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On Blue and Green Pigments from the St. George Cathedral of Veliky Novgorod

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A R T I C L E I N F O

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A B S T R A C T

This paper presents the first analytical data obtained from the examination of fragments of stunning Russian–Byzantine frescoes recovered from an archaeological excavation at Veliky Novgorod, one of the oldest cities in Russia and a UNESCO World Heritage Site. The archaeologists of the Institute of Archaeology of the Russian Academy of Sciences have been working on architectural excavations at Novgorod for more than 20 years. In the last seven years, they have unearthed fragments of frescoes in the layers of the twelfth century AD during excavation under the floor of the Cathedral of St. George in the Yuriev Princely Monastery (built in 1119).

As a first step of this complex research, we decided to concentrate on blue and green pigments. A selection of 30 samples and around 30 parts of wall paintings still in situ, subdivided by technique and color nuance, were first autoptically examined and, where possible, studied by optical microscopy. In this way typical details, such as the use of additives to the mortars, different ways of treating and mixing the colors, and pigment layers, were recognized. For the first screening, the analytical data were collected using a portable X-ray fluorescence device. They indicated the use of a variety of pigments and mixtures to obtain different nuances of color. The samples were then analyzed by scanning electron microscopy with energy dispersive spectrometry. All phases of the study were recorded and documented by photos and micrographs of the most significant details. The data are discussed in the text and help explain the working habits of the painters of the time.

1. The Cathedral of St. George

The Cathedral of St. George (Georgievskii Sobor, 1120–1130) is the main church of the Yuriev Monastery, located 2 km south of Veliky Novgorod on the left bank of the Volkhov River, close to its source: Lake Ilmen (Figure 1). Construction of this church began in 1119, probably simultaneously with the foundation of the monastery. The promoter of the huge stone cathedral was the Novgorod prince Vsevolod Mstislavich, and at that time the monastery was led by Abbot Kiriak (Anonymous 1950:21; Anonymous 2008). From the III Novgorod Chronicle (seventeenth century), it is known that a master named Peter built the cathedral and that the construction continued for about 11 years and was completed under Abbot Isaiah (Anonymous 2008). Upon completion of the construction, the interior of the church was decorated with fresco paintings. This must have happened before the summer of 1130 (Anonymous 1841:214), when the consecration of the cathedral took place.

By the beginning of the nineteenth century, the cathedral was dilapidated and needed thorough repair. On the initiative of Archimandrite Photius (1792–1838) (Ulybin, 2001, 2002), a major renovation of the temple was carried out in 1825–1827. The cracks in the walls and arches were repaired and the roof was replaced (Anonymous 2008:70–72; Valentin 1893). During the restoration of the cathedral, the frescoes of the twelfth century were knocked off the walls, since they did not correspond to the artistic ideas of the time of Archimandrite Photius. Afterward the cathedral was painted anew, with new plaster. An article dedicated to the renovation of the St. George Monastery under Archimandrite Photius was published by K. I. Maslov, who gave important archival information concerning the nineteenth-century reconstruction and painting of the cathedral (Maslov 1998:74–90).

The last repair of the wall paintings of the St. George Cathedral was carried out in 1898–1902. The plaster of the nineteenth century was replaced with new plaster, and almost the entire church was redecorated with oil paint (Kedrinsky 1902).

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Figure 1. The Cathedral of St. George (1119) in the Yuriev Monastery at Novgorod

The first research and restoration work in the St. George Cathedral of the St. George Monastery began in 1931, when the cathedral was transferred to the administration of the Novgorod State Museum. The work was carried out under the supervision of archaeologist M. K. Karger, a specialist for historical sciences at Petrograd University. In 1933–1935, he conducted archaeological excavations inside and close to the cathedral. As a result, the late layers in the western part of the cathedral were removed, and a significant part of the interior of the temple was lowered to the floor level of the twelfth century. He stopped his excavation at the large slabs of the floor level or, where there were no slabs, at the level of a lime-cement layer under the floor. Below this level, excavations were carried out only where the ancient floor was disturbed by burials (Karger 1946).

Karger's excavations discovered many fragments of the original fresco painting. Some of them preserved partial or full images of the faces of saints. Karger's article on the excavations of 1933–1935 in the St. George Cathedral is one of the most important sources for the history of culture, architecture, and painting of Old Rus' (Karger 1946).

In the 1950s, after the restoration, these rare materials, for which there are almost no parallels, were arranged in a museum set up in the cathedral, where sarcophagi of ancient burials were shown. V. L. Yanin, building on the work of Karger, carried out an additional inspection of the exhibited burials in the cathedral and published material from the cemetery of the Cathedral of St. George (Yanin 1988:89–118).

Later, a study on fresco paintings of the cathedral was published by V. D. Sarabyanov (1998, 2002, 2011). The researcher discussed two manners of representing the faces in the main nave of the cathedral. His article, devoted to the fate of the frescoes of the early St. George Cathedral, describes how in 1820, under Archimandrite Photius, the original frescoes were removed. The article mentions that the paintings of the time of Photius were recorded and removed at the beginning of the twentieth century (Sarabyanov 1998, 2002, 2011). Further, he describes the fragments of the original paintings, including those with faces, discovered during disassembly of the filling of the arches of the Orlov Building (built in the 1820s), located east of the St. George Cathedral (Sarabyanov 2012). The article suggests that new fragments of frescoes might be found in different places inside the monastery, in backfill containing the remains of the removed paintings of the twelfth century. The 2013–2020 archaeological research of the Institute of Archaeology of the Russian Academy of Sciences was carried out with the financial support of the Russian Foundation for Basic Research under the leadership of V. V. Sedov. A huge number of fragments of paintings—several tens of thousands—were rescued from the ground under the late floor of the cathedral (Sedov et al. 2014, 2016; Sedow 2020). They contain hundreds of faces and fragments of faces, fragments with painted and graffiti inscriptions, ornaments, parts of figurative compositions, and so on. The study of the newly discovered fresco ensemble began with art history studies (Etinhof 2016; Sedov and Etinhof 2016). This paper presents the very first analytical data obtained from the study of blue and green fragments from the cathedral.

2. Methods and Techniques

The fragments recovered from the Cathedral of St. George are copious. We are dealing with many tens of thousands of fragments, with widths ranging from 40 cm to a few millimeters, preserved in various deposits in the city of Novgorod. So it was important to decide how and where to begin our examination and analysis, obtain useful and manageable data, keep track of the entire bulk of materials, and at the same time collect data useful for comparison. We settled for what we consider the simplest, most versatile, and most adaptable approach and decided to take into consideration pigments of one or two colors at a time. In this way we could detect the use of different mixtures employed for obtaining the diverse nuances and shades of color. The second decision was selecting the colors to be studied first. We went for green and blue—the colors that in general show more nuanced variations and that might present more difficulties because of the many choices available to ancient painters.

Another important aim of this study is to distinguish, if possible, the fragments of later paintings mixed up with those of the early phase of the Church of St. George in the two excavated sites outside the sacred building: one immediately adjacent and the second around 20 m from the building.

A group of scientists carried out a scientific examination of plaster and pigments from the Cathedral of St. George. They employed seven different methods on 11 fragments of painting and on some of the figures still in situ in the tower (Philippova et al. 2022). These data represent a useful comparison to our results.

2.1. Microscopy, XRF, and SEM-EDS Analysis

After the autoptic examination, with the naked eye and by means of simple optical magnification devices, such as jeweler's lenses, a thorough examination was carried out with a portable digital microscope (ProScope) equipped with a support and different lenses (10x, 50x, 200x) and with a Levenhuk digital microscope. The main magnifications employed were 50x and 100x. The aim of the microscopic examination was to differentiate and document the structure and texture of the fragments and to make sure that the exact areas of the sample to be analyzed could be easily recognized and retrieved.

As with the first screening of the available samples from the various churches, both as fragments and in situ, we carried out portable X-ray fluorescence (pXRF) measurements using a Bruker Tracer 5i pXRF spectrometer with ARTAX advanced spectral analysis PC software. The micro X-ray tube has a rhodium anode. The measurements were carried out on an area with a diameter of 8 mm with 15 keV and 11.35 A. The acquisition time was 60 seconds per measurement. Several measurements were acquired on each fragment whenever needed—for instance, when different color nuances could be distinguished or when different structures were recognized in the layers of painting at the microscope. Plaster analyses were carried out as well to discriminate elements in the substrate that might have been measured together with those of the pigments.

The samples were then observed and analyzed with scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) to see if the differences could be confirmed. The mixtures were identified and dated. The samples—first as loose fragments and then as mounted cross sections, made conductive with a layer of carbon in the usual way—were observed and documented by backscattered electron imaging (BSE) and analyzed using a Tescan Vega Compact SEM with Tescan Essence EDS with the following operating conditions: 20 kV accelerating voltage, 12 mA beam current, 15.8 mm working distance, counts of 100 seconds per

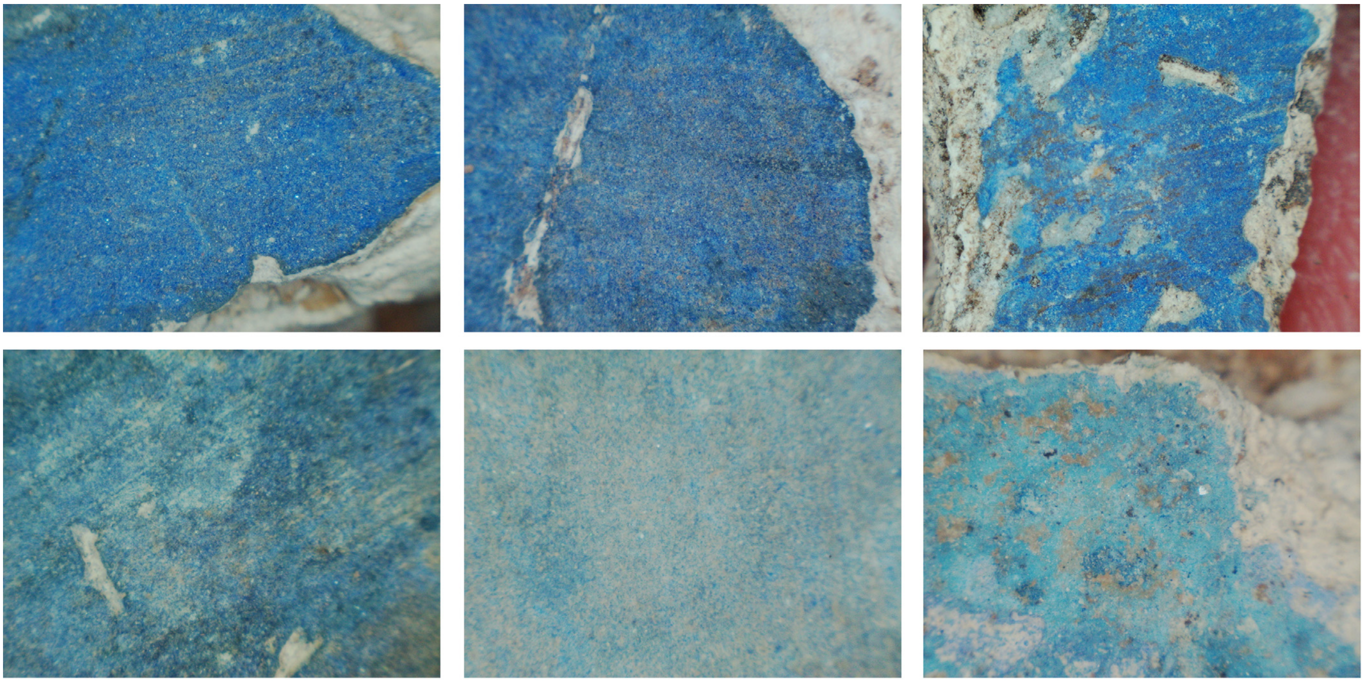

Figure 2. Some of the blue pigments from the Cathedral of St. George discussed in the text. The micrographs show the different ways of applying the pigments and the different colors and textures. The early ones show a more regular pigment layer and the strokes in one direction, even when damaged. The later fragments (second row, last two samples) have a mottled aspect and less regular pigment layers.

analysis, and dead time of approximately 25%. The measurements were processed using AZtecLiveLite EDS Software. As standards, we used pure pigments, bought from specialized workshops. We checked their composition first to see if there were any mixtures or additions.

3. Materials

3.1. Historical Green and Blue Pigments

In the case of green pigments, the possible palette includes malachite, Cu_2CO_3 $(OH)_2$; Egyptian green: calcium, Cu, and more than 4% flux (Schiegl and El Goresy 2006; Tite et al. 1987); green earth, consisting of celadonite (approximately $K[(Al, Fe_3+) (Fe_2+ Mg)](AlSi_3, Si_3)O_{10}(OH)_2$) with low Al content, and glauconite, similar to celadonite but with a large content of Al (approximately $(K, Na)(Fe_3+ Al, Mg)_3(Si, Al)_4O_{10}(OH)_2$), (Ospitali et al. 2008); and, finally, mixtures of yellow and blue.

In the case of blue pigments, the minerals and other ingredients employed can be azurite ($2CuCO_3$ $Cu(OH)_2$) (see Daniilia et al. 2000); Egyptian blue ($CaCuSi_4O_{10}$) (Ajò et al. 1996; Mirti et al. 1995; Pozza et al. 2000; Tite et al. 1987; Verri 2009); and the so-called *oltremare*—that is, lapis lazuli (or lazurite: $(Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)$) (Schmidt et al. 2009) but also, for instance, mixtures of black and white pigments of different kinds and mixtures of minerals and indigo or other colorants of organic origin (Aceto 2021; Brunon 2013, 2017; Casadio et al. 2004). Both Egyptian green and Egyptian blue (or cuprorivaite) are artificial, human-made pigments. They were quite common in antiquity and until later times, but they do not seem to have been in use at Novgorod. Obviously, the composition can vary (Schiegl and El Goresy 2006; Tite et al. 1987).

Ideally the pigments used for fresco paintings should be stable. That is, they should be resistant to humidity, air, and light and free of acidic components, both organic and inorganic. In reality, a range of unstable pigments was used for frescoes at different times and in different places.

The so-called earth pigments are very stable. These are for white, lime and kaolin; for yellow, red, and brown, the various ocher varieties and sienna, caput mortuum, and umbra; for green, malachite and green earth; and for blue, lazurite (also called lapis lazuli, azure, or *oltremare*). Unstable mineral pigments are, for instance, lead white and the orangey-red tetroxide called minium, which both turn to brown; azurite, which in the presence of humidity turns to green malachite and in the presence of sulfur turns to black; verdigris, which in the presence of humidity alters with whitish to pink crusts; and finally cinnabar, which under the action of humidity and sunlight turns to black.

Unstable pigments were employed for frescoes by using precaution and expedients, such as treating the pigment layers with resins or wax. Pliny states, “A surface painted with cinnabar is damaged by the action of sunlight and moonlight. The way to prevent this is to let the wall dry and then to coat it with Punic wax melted with olive oil and applied by means of brushes of bristles while it is still hot, and then this wax coating must be again heated by bringing near to it burning charcoal made of plant-galls, till it exudes drops of perspiration, and afterwards smoothed down with waxed rollers and then with clean linen cloths, in the way in which marble is given a shine” (Pliny, Nat. Hist., 33, 122).

The data obtained with pXRF measurements carried out on the walls of the church and the pXRF and SEM-EDS analyses on the selected samples permit a first screening and identification of the green and blue pigments from the Cathedral of St. George. An important result is that we can now distinguish the early fragments from the later ones.

4. Discussion of Results

4.1. Microscopy on Blue Pigment Layers from the Cathedral of St. George

A large group of fragments from the Cathedral of St. George in the Yuriev Monastery comes from the excavation immediately adjacent to the wall, carried out in 2020, and from one farther from the building, carried out in 2021. In the case of both sites, we suspected that some of the fragments might be of a later date.

A selection of blue samples from this excavation was examined at the microscope and showed that the blue paint on the fragments of the first group had been applied carefully with only one orientation (Figure 2: IUR ffw20mb1; IUR ow 20 DBm; IUR ow DB3s; IUR ow 20 DB1pm). In the case of the second group, the striation of the brush has different

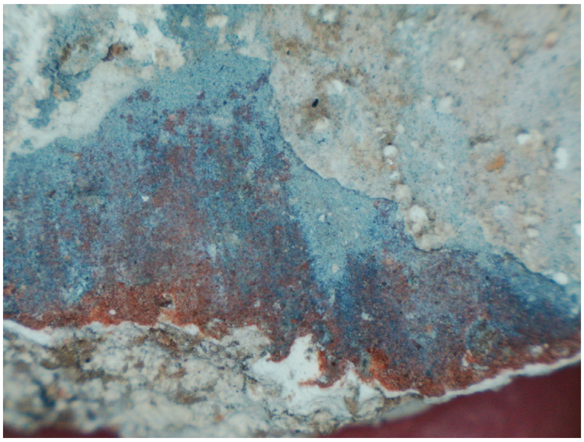

Figure 3. Detail (50x) of sample with blue and white pigments on a red underlayer (Iur OW 20 DLB3p).

Figure 4. Twelfth-century wall paintings preserved under the later floor, still in situ inside the St. George Cathedral after excavation. The red underlayer is exposed where the paint is damaged.

directions (Figure 2: IUR ow 20 GB1 l gray-blue; IUR ow 20 LBg1). In some cases, the pigment has a mottled appearance, with shiny quartz inclusions. That is, the sand employed as aggregate protrudes from the plaster and through the pigment layer, and more pigment layers can be recognized on the same specimen (Figure 2: IUR ow 20 LBg1). Further, some of the samples belonging to the second group show pigment layering on what looks like a kind of red underlayer (Figure 3).

A red pigment was also employed, apparently as a kind of preparation coating, under the *intonachino*—the last and finest plaster layer, about 3 mm thick (Figure 4)—but apparently only on the lower section of the wall, near the floor. The measurements carried out with pXRF on the red coating under the plaster still in situ identified an iron-based red pigment, most probably red ocher. The SEM-EDS analyses carried out on the red layer under the blue pigment confirmed that it consists of red ocher. We plan to determine the exact nature of this red pigment with more precision by using a different method, such as X-ray diffraction (XRD) in the near future.

Red underlayers under a pigment of a completely different color are known from earlier sites. For instance, in Italy, in the fragments of frescoes from the Caseggiato dei Lottatori at Ostia, dated to the second half of the first century AD, there were some red underlayers (Marano 2021:58–65, Figures, 3, 4, 5, 8). Further examples are fragments of Roman mural paintings collected from the excavations in the Patio de Banderas in the Reales Alcazares Palace in Sevilla, on which the underlayer was an iron-based mineral, on top of which was an Hg-based compound (Duran et al. 2011). Finally there were red underlayers under the pigments of paintings from the Sinop Batalar Church complex in northern Anatolia, dated to the second to fourth century AD (Bakiler et al. 2016:270–71). In short, this method was practiced in the entire Mediterranean, but it is less known in Russian-Byzantine mural paintings.

In all known Mediterranean cases, red ocher was the material employed for the underpaint. This practice was observed and has been known for a long time. In the sixteenth century, Cennino Cennini mentions the technique of applying secco layers on a red underpaint called *morellone* to obtain a darker blue hue (Cennini 2009). Also in the sixteenth century AD, Francisco Pacheco dal Rio (1594–1644)—a Spanish painter and teacher of Velasquez—recommends in his treatise *Arte de la Pintura* (1649) to add on the surface of the intonaco, on top of the preparatory drawing, a layer of lime and *almagra* (red ocher), but he states that only lime without red ocher should be used under green and blue (Pacheco 1959, II, 52).

Despite the very long use of this practice, the reason for employing a red pigment as underlayer for other colors, as well as the use of pink or yellow for the *intonachino* (see, e.g., Allag and Groetembril 2021; Dilaria et al. 2021:141; Marano 2021:58, Figure 3), has not been explained in a convincing way, at least up to now. The most common theory is that the red ocher layer would somehow protect the painting from humidity, but the mechanism remains unclear. Other scholars state that the idea was to deepen the color of the pigment or change its nuance. For instance, in the wall painting of the Spring of Peirene at Corinth, the underpaint is black under a layer of blue (Hill 1964), certainly to deepen the blue color.

A further theory explains the red underlayers as a kind of stabilization or even sanitization of the intonaco before the application of paint. This, together with the improvement of the application of color and the reduction in quantity of expensive pigments, while nonetheless achieving good coverage, might represent a good reason for the use of this kind of underlayer (Allag and Groetembril 2021:210). However, it must be noted that multiple layers also impede carbonation, and in many cases the secco technique was used.

4.2. Microscopy on Green Pigments from the St. George Cathedral

While rough mortars could not be found on all fragments, relatively thick layers of intonaco were examined on most specimens selected for analysis. The microscopic study and in some cases even the autoptic examination evidenced in the structure of the intonaco some recurrent differences among groups of fragments. The fragments that could be dated to that period—by comparing them with the remains of the twelfth century—show a compact lime preparation mixed with straw. The plaster preparations that can be dated to later phases of the cathedral consist instead of a different material mixed with rough quartz sand that often can even be seen on the surface and shows through the pigment layer.

The main group of green pigments from the excavation immediately outside the wall of the cathedral shows carefully applied layers with a single orientation of the brushstrokes. The green pigment layer seems to be less compact and stable and more prone to scratches than other pigments—for example, the blue. In some cases, the dark green and yellow-green pigments were applied on a red underpaint that is now visible where the upper layer is damaged (Figure 5). The pigment of a light green fragment, a single find for the moment, consists of a layer of light green pigment, apparently prepared by mixing green earth with

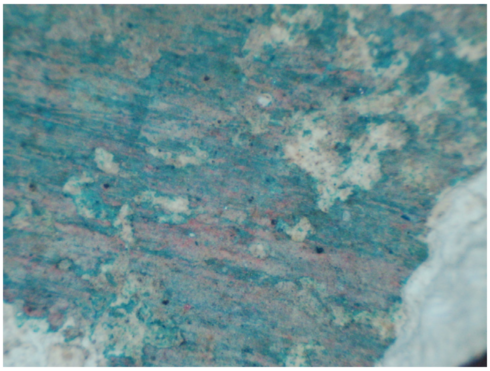

Figure 5. Green pigment (Iur OW 20 YG1g) on red underpaint (50x). The brush-strokes are oriented in one direction. The intonaco is compact and mixed with straw fragments and can be dated to the twelfth century AD.

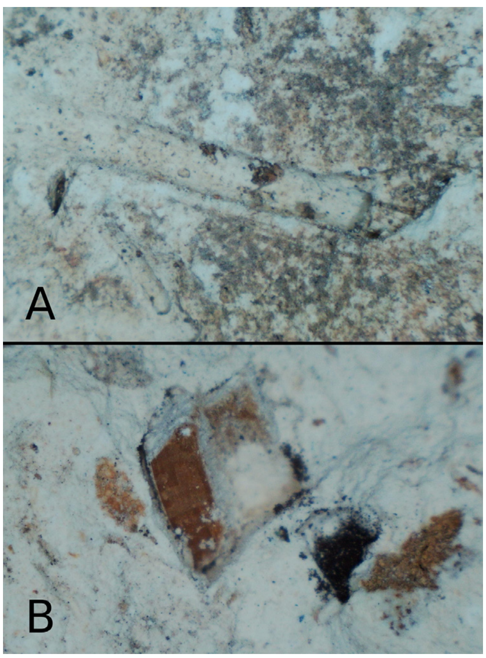

Figure 6. (a) Intonaco of fragment IUR ow 20 DB5 mixed with straw, as shown by the imprints preserved in the material (50x). (b) Detail (50x) of wooden fragment in the intonaco of a blue pigment from the St George Cathedral (IUR ffw 21 MBl).

lime and a small amount of dark blue pigment. The white upper layer on it is lime applied a secco. The green paint layer lies on a thin white layer of what looks like a lime preparation. The fabric of the intonaco is compact, with only some imprints and remains of straw and chaff. We date this kind of plaster to the first phase of paintings of the cathedral, in the twelfth century AD.

4.3. Intonaco of Blue and Green Fragments from the Yuriev Monastery Cathedral

In the group of blue-painted fragments with regularly oriented brush-strokes mentioned above, the *intonachino* underlying the pigment is very compact and measures only 2–3 mm in thickness. This kind of plaster contains only a tiny amount of very fine sand and was mixed with straw or, in some cases, with wood shavings (see Figures 6a and 6b). The binder is a weakly magnesian lime with a silica component.

The later fragments, with more irregularly applied paint, show a thicker substrate consisting of several layers, and the lime binder is mixed with a much coarser-grained quartz sand (Figure 7). As an example of later fragments, we took for the illustration a mottled light blue fragment, characterized by an intonaco applied in at least three layers (Figure 7). The upper one is a thinner lime preparation layer, under which small voids can be recognized at several locations, while the lower layers contain very characteristic inhomogeneous grains of medium- to very coarse-grained quartz sand. The voids at the contact line of the thicker layers are due to the loss of larger sand grains and brick fragments, originally pushed to the interface during the polishing process between each intonaco application.

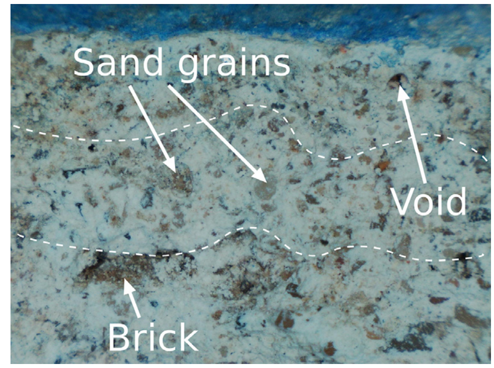

Figure 7. Fragment (IUR ow 20 LBg1) with mottled light blue paint; intonaco applied in three layers, as roughly indicated by the dashed lines; and aggregate of coarse-grained quartz sand and brick fragments (50x). This structure indicates a date later than the twelfth century AD.

The investigations carried out by Philippova et al. on 11 fragments from the St. George Cathedral showed calcite, clay minerals, and sand and did not identify organic binders such as fats, oils, waxes, and resins (Philippova et al. 2022:4–5, Table 2). We are planning further analyses by XRD, Raman, Fourier-transform infrared spectroscopy (FTIR), and gas chromatography–mass spectrometry to see if other mixtures and compounds can be identified in both pigments and plasters.

5. SEM-EDS on Blue and Green Pigments from the Cathedral of St. George

The pigments employed in mural painting were prepared and mixed on the working sites, and the final result of the various recipes was certainly not always the same or even completely homogeneous. Further, pigments, containers, brushes, and the entire environment were probably continuously contaminated with remains of different colors. We have to keep this in mind when trying to identify the palette of ancient recipes, especially when studying the fragments belonging to the later phase of the cathedral, as in that case we are mostly dealing with mixtures of pigments. We used a semiquantitative method, pXRF, for the first screening because with this technique, frescoes still in situ could be studied and compared with the fragments. Later, the samples were mounted in resins and studied by SEM-EDS.

5.1. Blue Pigments

The first XRF analyses carried out on the blue pigments recovered from the St. George Church came as something of a surprise. The results, albeit just qualitative, seemed to suggest that an unmixed lazurite pigment had been employed for the bright blue color of several fragments. Lazurite powder was in antiquity—and still is now—one of the most expensive pigments in circulation, as it was obtained by grinding and washing, or roasting and washing, the widely appreciated and precious lapis lazuli to get rid of the stone's pyrite inclusions and other impurities (Dussubieux and Golitko, 2017; Lo Giudice et al. 2009; Schmidt et al. 2009). The sources of lapis lazuli are not many. Generally in archaeology, the area of Badakhshan in Afghanistan is almost the only

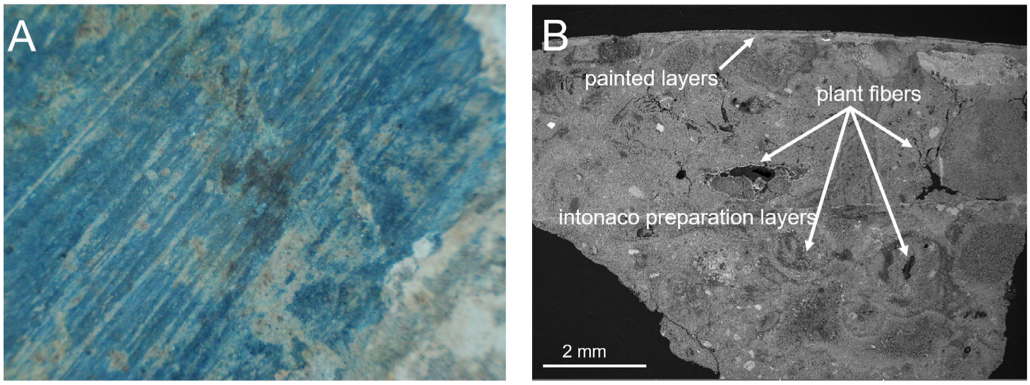

Figure 8. (a) Optical microscopy on blue pigment from the St. George Cathedral. (b) The cross-section stratigraphy shows an *intonachino* with very few grains of quartz (less than 5% volume). The underlying intonaco (plaster) contains straw and chaff and can be dated to the twelfth century AD.

one taken into consideration when discussing the provenance of this precious stone and pigment. However, other lazurite mining areas exist, and numerous studies discuss the provenance of lapis lazuli (Dussubieux and Golitko, 2017; Law 2014; Lo Giudice et al. 2009; Re et al. 2011, 2013; Salvadó et al. 2014; Schmidt et al. 2009). The main mines taken into consideration in the mentioned studies are located in the Pamir Mountains in Tajikistan and in the Sayan Mountains southwest of Lake Baikal in Siberia (Law 2014:423–24). Finally, there are some mines in Chile, which certainly cannot be a source for archaeological finds in Europe of this period.

SEM-EDS analysis is not sufficient for determining the source of this pigment, but it will be interesting to follow up on this question in the future. We plan to solve this problem using sulfur isotope analyses that can distinguish minerals from the different mines. The analyses will be carried out at the Laboratory of Isotope Geochemistry and Geochronology at the Russian Academy of Sciences in Moscow. For this we got hold of lapis lazuli samples from Shikhova in the Badakhshan region of Afghanistan, from Grevingk and Chistyakova in the Lake Baikal region, and from Lajvar Dara in the Pamir Mountains as comparisons.

From the studies of Roman pigments, we know that the costly lapis lazuli pigment was mostly employed mixed with abundant azurite or other additives to limit expense, but this does not seem to be the case in the twelfth century at the St. George Cathedral, where the bright blue pigment was mixed only with lime to achieve a lighter color or with a dark pigment (see below) when a darker hue was desired. The variations in the content of Na and K are due to the variability in the mineral, which besides lazurite and pyrites can contain sodalite, sanidine, nepheline, phlogopite, pyroxene, calcite, and sodalite. The analysis of the various grains inside the pigment had different compositions; sodalite, pyroxene, albite, phlogopites, and so on could be easily recognized. The presence of these minerals demonstrates the natural origin of the pigment.

The section of the blue sample (IUR DB Nov1a) that we consider as belonging to the earliest phase of the cathedral was examined in detail with SEM-EDS and showed a very regular layer of paint applied in only one direction, with a relatively thin *intonachino* with only rare quartz granules and with straw as aggregate (less than 5% volume; Figures 8 and 9). To counteract the shrinking of the lime binder, vegetable fibers such as straw and chaff were added. The color layers show a complex structure (Figure 10): the *intonachino* surface was prepared with the addition of a dark, finely ground pigment consisting of lime mixed with black charcoal, with a very reduced thickness under 100 microns. On this blackish dark gray layer, a thin layer of blue clay was applied as underpaint for the blue pigment. This is an interesting observation because blue clay is found in the area around St. Petersburg. The use of this uncommon material might represent a local solution in the painting technique of the early period of the cathedral. The blue layer applied on top of the blue clay measures less than 100 microns in thickness and is very rich in pigment, with less fine granules at the bottom and very fine granules in the upper portion. The pigment employed is lazurite with a medium granulometry. Grains with sharp cracked edges and secondary microfractures indicate that the stone was ground. The lazurite grains are the most abundant part of the pigment, but phlogopites are also present and show the elongated shapes and preferential cleavage typical of micas. Some pyrites granules have been also identified. The EDS spectra show the peaks of the most abundant phase present in the blue layer (Figure 11).

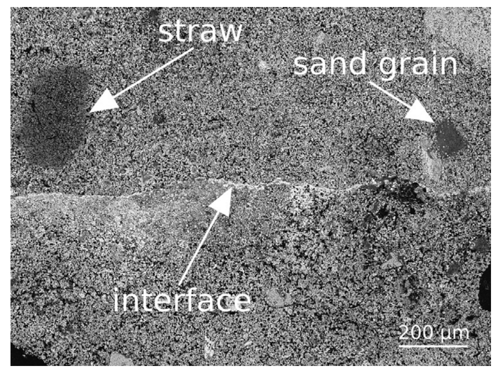

Figure 9. A micrograph shows the interface between *intonachino* and intonaco in sample IUR DB Nov1a. A straw stalk in section in the upper left corner and a small quartz sand grain on the right can be recognized.

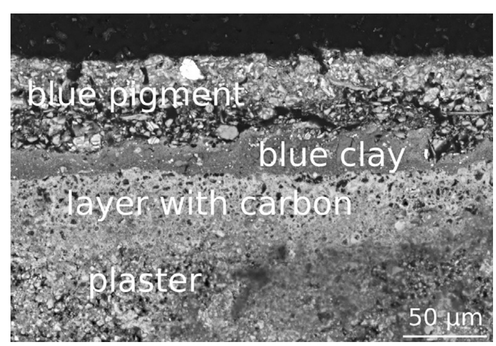

Figure 10. SEM micrography showing the complex stratigraphy of a blue sample with the *intonachino* preparation at the bottom, a layer of charcoal black mixed with lime, a blue clay layer, and blue pigment on top, with thicker granules of lazurite in the lower part and finer granules on top.

Analysis of the lazurite pigment gave the following mean results in weight percent: Na_2O, 9.7%; MgO, 1.8%; dAl_2O_3, 19.3%; SiO_2, 30%; SO_3, 7.5%; Cl_2O, 0.7%; K_2O, 2.9%; CaO, 21.8%; Fe_2O_3, 5.4%.

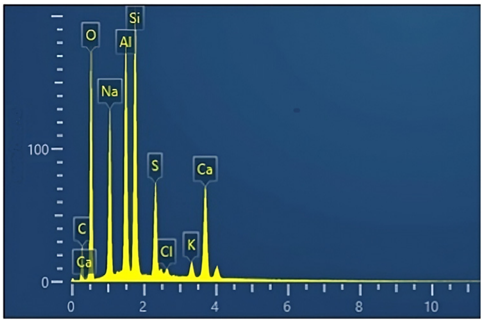

Figure 11. EDS spectra showing the main phase in the blue pigment: lazurite

Phlogopite ($KMg_3AlSi_3O_{10}(F,OH)_2$) fragments inside the pigment (together with other impurities, such as pyrites, albite, and sanidine) are natural components of this pigment (Figure 12). However, in the twelfth century only a natural pigment could be employed, as artificial lazurite was first invented in 1826. The late phases of the church can be easily distinguished by examining the plaster, as discussed in section 4.3. XRD, FTIR, and Raman are planned for the near future to better define the impurities in the pigment and to evaluate the degree of purification of the pigment (cf. Ballirano and Maras 2006; Salvadó et al. 2014).

Light blue sample no. 1472, from the excavation outside the wall of the Cathedral of St. George, differs from the blue fragments discussed above. The intonaco belongs to the group containing coarse quartz sand and is applied in layers (Figure 13). The last layer of pigment (lead white) was applied a secco.

Examination with SEM-EDS revealed that the light blue pigment was a mixture of lead white (2PbCO3 $Pb(OH)_2$) and white barium sulfate ($BaSO_4$) with azurite (($2CuCO_3$ Cu $(OH)_2$) and a small amount of lazurite (Figure 14a–b). Azurite was identified as rounded grains in a lead white pigment (Figures 14b and 15). The form of the grains is rather anomalous because ground azurite normally shows fragments with angular shapes. The rounded particles suggest that this azurite might be synthetic, and it is known that this artificial pigment was produced starting in the eighteenth century AD (Bevilacqua et al. 2019:52). Barium sulphate had already been mentioned by Agricola in the sixteenth century and was widely used as white pigment in the eighteenth century, but as it does not give good coverage and turns easily to gray, here it was mixed with lead white. The use of both artificial azurite and barium sulphate in the composition of this pigment, together with the kind of intonaco and the way the pigment is applied, represents a further reason for dating this fragment to a later period of the cathedral, most probably the end of the eighteenth century.

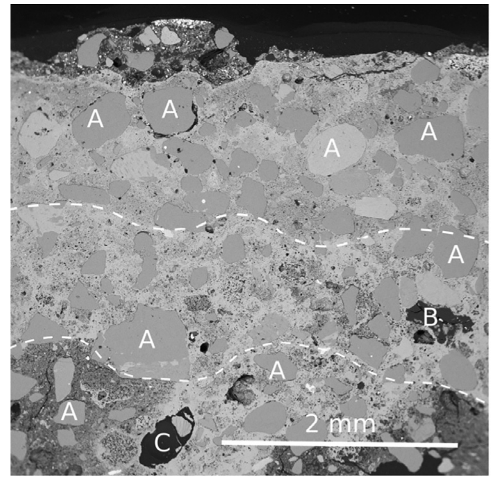

Figure 13. The micrograph shows the layers of the intonaco under a light blue pigment. The letter *A* marks the sand grains, *B* marks the brick fragments, and *C* shows the void left by a lost sand grain.

As already mentioned, the common characteristic of late fragments with a blue pigment is the addition of an abundant and rather coarse quartz sand to the intonaco, so that the quartz grains even protrude through the pigment layer. Shiny quartz grains are even visible on the surface of the pigment, and this seems to have been done on purpose, perhaps to confer a shiny aspect to the blue color under the light of lamps or candles. We suggest that the addition of quartz sand as an aggregate of the intonaco and as an ingredient and mean to obtain a shiny surface might be an eighteenth-century technique.

Analyses by Philippova et al. on a blue fragment identified lazurite with some kaolinite, clay, and calcite in the pigment and three layers: the lazurite pigment, the layer with carbon, and the intonaco (Philippova et al. 2022:5, 8). Apparently, the researchers did not see or notice the blue clay or took it as part of the substrate with carbon. However, the blue clay layer is quite visible on the micrograph we obtained by SEM (Figures 10 and 12a).

5.2. Green Pigments

The pXRF analyses carried out on the green samples from the St. George Cathedral showed that the main pigment employed for the green details was green earth. This natural pigment is very suitable for fresco painting because it is very stable and does not react with lime. Indeed,

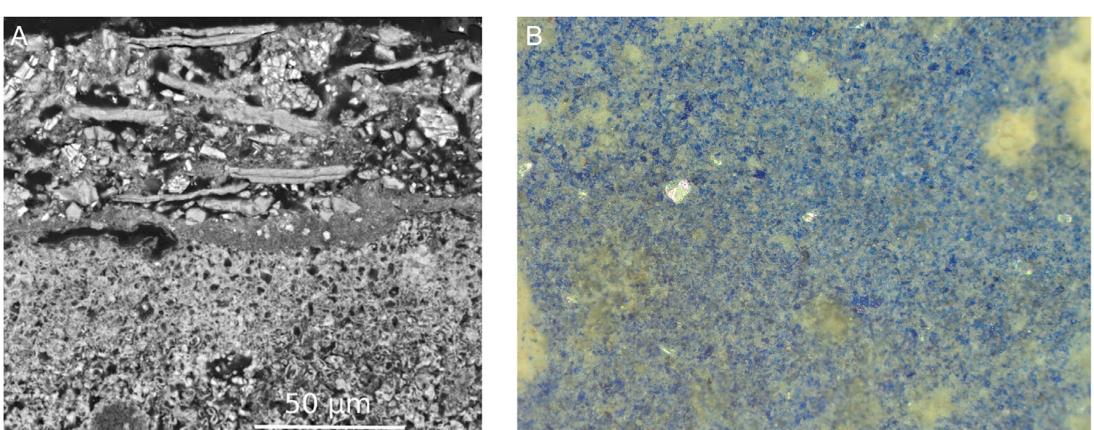

Figure 12. (a) The mottled, angular fragments in the blue pigment at the top consist of lazurite. The lamellar structure of the phlogopites can be easily recognized. The phlogopites can be seen at the microscope at 50x, and their sparkle is even recognizable with the naked eye.

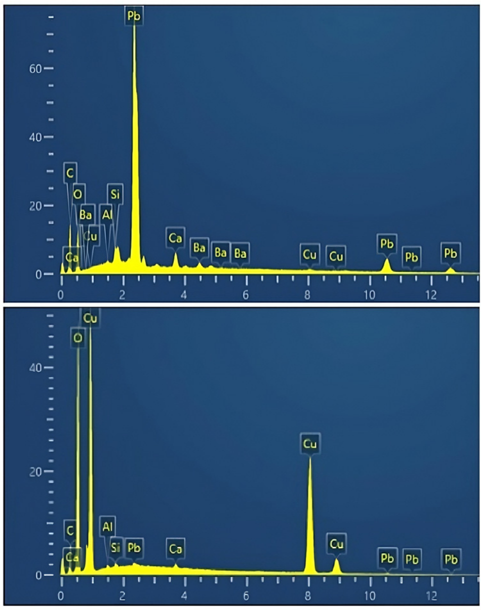

Figure 14. (a) Peaks show the presence of lead white and barium sulphate in a light blue pigment of a late date. The S peak is hidden by the Pb peak. (b) SEM-EDS analysis of the azurite grains in the light blue pigment. The small Pb amount comes from lead white in the pigment.

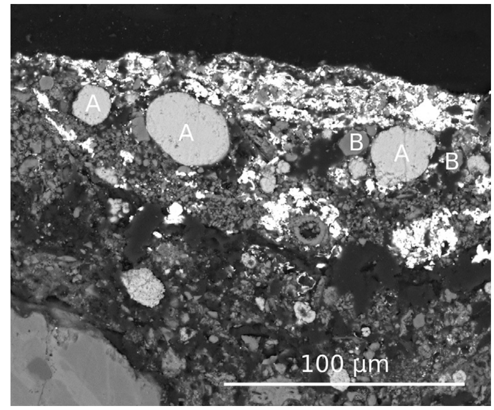

Figure 15. A micrograph shows the pigment layer of a light blue fragment in BS mode. The letter *A* marks the rounded grains of azurite, while the angular fragments marked *B* consist of lazurite. The white parts of the pigment consist of lead white.

green earth seems to be the most widely employed green pigment in Roman and Byzantine mural paintings, followed by Egyptian green and mixtures with malachite and verdigris (Delamare et al. 2002). The composition of green earth can be easily distinguished from that of other green pigments, but distinguishing its components is more complicated. The most common constituents of green earth are celadonite and glauconite, but serpentinite, smectite, and chlorite can also be present in the mixture (Béarat 1996; Moretto et al. 2011; Ospitali et al. 2008; Rafalska-Lasocha et al. 2010, 2012). The pXRF analysis could not distinguish between celadonite and glauconite. Therefore dedicated investigations with SEM-EDS were carried out. XRD measurements are also planned for the near future.

The examined sample (IUR DG Nov2a) shows a compact and uniform dark green layer (Figure 16a). As in the case of the blue pigment, the *intonachino* is very compact, with only very few quartz granules under 5% volume. Vegetable fibers such as straw and chaff were also added (Figure 16b). The structure is less complex than that of the blue pigment. Green earth is and always was much cheaper and more common than lazurite. It could be used as it was and in an abundant amount. The plaster preparation is the same one we encountered in fragments of the twelfth century, and a thin layer of blackish preparation containing charcoal was applied on top of the *intonachino*. The pigment employed was identified as green earth, as the analysis showed. The EDS spectrum of the green pigment indicates that the main component of the green earth is celadonite. That is, this pigment consists of better-quality green earth. Scholars agree that green earth consisting of high amounts of celadonite or mainly celadonite gives a better color and better properties to pigments than does green earth with high amounts of glauconite (e.g., Bevilacqua et al. 2019:115).

The EDS results of the analysis on the green pellets are as follows: MgO, 5.5; Al_2O_3, 5.9; SiO_2, 56.6; K_2O, 8.0; CaO, 0.5; TiO_2, 0.2; Fe_2O_3, 22.3.

The image in BS mode (Figure 17a) shows the typical structure of green earth, with rounded pellets with a diameter of around 30–40 microns. The green pigment is less finely ground than the blue. Figure 17B shows the peaks of green earth.

Only one of our pXRF analyses seemed to indicate that the green pigments were mixed Mn-Fe compounds when darker hues were desired. However, the sample on which the pXRF identified higher Mn and Fe has not been brought to the laboratory for SEM-EDS examination yet.

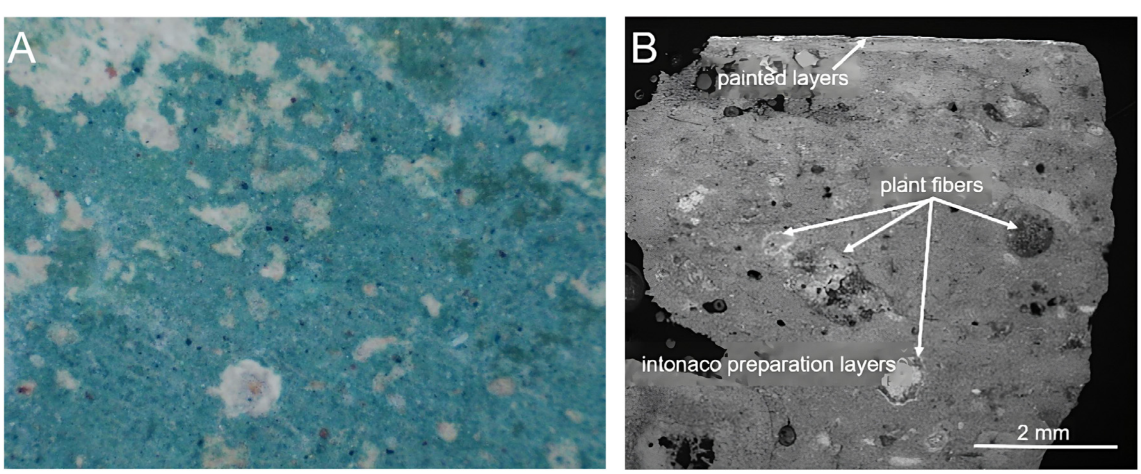

Figure 16. (a) Optical microscopy on a green sample from the St. George Cathedral. (b) Cross section of sample showing the stratigraphy: plaster with straw, preparation layer, and pigment.

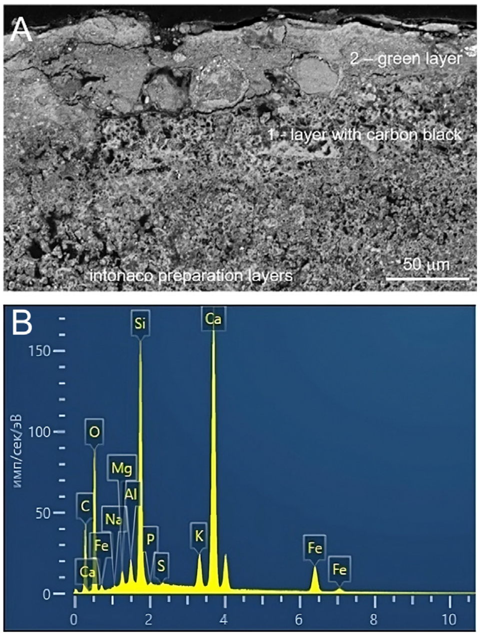

Figure 17. (a) SEM micrography in BS mode showing the upper layers with *intonachino*, a carbon black layer, and the green earth pigment layer. (b) EDS spectra showing the main phase of green earth.

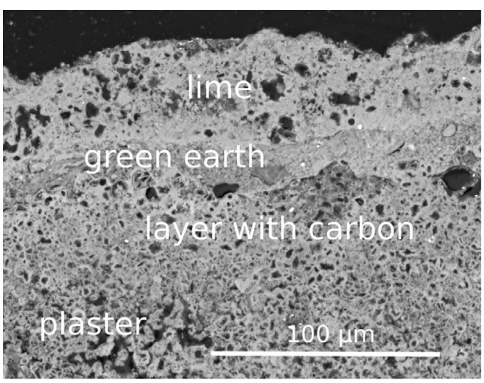

Figure 18. The light green fragment consists of a layer of green earth pigment on top of a layer of lime with carbon, covered by a layer of lime.

For the moment, we have only XRF data, and this result could not be confirmed.

The other fragments with a green earth pigment that we analyzed by SEM-EDS did not contain Mn and Fe, but green earth was applied on a layer of lime mixed with carbon. The green earth pigments containing Mn and Fe might perhaps be later restorations.

One of the dark green specimens shows a red underpaint, similar to that under the blue color (Figure 5) dated to the later phases of the cathedral. However, straw and only very small fragments of brick can be observed in the intonaco of this sample, which looks like a twelfth-century specimen both because of the intonaco structure and because the pigment is applied with regular strokes all in one direction. The fragment with a red underpaint clearly belongs to the twelfth-century phase.

Light green sample no. 1480 from the St. George Cathedral consists of green earth on which lime was applied. Its substrate is a lime intonaco mixed with straw and a few small fragments of brick, with no traces of the quartz sand inclusions present in the intonaco of the later fragments of the church. The pigment is green earth applied on a lime layer with carbon (Figure 18). The lighter color is given by a layer of lime, probably applied a secco on top of the green earth pigment.

The investigations carried out by Philippova et al. on a green fragment identified green earth, with the prevalence of celadonite over glauconite, and some calcite (Philippova et al. 2022:5–6).

6. Conclusions

The examination and analyses of around 60 samples from the Cathedral of St. George at Novgorod evidenced groups of fragments that can be distinguished by different techniques of paint application, mixtures of pigments, and preparation layers. This research is quite significant because already at this early stage, the different phases of wall paintings in the Cathedral of St. George can be distinguished and identified through different characteristics in techniques and pigment mixtures. This first screening of the available materials represents the basis for further studies that might deepen our knowledge of the habits and recipes employed by artists of the twelfth century and later.

The use of precious lazurite in the mural paintings of the churches of Novgorod demonstrates on one side the respect for the church shown by the population in general but also the wish of the donors to show their wealth and power. The origin of the lazurite, either coming from Siberia, the Pamir Mountains, or Badakhshan, will be determined by differentiating the samples with sulfur isotope analysis. Our data confirm the identification of Philippova et al. (2022) of lazurite and green earth as blue and green pigments employed in the St. George Cathedral. To be mentioned is also the analyses of Balakhnina et al. (2021) on the blue and green fragments from the contemporary Church of the Annunciation on the settlement at Novgorod, which also identified lazurite and green earth on the samples.

The identification of pigments such as artificial azurite and white barium sulfate on some of the fragments allows us to date them instead to the later phase of the cathedral.

While some of the pigments seem to remain the same during the entire century—lazurite for blue, and green earth for green—various ways of applying the color and the different recipes and aggregates of the plaster can be distinguished. The addition of lime to obtain lighter hues is certainly ubiquitous, while the employment of artificial azurite and barium sulfate must have been introduced toward the end of the eighteenth century or even later.

The use of manganese and iron compounds—sienna and Mn-rich earth—to obtain darker hues, as suggested by some pXRF measurements, might be an important detail reflecting the influence of the eastern Mediterranean world, certainly through the mediation of Byzantine painters who came to Russia, invited by local princes. However, this topic needs to be investigated by SEM-EDS and XRD in a second step of this research.

The use of local materials might be hypothesized too and represents one of the questions that will have to be tackled in the future.

Our data indicate that in the case of most of the top layers of paint—superimposed secco layers—the binding agent was lime.

The use of quartz sand in blue pigments is rather intriguing and seems to be not only an addition with technical reasons but also an aesthetic way to obtain a sparkling surface under the flickering light of lamps and candles during religious ceremonies. The aggregates in the intonaco and the binder-to-aggregate ratio have a strong impact on the aspect of the paint layer and can change the appearance and the texture of the surface.

Additions of sparkling materials to pigments are known from other times and places. For instance, tiny fragments of glass have been identified in the Roman frescoes at Dietikon in Switzerland. The analyst suggested that "Roman painters probably added crushed glass [to the pigment] to render their paint more brilliant" (Béarat 1996:86).

As a further remark we can mention that the addition of minute amounts of quartz is a characteristic feature of the Ruthenian-Byzantine frescoes as well (Rafalska-Lasocha et al., 2010, 2012). It seems that the wish of obtaining a sparkling surface in mural paintings was also common at Novgorod.

This preliminary research also helps in deciding which future investigations will be appropriate for collecting more data and information on this important material. Aside from polarized light microscopy (PLM), a key technique for the exact identification of the mortars and intonaco types, SEM-EDS for all samples, Raman, XRD, and FTIR are planned to fine-tune the determination of paint, organic and inorganic binders, aggregates, and intonaco layers. SEM with a microanalyzer is certainly the best choice for this type of research, as it reveals the succession of layers and the inclusions; can show the structure of organic materials, such as the possible use of particles of carbon obtained from burned wood (Eastaugh et al. 2004), burned bones, and so on; and can roughly identify pigments. In the case of crystalline materials, such as mineral pigments and their mixtures, we will try to identify the mineral phases and the size of the crystallites by XRD. This kind of analysis, combined with FTIR and Raman, will greatly help to exactly define the materials. All these examinations will be the next steps of our research.

Declaration of Competing Interest

The authors declare no conflict of interest.

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