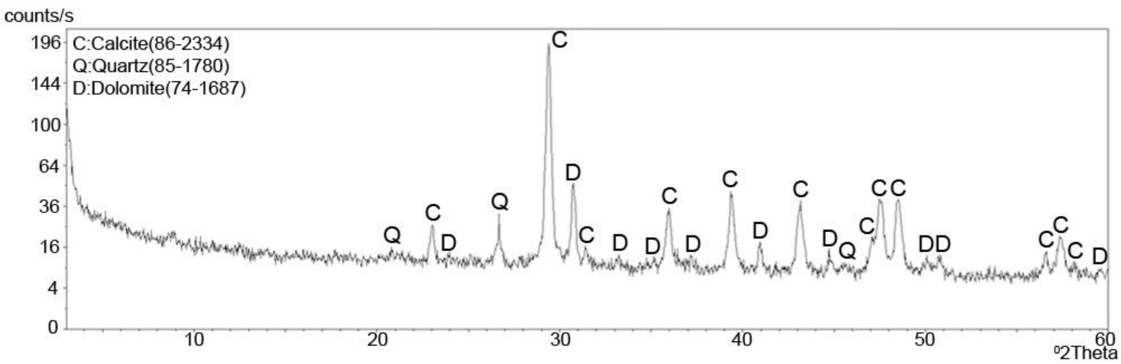


Figure 37. XRD pattern of yellow painting layer.

XRD analysis was confirmed by FT-IR analysis. According to FT-IR analysis on powdered yellow paint sample, CO_3□ stretching bands at 2518, 1794, 1437, 875, 713 cm^{-1} revealed the presence of calcite [2($CaCO_3$)] and at 1627, 1437, 1036, 875, 728cm^{-1} the presence of dolomite [$CaMg(CO_3)_2$]. In the spectrum, the peaks at 1036, 582, 470 cm^{-1} due to goethite {4[FeO.OH]}, and at 519 cm^{-1} due to α-quartz [3[SiO_2)] were inferred (Gadsden 1975) (Figure 38).

The infrared absorption bands of silica possibly have covered the strong peaks of yellow ochre (goethite) and quartz in the range of 1100 and 1000 cm^{-1} (Bikiaris et al. 1999).

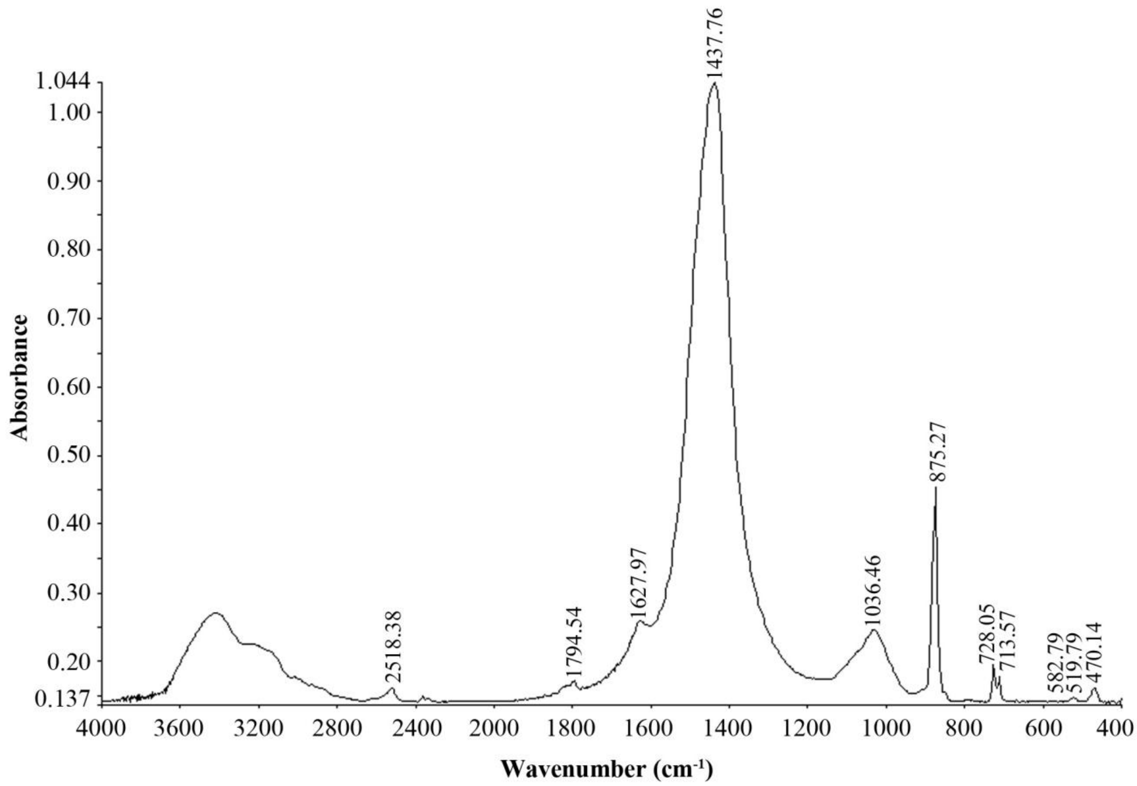
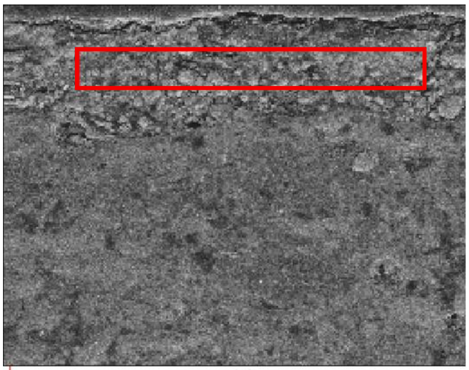


Figure 38. FT-IR spectrum recorded on a sample of the yellow painting layer.

The elemental composition of the yellow paint layer was determined by SEM-EDS analysis on polished section and powdered pigment sample. Henceforth, mainly calcium (Ca), iron (Fe) and magnesium (Mg) have been revealed (Figure 39, Figure 41). Besides this, the SEM-EDS analysis on powdered yellow pigment sample treated with dilute HCl have indicated the presence of mostly oxygen (O), iron (Fe) and silicon (Si) (Figure 40).

The analyses results on the yellow painting layer has shown the use of goethite-based yellow ochre (Fe_2O_3. H_2O silica and clay) for yellow pigment. Yellow ochre as an earthen pigment was used commonly in historic mural paintings (Daniilia et al. 2007, Daniilia et al. 2008, Brysbaert 2008). Yellow pigment was used by mixing with mainly dolomitic (magnesian) lime as binder. Lime (calcite) could have been also used as white pigment. The presence of quartz in painting layer may also have been stemmed from migration of clays within soil.



Element	%
CaO	65.65
Fe_2O_3	14.55
MgO	11.58
SiO_2	4.84
Al_2O_3	1.94
K_2O	1.45
Total	**100.00**

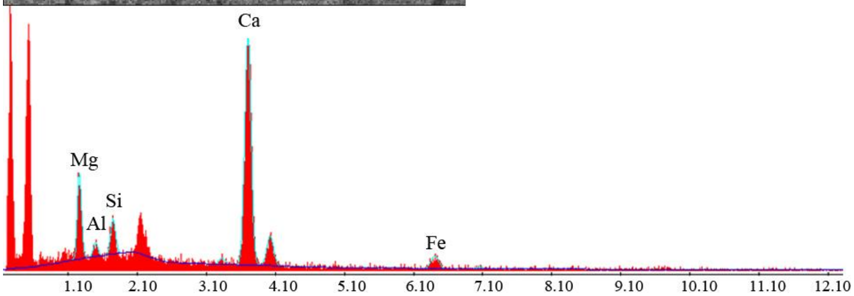


Figure 39. SE image and EDX spectrum of the yellow painting layer.

Element	%
O	45.63
Si	21.64
Fe	17.35
Al	6.25
K	2.16
P	1.93
Mg	1.42
Cl	1.08
Ca	1.04
Na	0.75
S	0.33
Total	**100.00**

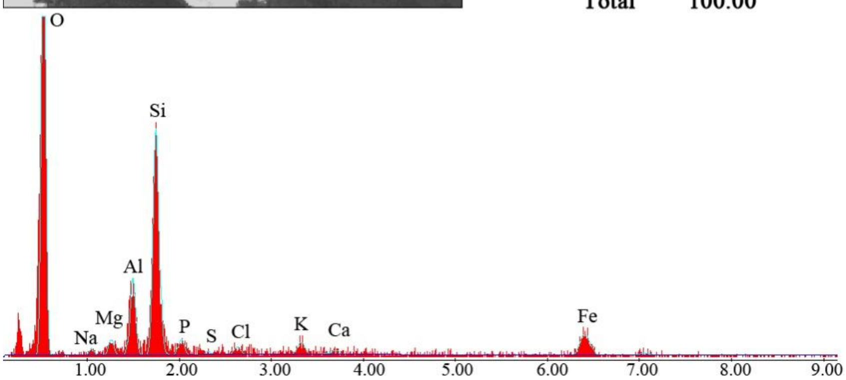


Figure 40. SE image and EDX spectrum of the yellow pigment.

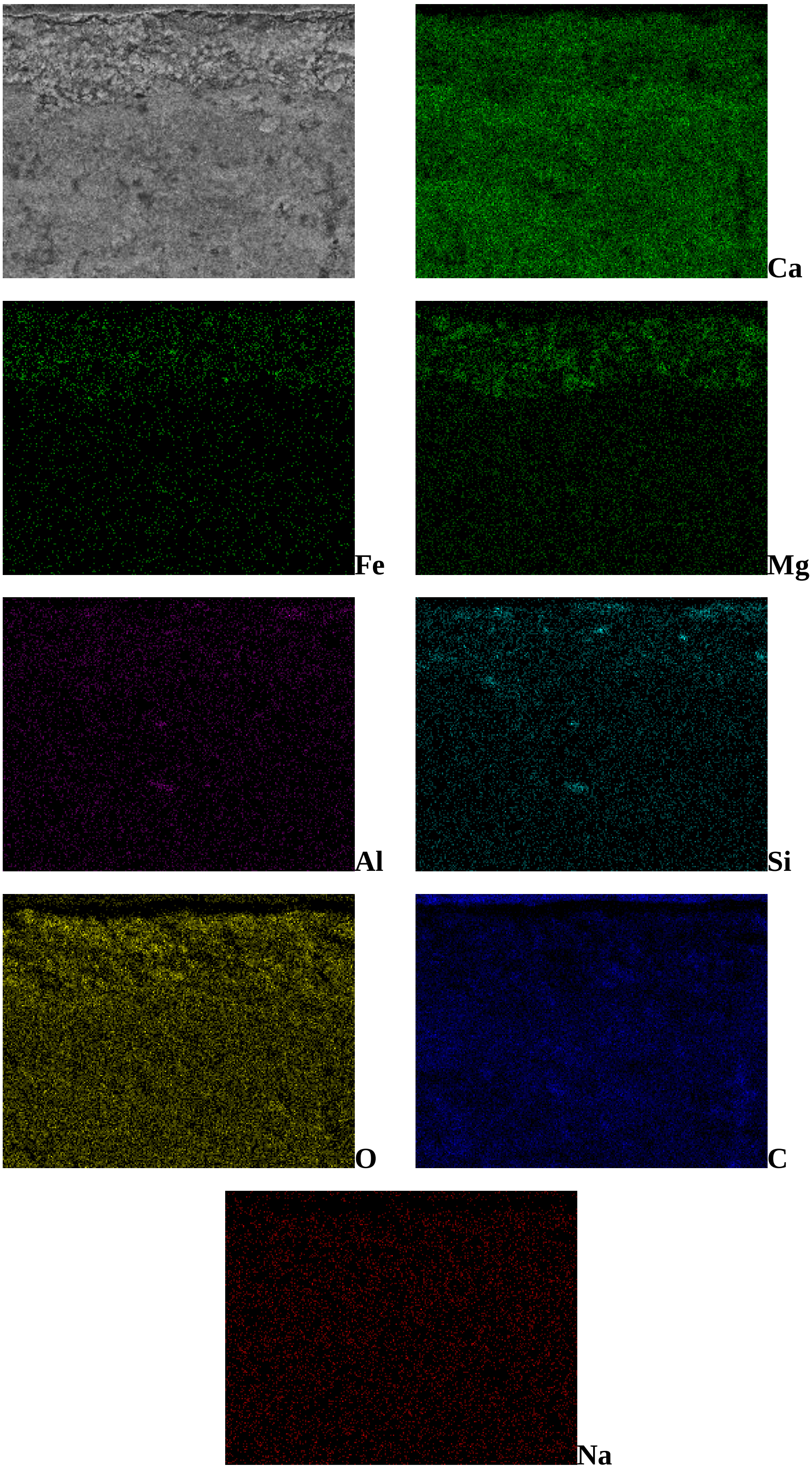


Figure 41. Mapping based on the chemical compositions of layers forming yellow wall painting.

c) Purple Painting Layer

Analyses of the polished section on optical microscope and SEM-EDS have indicated two paint layers, one red layer (*c.* 10 µm) and one purple layer (*c.* 10 µm). The purple painting was carried out in *lime-secco* technique over red painting layer, which was also executed on *lime-secco* technique (Figure 42).

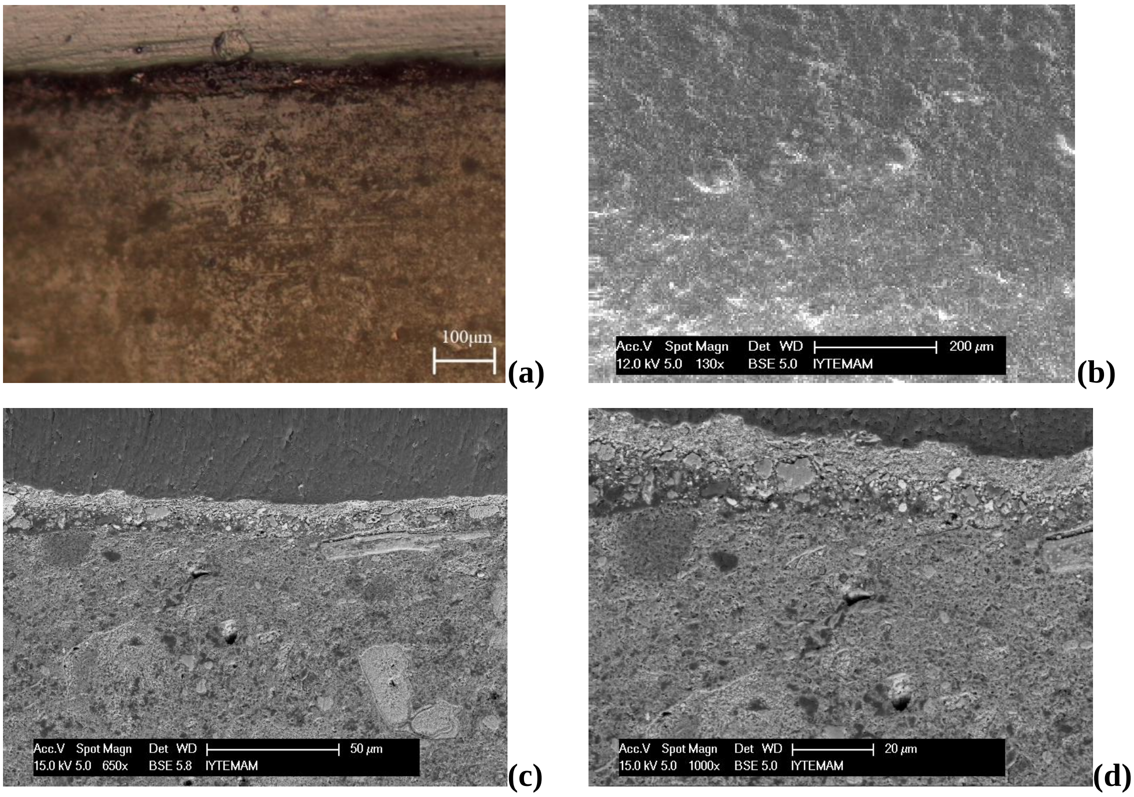


Figure 42. Optical microscope image (a), BSE images of surface in 130x magnification (b), in 650x magnification (c), and in 1000x magnification (d) of polished section of purple painted plaster.

The mineralogical composition of the purple paint was investigated by XRD analysis; hence, the surface of painting layer includes calcite, dolomite and quartz (Figure 43).

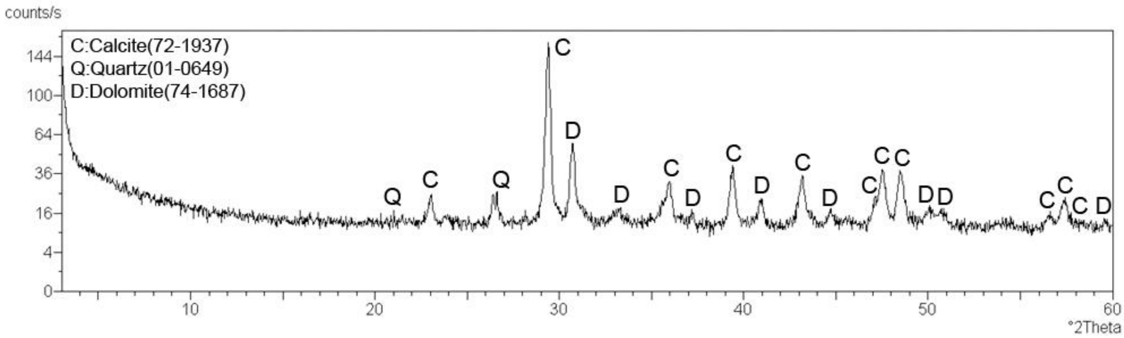


Figure 43. XRD pattern of purple painting layer.

FT-IR analysis on purple paint layer has inferred CO_3□ stretching bands at 2515, 1798, 1625, 1428, 1035, 873, 727, 713 cm^{-1}due to calcite [2($CaCO_3$)] and dolomite [$CaMg(CO_3)_2$]. Calcite and dolomite can be differentiated by the peaks observed at 727 and 713 cm^{-1}; 727 cm^{-1} is attributed to dolomite and 713 cm^{-1} is related to calcite. The absorption bands at 1102, 573, 546, 531, 471 cm^{-1} due to *caput mortuum* (purple ochre) (Bikiaris et al. 1999), Si-O stretching bands at 525, 447 cm^{-1} due to α-quartz [3[SiO_2)] were also observed (Gadsden 1975) (Figure 44). The infrared absorption bands in the broad range of 1000 and 1200 cm^{-1} are observed possibly due to silica.

The presence of hematite (Fe_2O_3), as the principal chromophore, and dolomite, as a binding medium in the surface of painting layer was observed in production purple-painted historic cave paintings of Clearwell Caves, where the caves contain dolomite, as a gangue mineral (Marshall et al. 2004).

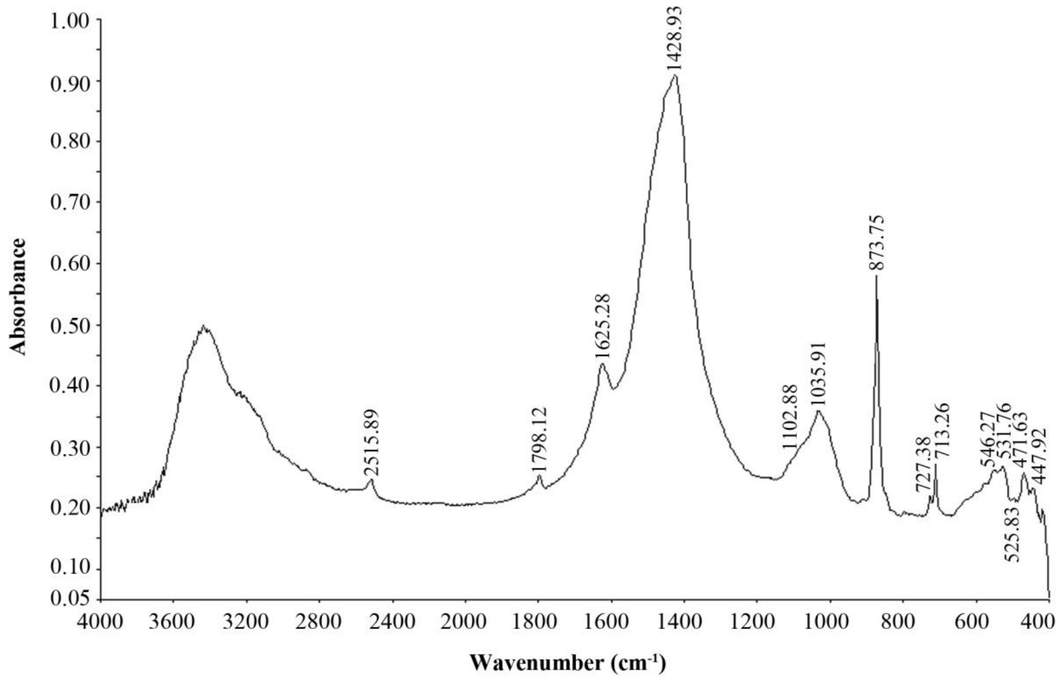
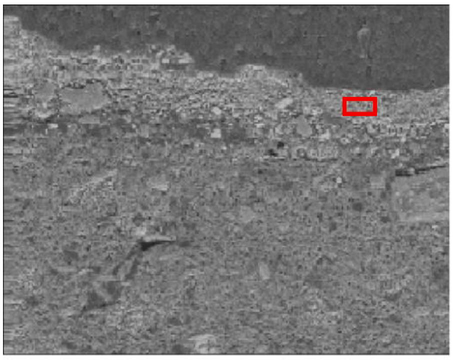


Figure 44. FT-IR spectrum recorded on a sample of the purple painting layer.

According to the SEM-EDS analyses on polished sections and powdered pigment samples of purple-painting layers, the prominent elements are calcium (Ca), iron (Fe), magnesium (Mg) and oxygen (O) (Figure 45, Figure 46, Figure 47). Thus, iron oxide could have been used in the preparation of purple pigment.

The high concentration of iron according to SEM-EDS analyses has indicated that iron-based purple ochre was used in the wall paintings of the church. Purple ochre, defined as *caput mortuum* in some sources, occurs as to the heterogeneity of particle sizes of hematite-rich pigments; the largest particle size leads to the darker hues (Eastaugh et al. 2004, Bikiaris et al. 1999). Although *caput mortuum* (Cardinal purple or Indian red) was rare and expensive in antiquity, this pigment was determined as one of the most commonly-used pigments in Byzantine hagiography (Daniilia et al. 2000, Bikiaris et al. 1999, Gettens and Stout 1957). An important example of the use of purple ochre as a pigment is observed in wall painting of the chapel of a Byzantine church now known as Kariye Camii (Gettens and Stout 1957).

The pigment of *caput mortuum* was executed after admixing with dolomitic (magnesian) lime and lime milk. As determined in mineralogical and chemical analyses, lime (calcite) could be used as white pigment, as well, and quartz might be stemmed from clays in soil.



Element	%
O	43.99
Ca	24.43
C	24.40
Mg	3.46
Fe	1.89
Si	0.91
Na	0.45
Al	0.38
K	0.27
Cl	0.13
Total	**100.00**

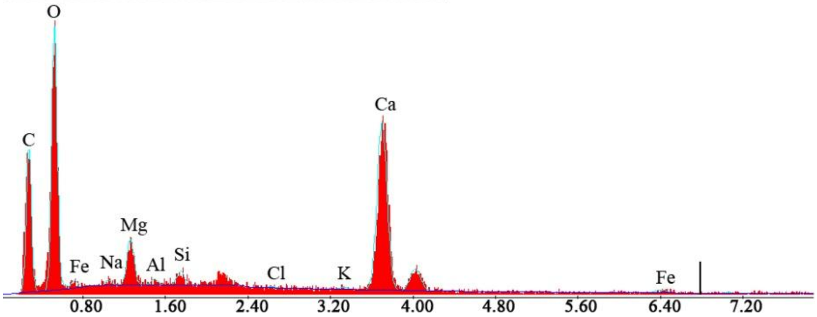
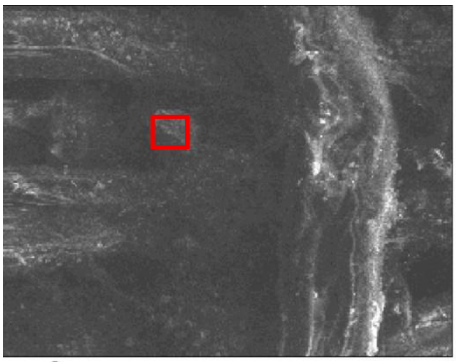


Figure 45. SE image and EDX spectrum of the purple painting layer.



Element	%
Fe	54.01
O	36.26
Si	5.74
Al	2.02
Mg	1.00
K	0.98
Total	**100.00**

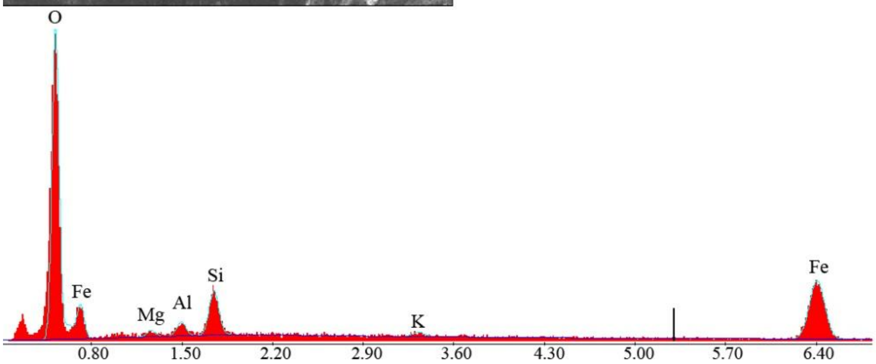


Figure 46. SE image and EDX spectrum of the purple pigment.

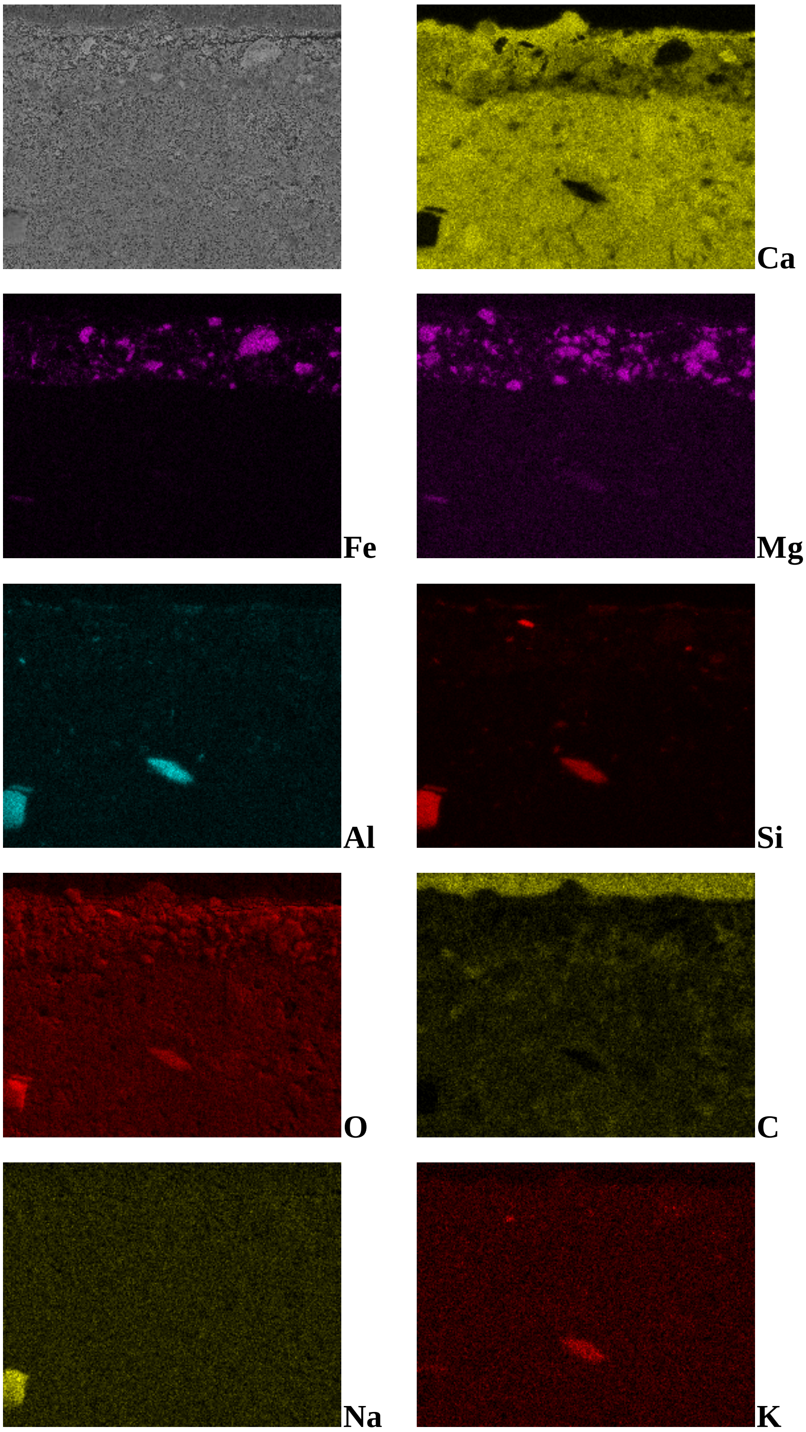


Figure 47. Mapping based on the chemical compositions of layers forming purple wall painting.

d) Green Painting Layer

According to optical microscope and SEM-EDS images of polished section, green painting (*c.* 25 µm) was brushed in *lime-secco* technique over black painting layer (*c.* 15 µm) (Figure 48).

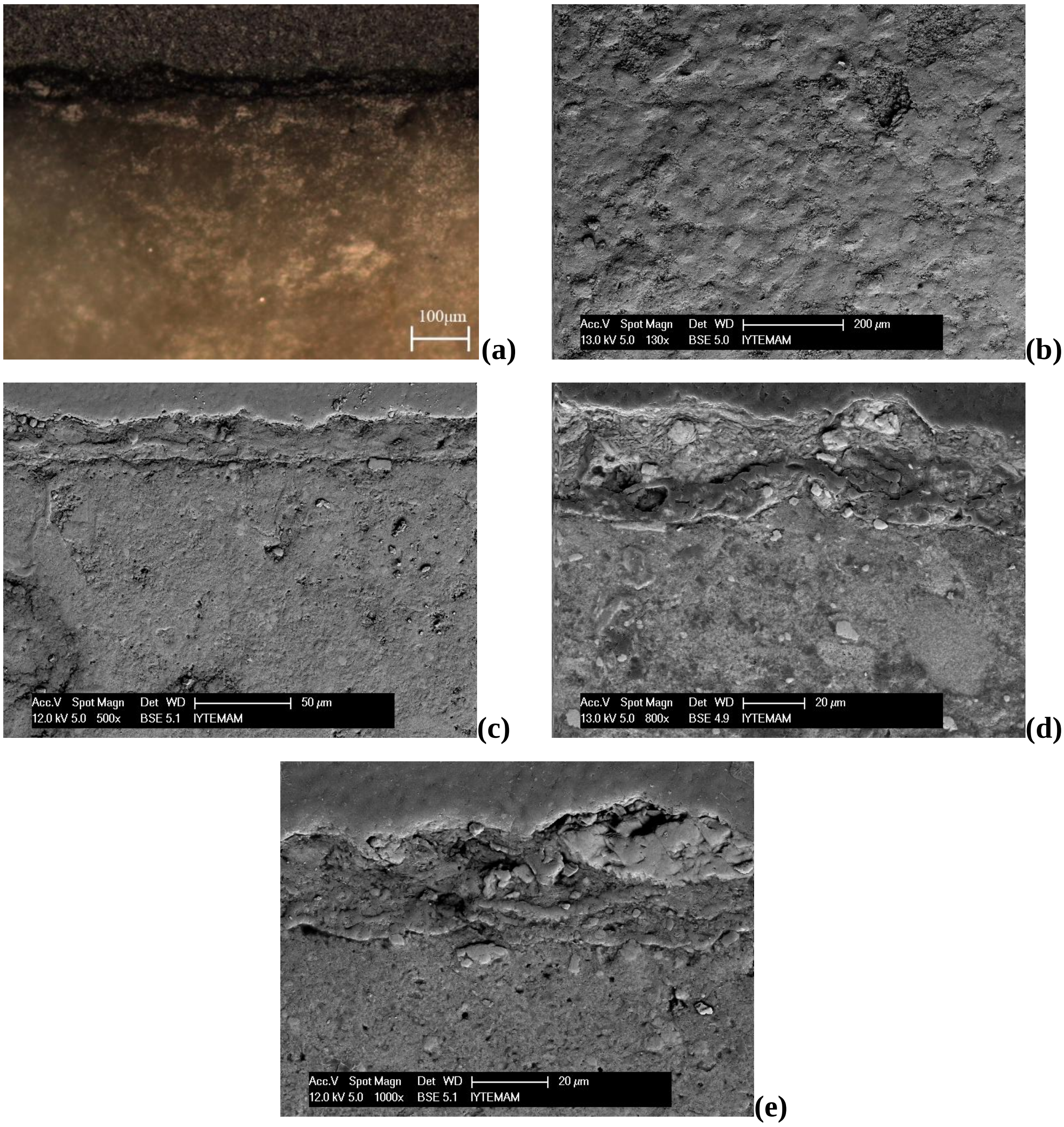


Figure 48. Optical microscope image (a), BSE images of surface in 130x magnification (b), in 500x magnification (c), and in 800x magnification (d), and in 1000x magnification (e) of polished section of green painted plaster.

The XRD analysis on surface of green-painted plaster has indicated that the mineralogical structure is composed of calcite, dolomite and quartz (Figure 49).

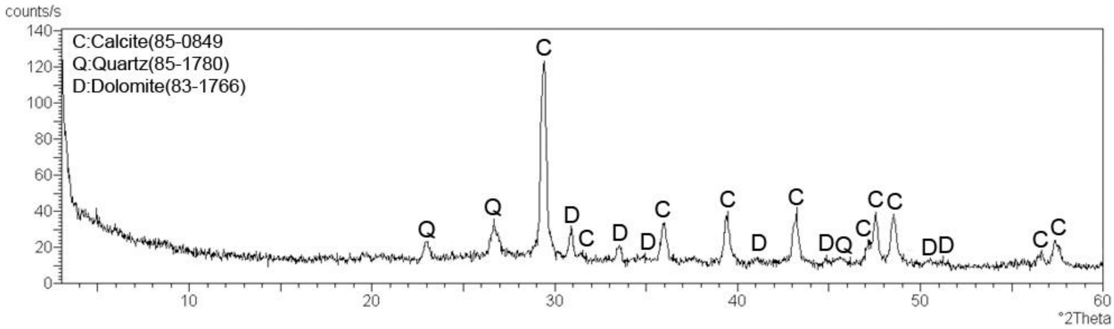


Figure 49. XRD pattern of green painting layer.

The FT-IR spectrum of the green paint, in parallel with XRD results, has demonstrated CO_3□ stretching bands at 2517, 1798, 1627, 1428, 873, 713cm^{-1}due to calcite [2($CaCO_3$)] and dolomite [$CaMg(CO_3)_2$]; additionally a shoulder dolomite peak was observed at 848cm^{-1}. Si-O stretching bands at 798, 775, 479, 454 cm^{-1} due to α-quartz [3[SiO_2)] were inferred, as well. FT-IR spectrum presented the characteristic bands of aluminosilicates (Si-O-Al) at 3558, 1627, 1024, 684, 454, 439 cm^{-1} due to glauconite {2[$(K,Na,Ca)_{1.2\text{-}2}(Fe^{III},Al,Fe^{II},Mg)_{4\text{-}}$ $(Si_{7\text{-}7.6}Al_{1\text{-}0.4}O_{20}(OH)_4$.$n$H2O]} and at 1118, 971, 684, 494, 439 cm^{-1} due to celadonite [$K(Mg,Fe^{II})(Fe^{III},Al)Si_4O_{10}(OH)$] (Figure 50) (Gadsden 1975).

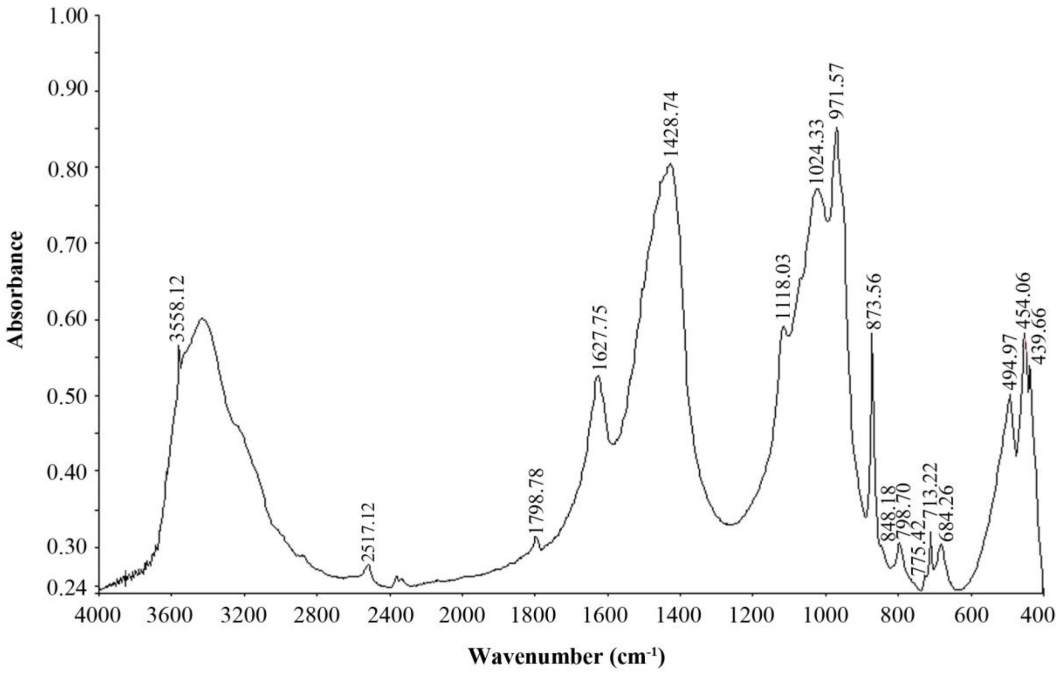
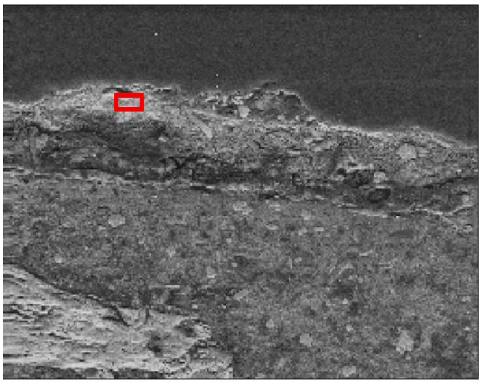


Figure 50. FT-IR spectrum recorded on a sample of the green painting layer.

The SEM-EDS analyses on polished green-painted *intonaco* section and powdered pigment sample have revealed the presence of mostly calcium (Ca), silicon (Si), magnesium (Mg), potassium (K), oxygen (O) and iron (Fe) as the elemental composition of the green painting layer (Figure 51, Figure 52, Figure 53).

The results of the analyses have assumed the use of typical green earth pigment (*terre-verte*) on the basis of glauconite and celadonite due to the presence of the high concentration of potassium. Green earth pigment as an earth-based pigment was used extensively in historic mural paintings in Byzantine art (Hein et al. 2009, Daniilia et al. 2007, Daniilia et al. 2000). Green earth pigment was admixed with dolomitic (magnesian) lime as binder. Green paint could have been lightened with lime as white pigment. The presence of quartz may have been resulted from the clays in soil.



Element	%
Ca	29.75
Si	23.51
O	19.78
Fe	13.67
K	8.52
Mg	2.58
Al	2.19
Total	**100.00**

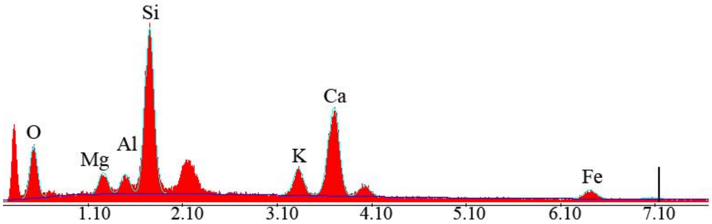
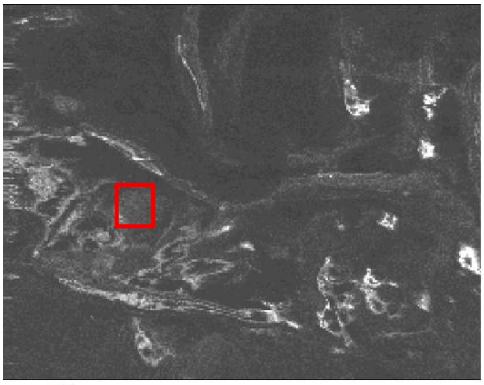


Figure 51. SE image and EDX spectrum of the green painting layer.



Element	%
O	59.18
Si	24.15
Fe	4.52
K	4.58
Mg	4.05
Al	3.52
Total	**100.00**

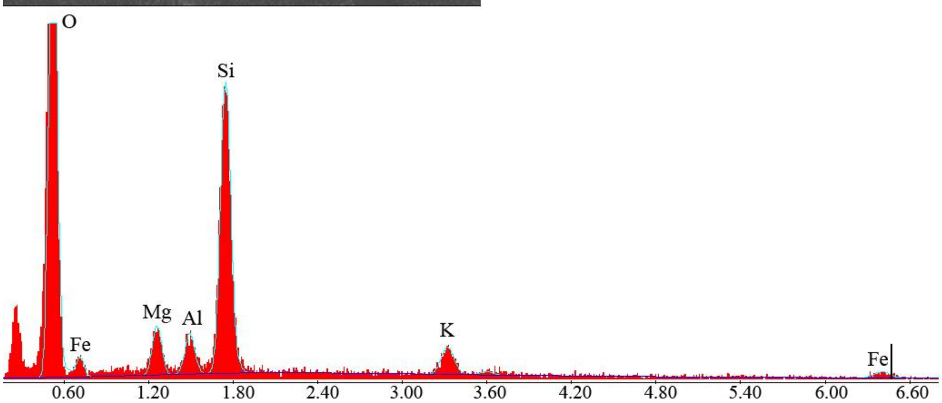


Figure 52. SE image and EDX spectrum of the green pigment.

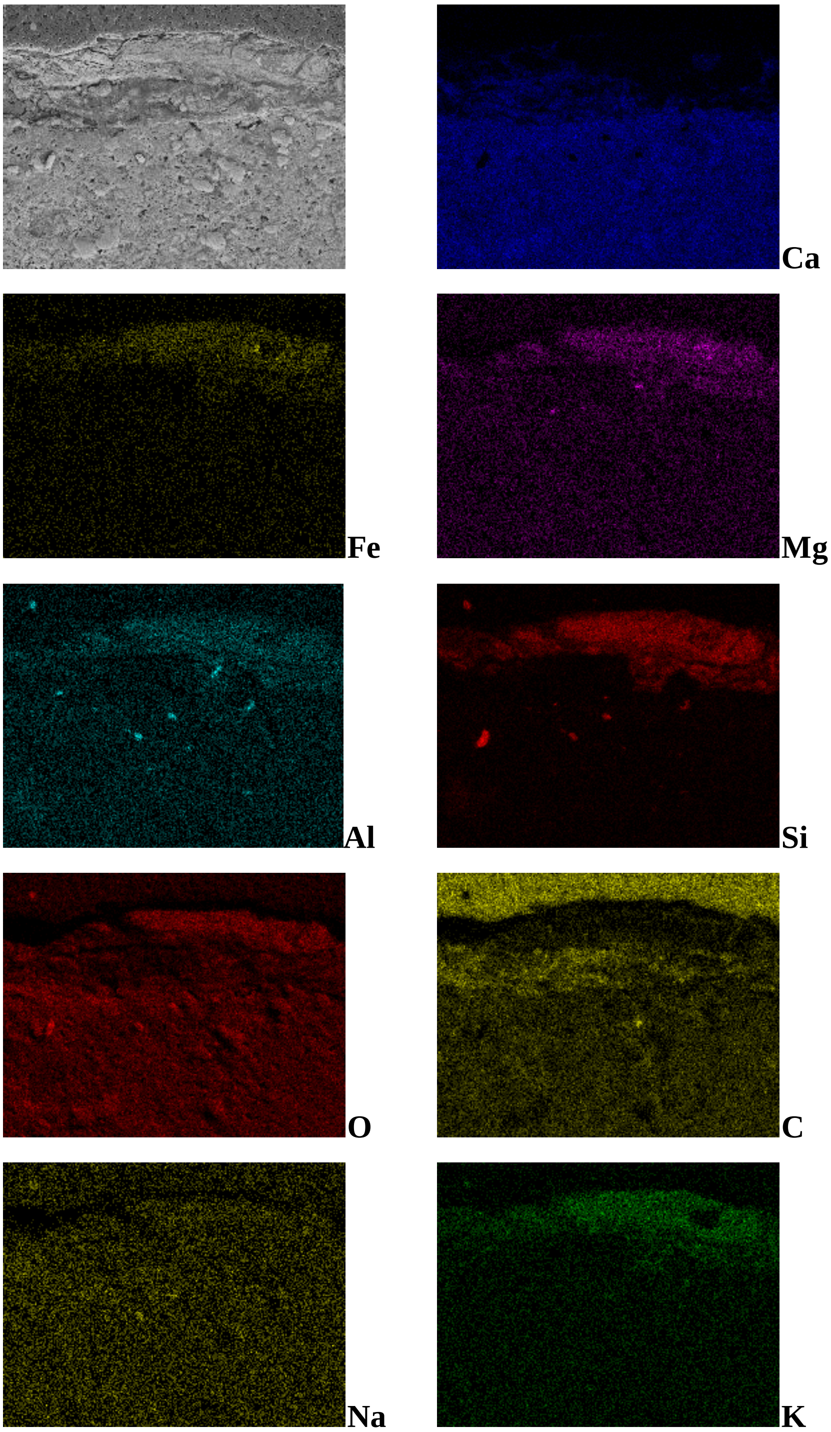


Figure 53. Mapping based on the chemical compositions of layers forming green wall painting.

e) Dark Blue Painting Layer

SEM and optical microscope analyses displayed that dark blue painting (*c.* 15 µm) was executed in *lime-secco* technique (Figure 54).

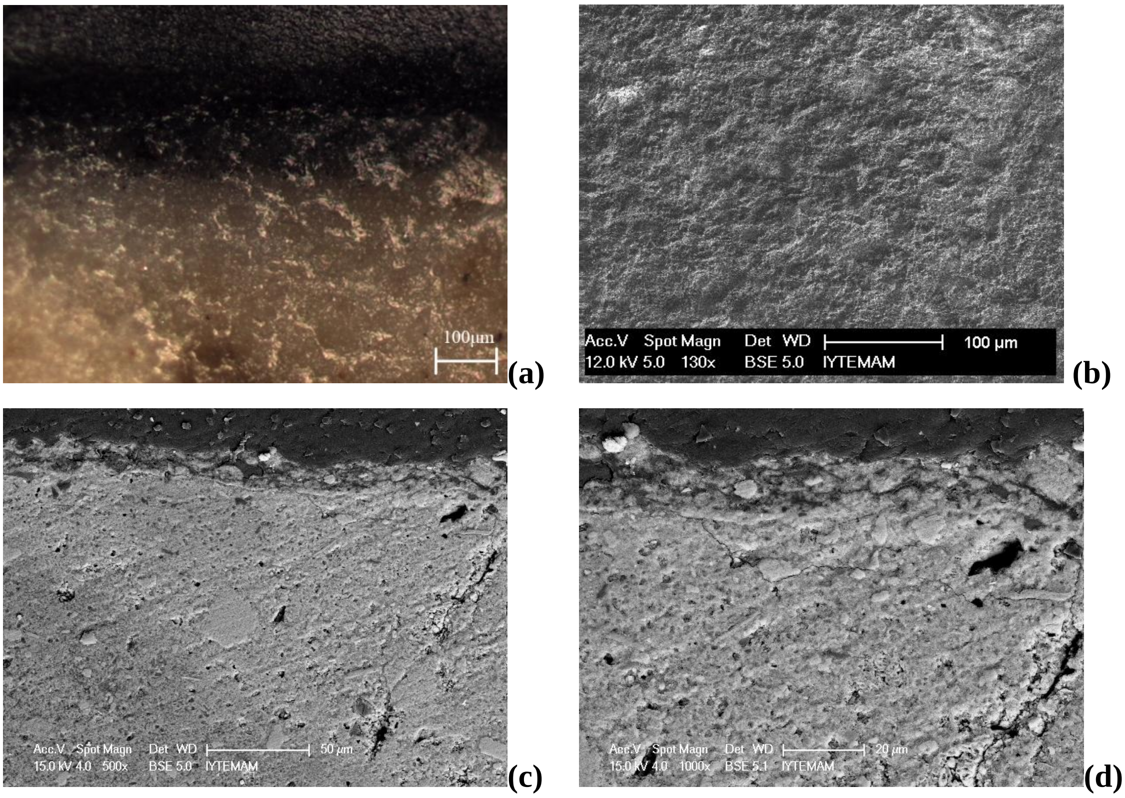


Figure 54. Optical microscope image (a), BSE images of surface in 130x magnification (b), in 500x magnification (c), and in 1000x magnification (d) of polished section of dark blue painted plaster.

XRD spectrum of the dark blue paint has demonstrated that the painting layer contains basically calcite (Ca), lazurite [Na8.16($Al_6Si_6O_{24}$)1.14S0.86], and quartz (Figure 55).

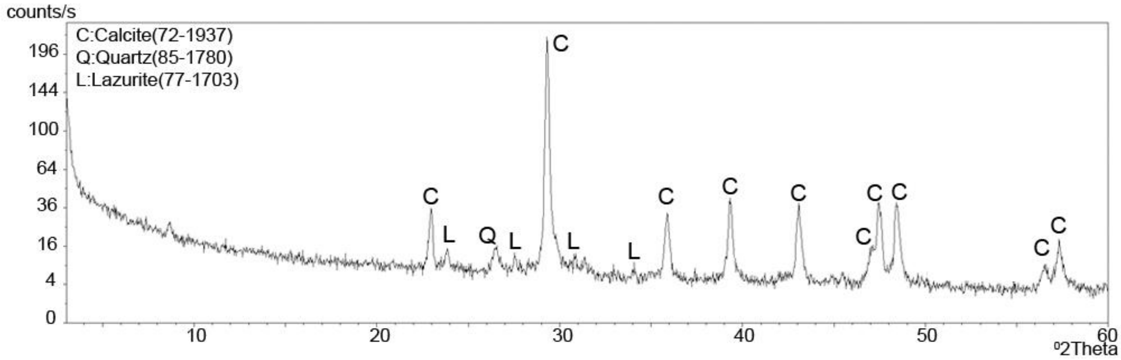


Figure 55. XRD pattern of dark blue painting layer.

XRD results were supported by FT-IR analysis. In the FT-IR spectrum on powdered dark blue paint sample, CO_3□ stretching bands at 2515, 1794, 1429, 873, 712 cm^{-1} due to calcite [2($CaCO_3$)] and Si-O stretching bands at 1078, 913, 668, 517, 462 cm^{-1} due to α-quartz [3[SiO_2)] were observed. The spectrum demonstrated the absorption bands at 1161, 1078, 1036, 471 cm^{-1} which could be indicative for the presence of lazurite (*lapis lazuli*) [$(Na,Ca)_8(Al,Si)_{12}O_{24}(SO_4,‘S’_n)$] (Gadsden 1975, Hein et al. 2009). The infrared absorption bands at 517, 471 cm^{-1} could be attributed to glaucophane {2[$Na(Mg,Fe^{II})_3Al_2Si_8O_{22}(OH)_2$]} (Gadsden 1975) (Figure 56).

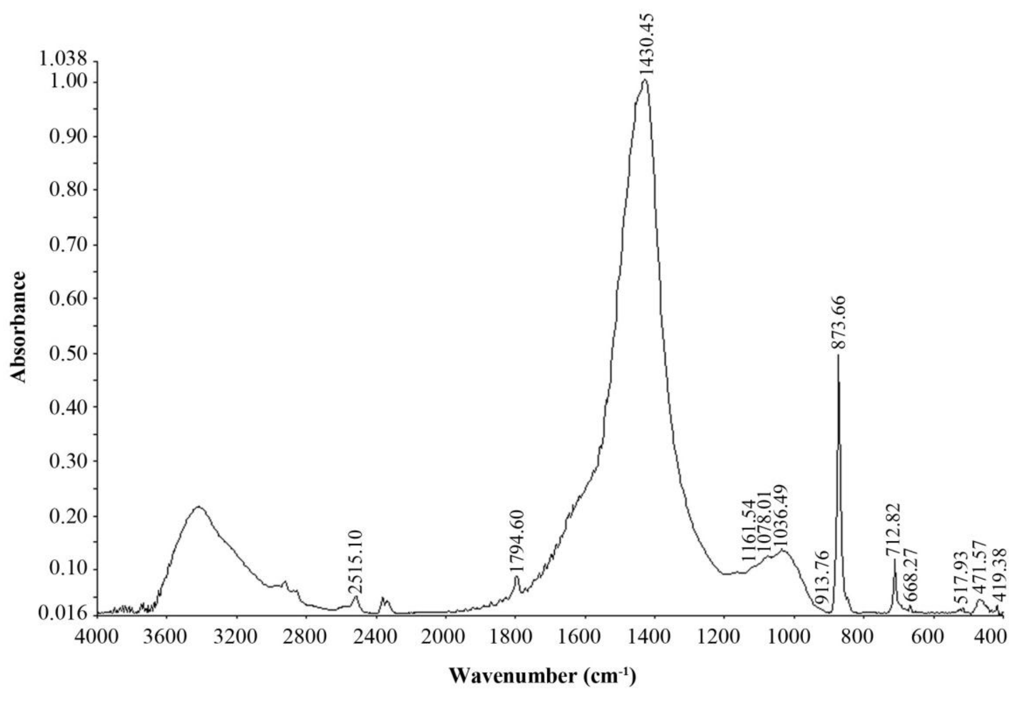


Figure 56. FT-IR spectrum recorded on a sample of the dark blue painting layer.

In parallel with mineralogical analyses, the SEM-EDS analyses on polished dark bluish-painted *intonaco* sample and powdered pigment sample have revealed the presence of mainly calcium (Ca), silicon (Si), oxygen (O), aluminium (Al) and iron (Fe) as the elemental composition of the dark blue painting layer (Figure 57, Figure 58).

As to the outcome of XRD and FT-IR analysis, lazurite, as the main mineral component of dark blue painting is the demonstration for the use of *lapis lazuli* (natural ultramarine) mixed with lime binder. Lazurite is constituted in metamorphosed lime-stones and marble, depending on penetration of an alkaline igneous; this procedure commonly occurs with calcite ($CaCO_3$) and pyrite (FeS_2) (Eastaugh et al. 2004b).

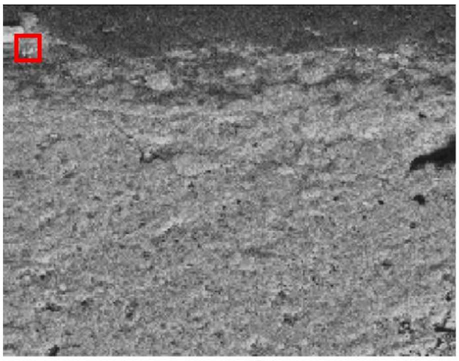
Lazurite exists at several locations worldwide and is most widely encountered in *lapis lazuli*. The best known mines, which have been worked for more than 6000 years, for *lapis lazuli* are at the Kokcha River valley in Afghanistan, and considered to be the source of most of the lazurite used in Europe during the Middle Ages and the early modern period. It is also found at Lake Baikal (Russia), Mt Vesuvius (Italy), Colorado and California (USA), the Chilean Andes, Argentina, Burma and Canada (Eastaugh et al. 2004b).

Lazurite was a precious pigment as it was expensive and rare; thus, it was often executed by mixing with other, less costly blue pigments such as azurite and indigo (Eastaugh et al. 2004b, tr. Veliz, 1986). It was often reserved for iconographically significant elements of wall paintings as to similar reasons (Gettens and Stout 1957). In the light of this knowledge, the dark blue paintings of the church could have been executed by mixing *lapis lazuli* (lazurite) and glaucophane.

The execution of two blue pigments, Egyptian blue (an expensive and rare pigment) and glaucophane (a local and abundant pigment), was attested in earlier studies on the mural paintings from the Greek Bronze Age (Filippakis et al. 1976, Profi et al. 1977).

In FT-IR and XRD analyses, quartz was determined due to possibly the presence of clays in soil.

Black pigment, used in dark blue painting could not be identified due to the fact that in FT-IR spectrum, the absorption bands of calcite covers any potential peaks from carbon (charcoal) black or bone black. On the other hand, the presence of carbon (C) was identified as to mapping analysis of the polished section on scanning electron microscope; thus carbon black, that is lime mixed with powdered charcoal, might have been used in dark blue paint (Figure 59).



Element	%
CaO	92.44
Fe_2O_3	2.11
MgO	1.65
NaO	1.36
K_2O	0.92
Al_2O_3	0.79
SiO_2	0.73
Total	**100.00**

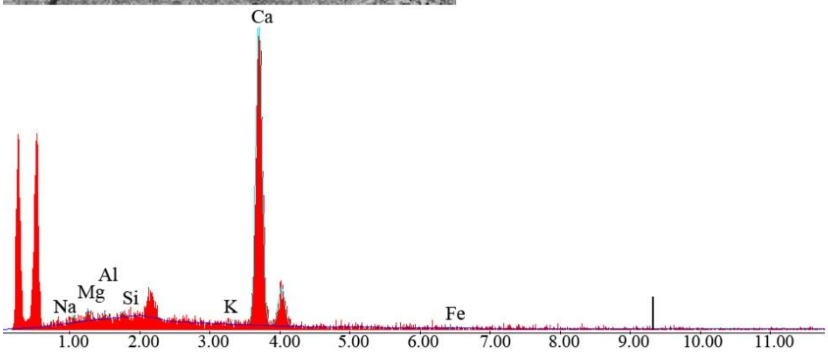
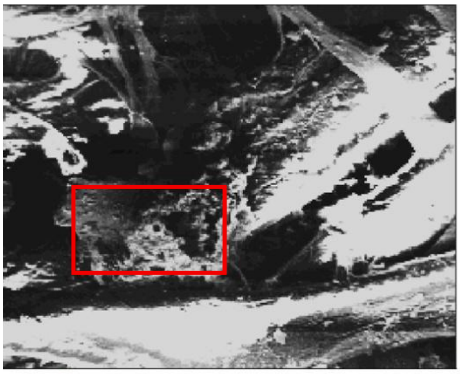


Figure 57. SE image and EDX spectrum of the dark blue painting layer.



Element	%
O	49.47
Si	29.10
Al	9.10
Fe	5.07
K	3.07
Mg	2.79
Ti	0.83
Ca	0.58
Total	**100.00**

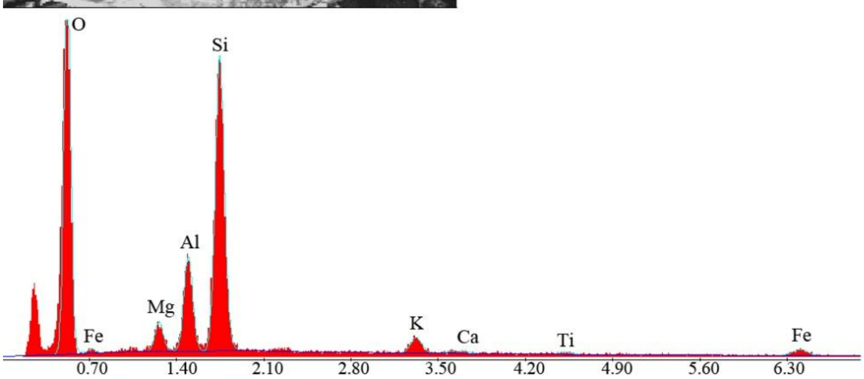


Figure 58. SE image and EDX spectrum of the dark blue pigment.

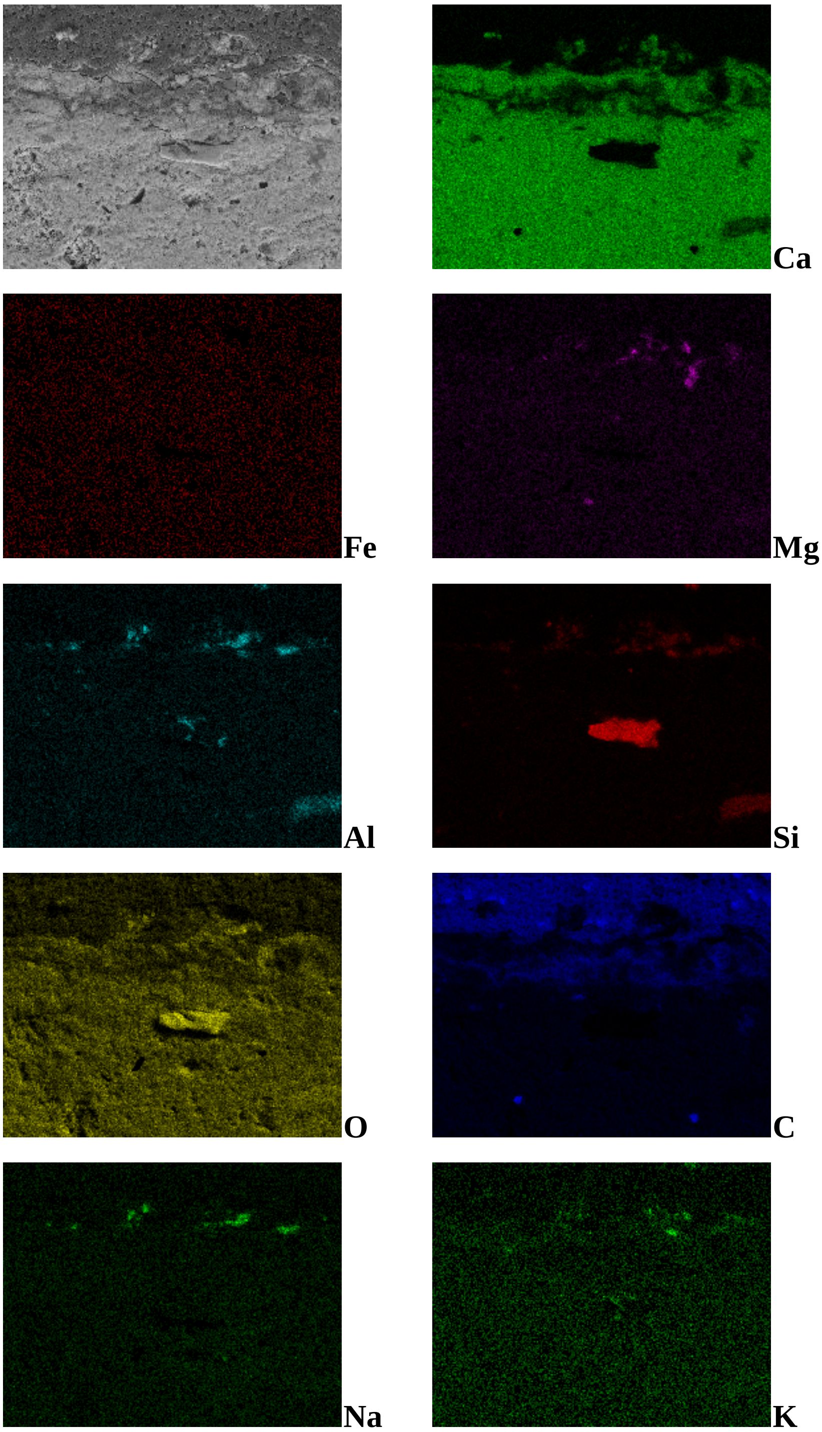


Figure 59. Mapping based on the chemical compositions of layers forming dark blue wall painting.

f) Blue Painting Layer

As shown in optical microscope image, blue painting (*c.* 10 μm) was fabricated in *lime-secco* technique over a black painting layer which is executed dry plaster (*c.* 20 μm) (Figure 60).

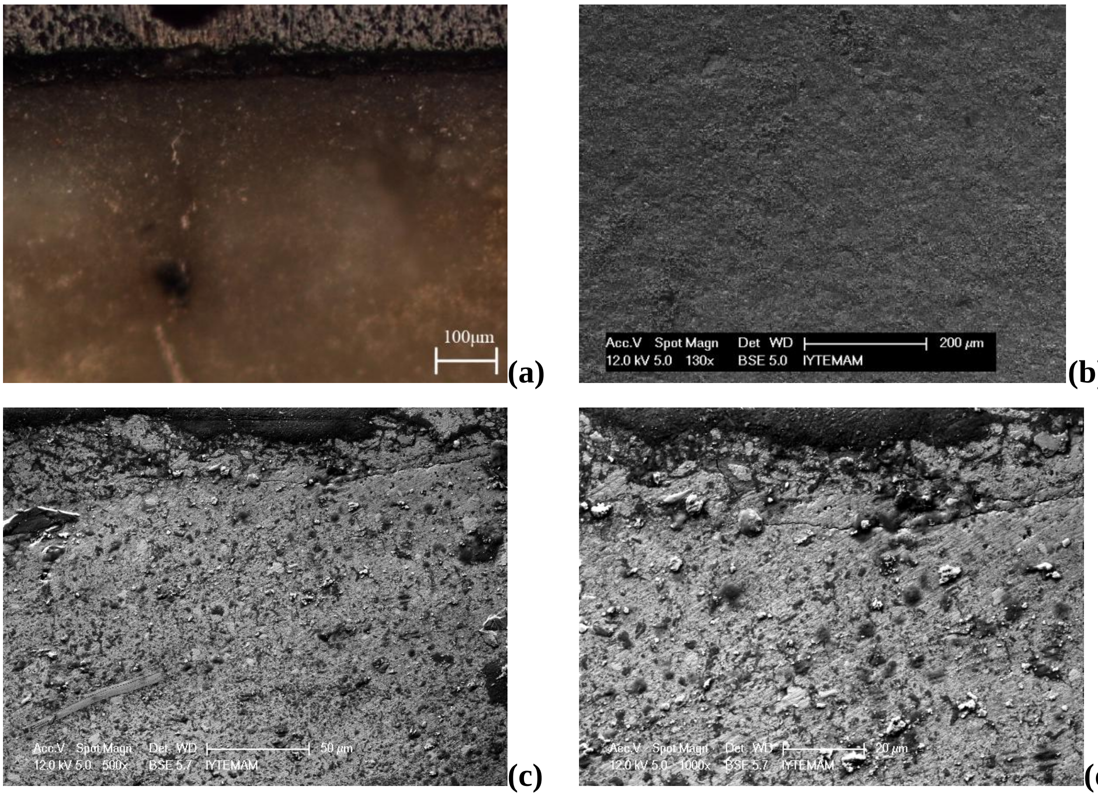


Figure 60. Optical microscope image (a), BSE images of surface in 130x magnification (b), in 500x magnification (c), and in 1000x magnification (d) of polished section of blue painted plaster.

The mineralogical composition of blue painting sample was investigated by XRD and FT-IR analysis. In the XRD spectrum, calcite ($CaCO_3$) and lazurite $[Na8.16(Al_6Si_6O_{24})1.14S0.86]$ were identified (Figure 61).

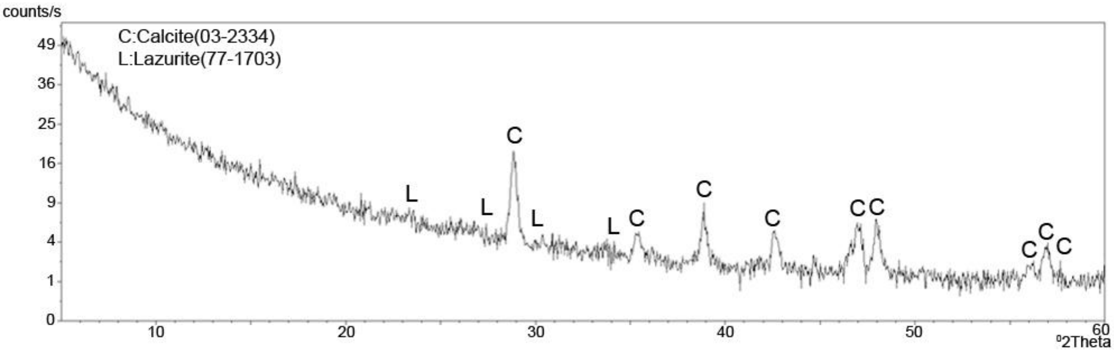


Figure 61. XRD pattern of blue painting layer.

FT-IR analysis of the blue paint supported the XRD results. In the FT-IR spectrum, CO_3□ stretching bands at 2504, 1793, 1426, 873, 712 cm^{-1}due to calcite [2($CaCO_3$)] and Si-O stretching bands at 693, 503 cm^{-1} due to α-quartz [3[SiO_2)] were inferred. The absorption bands at 1033, 930, 693, 438 cm^{-1} can be related to lazurite (*lapis lazuli*) [$(Na,Ca)_8(Al,Si)_{12}O_{24}(SO_4,‘S’_n)$] (Gadsden 1975, Hein et al. 2009). Besides this, the absorption bands at 1043, 873, 693, 438 cm^{-1} could be assigned to glaucophane {2[$Na(Mg,Fe^{II})_3Al_2Si_8O_{22}(OH)_2$]}were observed (Gadsden 1975) (Figure 62).

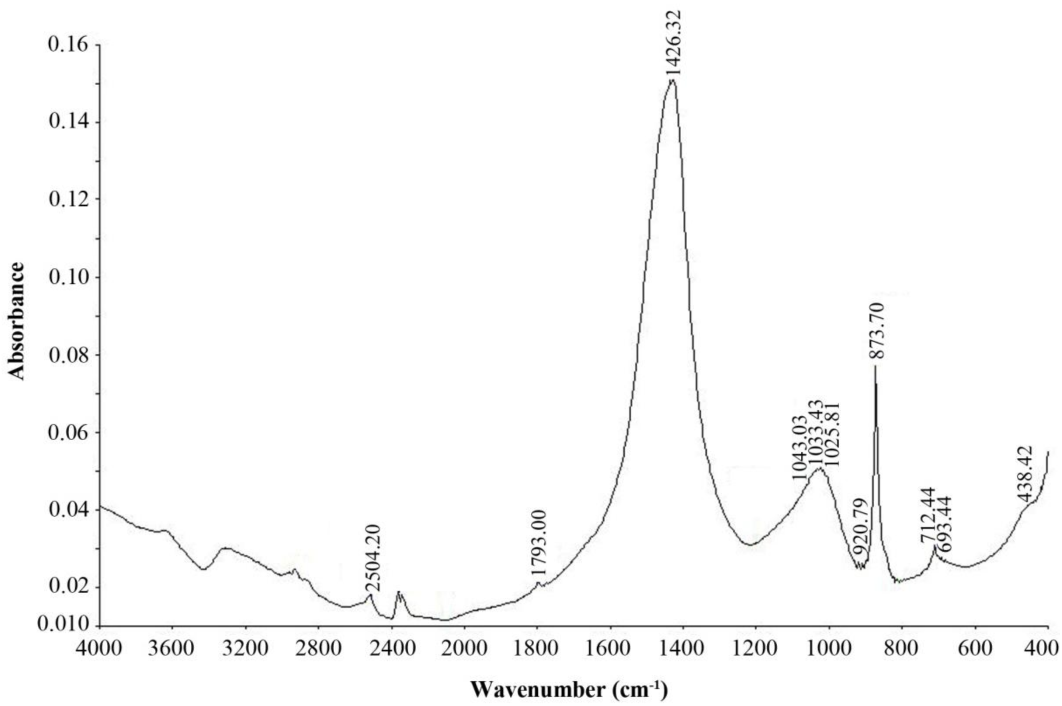
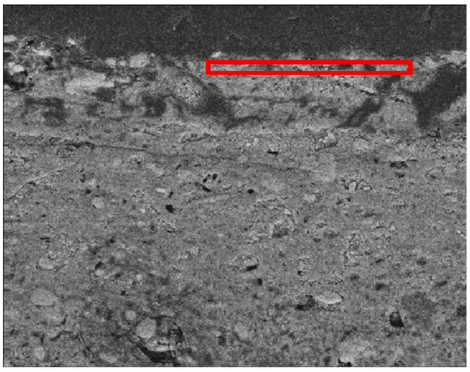


Figure 62. FT-IR spectrum recorded on a sample of the blue painting layer.

The SEM-EDS analysis carried out on polished cross section of the blue painting layer in order to determine the chemical composition have shown the main elements are calcium (Ca), silicon (Si), and oxygen (O) (Figure 63, Figure 65). Besides this, the analysis on the blue powdered samples, which were purified from calcium with the treatment of HCl, has demonstrated that iron (Fe), silicon (Si) and oxygen (O) are the main elements (Figure 64).

As to the FT-IR results the blue painting was fabricated from mix of *lapis lazuli* (lazurite) and glaucophane as blue pigments and lime milk as binding medium. Lime (calcite) can be used as white pigment for lightening. The presence of quartz may have been stemmed from the clays which migrated from the soil.



Element	%
Ca	34.81
O	28.26
C	28.22
Si	2.58
Al	1.69
Mg	0.99
Co	0.69
K	0.68
Fe	0.55
Total	**100.00**

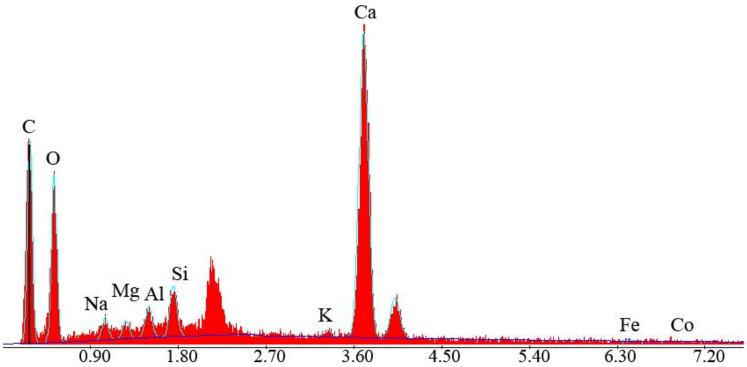
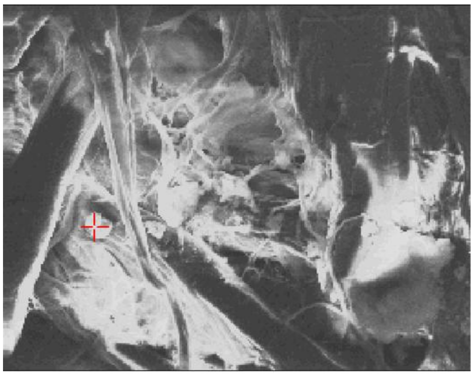


Figure 63. SE image and EDX spectrum of the blue painting layer.



Element	%
O	60.62
Si	24.91
Fe	11.41
Al	1.30
Na	0.98
Mg	0.78
Total	**100.00**

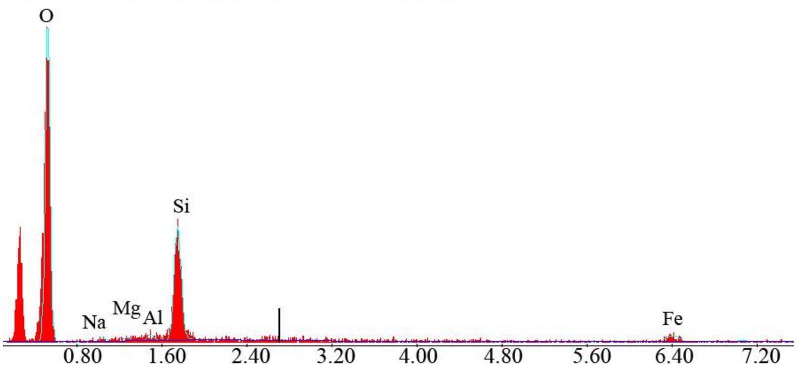


Figure 64. SE image and EDX spectrum of the blue pigment.

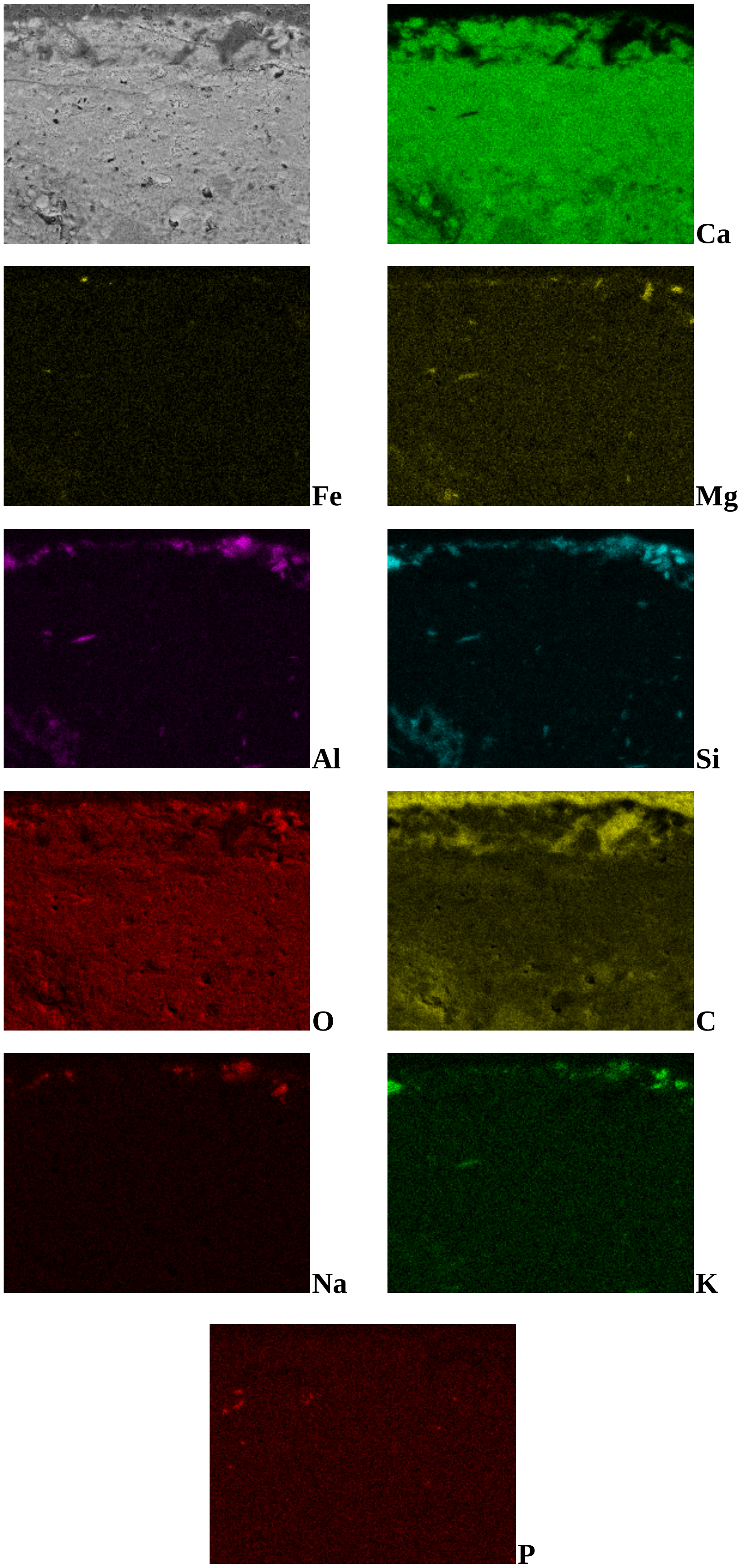


Figure 65. Mapping based on the chemical compositions of layers forming blue wall painting.

CHAPTER 5

CONCLUSION

This study was aimed at characterization of original materials and paintings techniques employed at fabrication of the wall paintings of Byzantine church in Kadıkalesi (Anaia).

Analysed wall painting samples were fragments of painted plasters which were found in earth during excavations; precise knowledge about the entire compositions is not available at present. Existing wall paintings on wall supports, arches and vaults have been detaching and the paints on surface renderings have been wiped out due to unfavourable environmental conditions; such as being under ground, being exposed to direct rain water, sun and other weather changes. Owing to these reasons, the church edifice could not be uncovered and the wall paintings have been left under ground deliberatively by the excavation team as a preservation precaution. Therefore, there is no information about the architectural characteristics of the church-monastery edifice yet.

According to macroscopic investigation *in situ*, the wall structure of the church was erected with alternating series of brick and stone- mainly cut-stone work, and the arches and the vaults were constructed with brick.

The structure of support of wall paintings is composed of two-layered plasters as of rough plaster (*arriccio*) and fine plaster (*intonaco*). Rough plasters are approximately 2.5cm in thickness and the thickness of fine plasters is 1.5cm in average. The fine plasters, which paintings were executed on, can be defined as high porous and low dense materials. According to several analyses, the fine plasters are almost consisted of pure lime with small amount of aggregates in small grain sizes.

Wall paintings in Byzantine church were executed in *lime-secco* technique: pigments which were admixed with mainly lime milk as binder were applied on lime-based fine plasters. Dolomitic lime, as binding medium was identified in yellow, green and purple painting layers in addition to lime milk.

On the basis of microscopic investigation on paint layers, the wall paintings were fabricated by using fundamentally earthen pigments; such as iron oxide-based pigments and aluminosilicate-based pigments. Red ochre (hematite) (Fe_2O_3) in red, yellow ochre (goethite) (Fe_2O_3. H_2O silica and clay) in yellow and caput mortuum (hematite in different grain sizes) in purple paintings were determined; and green earth (celadonite and glauconite) in green paintings, lazurite (*lapis lazuli*) and glaucophane in blue and dark blue paintings were identified.

In this case study, determination of dolomitic (magnesian) lime in paint layers indicated that the artists of the wall paintings of the Byzantine church improved the *lime-secco* technique. According to recent studies, use of dolomitic lime as binder prevented crazing on the surface of the paintings, and provided resistance and stability for the paint layers of the wall paintings. Besides this, identification of lazurite (*lapis lazuli*) as blue pigment is significant in the fields of archaeology and art history; as this determination can be deciphered as that Anaia (Kadıkalesi) and the church-monastery edifice are important in terms of marketing of lazurite, which was mostly conveyed from the mines of the Kokcha River valley in Afghanistan, in Mediterranean region during the Middle Ages.

Wall paintings of the church have been kept under soil as a conservation approach and precaution. However, a temporary shelter should be constructed in order to carry out the future *in situ* conservation works of the wall paintings and the church.

Soil in wall paintings which have been recently uncovered should be cleaned from soil with a soft brush; chemical cleansers reactions of which have not been established must be avoided.

Blistering and crazing have not been observed owing to application of wall paintings in lime-secco technique properly. In this sense, no problems existed about paint layers, except fading of paints which were exposed to direct sun light and rain water. However, detachment of rough plaster layers from wall supports and from painted fine plaster layers is a critical challenge. For this reason, plaster layers should be attached to wall supports and the adherence between rough and fine plaster layers should be implemented by using lime-based plasters and mortars; cement must not be used.

Consolidation and reintegration works, if necessary, on wall paintings and the church should be implemented to a minimum with the most proper materials and techniques in order to prevent reducing of material and authenticity, rather than using contemporary materials and technology effects of which are not known. Environmental conditions around wall paintings and the supporting structure should be monitored and controlled regularly.

This study has constituted a crucial stage in the context of determination of conservation approach. In the future phases of conservation works, other essential researches should be carried out precisely for the conservation of wall paintings of the church.

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