

OVERVIEW OF GILDING PRACTICE OF WALL PAINTINGS IN THE LATE BYZANTINE PERIOD OF SERBIA

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Abstract: In this paper are presented the techniques of the gilding practice recorded on the fresco fragments found in several Late-Byzantine churches – monasteries from Serbia. The fresco fragments with gilding analysed here were found during archaeological investigations in the monasteries Žiča, Mileševa and Banjska. They all belong to the time when these churches were built by Serbian kings, between the 13th and 14th centuries. On the cross-sections of the samples, observed with the optic microscope under normal and UV light, the gilding techniques with multi-layered preparations were revealed. Also, observations and measurements of each cross-section were made using scanning electron microscopy, coupled with energy dispersive X-ray fluorescence spectroscopy (EDX). The results showed that for the sample from Žiča we have the oldest proven occurrence of gilding with gilded tin, where the gold leaf is attached to the tin foil most probably with some kind of pre-treated oil. Also, an oil-based binder was used to attach the gilded tin foil to the bole ground. Until now the oldest known example has been found on the painting and wall decorations by Giotto di Bondone from the early 14th century. Samples from the Žiča monastery are dated to the early 13th century. In the other two churches, water gilding with gold leaves on bole grounds was detected. The quality of gold from which the leaves are made does not correspond to any contemporary coinage. Here we will discuss the possible origin of the gold for their production and show that they were made in goldsmith workshops, possibly from the Balkan region, since those were the places where the gold was refined, alloyed and could be obtained directly from the nearby mining sites.

Keywords: fresco, gilding, Byzantine, art, Serbia

Archaeological and conservation research, done in the late 20th century and in recent times in some of the most important late Byzantine churches in Serbia, yields interesting evidence about the gilding practice from the period between the beginning of the 13th and the first half of the 14th century. Here we will present archaeological finds of fresco fragments with gilded surfaces, from monasteries Žiča 1220/1221, Mileševa around 1227 and Banjska 1317, and contribute to already published research of our colleagues about gilding techniques on wall fresco paintings in the monasteries of Studenica, Mileševa, Sopoćani, Gradac and Banjska.^{1,2,3} All analysed fragments are recognised as remains of original fresco painting done at the time of their construction and are considered to represent the first and the oldest layers of wall decoration.

Gold is the metal that had been in use since the Neolithic, the oldest finds of gold objects being those from Varna cemetery, dated to around 5000 BC. Gold was found also as decoration on ceramic vessels from the Bubanj Hum I culture in Serbia.⁴ The evidence of gilding with gold leaves that can be thinner than 1 µm is found in ancient Egypt^{5,6} (Darque-Ceretti et al., Nicholson). Since then, right up to modern times, gold has been a material that represents high prestige and ranking. In Christian art it symbolizes the Uncreated Light and presence of divinity. In early Christianity it was used for large areas representing the sky, either on icons or in gilded mosaics in Byzantine churches. After the mosaic technique for decorating churches was nearly abandoned in the 13th/14th centuries,⁷ gilding was used in fresco painting usually just for saints haloes and minor details. Gold leaves were attached with organic binders to fine, prepared grounds. Records of gilding techniques on fresco paintings are preserved in artists' handbooks (Hermeneia in Greek) from 8th (Manuscript from Lucca) and later centuries.⁸ The famous one is Cennino Cennini's^{9, 10} *Il libro dell'arte* from the 14th century, where different gilding techniques, lamination gilding on tin foil and preparation of grounds and binders are described. For the period of interest, we must consider the writings of *Eraclius* on *De Coloribus et Artibus Romanorum* that consists of three books, first two written in the 10th century in Italy, and the third one probably added in France in the 13th century,¹¹ and the writing of

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- 1 T. Zorba et al., Technique and palette of XIIIth century painting in the monastery of Mileseva. *Applied Physics A*, 83/4 (Heidelberg), 2006, 719–725.
 - 2 A. Јеликић и Д. Станојевић, О злату на сопоћанским фрескама. *Саопшћења*, Републички завод за заштиту споменика културе, 49 (Београд), 2017, 57–74.
 - 3 I. Drpić, et A. Jelikić, On Large scale Gilding and Mosaic Simulation in Medieval Serbian Wall Painting. *Archaeometry* 63/4 (Oxford), 2021, 779–793.
 - 4 M. Gajić-Kvaščev et al., “New evidence for the use of cinnabar as a colouring pigment in the Vinča culture”, *Journal of Archaeological Science* 39.4 (London), 2012, 1025–1033.
 - 5 E. Darque-Ceretti, E. Felder and M., “Foil and leaf gilding on cultural artifacts: Forming and adhesion”, *Matéria* 16/1 (Rio de Janeiro), 2011, 540–559.
 - 6 E. D. Nicholson, “The ancient craft of gold beating”, *Gold Bulletin* 12/4 (Queensland), 1979, 161–166.
 - 7 G. Bustacchini, “Gold in mosaic art and technique”, *Gold Bulletin* 6/2 (Queensland), 1973, 52–56.
 - 8 O. Katsibiri, “Investigation of the technique and materials used for mordant gilding on Byzantine and post-Byzantine icons and wall paintings”, Doctoral dissertation, Northumbria University, Newcastle, November, 2002.
 - 9 М. Медиф, *Стари сликарски приручници (III)*, Републички завод за заштиту споменика културе, Београд, 1999, 267 и 413.
 - 10 C. Cennini, *The craftsman's handbook. Vol. 2*, New Haven, 1954.
 - 11 S. M. Viñas, “Original written sources for the history of mediaeval painting techniques and materials: a list of published texts”, *Studies in conservation* 43/2, 1998, 114–124.

Theophilus the Presbyter from the 12th century *Shedula Diversarum artium* – three books about wall paintings and paintings on wood, parchment, leather etc., on how to colour glass, make ceramics, but also on making art objects from different kinds of metals and how to prepare different alloys.¹² In his first book under passage XXIII, titled “About the golden leaves”, we find the oldest written explanation on how to make gold leaves by beating pure gold between the carefully prepared pieces of Byzantine parchment made of flax fibre and treated with burnt ochre.¹³ Although Theophilus does not mention that the gold for beating is actually a gold coin, it is widely accepted and more or less implied that gold leaves are made from gold coins. One of the reasons may be the easier control of the working process, as it was easy to calculate exactly how many leaves can be produced from one coin and how many leaves a man can make per day. This is known from writings in *Il libro dell’arte* (chapter CXXXIX) and may be also true from an earlier period based on the results of analyses of Byzantine gilded mosaic tesserae from the 4th to the 12th century,¹⁴ where it was found that the gold leaves were made of gold that can be compared to coins minted in Byzantium or as early Arab coinage (reused Byzantine coins¹⁵). In any case, the gold should be of the highest quality as suggested in these books.

Basically, there are two main techniques, water gilding and oil or so-called mordant gilding. Water gilding comprises the preparatory layer made of bole and the binding medium. The bole is a special kind of soft clay, orange-reddish to brown in colour, which contains iron oxides and aluminium silicates. The binding medium was usually egg white or weak size. After putting the bole with binder on the ground layer, which was calcium carbonate or gypsum, the gold leaf could be fixed to it by activating gluing properties using breath, with rakii (spirit) or with garlic juice, etc. The fixed gold was then burnished with some kind of special tool made of agate, semi-precious stone, or animal teeth to obtain the glossy look. With oil gilding (also called mordant gilding), the glossy shine was not possible to obtain because the technique includes the use of oil-resinous binders or just pre-heated oil with some kind of siccativ, usually lead white, minimum or verdigris over the prepared ground that could be with or without bole. The oil phase gets sticky after a certain time and that is when the gold leaf is applied. Burnishing was not possible due to the long time required for oils to completely dry out, so this kind of gilding was used usually for smaller decorations on paintings like crowns, jewellery presentations etc.

There is very little data on the analytical research of surviving gilded wall paintings from the Byzantine period. Besides the work of Katsibiri (2003) about the history of mordant gilding, with just a few examples from the Byzantine period, and the data on the quality of gold leaves in mosaic tesserae from the Byzantine period in Levant by Neri et al.¹⁶, other analytical works mostly concern Post Byzantine icons and wall paintings. Some information about the origin of gold, trade routes and organisation of crafts, such as goldsmiths that were engaged in purifying the gold and making

12 M. Медич, *Стари сликарски приручници (I)*, Завод за заштиту споменика културе, Београд, 1999, 234–295.

13 Ibid. 6)

14 E. Neri et al., “Glass and gold: Analyses of 4th–12th centuries Levantine mosaic tesserae. A contribution to technological and chronological knowledge”, *Journal of archaeological Science* 70 (London), 2016, 158–171.

15 A. Gondonneau and M. F. Guerra, “The circulation of precious metals in the Arab Empire: the case of the Near and the Middle East”, *Archæometry* 44(4) (Oxford), 2002, 573–599.

16 Ibid. 14)

the gold leaves (beating of gold), can be obtained in writings about the economy of the Byzantine Empire¹⁷ and the organisation of goldsmiths and goldsmithing in Byzantium.¹⁸

From recent examinations of original fresco paintings preserved on the walls in several churches in Serbia, the unique practice of imitating gold mosaics on large areas of the walls (backgrounds) has been identified. It was done with the so-called part gold¹⁹ – a gold leaf adhered to silver foil by beating and then stuck on the yellow preparatory layer, with adhesive. After fixing the part gold, the artist draws the lines imitating the mosaic tesserae (Drpić and Jelikić, 2021)²⁰. These pseudo mosaics with part gold were found in churches of monasteries Studenica, Mileševa, Gradac and Sopoćani, the latest one being the best preserved. In Banjska, the imitation of mosaics was made just with pure gold leaves. Here the gilding with gold leaves on tin foil from the Žiča monastery will be presented, as well as some specific features of gilding in Mileševa and Banjska not earlier observed.

Since the Kingdom of Serbia, then called the Kingdom of Raška, was established on the basis of Byzantine tradition and East Orthodoxy, it is no surprise that the most qualified Greek painters were invited to Serbia to paint the walls of representative churches built by Serbian kings. That resulted in many parallels that can be found between churches in modern Greece and Serbia from the period between the 13th and 15th centuries²¹. We hope that this overview of gilding practice in Serbia from the 13th to the beginning of the 14th century will contribute in a broader sense to the history of gilding practice in Byzantine art.

SAMPLES

Figure 1 shows the photos of five analysed samples under the OM.

Samples of fresco fragments from Žiča were found in two pits hidden in the floor of the Church of Ascension of our Lord. It is assumed that they were buried into the pits during the first renovation of the monastery at the beginning of the 14th century²². Fragments of fresco paintings are in very good state of preservation and on some of them it is visible that above the yellow or red ground layer there are two layers, one dark thick layer covered with a gold leaf. This was the first archbishopric of Serbia built by the first crowned king, Stefan Nemanjić, finished with fresco decoration in 1220 or 1221. It was built in order to celebrate Serbian independence from the Byzantine Empire and was intended as the place where Serbian kings should be crowned. Here we will discuss the sample with the red ground – sample no 1 in Figure 1.

17 A. E. Laiou, *The economic history of Byzantium: from the seventh through the fifteenth century* (Vol. 3). Washington, 2002.

18 A. Rhoby, "Gold, Goldsmiths and Goldsmithing in Byzantium", in *New Research on Late Byzantine Goldsmiths' Works (13th–15th Centuries)*, ed. A. Bosselmann-Ruickbie, Mainz, 2019, 9–20.

19 I. Osticioli et al., "The "oro di metà" Gilding in the Fifteenth-Century: A Multi-Analytical Investigation", *Heritage* 2/2 (Paris), 2019, 1166–1175.

20 Ibid. 3)

21 E. Oikonomopoulou et al., "An intercultural approach for the protection and promotion of common cultural heritage: the case of Byzantine monuments in Serbia", *International journal of heritage in the digital era* 2/4 (London), 2013, 547–568.

22 В. Обренија, "Две јаме у цркви Светог спаса у Жичи", у *Манасџир Жича : зборник радова*, Краљево 2000, 247–261.

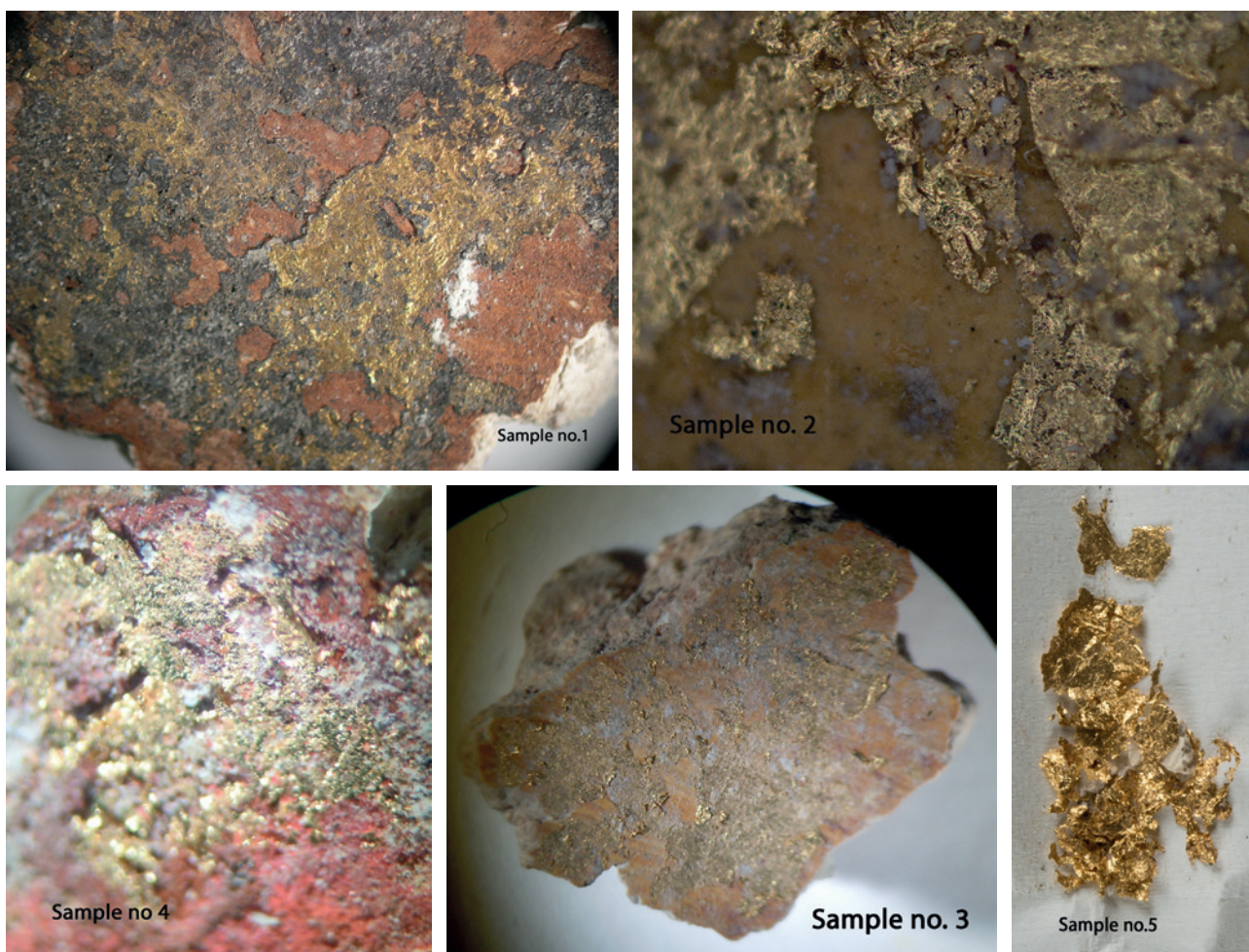


Fig. 1

The Mileševa Monastery was built by Prince Stefan Vladislav, son of Stefan the First-Crowned (later king 1234–1243). First it was built and fresco painted as a church with one dome in the nave between 1219–1228, and a little bit later, in 1235, the outer narthex was added upon which, during the 19th century restoration, a second dome was constructed on top. It was also partly repainted in the 16th century. Samples from the monastery of Mileševa, in the Church of Ascension Day, were found during excavations in the last decade of the 20th century²³, and were identified as the remains of the first reconstruction during the 13th century, since they were found in the area under the floor where the frescoes were damaged due to the opening of the entrance from the outer to the inner narthex (personal communication with PhD Bojan Popović). The sample analysed has a yellow ground and a gold leaf on top – sample no 2, Figure 1).

Banjska Monastery – St. Stephan church was built at the beginning of the 14th century between 1313–1317 by King Stefan Uroš II Milutin Nemanjić, as his burial church dedicated to St. Stefan. It was well known in traditional narratives that gold was extensively used through sayings about the interior being bathed in light and gold. Fresco fragments were found in several graves beneath the floor of the

²³ Д. Минић и В. Обренија, „Милешева археолошка истраживања у 1994”, *Гласник друштва конзерватора Србије* 19 (Београд), 1995, 82–84.

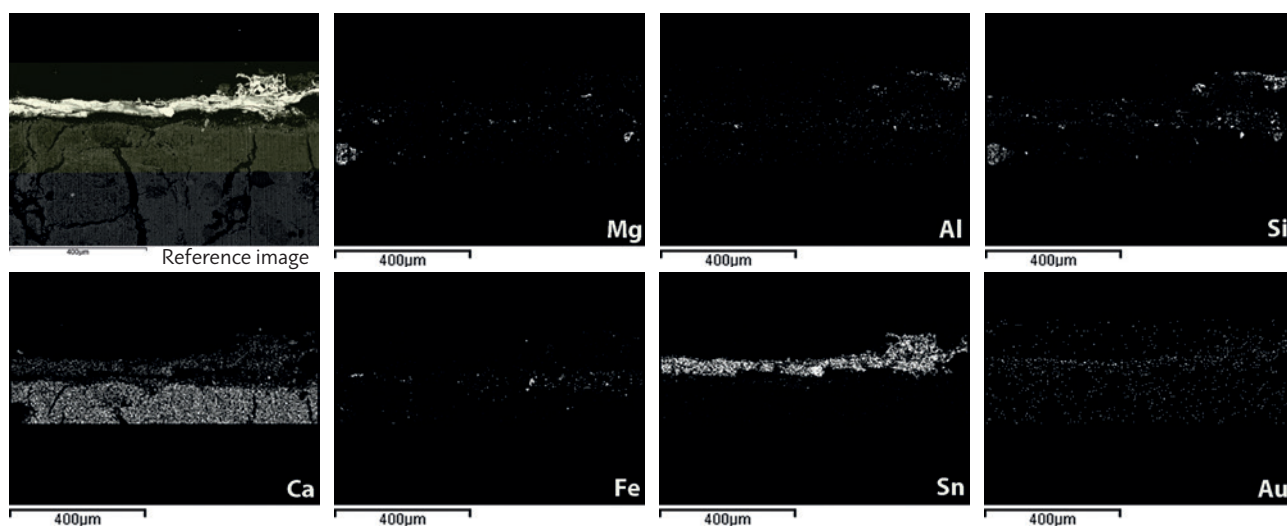


Fig. 2

church²⁴. Since the only surviving fresco painting which has been done until today is the original one, here there is absolutely no doubt that the fragments here analysed belong to the period of the building of the church. We analysed two fragments, one with the yellow ground – sample no. 3 and one with the red ground – sample no. 4 (Figure 1). We also analysed the detached gold leaves – sample no. 5 (Figure 1).

INSTRUMENTATION

Observation of whole samples was done with the optic microscope Olympus SZ16 and the images of samples were done with the Olympus Camedia digital camera. Cross-sections of the samples were observed on an Olympus BX51M microscope equipped with a UV lamp Olympus U-RFL-T under normal light in a dark field and under UV light without filters. Images of cross sections were obtained with the Olympus SC/180 camera equipped with cellSensStandard software for managing images.

SEM-EDX of gold leaves and EDX mapping of cross sections of the samples were done with a scanning electron microscope (JEOL JSM 6460 LV) equipped with an Oxford EDX analyser. Samples of cross sections were carbon-coated to eliminate charging effects. Fineness of gold was measured on uncoated samples by measuring five clearest spots on the gold leaf, with ion beam of about 1 µm in diameter and subtracting all elements different than Au, Ag and Cu that do not belong to the major composition of the gold (like Fe, Ca, O, etc.,) Finally, the results are normalised to 100 wt. %.

Cross sections are measured with SEM EDX on each characteristic layer that can be seen under the SEI. The measured areas, depending of the geometry of the sample, were usually about 20 × 10 µm big.

24 M. Поповић, „Средњовековне сахране у цркви манастира Бањске / Medieval Burials at the Church of the Monastery Banjska”, *Саопштења XLVIII* (Београд), 2016, 23–55.

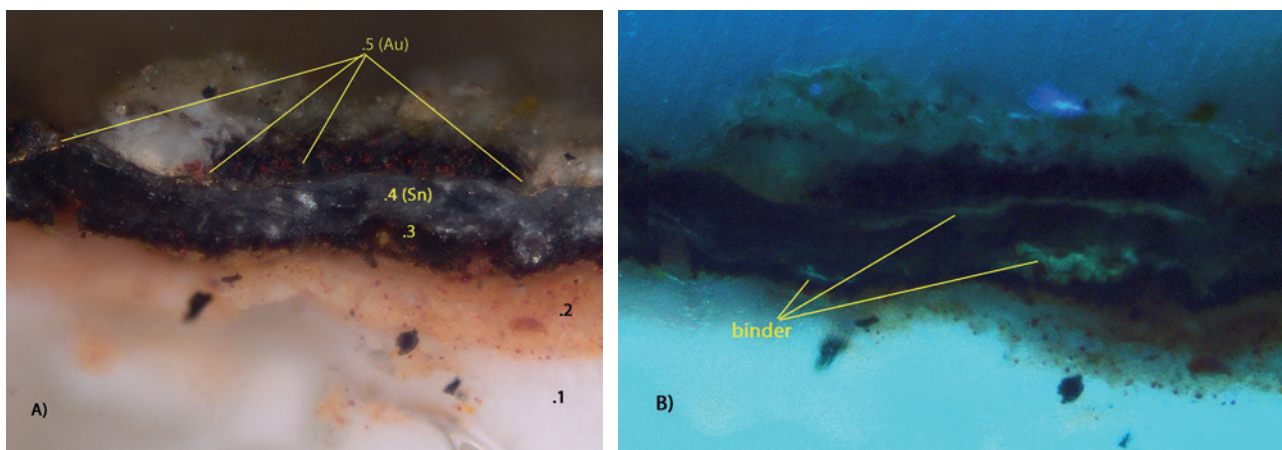


Fig. 3

RESULTS AND DISCUSSION

Žiča monastery

SEI EDX mapping of sample no.1 from Žiča is given in Figure 2. Observations with OM under normal light in dark field and under UV light are given in Figure 3.

With SEI EDX mapping we obtained the distribution of elements in the cross section of the sample. For sample no. 1 we can see, in Figure 2, that there is a high concentration of calcium in the bottom of the sample and that this layer is richer in Al, Si, Mg, Fe in the region of the contact zone with Sn. This layer represents the calcium carbonate ground with the aluminosilicates and iron minerals on the top. Above this region there is the Sn rich layer, representing the Sn foil and above that there is a very thin layer of Au representing the gold leaf.

In OM colour image of sample no. 1 (Figure 3), based on mapping, we can show the position of the layers detected. The lowest layer in Figure 3A represents the ground material in fresco painting made of calcium carbonate (lime); the second layer is red in colour and represents the preparatory layer for gilding – red bole rich in aluminosilicates with Fe minerals mixed with calcium carbonate; layer 3 looks like a binder and there is a thick black layer 4 that is the Sn foil above which we can see a very thin yellow gold leaf – layer no. 5. During the observation of sample no. 1, under UV light, we found yellowish fluorescence of the binder between gold leaf and tin foil (Figure 3B). Under UV light gold turns black when observed under the microscope so we are certain that this fluorescence derives from the binding medium used to fix the gold leaf to tin foil. In *Il libro dell'arte chapter XCIX. Come si fa lo stagno dorato, e come colla detta dorurata si mette d'oro fine*²⁵. Actually, Cennini describes the kind of glue, *colla detta doratura*, which needs to be left on the sun after being applied. This certainly points to the drying of oil, since proteinous binders would dry on the spot and wax, if applied, would melt in the sun. On mapping we did not find traces of proteinous matter like P, S or N, and yellow fluorescence points toward the oily binders²⁶. We conclude that some kind of oil was used to fix the gold leaf to the tin foil.

Between the tin foil, whose thickness ranges from 25–45 μm , and the red ground we can see yellow fluorescence with bluish tint, which also represents the bind-

25 Ibid. 10)

26 A. Mounier, L. Dayet, F. Daniel, and C. Belin, «Fluorescence UV des liants employés dans les dorures sur peintures murales médiévales», *ArcheoSciences. Revue d'archéométrie*, 35 (Rennes), (2011), 19–28.

ing media. In research by Holclajtner-Antunović, et al.²⁷, the gilded tin on yellow grounds from the same archaeological context was analysed and it was shown that it is made of clay rich in mineral goethite and aluminosilicates, that black layer is made of tin and the uppermost layer is made of gold with a small amount of silver. The binder was defined as a mixture of oil and resin. Since the fluorescence of our sample looks pretty same as in the mentioned work and concerning the fact that mixture of resin and oil may give a bluish tint,²⁸ we suppose that it is the same mixture of oil and resin that was used to fix the gilded tin foil to the red ground in the case of our sample no 1.

The earliest examples of proven gilded tin foils are the artworks of Giotto from the Chapel of the Scrovegni in Padua²⁹ and the Pentacost panel painting³⁰, dated to the beginning of the 14th century. The gilded tin was found for the rays directed towards the apostles from the dove, symbolising the Holy Spirit. There are also indications that the stars on another of Giotto's panel paintings, the Epiphany (1310–1320), were made with the same technique. There is only one mention of gilding on tin surviving on fresco painting from the 12th century church in Nogaro (France)³¹, but that mention is made in a sense that it may originate from 18th century intervention (addition of the gold stars) and this observation is not included in the conclusions, concerning the gilding techniques of Romanesque period. Fragments from Žiča predate Giotto's Pentecost by about one century, so we may say that these are the earliest proven examples of real gilded tin recorded on any kind of artwork.

Thickness of the gold leaf was measured on the Backscatter electron image of the sample, Figure 4.

The gold leaf that is about 1.7 μm thick, was subjected to detailed analyses by taking the whole sample no. 1 under the SEM-EDX analysis and examining five different spots of the gold leaf. The average weight percent values obtained for the gold leaf are 93.7% Au, 5.4% Ag, 0.9% Cu. These values can be expressed as the carats (one carat is 1/24 of pure gold or 4,1667%)³². In carats, the fineness of the gold from Žiča is approximately 22.3 carats.

We will now consider the possible coinage used to make these leaves. At the time when the Žiča monastery was built, the main gold currency in Europe was the Byzantine hyperpyron, the gold coin that was introduced by the Alexiuous I monetary reform in 1092. Initially, this was a gold coin of good quality of about 20.5 carats that was minted in Constantinople, but after its sack in 1204, in the 4th

27 I. Holclajtner-Antunović, et al., "Multi-analytical study of techniques and palettes of wall paintings of the monastery of Žiča, Serbia", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 156 (Amsterdam), 2016, 78–88.

28 A. Pelagotti et al., "A study of UV fluorescence emission of painting materials", in *Art '05–8th International Conference on Non-Destructive Investigations and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*, Lecce, Italy, (2005, May), p. A97.

29 R. Cesareo, "Non-destructive EDXRF-analysis of the golden haloes of Giotto's frescos in the Chapel of the Scrovegni in Padua", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 211–1 (Amsterdam), 2003, 133–137.

30 R. Billinge and D. Gordon, "The Use of Gilded Tin in Giotto's "Pentecost"". *National Gallery Technical Bulletin* 29 (London), 2008, 76–80.

31 A. Mounier, F. Daniel and F. Bechtel, "Gilding techniques in mural paintings: three examples from the Romanesque period in France", In *Proceedings of the 37th International Symposium on Archaeometry, 13th–16th May 2008, Siena, Italy*, ed. I. Turbanti-Memmi, Siena, 2011, 273–278.

32 See <https://www.britannica.com/technology/karat>

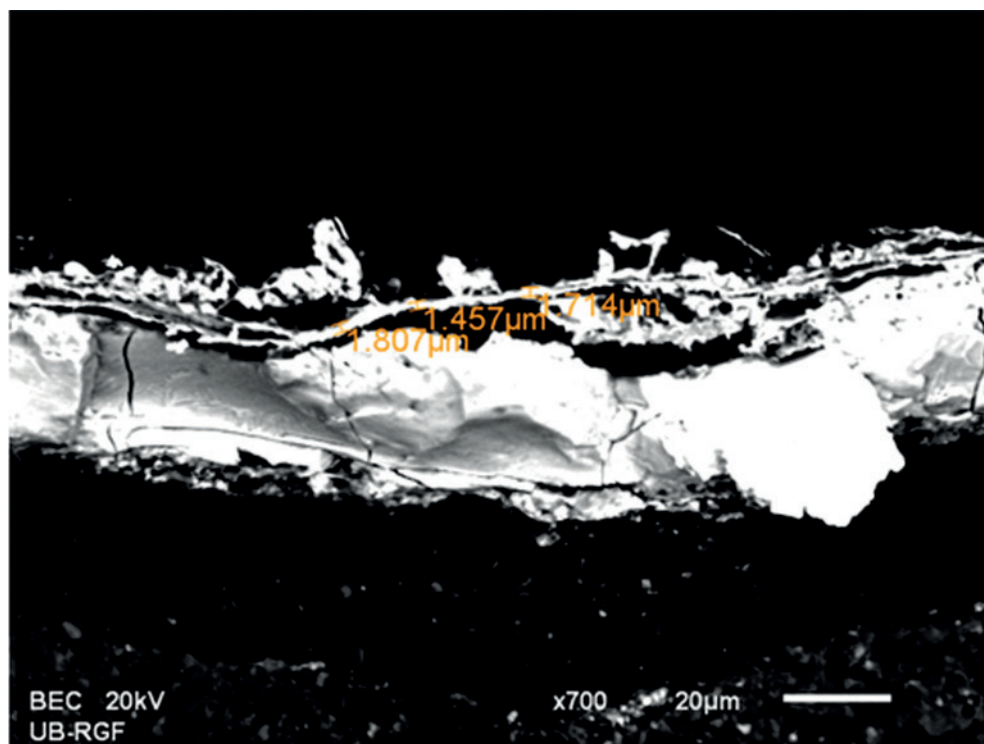


Fig. 4

crusade, it continued to be minted only by the exiled emperors of Nicaea from 1211 and debased to 18 carats during the rule of John III Ducas Vatatzes (1222–1254).^{33,34} Besides these, until 1231, when 20.5 carats Augustale was first minted by Frederic II in Sicily, there were no gold coins minted in this part of the Christian world.^{35,36} According to these values we may conclude that the gold from Žiča was of significantly higher purity than the available coinage. In the study that compares the Byzantine coinage and jewellery by Oddy and Niece (1986)³⁷ it was noted that a substantial number of items that belong to the period before the 10th century are made of 22 carat gold (around 92%), which was much less than 24 carat contemporary coinage. More than 90% of gold is also found in the jewellery from the 11th to the 13th centuries,³⁸ so it seems to be like a deliberate composition, no matter what the quality of the coinage was at the time. Since the goldsmiths were in charge of all operations that concerned gold, from refining to making objects made of gold and exchange of money, it would not be a surprise that they were able to make the adequate alloys for all purposes, either by recycling or making the alloy from pure gold. We suspect that this can be a plausible explanation for the composition of the gold leaves in Žiča.

33 P. Grierson, *Byzantine coinage* No. 4, Washington, 1999, 11.

34 A. M. Stahl, "Coinage and money in the Latin Empire of Constantinople", *Dumbarton Oaks Papers* 55 (Washington), 2001, 197–206.

35 M. Baldassarri et al., "X-ray fluorescence analysis of XII–XIV century Italian gold coins", *Journal of Archaeology* Article ID 519218, 2014, <https://www.hindawi.com/journals/jarchae/2014/519218/>

36 J. Weschke et al., *Gold coins of the Middle Ages from the Deutsche Bundesbank Collection*, Frankfurt, 1983.

37 A. Oddy and S. La Niece, "Byzantine gold coins and jewellery", *Gold Bulletin* 19/1 (Queensland), 1986, 19–27.

38 *Ibid* 18)

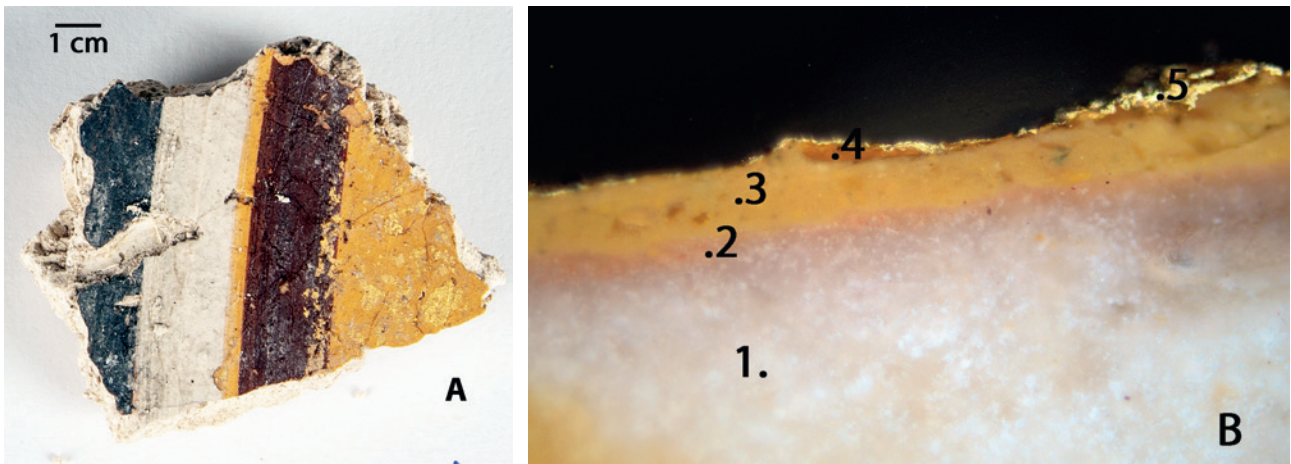


Fig. 5

Mileševa monastery

From the Mileševa monastery only one fragment with a gilded surface was analysed (Figure 1 and Figure 5).

This fragment consists of black, white and dark red stripes next to the yellow ground with traces of gold leaf above, Figure 5A. In the cross section of the gilded surface, Figure 5B, we can see five layers, the first one being the white one with occasional appearance of red spots (spot 1), above is a very thin pale red layer (spot 2), then a yellow pigmented layer (spot 3) above which there is a tiny light orange layer (spot 4) and finally a metal leaf (spot 5) on the surface.

SEM EDX results made on the cross section of sample no. 2 are given in Figure 6.

SEM EDX analyses (Figure 6), have shown that the first white layer is calcium carbonate and that the yellow layer about 30µm thick is kaolinic goethite,³⁹ the yellow clay composed of mineral goethite and aluminosilicates, better known as yellow earth or natural ochre pigment mixed with lime. Yellow ochre containing goethite was found also as the ground layer of mosaic imitations made with part gold in the same church⁴⁰. The gold leaf is characterised as pure gold. Although the picks of silver were showing up during collecting the point spectra of the metal, the

39 D. Hradil et al., "Clay and iron oxide pigments in the history of painting", *Applied clay science*, 22(5) (Amsterdam), 2003, 223–236.

40 Ibid. 3)

Fig. 6

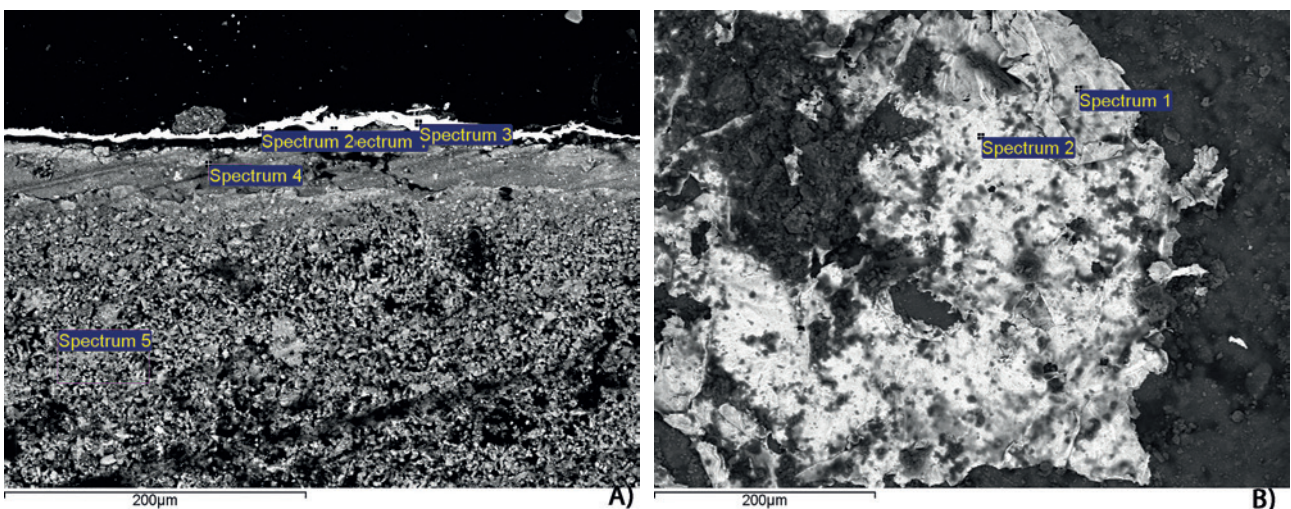


Table 1: elements detected on cross section of sample no. 2

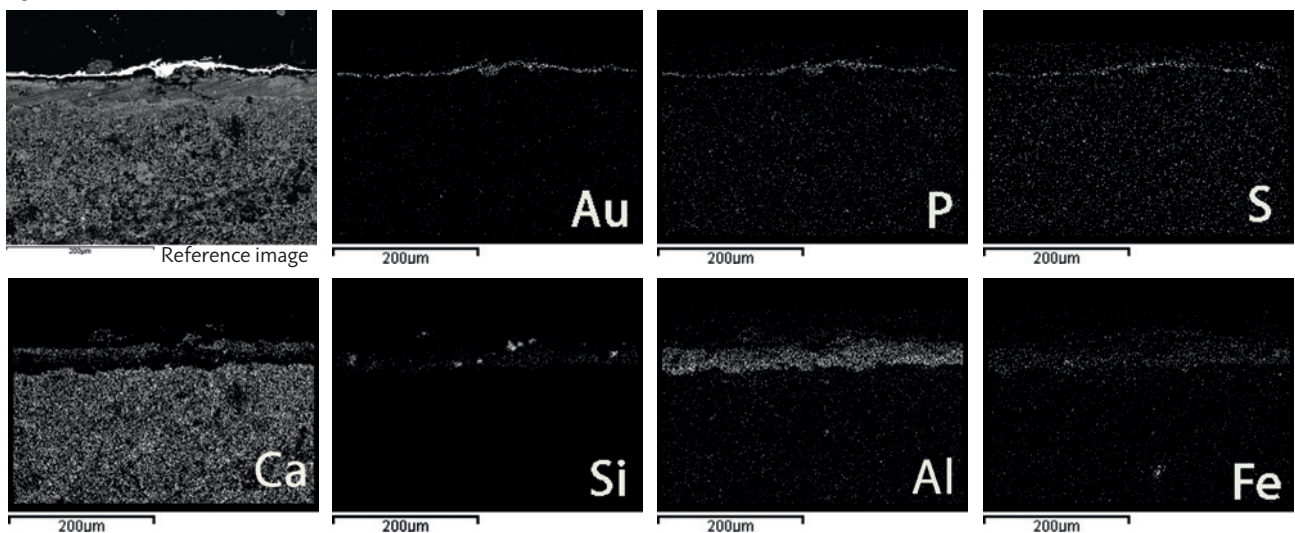
Spectrum	In stats.	O	Mg	Al	Si	K	Ca	Fe	Au	Total
Spectrum 1	Yes	8.35		0.46			0.66		90.52	100.00
Spectrum 2	Yes	4.44							95.56	100.00
Spectrum 3	Yes	6.00		0.48			1.01		92.51	100.00
Spectrum 4	Yes	48.84	1.21	11.34	16.69	0.63	14.53	6.75		100.00
Spectrum 5	Yes	58.42	1.55		1.34		38.68			100.00
Spectrum 6	Yes	58.28	1.13	1.26	1.92		37.41			100.00

quantification of this element Table 1 in Figure 6, and in 5-point measurements did not appear in the final result, so we assume that the silver and/or copper, if present, are below the limits of detection for the instrument (below 0,1%). We may say that the leaves are made of approximately 24 carat gold or to say pure gold for the time when they were produced. The same fineness of gold was found for part gold in mosaic imitations in this church. This causes us to believe that we can confirm that our fragments really belong to the period of the original decoration. As noted earlier for Žiča, we find it impossible that these gold leaves and part gold were made from coins. The first issues of 24-carat gold coins in the 13th century are the Florins or Genovini minted in today's Italy, from the year 1252, which is about 20 years after the completion of the first reconstruction of the Church of Ascension Day in Mileševa. Again, it is more probable that the pure gold leaves were made in a goldsmith workshop, this time from refined gold.

Mapping of the mentioned sample gave a better picture about the structure of the layers (Figure 7).

From Figure 7, we can see that the pale red layer is poor in aluminosilicates and that the iron is rather blurred between the yellow and the pale red region. Also, Fe can be found in higher concentration in the white layer in spots with characteristic red colour. The orange layer between the gold leaf and the yellow ground clearly shows the high concentration of sulphur and phosphorus (Figure 7). These two elements can be found in higher concentrations in binders of animal origin, such as egg white with a lot of sulphur and egg yolk, rich in phosphorus or in casein, a

Fig. 7



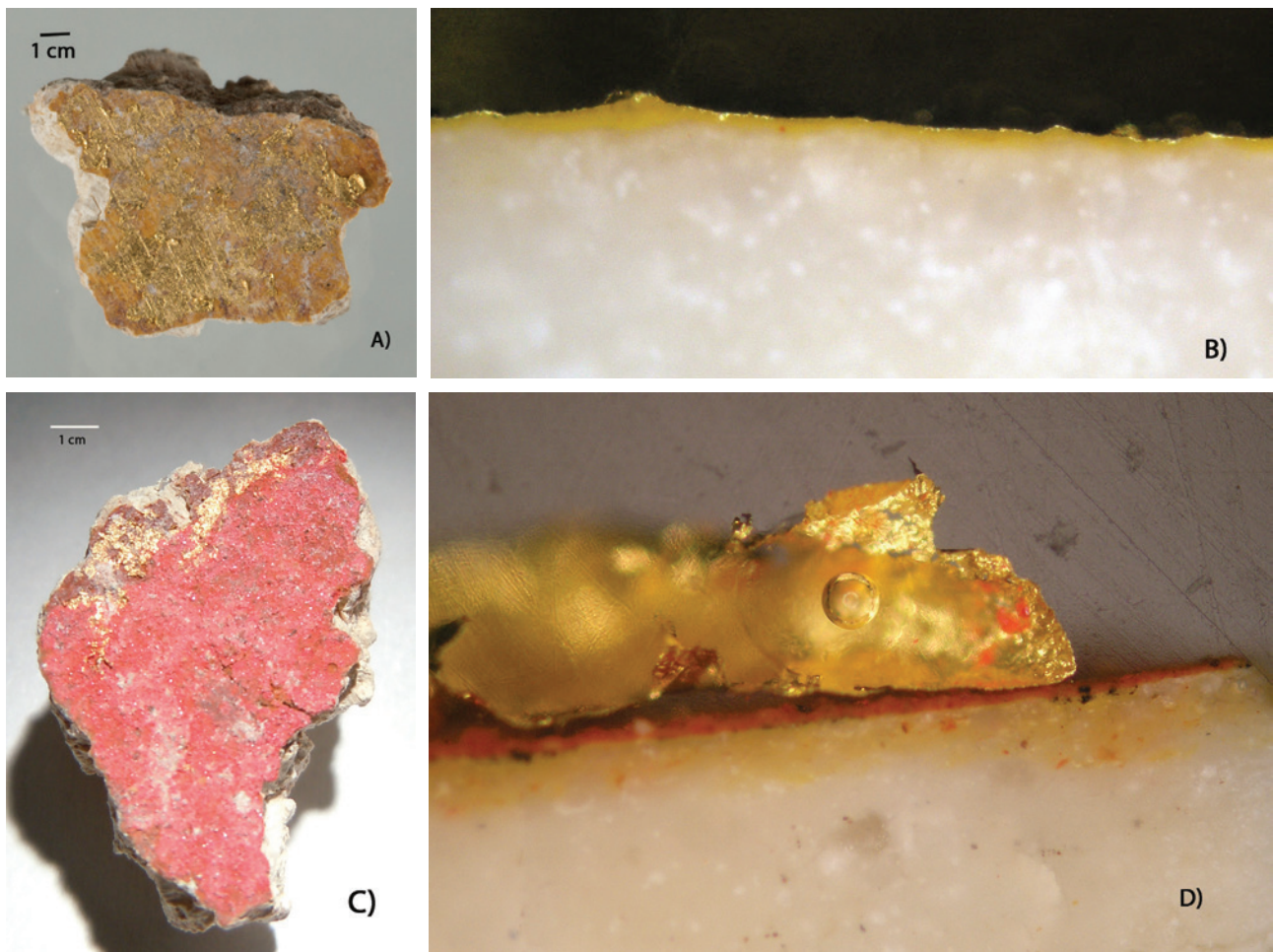


Fig. 8

kind of glair made out of phosphoproteins from milk. In old Hermineia, casein glue is never mentioned as an adhesive for gold leaves, most probably because of its low solubility in water⁴¹. When dried it becomes strong glue that is water repellent and as such it would be hardly reactivated in order to bind the gold leaf. Knowing that the egg white is almost free of phosphorus, in our opinion, it is more likely that the binder was made of whole egg, since the concentration of the sulphur and the phosphorus seems to be almost identical.

Banjska monastery

In Banjska monastery, two kinds of samples are recognised, ones with yellow ground beneath the gold leaf and another with red ground, Figures 1 and 8. Also, there were many detached gold leaves that were collected during archaeological excavations (Figure 1). There is a much greater number of yellow grounds than the red ones. Cross sections of sample no. 3 and sample no. 4, observed under the OM, are given in Figure 8. The mapping of these samples – SEI EDX results – are given in Figure 9 and the SEI image of sample no. 4 and the spot spectrum of clay mineral are given in Figures 10 and 11.

In the cross section of the samples, observed with OM, we can see that in the case of yellow grounds, a thin yellow ground is the only layer between the gold leaf and the white preparation Figure 8B. In the red ground layer there is a pale

⁴¹ C. N. Bye, "Casein and mixed protein adhesives" in *Handbook of adhesives*, ed. I. Skeist, Boston, MA, 1990. 135–152.

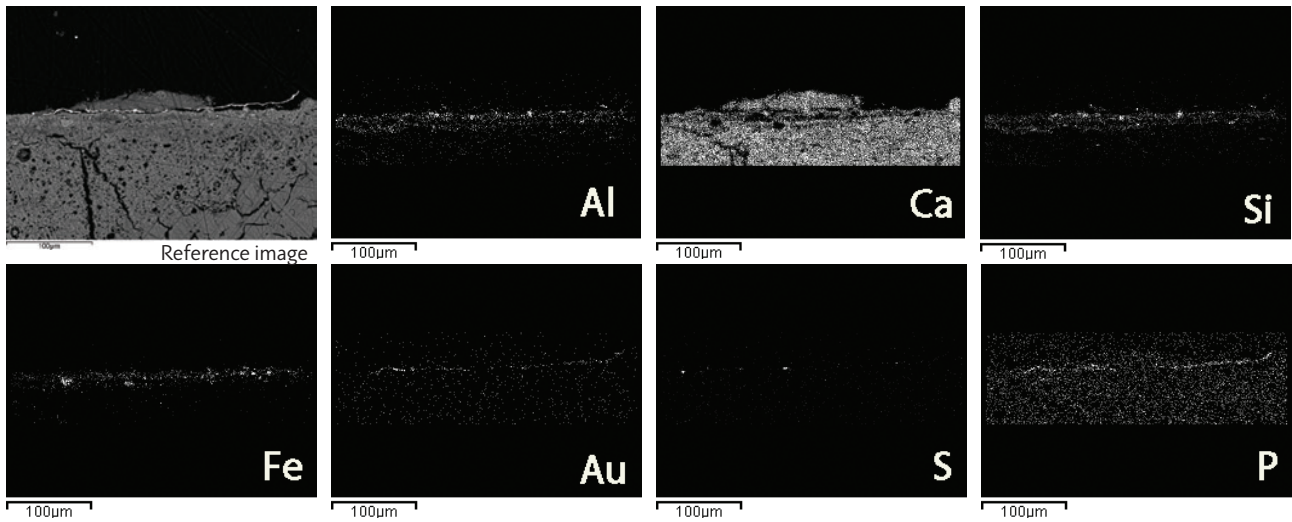
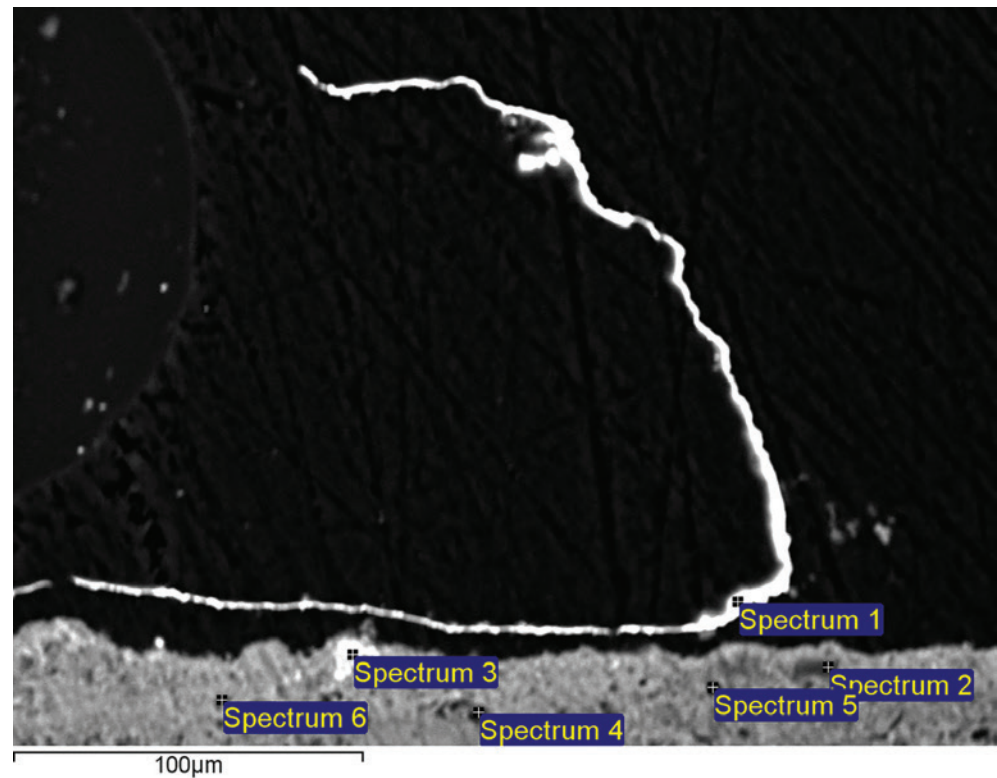


Fig. 9

yellow underlayer, Figure 8D. In both cases they contain some dark orange to red particles. SEI EDX mapping of sample no. 4, (Figure 9), has shown that the basic preparation is made of rather pure calcium carbonate and that either yellow or red layers are made of iron oxide minerals, predominately goethite, in the case of yellow, and hematite in the case of red, with some aluminosilicates. A minor amount of clay minerals containing Mg, K, Na was recorded by spot EDX analyses in the region of yellow and red layers, for example in spot 2 from Figure 10, and its spectrum is shown in Figure 11. The presence of a high amount of calcium in the red and yellow layers and almost absolute absence of sulphur on EDX mapping of sample no. 4 (Figure 9), indicates that the ground for gilding was made with natural red and yellow earth pigments with lime as the binder (*al fresco*). The same is the case in all other fragments, from the other two churches investigated here. On the

Fig. 10



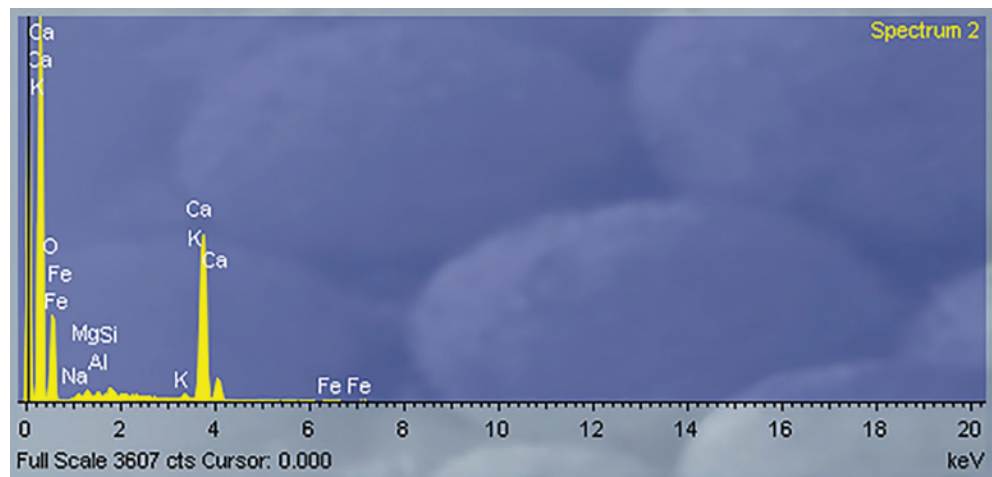


Fig. 11

EDX mapping (Figure 9), we can see an almost absolute absence of sulphur and the presence of a very thin layer rich in phosphorus. This may indicate the egg or casein glue. For the reason mentioned previously we suggest that the egg yolk was used as adhesive for gold leaves.

The gold leaves that are detached from the fresco fragments were collected and examined with EDX, sample no 5. Their average composition is 97.5% gold, 1.6% silver and 0.9% copper, in other words 23.2 carat gold, Figure 12.

Their thickness is about 0.5 μm . This composition is the closest to the Grosso of Lucca (23.7 carats), minted from 1246 or 1256 in the town of Lucca near Florence, which contains about 97% of Au and about 2% Ag with no copper reported⁴². That was the short-lasting coinage in a small number of pieces and probably decommissioned by the end of the century so it is hard to believe that it was available at the time of building the church of St. Stefan at the beginning of the 14th century. The Venetian gold Ducat that was minted from 1284 would be a second choice, but it was made of 24-carat gold (99.4 % of gold) slightly purer than the Florin from Florence that had 99% of gold, so it should also be ruled out as a possibility. The coinage of Byzantium at that time was of much lower purity. This unusual composition of the gold leaves in Banjska suggests that gold was not obtained from the recycling of jewellery (usually 22 carats) or from temporary coins, as expected. A parallel to this composition may be found in gilded mosaic tesserae from the Church of Mount of Olives in Jerusalem (samples A_JH10 and A_JH11), dated to 4th–6th centuries and several samples from St. Apollinare Nuovo in Ravenna from the 5th–6th centuries samples (RAN 13, RAN 14 and RAN15). Here we would add one tesserae from the church in Bethlehem (sample BEsc), built in the 12th century, for which Emperor Manuel I sent the tesserae and the mosaicists (workers). From the same study of Neri et al. (2016), there is one very similar sample from the Mosque of Damascus (DA18). In the 3D presentation of these samples (Figure 12), we can see that the closest to the Banjska gold is the sample from Bethlehem, the 12th century church. This particular sample is said to be a newly produced one and that the gold leaf could have been made by remelting the earlier 7th century coinage, from Islamic early coinage or from an unknown source of gold. The unknown source of gold appears to us very probable, given that in the 7th century gold coinage was made not only in Constantinople, which was the main mint, but

42 Ibid. 31)

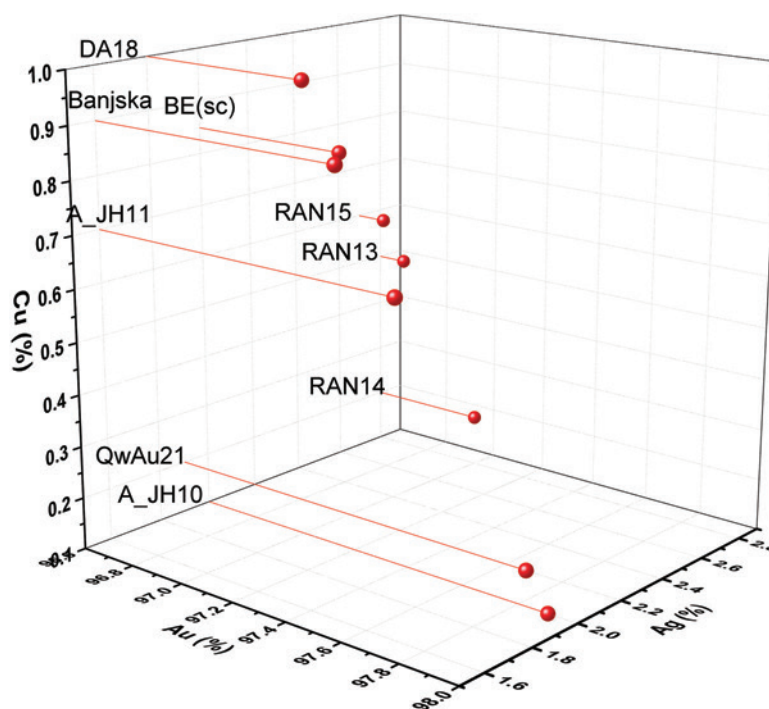


Fig. 12

also in several other provincial mints, among which is the one in Thessaloniki in the Prefecture of *Illyricum*⁴³. If the tesserae had been sent from Constantinople, that means that they could have been produced from any kind of gold existing in the Empire. On the other hand, Umayyads just recycled the Byzantine gold from the mint in Carthage, and at least initially used the same sources as the Byzantine Empire, before Arab occupation (Nubian, Red Sea, Ethiopian and Arabian-Yemen). We should also consider the samples from the 6th century Ravenna as they are completely in accordance with the Byzantine coinage of that time, characteristic of Justinian's renewal of the Empire, due to reconquest of the Balkans, North Africa, Italy and part of Spain. This resulted in new resources and the opening of many provincial mints.⁴⁴

It is well known that gold deposits are present in the Balkans – namely in Serbo-Macedonian-Rhodope Metallogenic Belt (SRMB)⁴⁵. The gold from these territories, from modern-day Serbia (*Illyricum*), Bulgaria (*Thracia*) and parts of North Macedonia and Thessaly in Greece could have served as the raw material for making gold in early, but also in the Late Byzantine period.

From the late 13th century, the Serbian Kingdom, under the rule of King Milutin, had its own silver and gold mines (Brskovo, Novo Brdo, Kopaonik etc.) and the mint of Serbian silver coins in the town of Brskovo^{46,47}. From there the silver was exported to Venice, through the towns of Dubrovnik (*Ragusa*) and Kotor, on the Adriatic

43 Ibid 17)

44 Ibid. 29)

45 A. Tsirambides and A. Filippidis, "Gold metallogeny of the Serbomacedonian-rhodope metallogenic belt (SRMB)", *Bulletin of the Geological Society of Greece*, 50/4 (Thessaloniki), 2016, 2037–2046.

46 М. Гогић, „Рударска производња у средњовековном Брскову”, *Историјски записи* 1 (Подгорица), 2010, 195–214.

47 Д. К. Којић, О саставу и обради племенитих метала из српских средњовековних рудника. *Зборник радова Византолошког института* 50/2 (Београд), 2013, 853–861.

coast. This was the time of prosperity of the Serbian Kingdom, economically founded on the trade in silver and other metals. This was due to the presence of Saxon miners from the middle of the 13th century, who brought new skills in mining to the Southern Slavic population⁴⁸. The position of the gold mines is not precisely defined in written sources, but from the point of geology, wherever silver was mined in polymetallic deposits, such as the ones in Serbia, there was some native gold to be found in the quartz veins on the surface or not deeper than 30 m from the surface. Some of them were in the vicinity of monastery Banjska and are included in the St. Stephen Chrysobull (charter of monastery Banjska issued by King Milutin)⁴⁹. Still, the refining of gold was a very specific operation needed to obtain pure gold from raw materials. That was done in goldsmiths' workshops connected to gold working and the production of other items made of gold. The refining of precious metals still existed in Constantinople, Thessaloniki and possibly Serres, in the late Byzantine period⁵⁰, after year 1261 and the recovery of Constantinople from the Crusaders. These sites were possibly the ones that were nearest to the places from where the gold ore was collected⁵¹. The latter two are being near the borders of Milutin's Kingdom to the South.

We do not know the origin of the gold from the fresco fragments in Banjska, but we can see that it was not made out of contemporary coinage and we can only hypothesise that the origin of the gold can be from Balkan ores, in general, or from the same sources as for the gold coinage in the Damascus mint, from an earlier epoch. Here we would like to emphasise that the most probable sources of gold in the West in the 12th century were those described by Theophilus in book III, chapters 46–49, naming the territory with the Biblical term Havilah (Middle East), from Spain, from river deposits and from the territories of the Arab Empire⁵². The main progress was made with new sources from Serbia (refining the gold-rich silver) and later from Hungary, Bohemia and Silesia. However, most of the supply came from Levant and Africa⁵³. At this stage more precise analyses of gold used in Byzantine Empire would be needed to further elaborate the origin of the gold used for the leaves in the church of St. Stefan in Banjska.

CONCLUSIONS

In this investigation on gilded fresco fragments found in three churches built by the Serbian kings of the Nemanjić Dynasty, between the 13th and the first decades of the 14th century, we gained better insight in the gilding practice of this period. Besides the technique of gilding, the quality of gold leaves gave some new insights into the production of gold leaves in this period. Historically, we can describe the period from the 11th century until the end of the Byzantine Empire as a period of gold shortage. However, this does not mean that gold was not circulated, traded,

48 M. D. Stojković, "The Influence of Saxon Mining on Development of the Serbian Medieval State", *Mining History* 18/5 (London), 2013, 35–44

49 В. Симић, Рудници злата у средњовековној Србији према савременом познавању наших рудишта, *Весник* 19, Београд, 1961, 325–346.

50 K. P. Matschke, "The Late Byzantine urban economy, thirteenth-fifteenth centuries", in *The economic history of Byzantium: from the seventh through the fifteenth century*. Vol. 39, ed. Laiou, Washington, 2002, 463–95.

51 Ibid 18)

52 D. Savoy, *The Globalization of Renaissance Art: A Critical Review*, Leiden, 2017, 144.

53 R. S. Lopez, "Back to gold", 1252. *The economic history review*, 9/2, Glasgow, 1956, 219–240.

objects made of gold gifted and so on. It was just evident that the supplies of raw materials were problematic in Byzantium, and that coinage was made of debased gold. From 1028 these coins – hyperpyron contained ~ 87 % gold and from the siege of Constantinople and revival of coinage in Nicea in 1211, they were debased constantly until the total collapse of the Empire. Meanwhile, in the West, the Republics of Genoa, Florence and Venice started to mint their own pure gold coins from the second half of the 13th century. The purity of the gold from the monasteries Žiča, Mileševa and Banjska does not fit any contemporary coinage.

For Žiča, 93.7% Au, 5.4% Ag, 0.9% Cu (~22.3 carat) gold leaves may be considered to derive from recycling of jewellery or as deliberate action of goldsmiths. Here we find the gold leaves fixed to the foil made of tin. We may say that this is the earliest confirmation of the use of this technique in art, predating the elaborated examples in Giotto's work by about a century. Based on observations under UV light, we can conclude that there are indications that the gold leaf was attached to tin foil with some kind of oil.

In Mileševa, gold leaves are made of 99% gold (24 carats) and for now we can only suppose that they came from the goldsmith workshop that had the access to such a kind of material. These fragments predate the minting of pure gold coins in the West by about twenty years since the first minting of Florins and Genovinis started in year 1252 and of Venetian Ducats in the year 1282.

Large parts of the Mileševa walls are gilded with part gold that was used to imitate mosaics, but here we found another kind of gilding as a part of wall decoration. Gold leaves are attached to the ground preparation with some kind of proteinous adhesive, most probably whole egg. The same kind of ground and the same quality of gold on this fragment and on part gold fragments from the first painting on the walls in this church, confirm the hypothesis that the archaeological finds are from the same period.

In the Banjska monastery, two kinds of ground layers were found, yellow and red. Beneath the red ground there is a light yellow underlayer. In both cases these are the natural iron oxide rich aluminium silicates known as the pigments yellow and red earths, on a support made of lime. Gold leaves with a thickness of about 0.5 µm were attached to the ground, most probably with egg yolk. Analysis of the leaves shows an average of 97.5% gold, 1.6% silver and 0.9% copper (23.2 carats). This composition does not match any contemporary coinage either. The only parallels could be found in some gold tesserae from a much earlier period, the latest being from the 12th century. It is interesting to point out that at the time when these tesserae were made, the gold for the Byzantine Empire was partly obtained from the Balkans. The other possibility is that the origin of this gold was the same as for the mints in Damascus in the 7th century. We hope that future investigation will give answers to this question.

We may conclude that between the 13th and the 14th centuries gold leaves were not made out of gold coins but could have been obtained in goldsmiths' workshops either by recycling of jewellery or from the raw gold obtained from the mining sites that was refined in these workshops.

Here we have shown that a different kind of gilding was practised in the Late Byzantine period, and that these techniques of gilding can be traced in artists' handbooks from the 10th to the 14th centuries. They show the great skilfulness of the artists that created these works and perhaps willingness to make some innovations (imitation of mosaics).

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ILLUSTRATIONS

1: Samples analysed: sample no. 1 from Monastery Žiča, sample no. 2 from Monastery Mileševa, samples no. 3, 4 and 5 from Monastery Banjska, Magnification 15x.

Анализирани узорци: узорак бр. 1 из Манастира Жича, узорак бр. 2 из манастира Милешева, узорци бр. 3, 4 и 5 из Манастира Бањска, Увећање 15x.

2: Mapping of sample no. 1 from Žiča: we can distinguish the Ca rich layer, layer rich in Fe, Mg, Al, Si and two metal layers, one with Sn and the other with Au.

Мапирање узорка бр. 1 из Жиче: можемо разликовати слој богат са Ca, слој богат са Fe, Mg, Al, Si и два метална слоја, један са Sn, а други са Au.

3: Sample no. 1 A) Under the normal light in the dark field, magnification 200x, B) Under UV light, fluorescence of the binder is visible in place of gold leaf and on the place where a tin leaf is attached to the ground layer, magnification 200x.

Узорак бр. 1 А) Под нормалним светлом у тамном пољу, увећање 200x, Б) Под UV светлом видљива је флуоресценција везива на месту златног листа и на месту где је калајни лим причвршћен за основни слој, увећање 200x.

Figure 4: Backscatter electron image of the sample no. 1, thickness of the gold leaf.

Слика повратног расејања електрона узорка бр. 1, дебљина златног листа.

5: A) Whole fragment from Mileševa. B) Cross-section of the gilded part, 100x, sample no 2.

А) Цео фрагмент из Милешеве. Б) Попречни пресек позлаћеног дела, 100x, узорак бр.2.

Figure 6: A) Cross section of sample no. 2. with marked points of measurement. B) Point measurements of golden leaves; Table 1) Results of the measured areas and points on SEI image of the cross section. We can see that in the area where the Au leaf was measured the elements like O, Al and Ca are detected. They are considered as impurities and subtracted so that in further discussion we consider the purity of gold leaf as 100 wt % of gold.

А) Попречни пресек узорка бр. 2. са означеним мерним тачкама. Б) Тачке мерења златних листова; Табела 1) Резултати мерених подручја и тачака на SEI слици попречног пресека. Можемо видети да су у области где је измерен Au лист детектовани елементи попут O, Al и Ca. Они се сматрају нечистоћама и одузимају се, тако да у даљој расправи сматрамо чистоћу златног листа као 100 тежинских % злата.

7: SEI EDX mapping of sample no. 2, from Mileševa.

SEI EDX мапирање узорка бр. 2, из Милешеве.

8: Samples from Monastery Banjska: A) Gold leaf on yellow ground, sample no. 3, B) Cross section of sample no. 3, C) Gold leaf on red ground, sample no. 4 D) Cross section of sample no. 4.

Узорци из манастира Бањска: А) Златни лист на жутој подлози, узорак бр. 3, Б) Пресек узорка бр. 3, В) Златни лист на црвеној подлози, узорак бр. 4 Г) Пресек узорка бр. 4.

9: Mapping of sample no. 4 from Banjska with SEI EDX.

Мапирање узорка бр. 4 из Бањске са SEI EDX.

10: SEI image of sample no. 4 with spots analysed

SEI слика узорка бр. 4 са анализираним тачкама

11: Spectrum of point 2 from Figure 10

Спектар тачке 2 са слике 10

12: 3D presentation – content of Au, Ag and Cu in the leaves of Byzantine period gilded mosaic samples and the gold from Banjska.

3Д приказ – садржај Au, Ag и Cu у узорцима листова позлаћеног мозаика из византијског периода и злату из Бањске.

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ПРЕГЛЕД ТЕХНИКА ПОЗЛАТЕ КАСНОВИЗАНТИЈСКИХ ЗИДНИХ СЛИКА ИЗ СРБИЈЕ

Резиме: У овом раду обрађују се подаци о карактеристикама техника позлате на фрагментима зидних слика који су пронађени током археолошких ископавања у црквама манастира Жича, Милешева и Бањска. Сматра се да ови фрагменти припадају првобитном сликарству у овим црквама. На овај начин желели смо да употпунимо сазнања о техникама позлате на овим просторима од почетка тринаестог до почетка четрнаестог века.

У манастиру Жича, на узорцима са жутом или црвеном подлогом, установљено је да се изнад подлога које се састоје од земљаних пигмената на бази оксида гвожђа и алумосиликата налазе калајне фолије које су позлаћене. Између калајне фолије и златног листића дебљине око 1.7 µм уочена је оранж флуоресценција што указује на везиво на бази уља. Ова техника описана је у Ченинијевом *Il libro dell'arte* поглавље XCIX. Златни листићи су чистоће 22,3 карата. Овим је доказано да је позлаћивање применом позлаћених калајних листића било у употреби почетком тринаестог века, скоро један век пре познатих примера код Ћота ди Бондонеа са почетка четрнаестог века. Из манастира Милешева, анализиран је један узорак, са жутом подлогом од земљаног пигмента на бази оксида гвожђа и алумосиликата. Везиво је највероватније од целог јајета а квалитет злата је 24 карата. Квалитет злата је исти као претходно описан на имитацијама мозаика од ламинираног злата на сребрним фолијама, детектованим на зидовима цркве. Ово говори у прилог томе да је овај узорак из периода, првог осликавања Милешева. У манастиру Бањска, присутни су фрагменти са жутом и црвеном подлогом на бази оксида гвожђа са алумосиликатима. Везиво је највероватније жуманце а чистоћа злата је 23,2 карата.

Састав златних листића не одговара ниједној актуелној продукцији златног новца из тог времена. Може се претпоставити да су листићи набављани директно из златарских радионица где је вршено пречишћавање злата, рециклажа и прављење легура, и то по правилу под строгим контролом државне управе. За Бањску можемо рећи да постоје индикације да злато може да потиче од сировина са простора Балкана или са простора из којих је ковница новца у Дамаску, током шестог и седмог века добављала сировине за производњу златног новца.

Кључне речи: фреска, позлата, Византија, уметност, Србија