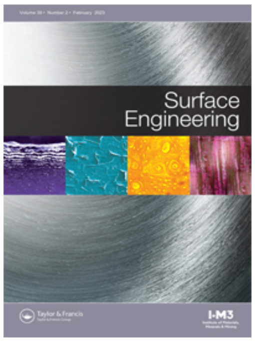


Surface Engineering

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/ysue20

Substrates and preparation layers under the wall paintings of the St George's Cathedral (1119 CE) at Veliki Novgorod

Alessandra R. G. Giumlia-Mair, Vladimir V. Sedov & Olga Etinhof

To cite this article: Alessandra R. G. Giumlia-Mair, Vladimir V. Sedov & Olga Etinhof (2023) Substrates and preparation layers under the wall paintings of the St George's Cathedral (1119 CE) at Veliki Novgorod, Surface Engineering, 39:2, 139-149, DOI: 10.1080/02670844.2023.2202007

To link to this article: https://doi.org/10.1080/02670844.2023.2202007

Published online: 03 May 2023.

SURFACE ENGINEERING
2023, VOL. 39, NO. 2, 139–149
https://doi.org/10.1080/02670844.2023.2202007

Substrates and preparation layers under the wall paintings of the St George's Cathedral (1119 CE) at Veliki Novgorod

Alessandra R. G. Giumlia-Mair [a,b], Vladimir V. Sedov[a] and Olga Etinhof[a]

[a]Institute of Archaeology, Russian Academy of Sciences, Moscow, Russian Federation; [b]AGM Archeoanalisi, Merano, Italy

ABSTRACT
The Cathedral of St. George is located in the Yuriev Monastery, in Novgorod, one of the capitals of ancient Rus (The Great Novgorod). The wall paintings were completed around 1120 CE. The Cathedral or its parts were renovated in different periods. The fragments of the twelfth-century frescoes were deposited under the new floor and in the area around the Cathedral. Archaeological excavations of the Institute of Archaeology of the Russian Academy of Sciences in Moscow brought to light a large number of fragments of frescoes. The Laboratory for Architectural Archaeology and Multidisciplinary Methods in Architectural Research of the Institute began to study the fragments in 2021 and presents here the first results of the research on substrate and preparation layers of the paintings. Our aim was tdistinguishing the different phases of the wall paintings. The plasters used in the twelfth century are different from the later ones and contain different aggregates.

ARTICLE HISTORY
Received 16 January 2023
Revised 27 March 2023
Accepted 9 April 2023

KEYWORDS
Frescoes; cathedral; Novgorod; substrates; mortar; aggregates; pigments; underpaint

Introduction

The Cathedral of St. George (Figure 1) is located in the Yuriev Monastery, to the south of the ancient town of Novgorod, one of the capitals of ancient Rus, now called Veliki Novgorod (The Great Novgorod). The church was founded in 1119 CE at the behest of the Prince of Novgorod, Vsevolod Mstislavich, and its wall paintings were most probably completed around 1120 CE.

In later periods the Cathedral or parts of it were renovated several times and, in 1902 the early frescoes were removed from the walls and were partly deposited under a new floor, built 1,5 m higher than the original floor. Other heaps of fragments were scattered in the area around the church in several places. The only preserved parts of the twelfth century frescoes inside the church are still visible *in situ* in the niches of some of the windows and on the parts of wall that had remained hidden under the new floor level. However, the paintings in the contemporary adjacent tower are still *in situ* and almost completely preserved. The excavations of the Institute of Archaeology that began in 2013 and are still ongoing, brought to light literally tens of thousands of fragments of wall paintings of the different periods from under the floor of the Cathedral and from other trenches dug in the area around it [1–4]. Many of the fragments show recognizable details, such as faces of saints (Figure 2), writings and graffiti recording births and deaths that coincide with the texts in the chronicles of the time. The finds are therefore very important for the reconstruction of the history of the period, for the history of Novgorod and for the study of Russian-Byzantine art.

In 2021 the team of the Laboratory for Architectural Archaeology and Multidisciplinary Methods in Architectural Research of the Institute of Archaeology of the Russian Academy of Sciences in Moscow, began to analyse the fragments of wall paintings of the different periods, with special attention to the substrates of the wall-paintings, the composition, preparation, structure and thickness of the plasters and mortar, its aggregates, other kinds of preparation layers, pigment layers and underpaint. Our first objective was that of finding a way to date the fragments. After detailed analyses we can now clearly distinguish the wall painting fragments from the different periods. The second aim was the reconstruction of the artists' working habits. To do this we have studied the painting techniques employed by the artists i.e. how they prepared the plasters, the substrate layers, the pigments and how these elements were worked and applied in the different periods of the Cathedral.

Our team consists of archaeologists, art historians and analysts, and we consulted different editions of ancient texts, for example, Vitruvius, Pliny, Cennino Cennini and Dionysos of Fourna, but also early Russian translations of ancient handbooks for artists that can be of help in understanding the different working stages of the Byzantine artists.

CONTACT Alessandra R. G. Giumlia-Mair giumlia@yahoo.it Institute of Archaeology, Russian Academy of Sciences, Moscow, Russian Federation; AGM Archeoanalisi, via della Costa 4, 39012 Merano, Italy

Figure 1. The Cathedral of St. George (Figure 1) in the Yuriev Monastery, Veliki Novgorod, seen from the river Volkhov.

Materials and methods

All samples have been examined with the naked eye, optical magnification devices, a digital microscope, and an optical microscope (henceforth OM). This kind of investigation is very important and allows a first screening of the materials. In the laboratory, we used several microscopes but mainly an Olympus BX51. When we were dealing with *in situ* paintings, as for example in the tower of the St. George's Cathedral, we employed a digital Proscope with 50 x magnification and a portable Levenhuk with variable magnification.

Subsequently, we analysed around 250 fragments of wall paintings of different colour and their substrates with a portable X-ray fluorescence spectrometry device (henceforth pXRF). As a comparison and to obtain measurements of well dated pigments, XRF measurements were also performed on several areas of different colour of the twelfth-century paintings still *in situ* in the church and in the tower. The aim of this kind of analysis was that of obtaining a first screening of the material and a first rough subdivision of the pigments into groups.

The XRF device employed was a portable Bruker Tracer i5 with Artax™ advanced spectral analysis PC software and a micro-X-ray tube with a rhodium anode. The measurements were carried out on an area with a diameter of 8 mm with 15 keV and 11.35 A. The acquisition time was 60 s per measurement. Several measurements were acquired on each fragment whenever this was needed, for instance, when different colour nuances could be distinguished, or when different structures had been recognised at the microscope in the layers of painting or in the intonaco. We use the mean of the various measurements.

The small samples taken from the fragments were then mounted in epoxy resins and polished by using 1200, 2000 and 4000 paper first and then diamond paste (3 and 1 micron) and finally made conductive with graphite. They were then analysed in the scanning electron microscope with energy dispersive spectrometry Tescan Vega Compact SEM with TESCAN Essence™ EDS with the following operating conditions: 20 kV accelerating voltage, 12 mA beam current, 15.8 mm working distance, counts of 100 s per analysis, dead time of approximately 25%. The measurements were processed using the AZtecLive-Lite EDS Software.

In this paper, we call *arriccio* or mortar the first, lower, rough layer, which is directly applied on the wall, *intonaco* or plaster the second finer preparation layer applied on top of the *arriccio*, and *intonachino* the last upper layer immediately under the pigment (Figure 3). The terms *arriccio*, *intonaco* and *intonachino,* and mortar, lower plaster and upper preparation plaster are equivalent, but the Italian terms

Figure 2. One of the fragments with the representation of a face with a halo around the head: an older woman wearing a transparent veil under a thicker cloth.

are conveniently short and commonly employed in the international bibliography [5]

Results

Plaster and aggregates

The autoptic and microscopic examination showed that the twelfth-century wall-paintings of the Cathedral of St. George mostly consist of three layers, applied on the church walls, which are built with rows of stones and plinths (i.e. Byzantine bricks with a flat and rectangular shape). The first layer, the *arriccio*, is applied directly to the masonry of walls and pillars of the church. This rather thick layer consists of lime with irregular, small and large inclusions of brick (plinth) fragments and sand. The second layer of the twelfth-century fragments is the *intonaco*. This layer is 4–5 cm thick, less than the *arriccio*, very white and it does not contain brick fragments, but only some straw (Figure 4). The third layer, the *intonachino*, is 3–5 mm thick, much thinner than the *intonaco*, and consists of fine slaked lime applied on the previous layer. In some cases, a much thinner lime wash was also added on the *intonachino* just before applying the pigments (Figure 5), most probably to humidify the drying layer.

The use of well refined and purified intonaco reminds of the procedure recommended by Cennino Cennini: An important passage in the famous Libro dell'Arte (The Book of the Art), written by him in Italian (end of the 14th – beginning of the fifteenth century AD), describes how slaked lime was prepared to be used as a pigment [6]. We can hypothesise that a similar, if less elaborate, procedure was used for the lime employed in the plaster or *intonaco*. He recommends taking white slaked lime, reduce it to powder and place it in water for eight days, changing the water every day and mixing the lime carefully, so that all 'fatness' (i.e. the impurities) is eliminated. After eight days, the lime should be formed into small loaves and left to dry in the sun on a roof. The longer the loaves are left to dry the whiter they become. When the loaves are completely dry, they are ground on a stone slab with the addition of water and new loaves are formed. This is repeated twice and then the lime is 'good to be worked on frescoes, i.e. on the wall without tempera (binding

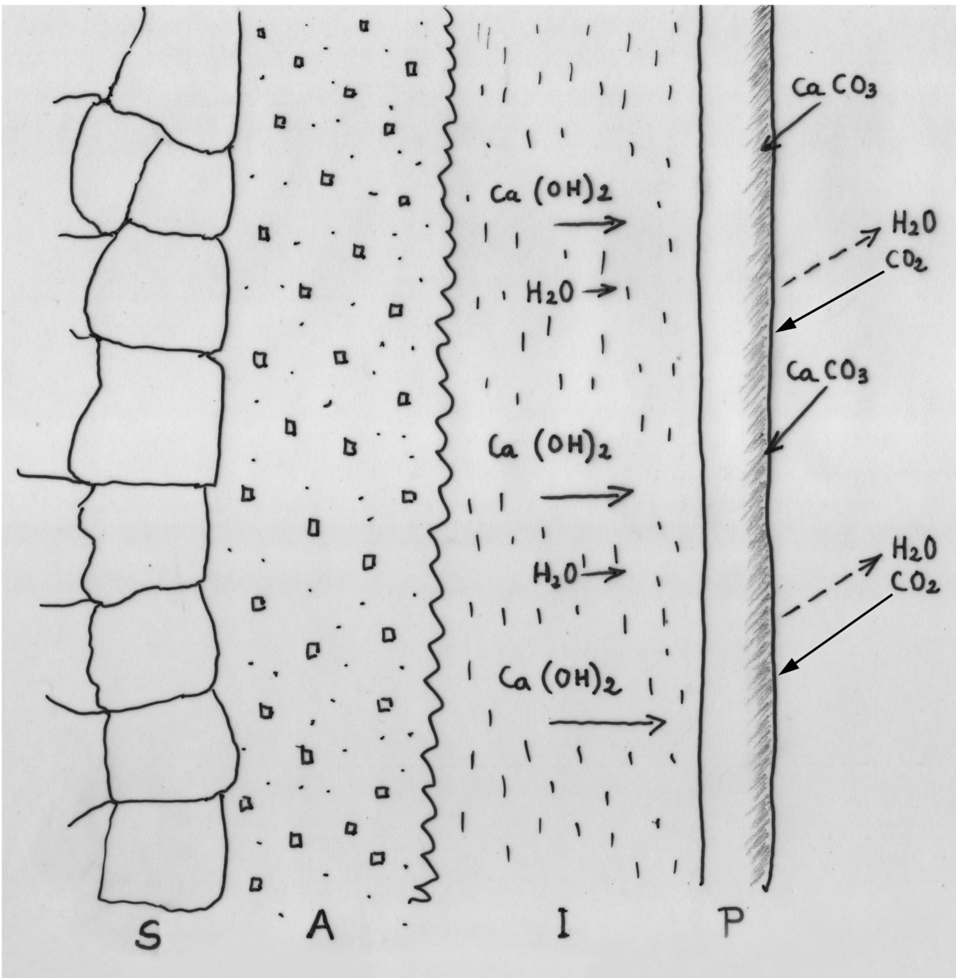


Figure 3. The drawing shows the typical scheme of the twelfth-century frescoes and the mechanism of the carbonation process of frescoes. From the left: support i.e. wall (S); mortar or *arriccio* (A); plaster or *intonaco* (I); pigment (darker) on upper preparation layer or *intonachino* (P).

material)'. As a final comment he adds 'and without this you cannot do anything, like for example skin tone and other mixtures of colours done on the wall, i.e. on fresco; and it never wants any kind of tempera'. (transl. A.Giumlia-Mair).

In the fragments with this very white and well refined plaster we identified some straw and a very small amount of clean sand and brick fragments as aggregates. It is important to note that this kind of plaster is always found on fragments with a pigment

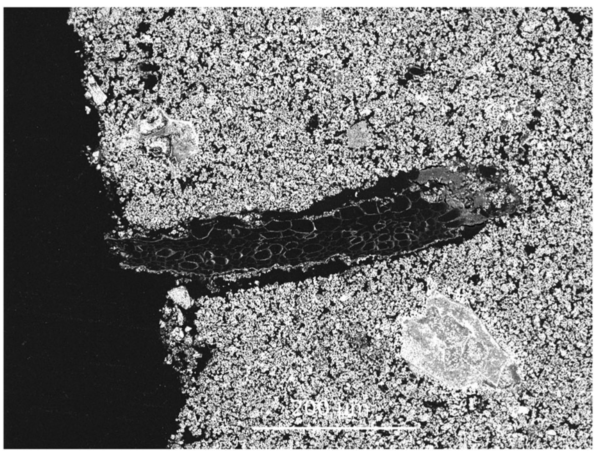


Figure 4. SEM micrograph showing a straw fibre in the plaster of a fragment of wall painting.

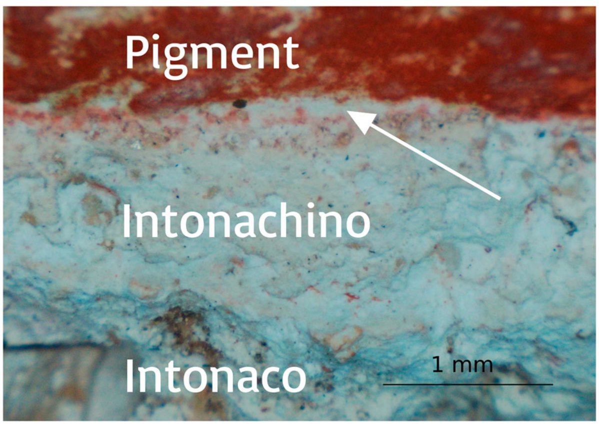


Figure 5. The photo taken at the microscope (x50) shows a layer of red ochre on a compact and very white layer of *intonachino*, under which the *intonaco* with more aggregates can be recognised. The arrow shows a thin layer of lime wash under the red pigment.

layer applied always in one direction and very regularly. This seems to be the typical way of applying pigments on the fresco remains of the twelfth century, while on other fragments the pigment is less homogeneous. The addition of straw as aggregate to the plaster can be also considered a technique of this period.

The text of Nectarius or Nektar, archbishop of Ohrid (1599), instructs to add straw, washed, and cut with a length of half a digit, and some sand to the lime, and leave it to rest for three days. After applying this mixture on the wetted wall, another layer of *intonaco* mixed with flax fibres must be applied on top of the first, so that it completely covers the lower layer. Finally, he stated that the last layer must be carefully levelled and smoothed, and immediately painted before it dries out [7]. A second important text, the Herminia (handbook in Greek) of Dionysius (or Denys) of Fourna i.e. Dionysius Furnoagraphiota (1670–1744), based on much older texts, describes a mixture of lime and straw for the lower layer, the intonaco, and a mixture of lime and flax for the finer upper layer i.e. the *intonachino* [7,8]. Indeed, in several samples dated to the twelfth century (i.e. IUR ow 20 DB5l, cat.n. 1468; and IUR R up1, cat.n. 1493) and in the white and compact plaster of the frescoes in the tower we identified fibres of flax on top of the intonaco mixed with straw (Figure 6).

Further, Dionysius of Fourna recommends applying intonaco in a layer of two or more *digiti* (one *digitus* corresponds cm 1.85 cm) on an abundantly wetted brick wall and adds that during the winter the intonaco should be applied in the evening and again in the morning, while in the good season the most convenient time can be chosen by the painter [7,8].

In two samples (IUR F 21 MB1l, cat. N. 1492, and IUR Rl, cat.n. 1493), we identified, in the same kind of white and compact plaster, a small amount of wood shavings (Figure 7), apparently from a carpenter's workshop, instead of straw. This kind of aggregate represents a cheap and useful substitute of straw and was possibly employed in a period in which straw was not readily available, for example in difficult or cold periods, when straw was a much-needed fodder for bovines and horses.

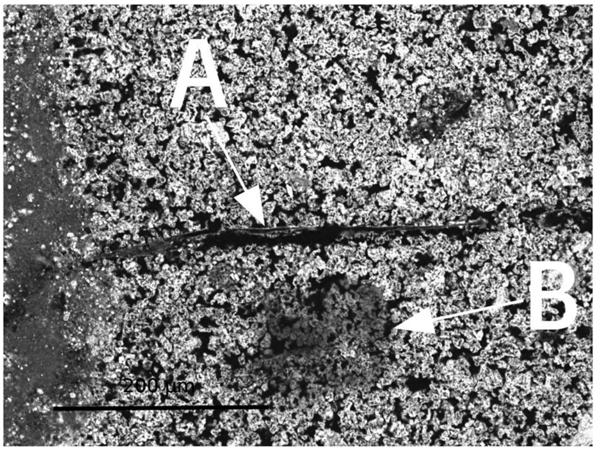


Figure 6. SEM micrograph showing a flax fibre (A) and a stem of straw in section (B) mixed as aggregates in the intonaco.

On samples on which the pigments are applied in a much more irregular way the plaster is also different: there are several layers, and it contains a large amount of rather rough sand (Figure 8), but no straw or wood. Further, these samples also show a layer of finer lime or possibly of lime milk under the pigments, which also seem to be applied in more layers. This indicates that tempera painting applied *a secco*, and not fresco was the technique used for these wall paintings. These fragments certainly belong to a later phase, perhaps to the fifteenth century additions and repairs in the church.

Red layers under the intonachino

In some of the fragments, apparently belonging to the twelfth-century phase of the frescoes in the Cathedral of St. George, the *intonachino* is well purified, and under this layer of preparation, which is around 3 mm thick, there is a very noticeable layer of red pigment (Figure 9). The Roman *intonachino* was sometimes coloured, mostly with a pink or yellow pigment, different from that painted on the top [9,10], but this seems to be an altogether different technique. In the St. George's Cathedral, the red pigment under the plaster layer is also still visible in some corners where part of the original twelfth-century frescoes was preserved under the floor, but has now lost the pigment and *intonachino* layer (Figure 10).

Red coatings under the *intonachino*, similar to those identified in the Cathedral of St. George, are known from earlier sites, for instance in Italy, in the

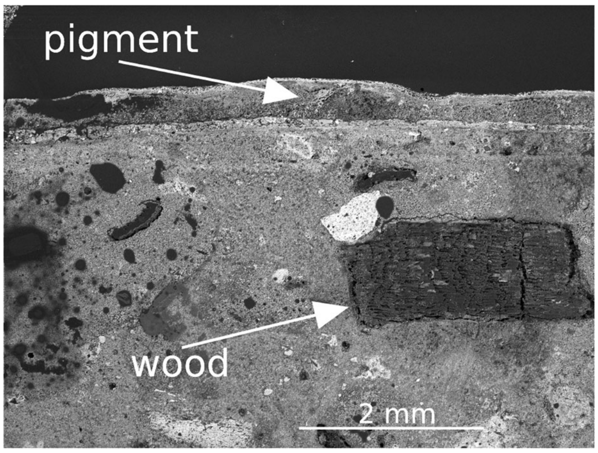


Figure 7. The photo taken at the microscope (x50) shows a fragment of wood shaving employed as aggregate in the intonaco of some of the twelfth-century fragments, possibly during in periods, when straw was needed as fodder.

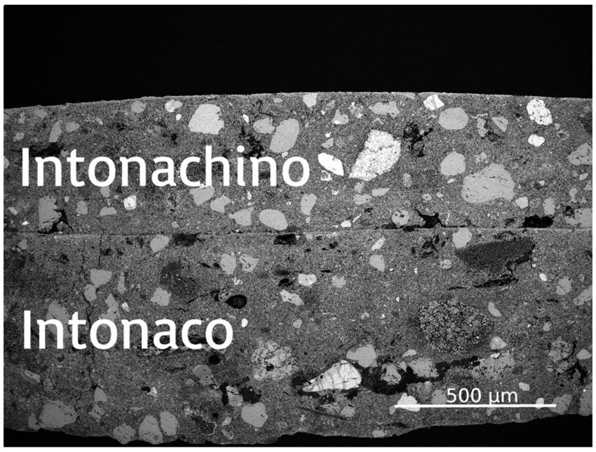


Figure 8. SEM micrograph showing an example of later wall painting with two distinct layers of preparation (*intonachino* and *intonaco*) and a large amount of rough sand, but no straw or wood in the *intonaco*.

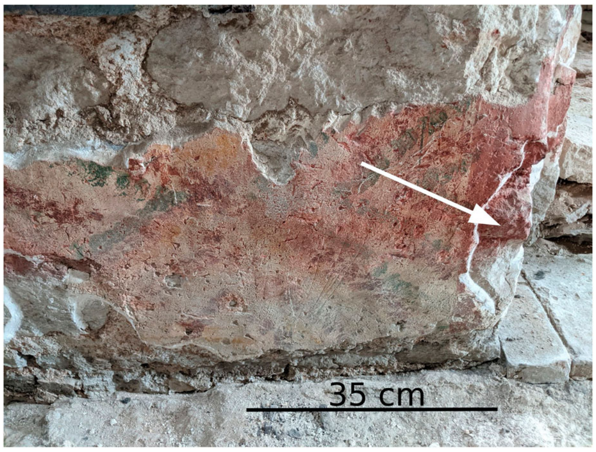


Figure 10. Detail of corner of a pillar that was hidden under the floor before the excavation, showing the red ochre pigment under the *intonachino* layer.

wall paintings from the famous Villa dei Papiri at Herculaneum, destroyed in the Vesuvius eruption of 79 AD [11,p.188), or in the fragments of frescoes from the Caseggiato dei Lottatori at Ostia, dated to the second half of the first century AD [12]. Red layers under the *intonachino* have been also identified in fragments of Roman paintings from the excavations in the Patio de Banderas, Reales Alcazares Palace in Sevilla [13] and in the paintings from the Sinop Batalar Church complex in Northern Anatolia, dated to the 2nd–4th century CE [9,29].

Discussion

In all these instances the material employed for the underpaint was red ochre and this is also the case in the St. George's Cathedral: our SEM-EDS analyses confirmed the use of red ochre under the *intonachino*.

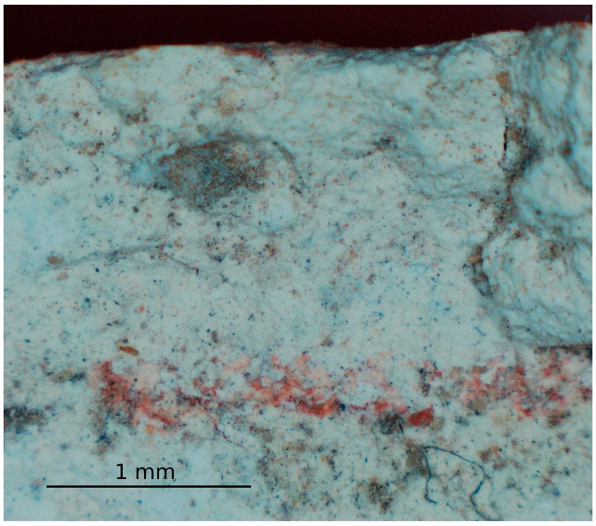


Figure 9. Microscope picture (x50) showing a fragment of wall painting with a layer of red ochre under the *intonachino*, possibly applied as protection from fungus or mould.

In the twelfth century there were not many choices of red pigments: the most common ones were iron oxides and hydroxides i.e. the earth pigments called red ochres (Fe_2O_3), known in mineralogy as hematite and goethite [14]. The second possibility was cinnabar or vermillion (Hg S, mercury (II) sulphide) that was in antiquity the second most expensive pigment after lazurite. For instance, as stated by Pliny (Natural History, 33, 118) in Roman times the refined cinnabar had a price established by law at 70 sesterces a pound to prevent the price going beyond limit. The most important mines exploited in antiquity were those of Almaden in Spain [15,16], and the precious cinnabar was adulterated in many ways [17], for instance by adding to it some minium (see below). The investigation by SEM-EDS did not reveal any mercury in the red pigment, and the use of the costly cinnabar hidden under the *intonachino* would not be logical or very credible.

The last red pigment in use at this time was minium (lead oxide, Pb_3O_4), both the natural and the artificial kind, obtained by heating lead minerals such as litharge and cerussite to ca. 425 and 430°C. However, no lead could be detected in the red layer under the *intonachino*. The EDS analyses on several areas of the red layer showed the typical peaks of ochre or, better, red earth, because it contains many impurities (Ca, Si, Al, Cl, K, Ti, Mg) (Figure 11). Therefore, we can safely conclude that the red pigment applied under the *intonachino* was red ochre, i.e. hematite (Fe_2O_3) or/and goethite (FeOOH), mixed with alumino-silicate as kaolinite or illite, quartz and calcium compounds.

The most common explanation for the presence of a red pigment in a place where it could not be seen is that the red ochre layer would protect the painting from humidity, but perhaps an even better interpretation is that the application of ochre might prevent the formation of fungus in the intonaco. It seems that the red layer under the *intonachino* was only applied on the lower part of the painted wall. The growth of

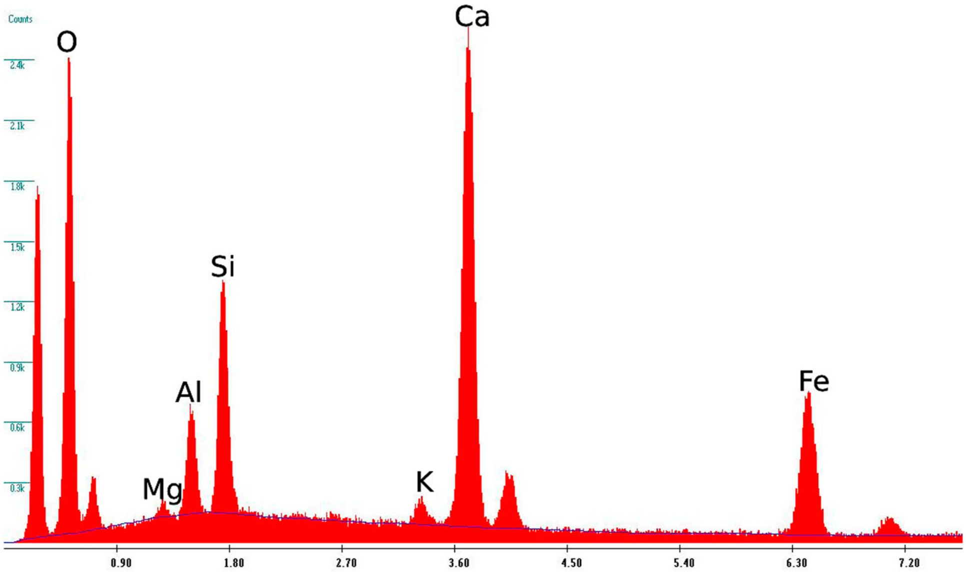


Figure 11. EDS analysis on the red pigment shows the typical peaks of red earth, i.e. hematite and goethite mixed with many impurities.

efflorescence and mould on painted walls must have been a very common and general problem, especially so in the relatively humid environment inside a church made of bricks. The presence of iron minerals in the red ochre (and possibly in yellow ochre too) seems to have acted as a kind of mould inhibitor. It is interesting to note that Fe_2O_3, hematite, mixed with impurities and clays ($Al_2O_3SiO_2$) represents the most important material that gives the colour to red ochre, and is also used in oil paintings, because it absorbs and dries out the oil of the pigments [18].

Underpaint

Underpaint layers have been used since antiquity. For instance, as early as the second century BCE, the blue pigment on the wall-paintings of the spring of Peirene at Corinth was deepened with a black underpaint (Hill 1964). In several cases even the *intonachino* was coloured, mainly with a pink or yellow pigment. The reason for this is still object of discussion [19–21]. The colouring of the upper layer of intonachino does not seem to have been in use at Novgorod in the twelfth century AD nor later, however, many of the fragments studied for this project present an underpaint layer, quite often in a colour which strongly contrasts with the pigment applied on the top. In the twelfth century, the most common underpaint is a grey layer, prepared by mixing lime with powdered charcoal that was used both as grey pigment and as an underpaint to deepen the colour, especially in the case of blue. In this paper we call it 'reft', because this is the term employed in ancient Russian texts that describe this pigment. The German monk Theophilus who wrote a treatise in Latin (*De diversis artibus* or *Schedula diversarum atrium i.e.* On various arts, 1122) calls it *veneda* and recommends that 'for the ground beneath azure and green, the pigment called veneda, mixed from black and lime, should be laid' (Theophilus, Div.Art., I, 15). We should note, however, that, as *reft* is present under most colours of twelfth century fresco pigments, it had perhaps a function similar to that of ochre as well (see for instance Figure 12).

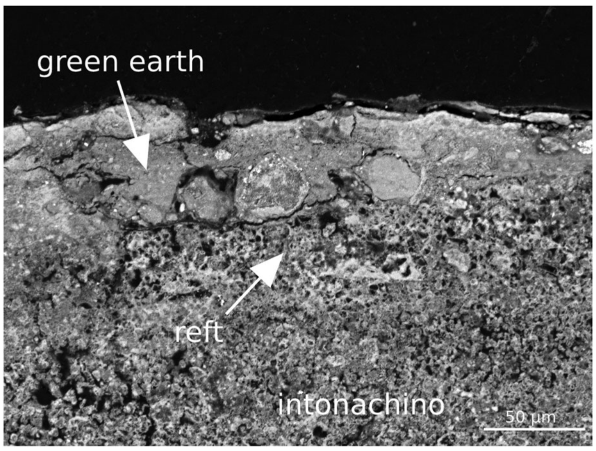


Figure 12. SEM micrograph showing the section of a green fragment of twelfth-century fresco. The upper layer is roughly ground green earth (celadonite and glauconite) on a layer of a grey mixture of lime and ground charcoal, called *reft* in ancient Russian texts.

A yellow ochre underpaint under a green earth pigment and even under blue (IUR f21 MG1, cat.n. 1496) has been also recognised on twelfth century fragments. This certainly changed the colour nuance of the pigment, but possibly also had the function of protection from fungus and humidity, like red ochre.

Some later blue fragments from the St.George's Cathedral, characterised by irregular strokes and pigment layers, and by a plaster containing a large amount of sand (Figure 13), show a dark red underpaint (for instance IUR ow 20 DLB3s, cat.n. 1475) of the kind called *morellone* by Cennino Cennini, who in his Treatise gives for this technique a recipe with two parts of *sinopia* (red ochre) and one part of black pigment, most probably vine black (i.e charcoal of grapevine wood) [22]. This mixture was employed in particular under blue pigments to deepen the colour. In this way less expensive pigments were used, the durability of the colour layer was improved, and the blue had a good coverage [21], but multiple layers also impede the carbonation. Certainly, this technique needed to be carried out with much skill and experience. In the St.George's Cathedral this technique has been identified only on fragments of later date.

It is quite interesting to note that the seventeenth century Treatise *Arte de la Pintura* (1649) (the art of painting) by the Spanish painter Francisco Pacheco dal Rio (1594–1644) mentions the use of adding on the surface of the intonaco, and on top of the preparatory drawing, a layer of lime and *almagra*, i.e. red ochre. However, he stated that only lime without red ochre should be used under green and blue pigments (Pacheco 1959, II, 52). Apparently, the opinion of the artists that painted the later frescoes in the St. George's Cathedral was different.

The SEM-EDS analysis of a twelfth century fragment sample with a blue colour (Figure 14) showed instead that under the actual blue pigment, consisting of lazurite i.e. ground lapis lazuli, a layer of greyish-blue clay was used on top of the *reft* layer (Figure 15), a technique very different from the one just described above that was employed in later times. Lazurite was the most expensive pigment, both in antiquity and until today, because not many deposits of lapis lazuli are known, and this mineral is also used as precious stone. The underpaint with blue clay improved the coverage, deepened the colour, and helped to economise because a lesser quantity of the expensive lazurite pigment could be employed. The SEM examination showed that the blue lazurite was applied on blue clay, which was itself applied on a layer of *reft*. The *intonachino* and *intonaco* are the well refined, very white plaster mixtures with only straw and a very small amount of sand, known from the twelfth century. The EDS analysis showed the typical lazurite peaks and following results: Na_2O 9.7; MgO 1.8; Al_2O_3 19.3; SiO_2 30.8; SO_3 7.4; Cl_2O 0.6; K_2O 2.8; CaO 21.8; Fe_2O_3 5.3. The EDS analysis of granules present in the lazurite identified some sodalite, tourmaline and phlogopites, which are typical components of lazurite.

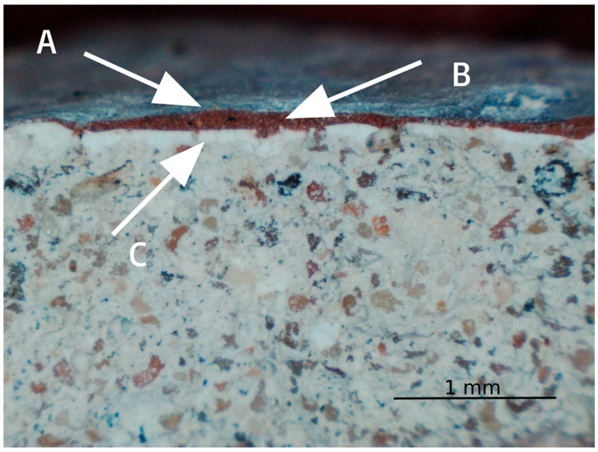


Figure 13. Microscope picture (x50) showing a fragment of later wall painting, possibly fifteenth century, characterised by the intonaco preparation with rough sand, with a layer of red earth (B) under a blue tempera pigment (A). No *reft* is used, but a thin, white layer of lime wash (C) can be recognised under the red.

Alterations on the frescoes

The most common damage on frescoes in general and in the Cathedral of St George as well is the efflorescence of gypsum ($CaSO_4$) i.e. the phenomenon of the so-called sulphatisation due to the centuries of use of lamps, candles, braziers and perhaps even torches, emitting sulphur in the air. The sulphur combines with the calcium present in the lime and forms gypsum that, helped by humidity, comes to the surface. The gypsum efflorescence produces dangerous damage, scaling and blackening of the wall paintings. For instance, the map obtained by SEM-EDS on a later sample with a blue pigment shows the presence of sulphur on lighter areas of the surface. The spots correspond to high SO_3 values (see table) and show the recrystallisation of gypsum. This kind of damage appears on several fragments. The analyses carried out on the spots 154, 155 and 156 indicate the presence of gypsum efflorescence, while the spot 153,

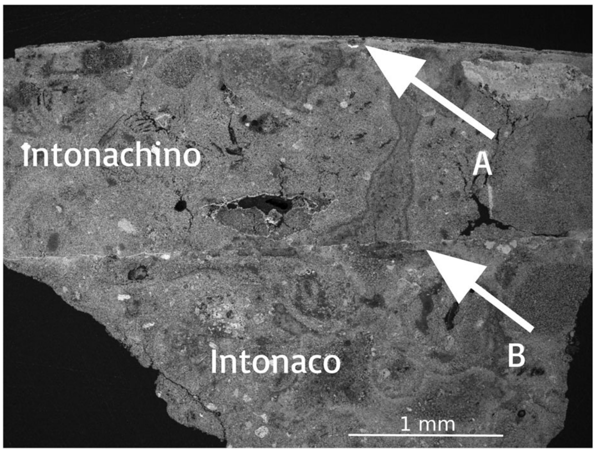


Figure 14. SEM micrograph showing a twelfth-century fragment with blue pigment and *intonachino* and *intonaco* with straw aggregates. (A) Pigment layers. (B) Interface between *intonachino* and *intonaco*.

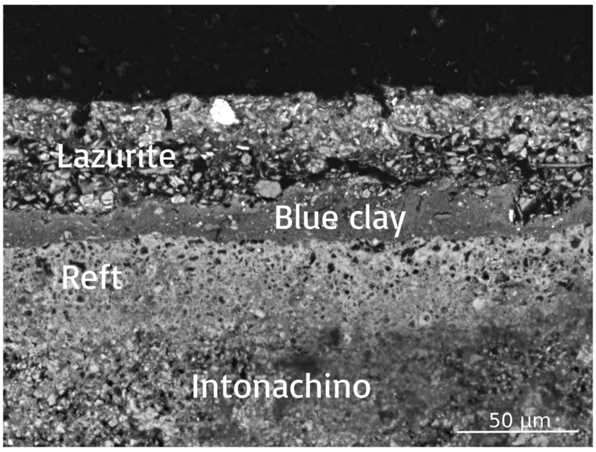


Figure 15. SEM micrograph showing a detail of the twelfth-century sample of Figure 14 with a layer of lazurite on a thin layer of blue clay (instead of red earth) and a *reft* layer with charcoal fragments applied on top of the *intonachino*.

158 and 159 shows the composition of the underlying intonaco with high CaO (Figure 16).

Other common alterations on frescoes are the formation of salts such as nitrates, oxalates, chlorides, sulphates and carbonates, however, these do not seem to have had a strong impact on the frescoes of the Cathedral in Novgorod.

Comparisons

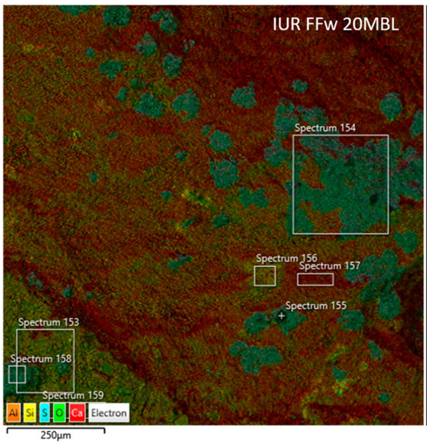
The pigments and the working method of the twelfth century artists who painted the frescoes in the Cathedral of St.George at Novgorod can be compared to those of contemporary important monuments, such as the frescoes our team recently analysed (November 2022, still unpublished) in the crypta of the Basilica of Santa Maria Assunta at Aquileia, Udine, Italy, the church of the Forty Holy Martyrs (1230 AD) i.e. one of the most important Bulgarian historical monuments, at the foot of Tsarevets on the left bank of the Yantra River, at Veliko Turnovo BG, [23] and to the paintings on the architectural pieces from the Palace of the Patriarch at Cividale, Italy [24], just to name only a few. In all these monuments the painters employed earth pigments such as ochres of different colours, white earth (calcite and kaolinite), green earth (a mixture of celadonite and glauconite), lazurite and carbon black applied on a very white plaster mixed with straw, flax or similar organic fibres. Both, plaster and the pigments were carefully polished, and highlights were added *a secco*, mostly with the addition of lime.

The pigments employed in the later phases of the Cathedral can be compared with those of the churches on the Mani peninsula in Greece [25], the ones of the fourteenth to seventeenth century AD churches at Kastoria [26] and those of the Protaton Church (1295 AD) of Mount Athos in Greece [27]. All of them are applied on a plaster with the addition of rough sand and are characterised by the use of more mixtures and later kinds of pigments, such as for instance artificial azurite and barium sulphate.

It is also interesting to note that the analyses carried out on 12 fresco fragments from the remains of a twelfth century AD church excavated at Smolensk, at Krasnoflotskaya Street 1–3, showed that the same kind of pigments, such as lazurite, green earth, ochre and carbon black, employed at Novgorod were in use at Smolensk as well, but the plaster was different, because the last layer under the pigments was kaolinite ($Al_2(Si_2O_5)(OH)_4$) [28].

Conclusions

The study carried out on the fresco remains from the excavations in and around the Cathedral of St.George at Novgorod helped to distinguish the earlier



	154	158	157	156	158	153	159
Na_2O	1.88	1.49	0.74	0.98	1.49	7.31	9.41
MgO	2.13	0.82	2.85	5.24	0.82	5.89	4.78
Al_2O_3	1.87	2.14	2.73	16.16	2.14	16.37	20.41
SiO_2	4.49	5.32	6.46	32.79	5.32	32.79	41.35
SO_3	38.11	51.36	1.50	0.84	51.36	13.97	6.77
K_2O	1.75	0.62	1.24	17.63	0.62	2.59	2.33
CaO	48.29	37.91	80.67	18.81	37.91	18.96	12.81
FeO	0.59	0.33	1.56	5.99	0.33	1.08	0.79

Figure 16. The map shows a gypsum efflorescence (sulphatisation), due to the use of candles, braziers or torches on top of the pigment of a later fragment, and the results of measurements on the various areas, showing high sulphur values. The 153, 158 and 159 measurements were carried out on the lime of the *intonachino*. (All photos by A. Giumlia-Mair. The drawing of Figure 4 is by AGM Archeoanalisi).

fragments of the twelfth century from those from later phases. Noticeable differences were observed in the structure and mixtures of the *intonaco* of the various periods and the aggregates added to the plasters were also different. While in the early phase the pigments were applied on an accurately purified layer of lime-based *intonachino* and were real fresco paintings, in the following centuries also tempera applied *a secco* was used. Further, the pigments of the twelfth century had been applied in a very regular way and always in the same direction, while the wall paintings of later periods show less regular pigment layers.

The SEM-EDS analyses revealed that in the early phase the most expensive pigment of the times i.e. lazurite, was applied using a complex method involving *reft* and blue clay as substrates. This method does not seem to have been observed before on Russian-Byzantine frescoes.

The comparison of the technologies employed for the preparation layers and in the application of the pigments with those of other monuments showed that the artists who painted the frescoes in the twelfth century in the St.George's Cathedral employed classical Byzantine methods and approaches to the paintings, while the later phases show significant changes in the painting techniques and in the use of pigments.

Acknowledgements

This research was carried out within the state assignment of the Ministry of Science and Higher Education of the Russian Federation. Theme: 'Pre-Mongol frescoes in Novgorod: archaeological context and scientific research: The frescoes of the St.George's Cathedral, Yuriev Monastery, 2013–2020 excavations'. Agreement N°075-15-2021-576.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Russian Academy of Sciences Moscow [grant number 075-15-2021-576].

ORCID

Alessandra R. G. Giumlia-Mair http://orcid.org/0000-0001-8185-1955

References

[1] Sedov VV, Kadeishvili EA, Vdovichenko MV. The frescoes of the 12th century on the walls of the Cathedral of St. George in the Yuriev monastery near Novgorod Veliky, discovered on the 2013 archaeological excavation. Conserv Stud Monuments Cult. 2014;7:15–19. СЕДОВ ВЛ.В., КАДЕЙШВИЛИ Е.А., ВДОВИЧЕНКО М. В. *Фрески XII в. на стенах Георгиевского собора Юрьева монастыря под Великим Новгородом, открытые в ходе археологических работ 2013 г.*, Реставрация и исследование памятников культуры. 2014;7:15–19.

[2] Sedov VV, Vdovichenko MV, Kadeishvili EA. Frescoes of the XII century on the walls of the St. George Cathedral of the Yuriev Monastery (according to the results of archaeological work in 2014). Restor Res Cult Monuments. 2016;8:11–17. СЕДОВ ВЛ.В., ВДОВИЧЕНКО М.В., КАДЕЙШВИЛИ Е.А. Фрески XII в. на стенах Георгиевского собора Юрьева монастыря (по результатам археологических работ 2014 г., *Реставрация и исследование памятников культуры. Вып.* 2016;8:11–17.

[3] Sedov VV, Etinhof OE. New data on architecture and frescoes of the Cathedral of St. George in the Yuriev Monastery. Archit Heritage. 2016;65:16–29. СЕДОВ ВЛ.В., ЭТИНГОФ О.Е. *Новые данные об архитектуре и фресках Георгиевского собора Юрьева монастыря*, Архитектурное наследство. 2016;**65**:16–29.

[4] Sedow W. Die Ausgrabungen in der St.-Georg-Kathedrale des Jurjew-Klosters in Welikij Nowgorod (2013–2016). In: Nawroth M, Wemhoff M, Makarow N, Kowal W, editors, Archäologie in mittelalterlichen Städten. Russland und Deutschland – ein Vergleich. Berlin: Staatliche Museen zu Berlin; 2020. p. 117–137.

[5] Weyer A, Roig Picazo P, Pop D, et al. European illustrated glossary of conservation terms for wall paintings and architectural surfaces. English definitions with translations into Bulgarian, Croatian, French, German, Hungarian, Italian, Polish, Romanian, Spanish and Turkish. Series of publications by the Hornemann Institute, Volume 17. Petersberg: M.Imhof Verlag; 2016.

[6] Cennini C. Il libro dell'Arte. Vicenza: Neri Pozza Editore; 2020; I, LVIII, 101–102.

[7] Mora P, Mora L, Philippot P. La conservazione delle pitture murali. Bologna: Editrice Compositori; 1999.

[8] Kakavas G. Dionysios of Fourna: artistic creation and literary description. Leiden: Alexandros Press; 2008. p. 288–291.

[9] Allag C, Grotembril S. Le rôle des sous-couches. In: Cavalieri M, Tomassini P, editors. La peinture murale antique: méthodes et apports d'une approche technique. Actes du colloque international, Louvain-la-Neuve, 21 avril 2017. Roma: Quasar; 2021. p. 205–212.

[10] Marano M. Mortars and pigments under the microscope. In: Cavalieri M, Tomassini P, editors. La peinture murale antique: méthodes et apports d'une approche technique. Actes du colloque international, Louvain-la-Neuve, 21 avril 2017. Roma: Quasar; 2021. p. 55–68.

[11] Amadori ML, Barcelli S, Poldi G, et al. Invasive and non-invasive analyses for knowledge and conservation of Roman wall paintings of the Villa of the Papyri in Herculaneum. Microchem J. 2015;118:183–192.

[12] Marano M. Mortars and pigments under the microscope. In: Cavalieri M, Tomassini P, editors. La peinture murale antique: méthodes et apports d'une approche technique. Actes du colloque international, Louvain-la-Neuve, 21 avril 2017. Roma: Quasar; 2021. p. 58–65. figs.3; 4; 5; 8.

[13] Duran A, Pérez-Rodríguez JL, Jimenez de Haro MdC, et al. Analytical study of Roman and Arabic wall paintings in the Patio De Banderas of Reales Alcazares' Palace using non-destructive XRD/XRF and

complementary techniques. J Archaeol Sci. 2011;39 (9):2366–2377.

[14] Eastaugh N, Walsh V, Chaplin T, et al. Pigment compendium: a dictionary and optical microscopy of historical pigments. Oxford: Butterworth-Heinemann; 2008.

[15] Giumlia-Mair A. (2009). The history of mercury production in the mine of Idrija, Slovenia. In: *Archaeometallurgy in Europe* 2007, 17–21 June, Aquileia, Italy, p. 68–78.

[16] Gliozzo E. Pigments – mercury-based red (cinnabar-vermilion) and white (calomel) and their degradation products. Archaeol Anthropol Sci. 2021;13(210):1–52. doi:10.1007/s12520-021-01402-4.

[17] Trinquier J. Cinnabaris et "sang-dragon »: Le « cinabre » des anciens entre minéral, végétal et animal. Rev Archeol. 2013;2013(2):305–346.

[18] Bevilacqua N, Borgioli L, Adrover Gracia I. I pigmenti nell'arte dalla preistoria alla rivoluzione industriale. Saonara: Il Prato editrice; 2019.

[19] Dilaria S, Sebastiani L, Salvadori M, et al. (2021). Caratteristiche dei pigmenti e dei tectoria ad Aquileia: un approccio archeometrico per lo studio di frammenti di intonaco provenienti da scavi di contesti residenziali aquileiesi (II sec. a. C. – V sec. d.C.). In: *La peinture murale antique: méthodes et apports d'une approche technique*, Actes du colloque international, Louvain-la-Neuve, 21 avril 2017, Quasar, Roma, p. 125–148.

[20] Marano M. Mortars and pigments under the microscope. In: Cavalieri M, Tomassini P, editors. La peinture murale antique: méthodes et apports d'une approche technique. Actes du colloque international, Louvain-la-Neuve, 21 avril 2017. Roma: Quasar; 2021. p. 58.

[21] Allag C, Grotembril S. Le rôle des sous-couches. In: Cavalieri M, Tomassini P, editors. La peinture murale antique: méthodes et apports d'une approche technique. Actes du colloque international, Louvain-la-Neuve, 21 avril 2017. Roma: Quasar; 2021. p. 210.

[22] Bevilacqua N, Borgioli L, Adrover Gracia I. I pigmenti nell'arte dalla preistoria alla rivoluzione industriale. Saonara: Il Prato editrice; 2019, 77–78.

[23] Sakellariou E, Torba T, Pavlidou E, et al. The Byzantine Church of "40 Holy Martyrs" in Veliko Turnovo, Bulgaria: pigments and technique. Am Inst Phys. 2010;1203:501–506. doi:10.1063/1.3322496.

[24] Roascio S, Zucchiatti A, Cagnana A. Study of the pigments in medieval polychrome architectural elements of "Veneto-Byzantine" style. J Cult Heritage. 2002;3:289–297.

[25] Hein A, Karatasios I, Mourelatos D. Byzantine wall paintings from Mani (Greece): microanalytical investigation of pigments and plasters. Anal Bioanal Chem. 2009;395:2061–2071.

[26] Jordanidis A, Garcia-Guinea J, Strati A, et al. Byzantine wall paintings from Kastoria, northern Greece: spectroscopic study of pigments and efflorescing salts. Spectrochim Acta A. 2011;78:874–887.

[27] Daniilia S, Tsakalof A, Bairachtari K, et al. The byzantine wall paintings from the Protaton Church on Mount Athos, Greece: tradition and science. J Archaeol Sci. 2007;34:1971–1984.

[28] 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. Heritage Sci. 2020;8:45. doi:10.1186/s40494-020-00389-w.

[29] Bakiler M, Kirmizi B, Ormanci Öztürk Ö, et al. Material characterization of the Late Roman wall painting samples from Sinop Balatlar Church Complex in the Black Sea region of Turkey. Microchem J. 2016;126:263–273.