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Systematic study of wall painting of the twelfth century from the Christ's Transfiguration Cathedral of the Mirozhsky Monastery in Pskov (Russia) by complementary physico-chemical methods

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Abstract

The unique pre-Mongolian twelfth century wall painting from the Christ's Transfiguration Cathedral of the Mirozhsky Monastery in Pskov (Russia) have been investigated. A little less than 200 XRF spectra were collected in situ by portable spectrometer. Moreover 19 samples were subjected to additional in-depth laboratory analysis by six complimentary physico-chemical methods: neutron activation analysis, Fourier transform infrared spectroscopy, micro-Raman spectroscopy, polished cross-sections, polarized microscopy, and chemical microanalysis. Pigments and plasters from the interior painting, fragments found during archaeological excavations, samples from exterior murals, and sample of salt efflorescence were analyzed. The samples included the author's twelfth century painting as well as late repaintings. The composition of pigments and the number of painting layers were determined. Conclusions about organic binder presence or absence, and the painting technique were drawn. The results obtained will be used for restoration and conservation works.

Keywords Old Russian pre-Mongolian wall painting, Components of paintings (pigments, plasters, and binders), NAA, XRF, FTIR, Micro-Raman spectroscopy, Polished cross-sections, Polarized microscopy, Restoration

Introduction

The work is devoted to the study of murals of one of the oldest churches in Russia—the Christ's Transfiguration Cathedral of the Mirozhsky Monastery (Pskov, Russia). This monument is of federal importance included in the UNESCO world heritage list in 2019. The Christ's Transfiguration Cathedral is a Byzantine-type church (Fig. 1a). The Cathedral was painted by Greek masters eight centuries ago. The murals' significance consists in their high artistic quality, in a well-developed iconographic concept, as well as in unique preservation: about eighty percent of the twelfth century painting cycles have survived to the present day (Fig. 1b).

The painting of the Cathedral has no parallel in Byzantine art of that time. They break new ground in Old Russian church decoration, defining the development trends of pre-Mongolian art in Old Russia. In the following centuries, the history of the murals is unknown. The first information about significant architectural changes of the Cathedral dates back to the sixteenth century. Most

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Fig. 1 View of the Christ's Transfiguration Cathedral of the Mirozhsky Monastery from the south-west (**a**), view of painting cycle (**b**), the "Last Supper" composition on west wall (**c**), the "Deisis" composition above the portal of the west narthex (**d**), fragment of the drum paintings with the figures of prophets (**e**)

probably that ancient painting had already been whitewashed by that time, since the architectural modifications completely ignored the painting structure [1].

The history of the discovery of the Christ's Transfiguration Cathedral original painting goes back to the nineteenth century. At that time, the Russian architect and restorer V.V. Suslov was tasked to uncover the twelfth century painting and investigate the Cathedral for its further restoration [2]. In the following few years extensive Cathedral research was carried out. A restoration plan was developed and implemented. All the original paintings were uncovered from various late overpainting. Of course, the past centuries could not pass without any traces, like abrasions and losses of the paint layer and plaster. Therefore, V.V. Suslov was accused of defacing ancient paintings and was suspended from the restoration. Instead of completing the restoration work, repairs were carried out in the church. Ancient painting was completely hidden under new repainting which repeated "old style" [3–5]. The work was performed under the leadership of Russian icon painter N.M. Sofonov. In 1968–1983, the first comprehensive works on the

restoration of the painting of the Cathedral were carried out by a team of painters and restorers led by D.E. Bryagin [6] (Fig. 2a). The Sofonov's repainting was partially removed, from those areas where the preservation of ancient painting did not cause any questions. During the uncovering, small areas of the Sofonov's repainting were left (Fig. 2b).

The lack of clear boundaries between paintings of different times made it difficult to study the original wall painting. So in 1993 a new stage of restoration of the Cathedral began under the leadership of Soviet and Russian art historian, painter, and restorer V.D. Sarabyanov [7]. This stage continues intermittently to this day. The main goal of present restoration is in the full uncover of all the twelfth century painting remaining fragments.

The aim of the study

The investigation of a monument is not just scientific interest. A restoration project should take into account the entire long life of the monument. Such the project cannot be created without the research stage, which is possible only at the interdisciplinary level employing exact sciences resources and using innovative equipment.

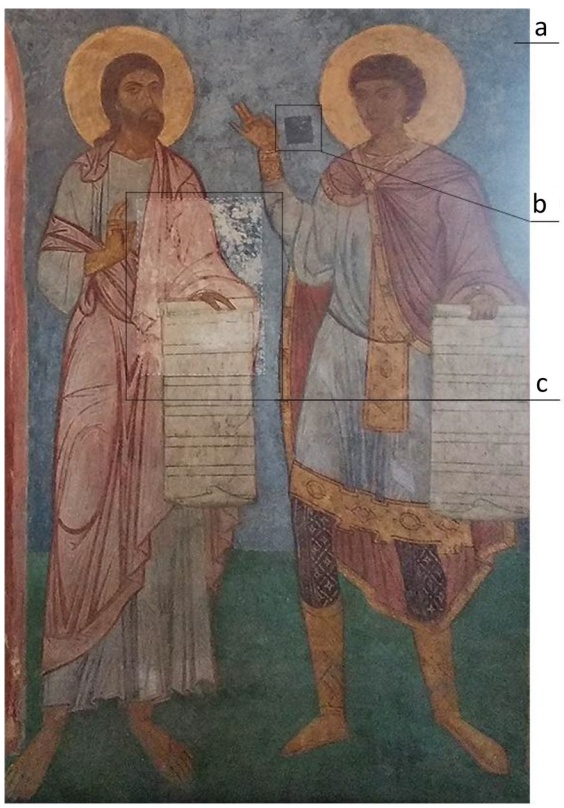

Fig. 2 Image of unknown prophets between the north-west and north windows of the drum. An example of painting fragments of different times: D.E. Bryagin's twentieth century restoration (**a**), N.M. Sofonov's nineteenth century repainting (**b**), V.D. Sarabyanov's trial uncovering area with twelfth century original painting (**c**)

At the end of the last century, studies of the Christ's Transfiguration Cathedral were carried out twice: in the 80 s under the leadership of D.E. Bryagin [8], and in the 90 s—under the leadership of Yu.M. Kuks [9]. The main tasks of the research part of D.E. Bryagin's works were to determine the composition of the primers and the set of pigments used. Yu.M. Kuks mainly identified the composition of the restorative consolidates, found out the layer ordering of the original painting, determined the repaintings, the composition of the primers and grounds.

Nowadays, a new stage of major restoration and conservation works is planned in the Christ's Transfiguration Cathedral. As mentioned above, restorers are faced with the task of restoring the author's twelfth century murals as completely as possible. First, art historians and restorers thoroughly inspect the monument and determine the state of the painting. For this purpose, some areas choose for trial uncovering (Fig. 2c) so as to show the most characteristic state of the author's color layer for this monument in not essential part of the painting. The next step is physico-chemical investigation. Only after this step laborious and complex restoration process be properly prepared and implemented.

Current investigation was carried out using seven complementary methods and modern equipment. Significant number of samples of different types expanded greatly the range of previous works and contributed to the addition and updating of information. The present study significantly differs from previous ones, since they were mainly aimed to work with preserved author's layer. With the help of modern spectrometer, the spectra collection was carried out at about two hundred points, which gives the authors the right to talk about mass analysis. Archaeological fragments found near the Cathedral during excavations in 2008–2009 and 2020–2021 were also studied.

This work was carried out by scientists from Frank Laboratory of Neutron Physics (FLNP) at Joint Institute for Nuclear Research (JINR) in cooperation with restorers from Interregional Agency for Scientific Restoration of Works of Art (IASRWA)—department of the Ministry of Culture of the Russian Federation.

Methods

The description of samples

Measurement points of various pigments for in situ XRF investigations on the interior walls of the Cathedral were chosen by the restorers from IASRWA in such a way as to study all possible colors. For comparison the XRF spectra of plasters were regularly collected in the places of losses. Also pigments and plasters from fragments found during archaeological excavations in 2008–2009 [10] and

2020–2021 were studied by portable XRF. The total number of XRF spectra measurement points was 189.

Specially selected samples (19 in total), including pigments and plasters from the inner and outer walls of the Cathedral, and salt efflorescence, were subjected to additional in-depth laboratory analysis by different methods. A detailed description of samples and methods used are provided in Table 1.

Portable X-ray fluorescence analysis

The elemental composition of pigments and plasters was determined by XRF portable spectrometer Bruker Tracer 5i under the following policies: a collimator with 8 mm diameter was used; a built-in video camera was used to position the spectrometer; the spectra of each color were collected at least in three measurement points, thus eliminating the possibility of outliers; the spectra were processed with Artax software.

Neutron activation analysis

The samples of plaster were prepared for irradiation in FLNP JINR. The surface of the samples was mechanically cleaned with a Dremel multifunctional tool equipped with a diamond-coated disc. Before processing each sample, the disc and the body of the instrument were wiped with cotton swabs soaked in ethanol. The samples were powdered and dried to a constant mass at 105 °C. Two subsamples of approximately 0.1 g were weighed and packed in plastic bags: the first subsample—to determine the mass fractions by short-lived isotopes (SLI) and the second one—for medium- and long-lived isotopes (MLI and LLI).

Samples were irradiated at the WWR-K reactor at the Institute of Nuclear Physics (INP), Almaty, Kazakhstan. To determine the elemental composition by SLI samples were irradiated for 60 s in a "dry" channel. Pneumatic transport system was used to deliver samples to irradiation zone and back. The approximate flux density of thermal neutrons in the "dry" channel is 4×10^{12} n/(cm^2 s), resonance ones – 4×10^{10} n/(cm^2 s). The SLI spectra were measured by the Canberra GC-2018 detector with the relative efficiency of 20% and the resolution of 1.8 keV for the Co-60 gamma line with energy of 1332 keV. To obtain MLI and LLI samples were manually loaded into

Table 1 Description of samples and methods used for investigation

Sample	Description	Methods
1	Plaster with green paint, a fragment of a painting from the archaeological excavations in 2020	PM, OM, micro-Raman, FTIR
2	Plaster with light-blue paint, a fragment of a painting from the archaeological excavations in 2020	PM, OM, micro-Raman, FTIR
3	Plaster with yellow paint, a fragment of a painting from the archaeological excavations in 2020	PM, FTIR
4	Salt efflorescence with blue paint, the lower row of the saints, the south part of the semicircle in the Cathedral central apse	FTIR, chemical microanalysis
5	Plaster with yellow paint, painting of the portal of the Cathedral west narthex	PM, OM, micro-Raman
6	Plaster with red paint, composition "Deisis", painting over the portal of the Cathedral west narthex	PM, OM, micro-Raman, FTIR
7	Olive-green paint, composition "Deisis", painting over the portal of the Cathedral west narthex	FTIR
8	Plaster with red paint, composition "Deisis", painting over the portal of the Cathedral west narthex	PM, FTIR
9	Plaster, central zakomara (arched gable) of the west facade of the Cathedral	PM, NAA
10	Plaster with red paint, painting of the central zakomara (arched gable) of the Cathedral west facade	PM, OM, micro-Raman, FTIR, NAA
11	Whitewash with red paint, painting of the south pilaster-strip of the Cathedral west facade	PM, FTIR
12	Plaster with orange-red paint, painting of the central zakomara (arched gable) of the Cathedral west facade	PM, OM, micro-Raman, FTIR, NAA
13	Plaster from the south slope of the lite opening in the upper part of the west wall of the west arm of the naos of the Cathedral	PM, OM, micro-Raman, NAA
14	Plaster with gray-blue paint, tunic of Prophet Solomon, the surface between the west and north-west windows of the Cathedral drum	PM, OM, micro-Raman, FTIR
15	Yellow-green paint, the himatius of Prophet Jonah, the wall surface between the south and south-west windows of the Cathedral drum	PM, OM, micro-Raman, FTIR
16	Plaster with light-green paint, the himatius of Prophet Habakkuk, the surface between the north-east and east windows of the Cathedral drum	PM, OM, micro-Raman, FTIR
17	Plaster with dark-purple paint, the chiton of the unknown prophet, the surface between the east and south-east windows of the Cathedral drum	PM, OM, micro-Raman, FTIR
18	Plaster with yellow paint, the himatius of Prophet Zechariah, the surface between the north and north-east windows of the Cathedral drum	PM, OM, micro-Raman, FTIR
19	Mortar from the south compartment	NAA

PM, Polarized Microscopy; OM, Optical Microscopy; FTIR, Fourier Transform Infrared spectroscopy; NAA, Neutron Activation Analysis

one of the "wet" channels for 1.5 h. In the "wet" channel the fluxes of thermal and resonance neutrons are approximately 6×10^{13} and 3×10^{12} n/(cm^2 s) respectively. The MLI spectra were collected six days after the end of irradiation, and the LLI—three weeks after irradiation, using the automatic spectra measurement system developed in FLNP JINR [11, 12]. The system includes the ORTEC GEM40P4-83 detector with the relative efficiency of 40% and the resolution of 1.85 keV for the Co-60 gamma line with the energy of 1332 keV.

Quality control was carried out using NIST standard samples. 1515, 1633C, 2709A, 2710A, 50C standard samples were used for the SLI; 1515, 1633C, 1944, 2586, 2709A, 2710A, 278—for MLI and LLI. Standards were weighed and packed in the same way as the studying samples.

The spectra were processed using the GENIE-2000 software. To calculate mass fractions of elements by the relative NAA method, Concentration program developed at the FLNP JINR was used [13].

Since there are few resonance neutrons in the irradiating channels of the WWR-K reactor, it is not possible to determine such an important macro-element as silicon. To assess the content of this element, the following actions were taken: the samples were ignited at a temperature of 1000 °C within two hours, the mass of the samples was fixed before and after ignition. The mass difference determined the amount of carbon dioxide released. The approximate silicon content was calculated on the basis that the sum of the mass fractions of all macrooxides (CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, SiO_2) and carbon dioxide in each plaster base should be 100%.

Polarized and optical microscopy

Visualization of the color layers and plasters was carried out using a LOMO L-215 POLAM microscope. Film polarizers rather than Nicol prisms are applied in the design of this instrument. A built-in MC-5.3 digital camera was used to take micro photos with a resolution of 5.3 megapixels. The images were processed in the MCview software. The magnification was selected experimentally to obtain the most informative photos.

Pigment species for PM were placed between the slide and the cover glasses using a Canada balsam as mounting medium. Pigments were identified according to methods from work [14]. Polished cross-sections were prepared as described in [15].

Micro-Raman spectroscopy

Measurements were performed on the polished cross-sections for each individual layer. Raman spectra were recorded with the Raman microscope RamMics M532/785 (EnSpectr) equipped with objectives of magnification of 10, 20, and 50×. Two single mode lasers emitting at 532 nm (spectral range of 160–4000 cm^{-1}, spectral resolution of 5–7 cm^{-1}) and 785 nm (spectral range of 200–2300 cm^{-1}, spectral resolution of 7–9 cm^{-1}) were used. The laser power was decreased from maximum to prevent pigment degradation. Depending on the signal intensity exposition time varied from 1 to 30 s and up to 1000 spectra were averaged. The spectra collection and processing was carried out with EnSpectr software.

Fourier transform infrared spectroscopy

ATR-FTIR (Attenuated Total Reflectance) spectra of pigments and plasters were measured using Invenio-R (Bruker) spectrometer in 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. For each sample 64 scans were summed. The spectra were collected and processed using Opus software. Individual compounds were identified using pigment libraries and the IRUG Internet database [16].

No special preparation was needed for pigments and plasters. A sample was scalped from wall painting fragment and placed on ATR crystal for analysis. Organic binder determination was guided by the following consideration: since organic binder may appear in micro or even trace amounts, their peaks in the spectra may be suppressed by the peaks of the main components, such as lime, sand, and clay. To obtain possible organic binder, extraction was carried out with various polar and non-polar solvents. To extract proteins and polysaccharides polar solvents were used. Extraction of fats, resins, and other substances insoluble in water was carried out with non-polar solvents. We have prepared two series of extracts: with deionized water (Direct-Q5UV (Millipore)) and with chemically pure chloroform. Sample powder was sonicated for 30 min at 45 °C. The chloroform solution was air dried, water extract was dried at 105 °C. Obtained dry residues were investigated by ATR-FTIR spectroscopy.

Chemical microanalysis

The sample 4 of salt efflorescence (Table 1) was subjected to chemical microanalysis in order to determine the anionic composition. Drop analysis based on following sensitive chemical reactions was carried out:

1. Dissolution in hydrochloric acid for carbonates identification

$$CO_3^{2-} + 2HCl = 2Cl^- + H_2O + CO_2\uparrow$$

2. Reaction of water extract with barium chloride to detect sulfates

$$SO_4^{2-} + Ba^{2+} = BaSO_4 \downarrow \text{(white)}$$

3. Reaction of water extract with silver nitrate to detect chlorides

$$Cl^- + Ag^+ = AgCl \downarrow \text{(white)}$$

All manipulations and observations were done using the stereoscopic microscope MSP-2 (LOMO).

Results

NAA

The elemental composition of the five plaster samples was determined by neutron activation analysis. The mass fractions of 36 elements were determined. The silicon content was calculated additionally. The results are summarized in the Table 2. The obtained data has been added to the created building materials database of the Old

Table 2 NAA data for plasters (in mg/kg)

Sample	Na	Mg	Al	Si	Cl	K	Ca
19	4020 ± 48	13,400 ± 1300	41,400 ± 950	171,000	< LOD	19,400 ± 660	174,000 ± 10,000
9	2500 ± 32	11,000 ± 1000	20,800 ± 480	85,100	242 ± 44	9860 ± 390	275,000 ± 16,000
10	1800 ± 23	7760 ± 800	12,200 ± 280	95,200	129 ± 36	6670 ± 300	246,000 ± 14,000
12	2860 ± 37	6250 ± 600	13,500 ± 310	237,000	101 ± 28	9740 ± 400	147,000 ± 8400
13	1510 ± 20	12,000 ± 1000	9280 ± 220	31,600	373 ± 48	5860 ± 290	321,000 ± 18,000

Sample	Sc	Ti	V	Cr	Mn	Fe	Co
19	6.64 ± 0.07	3410 ± 290	42.9 ± 1.7	54.0 ± 1.4	570 ± 31	21,700 ± 910	7.62 ± 0.14
9	3.39 ± 0.04	1820 ± 180	22.3 ± 1.0	38.6 ± 1.0	498 ± 27	12,000 ± 500	4.61 ± 0.08
10	1.49 ± 0.02	834 ± 110	9.61 ± 0.62	35.0 ± 0.9	280 ± 17	5050 ± 210	1.94 ± 0.04
12	1.55 ± 0.02	661 ± 93	8.98 ± 0.53	28.5 ± 0.7	267 ± 14	5780 ± 240	2.25 ± 0.05
13	1.52 ± 0.02	623 ± 100	11.6 ± 0.7	25.6 ± 0.6	389 ± 22	6430 ± 270	1.98 ± 0.04

Sample	Zn	As	Br	Rb	Sr	Zr	Mo
19	139 ± 6	2.56 ± 0.08	< LOD	73.2 ± 11.7	143 ± 13	149 ± 37	6.58 ± 0.66
9	34.0 ± 1.7	4.62 ± 0.12	1.29 ± 0.15	40.7 ± 6.5	164 ± 13	67.2 ± 18.1	3.67 ± 0.40
10	29.1 ± 1.4	1.58 ± 0.05	0.778 ± 0.093	21.4 ± 3.6	123 ± 10	53.1 ± 13.8	1.90 ± 0.25
12	22.8 ± 1.3	1.21 ± 0.04	1.60 ± 0.19	30.8 ± 4.9	127 ± 10	125 ± 31	1.84 ± 0.26
13	10.8 ± 1.4	1.97 ± 0.06	4.13 ± 0.50	12.0 ± 2.0	167 ± 13	27.9 ± 8.1	2.52 ± 0.30

Sample	Sb	Ba	Cs	La	Ce	Nd	Sm
19	0.213 ± 0.023	275 ± 28	1.95 ± 0.04	22.9 ± 0.5	45.6 ± 2.1	20.4 ± 1.9	4.7 ± 0.2
9	0.144 ± 0.033	135 ± 14	1.01 ± 0.02	12.2 ± 0.3	24.0 ± 1.1	13.4 ± 1.3	2.39 ± 0.1
10	0.363 ± 0.033	100 ± 10	0.378 ± 0.013	4.92 ± 0.10	12.5 ± 0.6	6.09 ± 0.73	1.20 ± 0.05
12	0.292 ± 0.035	176 ± 18	0.448 ± 0.014	7.36 ± 0.15	18.1 ± 0.8	6.74 ± 0.74	1.77 ± 0.08
13	0.140 ± 0.027	71.7 ± 7.9	0.231 ± 0.011	4.45 ± 0.09	10.5 ± 0.5	5.47 ± 0.66	1.14 ± 0.05

Sample	Eu	Tb	Yb	Lu	Hf	Ta
19	0.837 ± 0.033	0.545 ± 0.035	1.99 ± 0.13	0.283 ± 0.031	4.53 ± 1.36	0.671 ± 0.023
9	0.414 ± 0.020	0.287 ± 0.022	1.02 ± 0.07	0.141 ± 0.016	2.06 ± 0.62	0.339 ± 0.013
10	0.265 ± 0.014	0.125 ± 0.014	0.466 ± 0.035	0.0796 ± 0.0088	1.84 ± 0.55	0.157 ± 0.008
12	0.268 ± 0.015	0.144 ± 0.014	0.502 ± 0.037	0.0823 ± 0.0091	3.27 ± 0.98	0.231 ± 0.010
13	0.216 ± 0.013	0.142 ± 0.016	0.316 ± 0.027	0.0657 ± 0.0072	0.956 ± 0.287	0.156 ± 0.007

Sample	Au	Th	U
19	0.00166 ± 0.00055	6.40 ± 0.12	2.44 ± 0.06
9	0.01110 ± 0.00330	3.02 ± 0.05	1.40 ± 0.03
10	0.00304 ± 0.00091	1.44 ± 0.03	0.808 ± 0.023
12	0.00253 ± 0.00078	2.75 ± 0.05	0.981 ± 0.027
13	0.00288 ± 0.00086	1.29 ± 0.03	0.956 ± 0.026

LOD, limit of detection

Russian Cathedrals and can be used later as information for statistical analysis.

XRF

Research in the Cathedral drum

Twelfth century pigments A thorough analysis of the pigments and plasters composition in the Cathedral drum (Fig. 1e) was carried out. The results of semi-quantitative elemental analysis and conclusions about the possible mineral composition of the main colors are listed in Table 3. Since the elemental composition of pigments are compared with plaster one, the following notation have been used: element boldfaced if it has mass fraction greater than the same element in the plaster; elements in parentheses are not present in all MPs.

The dominant element in plaster base composition is calcium, thus lime is the main component of plaster. Observed silicon and aluminum indicate the presence of clay minerals and sand. No sulfur was found in the elemental composition of plaster base. But it can be seen that in all measuring points of different pigments high amounts of calcium and sulfur were determined. So we can conclude that gypsum located on the surface of the painting.

The increased levels of iron in yellow and red pigments indicate the usage of yellow and red ochres (main colored minerals are goethite α-FeOOH and hematite Fe_2O_3, respectively). The presence of silicon and aluminum in these paints indicates the presence of various clay minerals and sand.

High iron, silicon, and potassium content in the green pigment indicates the presence of green earth, which can contain such minerals as glauconite $((K,Ca)(Mg,Fe,Al)_2[(Al,Si)Si_3O_{10}](OH)_2)$ or celadonite $(K(Mg,Fe,Al)_2[Si_4O_{10}](OH)_2)$. In addition, copper was found in the composition of the one measuring green point.

No copper was determined in the blue colors. Nevertheless, content of iron, silicon, and aluminum are little more than in plaster. Thus, we can talk about the presence of lazurite $(Na_6[(Al,Si)O_4]_6S_2)$. Sulphur which forms polysulfide ions responsible for the blue color of lazurite, cannot be reliably identified by XRF because of high gypsum content on the wall surface.

It should be noted that in lighter-shade areas of painting a large calcium content was found (Table 3), which indicates that the paints were whitened with lime ($CaCO_3$). In such situation, it is difficult to determine the coloring base because of small amount of color pigment is required to change the paint hue.

In light-blue or gray-blue hues (for example, the chiton of Prophet Jonah) are even more difficult to determine the main coloring mineral. In terms of elemental composition, such paints have minimal differences from the plaster base. They could have been painted with lazurite mixed with lime, but the high content of gypsum on the wall surface prevents the determination of sulfur in the pigment. Also commonly used in Old Russia grey-blue pigment was spruce charcoal mixed with lime and called "reft"' [17]. But carbon could not be detected by XRF analysis.

In the composition of the pigment used for preliminary drawing (visible on the white scrolls of the prophets), an increased content of lead was found. Together with observed pale orange hue it can be conclude that the pigment is highly lightened red lead (Pb_3O_4) [18].

The light-green himatius of one of the prophets is characterized by a high content of calcium, that indicates the dilution of paints with lime.

Deep red clothes or folds on clothes are characterized by a significant iron content, several times higher than in yellow and red ochres (Table 3). While the content of manganese (which is part of umbers) is not high. Old Russian painters used pigment called "bagor" in wall painting, which has a dark red color of purple hue that is most probably analogous to caput mortuum. Such pigments are practically pure anhydrous iron oxide (Fe_2O_3), prepared by ignition of red ochres.

Prints of restoration The gray-blue hem of the Prophet Solomon tunic is located outside the trial uncovered areas and belongs to Bryagin's restoration. The pigment elemental composition showed the presence of a large titanium amount, most likely related to restoration paints. The elemental composition of this color is quite difficult for identification of specific pigments, so laboratory analysis is needed.

The above mentioned areas of Sofonov's repainting, left on the clothes and faces of the prophets between the north and north-east windows of the drum, were also examined. All the studied points are characterized by the presence of sufficient amount of lead, which may indicate the use of lead white $(Pb(CO_3)Pb(OH)_2)$. The absence of copper and chromium in the green areas allows to assume that the pigment in this case is glauconite or celadonite.

Entrance to the choir balcony

Investigation of the pigments elemental composition carried out on the west wall around the entrance to the choir balcony (Fig. 1c). The composition of the main colors is similar to the pigments from the drum (Table 3).

Lower row

Pigments The composition of the gray-blue background around St. Panteleimon slightly differ from the plaster composition. Exception is in increased lead content, so it

Table 3 Semiquantitative elemental composition data for in situ XRF analysis summarized for several measuring points (MPs)

Sample	MPs	Elements	Minerals	Sample	MPs	Elements	Minerals
Cathedral drum							
Plaster	4	Al, Si, P, S, K, Ca, Ti, Mn, Fe, Pb	Calcite/gypsum				
			Clay/quartz				
Main colors							
Yellow	9	Al, **Si**, P, **S**, K, Ca, **Ti**, Mn, **Fe**, **Pb**	Goethite	Red	3	Al, Si, P, **S**, K, Ca, Ti, Mn, **Fe**	Hematite
			Lead white or massicot				Clay/quartz
			Clay/quartz				Calcite/gypsum
			Calcite/gypsum				
Blue	5	**Al**, **Si**, **P**, **S**, **K**, Ca, **Ti**, Mn, **Fe**, Zn, Pb	Lazurite	Green Samples 15, 16	9	Al, **Si**, P, **S**, **K**, Ca, **Fe**, Ti, Cr, Mn, (**Cu**), Zn, Pb	Glauconite/celadonite
			Clay/quartz				Clay/quartz
			Calcite/gypsum				Calcite/gypsum
White	3	Al, Si, P, **S**, **K**, Ca, Ti, Fe	Calcite/gypsum	Black	3	Al, Si, P, **S**, **K**, Ca, Ti, Fe	Calcite/gypsum
			Clay/quartz				Clay/quartz
Light hue paints							
Light-blue	3	Al, Si, **P**, **S**, K, Ca, Ti, Mn, Fe, Zn, Pb	Calcite/gypsum	Light-yellow	6	Al, Si, P, **S**, K, Ca, Ti, Mn, **Fe**, Zn, Pb	Goethite
							Clay/quartz
							Calcite/gypsum
Pink	6	**Al**, **Si**, P, **S**, **K**, Ca, Ti, Mn, **Fe**, Zn, Pb	Hematite	Pile orange	3	**Al**, **Si**, P, **S**, **K**, Ca, Ti, **Fe**, Zn, Pb	Red lead
			Clay/quartz				Clay/quartz
			Calcite/gypsum				Calcite/gypsum
Composite paints							
Deep red (stripes)	8	**Al**, **Si**, **S**, P, **K**, Ca, Ti, Mn, **Fe**, Zn, Pb	Hematite	Purple red (violet) Sample 17	6	**Al**, **Si**, **P**, **S**, **K**, Ca, **Mn**, **Ti**, **Fe**, Zn, **Pb**	Hematite
			Clay/quartz				Clay/quartz
			Calcite/gypsum				Calcite/gypsum
Light-green Sample 18	9	Al, **Si**, P, **S**, **K**, Ca, **Ti**, Mn, **Fe**, Zn, Pb	Glauconite/celadonite				
			Clay/quartz				
			Calcite/gypsum				
Entrance to the choir balcony							
Plaster	2	Al, Si, K, Ca, Ti, Mn, Fe, Zn	Calcite/gypsum				
			Clay/quartz				
Yellow	4	Al, Si, P, K, Ca, **Ti**, Mn, **Fe**, Pb	Goethite	Green	9	Al, Si, P, **K**, Ca, Ti, Mn, Fe, Pb	Glauconite/celadonite
			Clay/quartz				Clay/quartz
			Calcite/gypsum				Calcite
Red	4	Al, **Si**, P, K, Ca, **Ti**, **Mn**, **Fe**, Pb	Hematite	Blue	6	Al, **Si**, P, S, K, Ca, **Ti**, Mn, **Fe**, Zn, Pb	Clay/quartz
			Clay/quartz				Calcite/gypsum
			Calcite/gypsum				
Deep red	4	Al, Si, P, K, Ca, Ti, Mn, **Fe**, Pb	Hematite				
			Clay/quartz				
			Calcite/gypsum				
Lower row							
Pigments							
Plaster	4	Al, Si, S, K, Ca, Ti, Fe	Calcite/gypsum				
			Clay/quartz				

Table 3 (continued)

Sample	MPs	Elements	Minerals	Sample	MPs	Elements	Minerals
Blue with salt efflorescence	3	Al, Si, **S**, P, K, Ca, Ti, Mn, Fe, **Pb**	Lead white	Blue	3	Al, **Si**, **S**, P, **K**, Ca, Ti, Mn, Fe, Pb	Lead white
			Calcite/gypsum				Calcite/gypsum
			Clay/quartz				Clay/quartz
Grey-blue	3	Al, Si, **S**, P, K, Ca, Ti, Mn, Fe, **Pb**	Lead white	Red	3	Al, Si, **S**, P, K, Ca, Ti, Mn, **Fe**, **Pb**	Hematite
			Calcite/gypsum				Lead white
			Clay/quartz				Clay/quartz
							Calcite/gypsum
Green	2	Al, Si, **S**, **P**, K, Ca, Ti, Fe, Pb	Glauconite/celadonite	Green	2	Al, Si, **S**, **P**, **K**, Ca, **Ba**, **Cr**, Mn, **Fe**, **Pb**	Chrome green
			Lead white				Lead white/barium white
			Calcite/gypsum				Calcite/gypsum
			Clay/quartz				Clay/quartz
Yellow	3	**Al**, **Si**, **S**, P, **K**, Ca, **Ti**, **Mn**, **Fe**, Pb	Goethite				
			Lead white				
			Clay/quartz				
			Calcite/gypsum				
Consequences of thermal exposure							
Yellow to red	9	Mg, Al, Si, S, K, Ca, Ti, Mn, **Fe**, Pb	Goethite or hematite				
			Clay/quartz				
			Calcite/gypsum				
Samples found during archaeological excavations							
Twelfth century							
Plaster	4	Al, Si, S, (P), K, Ca, Ti, Mn, Fe	Calcite/gypsum				
			Clay/quartz				
Yellow Sample 3	9	Al, Si, S, K, Ca, **Ti**, **Mn**, **Fe**	Goethite	Red	3	Al, Si, P, K, Ca, Mn, Ti, Fe, **Hg**	Cinnabar
			Clay/quartz				Hematite
			Calcite/gypsum				Clay/quartz
							Calcite/gypsum
Blue Sample 2	5	Al, **Si**, S, K, **Ca**, Ti, Mn, **Fe**, Zn	Clay/quartz	Green Sample 1	9	Al, **Si**, P, S, **K**, Ca, **Ti**, Mn, **Fe**, **Cu**, **Zn**	Glauconite/celadonite
			Calcite/gypsum				Clay/quartz
							Calcite/gypsum
Late centuries							
Plaster	4	Al, Si, S, K, Ca, Ti, Mn, Fe	Calcite/gypsum				
			Clay/quartz				
Yellow	9	Al, Si, S, K, Ca, Ti, Mn, **Fe**, **Pb**	Goethite	Red	3	Al, Si, S, K, Ca, **Fe**, Pb, Ba	Hematite
			Lead white or massicot				Clay/quartz
			Clay/quartz				Calcite/gypsum
			Calcite/gypsum				
Blue	5	Si, K, Ca, Fe, Ba, Pb	Clay/quartz				
			Calcite/gypsum				

can be assumed that in backgrounds lead white was used. Iron and lead were found in the composition of the pink pigment on the himatius, therefore, red ochre with lead white were applied [19]. A lead white is probably used by N.M. Sofonov's team. The green color on the sleeve and the hem of the chiton is different in their elemental composition. The pigment on the sleeve is glauconite or celadonite, since no elements except iron responsible for the green color have been found. On the contrary, chromium and barium were found in the pigment on the hem. These elements are not typical neither for twelfth century, nor for N.M. Sofonof's workshop. Also they were not found in other studied fragments. Thus the hem is probably toning with modern paints, possibly watercolors based on green chromium oxide and barium white.

Salt efflorescence A visual analysis of the lower row of the painting of the east wall of the south arm of the naos of the Cathedral revealed a salt crust on the surface of the painting. XRF analysis data show a significant content of sulfur and calcium. Thus it is most likely that the salt on the surface is calcium sulfate or gypsum.

Consequences of thermal exposure The study of the saint's nimbus with the yellow–red gradient (presumably arising due to exposure to high temperature from nearby icon lamp) by XRF method is not enough to solve the problem of change in coloration of painting. In this case, an increased iron content is observed in all measuring points, which means the use of ochre as a pigment. The level of iron content affects the saturation of the color: brighter yellow or red contains more iron. However, there is no rule that one of the colors should contain more iron. It is also difficult to identify the color by impurities of clay minerals. Thus, more sensitive elemental, molecular, and structural analysis is needed to determine and understand the processes of color transformation.

Archaeological samples

Architectural and archaeological excavations inside and outside the Christ's Transfiguration Cathedral were carried out in 2008–2009 and 2020–2021. Archaeologists have discovered a number of wall painting fragments with various pictorial layers (Fig. 3). Results of XRF analysis of such samples are summarized in Table 3.

Mercury and increased iron content were found in the red paint, which means, that presumably the painter used cinnabar (HgS) together with the red ochre. The data obtained are consistent with the 1980 report [8], which also mentions the discovery of cinnabar over red ochre. The yellow pigment is yellow ochre, since the iron content in the paint layer is higher than in the plaster base.

Fig. 3 Mural fragments found during archaeological excavations on the east side of the altar apse

It should be noted that mercury was found in one point of the yellow fragment, which probably got into the study area from the neighboring red part. The studied green fragment is identical in composition to the green-colored ground around the Prophet Habakkuk (?).

In some archaeological fragments linen fibers are visible. So, these samples date back later then origin Cathedral painting and probably belong to the painting from the zakomara (arched gable) of the east wall. A large amount of calcium and sulfur are found in the elemental composition of plaster, therefore, gypsum and lime can be used (Table 3). Also lead is presented in pictorial layers of all samples, most likely it is lead white. The red and yellow pigments are ochres, because they have an increased iron content. The presence of large amount of sulfur in plaster prevents reliable identification of blue pigment.

Microscopic study

Polarized microscopy was used to confirm, or in some cases, to refine the pigment composition. It is a simple but very visual tool which makes it possible to determine the mineral composition of the paints. And to determine number and order of paint layers, a study of polished cross-sections was carried out.

The most interesting samples concern the drum of the Cathedral and date from the twelfth century. These are samples from 14 to 18. Stratigraphy of the sample 14 (Fig. 4b) reveals three layers: plaster base, blue original layer and quite thick grey layer. In the third layer as well as on the top of fragment (Fig. 4a) grey, yellow, black, and white particles can be seen. Most probably it is restoration layer. The sample's slide contains blue transparent crystals which are not visible in crossed polarizers (Fig. 4c, d). These optical properties are features of lazurite. Also clusters of small red or yellow particles may be seen which retain color and transparency in the cross polarizers. These properties are typical for ochres. Black particles of elongated shape are coal.

The surface of sample 15 is not smooth: it looks like scaly (Fig. 4e). Cross section of this sample contains two identical light green layers (Fig. 4f). Between these layers there is white one. This stratigraphy may be due to consolidation of the color layer. Both on the surface and in the cross-section it can be seen that green color is composite and include light-green, dark-green, yellow, red, and blue crystals. In the micrograph of the sample's 15 slide all these particles can be seen: clusters of small particles of red and yellow ochres, blue lazurite crystals, as well as light- and dark-green particles that are getting more dark in cross polarizers like glauconite and celadonite (Fig. 4g, h).

The sample 16 contains single pictorial layer of light-green color over the plaster layer (Fig. 4j). The photograph from the sample 16 shows that the light-green pigment is mixed (Fig. 4i). The main part is light-green crystals. In addition, there are inclusions of yellow crystals and dark-green crystals. On the micrograph of slide two types of green earth crystals can be seen: most likely glauconite and celadonite (Fig. 4k, l). Crystals of glauconite looks like yellow ones and make up the bulk of the slide. Dark-green celadonite is much less common. Crystals of glauconite in the slide are quite similar to yellow ochre in color (Fig. 4k, l).

Deep red color of the sample 17 is also mixed (Fig. 4n). The three-layer structure was obtained for cross-section of this sample (Fig. 4m). First layer is plaster, middle layer is of grey-blue color, and top deep red layer contain blue inclusions. The main pigments according to polarized microscopy in this sample are red ochre and lazurite (Fig. 4o, p).

Cross-section of the sample 18 reveals only one yellow pictorial layer together with plaster base (Fig. 4q, r). And only yellow ochre was found in the slide (Fig. 4s, t).

Samples 1 and 2 are also dating back to twelfth century but were found during archeological excavations. In a micrograph of a cross-section of the sample 1 three layers can be clearly identified: plaster and two layers of black and green color. Polarized microscopic investigation of the pictorial layer shows that two types of green crystals can be distinguished. However, their optical properties suggest that these are glauconite and celeadonite, structurally related minerals. No black coal particles were found.

Cross-section of blue fragment 2 is similar to fragment 1 and also consists of three layers: plaster and two paint layers of black and blue color. There are quite large blue crystals in the top layer can be seen. The sample slide contains transparent blue crystals with sharp edges. The size of blue particles varies from very small to quite large. There are also no black coal particles were found.

Yellow ochre was identified in the slide of the sample 3 by polarized microscopy.

The sample 5 concerning to late repainting of the portal of the Cathedral. Cross-section shows two-layer structure, as well as polarized microscopy confirm the presence of yellow ochre.

Samples 6 and 8 are from outer wall painting. The sample 6 is highly unusual because it contains three color layers over the plaster base: green, yellow, and red in order from plaster. Red and yellow ochres as well as green earth were found in the slide. Only red ochre was found in the sample 8 according to polarized microscopy.

Samples 9–13 are also from outer walls, but from the central zakomara (arched gable). The cross-sections of

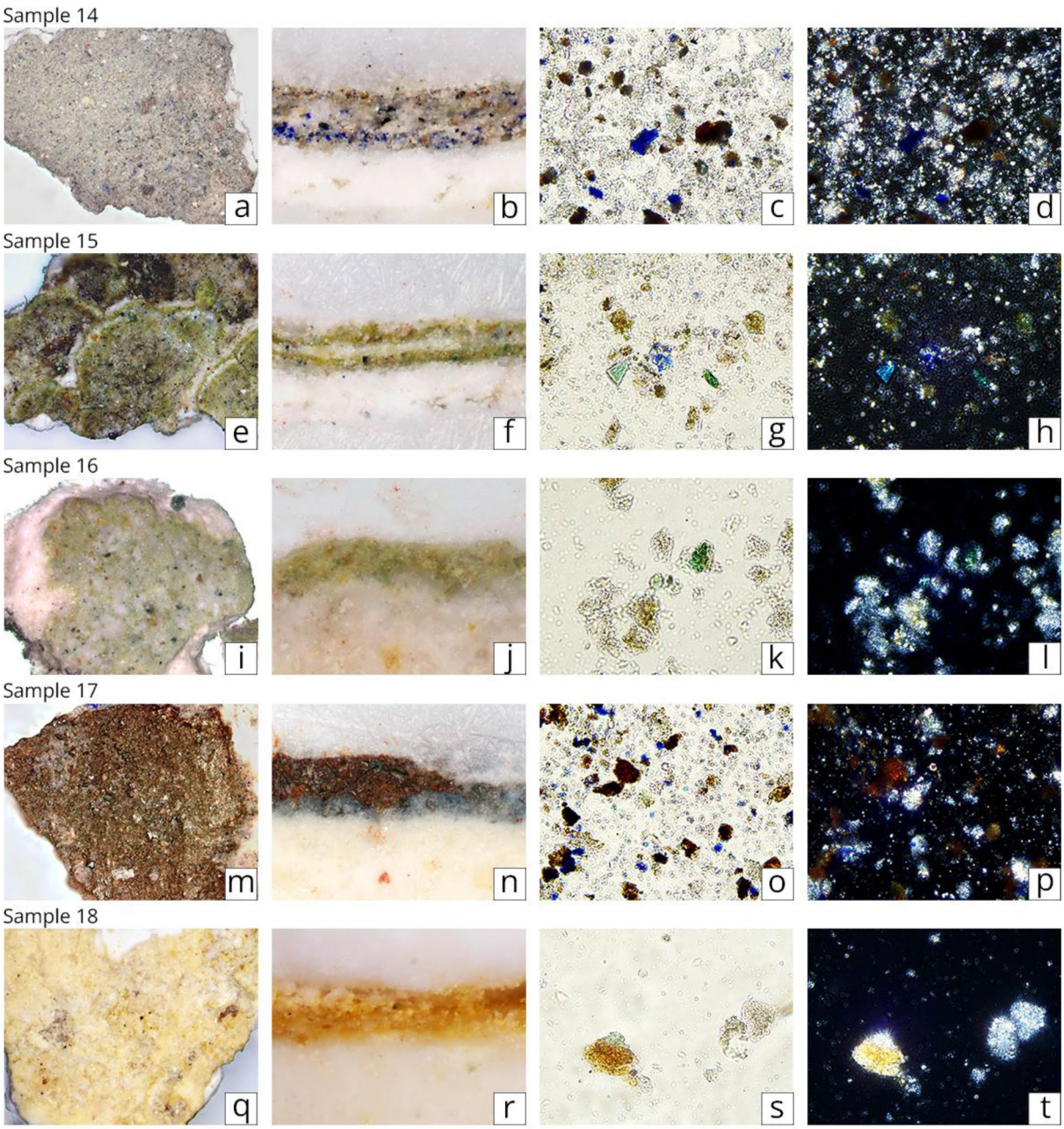

Fig. 4 Results of investigations of samples 14–18: optical microscopy micrographs made at × 100 magnification (**a**, **e**, **i**, **m**, **q**), polished cross-sections (**b**, **f**, **j**, **n**, **r**), pigments observed in plane polarized transmitted light (**c**, **g**, **k**, **o**, **s**) and between crossed polarizers (**d**, **h**, **l**, **p**, **t**)

samples 10, 12, 13 exhibit two-layer structures: paint and plaster. In red and orange colors red ochre with admixture of yellow one in the case of the sample 12 were identified by polarized microscopy.

Micro-Raman spectroscopy

Micro-Raman spectra were collected from each layer in all made cross-sections. In cases of mixed colors all possible crystals were analyzed. Results are summarized in the Table 4.

For the sample 1 plaster is almost pure lime, as no peaks of gypsum were found [20]. Black layer contains amorphous carbon [21]. Green color according to Raman spectroscopy is green earth [22]. But since the spectrum is very noisy, it is impossible to distinguish between glauconite and celadonite minerals. Spectra of plaster and

Table 4 Pigments detected in samples by optical and polarized microscopy and micro-Raman spectroscopy

Sample	Polarized microscopy	Optical microscopy of cross-sections		Micro-Raman spectroscopy	
		No and	color of layers	Pigments identified	Bands used for identification (cm^{-1})
1	Celadonite	3	Plaster	Calcite	153, 278, 711, 1085
	Glauconite		Black	Amorphous carbon	1315br (broad), 1591br
	Calcite			Calcite	151, 278, 722, 1086
	Quartz		Green	Celadonite/glauconite	168sh (shoulder), 198, 281, 345sh, 379, 393, 433, 537, 683
2	Lazurite	3	Plaster	Calcite	152, 279, 711, 1085
	Calcite		Black	Amorphous carbon	1313br, 1585br
	Quartz			Calcite	155, 279, 1087
			Blue	Lazurite	261, 283sh, 546, 598, 816, 1094, 1359, 1640, 1901, 2186
3	Yellow ochre	–		–	
	Calcite				
5	Yellow ochre	2	Plaster	Calcite	154, 279, 711, 1085
	Calcite		Yellow	Yellow ochre (goethite)	211, 301, 391, 475sh, 543
	Quartz			Massicot	143
				Calcite	280, 1085
6	Yellow ochre	4	Plaster	Calcite	151, 275, 710, 1084
	Red ochre			Gypsum	415, 492, 618, 669, 1006, 1132
	Glauconite		Green	Celadonite/glauconite	198, 278, 377, 541, 681
	Calcite		Yellow	Yellow ochre (goethite)	291, 405
				Calcite	277, 1084
				Gypsum	428, 607, 1006
				Titanium white (rutile)	445, 607
			Red	Red ochre (hematite)	224, 290, 408
				Amorphous carbon	1324br, 1597br
				Calcite	275sh, 1084
				Gypsum	408, 496, 616, 665, 1006
8	Red ochre	–		–	
	Calcite				
	Quartz				
9	Calcite	–		–	
	Coal				
10	Red ochre	2	Plaster	Calcite	152, 278, 711, 1084
	Calcite			Gypsum	413, 1006
	Quartz		Orange (red)	Red ochre (hematite)	221sh, 281, 412
				Calcite	154, 281, 711, 1084
				Gypsum	412, 492, 616, 1006, 1133
11	Red ochre	–		–	
	Calcite				
12	Yellow ochre	2	Plaster	Calcite	152, 710, 1084
	Calcite		Orange	Yellow ochre (goethite)	217, 281, 409, 608
	Quartz			Calcite	154, 281, 711, 1084
13	Calcite	3	Plaster	Calcite	152, 277, 710, 1084
	Quartz		Grey	Amorphous carbon	1317br, 1593br
				Calcite	153, 278, 710, 1084
				Gypsum	412, 492, 617, 668, 1006, 1133
			White	Calcite	277, 711, 1085
				Gypsum	202, 484, 629, 673, 1008, 1019
				Amorphous carbon	1317br, 1591br

Table 4 (continued)

Sample	Polarized microscopy	Optical microscopy of cross-sections		Micro-Raman spectroscopy	
		No and	color of layers	Pigments identified	Bands used for identification (cm^{-1})
				Titanium white (rutile)	441, 608
14	Lazurite	3	Plaster	Calcite	152, 278, 710, 1085
	Red ochre		Blue	Lazurite	263, 541, 579sh, 815, 1092
	Calcite		Grey	Amorphous carbon	1354br, 1594br
	Quartz			Calcite	144, 274, 1084
				Titanium white (rutile)	144, 247, 435, 609
				Celadonite/glauconite	432, 540
				Massicot	140, 293
				Gypsum	417, 488, 620, 667, 1005, 1111
15	Celadonite	2	Plaster	Calcite	152, 277, 711, 1084
	Glauconite		Light-green	Celadonite/glauconite	199, 275, 387, 531, 1052
	Yellow ochre			Yellow ochre (goethite)	381br, 484, 551sh, 1204br, 1271br
	Red ochre			Lazurite	263, 285sh, 544, 582sh, 824br, 1093, 1358br, 1641, 2186br
	Coal			Calcite	279, 1085
	Calcite			Prussian blue	275, 534, 2153
	Quartz			Chrome yellow	338, 401, 834
				Barium white	457, 615, 643, 985, 1086, 1138
				Titanium white (rutile)	142, 252, 609br, 834
				Lead white	1047
16	Celadonite	2	Plaster	Calcite	152, 277, 710, 1084
	Glauconite		Light-green	Celadonite/glauconite	386, 537
	Yellow ochre			Yellow ochre (goethite)	389
	Red ochre			Calcite	149, 277, 1085
	Calcite			Gypsum	1006
17	Red ochre	3	Plaster	Calcite	152, 278, 711, 1083
	Lazurite		Grey-blue	Amorphous carbon	1315br, 1595br
	Calcite			Calcite	148, 277, 1086
			Red	Red ochre (hematite)	221, 288, 401, 494, 607, 650, 1308br
18	Yellow ochre	2	Plaster	Calcite	154, 279, 710, 1084
	Calcite		Yellow	Yellow ochre (goethite)	395
	Quartz			Massicot	141, 279
				Calcite	152, 279, 710, 1085

black layers of the sample 6 are close to those in green fragment (the sample 1). And spectrum of top blue layer once more confirms the presence of lazurite [20, 23].

Raman spectroscopy of samples 14–18 from central drum reveals only calcite in plasters. However, the color layers of these samples contain traces of restoration materials. Thus, gypsum was found in surface layers in samples 14, 15, and 16, titanium white—in 14 and 15 samples, as well as barium white, Prussian blue, and chrome yellow in cross-section of 15 [20, 24]. Pigments such as red and yellow ochres, lazurite, glauconite/celadonite, amorphous carbon most likely belong to the original twelfth century painting.

The main result for samples from outer walls (6 and 10) consists in presence of gypsum in plasters and paints. The set of pigments identified by Raman spectroscopy: yellow and red ochres, green earth, coal—are widespread in wall painting.

FTIR

FTIR spectra for samples 14–18 were collected from the surface of the pictorial layers (Fig. 5a). In all cases, peaks of calcite and clay minerals prevent reliable identification of the pigments. In addition, significant protein content was found in all samples due to strong Amide I vibrations at 1640 cm^{-1} and satellite Amide II

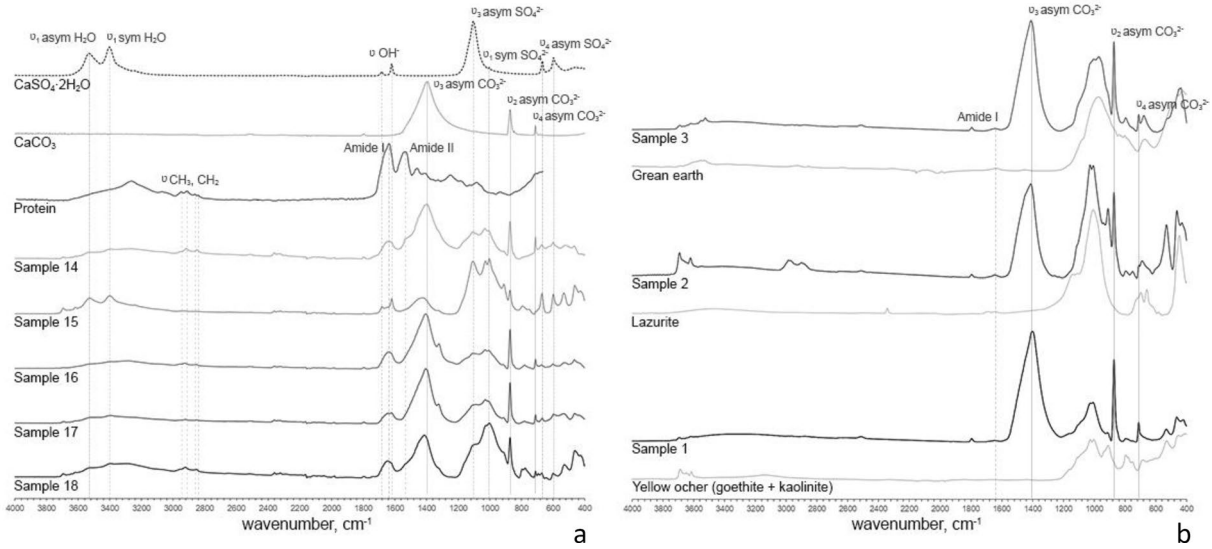

Fig. 5 FTIR spectra of organic binders in samples from the drum (**a**), some archaeological samples (**b**) and some suitable spectra from libraries

peaks at 1550 cm^{-1} are present in all spectra. Also significant amount of calcium sulfate dihydrate was identified [25].

FTIR spectroscopy investigation of samples 1–3 (Fig. 5b) suggests the presence of protein molecules as week peaks of Amide I vibrations were found in all spectra. So it can be concluded that such materials as egg white and/or egg yolk, casein etc. could be used as a binding medium or as a consolidant. Clarification of this issue requires additional research.

Samples 6–8, related to the "Deisis" composition above the portal of the west narthex of the Cathedral (Fig. 1d), are characterized by the presence of fats in the chloroform extracts (Fig. 6a), as well as proteins in aqueous extracts (Fig. 6b). So it can be suggested that egg yolk tempera paints were used for renovation of this composition. Another assumption is in consolidation the painting by the yolk during the restoration. The sample 5 also belongs to the "Deisis" composition, however, neither fats nor proteins are observed in the FTIR spectra of both extracts. That could be explained by insufficient amount of sample or a thin pictorial layer. Also it should be noted that high content of calcium sulfate was found in the FTIR spectra taken from the surface of the samples.

Samples 10 and 12 also belongs to the painting of the exterior walls of the Cathedral. Significant fat content was found in extracts obtained using chloroform from samples 10 and 12 (Fig. 6c), while water extracts practically do not contain organic substances (Fig. 6d). Thus it can be assumed that the painting of the central zakomara (arched gable) of the west facade was performed with oil paints.

A common feature of plaster samples 9 and 13 is the presence of polysaccharides or carbohydrates found in their aqueous extracts. Presumably, vegetable glue was used for the plaster base manufacture: gum or a decoction of cereals. However, the similarity of the binders used does not indicate the identity of the studied samples. Thus a significant amount of gypsum is present in the sample 9, while no gypsum was found in the sample 13.

Some of the salt efflorescence crystals (the sample 4) were also examined by FTIR spectroscopy. It is important to note that in addition to the expected salts of calcium sulfate (1092, 1002, 597 cm^{-1}) and carbonate (1416, 874, 712 cm^{-1}), peaks of bending vibrations of C-H bonds in CH_3– and CH_2= groups in the 3000–2800 cm^{-1} region were found. Together with Amide I (1645 cm^{-1}) and Amide II (1550 cm^{-1}) peaks this result allows to conclude that a significant amount of protein is present (Fig. 7).

Chemical microanalysis

To determine the anionic composition of salt efflorescence, the chemical microanalysis of the sample 4 was carried out. The studied sample practically does not dissolve in water. Adding 10% hydrochloric acid solution causes a moderate release of carbon dioxide indicating the presence of carbonate ions (lime). The

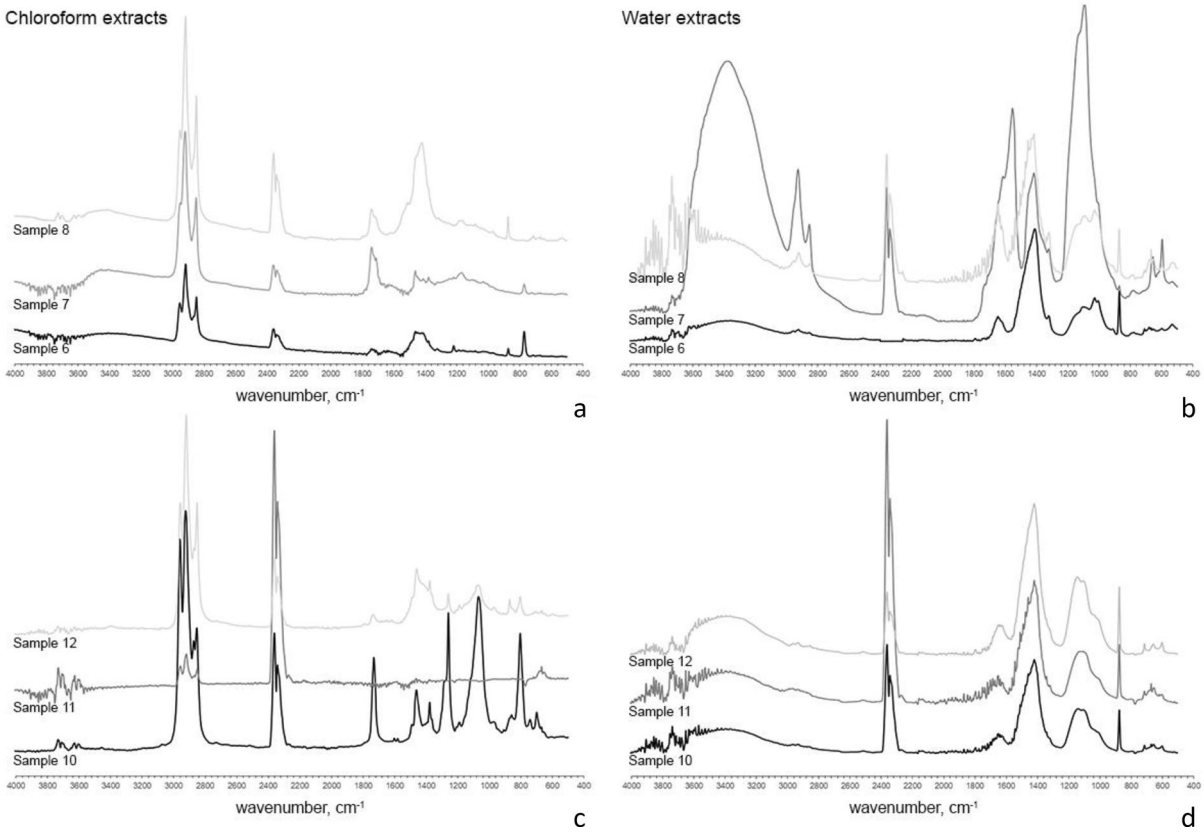

Fig. 6 FTIR spectra of organic binders in samples from outer walls: chloroform extracts (**a**, **c**) and water extracts (**b**, **d**)

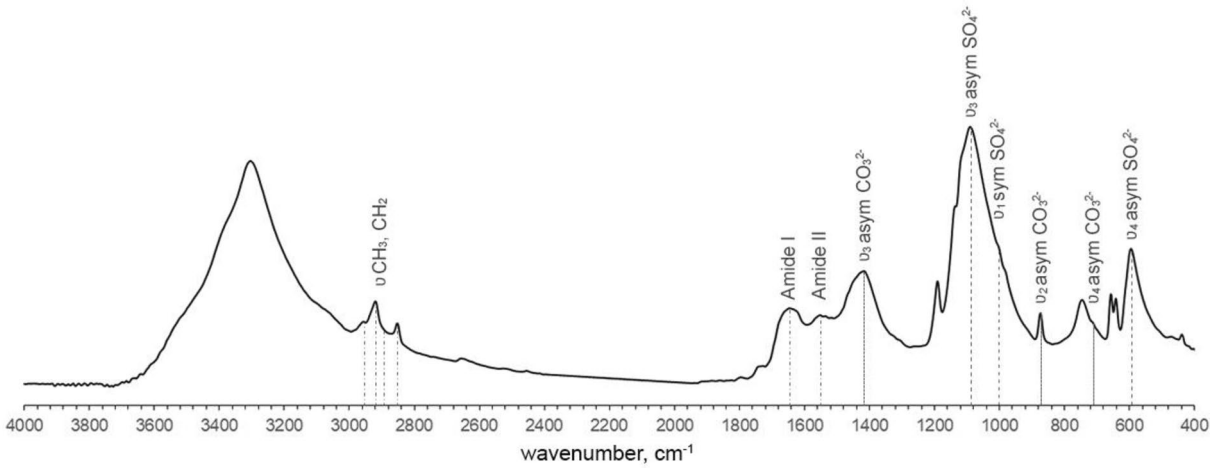

Fig. 7 IR spectrum of salt efflorescence (the sample 4)

reaction of water extract with barium chloride result in white precipitate ($BaSO_4$), which indicates the presence of sulfate ions in water extract. No visible changes occur after dropping silver nitrate solution to water extract. Thus there are no chlorides present.

Discussion

A project for the restoration of the unique cultural heritage site—the Christ's Transfiguration Cathedral of the Mirozhsky Monastery—is currently being prepared. The project implies the complete uncovering of

the ancient painting from all late additions and layering as it was done in some areas (above mentioned trial uncovering). However, traces of numerous restorations remain on the surface of the painting. They are not visible to the naked eye, but physico-chemical studies using modern equipment are capable of detecting these traces.

One of such imprint is gypsum. Lime-sand plasters are common to wall painting [17, 19, 26, 27]. The addition of gypsum to lime plaster is harmful to wall painting. Gypsum is a water soluble material. When exposed to moisture, freezing, and thawing the gypsum decrystallizes again, turns into powder, i.e. loses mechanical strength and deteriorates the painting [28]. This characteristic of gypsum is especially relevant the climate in the north-west of Russia with frequent transitions temperature through zero degrees Celsius.

The gypsum application technique in oil painting has been known since the middle of the sixteenth century, and the first mentions concern Italy and Spain. At the end of 17th–18th the addition of gypsum to levkas grounds found use even in Russian iconography, which, unfortunately, negatively affected their preservation. The first attempts to use gypsum in wall oil painting in Russia date back to the nineteenth century. Authors note that gypsum addition in plasters was possible only in heated churches [28].

Summarizing the above, we can assume that small gypsum additive in plasters [29] should be considered rather as an exception.

Often small amounts of gypsum are found on the surface of the color layer. This can be seen as the result of deterioration of lime plaster by sulfur dioxide [30].

Present in situ investigation shows that there is the quite large amount of sulfur on the surfaces of the walls. On the contrary, archaeological samples were not restored and no gypsum was found in them. Thus presumably gypsum was not used initially during the building and painting of the Cathedral in the twelfth century. We assume that the gypsum appeared on the walls of the Cathedral at nineteenth century during the restoration work under the leadership of N.M. Sofonov [31, 32]. The following uncovering of the ancient painting could not remove all traces of restoration materials. Investigations on the west wall once again confirms the later appearance of gypsum on the painting surface. Thus in those places where part of the upper layer of plaster could be removed during uncovering, much less gypsum was found.

Another important result to discuss is pigment set used by ancient artists. Red and yellow ochres are common pigments for medieval painting. They are stable and cheap thus most suitable for wall painting techniques. Green earths are very different in compositions and colors. Some researchers find glauconite in their studies, others find celadonite [33]. In our research we suggest using glauconite-rich green earth, as polarized microscopy revealed much more glauconite crystals compared to celadonite ones. Black pigment was identified by Raman spectroscopy as amorphous carbon. Presumably it is lamp black, because there are no large particles of coal were found by optical and polarized microscopy. Blue turns out to be very important since this color is very rare in nature. We found in the Christ's Transfiguration Cathedral lazurite. In the Ancient World and the Middle Ages it was very rare, because only one deposit in Badakhshan was known. So the ktitors of the Cathedral were powerful and rich. It is interesting that the use of lazurite in simultaneous paintings of Old Russian churches is no single [33–36].

Also some restoration paints were determined in areas of Sofonov's repainting, left on the clothes and faces of the prophets between the north and north-east windows of the drum during the restoration of D.E. Bryagin's team. Elemental composition of pigments showed the presence of large amount of lead, which may indicate the use of lead white, which is typical for N.M. Sofonov's workshop [37].

Organic binders are the important part of paints. In the samples related to the "Deisis" composition above the portal of the west narthex of the Cathedral, molecules of fats and proteins were found. It may indicate the presence of egg yolk, which could be used both for the preparation of tempera paints and for consolidation the painting. Analysis of samples from central zakomara (arched gable) of the west facade of the Cathedral shows that the painting was done with oil paints.

The analyzed plaster bases from the outer and inner walls of the Cathedral differ from each other in a various ratio of binder:filler. Lime is the main component of plasters. Also a significant amount of gypsum is present in the sample 9 taken from the outer wall of the Cathedral. In addition, in two samples 9 and 13 the similar binder based on polysaccharides or carbohydrates was found, therefore, it is most likely that vegetable glue was used for the manufacture of plaster: gum or a decoction of cereals.

Conclusions

The extensive physico-chemical study of unique paintings from the Christ's Transfiguration Cathedral of the Mirozhsky Monastery in Pskov (Russia) was carried out. Present state of the twelfth century unique painting uncovered from late overlapping layers was analyzed. In addition, nineteenth century N.M. Sofonov's repaintings, and twentieth century D.E. Bryagin's restoration, as well as exterior murals of the Cathedral and fragments of twelfth century paintings discovered

during archaeological excavations on the territory of the Mirozhsky Monastery were investigated.

Seven methods were used to carry out this study. Most of the fragments were investigated by in situ XRF analysis. To clarify questionable points, several samples were studied by neutron activation analysis, optical and polarized microscopy, Fourier transform infrared and Raman spectroscopy, and chemical microanalysis. The application of a variety of complementary methods provided a strong basis for representative results and allowed for in-depth conclusions to be drawn.

Elemental analysis of the main colors in the uncovered areas in the drum and several archaeological samples, presumably related to the original twelfth century painting, revealed the main used pigments: these are yellow and red ochres, green earth, lazurite, lime white, and "reft" (carbon black). A set of components in composite colors was determined.

The special attention is deserved with the fact of gypsum discovering by XRF, FTIR, and Raman spectroscopy since it is not typical material for the twelfth century in Old Russia.

Molecular analysis revealed the presence of significant amount of protein in samples taken from the drum of the Cathedral, so it is possible that such materials as egg white and/or egg yolk, casein etc. could be used as a binding medium or as a consolidant.

The salt efflorescence sample showed the presence of significant amount of protein in addition to the expected calcium sulfate and carbonate. So, it is possible to assume the consolidation of the pictorial layer in the lower row of the painting of the west arm of the naos of the Cathedral.

Molecular analysis of the paintings from the outer walls of the Cathedral showed the use of paints based on different types of binders.

Elemental composition of some plaster bases was determined by neutron activation analysis.

The study of murals by physico-chemical methods open up a new level in the knowledge about wall painting, which allowed to see the ongoing processes in painting most completely. The creation of a global analytical database, which previously did not exist in the field of studying and restoration of Old Russian wall painting, has begun. The database is necessary not only from the art history point of view for the theoretical study of murals, but also for the analysis of materials behavior for organization and conduct of restoration and conservation work.

Abbreviations

ATR	Attenuated total reflectance
FLNP	Frank Laboratory of Neutron Physics
FTIR	Fourier transform infrared spectroscopy
IASRWA	Interregional Agency for Scientific Restoration of Works of Art
INP	Institute of Nuclear Physics
IR	Infrared
JINR	Joint Institute for Nuclear Research
LLI	Long-lived isotopes
LOD	Limit of detection
MLI	Middle-lived isotopes
MP	Measuring point
NAA	Neutron activation analysis
NIST	National Institute of Standards and Technology
OM	Optical microscopy
PM	Polarized microscopy
SLI	Short-lived isotopes
UNESCO	United Nations Educational, Scientific and Cultural Organization
XRF	X-ray fluorescence spectroscopy
WWR	Water–water reactor

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OSP, AYuD contributed to experimental design, data collection, and processing. ABG contributed to samples collection and the art history context writing. SGL organized NAA. OSP and AYuD wrote and edited the manuscript. All authors read and approved the final manuscript.

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Declarations

Competing interests
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