

Isotopic Geochemistry Applied on Mortars of the Katholikon of the Monastery of Timios Prodromos in the Prefecture of Serres, Greece

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Abstract. The Monastery of Timios Prodromos is the most important Byzantine monument in the prefecture of Serres and one of the most important monastic foundations of Byzantine times in Northern Greece. It was founded in the late 13th century from Ioannikios and then renovated by his nephew, Joachim. The catholic dates back to the 14th century, and specifically between 1300-1333, under the rule of the second founder Joachim. Considering the pathology of Byzantine mural, for the most effective work on removal of over-paintings layer, fixing, restoration, recovery and maintenance of the painted surface and the substrate, it was decided the sampling from exact points of the mural painting representing the different phases, in order to determine their composition, the technology of construction materials, corrosion mechanisms and the proposal for restoration methodology. The methods to be used require very small quantities of material. The measurements are considered almost non-destructive and based on isotopic geochemistry. The techniques used are X-ray diffraction (XRD), scanning electron microscopy (SEM / EDXA) and isotopic analyzes (d18O and d13C) in a mass spectrometer (IRMS). The study of the samples was carried out by scanning electron microscopy with X-ray microanalyser and analysis of stable isotopes. The study shows that apart from the calcite present in all pigment samples, straw was used as a binder. There is also a mixing of dyes to produce the desired tint while in many cases there are different colour layers. The decay in the mural is extensive, especially in the lower layers of the wall, which have been severely affected by humidity and candle smoke. The creation of gypsum on the surface of the murals is intense and evident in most of the spectra taken

1. Introduction

The Monastery of Timios Prodromos, is the most important Byzantine monument in the prefecture of Serres and one of the most important monastic foundations of Byzantine times in northern Greece. It was founded at the end of the 13th century by Ioannikios, and was then restored by his nephew Joachim. It has the form of a closed fortification with the katholikon dominating in the middle of the lower courtyard. Its present form is the result of successive additions, renovations and interventions of various seasons. In the initial phase belongs the katholikon and the tower in the southwest corner. Decoration that is preserved in the catholic church is really important and impressive, but is also preserved in other buildings of the monastery. These frescoes date back to the 14th until 19th century and constitute a unique ensemble for studying the history and evolution of Byzantine and post-Byzantine painting in the region of Eastern Macedonia. Katholikon dates back to the 14th century, specifically between 1300-1333, under the rule of the second founder Joachim.



Considering the pathology of the Byzantine frescoes (falling materials, cracks of various types and progressive disintegration of the mortar of the remaining part of the monument) and a more efficient work on cleaning, removal of a layer of repairs, consolidation, restorations, retrievals and maintenance of painting surface and the substrate, it was decided taking samples from different phases of the frescoes to determine their composition, explore the technology of construction materials, corrosion mechanisms and the proposal for restoration methodology. The technical study of the chemical and mineralogical composition of mortars and pigments and their conservation status, using stable isotopes, is carried out in order to apply the research results to the restoration work for which the Ephorate of Byzantine Antiquities of Kavala is responsible. The main purpose of this study is to investigate the causes of disintegration of mortars and pigments in order to promote appropriate and specialized consolidation and restoration actions.

The methods used, require very small quantities of material. The measurements are considered almost non-destructive and based on isotopic geochemistry. The techniques used, are X-ray diffraction (XRD), scanning electron microscopy (SEM / EDXA) and isotopic analyzes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in mass spectrometer (IRMS).

The interpretation of the analytical results will lead to the development of proposals for maintenance materials and methods, preventive maintenance methods for the protection of monuments from climatic conditions and the suitability of existing materials and maintenance methods. The interpretation of the analytical results can be used for the development of archaeological research, as the study of the chemical, mineralogical and isotopic composition of the mortars can determine the origin and techniques of their construction.

2. Sampling

The mural has been performed with the fresco technique. It consists of the mortar (substrate) and the painting surface. The mortar is the wall plaster placed over its thick plaster and consists of 3 layers: the first is the thickest (about 10 mm), the second is 3 mm and the third is the 2 mm painting layer. The mortar consists of lime and straw. The painting surface of the wall painting consists of colours and natural minerals. The colours are joined to the water that is discharged through the surface of the mortar layer where it is concentrated and while it becomes dry, it stabilizes and becomes part of it. The result of this technique is called fresco and characterizes the Byzantine era. The work program included: samples of dyes, samples representative of the layers of construction of the mural, samples of recent interventions and repairs, samples representative of the conservation status of pigments and mortars. The samples were collected in section to represent moisture penetration from the outside. Sampling was carried out on the basis of the principle of extraction of the smallest possible quantity in order to minimize the intervention of the monuments.

Table 1: Sample description

Sample code	Origin	Description
C1	Nave	Mortar sample compounded with active material
C2	Nave, North wall	Sample of green pigment along with mortar. Strong corrosion is observed due to increased soot adherence
C3	Bottom part, North wall	Sample of pigment with a substrate over a wooden beam
C4	Sanctuary, Inner part	Probably dating back to 1803 AD and contains three phases

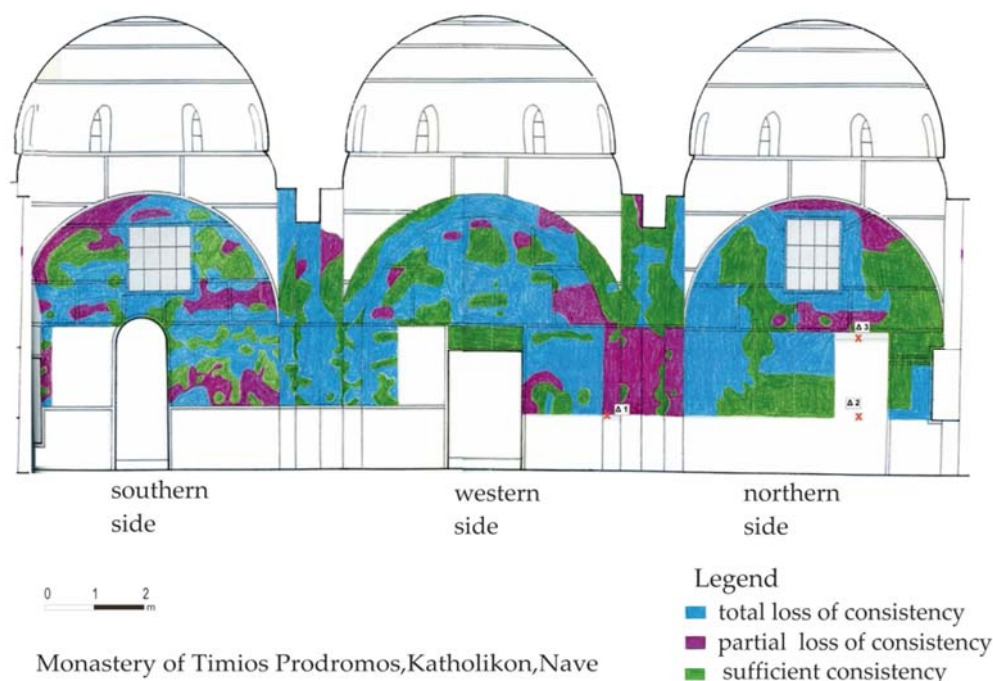


Figure 1: Sample presentation from the nave of the Monastery of Timios Prodromos

3. Methods of analysis – Sample preparation

Elemental and microform (SEM / EDXA) analysis was performed using a FEI / Quanta Inspect D8334 scanning electron microscope incorporating an X-ray energy dispersion microanalyser. The micro-morphological examination was performed by taking photomicrographs using back-scattering electrons, with its grey-colour graduations reflect the individual number of items. Elemental analysis was performed by sequentially scanning the electron beam on the surface of the sample. The pigment and mortar samples were stabilized to SEM stubs with a carbon footprint and placed in the scanning electron microscope for elemental and micro-morphological analysis.

Mineral analysis (XRD) was done using a Siemens D500 (Bruker AXS) diffractometer using $\text{CuK}\alpha$ -irradiation. Powder from the samples was used less than 0.063 mm. The isotopic analyzes were performed on Finnigan's Thermo Delta V Plus Isotope Ratio Mass Spectrometer (IRMS) and GasBench II instrumentation. Small quantities (<200 μg) of material were dissolved in orthophosphoric acid and the CO_2 produced was measured by the mass spectrometer. The isotopic ratios $^{13}\text{C} / ^{12}\text{C}$ and $^{18}\text{O} / ^{16}\text{O}$ were determined in relation to an international PDB standard. From each sample of mortar, 1-2 small samples were excised using a lancet, starting from the outside to the inside, in order to separate the pigments from the substrate. Each micro sample was placed in the pestle to form a homogeneous powder suitable for stable isotope analyzes. The isotopic analyzes were performed at the Stable Isotope Unit accredited according to ELOT EN ISO / IEC 17025: 2005. The Unit has successfully participated in international inter-laboratory trials and participates in international, transnational and national research programs.

4. Elementary, micromorphological and mineralogical approach

The application of elemental and micromorphological analysis to the scanning electron microscope makes it possible to determine the elemental composition, microstructure and morphology of the samples. Furthermore, elemental and micromorphological analysis can provide qualitative and quantitative information and be used diagnostically in determining the degree of diagnosis of the calcite matrix. Microscopic observation in the scanning electron microscope makes it possible to investigate the structure of the mortar.

More specifically, microscopic observation reveals information on resource allocation and resource relations with the other parts of the sample. The purposes of the analysis are:

- Determination of the mineral and chemical composition of pigments and mortars
- Determination of the size, shape and texture of the microstructures of mortar and pigments
- Determination of the erosion causes of pigment and mortar
- Diagnosis of recent interventions

Characterization of pigments

- Red pigments

The presence of Hg and S in SEM-EDS is a hallmark of the existence of the red pigment called cinnabar. The cinnabar is the main mercury (HgS), with bright red to orange reds. The word 'cinnabar' is probably of Indian origin and means "the blood of the dragon" or "red resin". It was known to the ancient Greeks from the 6th century BC. But strangely, its use in ancient Egypt has not been detected. Small pieces of ore, according to Vitruvius, were pulverized in a stone mortar and dust was produced, which was also the dye. It is a representative pigment of the Byzantine era. The detection of Fe in conjunction with the red shade of the sample leads to hematite (Figure 5). Hematite (α -Fe₂O₃) is anhydrous ferric oxide and gives pigments with red hue and metallic shine. The use of two kinds of red dye is an indication of successive layers of epigraphy. Sample B6 has been collected from a newer surgery segment as opposed to sample A4 representing the older segment, which is also evidenced by the experimental data.

- White pigments

Pb detection in sample B2 is associated with lead white pigment [Pb (PbCO₃ · Pb(OH)₂]. Extensive Pb detection in several samples, is an indication of the use of Pb white to illuminate shades.

- Yellow pigments

The presence of Fe in the A10 sample leads to the use of Fe₂O₃ (Hematite Fe₂O₃ or FeO(OH) limonite). The sample A10 has been collected from the form of Archangel Gabriel and dates back to the 15th century. The specimen has a strong soot-coat which is evidenced by the presence of sulfur which is the product of degradation of calcite. The yellow dye is typical of the late Byzantine era.

- Green pigmentation - greater intervention

Sample B8 is representative of a newer operation. The EDX spectrum depicted in Figure 8 is detected by the Fe elements combined with the Mo element (molybdenum) lead to the conclusion that this is a new material that indicates a newer operation.

- Blue pigment

The figure depicts the S and Na elements representing the blue ultra-marine dye in sample B3 (Figure 9). The chemical formula of the dye is Na₈-10Al₆Si₆O₂₄S₂-4. Blue dye is a sign of recent surgery as the dandelion lapis bulb is a younger dye that has been widely used after the Byzantine era, which is considered to be a sign of recent interventions.

- Binders

The binder consists of calcite and straw (Figure2). The mural has been performed with the fresco technique, so the plaster that is formed is created by lime (CaO) converted to calcium hydroxide (Ca (OH)₂) when mixed with water. The pigments applied on the liquid substrate during the drying process react with CO₂ and form a crystalline layer of CaCO₃ that makes fresco paintings very resistant to climatic conditions so they can be maintained for a long time. The binder contains straw (Figure 3).

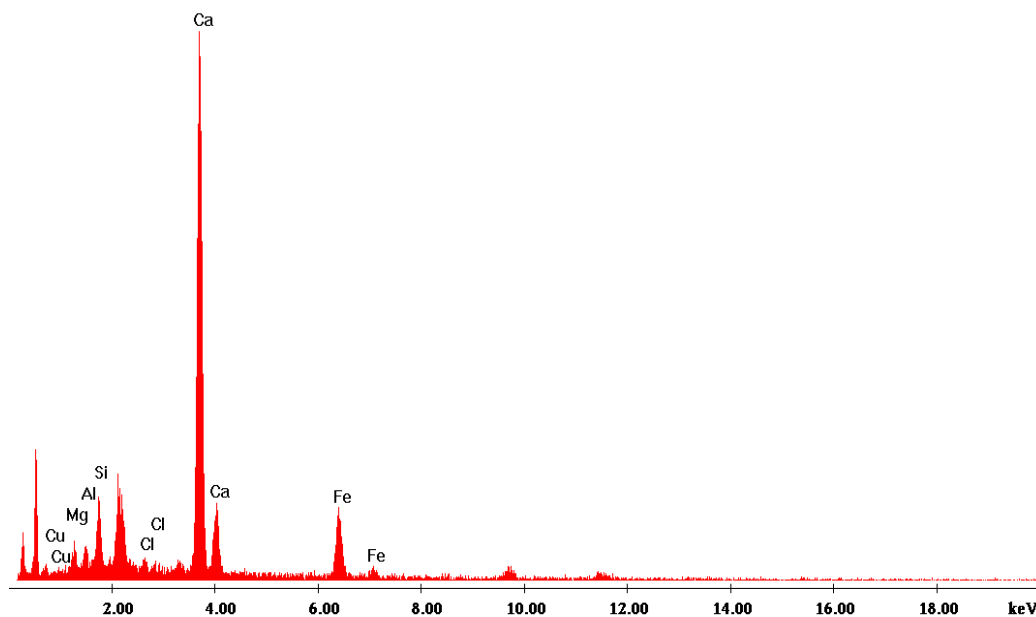


Figure 2: EDX spectrum of blue pigment (yellow pigment) in sample B3

- Corrosion products

Figure 3 shows the elements of calcium and sulphur associated with the presence of plaster in the layers of the mural. As mentioned above, one of the damages that a fresco can suffer is the absorption of moisture from the environment that occurs with the appearance of phosphates, nitrates, sulphates, carbonates and silicates on the surface. Especially gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is formed during the reaction of calcite (CaCO_3) and sulphur dioxide (SO_2), in the presence of relative humidity, an oxidation element and a catalyst (Fe_2O_3 or NO_2).

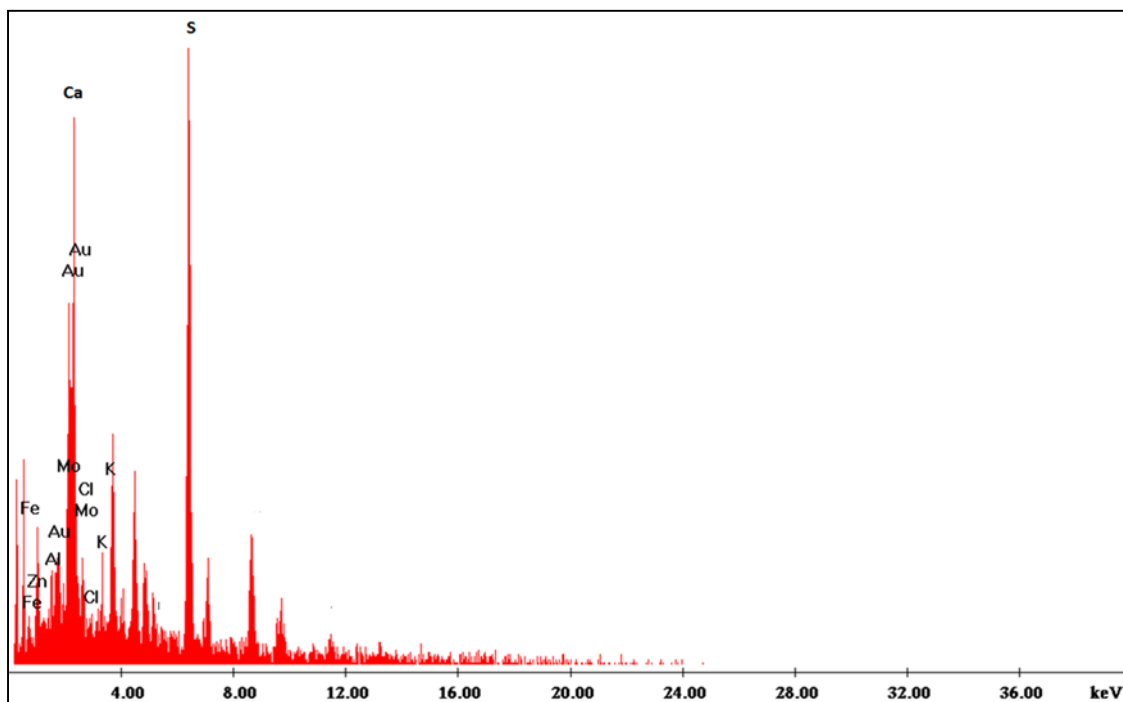


Figure 3: EDX spectrum representative of calcium sulphate

5. Analysis of stable isotopes

Measurements of stable isotopes of carbon and oxygen were performed on all samples, while 2-3 measurements were made on each sample. Prices range from -19.1 ‰ to 2.5 ‰ for oxygen and from -26.1 ‰ to 2.1 ‰ for coal (Table 2).

Table 2. Isotopic values of carbon and oxygen

Sample	Sample code	Method	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
A1	Narthex	N-10	-12.3	-9.4
A2	Narthex	N -10	-15.1	-17.1
A3	Narthex	N-10	-13.5	-19.6
A4	Narthex -1	N -10	-5.1	-15.8
A5	Narthex -1	N -10	2.7	-11.2
A6	Narthex -1	N -10	-9.8	-13.2
A7	Narthex -1	N -10	-12.9	-15.3
A8	Narthex -1	N -10	-12.5	-17.2
A9	Narthex -1	N -10	-14.1	-13.2
A10	Narthex -1	N-10	-16.4	-12.6
A11	Narthex -1	N-10	16.7	2.5
A12	Narthex -1	N -10	4.1	6.3
B1	Narthex 2 Mesonyktikon	N -10	2.1	9.3
B2	Narthex 2 Mesonyktikon	N -10	-15.4	-18.9
B3	Narthex 2 Mesonyktikon	N -10	-13.2	-19.1
B4	Narthex 2 Mesonyktikon	N-10	-13.5	-16.2
B5	Narthex 2 Mesonyktikon	N-10	-12.4	-11.2
B6	Narthex 2 Mesonyktikon	N-10	-9.8	-13.1
B7	Narthex 2 Mesonyktikon	N-10	-12.4	-15.1
B8	Narthex 2 Mesonyktikon	N-10	2.2	7.1
B9	Narthex 2 Mesonyktikon	N-10	-14.6	-13.3
C1	Nave	N-10	-26.1	-22.6
C2	Nave – North wall	N-10	-16.7	-12.2
C3	North wall – Bottom part	N-10	-14.1	-16.5
C4	Inner part of Sanctuary	N-10	12.3	14.2

Figure 4 gives the isotopic values of the samples as well as lines 1, 1A and 1B which can be used as tools for technology interpretation and mortar erosion. The CM point expresses the isotopic values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of calcite formed directly from the absorption of atmospheric CO_2 .

Line 1 shows deviation from the ideal conditions (point CM), indicating a continuous enrichment of $\delta^{13}\text{C}_{\text{co}_2}$ and $\delta^{18}\text{O}_{\text{co}_2}$.

Lines 1A and 1B are deviations from line 1.

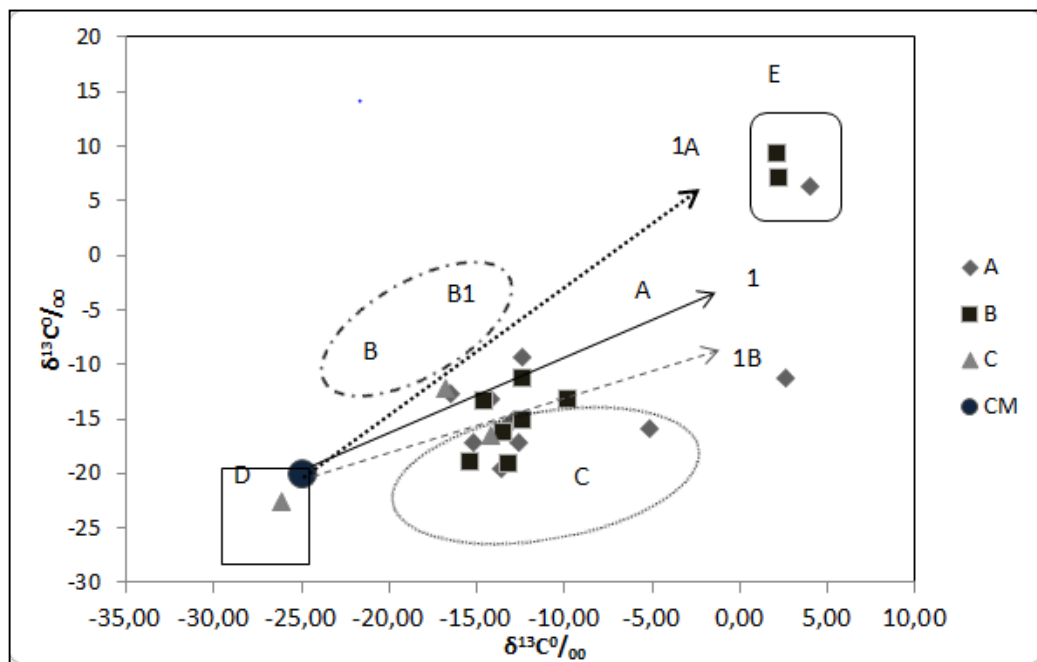


Figure 4. Isotopic values of the samples

These deviations, area A, show calcitic tissue formed from atmospheric CO₂ with varying proportions of limestone residues used for combustion (incomplete combustion products). Area B shows the participation of initial water in the melting phase of the mortar, possibly originating from isotopically heavier sources, e.g. evaporation or isotopically heavier meteoric water used in the preparation. Another possibility is the erosion of calcite from meteoric water. Area B1 shows the possible balance of calcite with silicate minerals. Area C shows calcified tissue formed with the participation of biogenic CO₂ significantly enriched in 16O over 18O and lesserly enriched at 12C than 13C. This position may also express calcium tissue formed from isotopically light re-condensed H₂O upon coagulation of the mortar or from partial secondary equilibrium of water with atmospheric CO₂. Area D indicates that part of the CO₂ was of biogenic origin during the thickening of plaster, with less diffusion effect along the mortar layer (eg only on the outside). Also area D can express the erosion of calcite with biogenic CO₂.

The samples analyzed in Figure 6 are placed in two areas A and C. The location of the points in the diagram, area C (figure 6), can be explained by the participation of biogenic CO₂ with secondary (recrystallization) equilibrium of water with atmospheric CO₂, Indicating extensive wear and tear from biological reasons and moisture. This secondary recrystallization of calcite, which also results in the creation of a black crust in the monuments, confirms that bio-corrosion is the main cause of the partial destruction of the monument.

Some of the samples studied are located in area A indicating that the calcium tissue was formed by the involvement of atmospheric CO₂ and the involvement of limestone used for combustion. These samples represent the original mortar. Conclusively, exploration of isotopic values indicates that mural repairs have affected the initial calcite composition to more positive values.

6. Restoration proposals

- Consolidation of the substrate with grouts

The following mortar composition is proposed:

- Hydraulic lime 100gr.
- Marble powder 80gr

- Primal AC572K 10 ml
- Sodium gluconate 1-3g
- Deionized water 100-150ml

Hydraulic lime is the bonding cement of the mixture and the marble powder is the filler material. Primal offers workability, adhesive properties and reduced shrinkage. Sodium gluconate is a fluidiser that reduces the amount of water and therefore shrinkage during curing.

- Consolidation of mural's layer

In areas where the original layer has remained, it is suggested to consolidate it with Paraloid B-72 2-5% dissolved in acetone. The paint surface has very small porosity, so it is recommended to fix with solutions and not with acrylic emulsions. Paraloid is an excellent quality maintenance material that retains its properties over time and is difficult to oxidize.

- Cleaning

Cleaning samples must be carried out using the following materials:

- White spirit
- Aromatic hydrocarbons (xylene, toluene)
- Alcohols (ethanol, methanol)
- Ketones (acetone, propanone)
- Chlorinated hydrocarbons (trichloroethane, trichloroethylene)
- Amides (dimethylformamide)
- Poor inorganic bases (ammonia)
- Amines (butylamine)

The choice of the appropriate solvent depends on the results of the specimens. Solvent application should in no way affect the painting surface. The mural has been performed with the fresco technique where lime is used as a binder. The above organic solvents are not expected to cause damage to the paint surface that has been performed with an inorganic binder.

- Removing repairs

The painting layer has been placed just above the original layer. The preservation of the repairs is against the principles of art conservation, while their technique and style are inferior to the original painting layer. Therefore, it is preferable to remove the repairs. Specimens of removal repairs may be carried out with the solvents proposed for cleaning along with simultaneous mechanical cleaning using a lance.

7. Conclusions

The study of the samples from the Monastery of Timios Prodromos near Serres, was carried out by scanning electron microscopy with X-ray microanalyser and analysis of constant isotopes. These two methods were complementary and gave us a large amount of information capable of leading, in the majority of cases, to safe conclusions about the identification of the materials, the technical design of the frescoes and the present situation. The study shows that in addition to the calcite present in all pigment samples, locally and straw was used as a binder. The study of the samples showed that there is mixing of pigments to produce the desired tint while in many cases there are different colour layers. Many samples of different red pigments were studied, for which SEM-EDS showed cinnabar and hematite (Fe_2O_3) in different proportions: the brightest specimens (orange-red) are more pronounced in contrast to cinnabar while the darkest shades come from pure hematite. The use of different pigments indicates newer interventions. In elemental analysis of the yellow samples Fe was detected with Ca demonstrating the use of limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$) as a yellow pigment. Blue ultra-marine was used in blue samples, indicating a newer operation. In addition, Pb detection in several samples, is an indication of the use of Pb white to illuminate shades.

The wear and tear in the mural is extensive and especially in the lower layers of the wall, which have been severely affected by moisture and candle fluff. The creation of gypsum on the surface of frescoes is intense and evident in most of the spectra taken.

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