

In situ Raman spectroscopy at the Voroneț Monastery (16th century, Romania): New results for green and blue pigments



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ABSTRACT

The Voroneț Monastery is one of the greatest cultural treasures of Romania, dating from the 15th century. In the present study, the green and blue pigments of its exterior frescoes (16th century) were analyzed through fibre-coupled Raman spectroscopy. A wide range of typical pigments, including malachite, basic Cu sulphates, azurite, lazurite, smalt, gypsum, anhydrite and calcite were found, together with other "rare pigments," such as conicalcrite and dolerophanite. The green pigment is either a mixture of malachite and conicalcrite or Cu sulphates while the blue pigment contains either lazurite, or a mixture of azurite and a minor quantity of smalt, gypsum and anhydrite. The identification of these pigments is very important for the restoration work, the monastery being a UNESCO World Heritage Site.

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1. Introduction

The Voroneț Monastery is one of the famous painted monasteries in the southern part of Bukovina, the north-eastern region of Romania. The monastery was founded by Stephen the Great, Prince of Moldavia, and erected between May and September 1488. Voroneț is internationally renowned for the bright hues of its exterior frescoes, the hundreds of well-preserved figures placed against a vivid blue background (the predominant colour of the artwork at Voroneț), and for the magnificent *Last Judgment* scene on the west wall (Supplementary data, Fig. S1). A small number of studies have been carried out on the paintings of the Voroneț Monastery. Using X-ray diffraction, Istudor [1–3] has identified the presence of malachite and green earth in the green pigment. For the blue pigment, a composition of azurite applied onto a charcoal background has been reported. Traces of smalt mixed with azurite have been found in both the interior and the exterior paintings.

Raman spectroscopy is a time-efficient, inexpensive and, above all, effective analytical method, widely applied in both Mineralogy and art. Numerous studies have focused on the determination of the Raman spectral characteristics of the minerals and synthetic compounds used as pigments in works of art [4–6]. The results of these

studies constitute a database for the non-invasive and non-contact Raman investigations carried out on valuable, sometimes impossible to move, artworks. Over the past three decades, numerous green and blue pigments used in the artworks of the Middle Ages and the Renaissance have been determined by means of Raman spectroscopy. Malachite, green earths, basic Cu sulphates, atacamite, clinoatacamite and copper phthalocyanine were used as green pigments [7–11]. Various green hues were achieved by mixing blue and yellow pigments, such as indigo and orpiment, lazurite and orpiment, or aerinite and goethite [10,13,14]. Different shades of green were also obtained using a mixture of green and blue pigments, such as malachite and/or green earths mixed with lazurite, azurite or indigo [7,10].

For the colour blue, azurite, lazurite, indigo and smalt were widely used in the painting of artworks. To obtain different shades of blue, these main pigments were mixed either together, in various proportions, or with other pigments of different colours, most frequently lead white, barite, calcite, cinnabar, red ochre, vermilion, malachite and black carbon [7,10,12,14]. The aim of the present study is to determine the composition of the green and blue pigments of the Voroneț Monastery using Raman spectroscopy.

2. Experimental

The Raman spectra were acquired using a Horiba Jobin-Yvon RPA-HE 532 Raman spectrograph with a multichannel air-cooled

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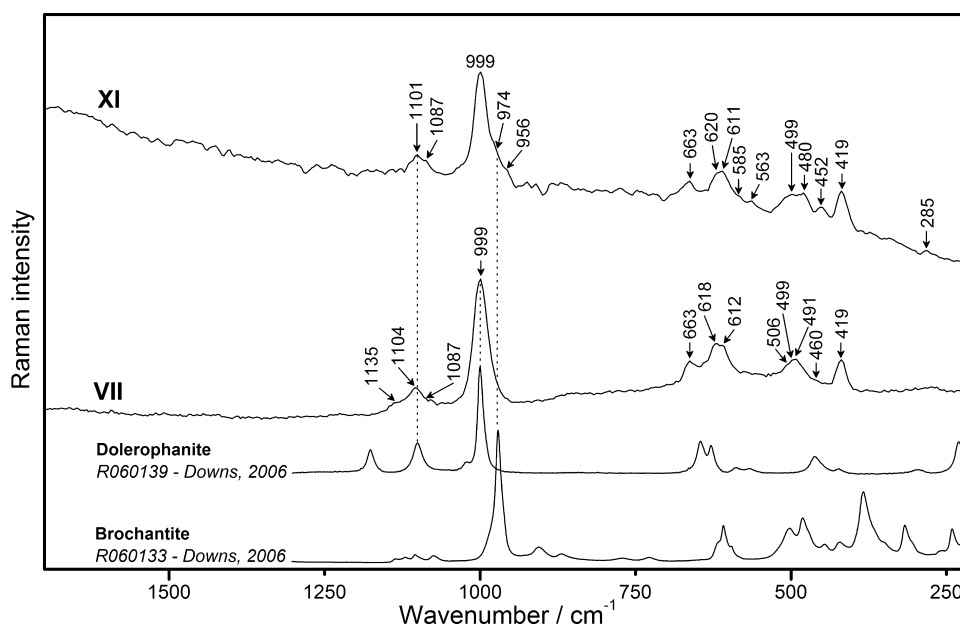


Fig. 1. Raman spectra of the green pigment in VII and XI points (Supplementary data, Fig. S3) and standard Raman spectra of dolerophanite and brochantite (Downs, 2006).

(-70°C) CCD detector (1024×256 pixels, size $26 \times 26 \mu\text{m}$, MPP selected chip, size $26.6 \times 6.7 \text{ mm}$). The excitation source was an Nd-Yag 532 nm laser with a nominal power of 100 mW. The spectra were obtained within the spectral range between 200 and 3400 cm^{-1} , with a spectral resolution of 3 cm^{-1} . The Raman system included a Superhead fibre-optic Raman probe for non-contact measurements, with an Olympus 50X LWD visible objective, $\text{NA}=0.50$, $\text{WD}=10.6 \text{ mm}$. The laser spot diameter on the sample was approximately $2\text{--}3 \mu\text{m}$ (the minimum theoretical spot diameter is $1.3 \mu\text{m}$). In order to improve the signal-to-noise ratio and to avoid any possible damage, the data were acquired through 2–20 second exposures and 10–50 acquisitions, at a laser power on the sample of 2–14 mW.

We solved the problem of straight light interference over the Raman signal using a paper cylinder liner attached to the objective. After focusing the laser, the liner was translated up to the sample. Thus, the straight light was stopped from reaching the CCD detector. The close-up photos were taken using a Sony DSLR-A100 + Sony 3.5–5.6/18–70 mm.

3. Results and discussion

The present study discusses only the Raman spectra acquired from the points in which green or blue layers appear. The measurement points are located on the exonarthex (the last part of the monastery to have been built), painted in 1547. Out of all the frescoes, we chose the following: the icon of St. Daniil the Hermit, found in the proximity of the main entrance of the church, in the southern part (Supplementary data, Fig. S2, positions I–VI); *The Last Judgment* scene, painted on the western façade (Supplementary data, Fig. S3, positions VII–IX), and a portion of the northern façade that is less well preserved because of harsh weather conditions (Supplementary data, Fig. S4, positions X–XII).

3.1. The green pigment

The green layers do not contain only one green pigment. The Raman spectra obtained, shown in Figs. 1–3, point to basic Cu sulphates, conicalcrite and malachite.

The minerals of the basic Cu sulphates group are the following: dolerophanite – $\text{Cu}_2(\text{SO}_4)\text{O}$, antlerite – $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$, brochantite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$, posnjakite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}$, langite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, and wroewolfeite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}$ [15]. These minerals are found in volcanic, hydrothermal and chemical-weathering environments. Dolerophanite is extremely rare, and it forms only during the oxidation of copper in the air, in the presence of sulphur oxides, as a volcanic sublimate. It does not form in aqueous environments.

Several Raman studies conducted on basic Cu sulphate minerals have been published [4–6,16–21]. For dolerophanite, the only data available are provided by Downs [19]. The four fundamental modes of vibration of the sulphate tetrahedral oxyanion occur at 981–983 (ν_1 – symmetric stretching), 450–451 (ν_2 – symmetric bending), 1104–1105 (ν_3 – antisymmetric stretching), and 611–613 cm^{-1} (ν_4 – antisymmetric bending) [5,22]. The shifting of the Raman bands over and above that which would be predicted for the fundamental modes of the sulphate anion may be attributed to several factors, including symmetry reduction, local stress in the crystals, and crystal orientation [5]. Furthermore, the intensity and position of the band varies based on crystal orientation and size, and the differences in resolution of the instruments used [5,6,18].

In the green layers from Voroneţ, basic Cu sulphate minerals (the antlerite–brochantite–posnjakite–langite series) are present only on the north wall of the monastery, and the Raman bands of these minerals are observed in the VII and XI spectra (Fig. 1). The Raman lines 999 (vs), 974 and 956 cm^{-1} are assigned to the symmetric stretching vibration of basic Cu sulphates (Supplementary data, Table S1). The 999 cm^{-1} band indicates the presence of dolerophanite. The 974 cm^{-1} band could be assigned to the brochantite–posnjakite–langite series, while the 956 cm^{-1} line is assumed to correspond, most likely, to langite (Fig. 1 – XI). We believe, however, that more minerals from the basic Cu sulphate group are present and that, as a result, the previously-mentioned Raman bands can be observed. The ν_2 symmetric bending modes are observed at 506, 499, 491, 480, 460, 452, and 419 cm^{-1} . These lines indicate the presence of at least two minerals from the basic Cu sulphate group, but most of the spectral lines can be assigned to brochantite (Supplementary data, Table S1). The 460 cm^{-1} band belongs exclusively to dolerophanite. The ν_3 antisymmetric stretching modes are either

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