# INSIGHTS INTO THE MINERAL PIGMENTS (CINNABAR, ORPIMENT AND LEAD- AND COPPER-BASED PIGMENTS) EMPLOYED IN THE CREATION OF WOODEN TRANSYLVANIAN ICONS DATED EIGHTEENTH TO EARLY NINETEENTH CENTURIES

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*Introduction*

This paper is a contribution to a wider study that aims to shed new light on Transylvanian icon painting from historical and scientific perspectives. The purpose is to uncover the origins and characteristics of the materials used, as well as to reconstruct the traditional techniques employed in icon painting.

To achieve this goal, a set of representative Transylvanian icons from the Museikon collection of the National Museum of Union Alba Iulia have been investigated using different micro-analytical methods to identify the materials and reconstruct the old techniques of icon painting in the region. Specific pigments and other painting materials that are related to local raw mineral or vegetal sources have been identified on the investigated Transylvanian icons, and parts of the results have already been presented and published: earth pigments prepared from local coloured earths,[1] plaster from gypsum of local origin[2] and some resins used to prepare the varnish which could have been harvested from local coniferous trees.[3]

This study focuses on a group of pigments found on the investigated Transylvanian icons: cinnabar, orpiment, lead- and copper-based pigments, which we hypothesise are related to local mineral deposits and mining exploitations in the region and could have been synthetised using local ingredients. We, therefore, have gathered documentary evidence as to their provenance, as well as to the methods of obtaining them known at the time. Our approach to the documentation and retrieval of the Transylvanian

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[1] Dumitrița Daniela Filip et al., "Local Raw Material Sources in the Color Pallete of the Transylvanian Icon Painters. The Reproduction of some Colored Earth Pigments of Local Provenience," *TS* 15 (2023):335-361; Dumitrița Daniela Filip et al., "Materie și Icoană: materiale și tehnica de pictare a icoanelor pe lemn din Transilvania în secolul al XVIII-lea" [Material Matter and Icon: Materials and Wooden Icon Painting Technique in the 18th Century Transylania], in Dumitrița Daniela Filip, ed., *Materie și Icoană: materiale și tehnica de pictare a icoanelor pe lemn din Transilvania în secolul al XVIII-lea* [Material Matter and Icon: Materials and Wooden Icon Painting Technique in the 18th Century Transylania] (Alba Iulia, Cluj-Napoca: Editura Muzeului Național al Unirii, Mega, 2023), 11-94.

[2] Filip et al., "Materie și Icoană," 29-34.

[3] A study based on experiments and the reproduction of historical varnishes followed by artificial ageing was undertaken and the research is still in progress. See Dumitrița Daniela Filip et al., "Study of Old Varnish Recipes used by The Transylvanian Icon Painters. Case study: Reproduction and characterization of varnishes used in 18th-century and early 19th-century icons from Museikon collection," *Apulum,* Series *Historia et Patrimonium* 60 (2023): 307-327.

icon painting techniques relies on three interconnected directions: the study of historical written sources, micro-analytical investigations (in this specific case, XRF and microscopic analysis) to confirm the documentary evidence, and field research in the region to map the natural resources necessary to the Transylvanian painters. We expect to better understand and contextualise the techniques of wooden icon painting in Transylvania through the correlation of the results obtained by this integrated approach. The identification of materials and their origin (local or imported) together with wooden panel manufacturing and painting techniques will ease the comparison of local icons both with the more known Greek and Russian ones and with those from the territories of the former Polish-Lithuanian commonwealth.

*The use of cinnabar, orpiment and lead- and copper-based pigments according to historical written sources*

As we previously presented in our studies,[4] we identified two types or groups of written sources that document both the theory and the practice of icon painting techniques in the eighteenth century and early nineteenth century. The first group consists of books/treatises of icon painting, namely different versions of the Hermeneia, with the most well-known version being that of Dionysios of Fourna.[5] The second group consists of archival documents that record the use of specific materials by the local masters. The main local source currently known is the testimony of master Grigore Ranite regarding one of his icons that was reported to have shed tears in 1764.[6]

The instructions given by the Hermeneia on the preparation methods of the pigments considered in this paper are briefly summarised in the following. Cinabbar was recommended to be used for the rendering of flesh tones and for painting garments, but it was also used as a colorant for red ink.[7] Dionysios gave instructions on the preparation of cinnabar from three chemical elements: quick-silver (mercury), brimstone (sulphur) and litharge (lead oxide).[8] He also mentioned the method based on grinding the mineral; for the same reasons a few centuries earlier, a Western master, Cennino Cennini, recommended the same method[9] to avoid buying a cinnabar adulterated with the cheaper red lead. Nineteenth-century written sources confirm that icon painters bought this pigment from local markets (Râmnic, Sibiu, Brașov).[10]

[4] Filip et al., "Local Raw Material Sources"; Filip et al., "Materie și Icoană," 12-13, 27-28.

[5] Dionisie din Furna, *Erminia picturii bizantine* [The Hermeneia of Byzantine Painting] (Bucharest: Sophia, 2000). Vasile Grecu made an inventory of the versions and sources of the Hermeneia. See Vasile Grecu, *Cărți de pictură bisericească bizantină* [Byzantine Church Painting Books] (Cernăuți: Institutul de Arte Grafice și Editura "Glasul Bucovinei"), excerpt from *Candela* 43 (1932): 105-137; Vasile Grecu, *Contribuții la studiul izvoarelor manualului de pictură bizantină* [Contributions to the Study of the Sources of the Byzantine Painting Manual] (Cluj: Cartea Românească, 1931), 1-7.

[6] The Testimony of master Grigore Ranite, *Documents from Blaj*, no. 449, fol. 7, Serviciul Județean Cluj al Arhivelor Naționale [Cluj County Service of the National Archives]; Ioan Chindriș, ed., *Icoana plângătoare de la Blaj 1764* [The Crying Icon of Blaj 1764] (Cluj-Napoca, 1997), 52-55.

[7] Dionisie din Furna, *Erminia,* 36-37, 50.

[8] Ibid., 48.

[9] Ibid., 58-59; Cennino Cennini, *Tratatul de pictură* [Painting Treatise] (Bucharest: Meridiane, 1977), 59-60.

[10] Ghenadie al Râmnicului, *Iconografia – arta de a zugrăvi templele și icoanele bisericești* [Iconography: The Art of Painting Temples and Church Icons] (Bucharest: Tipografia "Cărților Bisericești," 1891), 258-259.

Cinnabar (HgS) is a dense toxic red mineral found fairly widely, but not abundantly, distributed in the world. There are three types of mercuric sulphide pigments: 1. the natural, obtained by finely grinding cinnabar; 2. the synthetic form produced through the dry process, commonly known as vermilion; and 3. the synthetic variety created through a wet process, also referred to as vermilion.[11] Cinnabar has mainly been used to paint, to decorate architectural structures and mobile objects, to write (ink in manuscripts), to colour red lacquers and to serve for medicinal and cosmetic purposes. The earliest evidence of cinnabar's use as a colouring pigment is found in a painted plaster skull discovered in Kfar HaHoresh, Israel, dating back to the ninth millennium BC.[12] According to studies made so far, cinnabar was used as an artist's pigment up to modern times, when it became forbidden due to its toxicity.[13]

Lead white was the most used lead pigment and the most important of all white pigments. It was produced from early historical times until the nineteenth century, when zinc white and then titanium white replaced it.[14] The Hermeneia of Dionysios of Fourna gave instructions on the preparation of lead white from metallic lead strips and weak acetic acid solution (vinegar).[15] The result is a corrosion product of metallic lead exposed to the combined action of the acetic acid vapours, heat, carbon dioxide in the air and water vapour, which slowly transforms the lead to basic lead carbonate. Lead white, whose native mineral is cerussite ($PbCO_3$), was used from ancient times until the nineteenth century and was traditionally prepared from metallic lead and vinegar.[16] From the eighth century AD, its occurrence increased in every type of support and technique, such as to prepare grounds and gildings, paint in white and lighten other colours. Lead white can be transformed into several other Pb-based compounds, through heating and/or degradation (leading to colour change and darkening).[17]

Red lead, also known as minium, was mentioned in the Hermeneia of Dionysios of Fourna as a necessary ingredient for the preparation of: 1. poliment for gilding (in the composition of the clay bole), 2. adhesive for gilding (today known as mixtion) and 3. linseed oil varnish.[18]

Orpiment was indirectly mentioned by Dionysios, who drew attention to the fact that arsenic should not be used for fresco painting due to its lack of compatibility with fresh lime plaster.[19] Although orpiment was not mentioned for its use in panel painting, it was identified on the icons painted by

[11] Rutherford J. Gettens, Robert l. Feller, and W. T. Chase, "Vermilion and Cinnabar," *Studies in Conservation* 17 (1972): 45-69.
[12] Elisabetta Gliozzo, "Pigments – Mercury-Based Red (Cinnabar-Vermilion) and White (Calomel) and Their Degradation Products," *AAS* 13, 210 (2021): 1-53.
[13] According to Elisabeta Gliozzo, "Pigments-Mercury based," 2, cinnabar was banned for paints in 1990 due to its toxicity, while Rutherfort J. Gettens, Robert L. Feller, and W. T. Chase, "Vermilion and cinnabar," in Ashok Roy, ed., *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 2 (London: National Gallery of Art, Washington: Archetype Publications, 2012), 160, cited Eibner, who stated at the beginning of the twentieth century that it had no longer been available as an artist's pigment since 1880. See also Mauro Matteini, Rocco Mazzeo and Arcangelo Moles, *Chemistry for Restoration. Painting and Restoration Materials* (Florence: Nardine Editore, 2017), 50.
[14] Rutherford J. Gettens, Hermann Kuhn, and W. T. Chase, "Lead White," in Roy, ed., *Artists' Pigments*, 67-81; Matteini, Mazzeo, and Moles, *Chemistry for Restoration*, 22-23.
[15] Dionisie din Furna, *Erminia*, 49.
[16] Matteini, Mazzeo, and Moles, *Chemistry for Restoration*, 22; Gettens, Kuhn, and Chase, "Lead White," 69.
[17] Elisabetta Gliozzo, and Corina Ionescu, "Pigments – Lead-Based Whites, Reds, Yellows and Oranges and Their Alteration Phases," *AAS* 14, 17 (2022): 17-19.
[18] Ibid., 33, 34, 40.
[19] Ibid., 58.

Dionysios a few years after he wrote the treatise.[20] Two methods of obtaining orpiment are reported in the literature: 1. from the arsenic sulphide mineral ($As_2S_3$), by grinding or by levigation, and 2. by the sublimation of pyrites ($FeS_2$) or arsenopyrites (FeAsS).[21] Orpiment is a naturally occurring arsenic sulphide ($As_2S_3$) found widely in nature, but in relatively small deposits. Orpiment pigment was used by ancient Middle Eastern artists, but it did not attract significant attention from Western artists until the eighteenth century, when production of artificial arsenic trisulfide had begun.[22] However, due to its extreme toxicity, its use was largely abandoned, except for a very fine grade called king's yellow, which continued to be employed until the availability of cadmium yellow pigment.[23]

Natural and synthetic green and blue copper-based pigments were also used in icon painting. Instructions on the preparation methods of synthetic copper-based pigments were also given by Dionysios.[24] The process is based on a corrosion reaction of metallic copper exposed to a diluted acetic acid solution, such as grape pomace extract or vinegar. Copper-based green and blue pigments have been used since antiquity. They include natural minerals (malachite and azurite), their artificial analogues known as verditers, various basic copper chlorides and/or sulphates with uncertain origins, as well as synthetic pigments such as ancient Egyptian blue, verdigris (copper acetates), modern emerald and Scheele greens.[25]

Cinnabar, lead white and "grunspan" (a green copper-based pigment) were also mentioned by the master Grigore Ranite in a testimony.[26] The first two pigments were used both for rendering flesh tones and for painting garments, while "grunspan" was used only for painting backgrounds, garments and landscapes. Unfortunately, the icon he was referring to was lost during the inquiry for which his testimony was requested.

*The list of the investigated icons*

Nineteen Transylvanian icons from the Museikon collection selected[27] for this study and painted in the eighteenth century and early nineteenth century belonged to local parish churches, now located in Alba county, as presented in table 1. Some of them are presented in fig. 1. Fifteen icons were painted by nine of the most well-known local masters, who signed and dated some of them with inscriptions: Grigore Ranite, Iacov of Rășinari (Feisa), Gheorghe son of Iacov, Simon of Bălgrad (also known as Simon Oprovici of Craiova), Stan, Nistor Dascălul and Popa Ivan, masters from Rășinari, Simion Silghi Sălăgeanu and Popa

[20] Thomas Mafredas, Eleni Kouloumpi, and Stamatis C. Boyatzis, "Did Dionysius of Fourna Follow the Material Recipes Described in His Own Treatise? A First Analytical Investigation of Four of His Panel Paintings," *Heritage* 4 (2021): 3770-3789.

[21] Elisabeth West Fitzhugh, "Orpiment and Realgar," in Elisabeth West Fitzhugh, ed., *Artists' Pigments. A Handbook of Their History and Characteristics*, vol. 3 (London: National Gallery of Art, Washington Archetype Publications, 2012), 55; Mihail Mihalcu, *Fața nevăzută a formei și culorii. Enciclopedia îndeletnicirilor tehnico-artistice populare vechi românești de la A la Z* [Beyond Shape and Colour. The Encyclopaedia of Technical-Artists Folk Craft from A to Z] (Bucharest: Editura Tehnică, 1996), 11-12; Constantin Săndulescu-Verna, *Materiale și tehnica picturii* [Materials and the Painting Technique] (Timișoara: Marineasa, 2000), 89.

[22] Matteini, Mazzeo, and Moles, *Chemistry for Restoration*, 45.

[23] Britannica, The Editors of Encyclopaedia, "orpiment". *Encyclopedia Britannica*, accessed 23 January 2023, https://www.britannica.com/science/orpiment.

[24] Dionisie din Furna, *Erminia*, 48-49.

[25] Silvie Švarcová et al., "Pigments – Copper-Based Greens and Blues," *AAS* 13, 11 (2021): 2-11.

[26] The Testimony of Master Grigore Ranite, *Documents from Blaj*, no. 449, fol. 7, SJCJAN Archive; Chindriș, ed., *Icoana plângătoare de la Blaj 1764*, 52; Dionisie din Furna, *Erminia,* 36-37, 50.

[27] We extended our research, and in this study we present a larger number of Transylvanian icons investigated than those presented in Filip et al., *Materie și Icoană*, 49-51.

Nicolae of Feisa. The other four icons were painted by anonymous masters. They were included in the study to elucidate their identity and artistic paternity. The icons that were part of an assembly (e.g., iconostasis, namely royal icons) or group of icons and that do not have inscriptions were attributed and dated after correlating networks of information.[28]

Fig. 1. Some of the icons investigated: (a) icon GR; (b) icon AZ, for which green was made of an admixture of orpiment and copper based blue pigments; (c) icon IR, for the red background red lead alone was used; (d) icon GsI, for which copper-based pigments were identified. Credits Museikon.

Tabel 1. The Transylvanian icons investigated.

| Nr. crt. | Code | Icon | Provenance of the icon | Date of creation | Master |
|---|---|---|---|---|---|
| 1 | **GR** | The Descent of the Holy Spirit | Galda de Sus | 1736-1737 | Grigore Ranite |
| 2 | **IR1** | Mother of God with Child | Silivaș | 18th c. | Iacov of Rășinari (Feisa) |
| 3 | **IR2** | Jesus Christ | Fărău | | |
| 4 | **IR3** | Deisis | Biia | | |
| 5 | **GsI1** | Mamvri Supper | Berghin | 1790-1800 | Gheorghe son of Iacov |
| 6 | **GsI2** | Saint Nicholas | Berghin | 1790-1800 | |
| 7 | **GsI3** | Jesus Christ | Căpud | 1802 | |
| 8 | **PIR** | Mother of God with Child | Ghirbom | 1720-1740 | Popa Ivan from Rășinari |
| 9 | **SR** | Mother of God with Child | Afteia | 1767 | Stan of Rășinari |
| 10 | **NDR** | Archangel Michael | Sălciua de Sus | 1730-1750 | Nistor Dascălul of Rășinari |
| 11 | **SB1** | Mother of God with Child | Galda de Sus | 1782 | Simon of Bălgrad (Simon Oprovici of Craiova) |
| 12 | **SB2** | Jesus Christ | Mirăslău | 1795 | |
| 13 | **SSS1** | Mother of God with Child | Peleș | 18th c. | Simion Silaghi Sălăgeanu |
| 14 | **SSS 2** | Saint John the Baptist | Gârda | 1804 | |

[28] For the attribution of some icons we used the proposals of Ana Dumitran from the inventories and file of the icons of the National Museum of Union Alba Iulia, Museikon Department.

| | | | | | |
|---|---|---|---|---|---|
| 15 | **PNF** | Holy Trinity | Șilea | 1823 | Popa Nicolae of Feisa |
| 16 | **AZ** | Saint Nicholas | Zlatna | 18th c. | Anonymous |
| 17 | **AS** | Saint Nicholas | Sălișteа | 18th c. | Anonymous |
| 18 | **ASS1** | Saint Paraskeve | Sălciua de Sus | 18th c. | Anonymous |
| 19 | **ASS2** | Saint Demetrius | | | |

*Pigment identification by XRF analysis*

XRF analysis was carried out with a portable Micro-XRF Spectrometer Elio from Bruker. This non-contact measurement is non-invasive and completely non-destructive. No sample preparation is required. The spectrometer consists of an X-ray source with a Rhodium anode, operating at voltages ranging from 10 to 50 kV and a current capacity of up to 200 μA, yielding a maximum power of 4 W. Additionally, it features a Silicon Drift Detector with an active area measuring 25 mm². The emitted source is collimated, resulting in an analysis spot diameter of 1.2 mm on the sample at a working distance of 1.4 cm. The analyses were carried out at 40 kV and 40 μA, with an accumulation time of 60 seconds.

Microscopic observations were performed in the areas measured by XRF spectroscopy to better ascertain the colour. They were carried out at 50X and 200X magnification with a portable digital microscope, Dino-Lite AD7013MZ, with a resolution of 1.3 Megapixels.

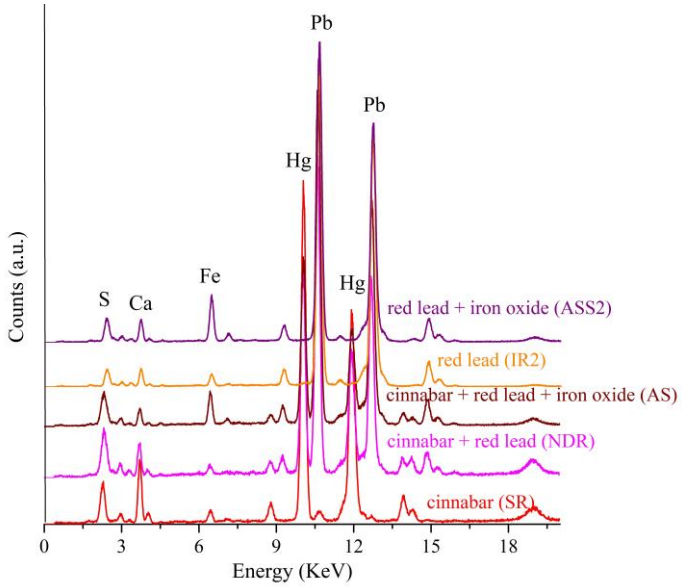



Fig. 2. XRF spectra of red hues found in Transylvanian icons (icons SR, NDR, AS, IR 2, ASS 2). Credits Cristina Carșote.

The use of c*innabar* (HgS) pigment, alone or in a mixture, was detected based on the identification of Hg in the XRF spectra. Cinnabar alone was found only for icon SR, while combinations of cinnabar with other red pigments were more frequent. Cinnabar and red lead mixtures were identified on six icons

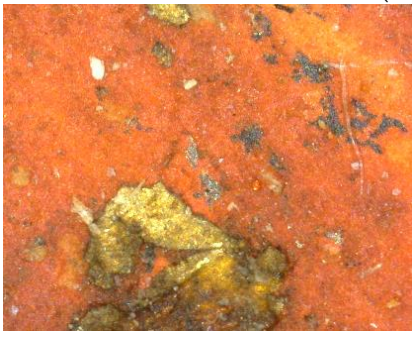
(SB1, GsI 1, IR 3, PIR, NDR, SSS 1) and cinnabar, red lead and iron-rich earth-pigment mixtures (ochre) were found on nine icons (R, AZ, AS, ASS 1, SB 2, IR 1, GsI 2, GsI 3, PNF). The presence of red lead alone was revealed on one icon (IR 2), whereas an admixture of red lead and ochre was identified on two icons (ASS 2, SSS 2). In fig. 2 the XRF spectra are shown of the red hues found in the Transylvanian icons (SR, NDR, AS, IR 2, ASS 2 icons), while fig. 3 emphasises the aesthetic/visual differences as revealed by the microscopic images.

Cinnabar (SR icon)

Cinnabar + red lead (NDR icon)

Cinnabar + red lead + iron oxide (AS icon)

Red lead (IR2 icon)



Red lead + iron oxide (ASS2 icon)

Fig. 3. Microscopic images of the red hues in Transylvanian icons (icons SR, NDR, AS, IR 2, ASS 2). Credits Cristina Carşote.

Lead white was found on all white-coloured areas of the icons, as expected. Its identification was based on the Pb signals in the XRF spectra of whites. Lead white served for the painting of different "white" objects and bright details, such as the light on garments, architectural elements, texts etc. The XRF spectrum of lead white from icon NDR and its microscopic image are presented in fig. 4.

Orpiment was detected only in 6 icons (PIR, NDR, AZ, AS, ASS 1, ASS 2), based on the identification of As signals in the XRF spectra taken on yellow and green colours. Orpiment alone was found on two icons (PIR, NDR), whereas an admixture of orpiment and iron-rich earth pigment (yellow ochre) was identified in three cases (AS, ASS 1, ASS 2). Orpiment combined with a copper-based blue pigment was used to obtain the green colour only on icon AZ. It is worth mentioning that yellow ochre was identified on three other icons (SB 2, IR 3, GR),[29] while the other 11 icons do not incorporate yellow

[29] Filip et al., *Materie și Icoană*, 46-48.

in their colour palettes. Fig. 5 shows the XRF spectra of yellow hues in icons PIR and AS, and of green colour in icon AZ, while fig. 6 presents the microscopic images corresponding to the analysed areas.

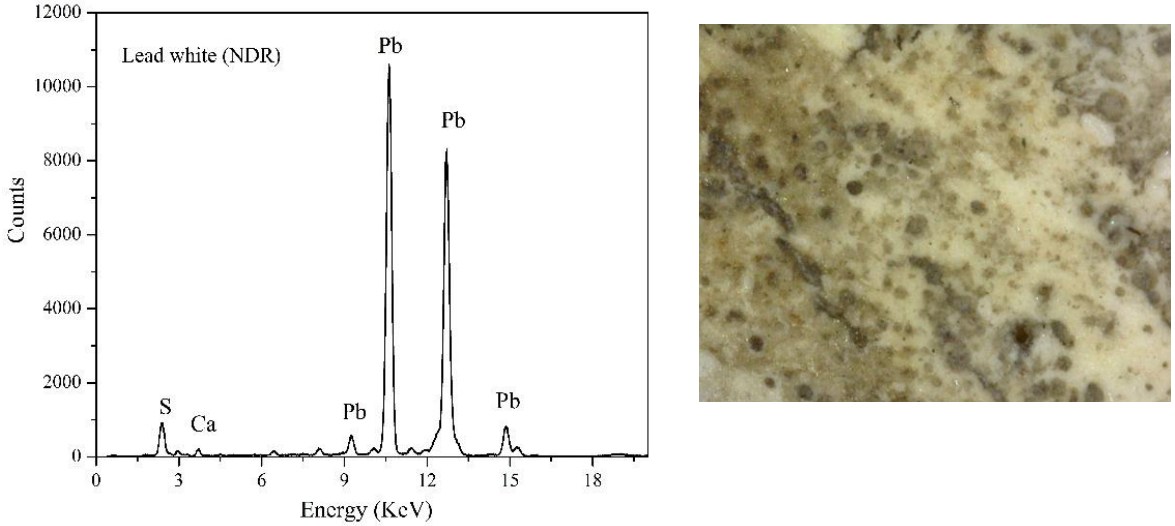



Fig. 4. XRF spectrum of lead white (icon NDR) and its microscopic image. Credits Cristina Carșote.

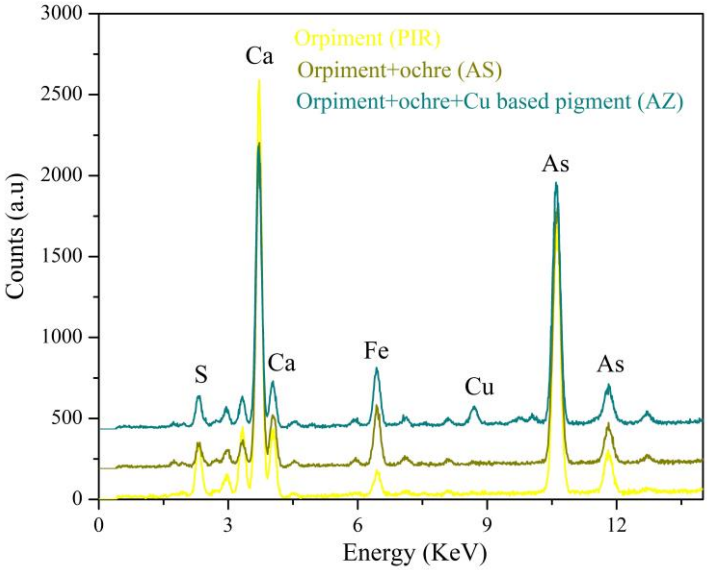
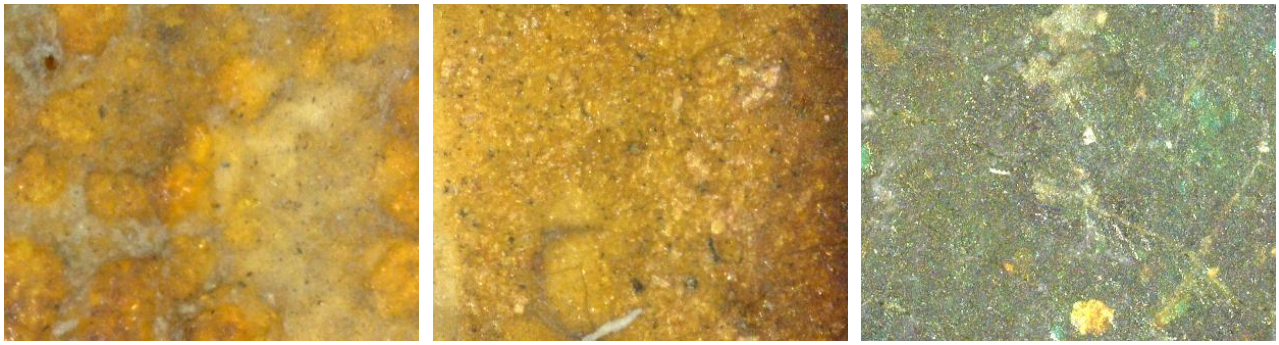



Fig. 5. XRF spectra of yellow hues (icons PIR and AS) and green colour (icon AZ). Credits Cristina Carșote

According to the XRF results, eleven of the investigated Transylvanian icons were painted using copper-based green pigments (SB 1, SB 2, R, SR, IR 3, SS1, SS2, NDR, GsI 1, GsI 3, PNF). Besides the green colour of the icon "Saint Nicholas" from Zlatna (AZ) obtained by mixing a copper-based blue pigment

with yellow orpiment, the remaining seven icons do not have green in their colour palettes. A copper-based blue pigment was also identified in icon GsI 1, specifically used for painting the blue garments. For the other Transylvanian icons, Prussian blue or ultramarine (identified by complementary FTIR analysis) were preferred for blue painting in backgrounds and garments.[30] The XRF spectra of copper-based green and blue pigments in icons SB1 and GsI 1 are presented in fig. 7, while the microscopic images of the analysed areas are illustrated in fig. 8.



Orpiment (PIR icon) | Orpiment + ochre (AS icon) | Orpiment + ochre +Cu based pigment (AZ icon)

Fig. 6. Microscopic images of orpiment, of orpiment and ochre and of orpiment and copper-based pigment in Transylvanian icons (PIR, AS, AZ icons). Credits Cristina Carșote.

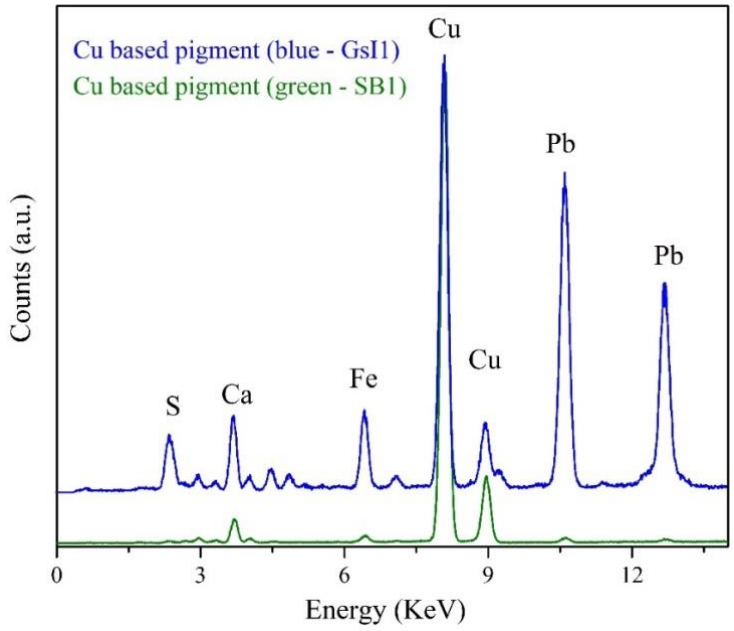
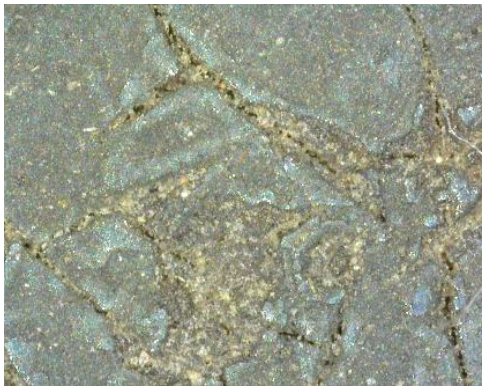



Fig. 7. XRF spectra of copper-based pigment in icons SB1 and GsI 1. Credits Cristina Carșote.

[30] See Filip et al., *Materie si icoană*, 43-45.

Copper-based pigment (green - SB1 icon)



Copper-based pigment (blue - GsI1 icon)

Fig. 8. Microscopic images of copper-based pigments in Transylvanian icons (icons SB 1, GsI 1). Credits Cristina Carşote.

In summary, it can be concluded that lead white was employed in all the Transylvanian icons investigated. Red lead and cinnabar mixtures were most frequently used. Copper-based green pigments were used with a high frequency for the painting of garments and landscapes (ground), while orpiment was used to obtain a light and vibrant yellow colour. It is worth noting that neither green nor yellow are present in the colour palettes of all the investigated icons. The copper-based blue pigment was identified only on a few of the icons.

When analysing the frequency of use of pigments in the icons we should keep in mind the symbolism of colours from a theological perspective: the colour palette in Eastern iconography was deliberately chosen for its symbolic value. Thus, on the one hand, white and black pigments are necessary to lighten or darken the other colours, while red and blue are among the most used colours, if not indispensable, to obtain the hues of garments for the icons of Jesus Christ, the Mother of God and of other categories of saints (martyrs, archangels, hierarchs etc).[31] On the other hand, green was mainly used to suggest land and vegetation (greenery) and, sporadically, in the painting of the garments of saints. After this detour into the correlating of theological meanings of colours and their frequencies of use in iconography, we may see that the symbolism of colours and their uses for specific purposes as presented in the Hermeneia are key to understanding why the investigated icons all have red in their colour palettes, while only half of them have green. What is important for our study is the use of specific red, yellow, white, green and blue pigments. We shall notice the frequent use of red lead and cinnabar. Although cinnabar was considered an expensive pigment, it was identified in sixteen out of the nineteen icons, very often in admixture with the other frequently used red pigment, namely red lead (minium). On the

[31] See the instructions from the Hermeneia regarding the colours of the garments of Jesus Christ, the Mother of God etc. Dionisie din Furna*, Erminia*, 147-148. For their symbolism in Christian art, see Dionysus the Areopagyte, *The Celestial and Ecclesiastical Hierarchy* (London: Skeffington and Son, Picadilly, W., 1894), 43, 48, 53. He spoke about noble symbols (sun, moon, stars) and inferior symbols (colours). In his book *The Celestial Hierarchy* he explained the means/symbolism of colours: If they are white, they are an image of light; if they are red, they represent fire; if they are yellow, they symbolise gold; if they are green, they represent youth and the flower of the soul; while dark blue stands for mystery and red for fiery movement.

contrary, cheaper pigments were used in the mass production of icons (i.e., Russian icons), as we have previously reported.[32]

By comparing the pigments identified in the 19 Transylvanian icons investigated with the pigments employed in the painting of the Russian mass-produced icons that were brought to Transylvania,[33] we observed that the cinnabar, orpiment and lead- and copper-based pigments often encountered in Transylvanian icons are very rarely used for icon mass production. This is another reason why we set out to document the presence and availability of these pigments locally. Our hypothesis is that the local abundances of minerals such as orpiment and cinnabar, and of lead- and copper-based minerals, facilitated their use in the local iconography of the time. *Local raw material deposits and the possible provenance of the pigments discussed*

Field research was carried out in the region in order to identify and map the local raw material sources suitable for icon painting. The collection of the Natural Science Museum of Aiud was studied to identify specimens of local minerals that could serve as raw material sources for pigments preparation. The mineral collection of the aforementioned museum is valuable for this research for several reasons: 1. the Natural Science Museum of Aiud is the oldest museum of this kind established in Transylvania, founded at the end of eighteenth century, and therefore, most of the items preserved there are almost contemporaneous to the investigated icons; 2. the minerals from the collection were brought from the most important historical mines located not only in Transylvania, but also in Banat and other former territories of the Habsburg Empire (Hungary, Slovenia, Austria); 3. numerous specimens of local minerals testify to their abundance in the region.[34]

As we have previously stated in our studies, diverse colours of earth pigments (yellow, red and brown ochres, green earth etc.) of local origin were employed by the masters in painting the investigated icons. These pigments of pedological origin, obtained from local sources, were reproduced and characterised.[35] They are wide spread in Alba county and easy to find. We extended our research on the pigments discussed in this paper to map the local resources that could supply the raw materials for their preparation.

As we have already stated, cinnabar and orpiment pigments can be prepared following two methods: 1. by grinding the minerals, or 2. by synthesis from the chemical elements, respectively by sublimation of pyrites ($FeS_2$) or arsenopyrites (FeAsS).[36] To reconstruct the first method, the raw minerals are needed, while for the second, the aforementioned elements. We may ask in this context: *did the Transylvanian masters have access to the mineral sources and to the other ingredients needed*? Hence, we need to zoom, on the one hand, into the geological formation and distribution in the area and, on the

[32] For more details see Dumitrița Daniela Filip, Cristina Crașote, and Elena Badea, "New Insights into the Transfer and Reception of Russian Icons in Transylvania Based on the Interdisciplinary Research of the RICONTRANS Project," in Ana Dumitran, and Dumitrița Daniela Filip, eds., *Russian Icons from Transylvania* (Cluj-Napoca: Mega, 2023), 81-82.

[33] For example, in the colour palette of Russian mass-produced icons (eighteenth-nineteenth centuries), investigated for ERC RICONTRANS project, orpiment and copper-based pigments were not identified, while cinnabar was identified on a few icons. See Filip, Carșote, and Badea, "New Insights," 78-86.

[34] For more details see Muzeul de Științele Naturii Aiud, Registru inventar [Inventory], vol. 2, 4933-14647 (1955), 12161-13805, pages 1242-1407.

[35] Filip et al., "Local Raw Material Sources"; Filip et al., *Materie și Icoană*, 46-50, 51-63, 71-74.

[36] Fitzhugh, "Orpiment and Realgar," 55; Mihalcu, *Fața nevăzută a formei*, 11-12; Săndulescu-Verna, *Materiale și tehnica picturii*, 89.

other hand, into the local natural resources related to the mining activities in the region (underground or surface exploitation) and map the natural resources taking into account the places where the icons were painted.

The *mineral cinnabar* is formed either in volcanic environments or by mineralisation.[37] There were reported important cinnabar occurrences at Izvorul Ampoiului (Metaliferi Mountains – part of the Apuseni Mountains) and Sântimbru Băi (Harghita Mountains), in the Gutâi mountains (Ilba, Baia Sprie, Cavnic, Băiuț) and near Brad (Hunedoara county).[38] Although there is no historical evidence yet discovered to confirm that cinnabar was exploited or mined for its use as a red pigment, we can hypothesise on the use of local cinnabar in icon painting, firstly taking into consideration the intense exploitation in the region and its availability on local markets. Studies made by V. Wollmann reported important mineral deposits of cinnabar located near Alba Iulia, at Zlatna (on the hills Dumbrava and Băbui-Vâltori, Valea Dosului) intensively exploited during the eighteenth century.[39] He mentioned an overproduction of mercury in 1750 due to the exploitation of cinnabar, and even samples of the mineral being sold on markets.[40] The Natural Science Museum of Aiud (Alba county) owns samples of cinnabar from Dumbrava – Valea Dosului (Alba county) and other samples of local provenance (fig. 9a).

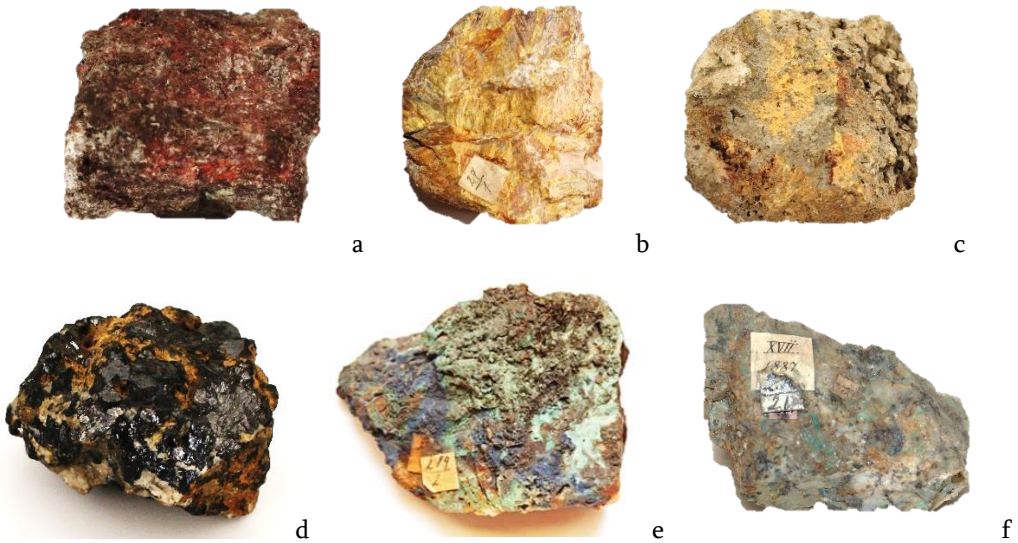


Fig. 9. Specimens of local origin: (a) cinnabar from Dumbrava-Valea Dosului (Zlatna, Alba county); (b) orpiment from Moldova Nouă (Caraș-Severin county); (c) from Baia Sprie mining region (Maramureș county); (d) cerussite from Baia de Arieș (Alba county); (e) malachite with azurite from Căzănești (Hunedoara county); (f) rock with malachite from Rimetea (Alba county), the Mineral collection, Natural Science Museum from Aiud. Credits Paul Scrobotă.

[37] Wolker Wollmann, "Exploatarea mercurului în Transilvania din epoca romană până la mijlocul secolului al XX-lea" […], *AUA hist.* 7 (2001): 151-152.
[38] Gheorghe C. Popescu et al., "The Gold Museum of Brad. Characterization and Classification of Native Gold Samples and Other Minerals," *Romania Journal of Mineral Deposits* 86, 2 (2013): 80; Wollmann, "Exploatarea mercurului," 151.
[39] Ibid., 156-157.
[40] Ibid., 157.

The pigment cinnabar could also be prepared following the technical instructions from the Hermeneia, as already presented. The process of preparation is based on three ingredients: quick-silver (mercury), brimstone (sulphur) and litharge (lead oxide II).[41] All the elements needed could be easily found in Transylvania.

We also have to take into consideration the trade networks inside and outside the Habsburg Empire and the possibility that imported cinnabar could also have been available in the region. What is important at this stage of the argument and that clarifies the use of cinnabar with such a high frequency in Transylvanian icons is its availability on local markets. When a product can be easily found and is accessible, then it is also affordable from a financial point of view. An important consumer of cinnabar was the printing press of Blaj. From its Inventory and financial documents, one can find that at the end of eighteenth century and early nineteenth century, large quantities of this pigment were bought and used to make the red ink needed for printing red letters, ornaments and other texts.[42] A worker category named "pelcarius ad rubrum" was specialised in preparing the red ink.[43] Another important detail mentioned in the inventory is the name of the market place that supplied the pigment for the industry: Sibiu.[44] It is also possible that the press bought cinnabar from local markets before the recorded years in the inventory. In fact, printing activity was undertaken before 1787, and is attested by documents dated 1747, presented by scholars who have studied the history of the printing press.[45]

Where *orpiment* is concerned, there is very little historical data with respect to its trade or mining exploitation in the region. For the seventeenth century, several studies have reported a document attesting that a Wallachian painter sent by Mihai Viteazul bought this yellow pigment from Venice.[46] Geological studies on its occurrences reported orpiment and realgar occurrences in volcanic regions and hydrothermal veins,[47] and in the Gutâi and Apuseni Mountains.[48] Mineral specimens (samples) from the mining region Baia Sprie (Maramureș county) and Moldova Nouă (Caraș-Severin county) are preserved in the collection of the Natural Science Museum of Aiud (fig. 9b-c). Among the items bought by the printing

[41] Dionisie din Furna, *Erminia*, 48.

[42] The inventory (1878-1821) and other related documents, preserved in the History Museum of Blaj, doc. no. 1269, were studied and published by Cornel Tatai-Baltă, and Teodor Smericinschi, "Din activitatea Tipografiei de la Blaj (1787-1821) reflectată de un material arhivistic" [From the Activity of the Printing Press of Blaj (1787-1821) Reflected by an Archival Material], *Apulum* 19 (1981): 239-258. See also Gabriela Mircea, "Amosfera de lucru cotidiană din cadrul vechii tipografii blăjene: utilizarea curentă a unor materiale și substanțe pe parcursul anilor 1787-1807" [Daily Working Climate from the Old Printing Press of Blaj: The Current Use of Some Materials and Substances Between 1787-1807], *Apulum,* Series *Historia et Patrimonium* 37, 2 (2000): 23-35; Gabriela Mircea, *Tipografia din Blaj în anii 1747-1830* [The Printing Press of Blaj Between 1747-1830] (Alba Iulia: Altip, 2008), 365.

[43] Tatai Baltă, and Smericinshi, "Din activitatea Tipografiei de la Blaj," 251. See also the Annex with Tables I and II of the employees, 255-258.

[44] Inventory, doc. no. 1269, fol. 253 v., apud ibid., 248.

[45] See Tatai Baltă, and Smericinshi, "Din activitatea Tipografiei de la Blaj," 240. They mentioned a document dated 14 July 1747, from fund *Mitropolia Română Unită Blaj – Cabinetul Mitropolitului* [Romanian Uniate Metropolitanate Blaj – The Metropolitan's Cabinet], doc. no. 26/1747, Serviciul Județean Alba al Arhivelor Naționale [Alba County Service of the National Archives].

[46] Mihalcu, *Fața nevăzută a formei*, 11-12; Corina Niculescu, *Icoane vechi românești* […] (Bucharest: Meridiane, 1971), 20; Săndulescu-Verna, *Materiale și tehnica picturii*, 135, footnote 4 cited a document from Hurmuzachi collection published in *Documente privind Istoria Românilor* [Documents Regarding the History of Romanians], XII, 602.

[47] Fitzhugh, "Orpiment and Realgar," 54. For orpiment occurrences in the Metaliferi Mountains see Udubașa et al., "Mineral Occurrences," 3-35.

[48] Popescu et al., "The Gold Museum of Brad," 81, 77.

press of Blaj was arsenic.[49] In fact, in the eighteenth century, English written sources started discussions on the preparation of orpiment from sulphur and arsenic.[50]

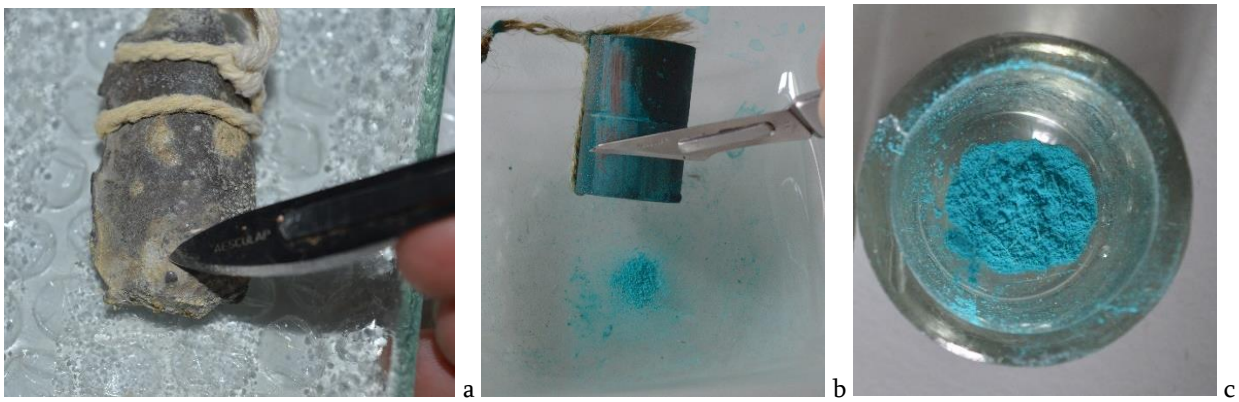
As far as the other two pigments, *lead white and copper-based pigments*, are concerned, they can be prepared following a process of the corrosion of the metals (Pb and Cu respectively) in the presence of acetic acid. For their preparation, the local masters needed metallic lead and copper, available in Transylvania. Lead white could also be obtained from the mineral cerussite.[51] Lead-based minerals were reported in the Apuseni Mountains.[52] Samples from the region (Baia de Arieș) are preserved in the collection of the Natural Science Museum of Aiud (fig. 9d). In the same time, at the end of eighteenth century, lead white produced in Austria was available on markets and it was not an expensive pigment.[53]

For the traditional method of preparation, metallic lead was needed, and this was available in the region. The printing press of Blaj was an important consumer of the metallic lead needed to make the type letters. It was bought from local markets (Alba Iulia, Sebeș, Mediaș) or from Baia Mare.[54] It is of interest to mention that the other ingredient – grape pomace – was readily available taking into account the vine-growing tradition in Transylvania. The Censum of 1733 mentioned the vine growers near Alba Iulia.[55] Thus, the ingredients for the preparation of lead white were available at that time. We followed the instructions from the Hermeneia and easily reproduced this recipe in the laboratory using both vinegar and grape pomace (fig. 10a).

Copper deposits were reported and exploited in the Apuseni mountains.[56] Samples of copper-based minerals (malachit and azurite) of local origin are preserved in the collection of the Natural Science Museum of Aiud (fig. 9e-f). These minerals are the raw materials for the natural copper-based pigments malachite and azurite. Banat was an important region where copper and iron were exploited.[57] Geological studies, as well as studies on the development of mining activities, based on archival documents, reported progress in the techniques of the mining industry between the seventeenth and nineteenth centuries. Thus, lead could be separated from copper and gold.[58] Taking all this into consideration, we may say that the icon painters of Transylvania had all the ingredients needed to prepare their own pigments.

[49] Tatai Baltă, and Smericinshi, "Din activitatea Tipografiei de la Blaj," 248.
[50] Fitzhugh, "Orpiment and Realgar," 55, mentioned by Robert Dossie in his book, *The Handmaid to the Arts*, written in 1758, who initiated discussion on the preparation of orpiment.
[51] Gliozzo, and Ionescu, "Pigments – Lead-based," 17.
[52] See the study of Udubașa et al., "Mineral Occurrences," 3-35.
[53] Cf. Gettens, Feller, and Chase, "Lead White," 68.
[54] Mircea, "Amosfera de lucru cotidiană," 25 who cited doc. no. 1269, fol. 250 v, 261 v, 281 v, 298 r, 302 v; Mircea, *Tipografia din Blaj*, 362-362, while Tatai Baltă, and Smericinshi, "Din activitatea Tipografiei de la Blaj," 248 cited from doc. no. 1269, fol. 264 v, 298 r and 250 v.
[55] Daniel Dumitran, "Societate urbană în Transilvania premodernă. O tipologie a orașelor" [Urban Society in Early Modern Transylvania. A Typology of Towns], *HU* 22 (2014): 117–135. See the Annexes, 134, according to the economic Censum of the social-working classes of Alba Iulia, dated 1733, winegrowers were recorded.
[56] Udubașa et al., "Mineral Occurrences," 3-35.
[57] Mircea Borcoș, and Gheorghe Udubașa, "Chronology and Characterisation of Mining Development in Romania," *Romanian Journal of Earth Sciences* 86, 1 (2012): 17-26, 21.
[58] Ibid., 20.

The copper-based green pigment used by Master Grigore Ranite appears in the aforementioned archival document under the name "grunspan".[59] This pigment is also known as verdigris or verderame, a synthetic copper-based pigment. As heritage science literature has reported, the name used for this particular pigment can indicate either the provenance, or the method used to prepare it.[60] It is known that "verdigris" is derived from the French name of the pigment (vet-de-Gréce), while "grunspan" (from Grünspan) comes either from "Spanich Grün", and indicating the provenance, or from "Kupferspäne", and indicating a preparation method using copper filings.[61] In the eighteenth century, France, and specifically the Montpellier vine region, was a great supplier of synthetic copper-based pigment.[62] The Transylvanian masters could prepare their own copper-based pigments following the instructions from the Hermenia, using as raw materials metallic copper and grape pomace. We could easily reproduce the recipe and obtain a very nice powdered pigment in the laboratory using metallic copper and fermented grape pomace (fig. 10b-c).



a b c

Fig. 10. Aspects from the process of the preparation of (a) lead white and (b)-(c) copper-based pigments. The metals were suspended in bottles with vinegar. The pigment is respectively a white or greenish blue corrosion layer formed on the metals as a result of a complex atmospheric corrosion process. The pigment was removed from time to time and a new corrosion layer then formed. Credits Dumitrița Daniela Filip.

*Conclusions*

The results presented in this paper are derived from the correlation of various data collected through an integrated research effort which includes insights from written sources on the theory and practice of icon painting, XRF investigations and microscopic observations conducted on selected Transylvanian icons, field surveys, and documentation of the mineral collection of the Natural Science Museum of Aiud. The pigments discussed in this study could be easily reproduced by following instructions found in the master source of the icon painters at that time, namely the Hermeneia, using raw mineral sources, locally

[59] The Testimony of master Grigore Ranite, *Documents from Blaj*, no. 449, fol. 7, SJCJAN Archive; Chindriș, ed., *Icoana plângătoare*, 52.
[60] Nicholas Eastaugh et al., *Pigment compendium. Optical Microscopy of Historical Pigments* (London: Butterworth-Heinemann, 2008), 78-87.
[61] Hermann Kühn, "Verdigris and Copper Resinate," in Roy, ed., *Artists' Pigments*, 131.
[62] Ibid., 132.

abundant and easily accessible. Consequently, the Transylvanian icon painters had two options: either to purchase the aforementioned pigments or to prepare them by themselves. This study sets the basis for a more in-depth comparative study of the mineral sources and pigments used in the painting of Transylvanian icons.

ACKNOWLEDGEMENTS:
Dumitrița Daniela Filip acknowledges the support of project POCU 153770, entitled *Accessibility of Advanced Research for Sustainable Economic Development – ACADEMIKA*, co-financed by the European Social Fund under the Human Capital Operational Program 2014–2020.
Elena Badea acknowledges the support of the grant of the Ministry of Research, Innovation and Digitization CNCS-CCCDI UEFISCDI, project number PN-III-P3-3.5E-EUK-2019-0211 (MUSEION), WITHIN PNCDI III.