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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

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Abstract

In 2012, the ruins of a temple of the old Russian period were found during archaeological research in the medieval historical territory of Smolensk. The archaeological complex consists of the ruins of an ancient temple, built in the middle of the XIIth century AD, and adjacent to it from the South-West of the territory, which housed the remains of the market XI–turn XIII–XIV centuries AD and necropolis XIII–XVI centuries AD. Chronologically diverse use of the investigated territory up to the XVIth century AD was determined by the nearby Church. Approximately 1000 fragments of wall paintings, 5 fragments window glass and 4 glazed floor tiles were found near the ruins of the Church building. For the first time fragments of wall paintings medieval of Old Russian temple were dated by the AMS radiocarbon dating and went through chemical-technological research (analysis of the plaster foundation, the definition of used pigments) by X-RAY diffractometry (XRD) and scanning electron microscopy (SEM/EDS). Optical microscopy also was used for visual observations of the samples of the wall painting. According to the results of the radiocarbon analysis, the fragments of the wall paintings were divided into two chronological groups. The earlier belongs to the last quarter of the XIIth–the first quarter of the XIIIth century AD. Samples of the wall paintings from the second group are dated back to the third quarter of the XIIIth century AD. A narrow range of Accelerator Mass Spectrometry (AMS) radiocarbon dating of fragments of the murals, obtained from carbonates due to the presence of high content of C14 isotope in carbon of the plaster, is simultaneous in age to the moment of creation of the plaster base. As a result of chemical and technological researches of the fragments of the wall paintings it was established that the plaster basis of the fragments of the wall painting consists of two layers. The plaster base contains organic binders. Chemical and technological analysis of pigments presents the following results: (1) the basis of the blue paint layer is ultramarine (mineral) and anatase (mineral); (2) the basis of the green paint layer is celadonite (mineral); (3) the basis of the brown paint layer is ochre (clay); (4) black particles in the colorful mixture of brown is an organic wood coal pigment.

Keywords: Russia, XIIth–XIIIth century AD, Church, Wall paintings, AMS radiocarbon dating, XRD, SEM/EDS and optical microscopy

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Introduction

Any remains of the temples, constructed in the period before the Mongol invasion to the lands of Rus' in 1237 AD–1240 AD, are considered rare archaeological findings. However, none of the previously known archaeological complexes associated with ancient Russian temples was examined using a complex of natural scientific research methods, including the parallel implementation of chemical and technological analysis of samples of wall paintings (the study of plaster base; determination of pigments used in paintings) and radiocarbon dating of carbon-containing mural fragments and masonry elements of the temple by atomic mass spectrometry.

In 2012 AD, 61 years after the last similar finding, the remains of a previously unknown old Russian church were unexpectedly discovered during archaeological excavations in the city of Smolensk at Krasnoflotskaya Street 1–3. The reconstructed area of this four-column single-domed temple with galleries is about 250–300 m². In the context of the historical topography, it was located on the site of the medieval territory named «Pyatnitsky End», on the right bank of the Pyatnitsky creek, which ran along the bottom of a ravine with the depth of 7–10 m. The territory on which the church was found adjoins the outer side of the tracing line of the destroyed section of the fortification wall of the Smolensk Kremlin, built in 1595 AD–1602 AD, not far from the place where the now-defunct Pyatnitskaya tower was previously located (Fig. 1), and is located on the left bank of the Dnieper river at a distance of about 150 m from the riverbank.

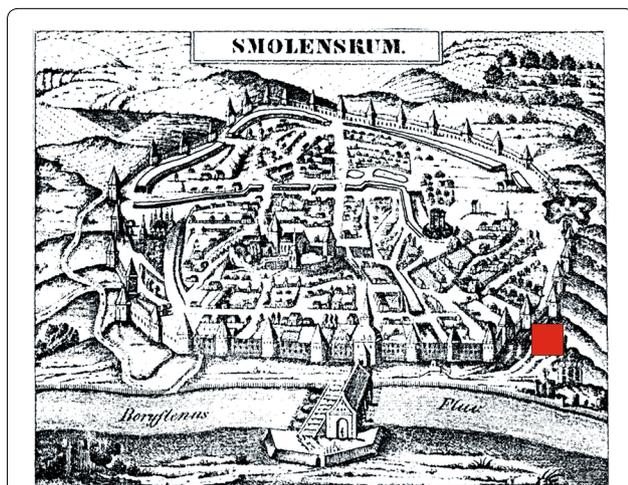
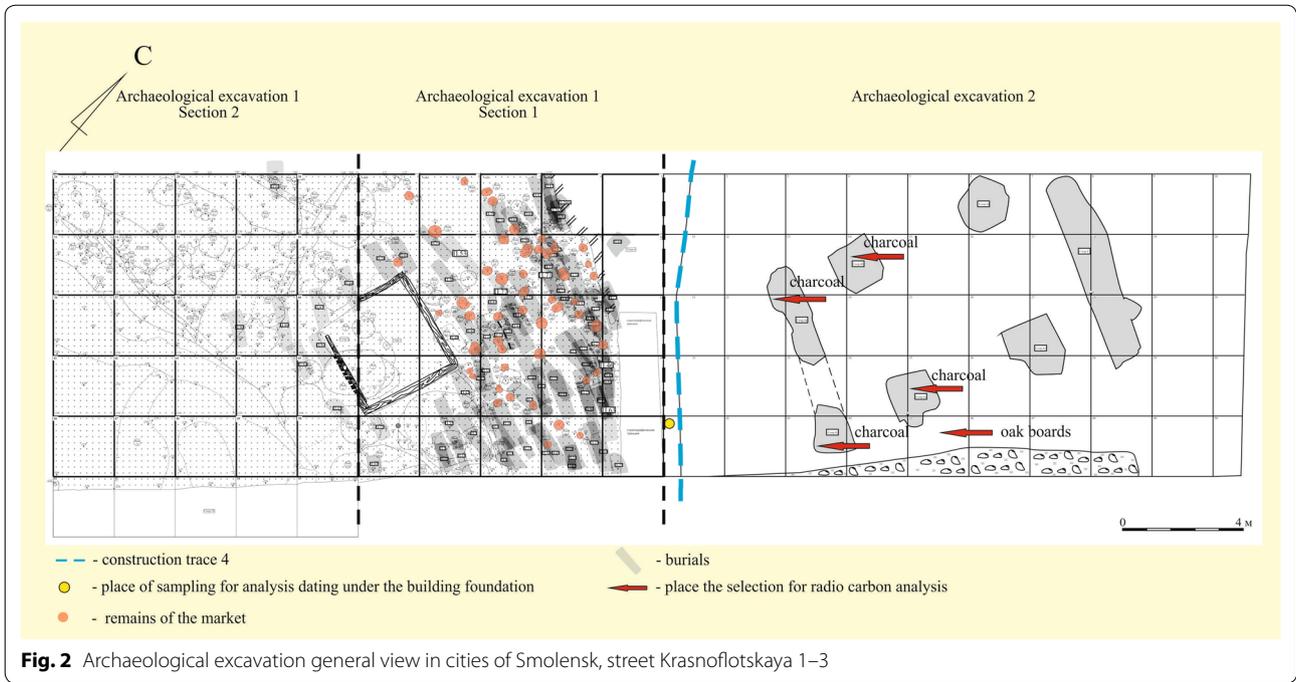


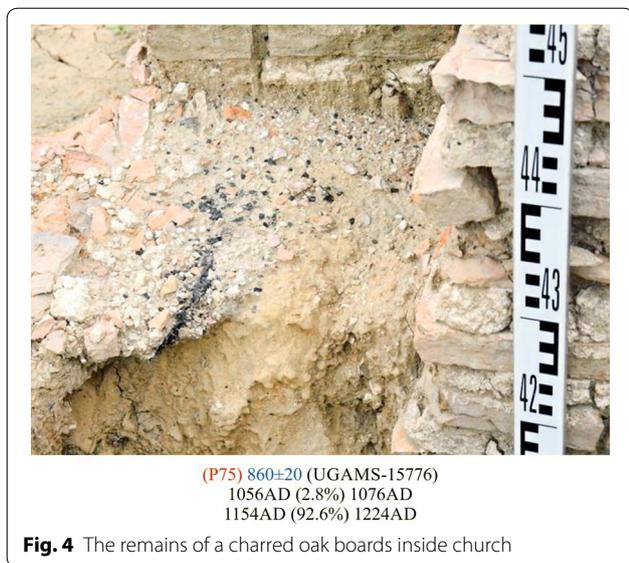
Fig. 1 Location of the investigated area on the plan of the city of Smolensk 1611 AD–1629 AD. A red dot marks the place of an archaeological dig in 2012

In 2012 specialists of the research team of the Capital Archaeological Bureau («CAB») carried out a preliminary clearing of the fragments of the found temple, after which these fragments were studied by a team of architectural archaeologists of the Institute of Archaeology of the Russian Academy of Sciences. At this time, the research group «CAB» conducted archaeological excavations on the territory adjacent to the temple. The study area near the temple (excavation 1) consisted of “Introduction” and “Results and discussions” sections with the total area of 205 m², measuring 10 × 10 and 10 × 10.5 m (Fig. 2), divided into squares of 2 × 2 m. Lithological deposits in the excavation with the capacity of up to 3.2 m were composed of sandy loam of brown and grey colour shades. The preserved cultural layer containing artefacts and buried objects of the Xth–XVth centuries AD: remains of buildings of a commercial space of the XIth–XIIIth century AD in the shape of 95 pillar holes and a necropolis of the XIIIth–XVth centuries AD, which included 91 burials (Fig. 2). The cultural layer was disassembled according to nominal layers (2–9) with the thickness of 0.20 m each with spatial instrumental organization of objects and findings [1, 2].

The most significant site going through the eastern wall of the investigated area (excavation 1, line of squares 10–15–20–25) was structure 4, with the area of 6.4 m² (Fig. 2). It was the south-western part of the galleries of the old Russian church, built chronologically later than the church itself, and dated back to the XIIIth century AD. The foundation of the galleries, cleared on the area of 6.4 m² and consisting of elongated boulders with smoothed edges with the longitudinal size of 11–23 cm, was cut into the ground from the level of layer 6 (– 108 to – 117 cm from the nominal zero) to the depth of 0.5 m to the levels, corresponding to layers 7–8.

A large number of objects related to the arrangement and decoration of this church was found in layers 6–8 of excavation 1: fragments of a wall painting, window glass, a part of a clay ceramic voice speaker (a clay jar built into the masonry of the walls, reversed into the inner part of the building. Voice speakers were used to reduce the load on the walls of buildings and to improve the acoustic properties of the premises), details of lead frames from windows and fragments of glazed tiles. In 2013 after the completion of the work of architectural archaeologists, the research team of «CAB» carried out the conservation of the discovered remains of the church, during which the samples of coal and wood from the masonry and structures of the Old Russian temple were selected for radiocarbon AMC dating. Wood from structures of the church was collected for dendrological analysis too. Pieces of charcoal selected for research were part of the masonry mortar of the temple for which they were





specially prepared. Fragments of the wooden boards from the temple taken for the research were severely charred, which indicates a fire in the temple, which destroyed its wooden structures.

Parts of stained glass, lead clips, glazed tiles (Fig. 3), oak board from the temple (Fig. 4) and fragments of wall paintings (Fig. 5) found during excavation 1, allow us to get a partial picture of its original arrangement. Wooden structures inside the church, according to the results of the dendrological analysis, were made of oak, floors and, perhaps, the elements of walls were decorated with glazed tiles of yellow–brown and dark red colors, small pieces of glass in lead clips about 10 cm long were used in the construction of the windows and the main color tones the wall paintings were dark blue and green.

Sample research methodology

The wall painting fragments were examined using radiocarbon AMC dating, XRD, SEM/EDS. Optical microscopy also was used for visual observations of the samples of murals. Several wall painting samples were used for radiocarbon AMS Dating. We had a possibility to study another 12 fragments of the wall paintings (Fig. 6) with an average size of about 5 cm² and 1.8–2.3 cm in thickness, representing the remains of non-reconstructed wall paintings from the background of decorative compositions and remains of clothes of the characters once depicted.

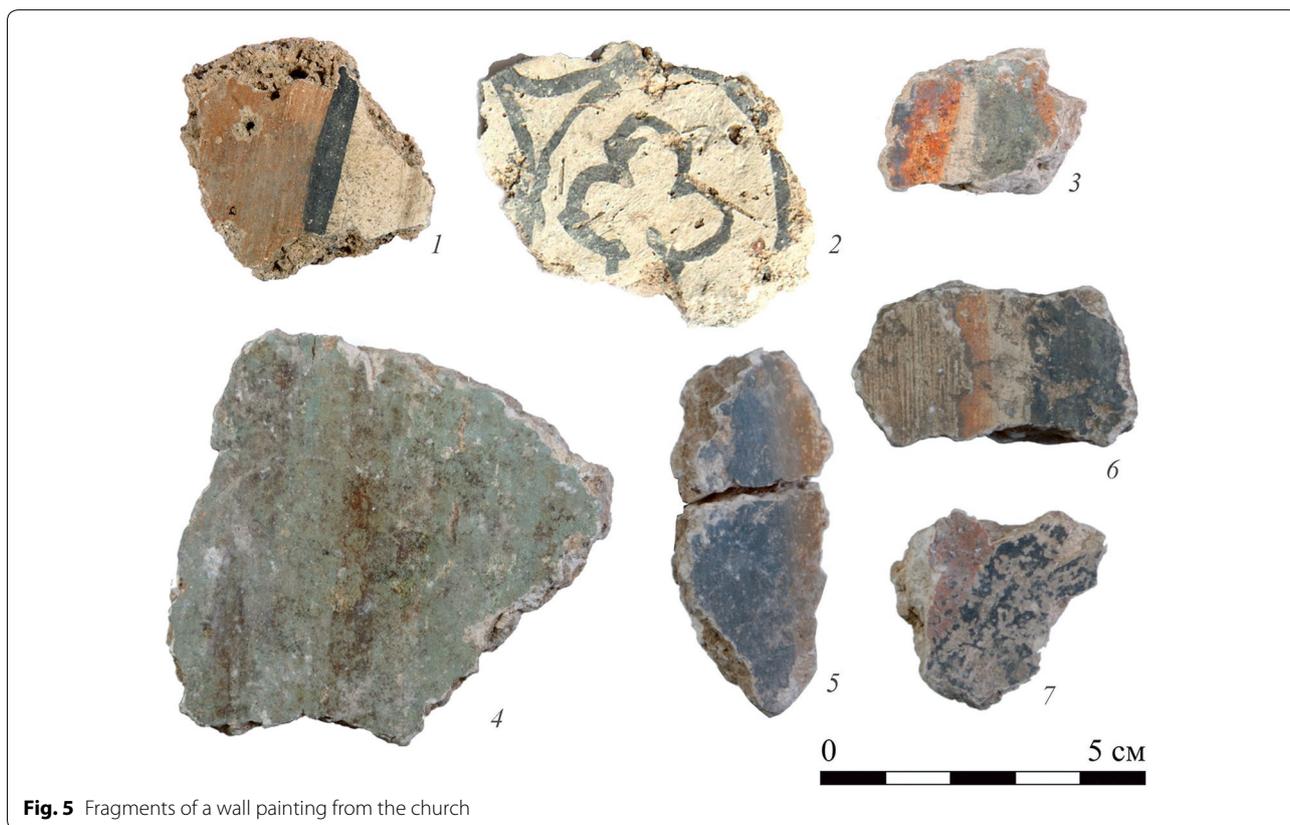




Fig. 6 The fragments of the wall paintings from the church which were studied. The red points indicate the analysis areas that were considered in the study of the composition of the paint layer for XRD and SEM/EDS methods

Radiocarbon AMS dating

To determine the radiocarbon age of the wall painting fragments, radiocarbon AMS dating of 4 samples of mural fragments, was carried out in the Center for Applied Isotope Studies (CAIS) at the University of Georgia, USA. The samples of carbonates and coal from the collected fragments of the mural were analyzed by the AMS technique according to the established method, normally used for fine art objects [3]. The samples were treated with 5% HCl at 80 °C for 1 h, then washed with deionized water through the fiberglass filter, and rinsed with diluted NaOH to remove possible contamination by humic acids. Samples were then treated with diluted HCl again, washed with deionized water, and dried at 60 °C. For AMS analysis, the cleaned samples were combusted at 900 °C in evacuated, sealed ampoules in the presence of CuO. The resulting carbon dioxide was cryogenically purified from the other reaction products and

catalytically converted to graphite using the method of Vogel et al. (1984) [4]. Graphite $^{14}\text{C}/^{13}\text{C}$ ratios were measured using the CAIS 0.5 MeV accelerator mass spectrometer. The sample ratios were compared to the ratio measured from the oxalic acid I standard (NBS SRM 4990).

Afterwards, the results of radiocarbon AMS dating of fragments of the wall paintings were compared with the results of radiocarbon dating by a similar method of samples taken from carbon-containing elements of the architectural remains of the temple—lime mortar masonry and burnt oak boards.

X-RAY diffractometry

In order to determine the composition and structure of the plaster base of the murals and pigments of blue, green, brown colors which were used in the creation of the murals of the church, samples no 1–12 (Fig. 6) were

analyzed. The studies were done on an ARL X'TRA X-ray diffractometer with Cu K α radiation (copper anode) and a 35 kV accelerating voltage; beam current was 40 mA; the angle range was 3–80°; at a 0.02° angle step. The weight of each of the samples was 10 mg. The compounds were identified using the PDF-2 database of the International Center for Diffraction Data (ICDD). When studying sample no 1 the diffractogram of the original fragment of the wall painting was taken, the ink layer on the surface was intact. From the surfaces of the wall painting fragments (samples no 1–12), a sample of the paint layer was mechanically taken out, which partially captured the trowel layer of the mural plaster base, which included kaolinite. The resulting sample was crushed to powder with a particle size of not more than 20 microns. The following sample of the plaster base with the size of 2 × 2 mm was taken from the internal parts of these fragment of the mural (sample no 1), which had not been exposed to the air: for this purpose, the wall painting sample was mechanically cleared from surface contaminants and dust.

Scanning electron microscopy

For the purpose of elemental analysis of the plaster base of sample no 1 and the qualitative comparison of the composition of the paint mixture of samples no 1, 3–12 (Fig. 6) these samples were analysed for on a Quanta 3D 200i scanning electron–ion microscope manufactured by FEI (Holland). The study was conducted in low vacuum mode in water vapor to avoid problems with electric charging of non-conductive samples, using reference samples in accordance with the algorithm proposed by Pukhov and Kurbatov [5]. When performing SEM/EDS analysis, the quantitative calculation of the element composition can be performed correctly under the following conditions: the sample has a homogeneous element composition within the scanning area of the electronic probe; the sample surface does not have roughnesses exceeding 30–300 nm in size, depending on the accelerating voltage used, i.e. the sample surface must be polished when analyzing at sufficiently large area.

Qualitative analysis of plaster base for sample no 1 was carried out in seven research areas (Fig. 10a). Sample preparation for elemental analysis consisted of sawing sample no 1 with a diamond wheel until it formed an even cut. No special preparation of samples to determine the chemical composition of pigments located on the surface of samples no 1, 3–12 was carried out. Due to subtlety and fragility of the colourful layers on the studied samples of the wall painting, it was impossible to polish them in the process of sample preparation. Therefore, the SEM/EDS analysis was held on the natural uneven surface of the paint layer, which prevented us from obtaining

the data for the appropriate quantitative calculation of the elemental composition of the studied paint layers on fragments of the wall painting.

Optical microscopy

Wall painting samples no 1, 7–9 (Fig. 6) were examined under a stereomicroscope LEICA MZ 125 (Germany) in a simple reflected and transmitted polarized light at a magnification of 40 times and were photographed from different angles using a KEYENCE VH-Z100UR (Microscope Multi Scan; Japan) optical microscope. The 3D magnification of the sample no 1 is demonstrated at the axes of the image. The structure of the plaster base of the wall painting fragments was studied too, as well as the pigments.

Results and discussions

Radiocarbon AMS dating

The radiocarbon dates of the mural fragments from the excavations in Smolensk contained in the plaster base, made from carbonates and coal, turned out to be about 30–160 years younger than the dates obtained for the carbon-containing samples from the masonry church solution, which has a calibrated 2 σ radiocarbon age around the middle of the XII century AD. (UGAMS-15774 P70 900 ± 20; UGAMS-15775 P85 940 ± 20) (Fig. 7). According to the results of radiocarbon AMC analysis, the wall painting fragments were divided into two chronological groups.

The earliest of them (Fig. 8, Table 1) is dated back to the last quarter of the XII—the first quarter of the XIII century AD (UGAMS-16215 no 6/2 880 ± 20; UGAMS-116216 no 4/8 880 ± 20; UGAMS-16217 no 1/10 890 ± 20). In general, it coincides in age with the radiocarbon date of oak wood coal, found inside the temple (UGAMS-15776 P75 960 ± 20, 2 σ 1056 AD (2.8%) 1076 AD, 1154 AD (92.6%) 1224 AD) (Figs. 4, 7). The radiocarbon age of the second group of wall paintings (Fig. 8, Table 1) belongs to the third quarter of the XIII century AD (UGAMS-112563 no 12/1 740 ± 20). A normal distribution of radiocarbon AMS dates was recorded: samples of materials used in the construction of the church studied in a similar way prove to be older than similarly studied samples of the wall painting fragments.

The same extremely minimal chronological error of ± 20 years was obtained for all AMC radiocarbon dates, which in fact is very unusual. This result is undoubtedly the consequence of the high quality of the used dating material, selected to minimize the influence of environmental factors, when all the pieces were taken from the inside of the fragments of the wall painting. We believe that the similar narrow value of

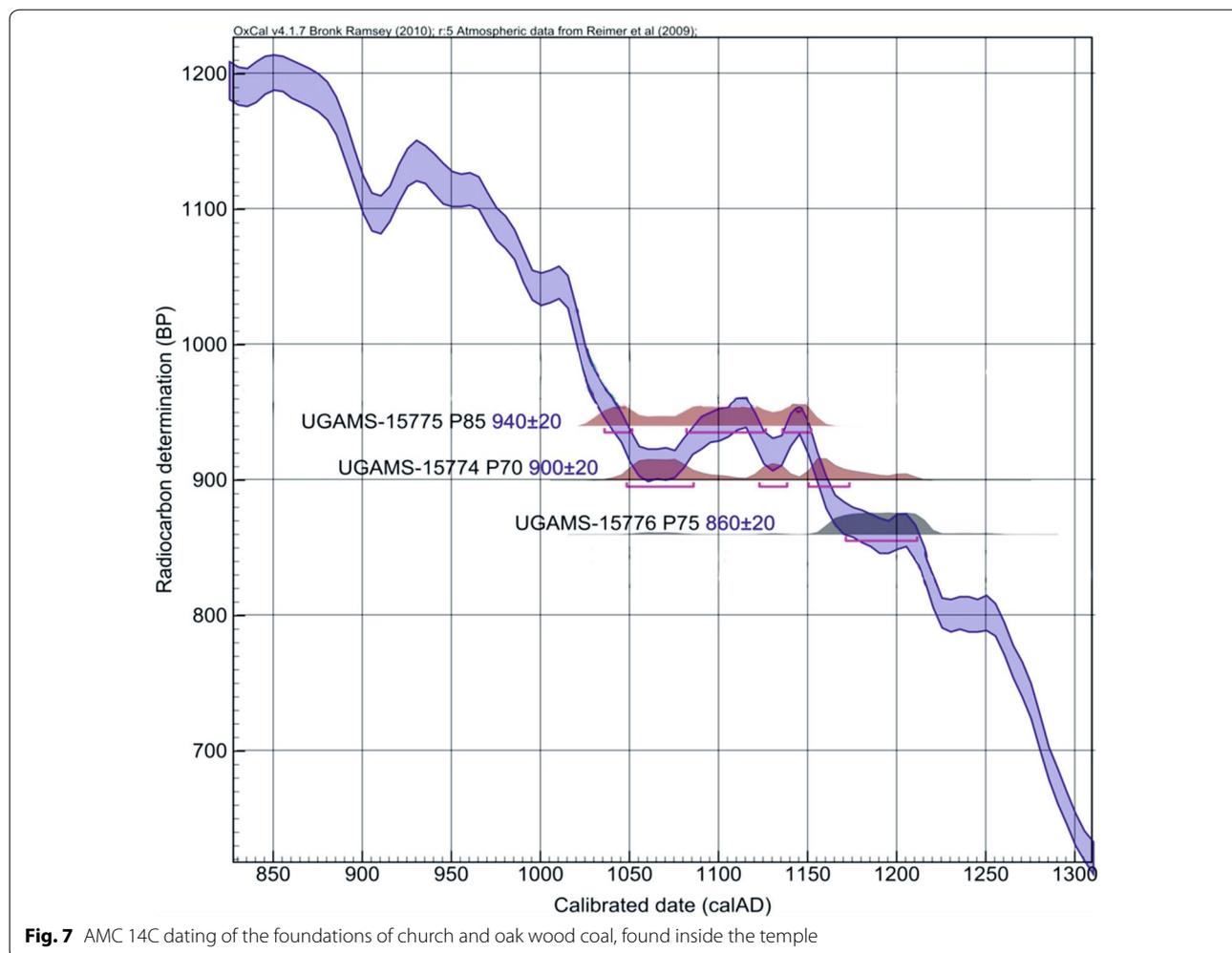


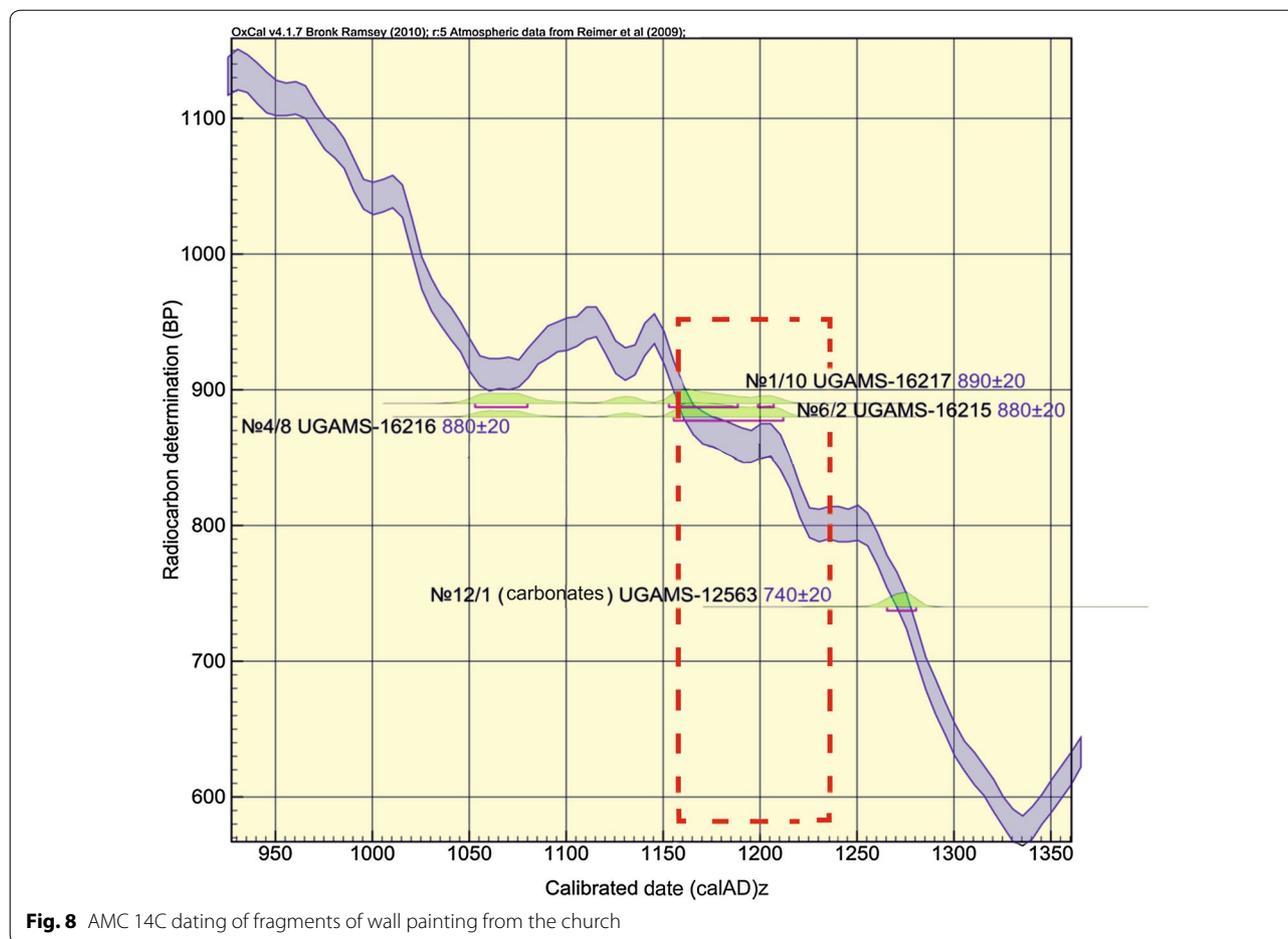
Fig. 7 AMC 14C dating of the foundations of church and oak wood coal, found inside the temple

the chronological error for all dated samples of wall painting (no 6/2, no 4/8, no 1/10, no 12/1) is explained by their highly uniform carbon saturation, dating back to the creation of the solution that served as the basis for the wall painting—for example, atmospheric carbon that got into this solution in the process of obtaining slaked lime.

Results of X-RAY diffractometry

A qualitative analysis of the fragment of the wall paintings (sample no 1) obtained using a diffractometer showed that its plaster base mainly consists of (CaCO_3) in the form of calcite and aragonite, which are known to have the same chemical composition, but at the same time possess different crystal lattice [6]. Also a small amount of quartz (SiO_2) was detected (Fig. 9a). The upper plaster layer of the mural plaster base consists of kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$). In samples no 4, 5 with blue colorful layer, ultramarine ($\text{Na}_4\text{Al}_6\text{Si}_8\text{O}_{23}\text{S}_4$) (Fig. 9b), in samples no 1, 10–12 ultramarine ($\text{Na}_4\text{Al}_6\text{Si}_8\text{O}_{23}\text{S}_4$)

and anatase peak (TiO_2) were detected (Fig. 9c). In the samples no 2, 6–9 of the mural, in the zone of brown colorful layer there is a high content of calcite (CaCO_3) and quartz (SiO_2), as well as traces of some amounts of kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$) (Fig. 9d). In sample no 3 of the wall painting, the zone of green colorful layer was explored. When conducting XRD analysis, glauconite, celadonite and chromceladonite have similar spectral characteristics. XRD analysis of sample no 3 gave the following result: $(\text{K}(\text{Mg},\text{Fe},\text{Al})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2)$. That is, based on the results of the XRD analysis of the green pigment, it is celadonite (Fig. 9e). Glauconite and celadonite are distinguished by the intensity of green color provided by Fe; there is no clear boundary between these substances from the mica category. As it is known, celadonite has a quality to retain color and keep it unchanged under the influence of air and light, and it was often used as a pigment mainly in wall paintings from Roman period [7–9] until XIV centuries in wall paintings in churches in Europe [10]. The green



lands as the pigments, mainly consisting of celadonite and glauconite, appear in Byzantine wall painting culture [11] and fragments of wall painting from Smolensk are undoubtedly related to them. Samples no 1–12 in the paint layer also contain trace contents of (SiO_2) and (CaCO_3), which were probably captured in samples of those paint layers from the plaster base during their selection (Fig. 9a–e).

Results of elemental analysis using scanning electron microscope

Qualitative analysis of the samples of the wall paintings using a scanning electron microscope confirms the data obtained using X-ray diffractometry. Elemental analysis demonstrates the presence of Al, Si, S, Na in the composition of samples no 4–5 which ensures the presence of ultramarine ($\text{Na}_4\text{Al}_6\text{Si}_8\text{O}_{23}\text{S}_4$) (Fig. 11a), as for the series of samples no 1, 10–12, in addition to the abovementioned elements, some Ti was also recorded, which indicates the presence of anatase (TiO_2) content in them (Fig. 11b). For samples no 2, 6–9, Al and Si were identified, which indicate kaolinite in the shape

of aluminosilicates ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$) which give brown color (Fig. 11c). In sample no 3, Mg, K, Si, Fe, Al were recorded, which corresponds content of celadonite or glauconite in the green pigment (Fig. 11d), but by XRD analysis it was determined that the green pigment is celadonite. Results of chemical elemental analysis for the plaster base of sample no 1 (Fig. 10a) demonstrate its typologically similar (Table 2), although heterogeneous composition with a high content of Ca and C as the main components, the fact of which indicates the presence of CaCO_3 in the sample. In addition, an extremely high carbon content of 8–28 Wt % may possibly indicate its organic origin, i.e. it appeared in lime solution after adding organic binders, or could have got into the lime from the atmosphere when it was extinguished. Manganese present in sample no 1 probably indicates the presence of clay materials in its composition in which it forms microcrystalline aggregations. (Table 2) [12]. The presence of Na, Al, and Si together with Mn allows one to presumably consider the concretion, studied in zone 1 of sample no 1, as manganese illite, belonging to the group of mica minerals of clay deposits (Figs. 10b, 11e, Table 2).

Table 1 AMS-radiocarbon dating of fragments of frescoes

Sample	Material	Laboratory number	$\delta^{13}C, \%$	Age ¹⁴ C	
				BP	BC/AD
(No 6/2) Wall painting fragment with blue pigment	Carbonates	UGAMS-16215	− 11, 9	880 ± 20	68.2% probability 1155AD (68.2%) 1212AD 95.4% probability 1048AD (17.9%) 1085AD 1123AD (4.5%) 1138AD 1151AD (73.0%) 1218AD
(No 4/8) Wall painting fragment with red pigment	Carbonates	UGAMS-16216	− 14, 9	880 ± 20	68.2% probability 1155AD (68.2%) 1212AD 95.4% probability 1048AD (17.9%) 1085AD 1123AD (4.5%) 1138AD 1151AD (73.0%) 1218AD
(No 1/10) Wall painting fragment with blue and red pigments	Carbonates	UGAMS-16217	− 13, 02	890 ± 20	68.2% probability 1053AD (24.7%) 1080AD 1153AD (37.7%) 1188AD 1199AD (5.8%) 1207AD 95.4% probability 1045AD (31.8%) 1095AD 1119AD (63.6%) 1215AD
(No 12/1) Wall painting fragment with blue and red pigments	Carbonates	UGAMS-12563	− 11, 8	740 ± 20	68.2% probability 1265AD (68.2%) 1280AD 95.4% probability 1240AD (1.2%) 1245AD 1251AD (94.2%) 1289AD

The possible high content in carbon of C14 isotope, simultaneous in age to the moment of creation of the plaster base, undoubtedly, was highly important to the accuracy of its radiocarbon AMC dating. This carbon, located in the lime layer of the mural, cannot be associated with the lime for the following reason: the results of radiocarbon AMC dating dated the age of the wall painting fragments back to the XIIth to XIIIth centuries. It is known that radiocarbon dating occurs on carbon isotope C14, which has a half-life of 5.700 ± 30 years (see Nubase-2016 database). The limestone formation period occurred approximately 300,000,000–150,000,000 years ago. Consequently we can state that no carbon suitable for the radiocarbon dating method could have been contained in plaster lime. However, the plaster is easily dated by the radiocarbon method and therefore contains a large amount of carbon introduced at the time of creation of the wall painting. Therefore the introduced carbon cannot have been a structural part of lime.

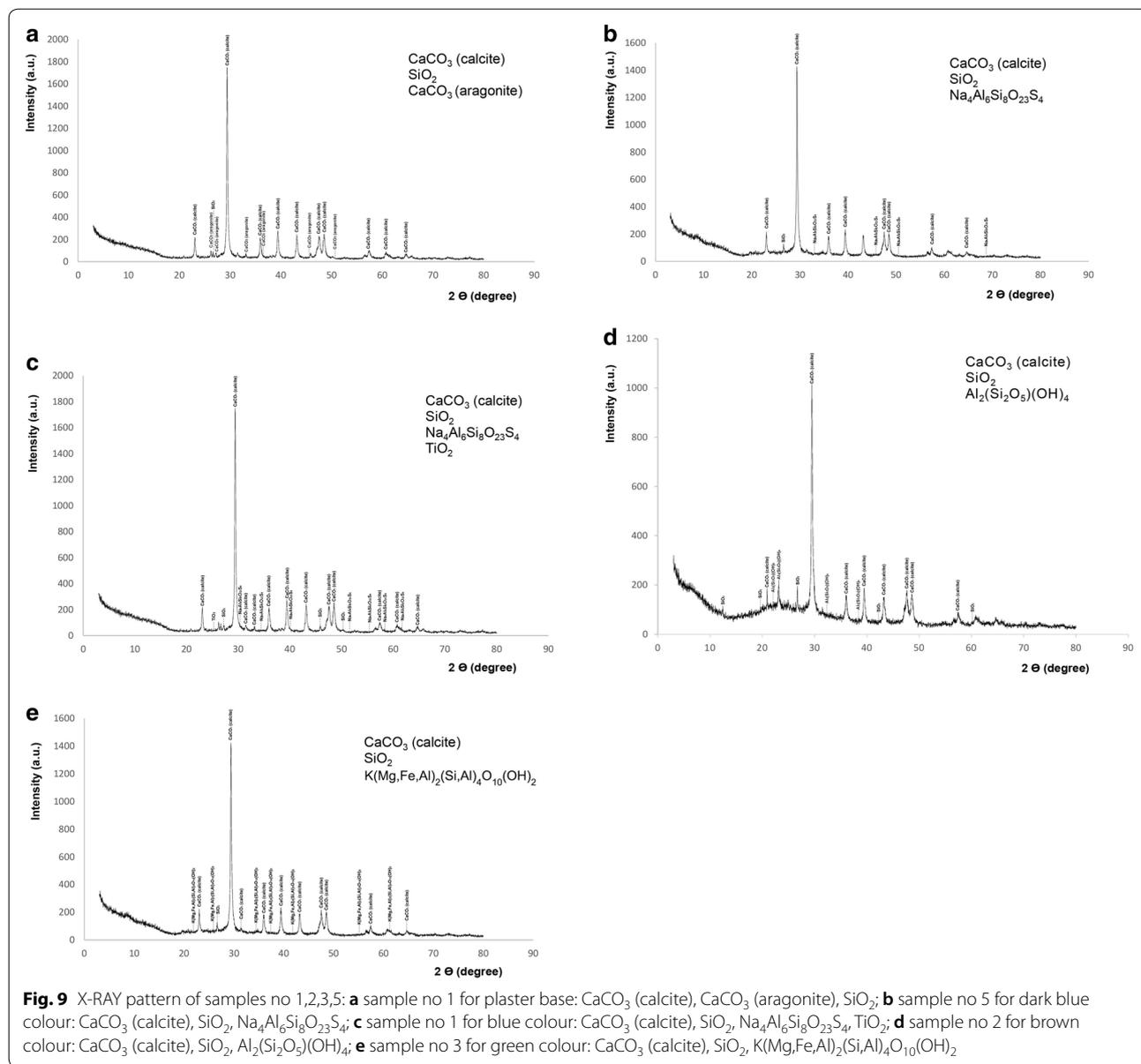
Results of visual observations using optical microscopes KEYENCE VH-Z100UR and LEICA MZ 125

The qualitative analysis of sample no 1 examined on a diffractometer and a scanning electron microscope, established the presence of ultramarine and anatase. The two-layer structure of the paint layer on sample no 1 was captured by 3D photograph, indicating the scale of the thickness of the paint layers using optical microscope

KEYENCE VH-Z100UR (Fig. 12). On this 3D photo the dark underlayer under the blue pigment consists of anatase. The blue-colored ink layer unevenly lying on top of the dark anatase underlayer, is ultramarine.

Optical microscopy method, by a KEYENCE VH-Z100UR and a LEICA MZ 125 optical microscopes, identified coal to form part of the paint layer in samples no 7, 8, 9. The visual criterion for determining coal in this case was the fact that the structure of black particles corresponded to the structure of wood materials. Results of the research by SEM/EDS and XRD methods did not detect a single pigment of black colour. It is known that organic pigments cannot be determined by SEM–EDS and XRD methods. Nevertheless, it is clearly defined when examining samples with the optical microscope in sample no 7–9. Consequently we can assume that the black pigment has organic nature, and identify it as coal, which particles have a fibrous composition, characteristic of the structure of wood.

The results of sample studies of plaster base sections from fragment no 1 using LEICA MZ 125 microscope revealed that the plaster base of the temple murals was two-layered. The lower, main layer of plaster consisted of unevenly mixed lime and clay-limestone rocks (Fig. 13) with a thickness of about 1.20 cm, with remains of straw filler 0.15 cm long and 0.02 cm thick. The second upper layer of plaster with a thickness of 0.15–0.20 cm was



mortar, containing a white lime compound with a shade of creamy color.

Conclusions

Consideration of the received radiocarbon AMC datings, allows us to outline the chronology of the temple construction in the ancient Russian period. According to the results of radiocarbon AMC dating, the construction of the temple took place around the middle—in the third quarter of the XIIth century AD. The wall paintings in the temple were created in the last quarter of XIIth—the first quarter of the XIIIth century AD. The likely renewal or addition to the wall paintings of the temple, determined

by the presence of fragments of the wall paintings of the group with a later radiocarbon age, occurred in the third quarter of the XIIIth century AD, which may have been related to the extension of the galleries of the church building.

The results of determining the composition of colourful mixtures by X-Ray diffraction, electron microscopy (SEM/EDS) and optical microscopy revealed that certain minerals (ultramarine, anatase, celadonite), clay (ochre), and organic wood coal pigment were used as pigments for creation of the murals under study. XRD method of studying of the green samples showed that the base of the green colourful layer is formed by celadonite. Anatase

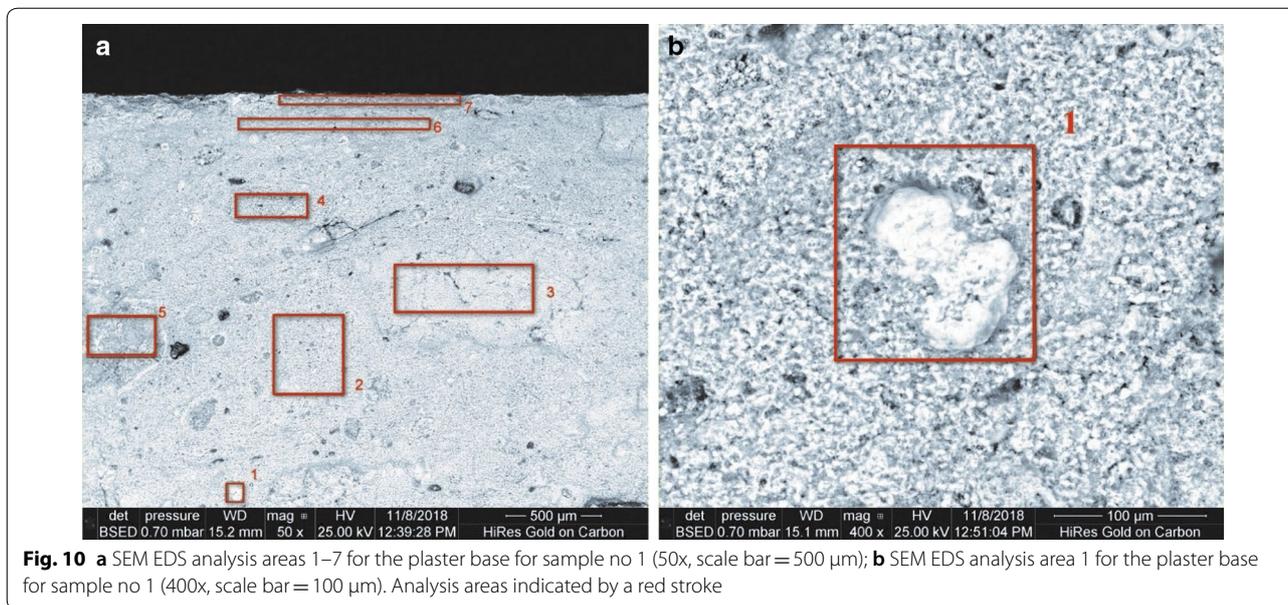


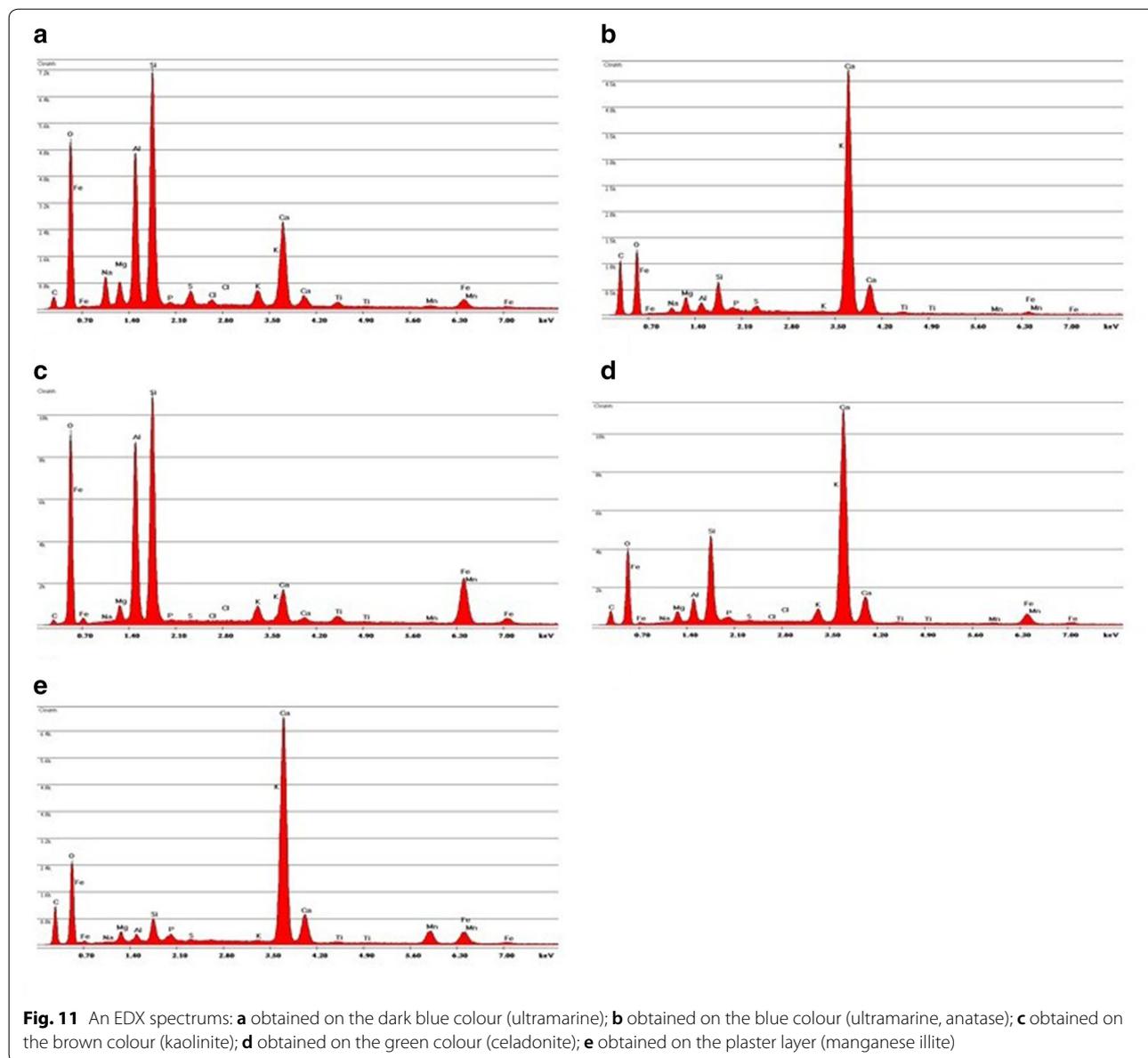
Table 2 The results of the elemental composition of the plaster base of sample No 1 by the XRD method

No zone	1	2	3	4	5	6	7
Element (Wt %)							
C	18, 14	26, 03	23, 04	23, 5	28, 09	25, 09	25, 91
O	49, 85	44, 82	46, 38	46, 3	43, 78	45, 04	44, 03
Na	0, 21	0, 24	0, 2	0, 13	0, 1	0, 21	0, 8
Mg	1, 06	1, 33	0, 87	1, 17	3, 27	1, 46	1, 44
Al	0, 63	0, 46	0, 23	0, 47	1, 17	0, 78	0, 77
Si	1, 78	1, 87	0, 62	1, 42	5, 26	2, 13	2, 2
P	0, 54	0, 29	0, 34	0, 27	0, 25	0, 28	0, 28
S	0, 13	0, 12	0, 11	0, 08	0, 05	0, 06	0, 42
Cl	0, 14	0, 16	0, 14	0, 17	0, 1	0, 09	0, 1
K	0, 15	0, 14	0, 09	0, 13	0, 13	0, 11	0, 12
Ca	21, 35	23, 75	27, 7	25, 9	15, 68	23, 68	23, 12
Ti	0, 22	0, 08	0, 02	0, 04	0, 07	0	0, 24
Mn	2, 93	0, 12	0, 03	0, 06	0, 02	0, 04	0, 04
Fe	2, 88	0, 57	0, 23	0, 39	2, 03	0, 52	0, 51

was first recorded as a pigment in ancient Russian wall paintings. Previously, anatase was considered only as a material used to produce titanium whites, which became widespread after the second half of the XIXth century. However, the presence of anatase in the palette of ancient artists was recorded in archaeological objects from different eras and civilizations. This mineral was found among pigments on the territories of Roman villas of the Iith century AD in England [13], as well as on polychrome decor of XVIth century Chinese porcelain originating from Portuguese ships sunk near the Cape of Good Hope [14].

The presence of blue colour ultramarine on the colourful layer of the studied fragments of the wall paintings is one of the earliest examples of this mineral being used in the paintings of ancient Russian temples as it was the most expensive pigment of the Middle Ages [15].

The creations of blue colour were also recorded in the study of XIVth century wall paintings from Patriarchate of Peć Monastery in Serbia, but there it was produced from cheaper pigments—coal and azurite [16]. This is explained by the fact that the clients who ordered those murals were not members of royal family. Expensive ultramarine is present only in the XIIIth century



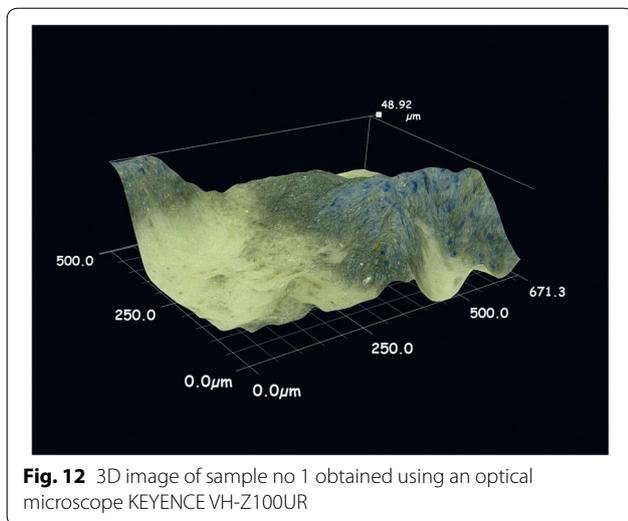
wall paintings of Serbian monasteries Žiĉa and Mileševa, painted by the order of kings of Serbia who had the financial ability to purchase them [17, 18].

In ancient Russian wall paintings of the XIth– XIIIth centuries AD, apart from this finding in Smolensk, pigment ultramarine is present only in Novgorod the Great churches, the customers of which were also princes: it is present on the murals of St. George's Monastery of St. George (built in 1119 AD), in the drum of St. Sophia Cathedral (built in 1045 AD–1050 AD), in fragments of XIIth century AD murals from the altar part of the Nikolo-Dvorishchensky cathedral (built in 1113 AD–1136 AD) [19]. From these historical analogies it can

be concluded that the creation of the church of Smolensk was ordered by a prince.

The two-layer structure of the plaster base is confirmed by XRD method and by optical microscopy.

The two-layer structure of the original plaster of the wall paintings foundation also exists in the Church of St. John the Theologian (built in 1173 AD), located 750 meters away from the explored territory. A large amount of carbon, up to 28 Wt%, recorded during elemental analysis on the electron scanning microscope proves the likely presence of an organic binder in the plaster base of the murals.



Abbreviations

XRD: X-RAY diffractometry; SEM/EDS: Scanning electron microscopy/energy dispersive x-ray spectroscopy; AMS radiocarbon dating: Accelerator mass spectrometry radiocarbon dating; CAB: The capital archaeological bureau; CAIS: Center for applied isotope studies; ICDD: International center for diffraction data.

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Competing interests

The authors declare that they have no competing interests.

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