LAZURITE AT NOVGOROD: TECHNIQUES, MIXTURES, PROVENANCE

LAZURIT NOVGORODBAN: TECHNIKÁK, KEVERÉKEK, SZÁRMAZÁS •

GIUMLIA-MAIR, Alessandra R.G.[1, 2*]; DUBININA, Elena[3]; VDOVICHENKO, Marina V.[1]; ZUBAVICHUS, Evgenius[1]; RICCARDI, Maria Pia[4] & MUSA, Maya[4]

[1]Institute of Archaeology, Russian Academy of Sciences, Moscow, Russian Federation

[2]AGM-Archeoanalisi, Merano, Bolzano, Italy

[3]Institute of Geology, Russian Academy of Sciences, Moscow, Russian Federation

[4]Dipartimento di Scienze della Terra, Università di Pavia, Pavia, Italy

*E-mail: giumlia@yahoo.it

Abstract

An extensive collection of wall-painting fragments that in the 19th century was removed from the walls and buried under the floor of the Cathedral of St. George was collected during the 2013-2023 architectural and archaeological excavations on the area of the St. George's Monastery at Veliky Novgorod (Russia), conducted by the Institute of Archaeology of the Russian Academy of Sciences. Among the pigments there were different kinds of blue, but the most common was rather pure lapis lazuli (lazurite), identified with XRF, SEM-EDS and XRD. Lazurite was the most valuable and expensive ancient pigment, as it was extracted and imported from few deposits, the most important of which was that of Sar-e-Sang in the Afghanistan region of Badakhshan.

Lazurite contains a significant amount of sulphur; therefore, the $\delta^{34}S$ values of the blue pigment can be used to identify the lazurite deposit. The sulphur isotope analysis was carried out using the CF IRMS technique with FlashHT element analyzer. Lapis lazuli reference samples from Badakhshan (from +15.7 to 22.3‰), Tajikistan (+17.6‰), and the Baikal (+45.4‰) deposits were analyzed and compared with the sulphur isotope composition of the blue pigment employed at Novgorod. The $\delta^{34}S$ values of blue pigment from fresco fragments (from +21.1 to +23.5 ‰) are close to the Badakhshan lapis lazuli reference samples. Therefore, we can confirm that the origin of the blue pigment employed at Novgorod was the region of Badakhshan in Afghanistan.

Kivonat

Az Orosz Tudományos Akadémia Régészettudományi Intézetének munkatársai 2013 és 2023 között intenzív építészeti és régészeti feltárás végeztek a Velikij Novgorodban (Oroszország) található Szent György-katedrálisban, amely során olyan falkép töredékeket gyűjtöttek nagy számban, amelyeket a 19. században távolítottak el az épület faláról, majd a katedrális padlója alá temettek el. A pigmentek között többféle típusú kék színt találtak, de a leggyakoribb a meglehetősen tiszta lapis lazuli (lazurit) volt, amit XRF, SEM-EDS és XRD módszerekkel azonosítottak. A lazurit volt a legértékesebb és legdrágább korabeli pigment, mivel kevés lelőhelyről termelték ki és importálták. A források közül a legfontosabb az afganisztáni Badakhshan régióban található Sar-e-Sang lelőhely volt.

A lazurit jelentős mennyiségű ként tartalmaz, ezért a kék pigment $\delta^{34}S$ értékei felhasználhatók a lazurit lelőhelyének azonosítására. A kénizotóp vizsgálata FlashHT elemanalizátorral ellátott CF IRMS technikával történt. A Badakhshanból (+15,7 és 22,3‰ között), Tádzsikisztánból (+17,6‰) és a Bajkál-tó vidéki lelőhelyről (+45,4‰) származó lapis lazuli referenciamintákat elemeztük és összehasonlítottuk a Novgorodban alkalmazott kék pigment kénizotóp-összetételével. A freskótöredékekből származó kék pigment $\delta^{34}S$ értékei (+21,1 és +23,5‰ között) közel állnak a badakhshani lapis lazuli referenciamintákéhoz, ezért megerősíthetjük, hogy a Novgorodban használt kék pigment eredete az afganisztáni Badakhshan régió volt.

KEYWORDS: FRESCOES, NOVGOROD, ST. GEORGE'S CATHEDRAL, XRF, SEM-EDS, XRD, CF IRMS

KULCSSZAVAK: FRESKÓ, VELIKIJ NOVGOROD, SZT. GYÖRGY-KATEDRÁLIS, XRF, SEM-EDS, XRD, CF IRMS

• How to cite this paper: GIUMLIA-MAIR. A.R.G.; DUBININA, E.; VDOVICHENKO, M.V.; ZUBAVICHUS, E.; RICCARDI, M.P. & MUSA, M., (2024): Lazurite at Novgorod: Techniques, Mixtures, Provenance, *Archeometriai Műhely* **XXI/3** 295–306.
doi: 10.55023/issn.1786-271X.2024-024

Introduction

Some time ago three of the authors, together with Prof. Vladimir Sedov, published a paper presenting the first data from the analyses carried out on fragments from the Cathedral of St. George (Giumlia-Mair et al. 2022). A second paper, dealing with the preparation layers of the murals, was published one year later (Giumlia-Mair et al. 2023a). A further paper presenting the latest analyses of earlier and later pigments and on the differences in the plasters has been recently published in this journal as well (Giumlia-Mair et al. 2023b). The present paper focuses on lazurite pigments, and the aim is that of deepening the knowledge on the blue colour pigments, the mixtures, how they were applied and especially the provenance of the pigment. The analyses were carried out with different methods: XRF, SEM-EDS, Raman, and CF IRMS technique with FlashHT element analyzer. The most important analysis for this paper is the isotopic study of the sulphur present in the pigment that determined the provenance of the lazurite samples from the fragments of the wall-paintings.

The history of the monument

The Cathedral of St. George in the Yuriev Monastery in Novgorod is one of the oldest surviving architectural monuments in Russia. Several researchers addressed various aspects of the temple in the past (Karger 1946; Sarabyanov 1998; Sarabyanov 2002; Lifshits et al. 2004; Sarabyanov 2012; Sedov et al. 2014, 2015, 2016, 2019).

The beginning of construction by order of prince Vsevolod Mstislavich in 1119 is known from the Novgorod chronicle. The cathedral was consecrated in 1130, but there exists no written evidence on the wall-paintings that were certainly completed around 1130. The wall-paintings of the 12th century were renovated at the turn of the 17th–18th centuries and again later in the 18th century (Sedov 2021; Etinhof 2016). The paintings were first removed from the walls in the 1820s and were buried under the new iron floor. In 1825-1827 the cathedral was re-painted, however in 1898-1902 these murals were also removed. The wall-paintings now visible in the Cathedral were depicted in 1902.

The study of the pre-Mongolian wall-paintings was one of the main goals of the architectural and archaeological excavations in 2013-2023. These paintings are one of the earliest monumental ensembles of pre-Mongolian Russia, the time of the birth of Russian art. They have exceptional artistic quality, testifying to their creation by talented and experienced artists coming to Novgorod from Kiev or even Byzantium.

The excavations

Fragments of the 12th century paintings were first discovered during the 1930s research by M. K. Karger, who removed the cast-iron floor of the 19th century in the two western transepts and found a 25–30 cm thick filling of "fragments of plaster with fresco painting" (Karger 1946). The most significant fragments were published in 1946 in the journal "Soviet Archaeology", as first presentation of pre-Mongolian paintings to the scientific world. Later, there were single finds of fragments around the monastery, and in the 1990s, during the repair of the Oryol building; more were discovered in its vaults and in a trench along it (Etinhof 2016). In 2013, the team of the Institute of Archaeology of the Russian Academy of Sciences, led by V. V. Sedov, laid a pit in the central apse, and discovered 12th century fragments under the cast-iron floor of the 1820s. About 60 trays (0.47 x 0.65 m) were collected from one pit and transferred to the Novgorod Museum, but among them there were no exceptional specimens.

The 2014-2015 excavations in the interior of the Cathedral yielded instead amazing results with over one hundred thousand fragments gathered in the eastern half of the temple. Among them are more than one hundred fragments of faces and parts of faces and bodies (**Fig. 1.**). Historically important graffiti inscriptions were also recovered (Gippius & Sedov 2015). Between 2015 and 2021, more excavations were carried out around the cathedral. The collection was annually augmented by 30–50 trays. In 2022, a new layer with fragments was recorded in a pit to the east of the St. George's Cathedral and yielded 120 trays of fragments (measuring 0.26 x 0.41 m).

Fig. 1.: The photo shows a number of boxes filled with fragments and one of the boxes containing blue fragments

1. ábra: Faltöredékekkel teli tartódobozok, amelyek egyike kék színű töredékeket tartalmaz.

HU ISSN 1786-271X; urn: nbn: hu-4106

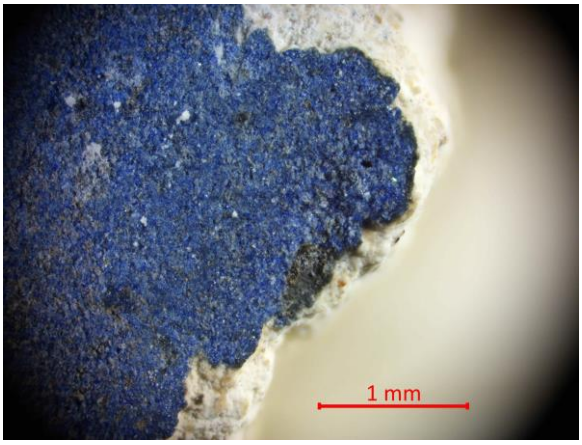


Fig. 2.: Optical microscopy shows the blackish substrate (called *reft*) under the lazurite pigment. Fragment No. 3481.

2. ábra: A lazurit pigment alatt látható fekete aláfestés (*reft*) optikai mikroszkópos felvétele. 3481-es minta.

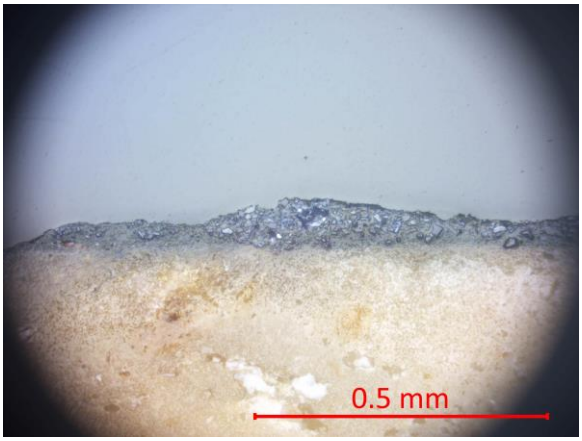


Fig. 3.: In the case of fragment No. 1469 the lazurite pigment had been applied directly on plaster, without any blue clay or *reft* substrate (optical microscopy, carried out with a Modular Microscope ADF W300 in reflected light, and micro photos taken with a microscope camera ADF STD 16).

3. ábra: Az 1469-es minta esetében a lazurit pigmentet közvetlenül a vakolatra vitték fel, kék agyag vagy *reft* aláfestés nélkül (ADF W300 moduláris mikroszkóppal visszavert fényben végzett optikai mikroszkópos vizsgálat, ADF STD 16 mikroszkópos kamerával készített mikrofotó)

In 2023, the excavation area was enlarged and about 400 trays of wall painting were recovered. More fragments might be under the pavement of the paths. We hope to extract the part under the lawn in the next archaeological seasons.

Lazurite pigments at Novgorod

The area of wall-paintings with lapis lazuli as calculated from the blue fragments recovered up to now (about 7% of all collected fragments) was at least around 70–80 m^2. The surface painted with the blue pigment would have covered around 180 m^2 and, in the entire temple, it would have been around 226 m^2. As an average layer is around 50 µm (0.05 mm) thick, the lazurite employed for the entire painted surface inside the church would be 9.2 liters of dry lazurite (without taking the binder into account). This indicates an unprecedented rich order, made by prince Vsevolod Mstislavich, for a monumental painting in the Cathedral. As discussed elsewhere (Giumlia-Mair et al. 2023b), the analyses showed that the blue pigment, applied for the 12th century paintings, consists of lazurite, i.e., ground lapis lazuli. Further studies showed that the lazurite was employed in different ways to achieve a variety of nuances.

In our 2023 publication (Giumlia-Mair et al. 2023b) we pointed out that, contrary to what was stated in a previous article reporting the opinion of a conservation expert based only on naked eye and microscopy observations (Etinhof 2022), most of the fragments painted with lazurite show a dark substrate, called *reft* in all Russian literature (**Fig. 2.**). Most of them also show a special preparation with a layer of blue clay under lazurite and reft (see Giumlia-Mair et al. 2022, 114, fig.10). It is generally thought that *reft* was a mixture of calcium carbonate white and powdered charcoal (Giumlia-Mair et al. 2023a, 2023b). Only in very few specimens, for example No. 1469 (**Fig. 3.**), the lazurite layer was directly applied on the white plaster, typical for the 12th century, with only very little straw, wood shavings or fine sand grains as aggregates. For this paper we analysed several blue-painted fragments dated to the 12th century. When a more intense blue was required, the painter added a dark layer (the one we call *reft*) under the lazurite fragment, however the SEM failed to recognize fragments of powdered charcoal in the blackish layer under the lazurite (see **Fig. 4.**). This means that, instead of charcoal, some soot (i.e. amorphous carbon) was mixed with the blue clay (or part of it), employed as a substrate for the lazurite. As discussed elsewhere, on one of the late samples a mixture of synthetic azurite, lead white, white barium sulphate and a small amount of lazurite were identified (Giumlia-Mair et al. 2022). Because of the technique employed in applying the pigment, the plaster rich in rough sand as additive, and the synthetic azurite and barium sulphate white, we date the mixture to the renovations that happened at the turn of the 17th–18th or later in the 19th century (see also Giumlia-Mair et al. 2022, 115, figs. 13-15).

HU ISSN 1786-271X; urn: nbn: hu-4106 © by the author(s)

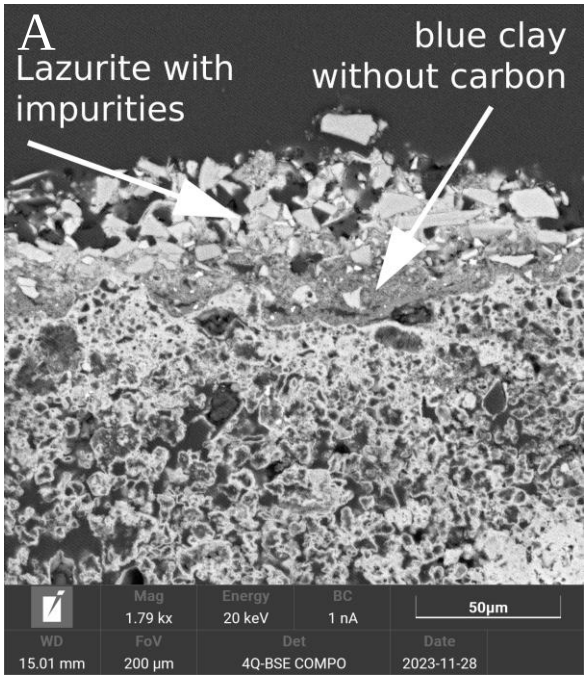
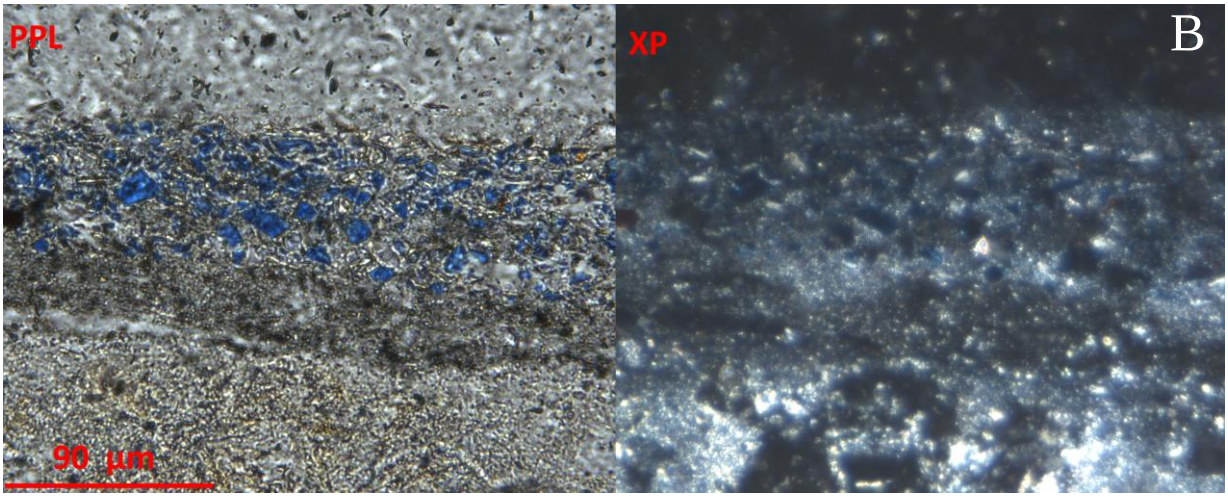


Fig. 4: Cross section of fragment No. 3481 (see also Fig. 2). (A) SEM-BSE micrograph showing the stratigraphy: the upper layer consists of natural lazurite containing phlogopites, sodalite, diopside and other minerals, applied on a thin layer of blue clay. The SEM examination did not show charcoal particles in the black lower layer, visible instead, for example, in sample No. 1502. The black colour is probably due to an admixture of the clay with soot (amorphous carbon). (B) Cross section with PPL and XP showing the lazurite pigment layer and the *reft* layer.

4. ábra: A 3481. sz. minta keresztmetszete (lásd még a 2. ábrát). (A) A rétegrendet mutató SEM-BSE felvétel. A felső réteg természetes lazuritból áll, amely flogopitot, szodalitot, diopszidot és más ásványokat tartalmaz, és vékony kék agyagrétegre van felhordva. A SEM-vizsgálat nem mutatott ki faszénszemcséket az alsó fekete rétegben, amelyek például az 1502. sz. mintában láthatóak. A fekete szín valószínűleg az agyag korommal (amorf szénnel) való keveredésének köszönhető. (B) A lazurit pigmentréteget és a *reft* réteget mutató optikai mikroszkópos (PPL és XP) felvételek.



Further, on a preparation dated to later phases, powdered charcoal mixed with a small amount of lazurite, was employed to achieve a deep bluish colour (**Fig. 5.**). Optical microscopy and SEM-EDS showed a thick substrate of red ochre with charcoal under the bluish layer.

One of the most important observations is that, even in the case of later specimens, the blue colour was always obtained by mixing at least some lazurite with other pigments or *reft*.

For the characterization of the phases micro-Raman spectroscopy has been also applied without sample preparation. We focused the laser source (532 nm) by the optical system (80x magnification) on the blue crystals and obtained the spectra of **Fig. 6A**.

The Raman bands at 257, 280, 546, 584, 804, 1091, 1120 and 1640 cm^{-1} are ascribable to the lazurite phase. On the other hand, when analysing the darker blue-greyish samples, we detected characteristic bands corresponding to G and D vibrational modes in graphite structure (**Fig. 6B)**.

The broad aspect of those bands must also be noted, as it suggests low crystallinity of the graphite or only hexagonal carbon-carbon bonds as per graphene disorder layers (Zaitsev 2010). Thus, the Raman data acquired on the samples' surface without preparation, confirmed the interpretation of the previous analyses.

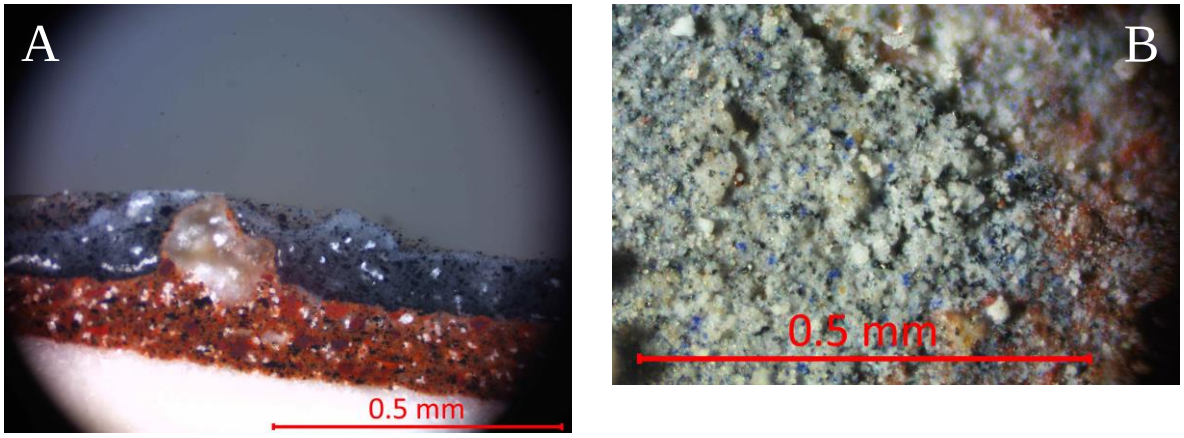


Fig. 5: Later dated fragment No. 1502. (A) Optical microscopy showing a layer of blue pigment consisting of a mixture of calcium carbonate, powdered charcoal and a small amount of lazurite applied on a red layer of red ochre mixed with powdered charcoal. A large quartz sand grain and small charcoal inclusions can be recognized in both pigments. (B) The higher magnification shows both the lazurite and the charcoal particles in calcium carbonate.

5. ábra: A későbbre datált 1502. sz. minta optikai mikroszkópos vizsgálata. (A) A kék pigmentréteget, amely kalcium-karbonát, faszénpor és kis mennyiségű lazurit keverékéből áll, vörös rétegre vittek fel, amely faszénporral kevert vörös okkerből készült. Egy nagyméretű kvarc homokszemcse és apró faszénzárványok felismerhetők mindkét rétegben. (B) A nagyobb nagyításon mind a lazurit, mind a faszénszemcsék jól megfigyelhetők a kalcium-karbonátban.

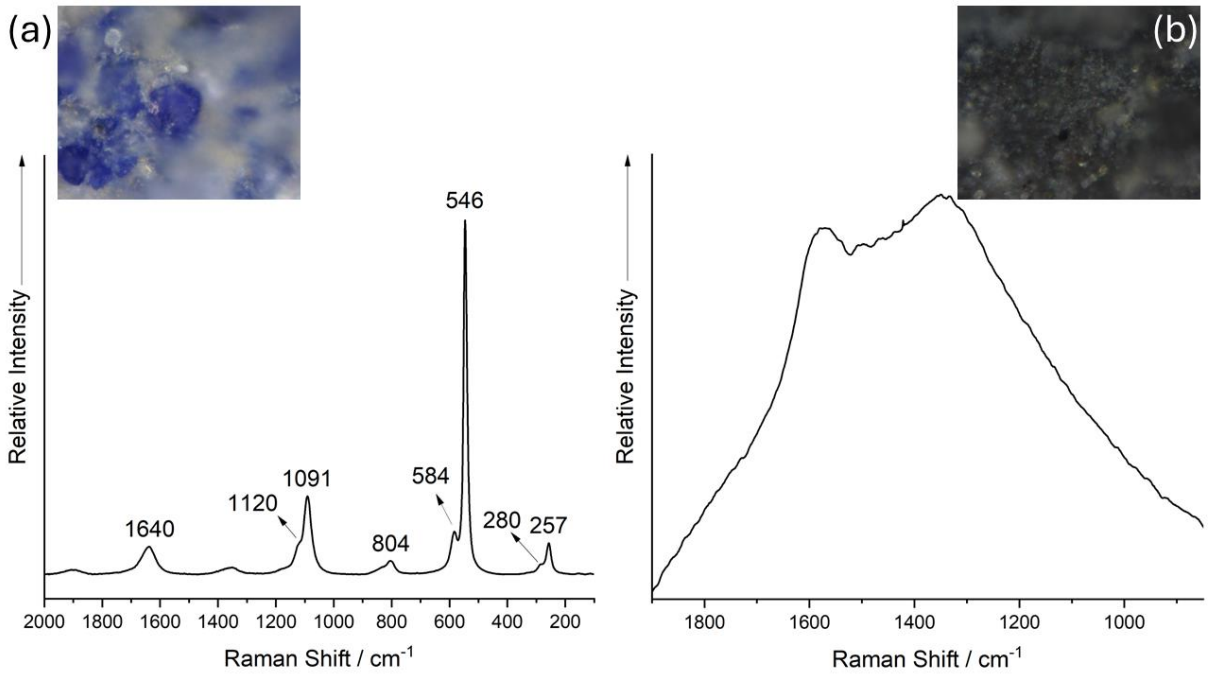


Fig. 6: Raman spectra acquired by focusing the source on the blue crystal (A) and on the darker grey ones (B), corresponding to lazurite and graphene, respectively. The 532 and the 633 nm Raman laser sources have been focused by 80x objective on the crystals shown in the micrograph images.

6. ábra: A kék kristályra (A) és a sötétebb szürke kristályokra (B) fókuszálva felvett Raman-spektrumok, amelyek lazuritnak, illetve grafénnek felelnek meg. Az 532 és a 633 nm-es Raman-lézerforrást 80x objektívvel fókuszáltuk a mikroszkópos képeken látható kristályokra.

HU ISSN 1786-271X; urn: nbn: hu-4106 © by the author(s)

The provenance of the lazurite pigment

Lazurite had to be imported from far away and was expensive, indeed the most precious pigment in use in antiquity. Now lapis lazuli is also found in Siberia, near Lake Baikal. It is known that the exploitation of the Baikal deposit began no earlier than the 18th century, but, as there are other possibilities, such as for instance the deposits in Tajikistan, and the minerals from the various deposits differ from each other, it still seemed useful to investigate the place of origin of the blue pigment from the Cathedral. Numerous studies for the determination of the provenance of lazurite exist, so that only a few can be mentioned here (see for example Guidorzi et al. 2022; Lo Giudice et al. 2009; Schmidt et al. 2009; Re et al. 2011, 2013; Law 2014). Several methods have been used to determine the origin of the mineral: more traditional like Raman, X-ray diffraction, micro-XRF, but also particle-induced X-ray emission (PIXE), particle-induced gamma-ray emission (PIGE), prompt-gamma activation analysis (PGAA) and ionoluminescence (IL). To confirm the origin of our lapis lazuli, we needed samples from various deposits, which were kindly provided by the A. E. Fersman Mineralogical Museum. After consultations with the museum staff and geologists, it was decided to conduct an isotopic analysis on the sulphur from the lapis lazuli admixture for determining its provenance. This analysis is relatively innovative in the study of pigments (Law 2014) and was carried out by E. O. Dubinina, Laboratory of Isotope Geochemistry and Geochronology of the Institute of Geology of Ore Deposits of the Russian Academy of Sciences, co-author of this article, and a specialist in sulphur isotopes. Three samples of blue pigment from the Cathedral and five samples from modern lapis lazuli deposits, such as the Pamirs and Siberia were provided.

Sulphur isotope composition of natural lapis lazuli and pigment of the wall-paintings

Rationale for the approach

The main feature of lapis lazuli is the diverse content of different forms of sulphur in the mineral molecule - from reduced (S^{2-}) to completely oxidized, or as sulphate (SO_4^{2-}). Between these forms of sulphur, a significant thermodynamic isotope fractionation takes place. For example, at 400 °C the isotopic fractionation of sulphur $\Delta^{34}S$ ($\approx\delta^{34}S(SO_4^{2-})$- $\delta^{34}S(S^{2-})$) between its oxidized and reduced forms is 20.3‰, at 600 °C it is 11.3‰, and at 800 °C - about 6‰ (Sakai 1968). Consequently, the amount ratio of the sulphur reduced to oxidized in the mineral molecule will affect the total sulphur isotopic composition of lapis lazuli if it was formed under open system conditions. As a rule, the lapis lazuli formation is associated with high temperature metasomatism (Korzhinsky 1947, 1953; Blaise & Sesbron 1966; Efimov & Suderkin 1967; Davydchenko 1972), which is quite consistent with the conditions of an open system. In turn, the ratio of reduced and oxidized forms of sulphur in the mineral is determined, first of all, by the redox conditions of lapis lazuli formation, and this parameter can also be a diagnostic feature of a particular deposit.

Therefore, the isotopic composition of sulphur in lapis lazuli is a reliable parameter. On one hand, it reflects the isotopic composition of sulphur in mineral-forming solutions. On the other hand, it also shows the redox conditions and temperature of mineral deposition. In addition, the total sulphur content in lapis lazuli can also be a diagnostic feature, since it is determined by the sulphur content in the rock through which high temperature metasomatism occurs (Korzhinsky 1947, 1953; Khoreva 1955). Thus, when identifying lapis lazuli and blue pigments from archaeological samples, it makes sense to determine not only the $\delta^{34}S$ values in lapis lazuli, but also to estimate the total sulphur content in the same sample in order to use two diagnostic features instead of one. In the case of a pigment, this approach works only for samples consisting of almost pure lapis lazuli.

One of the methodological problems is the presence in lapis lazuli of thin invisible inclusions of pyrite, which are difficult to physically separate from the mineral. The methodological recommendations to remove pyrite before the sulphur isotope analysis of lapis lazuli (Law 2014) are certainly correct, but when analysing lapis lazuli to solve problems of its provenance the removal of pyrite is not necessary. Firstly, the amount of invisible pyrite is a feature of specific lapis lazuli deposits, and secondly, we would have to assume that during the manufacture of pigments in the 12th century, special and efficient operations were carried out to completely separate pyrite and lapis lazuli. It is just possible that the flotation method was used to purify the ground raw material, however this method does not eliminate microscopic inclusions of dispersed pyrite. Nevertheless, we have to keep in mind that, if in the laboratory the flotation purification of a sample is applied, it would be a subjective factor that is difficult to correlate both with natural variations in the parameters (content, isotopic composition) of sulphur in the sample, and with the variations in the archaeological materials.

According to Law (2014), the sulphur isotopic composition of pyrite impurities is close to the isotopic composition of lapis lazuli due to the high-temperature origin of this mineral. For Badakhshan lapis lazuli, the difference between the $\delta^{34}S$ values of lapis lazuli and pyrite is 4.6‰, and for lapis lazuli from Tajikistan it is 6.6‰ (Law 2014). With

HU ISSN 1786-271X; urn: nbn: hu-4106 © by the author(s)

such a difference in the isotopic composition of sulphur, pyrite impurities can affect the results of isotopic analysis, which is currently carried out with an accuracy of ±0.3‰ (1σ), when the pyrite amount exceeds ≈2%. However, in this case the pyrite content in the sample is visible, and it renders possible to mechanically clean it.

These considerations elucidate the approach used in our work to identify the 12th century pigments from the Cathedral of St. George. At first, we analysed some samples of natural lapis lazuli from known deposits in Afghanistan, Tajikistan, and Russia, to obtain the diagnostic sulphur characteristics ($\delta^{34}S$ and C(S)) of lapis lazuli of different origins.

Analytical procedures

The sulphur isotope analysis was carried out by isotope mass spectrometry in a constant flow of helium (CF-IRMS) on a DELTA V+ mass spectrometer combined with a FlashHT1112 elemental analyzer (Thermo, Germany) in the Laboratory of Isotope Geochemistry and Geochronology of the IGEM RAS (Moscow). The calibration of the measured $\delta^{34}S$ values relative to the international standard VCDT was carried out by analysing IAEA reference materials (S-1, S-2 and S-3) that were analysed simultaneously with the studied samples.

The top layer of blue pigment was scraped off the surface of the fresco fragments using a diamond needle. The scraping depth was controlled under a binocular lens. The substance obtained was ground to a fine powder in an agate mortar. Samples of natural lapis lazuli were ground in the same way. The weight of both lapis lazuli and pigment samples was exactly the same (0.9 mg). The same portion (0.9 mg) of the V_2O_5 oxidizing agent (analytical grade) was added to each sample. The mixture of the sample and the oxidizing agent were placed in a tightly packaged tin container. The containers were placed, together with the standards put in similar containers, into the autosampler (AS-2000) for solids mounted on a FlashHT1112 peripheral device. The samples packed in tin containers were loaded by autosampler into a quartz reactor, filled layer by layer with tungsten oxide and electrolytic copper and heated to T = 1020 °C. The entire system was purged with high purity helium (grade 6.0) with the rate of 90 ml/min.

When the sample entered the reactor, a small portion of oxygen was supplied, resulting in instant high-temperature (1800 °C) combustion of the sample container. The released gas passed through the appropriate layers of the reactor in a helium flow, a special dehydrator, and entered a chromatographic column heated to 105 °C.

Table 1.: Isotopic composition ($\delta^{34}S$) and sulphur content (C(S)) in samples of natural lapis lazuli and blue pigment of the frescoes of the Cathedral of St. George (Novgorod).

1. táblázat: Természetes lapis lazuliból és a Szent György-katedrális (Novgorod) freskóinak kék pigmentjéből származó minták izotópösszetétele ($\delta^{34}S$) és kéntartalma (C(S)).

Sample No.	Sample description	C(S), µg/mg	$\delta^{34}S$ (VCDT), ‰
Natural lazurite samples			
FN-807	Baikal (Slyudyanka), Russia	32	45.3
FN-804_900	Baikal (Malaya Bystraya), Russia	32	45.4
FN-808	Badakhshan, Afghanistan	8	22.3
FN-805	Badakhshan, Afghanistan	20	15.7
FN-806	Lyajvar-Dara, Tajikistan	12	17.6
Blue pigment samples of the frescoes of the Cathedral of St. George			
Lasur_2021	Novgorod, Russia	11	22.6
Lasur_21B17		15	23.5
Lasur_21BI47		14	21.1

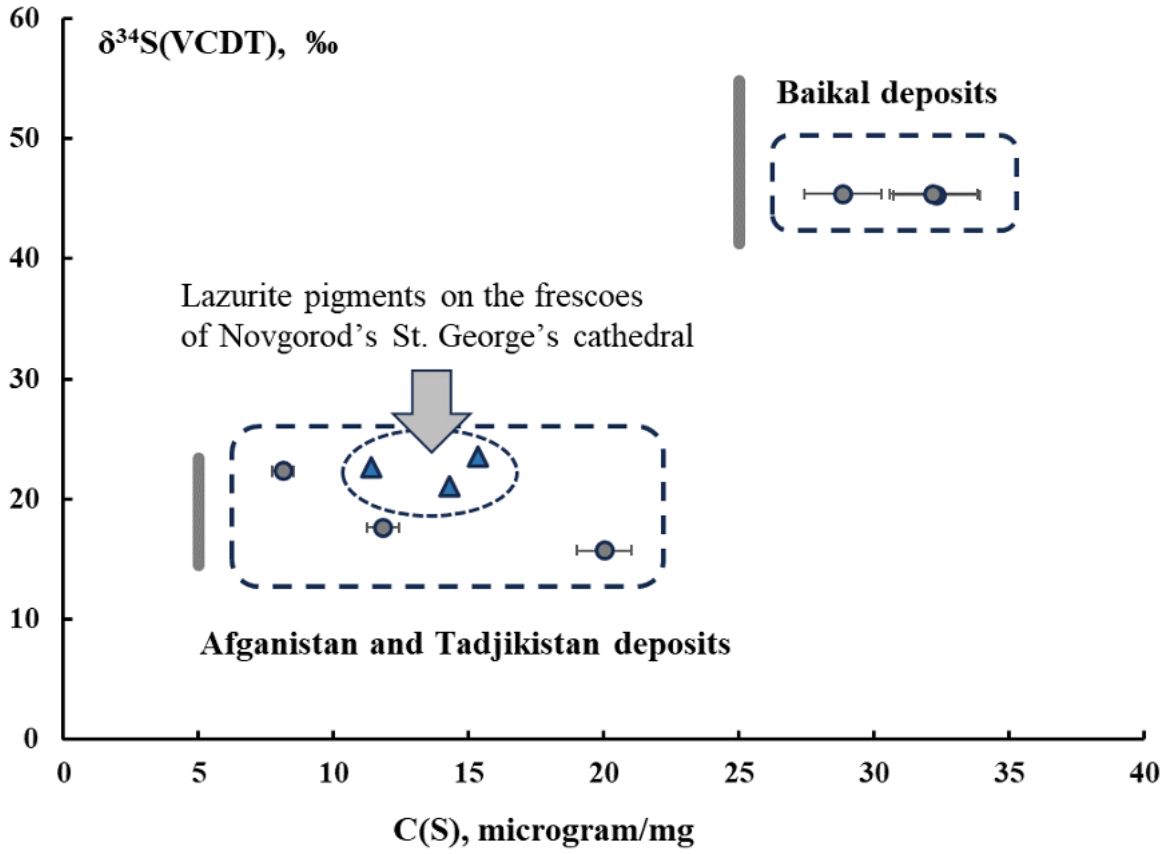


Fig. 7.: Diagnostic diagram C(S)-$\delta^{34}S$ for natural lapis lazuli. Data are applied for the pigment of the frescoes of the Cathedral of St. George (12th century, Novgorod), which fully correspond to the composition of lapis lazuli of Afghan and Tajik origin. Thick vertical lines are the interval of variations in the $\delta^{34}S$ value for lapis lazuli of the corresponding deposits according to Law (2014).

7. ábra: A természetes lapis lazuli C(S)-$\delta^{34}S$ diagnosztikai diagramja. Az adatokat a Szent György-katedrális (12. század, Novgorod) freskóinak pigmentjére alkalmazzuk, amely teljes mértékben megfelel az afgán és tádzsik eredetű lapis lazuli összetételének. A vastag függőleges vonalak a megfelelő lelőhelyek lapis lazulijának $\delta^{34}S$-értékében a Law (2014) szerinti eltérések intervallumát jelölik.

As a result of chromatographic purification, the sample, represented by a portion of SO^2 gas in a helium flow, was transferred through the ConFloIV gas commutator device to the inlet system of the DeltaV+ mass-spectrometer (Thermo, Germany). The accuracy of the $\delta^{34}S$ value determination obtained by the multiple analyses of IAEA standards, was ±0.3‰ (1σ). The sulphur concentration was determined by calibrating the chromatographic peak area with the accuracy ±5% (1σ). The results of the isotopic composition measurements ($\delta^{34}S$ in per mil, ‰) and sulphur content (C(S) in micrograms of sulphur in one mg of the sample are given in **Table 1.**

Analysis of natural lapis lazuli

As follows from **Table 1.**, lapis lazuli from the Baikal deposits contains the maximum amount of sulphur (32 μg/mg). Lapis lazuli from Afghanistan (Badakhshan) and Tajikistan (Lyajvar-Dara) are characterized by sulphur contents 2 to 4 times lower. The isotopic composition of sulphur also differs: the highest $\delta^{34}S$ values are characteristic of lapis lazuli from the Baikal deposits (≈ 45‰), and the lowest for deposits of Afghanistan and Tajikistan (15.7–17.6‰). Based on these data, it is possible to draw up a preliminary diagnostic diagram, which can later be supplemented by the results obtained both for lapis lazuli from other deposits and pigments from known archaeological objects (**Fig. 7.**). Unfortunately, the few published data do not contain information about the sulphur content of the sample and cannot be plotted on this chart. However, for comparison, we present the intervals of variations in $\delta^{34}S$ values from the review by Law (2014). Our preliminary data show that for lapis lazuli of Afghan and Tajik origin there is an inverse correlation between C(S) and $\delta^{34}S$ values, which can be explained by variations in the content of trace pyrite in the sample. This explains why the $\delta^{34}S$ value decreases with increasing sulphur content. For the Baikal samples, such

relationship between the C(S) and $\delta^{34}S$ values was not found. This may be due to the minor effect of dispersed pyrite impurities compared to the high sulphur background in lapis lazuli from Baikal deposits.

Analysis of pigments from the Cathedral of St. George (Novgorod)

The data obtained by analysing scrapings of fragments with blue pigment from the Cathedral of St. George in Novgorod are fully consistent with the composition of natural lapis lazuli of Afghan or, possibly, Tajik origin (**Fig. 8.**). However, the greatest agreement is observed between the samples from the Cathedral ($\delta^{34}S$ from 21.1 to 23.5‰) and the Afghan lapis lazuli sample FN 808. It is interesting that the sulphur content in this sample is minimal (C(S) = 8 μg/mg). Apparently, the lapis lazuli was carefully chosen for producing pigments with a minimal amount of pyrite impurities, as they worsen the properties of the pigment. Therefore, we can assume that when selecting raw materials for the blue pigment, lapis lazuli with few foreign inclusions, including pyrite, would be favoured. The sulphur content in the scrapings from the Novgorod samples is close to the sulphur content in samples of pure Afghan lapis lazuli. This indicates that the composition of the pigment is close to that of pure natural lapis lazuli.

Conclusions

The blue pigments employed in the 12th century in the mural paintings of the Cathedral of St. George at Novgorod consisted of lazurite, mainly applied in combination with *reft*, the mixture of calcium carbonate white and powdered charcoal or soot, and mainly with a substrate of blue clay. In very few cases the lazurite pigment was applied on the plaster, without any preparation underneath.

After XRF and SEM-EDS it was decided to determine the provenance of the lazurite in use at the St. George Cathedral by isotopic analysis of sulphur. The investigation was carried out by CF IRMS technique with FlashHT element analyzer at the Laboratory of Isotope Geochemistry and Geochronology of the Institute of Geology of Ore Deposits of the Russian Academy of Sciences, by E. O. Dubinina. The results of the analysis indicate that the lapis lazuli employed as a pigment at Novgorod came from the deposits in the region Badakhshan in Afghanistan.

Contribution of authors

Alessandra Giumlia-Mair Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition. **Elena Dubinina** Formal analysis, Investigation. **Marina Vdovichenko** Formal analysis, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Funding acquisition. **Evgenius Zubavichus** Formal analysis, Investigation. **Maria Pia Riccardi** Formal analysis, Investigation. **Maya Musa** Formal analysis, Investigation.

References

BLAISE, J. & CESBRON, F. (1966): Donnees mineralogiques et petrographiques sur le gisement de lapis-lazuli de Sar-e-Sang, Hindon-Konch, Afghanistan. *Bulletin de la Societe Francaises de Mineralogie et Cristallographie* **89** 333–343.

DAVYDCHENKO, A.G. (1972): Some features of high-temperature metasomatic mineral formation in dolomite marble strata during the regressive stage of ultrametamorphism (Southwestern Pamirs). *Metamorphogenic formation* **2** Naukova Dumka Publishing House, Kiev, 137–145. / ДАВЫДЧЕНКО, А.Г. (1972): Некоторые особенности высокотемпературного метасоматического минералообразования в толщах доломитовых мраморов в регрессивный этап ультраметаморфизма (Юго-Западный Памир). *Метаморфогенное образование* **2** издательство «Наукова думка», Киев, 137–145.

EFIMOV, I.A. & SUDERKIN, A.I. (1967): The Sary-Sang lapis lazuli deposit in Northern Afghanistan. *Bulletin of the Academy of Sciences of the Kazakh SSR* **8 (268)** 64–66. / ЕФИМОВ, И.А. & СУДЕРКИН, А.И. (1967): Месторождение ляпис-лазури Сары-Санг в Северном Афганистане. *Вестник Академии наук Казахской ССР* **8 (268)** 64–66.

ETINHOF, O.E. (2016): On the frescoes of the St. George Cathedral in the St. George Monastery at Novgorod. *Opus mixtum* **6** 190–201. / ЭТИНГОФ, О.Е. (2016): О фресках на оса Георгиевского собора Юрьева монастыря в Новгороде. *Opus mixtum* **6** 190–201.

ETINHOF, O.E. (2022): New finds of frescoes of St. George's Cathedral of the Yuriev Monastery and the artel of painters in the Novgorod land of the first half of the XII century. *Bulletin of St. Petersburg University. Art history* **12/3** 464–486. / ЭТИНГОФ, О.Е. (2022): Новые находки фресок Георгиевского собора Юрьева монастыря иартели живописцев в Новгородской земле первой половины XII в. *Вестник Санкт-Петербургского университета. Искусство ведение* **12/3** 464–486.
https://doi.org/10.21638/spbu15.2022.304

GIPPIUS, A.A. & SEDOV, V.V. (2015): Graffiti inscription of 1198 from St. George's Cathedral of St. George Monastery, The City and regions of Medieval Russia. In: GAIDUKOV, P.G. ed., *Archaeology, history, culture*. Vologda, Moscow,

478–490. / ГИППИУС, А.А. & СЕДОВ, Вл.В. (2015): Надпись-граффито 1198 года из Георгиевского собора Юрьева монастыря, Городаивеси Средневековой Руси. Города и веси Средневековой Руси. In: ГАЙДУКОВ, П.Г. ред., *Археология, история, культура.* Вологда, Москва, 478–490.

GIUMLIA-MAIR, A.R.G., SEDOV, V.V., VDOVICHENKO, M.V. & RICCARDI, M.P. (2022): On Blue and Green Pigments from the St. George Cathedral of Veliki Novgorod. *Advances in Archaeometerials* **3/2** 109–119. https://doi.org/10.1016/j.aia.2023.06.001

GIUMLIA-MAIR, A.R.G., SEDOV, V.V. & ETINHOF, O. (2023a): Substrates and preparation layers under the wall paintings of the St. George's Cathedral (1119 CE) at Veliki Novgorod. *Surface Engineering* **39/2** 139–149. https://doi.org/10.1080/02670844.2023.2202007

GIUMLIA-MAIR, A.R.G., VDOVICHENKO, M.V. & RICCARDI, M.P. (2023b): Optical Microscopy, XRF and SEM-EDS on Wall Painting Fragments from the St.George's Cathedral at Novgorod. *Archeometriai Műhely* **XX/4** 269–279. https://doi.org/10.55023/issn.1786-271X.2023-023

GUIDORZI, L., RE A., ANGELICI D., LEMASSON, Q., PACHECO, C., PICHON L., MOIGNARD, B., GALLO L. M., COSTA E., COSSIO, R., LO G.A., (2022): A provenance study on the lapis lazuli collection from the Regional Museum of Natural Sciences in Turin. *Journal of Physics. Conference Series* **2204** 012092. https://doi.org/10.1088/1742-6596/2204/1/012092

KARGER, M.K. (1946): Excavations and restoration work in the St. George Cathedral of the Yuriev Monastery in Novgorod. *Soviet Archaeology* **VIII** 175–224. / КАРГЕР, М.К. (1946): Раскопки и реставрационные работыв Георгиевском соборе Юрьева монастыря в Новгороде, *Советская археология* **VIII** 175–224.

KHOREVA, B.Ya. (1955): Paragenetic analysis of mineral associations of one lapis lazuli deposit. *Petrographic collection* **1** Gosgeoltehizdat, Materials of VSEGEI, issue 4, 182–190. / ХОРЕВА Б.Я. (1955): Парагенегический анализ минеральных ассоциаций одного лазуритового месторождения, *Петрографический сборник* **1** Госгеолтехиздат, Материалы ВСЕГЕИ, вып. 4, 182–190.

KORZHINSKY, D.S. (1947): Bimetasomatic phlogopite and lapis lazuli deposits of the Archaea of the Baikal region. In: ZAVARITSKY, A.N. & PREOBRAZHENSKY, I.A. eds., *Proceedings of the Institute of Geological Sciences* **29**, Moscow, Publishing House of the USSR Academy of Sciences 187. / КОРЖИНСКИЙ, Д.С. (1947): Бимета-соматические флогопитовые и лазуритовые месторождения архея Прибайкалья, In: ЗАВАРИЦКИЙ, А.Н. & ПРЕОБРАЖЕНСКИЙ, И.А. ред., *Труды института геологических наук,* **29**, Москва, Издательство Академии наук СССР, 187.

KORZHINSKY, D.S. (1953): An essay on metasomatic processes. In: ВЕТЕКНТІN, A.G. & SOKOLOV, G.A.M. eds., *The main problems in the doctrine of magmatogenic ore deposits*. Publishing House of the USSR Academy of Sciences, Moscow, 332–352. / КОРЖИНСКИЙ Д.С. (1953): Очерк метасоматических процессов, In: БЕТЕХТИН, А.Г. & СОКОЛОВ, Г.А.М. ред., *Основные проблемы вучениио магматогенных рудных месторождениях*. Издательство Академии наук СССР, Москва, 332–352.

LAW, R. (2014): Evaluating Potential Lapis Lazuli Sources for Ancient South Asia Using Sulfur Isotope Analysis. In: LAMBERG-KARLOVSKY, C.C., GENITO, B. & CERASETTI, B. eds., "- *My Life is like the Summer Rose - Maurizio Tosi el'Archeologia come modo di vivere*", Papers in Honour of Maurizio Tosi for his 70th birthday, *BAR International Series* **2690**, Oxford, 419–430.

LIFSHITS, L.I., SARABYANOV, V.D. & TSAREVSKAYA, T.Yu. (2004): *Monumental painting of Veliky Novgorod the end of the XI — first quarter of the XII century*. Dmitry Bulanin (Publisher), St. Petersburg, 887 pp. / ЛИФШИЦ, Л.И., САРАБЬЯНОВ, В.Д. & ЦАРЕВСКАЯ, Т.Ю. (2004): *Монументальная живопись Великого Новгорода конец XI — первая четверть XII века*. Дмитрий Буланин, Санкт-Петербург, 887 pp.

LO GIUDICE, A., RE, A., ANGELICI, D., CALUSI, S., GIUNTINI, L., MASSI, M., OLIVERO, P., PRATESI, G., ALBONICO, M. & CONZ, E. (2009): Multitechnique characterization of lapis lazuli for provenance study. *Analytical and Bioanalytical Chemistry* **395** 2211–2217. https://doi.org/10.1007/s00216-009-3039-7

RE, A., LO GIUDICE, A., ANGELICI, D., CALUSI, S., GIUNTINI, L., MASSI, M. & PRATESI, G. (2011): Lapis lazuli provenance study by means of micro-PIXE. *Nuclear Instruments and Methods in Physics Research B* **269** 2373–2377. https://doi.org/10.1016/j.nimb.2011.02.070

RE, A., ANGELICI, D., LO GIUDICE, A., MAUPAS, E., GIUNTINI, L., CALUSI, S., GELLI, N., MASSI, M., BORGHI, A., GALLO L.M., PRATESI, G. & MANDÒ, P.A. (2013): New markers to identify the provenance of lapis lazuli: trace elements in pyrite by means of micro PIXE. *Applied Physics A* **111** 69–74. https://doi.org/10.1007/s00339-013-7597-3

SAKAI, H. (1968): Isotopic properties of Sulphur compounds in hydrothermal processes. *Geochemical Journal* **2** 29–49.

SARABYANOV, V.D. (1998): Frescoes of the XII century in the main part of St. George's Cathedral of the St. George Monastery. In: LIKHACHEV, D.S. ed., *Cultural monuments. New discoveries: writing, art, archaeology*. Nauka, Moscow, 232–239. / САРАБЬЯНОВ, В.Д. (1998): Фрески XII в. восновномобъеме Георгиевского собора Юрьева монастыря. In: ЛИХАЧЕВ, Д.С. ред., *Памятники культуры. Новые открытия: письменность, искусство, археология*. Наука, Москва, 232–239.

SARABYANOV, V.D. (2002): Murals of the north-western tower of St. George's Cathedral of the Yuriev Monastery. In: ETINHOF, O.E. ed., *Ancient Russian art: Russia and the countries of the Byzantine world. XII century*. Dmitriy Bulanin, St. Petersburg, 365–398. / САРАБЬЯНОВ, В.Д. (2002): Росписи северо-западной башни Георгиевского собора Юрьева монастыря. In: ЭТИНГОФ, О.Е. ред., *Древнерусское искусство: Русь и страны Византийского мира. XII век*. Дмитрий Буланин, Санкт-Петербург,365–398.

SARABYANOV, V.D. (2012): Of the ancient murals of St. George's Cathedral of the Yuriev Monastery in Veliky Novgorod. In: NERSESYAN, L.V. ed., *The history of collecting, storing and restoring monuments of ancient Russian art*. INIKO, Moscow, 357–366. / САРАБЬЯНОВ, В.Д. (2012): Осудьбе древних росписей Георгиевского собора Юрьева монастыря в Великом Новгороде. In: НЕРСЕСЯН, Л.В. ред., *История собирания, хранения и реставрации памятников древнерусского искусства*. ИНИКО, Москва, 357–366.

SCHMIDT, C.M., WALTON, M.S. & TRENTELMAN, K. (2009): Characterization of Lapis Lazuli Pigments Using a Multitechnique Analytical Approach: Implications for Identification and Geological Provenancing. *Analytical Chemistry* **81** 8513–8518. https://doi.org/10.1021/ac901436g

SEDOV, V.V. (2021): The staircase tower of St. George's Cathedral of the Yuriev Monastery: archaeology, architecture and frescoes. *Russian archaeology* **4** 132–143. / СЕДОВ, ВЛ.В. (2021): Лестничная башня Георгиевского собора Юрьева монастыря: археология, архитектура и фрески. *Российская археология* **4** 132–143.

SEDOV, V.V. & VDOVICHENKO, M.V. (2015): Excavations of the St. George Cathedral of the Yuriev Monastery in Veliky Novgorod in 2014, Novgorod and the Novgorod land. *History and Archaeology* **29** Veliky Novgorod, 98–122. / СЕДОВ, ВЛ.В. & ВДОВИЧЕНКО, М.В. (2015): Раскопки Георгиевского собора Юрьева монастыря в Великом Новгороде в 2014 г., Новгород и Новгородская земля. *История и археология* **29** Великий Новгород, 98–122.

SEDOV, V.V. & VDOVICHENKO, M.V. (2019): Works of the architectural and archaeological detachment in Veliky Novgorod. In: MAKAROV, N.A & KOROL, G.G. eds., *New archaeological projects. Recreating the Past*. IA RAS (publisher), Moscow, 168–174. / СЕДОВ, ВЛ.В. & ВДОВИЧЕНКО, М.В. (2019): Работы архитектурно-археологического отряда в Великом Новгороде. In: МАКАРОВ, Н.А & КОРОЛЬ, Г.Г. ред., Новые археологические проекты. Воссоздавая прошлое, ИА РАН (издательство), Москва, 168–174. https://doi.org/10.31857/S086960630016578-4

SEDOV V.V., KADEISHVILI, E.A. & VDOVICHENKO, M.V. (2014): Frescoes of the XII century on the walls of St. George's Cathedral of St. George Monastery near Veliky Novgorod, discovered during archaeological work in 2013. *Restoration and research of cultural monuments* **7** 15–19. / СЕДОВ, ВЛ.В., КАДЕЙШВИЛИ, Е.А. & ВДОВИЧЕНКО, М.В. (2014): Фрески XII в. на стенах Георгиевского собора Юрьева монастыря под Великим Новгородом, открытые входе археологических работ 2013 г. *Реставрация и исследование памятников культуры* **7** 15–19.

SEDOV, V.V., VDOVICHENKO, M.V. & KADEISHVILI, E.A. (2016): Frescoes of the XII century on the walls of St. George's Cathedral of the Yuriev Monastery (based on the results of archaeological work in 2014). *Restoration and research of cultural monuments* **8** 11–17. / СЕДОВ, ВЛ.В., ВДОВИЧЕНКО, М.В. & КАДЕЙШВИЛИ, Е.А. (2016): Фрески XII в. настенах Георгиевского собора Юрьева монастыря (по результатам археологических работ 2014 г.). *Реставрация и исследование памятников культуры* **8** 11–17.

ZAITSEV, A.M. (2001): Scattering. In: ZAITSEV, A.M. ed., *Optical proprieties of Diamond*. Springer Verlag, Heidelberg, 69–124. http://dx.doi.org/10.1007/978-3-662-04548-0

HU ISSN 1786-271X; urn: nbn: hu-4106