OPTICAL MICROSCOPY AND SEM-EDS ON WALL-PAINTING FRAGMENTS FROM THE ST. GEORGE'S CATHEDRAL AT NOVGOROD

A NOVGORODI SZT. GYÖRGY KATEDRÁLIS FALKÉPTÖREDÉKEINEK VIZSGÁLATA OPTIKAI MIKROSZKÓP ÉS PÁSZTÁZÓ ELEKTRONMIKROSZKÓPOS ENERGIA DISZPERZÍV SPEKTROSZKÓPIA SEGÍTSÉGÉVEL •

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Abstract

This paper presents the latest data obtained from the analyses of fragments of Russian-Byzantine wall paintings recovered from the architectural excavations carried out in the church of St. George in the Yuriev Princely Monastery built in 1119 at Veliky Novgorod, one of the oldest cities in Russia and UNESCO World site. In the last 7 years the archaeologists of the Institute of Archaeology of the Russian Academy of Sciences in Moscow excavated the 12th century layers and extracted a large number of wall-paintings fragments, which are extremely important for the reconstruction of the history of Novgorod and for the study of Russian-Byzantine art in general. The pigments employed for the paintings and the painting techniques, together with color layers, substrates and mortars, have been studied and analyzed in the last two years in the Laboratory of the Architectural Archaeology and Multidisciplinary Methods for Architectural Research, Institute of Archaeology of the Russian Academy of Sciences. The employed analytical methods were optical microscopy (OM), X-ray Fluorescence Spectrometry (XRF) and Scanning Electron Microscope with Energy Dispersive Spectrometry (SEM-EDS). OM permits to distinguish the superficial painting method, the inclusions in the mortars, the intonaco *and* intonachino *layers and the various substrates. XRF was applied for a first screening of the fragments and for the first pigment identification. The samples of painted mortar were then mounted in epoxy resin and polished for the analysis with SEM-EDS. The analytical data we possessed up to now indicate a very classical Byzantine technique with the use of expensive pigments such as lazurite and cinnabar, but also green earth, various types of ochres and mixtures of pigments. Special care was taken for the identification of the substrates.*

Kivonat

Veliky Novgorod Oroszország egyik legrégebbi városa és az UNESCO Világörökség kiemelt helyszíne. Ez a tanulmány az ott 1119-ben épült Jurjev hercegi monostor Szent György-templomának műemléki ásatásaiból származó orosz-bizánci falfestmények töredékeinek legfrissebb elemzési adatait mutatja be. Az elmúlt 7 évben a moszkvai Orosz Tudományos Akadémia Régészeti Intézetének kutatói feltárták a 12. századi rétegeket és nagyszámú falképtöredéket emeltek ki. A leletek rendkívül fontosak Novgorod történetének rekonstrukciója és általánosságban az orosz-bizánci művészet tanulmányozása szempontjából is. A festményekhez felhasznált pigmenteket és festészeti technikákat, beleértve a festett-, hordozó rétegeket és habarcsokat, az elmúlt két évben az Orosz Tudományos Akadémia Építészeti Régészeti és Multidiszciplináris Építészeti Kutatási Módszerek Laboratóriumában tanulmányoztuk és elemeztük a következő analitikai módszerekkel: optikai mikroszkópia (OM), röntgen fluoreszcencia spektrometria (XRF) és a pásztázó elektronmikroszkópia energiadiszperzív spektrometriával (SEM-EDS). Az OM lehetővé teszi a felszíni festéstechnikai módszerek, a különböző összetételű

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habarcsok, az intonaco *és* intonachino *rétegek, valamint további hordozórétegek megkülönböztetését. XRF-et alkalmaztunk a töredékek első szűrésére és az előzetes pigmentazonosításra. A festett habarcs mintákból ezután epoxigyantába ágyazott, polírozott keresztmetszet-csiszolatokat készítettünk a SEM-EDS elemzéshez. Az eddig rendelkezésünkre álló analitikai adatok egy klasszikus bizánci festési technikát mutatnak, drága festékanyagok, például lazurit és cinóber felhasználásával, de zöldföldet, különféle okkerfajtákat és pigment keverékeket is használtak. Különös gondot fordítottunk a rétegrend azonosítására.*

KEYWORDS: WALL-PAINTING; RUSSIAN-BYZANTINE; FRESCOES; PIGMENTS; MORTARS; SUBSTRATES

KULCSSZAVAK: FALKÉPEK; OROSZ-BIZÁNCI; FRESKÓ; PIGMENTEK; HABARCSOK; HORDOZÓRÉTEGEK

Introduction

In this paper we present the analytical data collected by the team of the Laboratory of the Architectural Archaeology and Multidisciplinary Methods for Architectural Research, Institute of Archaeology of the Russian Academy of Sciences since 2021, when we began with the systematic analysis on the fragments of wall-paintings from the Cathedral of St. George (1120 AD) in the Yuriev Princely Monastery at Novgorod, one of the ancient capitals of Russia and UNESCO site.

While several exhaustive studies on the paintings of the churches of Novgorod exist (s. for instance Sarabyanov 1998; 2002; 2012; Lifshits et al. 2004; Etinhof 2022; Sedov et al. 2014; 2016; Sedov & Vdovichenko 2015; 2019), the only studies carried out up to now on the fragments from this church were those of Voronin and Kabanova (2020) with analyses by XRD and SEM-EDS of 19 fragments of wall painting dated to the 12^{th}-13^{th} century AD, and Philippova et al. (2022), carried out with Neutron Activation Analysis (NNA), SEM-EDS, PGAA, FTIR and Raman, however on only 11 samples from the Cathedral of St. George. We can also mention the study of Balakhnina et al. (2021) that analyzed by Raman spectrometry seven samples from the almost contemporary Church of the Annunciation on the Gorodishe (Hillfort) at Novgorod (12^{th} century).

Up to now we carried out around 600 analyses by using XRF and SEM-EDS and more are planned for the future, as part of a research project of the Laboratory of Architectural Archaeology and Interdisciplinary Study of Architectural Monuments of the Institute of Archaeology, Russian Academy of Sciences, in Moscow. We published part of our analytical data in two previous papers (Giumlia-Mair et al. 2022; 2023), one focusing on several selected blue and green pigments, and the second on the preparation layers and substrates identified up to now on the fragments. In the present paper we discuss our latest analytical data.

In the last 9 years the excavations of the Institute of Archaeology brought to light literally several tens of thousands of fragments of all colors and sizes, dug out from under the floor of the Cathedral and from various areas outside of the building (Sedov & Etinhof 2016; Sedow 2020). The excavated materials are now kept in boxes in five different large deposits at Novgorod and, temporarily for study, also at the Institute of Archaeology of the Russian Academy of Sciences in Moscow. The excavations are still ongoing and in the last days of the 2022 expedition a new deposit of fragments was discovered and partly unearthed. The excavations in this area will continue in the 2024 archaeological campaign.

Our first examinations and analyses by XRF showed differences in the materials and technology used for the various fragments, because the Cathedral had been renovated at different times and in different parts, for example in the 14^{th}–15^{th} century AD and again in the 19^{th} century (Valentin 1893; Anonimous 2008, 70–72; Maslov 1998, 74–90). The attribution of the various fragments to the different phases, i.e. 12^{th}, 14^{th}–15^{th} and 19^{th} centuries, represents one of the major challenges of this research, because the wall-paintings of the 12^{th} century and of later times were removed from the walls of the Cathedral in 1898–1902, left mixed up under the new floor and heaped up in the different locations around the building. At that time, extensive renovations were carried out and most parts of the church were plastered anew and re-painted with the oil-paintings that are still in place today (Kedrinsky 1902). The only parts of the Cathedral that still preserve the 12^{th} century frescoes in situ are the tower, the lower part of the walls that were hidden under the new floor, and some of the window niches. Our study is, therefore, extremely important for the understanding and the reconstruction of the techniques employed on the earlier wall paintings of the Cathedral.

Because of space limits it is not possible to discuss here comparisons to other churches at Novgorod and their paintings; however, it is the authors' intention to carry out such comparisons in the future.

Methods of analysis

The fragments were first examined autoptically with the naked eye and with simple optical magnification devices, then with a portable digital microscope Proscope Bodelin with 10x, 50x, 100x, 200x magnifications. The main magnification employed was 50x. In this way we could document the differences in the texture of the plaster and in the way of applying the paint.

After the optical examination we began the first screening of all samples and of the paintings *in situ* with a portable X-ray fluorescence spectrometer (henceforth pXRF), Bruker Tracer i5 with Artax™ advanced spectral analysis PC software and a rhodium anode with 15 keV and 11.35 nA. The area of measurement had an 8 mm diameter. The acquisition time was 60 s per measurement.

Finally, we employed a scanning electron microscope with energy dispersive microanalyzer (henceforth SEM-EDS): Tescan Vega Compact with TESCAN Essence™ EDS under the following operating conditions: 20 kV accelerating voltage, 12 mA beam current, 15.8 mm working distance, counts of 100 s per analysis, dead time of approximately 25%. The measurements were processed using the AZtecLiveLite EDS Software. Further, X-ray diffraction spectrometry, Inductively Coupled Plasma Mass Spectrometry (henceforth ICP-MS) and Raman spectrometry will be performed on several samples in the near future to deepen our knowledge of the techniques employed and for a better identification of pigments and binders.

Results and discussion

In our research we employ the Italian terms "*intonaco*", widely used in several languages, for the plaster preparation on top of the rough mortar applied on the walls, and "*intonachino*" for the upper, refined layer under the pigment (Winfield 1968, 66; Mora et al. 1999, 28-29, 160). It has to be noted that the "*intonachino*" is not a simple thin lime wash, but a well purified lime layer, applied on top of the plaster with much less additives than the "*intonaco*". The examination by optical microscopy and with the digital microscope showed that the *intonachino* is not present in all samples and it represents one of the most important features that permit to distinguish the various phases of paintings of the St. George's Cathedral. We must also keep in mind that different parts of the church might have been decorated in the same period by different artists: both Greek Byzantine painters and local painters, who perhaps employed different techniques and even different pigments, as well as different mixtures for plaster and mortars. The optical examination is extremely valuable for the distinction of the materials, as it permits to discriminate between the different periods. In fresco paintings the cases of a "pure" fresco, i.e. of paint directly applied on the wet lime plaster, are quite rare, but this mostly depends on the location and the date. In most cases the first layer is applied with *a fresco* technique, and the outlines, the different shades, and nuances of color as well as details of faces and garments are added *a secco* (see for example Amadori et al. 2015, 190-191).

Nevertheless, in general, the wall-paintings are called frescoes even when *a secco* layers are present. On our samples some details were added with *a secco* technique, but we call our wall-paintings frescoes, because the layers in contact with the *intonachino* or the *intonaco* were mostly painted with the fresco technique. This is in particular true for the fragments belonging to the 12th century phase, on which we mainly focus on in this paper, while in some cases the later paintings were applied a *secco*. The later fragments and techniques will be discussed elsewhere in a future publication, as we need more research on them.

A further important difference that distinguishes the phases of painting is the kind of *intonaco* used in the various periods. The *intonaco* of fragments we analyzed that can be stylistically and technologically dated to the 12th century contain only few small grains of quartz sand and vegetable fibers of various kinds. The microscopic examination allowed us to recognize straw and wood splinters looking like crushed wood shavings from a carpenter shop. Apparently, when straw was not available, the artists turned to wood splinters as a substitute for it (**Fig. 1.**). Where the frescoes are damaged in the tower some flax is visible under the *intonachino*. Oakum of linen was also found inside the *intonaco* of some fragments. In the ancient literature we find mentions of straw as addition to lime together with some sand in the texts of Nectarius or Nektar, archbishop of Ohrid (1599) translated into Russian (Petrov 1899). In the same text he instructs to add oakum of linen to the last layer (*intonachino*) that should be applied on top of the plaster with straw. A further literary source, the writings of Dionysius (or Denys) of Fourna (c.1670 – after 1744) also recommends a mixture of lime and straw for the *intonaco* and a mixture of lime and oakum of linen for the *intonachino* (Durand 1845, 56-57; Mora et al. 1999, 126-127). Our findings seem to perfectly coincide with the descriptions given by Nectarius and Denys of Fourna.

The materials employed for *intonaco* and *intonachino* under the pigments of the frescoes i.e., the lime and the aggregates, were in antiquity normally collected from local sources in the vicinities of the churches in which they were employed and depended therefore on the geology of the area. While the early *intonaco* is quite fine, white, and contains mostly only straw and a small amount of fine sand (see **Fig. 1.**), the *intonaco* of later wall-paintings contains a large amount of rougher sand and some brick fragments (**Fig. 2.**), making thus the distinction between the various phases more evident.

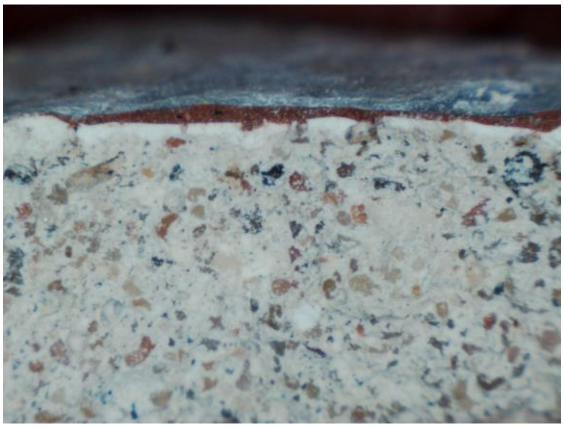

Fig. 1.: Detail of *intonaco* of later phases, not polished, with large amount of rough quartz sand visible on the fracture, white *intonachino*, a red underlayer and blue pigment on top. Magnification 50x (Photo by authors)

1. ábra: Későbbi fázisból származó festett vakolatminta (*intonaco*) keresztmetszetének részlete, csiszolás nélkül, a törésfelületen nagy mennyiségű durva kvarchomok töltőanyag látható, a vékony fehér intonachino rétegen vörös aláfestés kék színű festékréteggel. 50x nagyítás (A szerzők fotója)

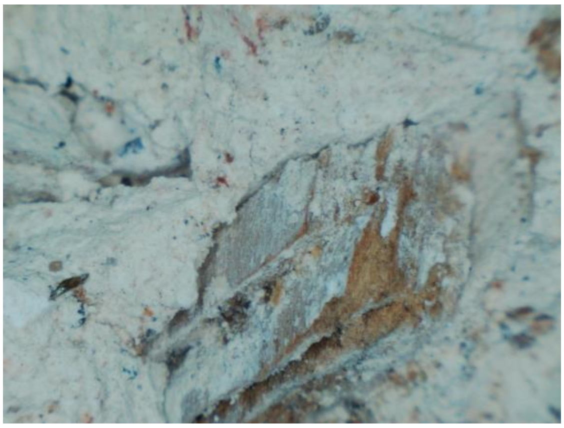

Fig. 2.: Fragment of wood inside the 12th century *intonaco*. The fragment is not prepared to show the wood fragment as found. The plaster is very white, with only few wood fragments and no sand. Magnification 50x (Photo by authors)

2. ábra: Fatöredék a 12. századi *intonaco* rétegben. A mintát nem preparáltuk, hogy az eredeti állapot bemutatható legyen. A vakolat nagyon fehér, csak kevés fatörmelékkel és kvarchomok töltőanyag nélkül. 50x nagyítás (A szerzők fotója)

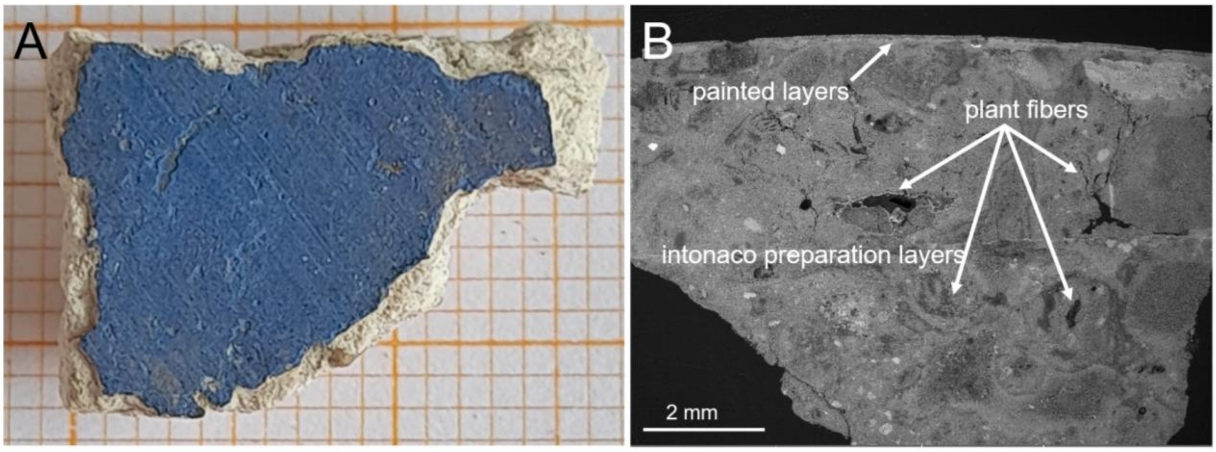

Fig. 3.: Blue pigment on a 12th century fragment: (a) the surface, the color is evenly applied, the brushstrokes went in one direction; (b) a SEM-BSE image of its intonaco with straw inclusions and very few grains of fine sand. The pigment layer is visible at the top as thin layer on a lime wash (Photo by authors, Giumlia-Mair et al. 2022).

3. ábra: Kék festékréteg egy 12. századi töredéken: (a) a felszín, a színt egyenletesen hordták fel, jól átható az ecsetvonás iránya; (b) az *intonaco* SEM-BSE képe szalmatöredékekkel és nagyon kevés finomszemcsés kvarchomokkal. A vékony kék pigmentréteg egy meszelés rétegen látható (A szerzők fotója, Giumlia-Mair et al. 2022).

As a final difference, also the technique employed in the application of pigments on the intonaco can be used as distinguishing characteristic: the pigments of the 12th century are applied with regular brush strokes that go always in one direction, at least on the portion of the same color (**Fig. 3.**), while in the case of the later paintings the pigments are much more irregularly applied. This characteristic, together with those of the plaster allow us to distinguish the habits and working procedures used in the execution of the wall-paintings. More data on the various substrates are given elsewhere in greater detail (Giumlia-Mair et al. 2023).

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Pigments and substrates

In general, we can assert that in the Russian-Byzantine art of frescoes of the 12th century as employed in the St.George's Cathedral at Novgorod the artists employed very classical natural earth pigments: ochres of different color, going from pale yellow, to darker yellow, through orangey red, red, red-brown and dark brown, green earths. In addition, also cinnabar, calcium carbonate white and blue lazurite were used.

Red pigments

The analyses by XRF and SEM-EDS showed that the most common red color is red earth, i.e. mixtures of red ochre (**Fig. 4.**) that, as mentioned before, was also employed as red underpaint. Nevertheless, minium, i.e. the orangey red mixture, commonly consisting of Pb_3O_4 and PbO, was also identified. Apparently, minium was employed more often on later fragments of wall-paintings, as indicated by the texture of the intonaco and the technique employed in the application of the pigment.

Cinnabar HgS and/or cinnabar mixtures are present too (**Fig. 5.**), sometimes mixed with calcium carbonate white to obtain the flesh color used for faces and bodies.

Fig. 4.: The most common red pigment is red ochre, i.e. red earth consisting of mixed iron oxides. The pigment layer is damaged, but the regular strokes can still be recognized. The plaster is white, compact and without sand. Magnification 50x. (Photo by authors)

4. ábra: A leggyakoribb vörös pigment a vörös okker, azaz a vegyes vas-oxidokból álló vörös földfesték. A pigmentréteg sérült, de a szabályos ecsetvonás még felismerhető. A vakolat fehér, tömör és homokmentes. Nagyítás 50x. (A szerzők fotója)

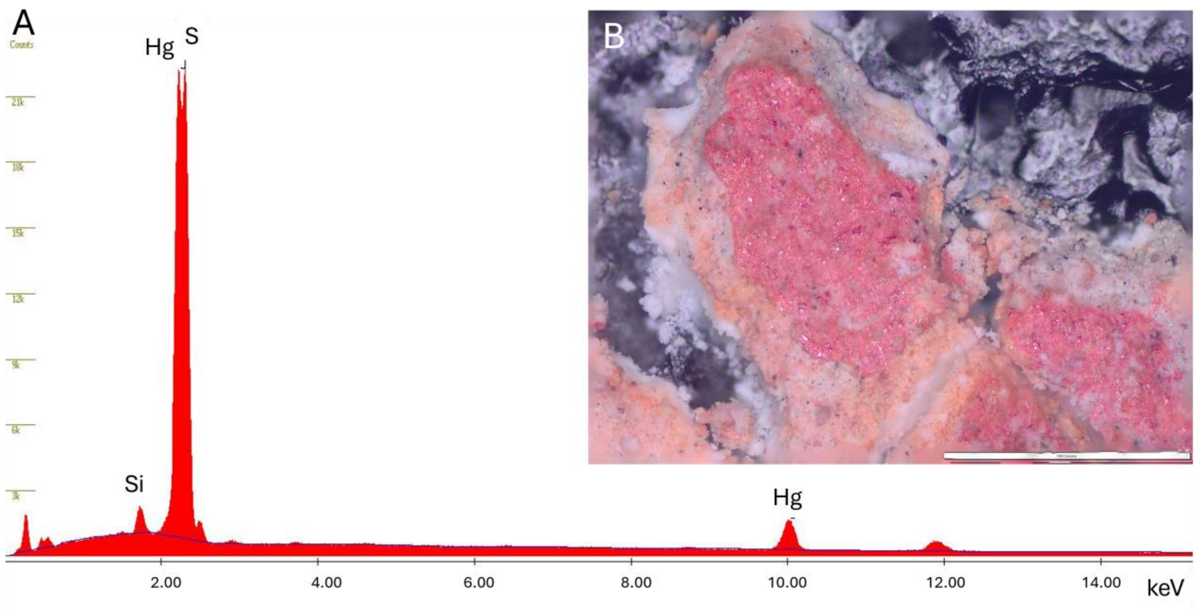

Fig. 5.: The cinnabar pigment: (a) its SEM-EDS spectrum (figure by authors); (b) Fragments of wall-painting with a cinnabar pigment on a layer of red ochre. Small crystals of cinnabarite can be recognized in the paint. (Photo by E. Zubavichius)

5. ábra: A cinóber: (a) SEM-EDS spektruma (az ábra a szerzők munkája); (b) Falképtöredék cinóber pigmenttel, vörös okker rétegen. A festékanyagban kis cinnabarit kristályok találhatók. (E. Zubavichius fotója)

Green pigments

All measurements of green fragments both by XRF and SEM-EDS have shown that the green pigments are mostly green earth, a rather common natural pigment employed since prehistory all over Europe. Green earth normally consists of green minerals such as celadonite $K(Mg,Fe^{2+})Fe^{3+}(Si_4O_{10})(OH)_2$ and glauconite $(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$. (**Fig. 6.**). The SEM-EDS results also show a peak of lead, most probably white lead used to lighten the green pigment, however, as white lead was not identified on other 12th century fragments, but on later samples only, we suppose that in the case of this particular fragment the pigment was integrated in a later phase. The planned Raman and X-rays diffraction analyses (henceforth XRD) will show which kind of mixture was used. Our XRF analyses showed that the painters, at least in one case, employed mixtures of green earth with black manganese salts that darkened the pigment. Up to now, this mixture was identified on only one sample (that might perhaps be a late addition) and needs to be confirmed by finding more instances of its use. On the contrary, to achieve a lighter color the painters mixed green earth with calcium carbonate white or even with lime.

Further, in only one case we identified with an XRF measurement some noticeable traces of copper, that suggested the use of copper carbonate (malachite, $Cu_2CO_3(OH)_2$) or other copper greens and perhaps of the artificially prepared pigment called Egyptian green, consisting of calcium, Cu and more than 4% of flux (Tite et al. 1984; Schiegl & El Goresy 2006). In this case, however, as among around over 100 measurements of green fragments no other traces of copper could be determined, at least up to now, we suppose that this was a much later retouching of a green pigment in only one spot. It is also possible that in later phases copper-based greens might have been applied a *secco* as retouching and, being less stable and resistant, went lost in the long period in the soil.

Blue pigments

With a slight surprise, because we know that for example the Romans, but also later artists, tended to dilute and stretch the expensive lazurite with the much cheaper blue copper carbonate azurite ($2CuCO_3{\cdot}Cu(OH)_2$) (see Daniilia et al. 2000); or even with Egyptian blue (or cuprorivaite, $CaCuSi_4O_{10}$) (Tite et al. 1987; Mirti et al. 1995; Ajò et al. 1996; Pozza et al. 2000; Verri 2009) an artificial, man-made pigment, we discovered that all early blue pigments consist of lazurite, i.e. lapis lazuli $(Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)$ (**Fig. 7.**). This was the most precious and expensive pigment used throughout antiquity and until today, as it consists of ground and refined lapis lazuli that with all probability had to be imported from Afghanistan. The second most expensive pigment, because of its rarity, was the already mentioned cinnabar. Lazurite is however also found in Siberia, near Lake Baikal, which would be closer to Novgorod than Badakhshan, the lapis lazuli region in Afghanistan. Beside Lake Baikal, which would be the closest, there are also other occurrences in other regions, for instance in Tajikistan, therefore we thought that it would be useful to investigate the origin of the lazurite so lavishly employed at Novgorod. As lazurite minerals of various provenance have a distinctive composition, we are planning to send some small samples to the Geology Department of the Academy of Sciences of Moscow to undergo some tests and analyses by ICP-MS and, hopefully, determine the provenance of this precious material.

Substrates

As mentioned above, we recently published a paper on substrates and preparation layers we have been able to determine among the fragments from Novgorod at our disposal. Therefore, in this paper we only give a short overview on the identified substrates and add some new data to the topic we already published (Giumlia-Mair et al. 2023).

Under many of the earlier pigments a grey substrate can be recognized at the microscope, and the SEM-EDS analyses have shown that it consists of calcite ($CaCO_3$) mixed with powdered charcoal.

It has to be noted that a previous paper by one of the colleagues belonging to our team reported the opinion of the conservation expert from Novgorod and stated that no reft seemed to be employed under blue pigments (Etinhof 2022), however, our examinations and analyses have proven the opposite: a dark layer of reft is always present under dark blue and quite often also under lighter blue pigments. The carbon particles can be easily recognized at the optical microscope and at the SEM (**Fig. 6.b and 8.**). This mixture is called *reft* in the ancient Russian texts describing the technology of frescoes and corresponds to the better known (in the West) *veneda* mentioned by the monk Theophilus (1122; Hawthorne and Smith 1979; Brepohl 1999), who recommends a mixture of lime and black under blue and green pigments (Theophilus, Div.Art., I, 15).

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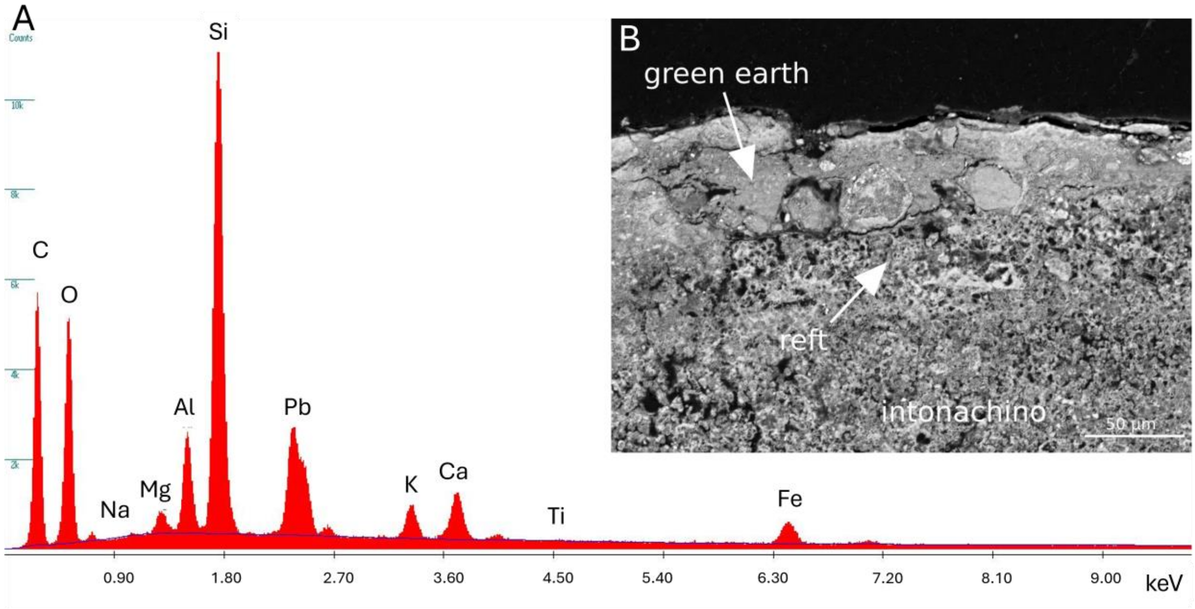

Fig. 6.: Green earth pigment: (a) its SEM-EDS spectrum (figure by authors); (b) SEM-BSE image of a section of *fresco* with a layer of green earth. Between pigment and *intonaco* there is a substrate of lime and charcoal (*reft*). (Photo by authors)

6. ábra: A zöldföld: (a) SEM-EDS spektruma (az ábra a szerzők munkája); (b) SEM-BSE kép egy zöldfölddel megfestett freskótöredékről. A pigment és az *intonaco* között mész és szén keverékéből álló réteg (reft) található. (A szerzők fotója)

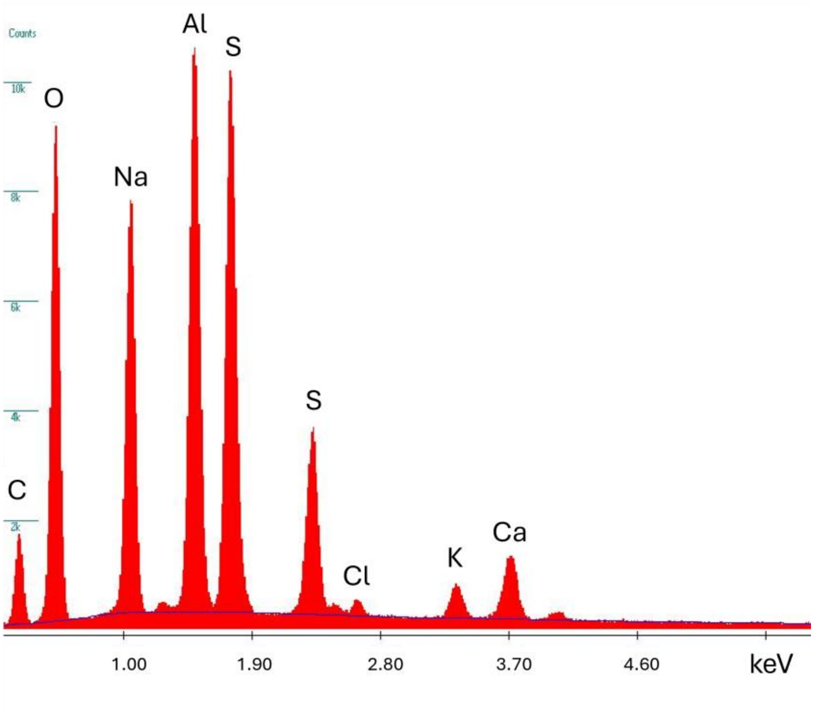

Fig. 7.: SEM-EDS spectrum of lazurite. (Figure by authors)

7. ábra: A lazurite (természetes ultramarine) SEM-EDS spektruma. (Az ábra a szerzők munkája)

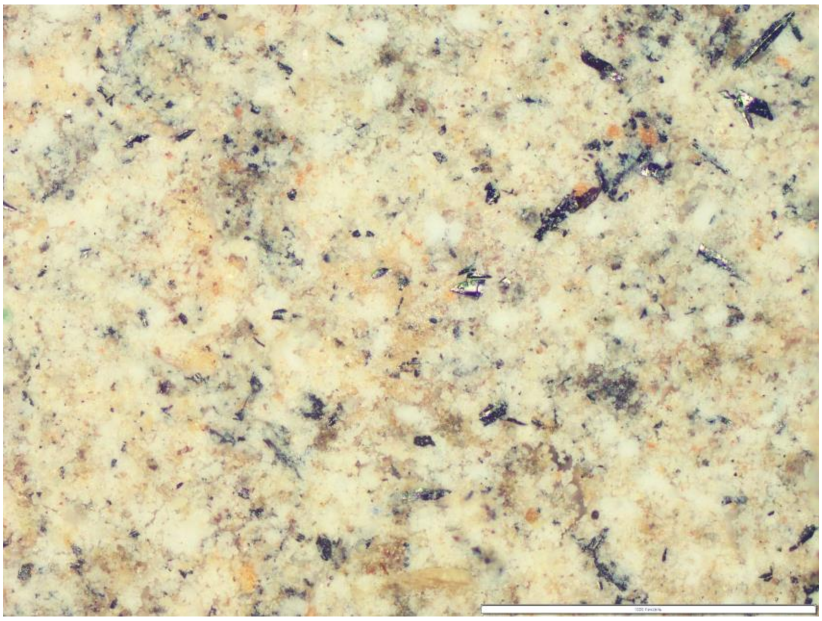

Fig. 8.: Shiny black fragments of powdered charcoal in lime: *reft* or *veneda*. This sample had originally a yellow ochre layer on top of the reft. Some remains are still recognizable. Magnification 100x (Photo by E. Zubavichius)

8. ábra: Fényes fekete porított növényi szén töredékek mészben: *reft* vagy *veneda* réteg felülete. Ennél a mintánál eredetileg egy sárga okkerréteg volt festve a reft rétegére. Az okkerréteg maradványa nyomokban még felismerhető. Nagyítás 100x (fotó: E. Zubavichius)

A further color that could be identified on some of our fragments and was employed particularly under the blue pigment is the so-called *morellone* (see **Fig. 2.**), mentioned by the famous Florentine painter Cennino Cennini or Cennino d'Andrea Cennini (ca. 1370-1440) who wrote a well-known Treatise: *il Libro dell'Arte,* i.e. the Handbook of the (Painter's) Craftmanship (1437). In his work Cennini gives a recipe for the production of *morellone,* as consisting of two parts of *sinopia* (red ochre, i.e. iron oxide) and one part of black. This mixture was employed to deepen the nuance of the pigment applied on top of it (Cennini 1960; 2017; 2020; Bevilacqua et al. 2019, 77-78). Interestingly the Spanish treatise *Arte de la Pintura* (1649) (the art of painting) by Francisco Pacheco dal Rio (1594–1644) instructs the readers to apply a layer of red ochre on a layer of lime (*intonachino* or perhaps a kind of thinner lime wash) apparently under all colors except under blue and green, under which only a white layer of lime should be used (Pacheco 1959, II, 52).

On the analyzed wall-paintings of the St. George's Cathedral yellow underlayers of yellow ochre were sometimes applied under green earth and had the function of changing the green nuance and rendering it "warmer" and lighter.

Conclusions

Our research has shown that among the fragments of frescoes recovered from the excavations in the St. George's Cathedral and in the vast area around the building two or more phases can be recognized. One of the main characteristics for the discrimination of the different phases is the texture of the *intonaco*: the ones dated to the 12th century are finer and white, mixed with natural fibers such as straw and oakum of linen, and sometimes wood splinters, while those from later phases are rougher, without *intonachino* and mixed with thick quartz sand. A further distinction can be made by examining how the paint was applied: on the early fragments the brush strokes are quite regular and go in one direction, while the later ones are applied in a much more irregular way (see Giumlia-Mair et al. 2023, fig. 2a, b, c, d, e). This was always confirmed by the combination with the type of plaster that was clearly of the early period, almost without sand and with only some straw or wood shavings as additives.

The analyses carried out on the pigments showed that the Russian-Byzantine artists employed classical earth pigments, such as ochres for red, yellow, and brown, green earth for the green, as well as calcium carbonate white, cinnabar, used especially for skin color, and the precious lazurite for blue.

Many of the early pigments are applied on a layer of the so-called *reft*, a mixture of lime and charcoal powder that probably had not only the task of darkening and deepening the color of the pigments, but as a natural adsorbent certainly also the practical function of protecting the wall-paintings from humidity and the formation of mold. Its action might be similar to that of bio-char, widely employed today both in agriculture as hygroscopic material, but also as a concrete additive, because of its permeability reduction (Arvaniti et al. 2015). As some authors have suggested (Allag and Groetembril 2021, 210), the red ochre layer, identified in particular under the blue pigment lazurite, but not only, seems to have, besides that of deepening the nuance of blue, a similar protective function for the pigment layers.

The analyses by ICP-MS of the lapis lazuli samples at the Institute of Geology of the Russian Academy of Sciences in Moscow, will hopefully give indication on the provenance of the lazurite.

Our research on the wall-paintings of the Cathedral is continuing, in the future, we are going to compare our results with those of available previous researches by other authors, and we also plan to analyze the pigments from other churches, in particular those from the Church of the Annunciation on the Rurikovo Gorodišče, built in 1103 (Balakhnina et al. 2021), and Our Saviour on the Nereditsa Hill, built in 1198, both at Novgorod, as well as the 12th century wall paintings in the crypta of the basilica of Aquileia in Italy, allegedly painted by Byzantine artists, and several fragments of wall paintings from the church of Studenica in Serbia. In this way we can cover the entire century and at the end of the project we might possibly understand the evolution in technique and pigments of this period and the differences and similarities between the painting habits of the artists who painted the frescoes in the St. George's Cathedral and those of contemporary artists in different countries.

Contribution of authors

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