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Pigment Mineralogy, Chemical Composition and Stratigraphy of Wall Paintings in the Church in Włościejewki, Poland

Mineralogia pigmentów, skład chemiczny i stratygrafia malowideł ściennych w kościele we Włościejewkach w Polsce

Keywords: pigments, thin section, wall paintings, microstratigraphy, petrography

Słowa kluczowe: pigmenty, płytki cienkie, malowidła ścienne, mikrostratygrafia, petrografia

Introduction: Purpose and aim

This study is focused on the technological layers in wall paintings of the Church of the Immaculate Conception of the Blessed Virgin Mary in Włościejewki. The majority of structures built in this region (located in the present-day Greater Poland Voivodeship) in the sixteenth century or earlier have been repeatedly rebuilt, and the original painting layers have not been preserved to the present day.[1] Therefore, this is an extraordinary opportunity to examine the original structure of sixteenth-century painting layers. The aim of the work was to study and analyze wall painting layers with a particular emphasis on the mineralogy and chemical composition of pigments used in paintings. Performing a comprehensive analysis of the structure and the stratigraphy of wall paintings in terms of correlation with the time of their creation was another indirect goal. In the years 2005–2010, the walls of the church were subjected to comprehensive restoration treatments, the only advanced procedures to be performed on them to date. Stratigraphy of the painting layers showed that, since the sixteenth century, they had been repeatedly repainted using various techniques. No documentation exists regarding the original painting layers, and the paintings have not been previously described for research, conservation, nor subjected to physicochemical testing.

Historical context of the building

The village of Włościejewki (Fig. 1. A), in the Greater Poland Voivodeship, is located approximately 60 km to the south of Poznań. Its first mention, under the old name of Vloszczegow, appeared in the year 1382.[2]

The building is located on a hill with a high eastern escarpment, formerly a watercourse valley. The first mention of a church in Włościejewki comes from the year 1417. The existing late Gothic shape of the church comes from the sixteenth century, and has been partially destroyed during a fire in the early seventeenth century. It is a single-nave church with an indoor presbytery and without a cellar. Red Gothic brick was used as building material, along with sand-lime plaster. The old brick system has remained intact in the inner walls, while the external walls have been transformed with modern bricks.[3] Gothic bricks have a different dimension.

During conservation, fragments of the original geometric painting décor were uncovered from under the modern painting layers (Fig. 2. A). In the presbytery, above the original passage from the sacristy to the church,

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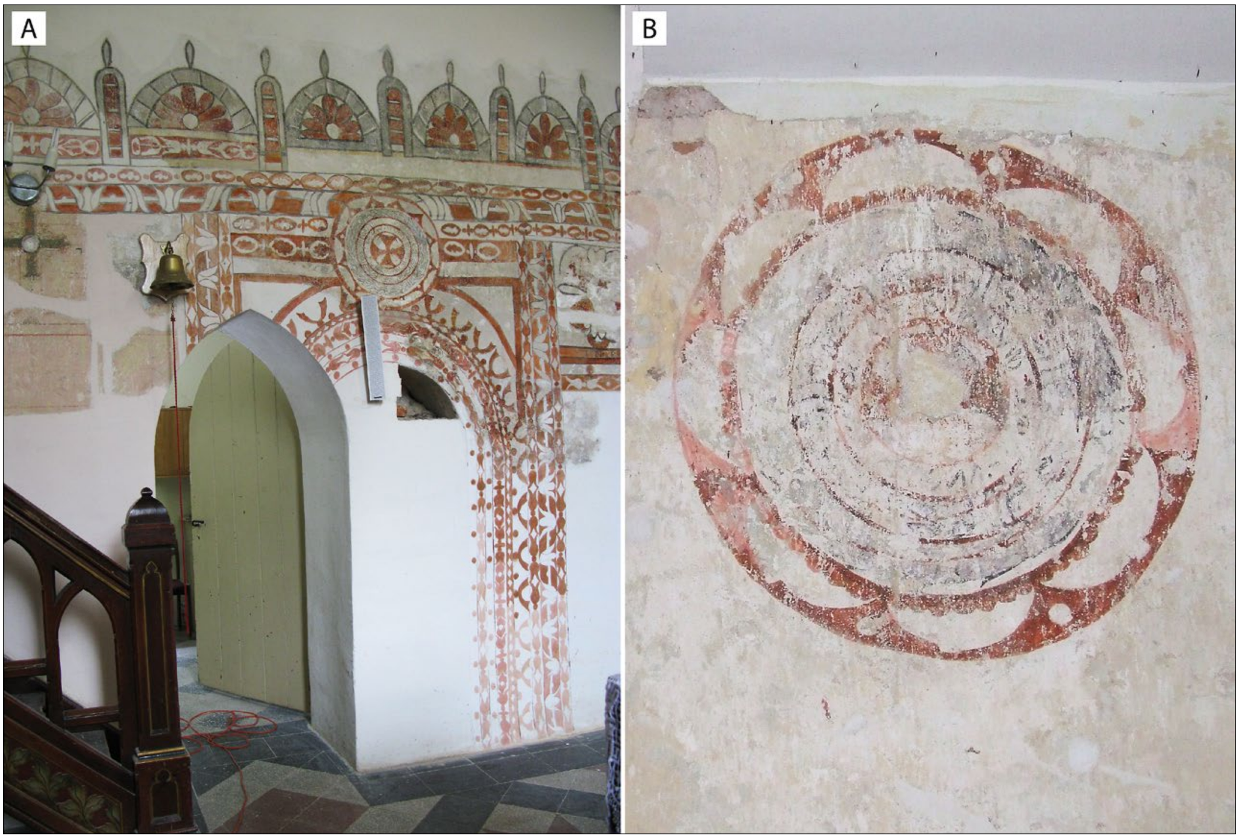

Fig. 1. A – original sixteenth-century ornaments, B—consecration cross from the sixteenth century.

that was likewise discovered, there is a symmetrically located consecration cross, richly decorated, in the form of a laurel wreath, with a Maltese cross and texts in Latin and Greek. Another consecration cross was discovered on the southern wall (Fig. 2. B). A considerably more modest consecration cross, located under the music choir at the entrance, is related to the second consecration of the church, which took place after the seventeenth-century fire. There is no record of either the local artist, the materials that were used, or any earlier paintings.

Wall painting technique

For centuries, the most popular technique used to make paintings on wall surfaces was the fresco technique. It is characterized by the presence of calcium carbonate in all technological layers. The main focus of this study was to determine the original, primarily used technique from the sixteenth or early seventeenth century. On brick walls with lime-sand joints, sand-lime plaster (arriccio) was applied, with medium and fine sand grains. The next step was to impose fine-grained lime whitewash (intonaco) and the polychromies of the background, details of walls, ceilings and vaults, mainly using dry fresco technique.[4]

Conservation background

Many factors contributed to the poor condition of the building's walls. The drainage of rainwater and roofing had been neglected for a long time. The lack of regular maintenance of drainage systems led to the flooding of the facade and permanent dampness, which resulted in the dissipation of internal plasters and the weakening of the brick foundation. Undrained water penetrated deep into the sand-lime plaster, causing its discoloration. An increase in salinity and salt crystallization increased the volume of individual layers and caused the fragments of the painting to lose their adhesion to the base surface and detach themselves from it. Initially blisters appeared, then a clear delamination, which eventually resulted in a complete deformation and even fragmentation of the painting.[5]

Methods and materials

The use of thin-section petrography analysis for studying historical objects has become a standard.[6] Despite its invasiveness, petrographic comparative analysis is valuable for recognizing and understanding the subject under study. Insight into the microstratigraphy of a painting, which facilitates the characteristics of all paint layers is particularly valuable. Thin sections are valuable as research and educational material. Thin-section analysis, combined with methods like SEM, X-ray fluorescence spectrometer (XRF), or micro-Raman spectroscopy, gives valuable results, as demonstrated in earlier studies conducted by Appolonia et al., Magon and Del Lama, Mugnaini et al. and many others.[7]

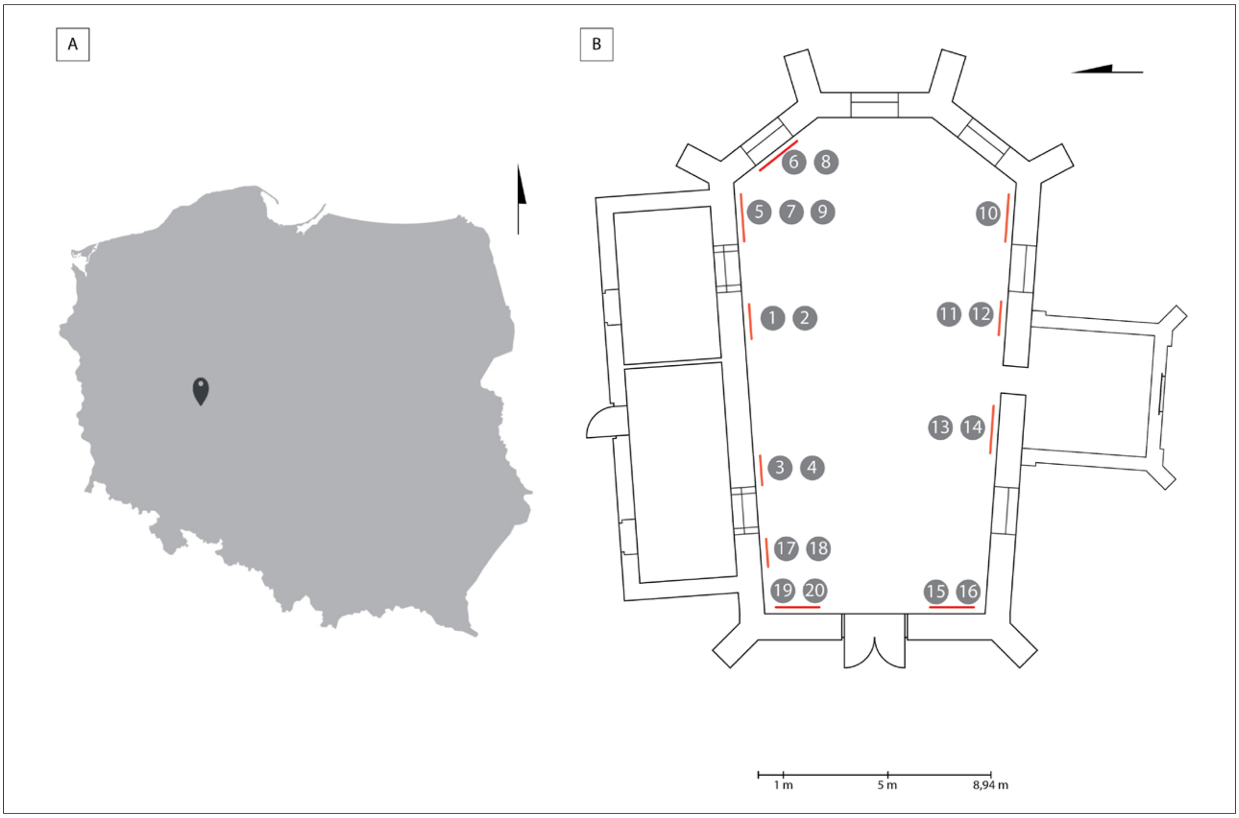

Fig. 2. A—church location, B—top view, sampling locations.

Methods

The size and number of samples taken was limited due to the condition of the building's walls and its historical value. The collected samples were selected from the most representative ones and most diverse in terms of color. The sampling sites were documented, photographed, and the samples were described using macro and microscopy. The first observations were carried out using an OLYMPUS SZX9 stereoscopic microscope. This made it possible to select the samples from which the thin sections were made to carry out observations with a polarizing microscope. Observations of the pigment layer were made with an OLYMPUS AX70 PROVS petrographic microscope. This microscope was equipped with a DP50 digital camera. Documentation photographs were taken in reflected and passing light, polarized, with parallel (PPL) and crossed nickels (XP).

The next step was to analyze the chemical composition of the pigment using a HITACHI 3700N scanning electron microscope, equipped with an EDS detector. Before inserting the sample into the SEM vacuum chamber, the thin sections were sprayed with graphite. The samples were tested under low vacuum conditions. The tests were carried out at the SEM-EDS laboratory of the Adam Mickiewicz University in Poznań.

Summary and results

Pigment samples were collected during the last stage of conservation work—the uncovering and renewal of paintings. The thickness of the samples varied depending on the condition of the plaster.

Optical tests

We selected samples representative for each color to make thin sections. All thin sections were observed in polarized transmitted and reflected light. Reflected light turned out to be more favorable for the observation of the pigments, while transmitted light was more favorable for the observation of the structure of the painting layers. This was related to the amount and type of pigment used. This paper presents a detailed description of selected representative samples.

Composition of technological layers supporting the painting layers

Plaster (arriccio)

In this case, we see plaster as one of technological painting layers applied directly to the brick wall, with an average thickness between 2–4.5 mm. Plasters from various samples seemed to be similar in terms of chemical composition of minerals and in structure, while their texture differed (Fig. 5.) The time of construction and the manner of preparing the walls, as well as the location of the sample and the related moisture content could have influenced the variabili-

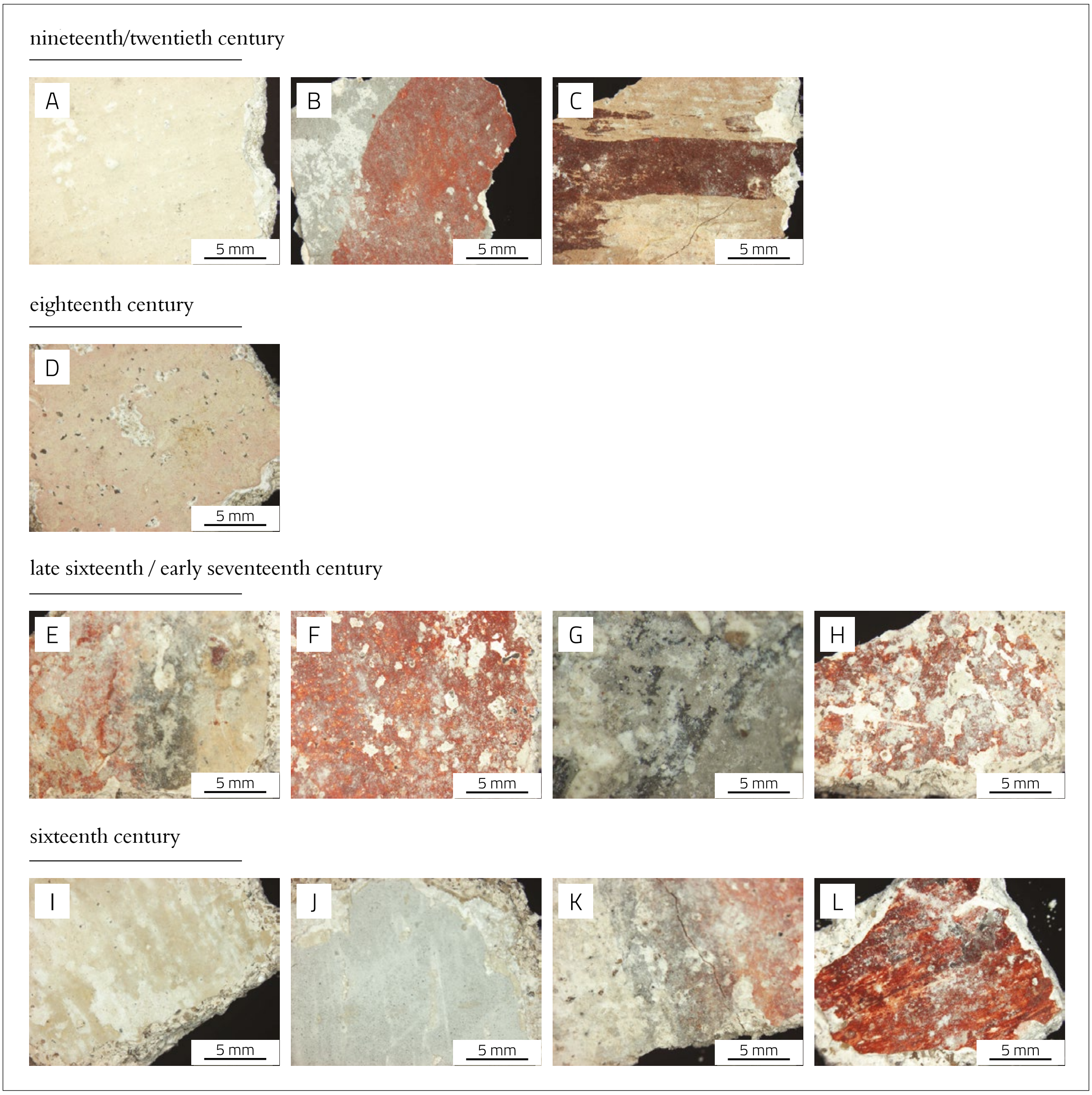

Fig. 3. Surface of the samples, pigment coating, A—sample No. 19, B—sample No. 1, C—sample No. 3, D—sample No. 4, E—sample No. 8, F—sample No. 13, G—sample No. 15, H—sample No. 16, I—sample No. 6, J—sample No. 9, K—sample No. 10, L—sample No. 5.

ty of the texture. An analysis of the plaster filler grains fraction was carried out. However, the largest number of counts amounted to 191, therefore these measurements cannot be considered statistically representative, but give us a general view of the tested samples. Studies of plaster grain fractions distinguished sample No. 19 (turn of the nineteenth and twentieth century), which, with the highest number of measurements, had the lowest average filler grain diameter of 0.37 mm and the lowest standard deviation of 0.14. Samples from the sixteenth century had an average filler grain diameter of 0.47 mm—medium sand grains,[8] and a standard deviation of 0.28. The results obtained from the measurements of the remaining plasters were similar, which is why we can assume that the plaster had been made in similar conditions using similar materials, and the sand came from the same source. Sample No. 19 undoubtedly contains a typical lime plaster, as shown by mapping results. Other examined samples from the sixteenth century showed small amount of magnesium. However, the Mg content in the samples did not exceed 5%, which allowed us to classify the plaster as based on quicklime for all samples.[9] The plaster layers had the highest porosity of all of the observed technological layers. The observed filler was fine-grained quartz sand, there were single grains of feldspars, ferrous and clay minerals. Another characteristic feature of the plasters was the presence of straws, hair and fibrous elements used as fillers. They were observed in all samples with plaster (from sixteenth and the turn of the sixteenth and seventeenth century), except samples No. 1 (eighteenth century), 19, and No.20 (turn of the nineteenth and twentieth century).

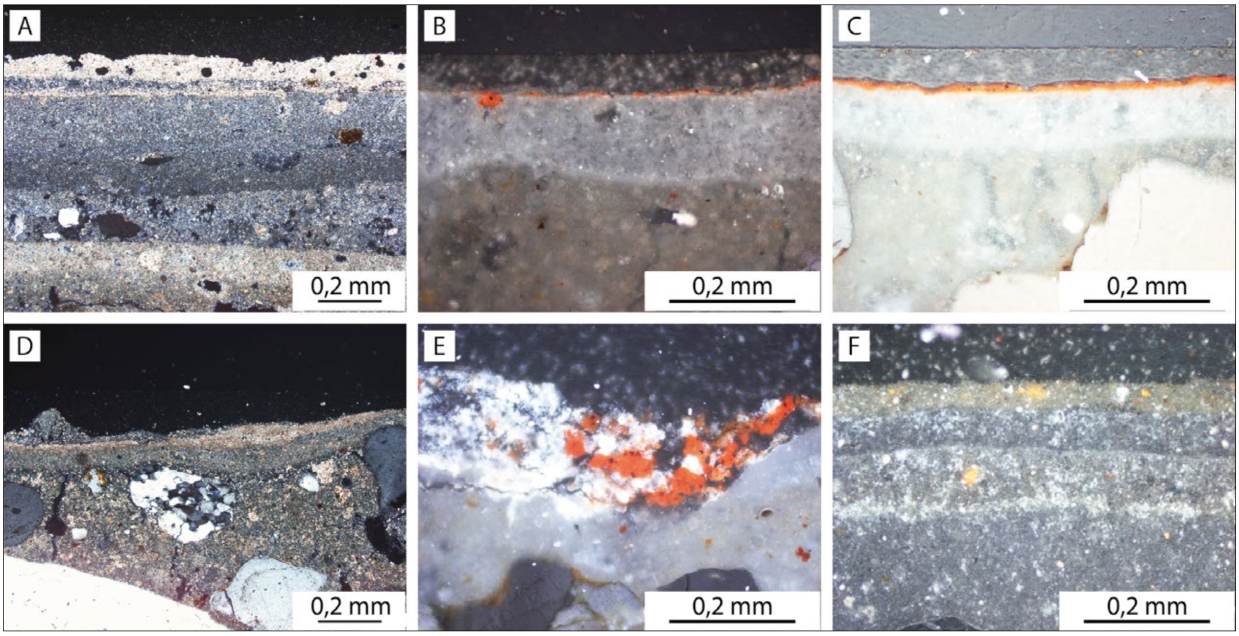

Fig. 4. Thin-section photos, stratigraphy and pigments, A—sample No. 9, transmitted light; B— sample No. 10, reflected light; C—sample No. 13, reflected light, D—sample No. 15, transmitted light; E—sample No. 16, reflected light; F—sample No. 19, reflected light.

Whitewash (intonaco)

It is a fine or very fine crystalline layer, with an average thickness between 0.1 and 0.2 mm. The main building element is $CaCO_3$. The mapping test and the microphotographs clearly revealed the line between plaster and whitewash, showing that they were distinctive, separately produced layers (Fig. 5. A, B). Whitewash in the observed samples was almost not porous at all (Fig. 4. B, C). In some of the tested samples, the whitewash was gently colored to replace the pigment layer. Observations and conservation studies suggested the presence of calcium and casein used as binder, which would explain the presence of characteristic elements such as sulfur and phosphorus in the technological layers, but mapping and chemical tests showed only small admixtures of sulfur, equally indicative of the presence of gypsum crystals and walls salination. Therefore, the presence of admixtures of protein and casein binders could not be unambiguously determined.

Sample description

Observations showed that relations between layers and microstratigraphy observation are important. Arriccio, intonaco, and pigments are components of a dynamic system where, to a certain degree, all the elements affect one another.

Samples from the sixteenth century

The oldest discovered wall paintings featured a characteristic red (Fig. 3. L), black, and white, geometrical pattern. Layers from this period have remained only on the north wall, at the presbytery. Two samples were distinguished, one from the niche (Fig. 3. I) and the second from the old passage (Fig. 3. J).

Sample No. 9 (pigment: light blue, sixteenth century)

The place of collection was the door frame of the former Gothic passage connecting the sacristy with the nave of the church. Microscopic observations in this thin section showed a varied structure in cross-section. Observations in reflected light revealed two not very clearly separated layers of bright pigment; the upper layer was found to contain very fine grains with an isotropic character. Underneath there were three layers of plaster containing several grains of quartz sand (Fig. 4. A). The sample, observed with a SEM microscope, showed the presence of four technological layers (Fig. 5. A). The tests indicated the presence of calcium, silicon, aluminum, iron, as well as traces of chlorine, sodium, and potassium. The chemical image made by profiling demonstrated a large, but variable calcium content depending on the layer. It coincided, to a large extent, with the oxygen curve. The individual layers were very finely crystalline.

Sample No. 10 (pigments: red, black, white)

Sample taken from the consecration cross on the south wall, about two meters above the floor level. Three layers were visible: plaster, whitewash, and pigment. Sand grains were observed to pierce the colored surface and disturb its smoothness (Fig. 3. K). Observations of sample No. 10 in reflected light clearly showed the presence of one thin, intensely colored, red-orange pigment layer, not perfectly continuous. A uniform, whitewash layer was visible below, and in the next, lower layer of the plaster, there were

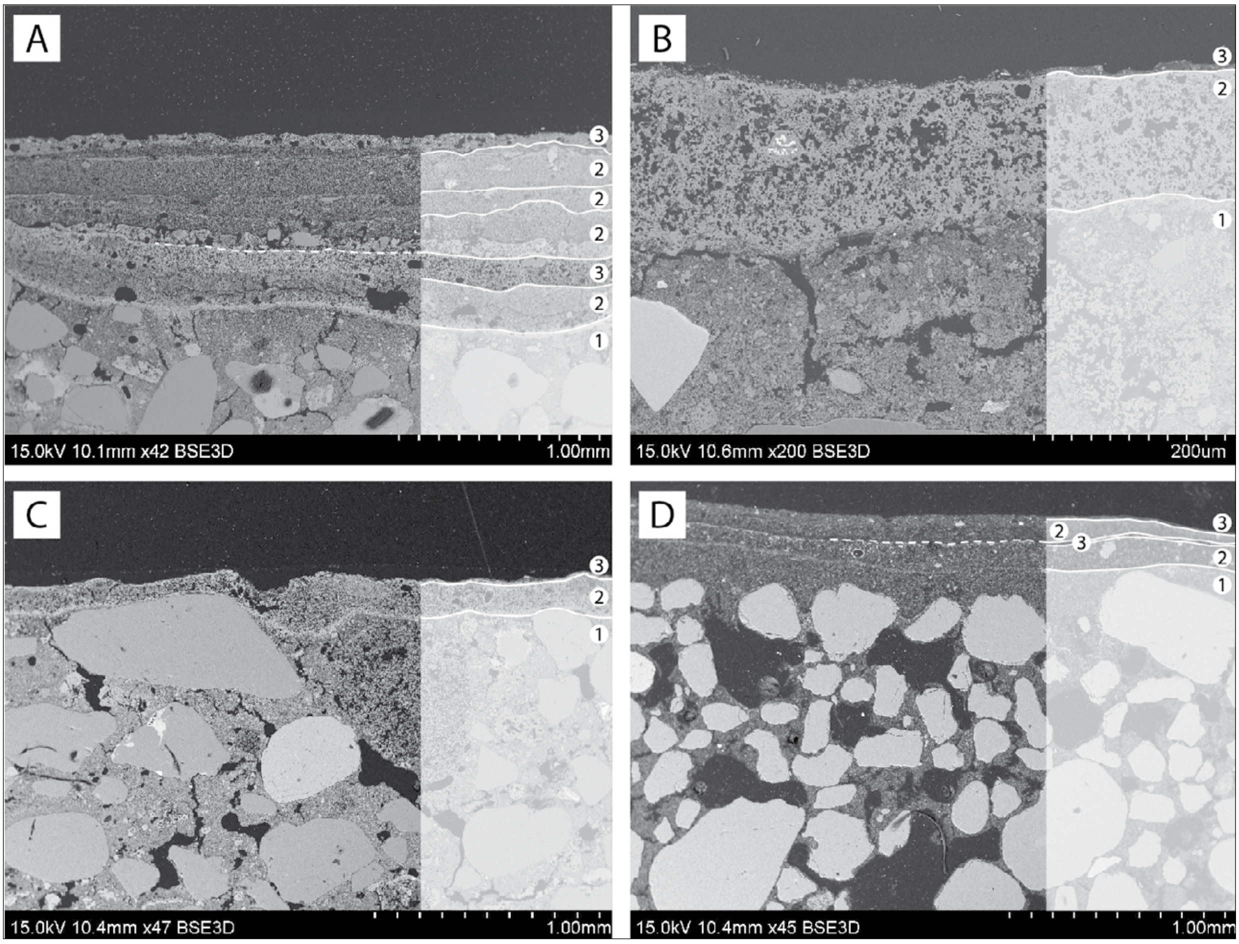

Fig. 5. Structure of the painting. A—sample No. 9, B—sample No. 10, C—sample No. 13, D—sample No. 19; 1—plaster, 2—whitewash, 3—pigment.

single fine quartz grains (Fig. 4. B). **SEM / EDS test results:** Observations of the sample with a BSE detector revealed the existence of one more clear, thin pigment layer. It was observed to consist of very fine-crystalline particles, below which there was a visible whitewash layer, also very fine-crystalline and porous. Below the plaster layer with distinct mineral grain with medium and fine (sand fraction size) minerals, combined with a fine crystalline binder, there were visible, elongated voids (Fig. 5. B). Data obtained by mapping showed the presence of elements such as calcium, aluminum, silicon, magnesium, oxygen, and some concentrated amounts of iron. The largest amount of calcium was observed in whitewash and plaster, the concentration of iron often overlapped with the presence of oxygen, most likely forming iron oxides. The presence of bromine is visible throughout the sample. Point and area tests on the surface layer of pigment showed the presence of iron, silicon, magnesium, and traces of titanium and arsenic.

Samples from the turn of the sixteenth and seventeenth century

In the group of samples from this period, only one came from an ornament (sample No. 8), and all others were collected from consecration crosses.

Sample No. 13 (pigment: red)

Three basic technological layers were observed and the sample surface was found to be inhomogeneous and to possess cavities (Fig. 3. F). The red-orange pigment observed in reflected light (Fig. 4. C) displayed a homogeneous structure, evenly distributed over the entire area. Underneath, there was a uniform, even layer of whitewash, in the next layer of plaster there were various sizes of quartz grains near the pigment layer. **SEM / EDS test results:** Observations conducted using an electron microscope revealed the presence of one thin, vast, dense and homogenous, very fine crystalline layer of pigment. It was slightly lighter than the lower whitewash layer. The color difference showed a different chemical composition (lighter areas mean heavier elements). A smooth transition of the pigment was visible and, combined with the whitening layer, it had a slightly higher porosity, and was distinguished by color. The layer of plaster underneath contained grains of sand with medium and fine fractions, and an average level of coating (Fig. 5. C). Point and area tests showed the presence of elements such as iron, silicon, aluminum, oxygen, titanium, magnesium, calcium, trace amounts of sodium and sulfur, in the pigment layer. Observations conducted using the mapping method showed a significant ac-

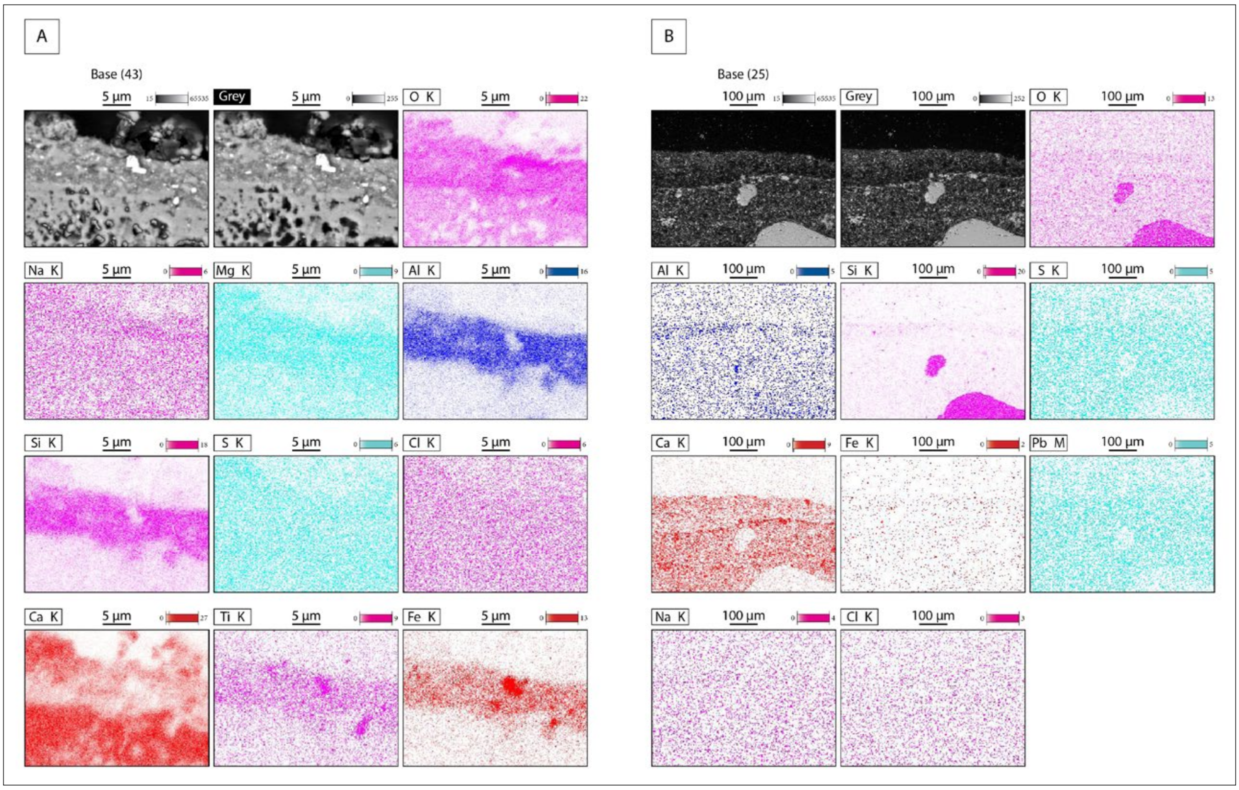

Fig. 6. Mapping: A—sample No. 16. X-ray mapping, BES image—mag: 4000, kV 15.0; B—sample No. 19, X—ray mapping, BES image—mag: 190, kV 15.0.

cumulation of calcium in whitewash and plaster layers, an even distribution of sulfur and chlorine on the entire surface of the sample, and a horizontal distribution of elements such as iron, silicon, clay, aluminum, oxygen, titanium, consistent with the pigment layer.

Samples No. 15 (black) and No. 16 (red)

Both samples were taken from a consecration cross located to the south from the main door. Sample No. 15 is gray-black with a red line (Fig. 3. G), and was observed to feature a strongly compact plaster, with visible straws in its cross-section. Its surface is uneven, damaged. Sample No. 16 is red (Fig. 3. H), and was observed to feature much more brittle plaster in pale pink, its surface was badly damaged and there were numerous deep defects on the surface.

Sample No. 15

The layer of plaster is clearly defined. A whitewash layer containing numerous fine quartz grains of varying degree of roundness was observed. On the top of the sample there were three thin layers of dye. The thickness of the layers was not equal. While observing the sample in reflected light from the bottom, we observed a distinct grayish beige staining layer, then a discontinuous layer of dark pigment, and another layer of gray-white pigment (Fig. 4. D). **SEM / EDS test results:** Studies with the BSE detector showed the presence of one layer of fine crystalline pigment. It occurred discontinuously on the porous whitewash layer and was highly concentrated. Point and area tests showed the presence of calcium, iron, silicon, magnesium aluminum and molybdenum. This is a gray-black specimen where we would expect the presence of carbon. However, due to the graphite spray, it was not included in the analyses.

Sample No. 16

Observations made in reflected light (Fig. 4. E) showed a clear, uniform layer of red pigment. We noticed the presence of one large lenticular accumulation of pigment in the whitening layer. In the bottom layer of plaster there were quartz grains of medium roundness, and in many places they penetrated into the whitewash layer. **SEM / EDS test results:** The observed cross-section of the sample showed a finely crystalline, thin and concentrated layer of pigment, an equally finely crystalline and porous layer of whitewash, and a fine and medium-crystalline layer of plaster with sand grains. The profile test performed on the vertical section of the pigment showed that the concentration of iron was uniform, the concentration of silicon and aluminum was the largest in the middle part of the vertical profile, and that calcium content increased near the whitening layer. Similarly, grouping elements could be observed thanks to mapping (Fig. 6. A): silicon, aluminum, and magnesium in the middle part of the profile, calcium in the bottom, and a large amount of oxygen was present uniformly throughout the sample area. Iron and magnesium formed a concentration band in the middle part, while chlorine and sodium were observed in the whole sample.

Samples from the eighteenth century

Sample No. 1 (pigment: light pink)

Taken from the southern wall, two meters above the floor, to the left of the entrance to the sacristy. Three clear layers were visible in the cross-section: a plaster, whitewash and pigment layer. The colorful, smooth surface of the fresco was observed to be disturbed by quartz grains, analogous to those found in the plaster (Fig. 3. D). **SEM / EDS test results:** The top pigment layer was tested directly on the sample. On the surface, very small parallel creases could be observed, while larger approximations showed delicate cracks parallel to the scratch marks. Spot and area tests show the presence of calcium, silicon, sulfur, iron, and barium.

Younger nineteenth- and twentieth-century samples

Sample No. 3 (pigments: light blue, first half of the twentieth century)

Collected at the entrance to the sacristy on the right side, two meters above the floor level, the pigment adheres to a very thin layer, displaying a smooth surface, few fine quartz grains were visible, the red color had been added to blue (Fig. 3. B). **SEM / EDS test results:** The sample was tested in low vacuum conditions. The surface of the pigment sample was observed to be fine crystalline, with two distinct zones visible: a light gray zone on the right and a dark gray zone on the left, singular darker areas were the remains of the layers covering the painting. On the lighter surface, parallel cracks were visible. We know from macroscopic studies that both zones represent a different color. Blue field point tests indicated the presence of calcium, silicon, aluminum and zinc, iron and barium.

Sample No. 4 (pigments: beige, brown)

The sample was very thin, the pigment was devoid of substructure (whitewash, plaster). This made it impossible to make a cut. The ample included for its distinctive color, it is a thin sample, a few millimeters thick (Fig. 3. C). **SEM / EDS test results:** The pigment surface layer was tested. The observation of the surface with the BSE detector featured two functions of testing the chemical composition at given points and on the designated area. Examination of the sample in terms of the content of elements showed: zinc, iron, calcium, sulfur, silicon, magnesium, sodium, potassium, manganese, barium.

Samples No. 19 (pigment: light yellow)

Samples collected from the back wall of the choir. The sample was compact, the surface was affected by sand grains breaking through the surface of the pigment (Fig. 3. A).The plaster was very compact, slightly colored, and contained medium fractions of quartz grains. Microscopic examination in reflected light showed that there were two layers in the cross-section with a coloring function (light yellow), (fig 4. F). **SEM / EDS test results:** Testing with a BSE detector showed two layers of pigments, they were separated by a delicate whitewash layer, they were very finely crystalline with low porosity. The plaster was well-packed, sorted with sand grains, basic quartz. Both layers were similar in texture and structure. Point tests showed the presence of silicon, aluminum, iron, traces of sulfur and chlorine. Mapping tests (Fig. 6. B) showed two layers with a significant concentration of calcium in the lower layer and a decrease of calcium in the upper layer. Other elements such as oxygen, silicon, aluminum, and iron were observed to be evenly distributed.

Discussion

Studies of painting layers and pigments confirmed the chronology suggested by conservators. Microscopic observations added several new facts about the techniques of creating paintings, in particular the nature of plasters and the type of filler, and the small chemical diversity of the pigments. To determine exactly whether the paintings in Włościejewki contained admixtures of an organic binder, it would be valuable to apply additional methods, for example the use of gas chromatography or a Raman spectroscope used by Trąbska[10] or Holclajtner-Antunović et al.[11]

The red pigment (samples No. 2, 5, 13, 16, 18)

It comes from the oldest paint layers, having one layer of pigment. Studies showed that the coloring substances used had been iron oxides, probably hematite Fe_2O_3. Chemical tests also showed the occurrence of hematite varieties, with admixtures of aluminum and titanium. The occurrence of $FeTiO_3$ ilmenite and aluminum oxides was also likely.[12] Results obtained by Trąbska in red pigments indicated the presence of red ferric pigments based mainly on goethite and hematite, which are natural components of red ochre. Trąbska[13] also noticed a significant amount of lead pigments (minium, lithargite, plattnerite) in medieval wall paintings in churches in Lesser Poland.

The gray-black pigment (samples No. 7, 15, 17, 14)

The ornaments were made of lime with an admixture of carbon pigment, corresponding to the period of creation of black dyes based on carbon with admixtures. Bony black can be ruled out because phosphorus was not found. However, there were small amounts of molybdenum, iron and aluminosilicates (clay minerals). Hematite and manganese oxides may be present in small amounts. Carbon black is a classic pigment that was also present in the Žiča monastery wall paintings[14] and locally in the Church of Saint Simon and Saint Jude Thaddeus in Kosieczyn[15] or in polychromes in the interiors of tenement house No. 43 in the Old Market Square in Poznań examined by Filipiak.[16]

Three-colored red-black-white pigments (samples No. 8, 10, 12)

The analyses showed the presence of iron red oxide, titanium, perhaps ilmenite. The black dye, similar to the grey-black samples mentioned above, is not clearly defined. White color is represented by lime whitewash.

Pale Pink pigment (sample No. 1)

Pale pink was made by a blend of whitewash with a red ferric pigment. Research indicates that iron oxide is the factor that gives color to the layer. Mixing whitewash with pigment was also noticed by Holclajtner-Antunović et al. (2016).

Light blue (sample No. 3)

Profile test using SEM shows that both are pigment based on iron and zinc oxides.

Beige (with brown) pigment (sample No. 4)

Coming from a repainting from the first half of the twentieth century. Large amounts of iron and manganese may indicate that the pigment used is a mixture of iron oxides and manganese oxides umber type pigment.[17]

Light yellow pigment (sample No. 6)

Sample from the oldest original interior design of the building, with characteristic fibrous elements in the plaster. It is whitewash colored by iron oxides.

Light blue pigment (sample No. 9)

Has two layers of pigment, the top light blue and visible underneath, in thin section light yellow, probably analogous and equal age with that coming from sample No. 6. Pigment is spread in whitewash slightly colored yellow by iron oxides and hydroxides, possible presence of limonite.

Light yellow and light blue pigments (samples No. 19 and No. 20)

Taken from the mezzanine of the choir where the walls were renovated and repainted. The sectional tests in the cut showed the presence of two colored layers, however the pigment was not clearly accumulated but dispersed throughout the patch. Testing using SEM/EDS indicated that the coloring agents wereiron oxides and hydroxides, iron oxides yellow. The occurrence of lead was also claimed, which can be identified with the presence of lead oxide PbO.

Presence of barium traces in some samples (No. 1, No. 3, No. 4) might be interpreted as using a barium hydroxide solution, a common practice of wetting the plaster and whitewash before applying the painting.

Correlation

Pigments originating from the sixteenth and from the turn of the sixteenth and seventeenth century were dominated by red pigments. Samples No. 2 and No. 5 came from ornaments, while samples No. 8, 10, 11, 13, 16, 18 came from consecration crosses. Similar parameters of the plaster and micro and macroscopic observations indicated the same age, origin and manner of making the tested samples.

Black pigments co-existed with red pigments as part of the same ornaments and patterns. As in the case of red pigments, the test results showed the same age, origin and manner of making the tested samples.

Samples with light yellow and light blue pigments did not form the characteristic painting décor of the church, they came from the oil cavity (No. 6) and passages (No. 9). The cross-sections of the samples showed that the light yellow and then light blue layers were initially applied. In samples No. 6 and No. 9 there are analogous layers of light yellow pigment, the light blue paint layer is present in the sample No. 9 as the outer layer. The white pigment in samples No. 10 and No. 11 co-exists with red and black pigments as part of the same ornaments and designs.

Observations of No. 19 and No. 20 samples from the choir show the same origin and technique. In the cross section of the sample No. 19, analogous layers are visible, also the plaster shows similar characteristics in the micro and macroscopic observations. Samples No. 3 and No. 4 come from the same twentieth century painting layer, which was documented on photographs, however, the samples were not taken together with the older layers. Sample No. 1 was the only sample from the eighteenth century painting layer. Stratigraphy observations confirmed that sample No. 1 was younger and adhered to samples from the sixteenth and the turn of sixteenth and seventeenth century.

Conclusions

The plaster in all tested samples was lime plaster. Plaster filler consisted mainly of quartz grains, additionally grain of feldspar, carbonates, clays and granitoids. The predominant fraction of the filler was medium-grained sand. In addition, in older plasters (samples No. 2, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18) we found fibrous admixtures, straw, and hair. There was a thin layer of fine-crystalline lime whitening in all samples, indicating the technique of performing according to the principles of dry fresco. Thanks to the conducted research, analysis, and correlation of samples, the following can be concluded:

Red pigments from samples No. 2, 5, 10 (sixteenth century), 8, 12, 13, 16, 18 (turn of the sixteenth and seventeenth century) are red ochre: iron red (Fe_2O_3 Hematite, $FeTiO_3$ ilmenite) with aluminosilicates (clay minerals), and aluminum oxides.

Gray-black pigments from samples 7, 10 (sixteenth century), 8, 12, 15, 17, 14 (turn of the sixteenth and seventeenth century) are black carbon with iron and manganese oxides.

The light yellow pigment in the tricolor sample No. 8 was yellow ochre, formed by iron oxides and hydroxides.

White in the form of lime whitewash occurred in the tricolor sample No. 10 (sixteenth century) and No. 11 (turn of the sixteenth and seventeenth century).

The light pink pigment from sample No. 1 (eighteenth century) was a whitewash tinted with iron oxides.

The light blue pigment of sample No. 3 (first half of the twentieth century) consisted of iron oxides and zinc oxides.

The brown pigment in sample No. 4 (first half of the twentieth century) was umber created by mixing iron and manganese oxides.

The light yellow pigment from sample No. 6 (sixteenth century) was yellow ocher that consisted of lime whitewash tinted with iron oxide and hydroxide, with a possible presence of limonite.

The light blue outer pigment from the sample No. 9 (sixteenth century) is whitewash colored with iron compounds, possible admixtures of aluminosilicates (clay minerals). The inner, light yellow color layer, which was analogous to the pigment layer of sample No. 6, was yellow ocher, colored by oxides and hydroxides of iron, with the possible presence of limonite.

Light yellow sample No. 19 and light blue No. 20 (eighteenth/nineteenth century) were yellow ocher formed by iron oxides and hydroxides with additions of lead oxide PbO.

The interpretation proposal is highly probable. Tests of wall painting layers confirmed the chronology suggested by conservators. Microscopic observations have added new facts about painting techniques used in Włościejewki, in particular concerning the nature of mortars and the type of fillers. We can say that the technique has not changed significantly for centuries. Another interesting fact is the slight chemical variation of the oldest pigments, and their visual and technical modesty and simplicity.

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Abstract

The sixteenth-century geometrical polychromies that were discovered during conservation works in a medieval church in Włościejewki provided an extraordinary opportunity to examine the original structure of old painting layers and compare them with newer ones. Scientific research was carried out to obtain and confirm the stratigraphy of the paintings and enhance the knowledge about the techniques and pigments that had been used there. This paper presents a mineralogical and petrographic characteristic of the materials. The analysis was performed in painting layers such as: plaster, whitewash and pigment. They originated from layers created between the sixteenth and nineteenth century. Four microscopic observations of thin sections were made, using reflected and transmitted light. Samples that turned out to be too fragile were examined using a scanning microscope equipped with an EDS detector. The research also described in detail the plaster and the whitewash. Monochromes of the background, details of walls and ceilings were made on lime whitewash using the dry fresco technique. The study illustratively demonstrates the structural and textural variability of the painting layers through the ages. The study's findings show a slight variability of the pigments, mainly iron oxides based pigments.

Streszczenie

Szesnastowieczne polichromie geometryczne, które odkryto podczas prac konserwatorskich w średniowiecznym kościele we Włościejewkach, dostarczyły nadzwyczajnej możliwości zbadania oryginalnej struktury starych warstw malarskich i porównania ich z nowszymi warstwami. Przeprowadzono badania naukowe, aby otrzymać i potwierdzić stratygrafię malowideł i pogłębić wiedzę na temat użytych technik i pigmentów. Niniejszy artykuł prezentuje mineralogiczną i petrograficzną charakterystykę zastosowanych materiałów. Analizę przeprowadzono na takich warstwach malarskich, jak: tynki, farba wapienna i pigmenty. Zostały one pobrane z warstw wytworzonych pomiędzy XVI i XIX wiekiem. Wykonano cztery obserwacje mikroskopowe na preparatach, wykorzystując światło odbite i przechodzące. Próbki, które okazały się zbyt delikatne, zostały przebadane przy użyciu mikroskopu skanującego wyposażonego w detektor EDS. Badanie również szczegółowo opisało tynk i farbę wapienną. Monochromie tła, detale ścian oraz sufitów wykonano na farbie wapiennej przy użyciu techniki suchego fresku. Badanie ilustratywnie przedstawia strukturalne i teksturalne zróżnicowanie warstw malarskich w różnych wiekach. Wyniki pokazują nieznaczne zróżnicowanie w pigmentach, głównie opartych na tlenkach żelaza.