Heritage Science

RESEARCH ARTICLE

Open Access

Comprehensive study of 12th century wall painting fragments from the St. George Cathedral of the Yuryev Monastery in Veliky Novgorod (Russia) using complementary physico-chemical methods

O. S. Philippova[1], A. Yu. Dmitriev[1*], T. J. Tsarevskaya[2] and S. O. Dmitrieva[3]

Abstract

A total of 7 complementary methods have been applied to investigate unique pre-Mongolian 12th century wall paintings from the St. George Cathedral of the Yuriev Monastery in Veliky Novgorod, Russia. Both archaeological samples from the main space of the Cathedral and fragments in situ in the stairs tower of the Cathedral were studied. For the first time in Russia, sensitive neutron methods were used to study the elemental composition of pigments and plasters—neutron activation analysis and prompt gamma activation analysis. This research made it possible to determine elemental and mineral composition of the pigments and plasters used during creation of wall paintings; identify the technique of paintings; make assumptions about the different time of the paintings creation in the main space of the Cathedral and in its stairs tower; as well as reconstruct the presumable original view of the painting of the St. George figure. The discovery of the expensive lazurite pigment attested to the high status of the ktetor of the Cathedral's murals. The obtained data were compared with Byzantine and Italian paintings of the same period churches.

Keywords: Old russian wall paintings, Pigments, Plasters, Multi-analytical investigation, Elemental and mineral analysis, Painting technique

Introduction

We can not only admire today the antiquity and beauty of art works. Modern methods of physico-chemical researches make it possible to see the invisible—what is under the layers of paint available to the human eye. Researchers from different countries paid special attention to the possibility of studying medieval wall paintings with this approach. The use of complex research methods allows to determine the composition of the plaster serving as the wall painting base [1], discover the technique and sequence of paint layers [2], and clarify the detailed composition of each individual pigment [2, 3]. Such studies have multifocal aims. They can help to determine the specific of painting techniques, make indirect assumptions about the social status of ktetors. In some cases, on the basis of pigments composition, it is possible to propose a hypothesis about the national school or clarify a work of art creation time. Finally, scientific data can provide important conclusions for subsequent restoration of a monument or visual reconstruction of painting original appearance.

The object of our research was a unique architectural monument from the UNESCO list of world heritage sites—St. George Cathedral—the catholicon of the Yuriev Monastery in Veliky Novgorod (Russia) (Fig. 1).

*Correspondence: andmitriev@jinr.ru; ru-day@list.ru
[1] Joint Institute for Nuclear Research, Joliot-Curie Str. 6, 141980 Dubna, Russia
Full list of author information is available at the end of the article

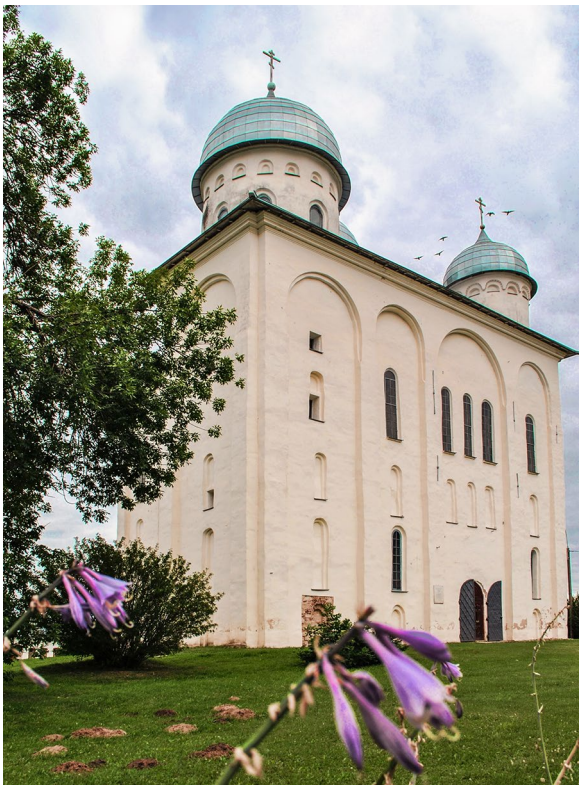

Fig. 1 St. George Cathedral of the Yuryev Monastery. View from the northwest

This monument is the largest of four stone churches built in Novgorod in first half of 12th century. The foundation of the monastery catholicon (1119) is mentioned in the chronicle, so we know the eminent ktetors: prince Mstislav the Great, known in Europe as Harold (grandson of the last Anglo-Saxon king Harold Godwinson) and his son Vsevolod. A later chronicle even reports the name of the architect—Peter—the earliest mention of the architect's name in Old Russia. The Cathedral was painted before its consecration in 1130, wall paintings covered all the walls of the church, neighboring southwest stairs tower and the cupola that crowns the tower.

Earliest wall paintings preserved on the walls without any serious changes about 700 years. However, the building suffered from at least two fires: in 1551 the original roof burned down, and was replaced by a tent-formed one; in 1675 the cupolas and roofs burned down again [4]. In the first half of 19th century, it was decided to replace wall decoration of interior totally. The wall paintings were knocked down and used as a base layer under the new floor. The walls were covered with oil painting, which was replaced by the painting in the Keim technique («Künstlerfarben», so called «liquid glass») in the beginning of 20th century. The original 12th century wall paintings preserved 'in situ' only in the stairs tower. The Cathedral was damaged during the Second World War; since the Nazis made an observation post in the stairs tower, old wall paintings were smoked, but unlike many Novgorod churches, survived and were restored later. A group from the Institute of Archeology of the Russian Academy of Sciences, headed by Vladimir Sedov, carried out excavations in and around the Cathedral in 2013–2017. This group discovered in the eastern part of the Cathedral below the floor level a huge number of pieces of knocked down 12th century wall paintings [5]. Some of these fragments are quite large and represent the faces of saints with a perfectly preserved high quality painting [6]. The unique complex of the ruined original murals of the Cathedral has just begun to be explored, there is a great work ahead for restorers who can gradually assemble fragments into larger elements of compositions. A similar experience in Russia has already been carried out with the 14th century wall paintings of the Savior on Kovalevo Church, where it was possible to collect from wall painting fragments not only whole saints figures, but individual evangelic scenes [7, 8], as well as the Assumption Church on Volotovo field [9].

It is extremely important to study found painting fragments using natural sciences methods. Physico-chemical research can give information about the painting technique, about the pigments composition and indirectly about the ktetors status (the usage of common or rare expensive pigments can help to make this conclusion), as well as the composition and technique of plaster making.

This work continues the investigation presented in IX Scientific Conference "Novgorod and Novgorod Land. Art and Restoration" [10]. It should be noted that 12th century wall paintings is exclusive part of Medieval Russian heritage. Many artistic traditions in 13th century were disrupted with the Mongol invasion. Besides a significant part of the pre-Mongolian monuments were destroyed during the Second World War, and only some preserved churches maintain elements of their original wall painting ensembles.

The aim of the work is to thoroughly investigate the 12th century fragments of wall painting from the St. George Cathedral of the Yuryev Monastery using complementary physico-chemical methods. The determination of the elemental, molecular and mineral composition of the mural fragments would make the conclusion about the pigments, the components of the plaster bases, as well as the presence and type of binders in the paints and plasters. The results of the investigation would help to identify the sequence of pictorial layers and the features of its technique related to various workshops; would permit to detect the changes occurred with paints within eight centuries and to reconstruct the presumable

original appearance of the painting fragment; would provide an opportunity to determine the socio-cultural features of creating the unique mural ensemble; would serve as a reliable basis for restoration and conservation work; would replenish the pigments database of Old Russian wall paintings.

Subjects of research, methods and tools

Archaeological wall painting fragments with a well-preserved pictorial layer were selected for investigation in laboratory conditions. These fragments are among those that were found during archaeological excavations in 2015 in the Cathedral main space: the central space, the altar, the altar apse, the prosthesis, and the diaconicon [5]. A total of six unicolor fragments (Fig. 2a) were selected: yellow, red, green, blue, black and orange. Also five multicolored fragments (Fig. 2b) were studied, on the surface of which two or more colors are clearly distinguishable, as well as five samples of archaeological plasters.

In situ spectra measurements (Fig. 2c) were carried out directly in the tower: on the stair walls, as well as on the cupola that crowns the tower, where 12th century murals have been preserved.

X-ray fluorescence analysis (XRF)

X-ray fluorescence analysis was performed using a portable Tracer 5*i* spectrometer (Bruker), via the built-in semi-quantitative calibration application oxide3phase. The investigation does not require any special sample preparation, except for cleaning from visible contaminations. Positioning of the spectrometer was carried out by built-in camera. A 8 mm collimator was used to measure the spectra. Artax program was applied to process the spectra.

Neutron activation analysis (NAA)

NAA is infrequently used method for the pigments elemental composition determination [11]. Samples preparation for irradiation included careful scraping of the paint layers with an alcohol-cleaned scalpel, grinding of the paint layers and plasters in an agate mortar and drying to a constant weight at 105 °C. The samples were irradiated at IBR-2 reactor in JINR [12]. NIST standard samples (1486, 1632E, 1633C, 1635A, 1944, 2586, 2709A, 278, 2782, 2710A, 50C) were irradiated together with the studied samples both for elemental mass fractions calculations by the relative approach of NAA method [13], and for quality control.

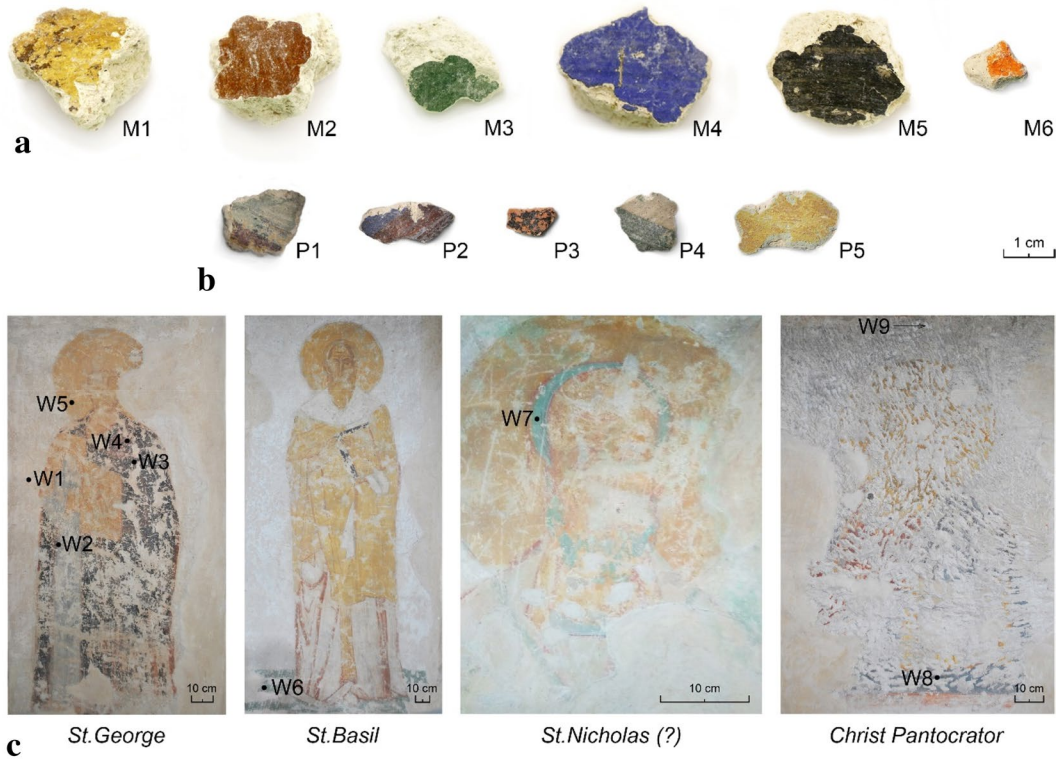

Fig. 2 Investigated samples: archaeological unicolor (**a**) and multicolored (**b**) fragments; points of in situ measurements in the Cathedral tower (**c**)

The induced activity spectra were collected using Canberra HPGe detectors GC10021 and GC4018. Various hardware (sample changer [14, 15]) and software (program for mass fractions calculation [16, 17], the NAA database [18], sample weights registration tool [19]) were used for NAA automation.

Prompt gamma activation analysis (PGAA)

PGAA was carried at IBR-2 reactor. Samples for irradiation were prepared in the same way as for NAA. The spectra were collected using radiation-resistant HPGe detector Canberra GR7023. The mass fractions were calculated by the absolute approach of PGAA method [20, 21] using special software. NIST 2430 standard sample was used for quality control.

Scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDX)

SEM-EDX analysis was carried out using Hitachi TM3030 Plus Tabletop Microscope operated in a high vacuum mode at 15 kV accelerating voltage. The same samples were used for SEM-EDX and stratigraphy analysis.

Fourier transform infrared spectroscopy (FTIR)

Unicolor samples were analyzed using Invenio-R spectrometer (Bruker) equipped with ATR (attenuated total reflectance) accessory and DTGS (deuterated triglycine sulfate) detector. The paint layer was accurately scalped for it. A total of 64 scans were taken for each sample in a 350–4000 cm^{-1} spectral range with resolution of 4 cm^{-1}.

Certain pigments in polished cross-sections were investigated using FTIR microscope Lumos (Bruker) equipped with MCT (mercury cadmium telluride) detector (co-adding 64 scans, wavenumber range 350–4000 cm^{-1}, resolution of 4 cm^{-1}). Measuring points were selected using integrated camera.

To determine organic binders in plaster samples the following probe preparing was made. In order to extract polar and non-polar components ultrapure water (Millipore Direct Q5) and chemical pure chloroform were used, respectively [22]. About 0.5 g of the fine powders of plaster samples were put in a glass vials, 2 ml of solvent were added. For the first time extraction was carried out for about 24 h with occasionally stirring. Water soluble fraction was dried at 105 °C. Dry residue was used for FTIR analysis (co-adding 64 scans, wavenumber range 350–4000 cm^{-1}, resolution of 4 cm^{-1}).

For the second time vials with samples and solvents were sonicated for 2 h at 70 °C. Then the solution was centrifuged for 2 min at 5000 rpm. Several drops of chloroform soluble fraction were placed directly on ATR crystal and air dried. A total of 128 scans were taken for each sample in a 350–4000 cm^{-1} spectral range with resolution of 2 cm^{-1}. For water extracts one drop was poured out on ATR crystal. Spectra were collected for liquid sample with the same parameters using pure water as background.

The spectra were processed using Opus software, the identification of compounds was performed with additionally purchased pigment libraries and the IRUG Internet database [23].

Raman spectroscopy

Raman spectra were collected using LabRAM HR spectrometer (Horiba) (He–Ne laser excitation wavelength 633 nm, 1800 grating, confocal hole—100 μm, and 50× magnification objective). No additional sample preparation was used; spectra were collected from the surface of pictorial layer. Compounds identification was performed with IRUG Internet database [23].

Optical microscopy and stratigraphic investigations

Reflected-light optical microscopy (OM) was applied for determination the number and order of the painting layers. Micro-probes were taken from the wall painting fragments in such a way as to capture all available layers of painting and partially the plaster. Then they were embedded in magnesian cement, air dried and polished with abrasive paper [24]. Cross-sections were studied under a microscope both in visible (Polam 215) and ultraviolet light (Olympus). The micrographs were taken using Nicon, Canon and the MC-5.3 (LOMO) cameras and processed via MCView software. For all archaeological fragments cross-sections were made for stratigraphic analysis to determine the number and order of paint layers and identify the painting technique.

Table 1 provides a summary of the methods used and the number of samples investigated by these methods.

Results

Investigation of the plaster

Elemental composition was determined for the following number of archaeological plaster samples: for two samples by NAA, for three samples by PGAA and for five samples by XRF. Table 2 presents weighted average values [25] of the elemental mass fractions for investigated samples. The data of three methods used are in good agreement with each other, the discrepancies do not exceed 1–3 σ.

The composition of the plaster was confirmed by IR spectroscopy. In addition to main calcite peaks (1793, 1397, 871, 712 cm^{-1}), a strong broad absorption band of a complex shape at 1200–900 cm^{-1} is present on the spectra. This is stretching vibrations of E–O–E bonds (E = Al, Si), characteristic of clay minerals or sand.

Table 1 Summary table of the methods used and the samples studied

Samples	Methods						
	NAA	PGAA	XRF	SEM EDX	Stratigraphy and optical microscopy	FTIR	Raman spectroscopy
Archaeological unicolor pigments from the main space	1	1	6	1	7	7	6
Archaeological multicolored pigments from the main space				2	5	1	
Archaeological plasters from the main space	2	3	5			2	
Pigments from the tower			8				
Plasters from the tower			1				

Besides, a broad band around 3390 cm^{-1} is responsible for the bending vibrations of OH groups in clay minerals.

No CH_3–, CH_2 = stretching vibrations were detected in 3000−2800 cm^{-1} region in chloroform extract. Thus, no organic binders soluble in $CHCl_3$ (fats, oils, waxes, resins) were found in the studied plaster sample. First experiment with water extract reveals no peaks in 3000−2800 cm^{-1} region. But more intensive extraction conditions provide another result: week peaks in 3000−2800 cm^{-1} region were found, which could mean the presence of trace amounts of water soluble compounds like decoctions of cereals and herbs, proteins, or polysaccharides. Besides, low concentration of organic compounds and strong peaks of water prevent reliable identification of compound type.

Investigation of unicolor archaeological samples

Elemental and mineral analysis of unicolor archaeological samples

Based on the elemental composition data by XRF, mineral composition of used paints was suggested (Table 3). Paints and plaster mineral composition were confirmed by vibrational spectroscopic data (Fig. 3).

Yellow and red pigments are characterized by increased iron content, which means the usage of yellow and red ochers. Goethite (α-FeOOH) is the base of yellow ocher, while hematite (Fe_2O_3) contributed to red ocher. Both ocher pigments have infrared spectral similarities and differences. Main vibration frequencies of calcite are presented at 1795, 1412, 873, 712 cm^{-1} in both spectra (Fig. 3a and b). Also broad bands of complex shape were detected at 1150–900 cm^{-1} region for both ochers. These peaks are stretching vibrations of the E–O–E bonds (E = Si, Al) of tetrahedral [SiO_4] and octahedral [$Al(OH)_6$] fragments in quartz and aluminosilicates. By the degree of peaks resolution and the intensity ratio, one can speak of the main structural features of clay minerals. Thus, the presence of resolved peaks at 1027 and 1007 cm^{-1} in yellow ocher spectrum indicates the existence of the most ordered clay mineral kaolinite [26]. On the contrary, broadening of absorption bands in the red ocher spectrum is a result of the isomorphic substitution of Si by Al in tetrahedral positions with formation of disordered structure, which is common with such minerals as montmorillonite or muscovite. Moreover, well resolved inner and outer stretching vibrations of hydroxyl groups in the 3700–3600 cm^{-1}region in the yellow ocher spectrum confirm the presence of kaolinite. The minerals goethite and hematite have characteristic stretching vibrations Fe-O…Fe bands in the far spectral region: 466 cm^{-1} for α-FeOOH and 445 cm^{-1} for Fe_2O_3.

Raman spectroscopy data confirm the usage of yellow and red ochers (Table 3). The spectra of both samples contain main calcite peaks in addition to goethite (294, 388, 561 cm^{-1}) and hematite (226, 293, 408, 513, 610, 652, 1309 cm^{-1}), respectively. An important result is in contribution of 146 and 281 cm^{-1} bands to yellow lead oxide—massicot in yellow sample spectrum.

Green pigment is also characterizing by a significant iron amount. Together with an increased silicon and potassium content, this may indicate the presence of a hydromica group mineral: glauconite or celadonite ("green earth"). It should be noted, Fe/Mg ratio for investigated green pigment is 3.6. Accordingly [27], that is much closer to celadonite (3.2) than to glauconite (8.6). A detailed examination of the green pigment IR spectrum (Fig. 3c) confirms the presence of celadonite [28]. Well resolved absorption band at 967 cm^{-1} represents a very low degree of isomorphic substitution of Si by Al in the Si-O layer, which is characteristic of more ordered celadonite structure. Resolution of M-OH bending vibrations (M = Mg, Fe, Al) at 550–400 cm^{-1} indicates that a divalent and trivalent cations occupied different crystallographic positions in the octahedral layer. Moreover, OH-stretching vibrations at 3554 and 3526 cm^{-1}

Table 2 Plasters elemental composition according to PGAA, XRF, and NAA, mg/kg

	PGAA	XRF	NAA
H	5430 ± 380		
C	137000 ± 25000		
Mg	26400 ± 4300	24000 ± 6200	
Al	12700 ± 2000	15400 ± 900	
Si	19000 ± 2000	24100 ± 1500	
S	599 ± 272	758 ± 165	
Cl	129 ± 11		
K	1870 ± 530	2460 ± 140	1450 ± 100
Ca	310000 ± 20000	364000 ± 2000	282000 ± 37000
Sc			1.31 ± 0.12
Ti	454 ± 23	246 ± 57	
Mn		341 ± 29	
Fe	7740 ± 1020	7500 ± 400	5840 ± 360
Co			1.96 ± 0.23
Ni			5.12 ± 0.38
Cu		10.6 ± 2.4	
Zn		11.7 ± 3.3	10.8 ± 0.9
As			0.724 ± 0.040
Br			1.31 ± 0.39
Rb			4.17 ± 1.08
Zr			19.8 ± 6.8
Mo			0.259 ± 0.042
Sb			0.101 ± 0.044
Cs			0.0461 ± 0.0128
Ba			94.8 ± 20.2
La			8.49 ± 0.47
Ce			17.1 ± 1.1
Nd			3.54 ± 0.74
Sm	1.76 ± 0.19		1.34 ± 0.15
Eu			0.297 ± 0.027
Gd	1.28 ± 0.17		
Tb			0.160 ± 0.017
Yb			0.313 ± 0.032
Lu			0.062 ± 0.006
Hf			0.615 ± 0.145
Ta			0.121 ± 0.016
W			0.145 ± 0.034
Au			0.00331 ± 0.00079
Th			1.09 ± 0.10
U			0.467 ± 0.040

are narrow and well-resolved, instead of broad diffuse peak specific for glauconite. The absence of the Fe^{3+}-OH bending vibrations at 815–810 cm^{-1} typical for glauconite confirm the presence of celadonite again. IR spectrum of green sample also contains calcite peaks (1795, 1412, 872, 712 cm^{-1}).

A significant sulfur content and copper absence in blue pigment is observed. This indicates that complex framework aluminosilicate of sodalite group named lazurite ($(Na,Ca)_8[AlSiO_4]_6S_2$) was used. Deep blue to violet color of lazurite is associated with polysulfide ions. It should be noted that a weak band at 581 cm^{-1} can be assigned to antisymmetric stretching vibrations of polysulfide ion (Fig. 3d) [29, 30]. Broad bands at 1100–900 and 670–625 cm^{-1} was assigned to stretching and bending vibrations of the aluminosilicate framework, respectively, which is typical for sodalite group minerals. Besides, absorption peaks at 3698 and 3621 cm^{-1} are similar to the bands in the yellow pigment spectrum, which were previously attributed to hydroxyl groups vibrations in kaolinite. Also FTIR analysis gave information about the presence of calcite (1795, 1413, 873, 712 cm^{-1}) in blue pigment. The Raman spectrum of blue pigment turned out to be of low quality, but still contains lines at 547, 1091 cm^{-1}, which are characteristic of lazurite. Summarizing all data, we conclude that blue color of the Yuryev Monastery wall paintings was created on the basis of lazurite.

Elemental composition of orange fragment obtained by XRF suggests using red lead. IR spectrum of Pb_3O_4 contains only 2 weak vibrations at 1398 and 679 cm^{-1}, which are impossible to detect against high lime content. As a result, in the orange pigment IR spectrum only calcite reliably identified (1795, 1403, 872, 712 cm^{-1}). Broad peaks at 3500–3300 and 1200–900 cm^{-1} indicate the presence of clay minerals and sand. On the contrary, orange fragment Raman spectrum turned out to be very insightful and red lead was determined by a large number of intense peaks: 86, 122, 152, 222, 312, 391, and 549 cm^{-1}.

XRF of black wall painting fragment reveals no characteristic elements against the plaster content. The black pigment elemental composition was additionally investigated by neutron methods: NAA and PGAA (Table 4). It is important that the mass of black pigment was too small to calculate the mass fractions of a sufficient number of elements using PGAA method. But the main result is in detection of a significant amount of carbon, which indicates the usage of carbon black or "reft' " pigment. According to researchers of Old Russian painting, "reft' " – the most common pigment in Russian wall painting which is spruce charcoal mixed with lime [31, 32]. The Raman spectroscopy confirms this suggestion. Thus, in addition to calcite peaks (163, 1086 cm^{-1}), there are vibrations at 1335, 1620 cm^{-1}, which are characteristic of carbon black [33].

Table 3 Results of the archaeological pigments and plaster physico-chemical analysis

Sample	Description	XRF analysis		FTIR spectroscopy		Raman spectroscopy		Optical microscopy
		Elements found	Pigment suggestion	Infrared bands (cm^{-1})	Mineral	Raman bands (cm^{-1})	Mineral	Thickness, µm
	Plaster	Ca, Si, Al, Mg, Fe, *P, K, Cl, S, Mn, Ti*	Lime, sand	1793, 1397, 871, 712; 3390[b], 1077[c], 1016[b], 613[b]; 1156[c]	Calcite; Clay minerals; Quartz			–
M1	Yellow	Ca, Si, Al, Fe, Pb, *S, K, Ti, P, Cr, Mn*[a]	Yellow ochre, lime, white lead or massicot	1795, 1410, 873, 712; 3695, 3619, 1105[c], 1027, 1007, 913, 534; 695, 433; 3300[b], 796, 749, 466	Calcite; Kaolinite; Quartz; **Goethite** [d]	148, 281, 1087; 294, 388, 561; 146, 281	Calcite; **Goethite; Massicot**	25
M2	Red	Si, Ca, Fe, Al, Mg, K, *P, S, Ti, Pb, Mn, Sr, Cl, Ba, As*	Red ochre, lime	1795, 1413, 873, 712; 1032[b]; 1162, 796, 777, 694, 519; 445	Calcite; Clay minerals; Quartz; **Hematite**	154, 293, 1086; 226, 293, 408, 513, 610, 652, 1309	Calcite; **Hematite**	50
M3	Green	Si, Ca, Fe, Al, K, Mg, *Pb, P, S, Ti, Mn, Sr, As*	Green earth, lime	1795, 1412, 872, 712; 3350[b], 1102[c], 1010[c]; 3554, 3526, 967, 797, 679, 487, 449, 438	Calcite; Clay minerals; **Celadonite**			30–40
M4	Blue	Si, Ca, Al, Mg, K, S, Fe, *P, Ti, Cl, Sr, Ba*	Lazurite, lime	1795, 1413, 873, 712; 3696[b], 3620, 1088[c]; 797, 779, 695, 519[c]; 1001, 654, 577, 534, 441	Calcite; Clay minerals; Quartz; **Lazurite**	1091; 547, 1091	Calcite; **Lazurite**	2 layers total 40 µm
M5	Black	Ca, Si, Al, Mg, Fe, *K, P, Ti, Mn, S, Pb, Sr*	"Reft'" (carbon black), lime	1795, 1409, 872, 711; 3695, 3620, 1095[c], 1029, 1007, 911, 536; 789, 751, 466	Calcite; Kaolinite; Goethite	163, 1086; 1335, 1620	Calcite; **"Reft'" (carbon black)**	20–50
M6	Orange	Ca, Pb, S, Si, Al, As, Fe, *P, K, Cl, Ti, Mn*	Red lead, lime, clay minerals	1795, 1403, 872, 712; 3410[b], 1079[c], 1030, 781, 527; 1160	Calcite; Clay minerals; Sand	86, 122, 152, 222, 312, 391, 549	**Red lead**	40–60

[a] Elements with content less than 1 mass% are marked italic; [b]appears as a wide peak; [c]appears as a shoulder; [d]colored components mark bold

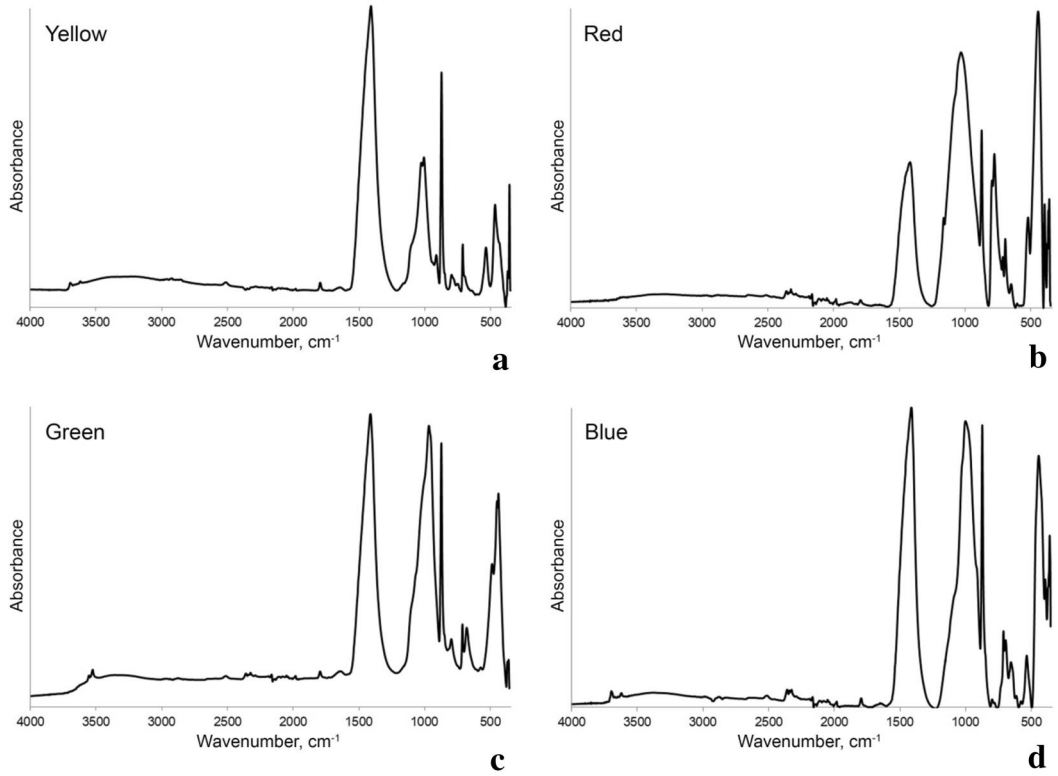

Fig. 3 ATR-FTIR spectra for unicolor archaeological samples with yellow (**a**), red (**b**), green (**c**), and blue (**d**) surface

Stratigraphic analysis of unicolor archaeological samples

Figure 4 shows cross-sections micrographs for unicolor fragments taken at a 200× magnification. All fragments, except of blue one, are two-layer and contain a top paint layer and a plaster one. Boundaries between the layers are well-defined. Three layers are clearly visible on the micrograph of blue-colored cross-section. The top blue layer is lazurite, middle gray-black one is presumably "reft' " (carbon black), and the third white layer is lime plaster.

The paint layers average thickness is determined from the obtained micrographs (Table 3) and ranges from 20 to 50 μm for different colors. Under lazurite layer with a thickness of no more than 10 μm, black 30 μm thick layer was applied.

For blue-colored fragment (Fig. 5a) an additional M4a cross-section was made to study the elemental composition using SEM-EDX with following mapping. The selected area for mapping is marked in micrograph Fig. 5b. Some element distribution maps are shown in Fig. 5d. Obtained data make it possible to conclude that blue pigment is lazurite, since such elements as sodium, silicon, aluminum and sulfur are mainly concentrated in the surface layer. In addition, silicon and aluminum are also presented in a gray-black layer, therefore, clay and/or sand are included in the "reft' " (carbon black). The distribution of calcium is uniform, so both pigments were mixed on the lime basis. FTIR data confirm this assumption (Fig. 5c). The spectrum of the blue area can be resolved into two main components: calcite and lazurite.

Multicolored archaeological samples investigation

Multicolored sample P1 exhibit two main colors: green and deep red, with traces of black on the green part (Fig. 6a and b). Yellow layer can also be observed under the top paint layer. Two cross-sections P1a and P1b were made from different areas of P1 fragment, which are similar in layer ordering. The bottom layer is a white plaster without inclusions. Following yellow layer is rather thick. Next white layer appears again. The final fourth layer (green for P1a, and red-brown for P1b) is very thin for both cross-sections (Fig. 6a and b).

On the surface of P2 two colors can be observed: blue and deep red (Fig. 6c). Moreover, deep red layer is applied over the blue one. Cross-section was made in such a way as to pick up both color layers. OM showed the presence of four layers: lower white plaster layer, second layer of black color, presumably "reft' " (carbon black), third layer containing bright blue lazurite crystals, and upper red layer, most likely hematite.

Table 4 Black pigment elemental composition according to PGAA, XRF, and NAA, mg/kg

	PGAA	XRF	NAA
H	10660 ± 300		
C	637000 ± 469000		
Na			1420 ± 50
Al		66300 ± 2800	
Si	71600 ± 10300	102000 ± 2000	
P		2760 ± 380	
S		2570 ± 260	
Cl	584 ± 58		
K		7520 ± 190	4870 ± 410
Ca	370000 ± 39000	266000 ± 1000	304000 ± 55000
Sc			4.10 ± 0.12
Ti	2975 ± 417	4470 ± 290	
Cr			49.7 ± 2.3
Mn		989 ± 75	
Fe		7410 ± 170	7210 ± 440
Co			2.86 ± 0.25
Ni			6.77 ± 1.02
Cu		55.0 ± 9.0	
Zn		97.0 ± 13.0	63.8 ± 3.5
As			3.78 ± 0.17
Br			3.36 ± 0.30
Rb			12.5 ± 2.1
Sr			645 ± 43
Zr			72.3 ± 8.0
Mo			6.17 ± 1.11
Ag	1130 ± 100		
Sn			162 ± 50
Sb			1.07 ± 0.096
Cs			0.143 ± 0.007
Ba			262 ± 14
La			14.5 ± 0.7
Ce			22.2 ± 3.3
Nd			18.5 ± 2.8
Sm	7.81 ± 1.68		6.26 ± 0.75
Eu			1.46 ± 0.09
Gd	1.28 ± 0.17		
Tb			0.581 ± 0.027
Yb			1.49 ± 0.26
Lu			0.266 ± 0.029
Hf			2.35 ± 0.19
Ta			0.494 ± 0.016
W			0.444 ± 0.129
Hg			42.0 ± 1.9
Pb		823 ± 48	
Th			4.31 ± 0.16
U			1.50 ± 0.10

Sample P3 has a bright orange color layer on top of which a fragmentary black paint is occur (Fig. 7a). Cross-section containing both orange and black colors was prepared. Unfortunately, it turned out impossible to pick up all the layers, thus there is no plaster on the micrographs. However, orange and black layers are well-defined (Fig. 7c). Investigation under ultraviolet (UV) light showed slight luminescence from orange layer (Fig. 7d).

P3 sample was subjected to SEM-EDX (Fig. 7e). Orange layer contains lead and represents red lead. Lime plaster remains can also be seen on the calcium map. The black layer did not show any characteristic elements. So black pigment is based on coal, but it was not possible to distinguish a clear layer on the carbon map because carbon is also part of the lime binder. Orange pigment IR spectrum contains only two lines at 1398 and 679 cm^{-1}, which are characteristic of red lead (Fig. 7b).

Sample P4 has a clear boundary between two colors (Fig. 8a). The beige paint is most probably applied over the green one. A probe was taken from the beige side. There are three well-defined layers on the cross-section micrograph under visible light (Fig. 8b). The first white layer is a plaster. Next two paint layers are followed, saturated green, and pale yellow. Note that ultraviolet analysis did not reveal any significant results for this sample (Fig. 8c), as for all multicolored samples except P3.

Elements distribution maps showed that iron, potassium, silicon and aluminum are mainly concentrated in the green layer, thus the green pigment is celadonite (Fig. 8d). The low calcium content in this layer indicates that the paint was not diluted with lime. Elemental composition of beige layer is indistinguishable from the plaster. Probably small amount of pigment mixed with lime was required to achieve the desired shade of paint.

Sample P5 has a yellow paint layer, however, green color can be seen at the edges and chips (Fig. 6d). P5 cross-section micrograph shows three layers: white plaster, pale green, and yellow.

XRF pigments investigation in the tower

The main colors in the stairs tower were studied in situ by XRF. Measurement points are shown in Fig. 2c. Obtained data are presented in Table 5. For plaster sample found elements are listed. For the pigment quantity of found elements are compared with the corresponding values in plaster. On the basis of this data the most probable pigments were suggested. Yellow and red pigments are represented by ochers. Green color occurs due to green earth. Reds and browns contain large amounts of lead, most likely as white lead. However, it was not possible to identify the blue pigment. One of the reasons may be

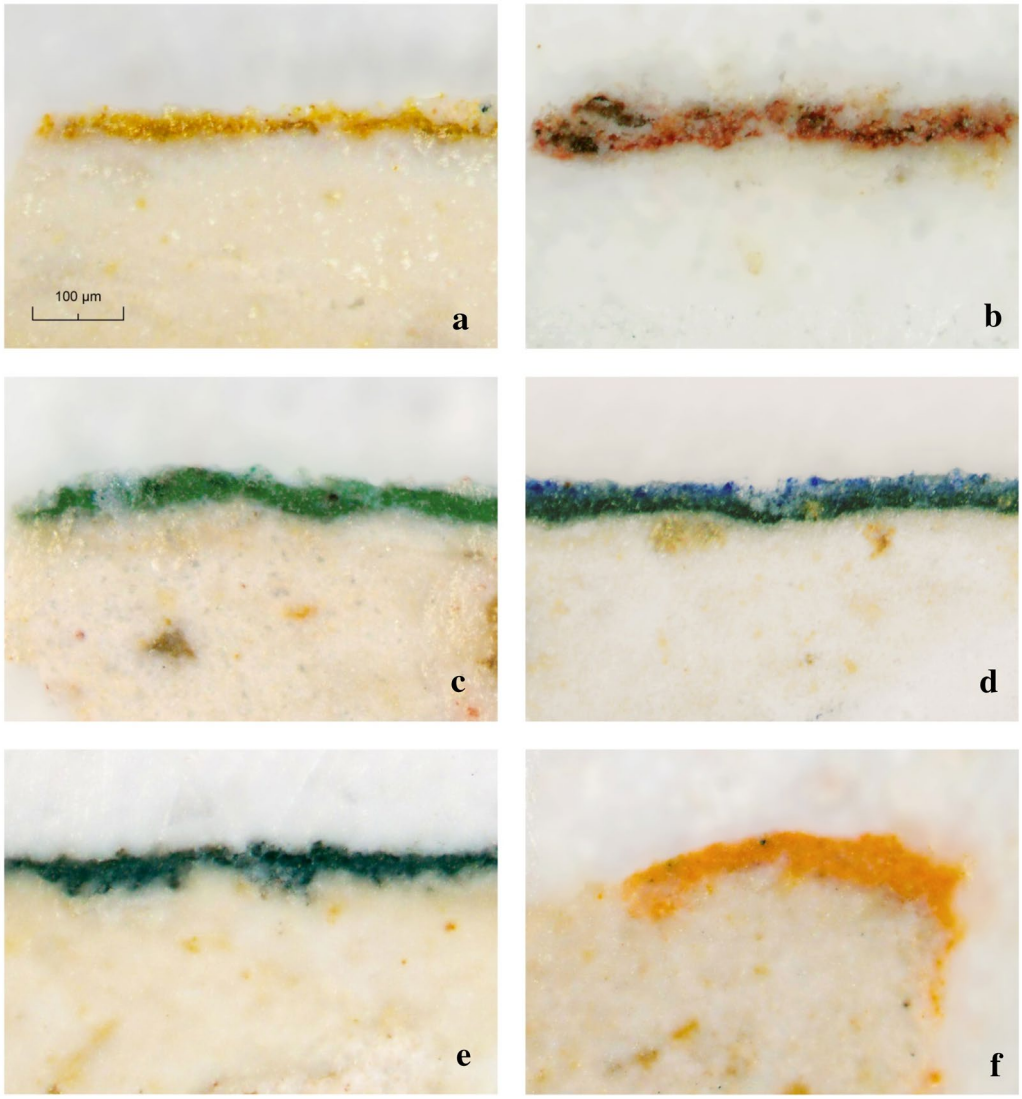

Fig. 4 Views of unicolor fragments and cross-sections micrographs: **a** M1, **b** M2, **c** M3, **d** M4, **e** M5, **f** M6

the presence of gypsum on the top of murals since a large sulfur quantity was determined in all spectra.

Discussion

Materials of archaeological fragments

Plasters

The data of three methods of elemental analysis showed good results convergence (Table 5). Also, it should be noted that these methods complement each other, expanding the range of determined elements. Thus, 40 elements mass fractions were determined in total.

According to elemental analysis, calcium, which forms the basis of lime, predominates in the plaster. Magnesium is often found as an impurity in calciferous rocks. Silicon and aluminum, which are the basis of clay minerals and sand, are present in the plaster in relatively small quantities. Iron, manganese, and titanium are also determined among the micro-impurities. So, the plaster consists almost entirely of lime. The plaster composition of all fragments is almost identical, that may indicate wall paintings creation simultaneity in the Cathedral main space, and, therefore, involving of a fairly large workshop. It should be noted that the researchers of fragments of paintings of the late 12th–13th centuries in the pre-Mongolian church of Smolensk assert that the plaster base of studied fragments consists of $CaCO_3$ in the form of calcite and aragonite [34].

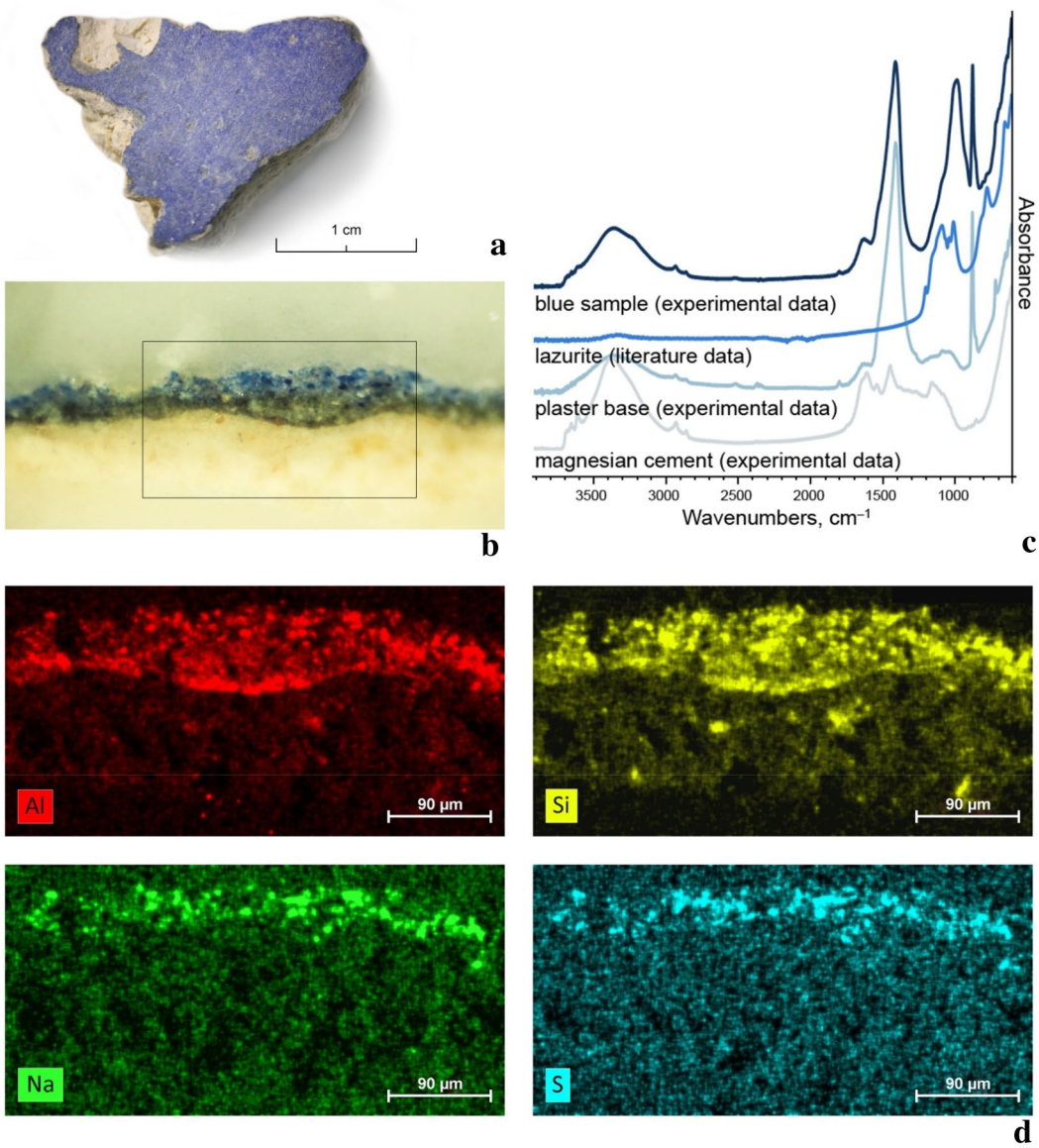

Fig. 5 View of blue M4a sample (**a**), cross-section (**b**), micro-FTIR spectra (**c**) and distribution maps of Al, Si, Na, and S (**d**)

The detected traces of organic binders supplement our understanding of the pre-Mongolian plasters composition. This is interesting within the controversy about the necessity of organic binders use. Previous investigations report the use of various organic materials for plasters. Pliny the Elder mentioned the milk [35] in a story about Ancient Greek painters. Plant binders was used in Indian medieval cave painting. The late data from Old Russian sources (the «Nectarios Typicon» of the 16th century) indicate the need of vegetable binders for plasters manufacturing (gluten glue from barley and oat flour). However, the limited restorer studies data do not reveal organic binders [36]. We were able to establish only the fact of water-soluble organic binders presence. Determination of the organic binders type requires further investigation.

Pigments

For all studied unicolor archaeological fragments, the elemental and mineral composition was determined by XRF and vibrational spectroscopy respectively. Additionally, the paint layers thickness was measured using polished cross-sections technique (Table 2).

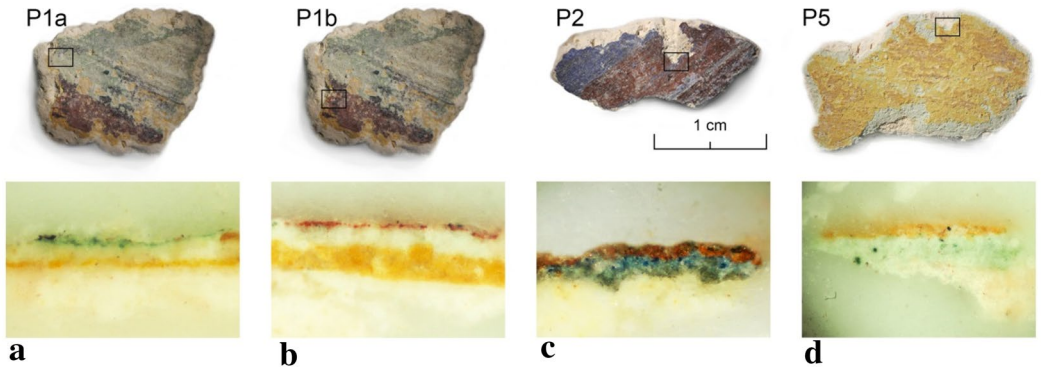

Fig. 6 View and cross-sections for multicolored samples P1a (**a**), P1b (**b**), P2 (**c**), and P5 (**d**)

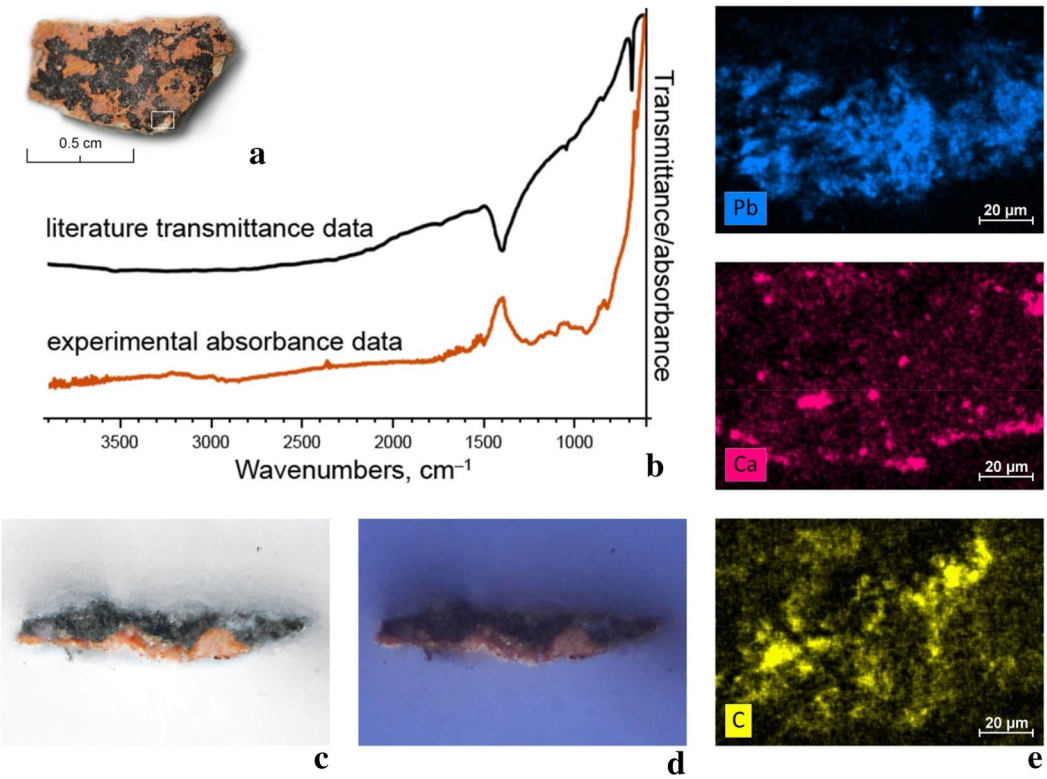

Fig. 7 View of multicolored P3 sample (**a**), FTIR spectra from orange layer (**b**), cross-section view under visible (**c**) and UV (**d**) light, and distribution maps of Pb, Ca, and C (**e**)

Yellow and red pigments are represented by ochres. These pigments are most common for medieval painting of Byzantine circle monuments, that can be found within Byzantium, Southern Slavs lands, and Southern Italy [37]. The researchers note that the stability of such materials as goethite and hematite makes them the most suitable for the wall painting techniques [2].

Minerals from hydromica group, glauconite and celadonite, have green color, same elemental composition and structure; particular mineral identification is fraught with difficulties. Thus, in work [37] only one green pigment glauconite is mentioned in 12th century Novgorod wall paintings. Therefore, our detailed examination of the IR spectra allowed us to identify celadonite in the

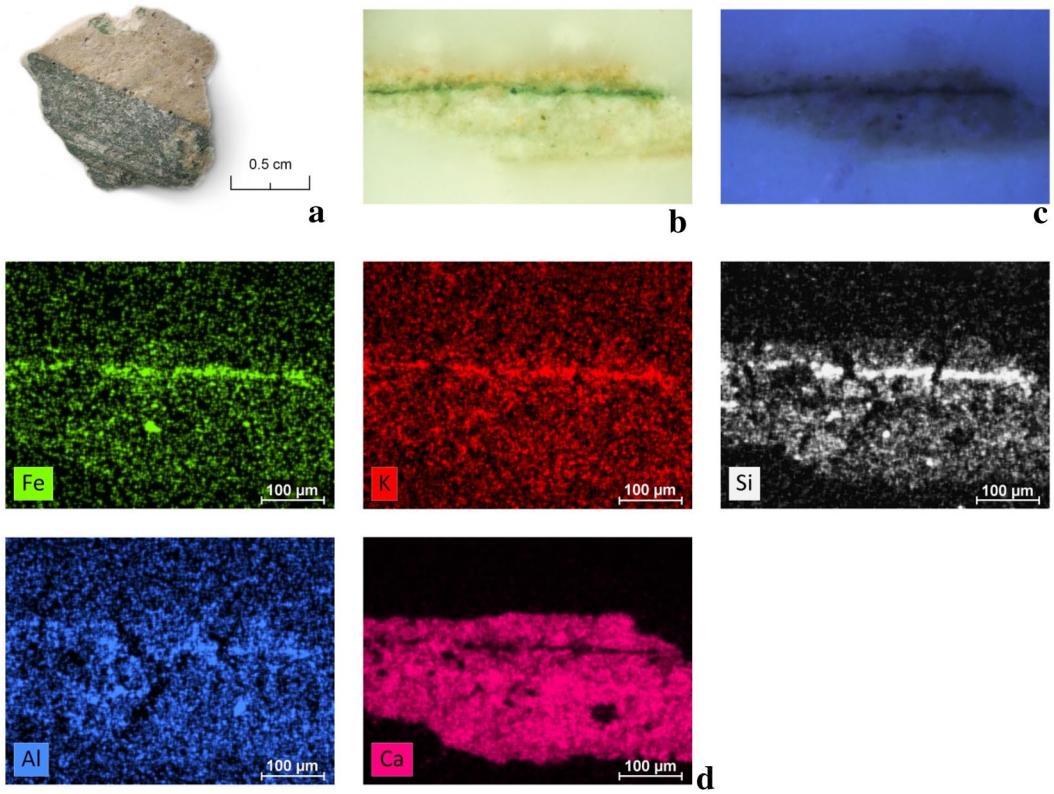

Fig. 8 View of multicolored P4 sample (**a**), cross-section under visible (**b**) and UV (**c**) light, distribution maps of Fe, K, Si, Al and Ca (**d**)

paintings of the St. George Cathedral. The researchers of the late 12th–13th centuries wall paintings from the ruins of the previously unknown Old Russian church in the city of Smolensk also discovered celadonite [34].

While examining blue fragment, the two-layer paint structure was found. The stratigraphy shows that there is black color layer under blue lazurite. A similar two-layer structure ("reft' " (carbon black) as the lower layer and lapis lazuli on top of it) was found in the famous painting of the beginning of the 13th century in the Princely Church of Mileševa (Serbia) [38]. In Old Russian paintings, we can also find a lower layer hidden under the blue color of the painting, consisting, however, of anatase, on top of which an nonuniformly lying lazurite is applied (a fragment of paintings from the late 12th–13th centuries from a destroyed church in Smolensk) [34].

It was a traditional method in 12th century to save imported lazurite and make blue color brighter and more stable. Lazurite was a very expensive material for Ancient World and Middle Ages, since only one deposit in Badakhshan was known. Ancient authors called it sapphire and noticed its purple hue, while pyrite inclusions were perceived as gold dust [35]. Thus, lazurite was not usually used in medieval wall painting, both due to its high cost and the difficulty of separating it from impurities. The need to use blue color in the backgrounds of Byzantine circle wall paintings was incompatible with the cost of such mineral amount. Italian authors give examples of rare use of lazurite in passing rich Byzantine monasteries [2]. In Old Russian painting, blue color effect was more often obtained due to the usage of spruce charcoal mixed with lime white ("reft' ") [37]. However, lazurite was found in some early Novgorod 11th–12th centuries monuments like St. Sophia and Nikolo-Dvorishchensky Cathedrals [37], and also in the paintings of the end of the 12th–13th centuries from the ruined church in Smolensk [34]. Therefore, our study confirms that St. George Cathedral becomes the third Novgorod monument where expensive imported lazurite was discovered [39]. Of course, only reach and respectable ktetors could afford to use such material.

Note that the investigated sample of blue color represents one of the numerous identical fragments of old painting, knocked down in the first half of the 19th century and buried under the newly made floor. By the shade of blue, these fragments are visually identical. There are quite large fragments among the pieces of plaster with a blue color layer, which suggests that these pieces were

Table 5 Pigments analysis results in the stairs tower by XRF

Sample	Description	Elements found	Pigment
W1	Plaster	Ca, S, Si, Al, Fe, K, Ti, Mn, Zn	Lime, gypsum, sand
W2	Light blue	> Ti, Si, Fe ≈ Al, K, Mn, Zn < Ca, S	Lime, gypsum, sand
W3	Dark brown	> Si, P, Pb, Fe ≈ Al, K, Ti, Mn, Zn < Ca, S	Red ochre, white lead, lime
W4	Deep red	>> Si, Fe > K, P, Ti, Pb ≈ Al, Mn, Zn << Ca, S	Red ochre, white lead, lime
W5	Yellow	> Fe ≈ Ca, Al, K, Si, Ti, Zn < S, Mn	Yellow ochre, lime
W6	Green	> Fe, K ≈ Si, Ti < Al, Mn, Zn << S, Ca	Glauconite or celadonite, lime
W7	Dove color	>> Fe, K > Si, P ≈ Al, Ca, Ti, Mn, Zn < S	Glauconite or celadonite, lime
W8	Blue	>> Ti, Si, Al, K, Fe > Zn ≈ Ca, Mn << S	
W9	Blue	>> Cu, Pb, As ≈ Al, K, Ca, Ti < Si, S, Mn, Fe, Zn	Azurite (?)

In this table, the following conventions are used for the mass fraction of an element from the pigment composition compared with the mass fraction of the same element from the plaster base composition:

- Element from the pigment composition of the marked with ">" has mass fraction value greater than the same element from the plaster base composition;
- Element marked with ">>" has mass fraction value that is more than an order of magnitude greater than the same element mass fraction in the plaster base;
- Element marked with "<" has mass fraction value less than in the plaster base;
- Element marked with "<<" has mass fraction value that is more than an order of magnitude smaller than in the plaster base;
- Element marked with "≈" has mass fraction value that is similar to the same element value in the plaster base;

most likely part of the background. Based on these data, it can be assumed that rare and expensive mineral lazurite may have been used for the bright blue background in St. George Cathedral painting. This assumption needs further verification, but it is consistent with historical information about the high status of the painting ktetors, Russian princes.

Painting technique

A detailed investigation of cross-sections micrographs allows us to draw conclusions about the painting technique. So in some photos of unicolor samples (for example, red Fig. 4b, green Fig. 4c) one can see a thin carbonation layer, indicating al fresco technique. Another characteristic of al fresco technique is diffusion between the paint layer and the plaster.

In this case penetration of color particles into the plaster should be observed. The diffusion is visible most clearly on the blue colored sample. Here, apparently, the initial "reft' " (carbon black) layer was applied in the al fresco technique (Fig. 5b). The results of using the al fresco technique (diffusion and carbonation layer) are demonstrated by stratigraphic studies of Casa di Marco Lucrezio fresco painting in Pompeii [40] and in wall paintings of the old katholikon of St. Stephen's monastery at the Meteora [41].

Besides, observed differences in thickness of various paint layers may indicate the use of mixed techniques in the painting of St. George Cathedral. It should be noted that for same period Italian murals the thickness of the paint layers ranges from 20 to 50 μm [2]. Thin color layer for yellow sample (25 μm) indicates low pigment diffusion (cross-reference it with the sample of red color, which is much thicker—60 μm). Therefore, painting was done over already dried plaster. Usually such thin paint layers were applied as secondary ones over the main

paint layer. Researchers find a similar multi-layered technique in other monuments of Novgorod painting of the 12th century. Thus, the authors of the work [37] provide data on fragments of paintings from the excavations in the altar part of the Nikolo-Dvorishchensky Cathedral, paintings in the drum of St. Sophia Cathedral and in the composition "St. Constantine and Helena" from the same church. They conclude that painting on wet plaster had limited use. Of course, the marking of compositions was carried out on fresh plaster when the first light yellow or pale brown layer was applied; perhaps the first preparatory drawing was carried out at that time. Nevertheless, most of the painting was completed on already dried plaster. Multilayered mixed painting technique is found in the 12th century not only in Novgorod churches—for example mixed painting techniques we can see in the study of the 12th century Church of Santa Maria di Cerrate (Italy) [2], 13th century Minorite Church of St. Francis of Assisi (Koper, Slovenia) [42].

Multicolored samples

Multicolored samples stratigraphy revealed the presence of several paint layers. Most likely, upper layer represents ornament fragments, borders or any other decorative elements applied over the main background color.

From this point of view, P1 sample stands out noticeably (Fig. 5): its stratigraphy shows two plaster layers. We can presume several ways to explain it. Firstly, middle yellow layer could be a preliminary drawing. After that a thin plaster layer was applied, and the finishing color was painted over it. Secondly, the upper green or red color could be a repainting to correct mistakes of less experienced workshop members. Such layering could arise due to using of preparatory drawing [37] or in the process of details clarifying (ornaments, folds of clothing). However, in order to discourse more with reason of a particular cross-section, it is necessary to have a holistic view of the depicted on wall painting scene, which is impossible at the moment.

Comparison of wall paintings from the stairs tower, and the main space

Comparing the elemental composition of pigments from the stairs tower and the Cathedral main space, it is possible to find out both similarities and differences. The main similarity: ochres and colored earths as the cheapest and most common pigments were used for yellow, red and green colors. The main difference for yellow color is in the presence of significant amount of lead in the archeological fragment. No lead was found in the tower on St. George yellow nimbus. On the contrary, significant lead content was determined in red pigment on the St. George's vestments, while the red-colored fragment from the main space does not contain lead. It should be noted that the high content of gypsum, most likely of restoration origin, prevents reliable determination of lazurite in tower wall paintings. However, copper was found in one spectrum in the tower. Perhaps azurite was used there as a blue pigment. According to the restorer Tatiana Romashkevich, it could have been lost during the use of certain solvents by restorers [43]. So, we can suggest different periods and, perhaps, different ktetors of Cathedral and stairs tower decoration.

This assumption correlates with the conclusions of the stylistic and iconographic analysis of the tower wall paintings. From the point of view of the program, the painting provides a special independent and complete idea, artistically also having significant differences from the decoration of the main space of the Cathedral [43, 44]. The staircase painting includes quite rare symbolic plots on the theme of spiritual ascent through repentance (acts of Samson, allegories of sins and virtues in the form of animals and birds). A staircase leads to the cupola chapel located at the top of the tower, apparently intended for solitary monastic prayer and restricted worships. The severe style of painting corresponds to the chapel functions—all images are made against the background of the white tone of levkas (thin top layer of plaster), based on limited color, flatness and a system of linear highlights. Our research confirms that a different technique and pigments were used for these murals compared to the main space of the Cathedral.

Moreover, it was possible to clarify the features of the dyes mixing technology for special color hues of some wall paintings. For example, it was shown how the pre-Mongolian masters achieved an exquisitely dove color (the St. Nicholas' hair hue in the tower cupola). For this purpose, the painters mixed green earth with lime white and added charcoal.

The absence of gypsum in the tower knocked-down wall painting (Fig. 2c, Christ Pantocrator) confirms the assumption of later gypsum plaster application. However, researchers who analyzed similar wall paintings in Southern Italy churches (painted by Byzantine masters) reach a conclusion that gypsum could be used in 12th century by Byzantine painters. For example, gypsum was found in the wall paintings of Santi Stefani crypt (10th–14th centuries), where its layer does not exceed 60 μm depth. Authors suggest the process of sulfation [3].

Also we determined elemental composition in some points on the stairs ornaments. But unfortunately the minimum thickness of the paint layer on the stairs of tower did not allow us to determine the pigments elemental composition: the signal from the color fragments does not differ from the pure plaster one. Probably, the minimum thickness of the paint layer was the result

Fig. 9 St. George wall painting digital reconstruction. View at the present time (**a**) and the possible original coloration (**b**)

of washing-off. Another point of view is expressed by Vladimir Sedov. He suggests that the tower painting was created starting from the cupola space, the walls of the spiral staircase were not decorated completely [45].

Digital reconstruction

On the basis of elemental and mineral compositions it became possible to reconstruct the one wall painting color palette at the moment of its original creation. Note that the authors have no knowledge of the methodological descriptions of such reconstructions. The study results showed that St. George figure was initially depicted in bright red vestments modeled with white highlights and most probably adorned with ornament. In such a way this saint figure is depicted on the wall painting of 12th century St. George Church in Staraya Ladoga. The white lead turned black over the time as a result of a chemical [46] or biochemical [47] decomposition that completely changed the wall painting color expression. Figure 9 shows St. George view at the present time (a) and the possible original coloration (b). Cases of such transformation could observed in the monasteries of Georgia [48] and Strechau castle, Styria, Austria [49].

Conclusions

The comprehensive study of the 12th century unique wall paintings was carried out. The elemental, mineral, and molecuar composition of plasters and paints was determined. It allowed to draw conclusions about the main pigments used for the St. George Cathedral painting. The obtained data became the first step for creating a pigments database of Old Russian monuments.

Some pigments used in the wall paintings are rare for Old Russia, and this peculiarity indirectly points the social status of the ktetor. The presence of expensive imported lazurite indicates the rich interior decorations, and most probably, denotes the work of a highly professional workshop.

Comparison of the pigments composition from the Cathedral main space and its stairs tower allows us to make reasonable assumptions about the different

periods of wall paintings decoration and/or the participation of different workshops.

Number, thickness, and order of the paint layers as well as the processes of carbonation and diffusion were revealed as the stratigraphic analysis results. It is shown that the most multicolored wall painting fragments consist of two or more layers. Obtained results provide the assumption that paintings of St. George Cathedral were performed in combined techniques of al fresco and fresco-secco.

Moreover, received data open the way to carry out quite significant and essential experiment. It was possible to partially reconstruct the original color image of St. George in the stairs tower, namely the bright red color of the vestments, which finds analogies among the 12th century wall paintings of Veliky Novgorod.

Abbreviations

ATR: Attenuated Total Reflectance; DTGS: Deuterated TriGlycine Sulfate; FTIR: Fourier Transform InfraRed Spectroscopy; IR: InfraRed; JINR: Joint Institute for Nuclear Research; MCT: Mercury Cadmium Telluride; NAA: Neutron Activation Analysis; NIST: National Institute of Standards and Technology; OM: Optical Microscopy; PGAA: Prompt Gamma Activation Analysis; SEM-EDX: Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy; UNESCO: United Nations Educational, Scientific and Cultural Organization; UV: UltraViolet; XRF: X-Ray Fluorescence Spectroscopy.

Acknowledgements

The authors thank T.A. Romashkevich and E.A. Morozova.

Authors' contributions

OSP, AYD contributed to experimental design, data collection and processing. TJT, SOD contributed to the art history context of the work. All authors contributed to writing and editing the manuscript. All authors read and approved the final manuscript.

Funding

This research received no external funding.

Availability of data and materials

All research data obtained during this study are included in this article. Raw data are available on request.

Declarations

Competing interests

The authors declare that they have no conflict of interests.

Author details

[1]Joint Institute for Nuclear Research, Joliot-Curie Str. 6, 141980 Dubna, Russia. [2]State Institute for Art Studies, Kozitsky Pereulok 5, 125009 Moscow, Russia. [3]Dubna State University, Universitetskaya Str. 19, 141980 Dubna, Russia.

Received: 26 November 2021 Accepted: 13 March 2022
Published online: 08 April 2022

References

1. Iordanidis A, Garcia-Guinea J, Strati A, Gkimourtzina A, Papoulidou A. Thermal, mineralogical and spectroscopic study of plasters from three post-Byzantine churches from Kastoria (northern Greece). J Therm Anal Calorim. 2011;103:577–86. https://doi.org/10.1007/s10973-010-1055-7.
2. Vasco G, Serra A, Manno D, Buccolieri G, Calcagnile L, Buccolieri A. Investigations of byzantine wall paintings in the abbey of Santa Maria di Cerrate (Italy) in view of their restoration. Spectrochim Acta Part A Mol Biomol Spectrosc. 2020;239: 118557. https://doi.org/10.1016/j.saa.2020.118557.
3. Fico D, Pennetta A, Rella G, Savino A, Terlizzi V, De Benedetto GE. A combined analytical approach applied to Medieval wall paintings from Puglia (Italy): the study of painting techniques and its conservation state. J Raman Spectrosc. 2016;47:321–8. https://doi.org/10.1002/jrs.4813.
4. Secretar LA. Monasteries of Veliky Novgorod and its environs (in Russian). Moscow: Severnii Palomnik; 2011.
5. Sedov VV, Vdovichenko MV. Archaeological work in the St. George Cathedral of the Yuriev Monastery and in the St. Panteleimon Monastery in 2015 (in Russian). Mater XXX Sci Conf "Novgorod Novgorod land Hist Archeol. Veliky Novgorod: Novgorod State United Museum; 2016. pp. 58–73.
6. Tsarevskaya T. Recent Information about the Original Paintings in St. George Cathedral of Yuriev Monastery in Novgorod the Great (in Russian). Art Christ World. 2016; pp. 195–207.
7. Dmitrieva S. Frescoes of the Transfiguration Church in Kovalyovo near Novgorod; 1380 (in Russian). Moscow: Galart; 2011.
8. Grekov AP. Frescoes of the Church of the Transfiguration of the Savior in Kovalyovo (in Russian). Moscow: Iskusstvo; 1987.
9. Anisimova TI. Restoration of ruined painting in Novgorod (in Russian). Proc All-Russian Conf study, Preserv Restor Monum Paint. Veliky Novgorod: Novgorod State United Museum; 2015. pp. 48–58.
10. Philippova OS, Dmitriev AY, Tsarevskaya TJ, Dmitrieva SO. Investigation of the pigments elemental and molecular composition of the frescoes of the St. George Cathedral of the Yuryev Monastery, and changes in coloration of medieval fresco painting—possibilities of physico-chemical methods (in Russian). In: press. Proc IX Sci Conf "Novgorod Novgorod land Art Restoration. "Veliky Novgorod: Novgorod State United Museum; 2021.
11. Chung Y-S, Kim S-H, Sun G-M, Lim J-M, Moon J-H, Kim Y-J, et al. Application of instrumental neutron activation analysis for the examination of oil pigments. Radiochim Acta. 2011;99:601–5. https://doi.org/10.1524/ract.2011.1849.
12. Bulavin M, Kulikov S. Current experiments at the irradiation facility of the IBR-2 reactor. J Phys Conf Ser. 2018;1021:12041. https://doi.org/10.1088/1742-6596/1021/1/012041.
13. Kuznetsov RA. Activation analysis (in Russian). Moscow: Atomizdat; 1974.
14. Pavlov SS, Dmitriev AY, Frontasyeva MV. Automation system for neutron activation analysis at the reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna. Russia J Radioanal Nucl Chem. 2016;309:27–38. https://doi.org/10.1007/s10967-016-4864-8.
15. Pavlov SS, Dmitriev AY, Chepurchenko IA, Frontasyeva MV. Automation system for measurement of gamma-ray spectra of induced activity for multi-element high volume neutron activation analysis at the reactor IBR-2 of Frank Laboratory of Neutron Physics at the Joint Institute for Nuclear Research. Phys Part Nucl Lett. 2014;11:737–42. https://doi.org/10.1134/s1547477114060107.
16. Dmitriev AY, Borzakov SB. Software for calculation of elements mass fractions in investigated samples by absolute method of neutron activation analysis. Phys Part Nucl Lett. 2019;16:772–8. https://doi.org/10.1134/s1547477119060438.
17. Dmitriev AY, Pavlov SS. Automation of the quantitative determination of elemental content in samples using neutron activation analysis on the IBR-2 reactor at the Frank Laboratory for Neutron Physics, Joint Institute for Nuclear Research. Phys Part Nucl Lett. 2013;10:33–6. https://doi.org/10.1134/s1547477113010056.
18. Dmitriev AY, Pavlov SS. Software for automation of neutron activation analysis at the IBR-2 reactor of FLNP, JINR. J Nucl Meas Inf Technol. 2012;4:54–66.
19. Dmitriev AY, Dmitriev FA. Automation of registration of sample weights for high-volume neutron activation analysis at the IBR-2 reactor of FLNP, JINR. Proc XXIII Int Semin Interact neutrons with Nucl. Dubna; 2016. p. 384–7. http://isinn.jinr.ru/proceedings/isinn-23/pdf/Dmitriev.pdf.
20. Révay Z, Lindstrom RM, Mackey EA, Belgya T. Neutron-induced prompt gamma activation analysis (PGAA). Handb Nucl Chem. 2011. p. 1619–72.
21. Molnár GL. Handbook of prompt gamma activation analysis. In: Molnár GL, editor. Handb. Prompt gamma act. anal. Dordrecht/Boston/London: Kluwer academic publishers; 2004.

22. Corso G, Gelzo M, Sanges C, Chambery A, Di Maro A, Severino V, et al. Polar and non-polar organic binder characterization in Pompeian wall paintings: Comparison to a simulated painting mimicking an "a secco" technique. Anal Bioanal Chem. 2012;402:3011–6.
23. Home|IRUG (cited 2021 Sep 13). http://irug.org/.
24. Lungina LN, Bratushko YI. The role of polished cross-sections studies for the examination of painting (in Russian). Proc 5th Sci Conf "Examination Attrib Work Anc Russ art." 2001. p. 267–70.
25. Malkin ZM. On computation of the error of the weighted mean (in Russian). Issues Publ by IAA RAS. St. Petersburg: the Central Astronomical Observatory of the Russian Academy of Sciences at Pulkovo; 2001;137: pp. 1–13.
26. Plyusnina II. Infrared spectra of minerals (in Russian). Moscow: Moscow University Press; 1977.
27. Hradil D, Grygar T, Hradilová J, Bezdička P. Clay and iron oxide pigments in the history of painting. Appl Clay Sci. 2003;22:223–36.
28. Buckley HA, Bevan JC, Brown KM, Johnson LR, Farmer VC. Glauconite and celadonite: two separate mineral species. Mineral Mag Mineral Soc. 1978;42:373–82. https://doi.org/10.1180/minmag.1978.042.323.08.
29. Chukanov NV, Vigasina MF, Zubkova NV, Pekov IV, Schäfer C, Kasatkin AV, et al. Extra-framework content in sodalite-group minerals: complexity and new aspects of its study using infrared and Raman spectroscopy. Minerals. 2020;10:1–17.
30. Chukanov NV, Sapozhnikov AN, Shendrik RY, Vigasina MF, Steudel R. Spectroscopic and crystal-chemical features of sodalite-group minerals from gem lazurite deposits. Minerals. 2020;10:1–23.
31. Filatov VV. The technique of ancient Russian monumental painting. Overview information (in Russian). In: Tech Technol sacred art Christ world From Antiq to Mod. Indrik; 2012.
32. Sarabyanov VD. Christ's Transfiguration Cathedral of the Mirozhsky monastery (in Russian). Moscow: Severniy palomnik; 2009.
33. Smith GD, Clark RJH. Raman microscopy in archaeological science. J Archaeol Sci. 2004;31:1137–60.
34. Voronin K, Kabanova M. Chemical-technological research and radiocarbon AMS dating of wall painting fragments from the ruins of the XIIth-XIIIth centuries AD church from archaeological excavations in the city of Smolensk, Russia. Herit Sci. 2020;8:45.
35. Pliny the Elder. Natural History. Translated by Rackham H, Jones WHS, Eichholz DE. Loeb Classical Library; 1938–1962.
36. Viner A. Fresco and tempera painting: materials and techniques of Old Russian wall painting of the 11th–17th centuries (in Russian). Moscow-Leningrad: Iskusstvo; 1948.
37. Grenberg YI, Pisareva SA. Wall painting of Old Novgorod in the aspect of technological research (in Russian). Artist Herit storage, Res Restor Collect Artic. Moscow: GOSNIIR; 1991. pp. 53–62.
38. Zorba T, Pavlidou E, Stanojlovic M, Bikiaris D, Paraskevopoulos KM, Nikolic V, Nikolic PM. Technique and palette of XIIIth century painting in the monastery of Mileseva. Appl Phys A. 2006;83:719–25.
39. Bobrov FY, Grigorieva IA, Parfenov VN. Study of the ground fragments with a colorful layer of wall paintings from the St. George Cathedral of the Yuriev monastery (Novgorod) and the Church of Mar Girgis,12th c. Rachkida (Lebanon) (in Russian). Saint Petersburg; 2016.
40. Knuutinen U, Mannerheimo H, Hornytzkyj S. Project report of pigment analyses of the fourth style wall paintings in the Casa di Marco Lucrezio (IX 3, 5.24) in Pompeii. 2007;22.
41. Daniilia S, Minopoulou E, Andrikopoulos KS, Tsakalof A, Bairachtari K. From Byzantine to post-Byzantine art: the painting technique of St Stephen's wall paintings at Meteora, Greece. J Archaeol Sci. 2008;35:2474–85.
42. Levstik MG, Mladenovič A, Križnar A, Kramar S. A raman microspectroscopy-based comparison of pigments applied in two gothic wall paintings in Slovenia. Period di Mineral. 2019;88:77–86.
43. Sarabyanov VD. Paintings of the north-western tower of the St. George Cathedral of the Yuriev Monastery (in Russian). Old Russ art Russ Ctries Byzantine world 12th century. St. Petersburg: Dmitry Bulanin; 2002. pp. 365–98.
44. Sarabyanov VD, Smirnova ES. The history of Old Russian painting (in Russian). Moscow: Saint Tikhon's Orthodox University; 2007.
45. Sedov VV. Staircase turret of the St. George's Cathedral in the Yuriev Monastery: archaeology, architecture and fresco painting (in Russian). Ross Arheol. 2021;132–43.
46. Giovannoni S, Matteini M, Moles A. Studies and developments concerning the problem of altered lead pigments in wall painting. Stud Conserv. 1990;35:21–5.
47. Petushkova JP, Lyalikova NN. Microbiological degradation of lead-containing pigments in mural paintings. Stud Conserv. 1986;31:65–9.
48. Dneprovskaya MB, Dubik OY. Compehensive analysis of pigments of the wall paintings of the Church of the Theotokos from Bertubani (David-Gareji, historical Georgia) (in Russian). Artist Herit storage, Res Restor Collect Artic. 1995. p. 44–56.
49. Koller M, Leitner H, Paschinger H. Reconversion of altered lead pigments in alpine mural paintings. Stud Conserv. 1990;35:15–20.

Publisher's Note