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FIRST FINDINGS OF RAMAN MICROSCOPY CONDUCTED ON EARLY CHRISTIAN MURALS IN EGYPT

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Abstract

This short report presents the first findings obtained through the application of Raman microscopy to analyse early Christian murals in Egypt. The samples were studied by a micro-Raman instrument, while the scanning electron microscope (ESEM-EDX) was applied to allow the accessing to the chemical composition of the samples. The identified pigments were red ochre (with different hues), yellow ochre and carbon black (from vegetable origin). A high quantity of TiO_2 anatase polymorph was detected in the red pigment samples. The analyses showed that calcium carbonate (calcite) was used to build up the underlying layers. Further analyses on multi-chromatic layers are in progress.

Keywords: Early Christian, Egypt, pigments, plasters, Raman microscopy

1. Introduction

Early Christian wall paintings are rare examples of the technology and materials in this period. El-Bagawat cemetery is almost the oldest Christian cemetery in the world. It is located in El-Kharga Oasis in the Western Desert of Egypt. Actually, it is believed that the early date of the cemetery goes back to the 4^{th} century AD, while the mud brick structures are from the 7^{th} century AD [1, 2]. The cemetery contains sixty three chapels, only a few are painted with biblical scenes. The most well-known examples are the chapel of the 'Exodus' and the chapel of the 'Peace'. In recent decades, Raman microscopy has been applied successfully to analyse painting materials [3-5]. This tool is a non-destructive one and no sample preparation is required. The microscopic unit attached to the Raman instrument permits the focusing of laser radiation on selected points on the samples, and also to monitor any changes may occur [6]. In the present study, the first micro-Raman analysis of paint layer samples collected from early Christian murals from El Bagawat cemetery is reported. Figure 1 shows some of the painted plasters in chapel number 25 in the cemetery.

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Figure 1. View of the murals paintings in El-Bgawat cemetery, Western Desert of Egypt.

2. Materials and methods

2.1. Samples

Few grains (milligrams), representing some chromatic colours at the selected chapel (red, yellow, and black colours), were carefully chosen for analysis.

2.2. Analytical methods

2.2.1. Optical microscopy

Preliminary observation was applied as initial step on the samples using a stereomicroscope (Olympus SZ-40) equipped with an Olympus DP10 digital camera.

2.2.2. Raman microscopy

The Raman spectra were recorded using a Renishaw InVia Raman spectrometer in the near infrared excitation line (785 nm) of a diode laser source. The instrument is equipped with Peltier cooled charge coupled device (CCD 576x400 pixels). A Leica DMLM microscope with a XYZ motorized stage with 200 and 500 magnification objectives is equipped to Raman spectrometer which can provide a sample irradiation diameter of up to 1 μm. In respect to the nature of samples, lower laser powers (up to 0.5 mW) have been operated. The exposure time of the CCD was kept on 20s per scan, while normally 5 up to 20 accumulations were co-added to produce the final spectrum in order to improve the signal-to-noise ratios.

2.2.3. Scanning electron microscopy (ESEM-EDX)

For more data on the microstructure and microanalysis of the samples, an environmental scanning electron microscope (Philips XL-30) was used. The X-ray microanalysis was carried out using an EDX detector (EDAX, Apollo SDD 10) with 20 kV accelerating voltage and pressure of 3.0 Torr. The GENESIS spectrum 6.x software, provided by EDAX Company, was used to obtain the EDX data.

3. Results

3.1. The microscopic examinations

Figure 2 shows a stereomicroscopic image obtained on the plaster sample. Under microscope, the stratigraphic sequence of the plaster can be observed. Two main layers can be easily distinguished, the first one (No. 1) is a well smoothed lime-based layer (the preparatory layer) which lies on a second thick coarse layer (No. 2) containing large siliceous grains.

Figure 2. A stereomicroscopic image obtained on the plaster sample.

3.2. Micro-Raman spectra

Several grains on the painted layers were chosen for analysis. The Raman spectrum recorded on the pinkish pictorial layer (Figure 3a) shows bands at 298, 414 and 617 cm^{-1} which all are for hematite (α-Fe_2O_3). The band at 414 cm^{-1} is probably attributed to a well-crystallized hematite [7].

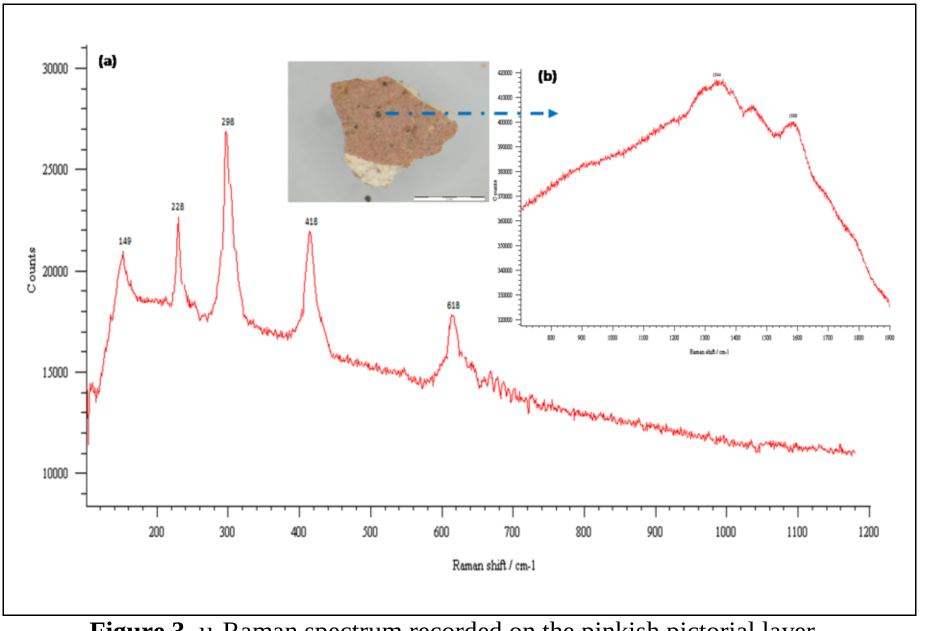

Figure 3. μ-Raman spectrum recorded on the pinkish pictorial layer (0.5 mW, 5 scans of 20s).

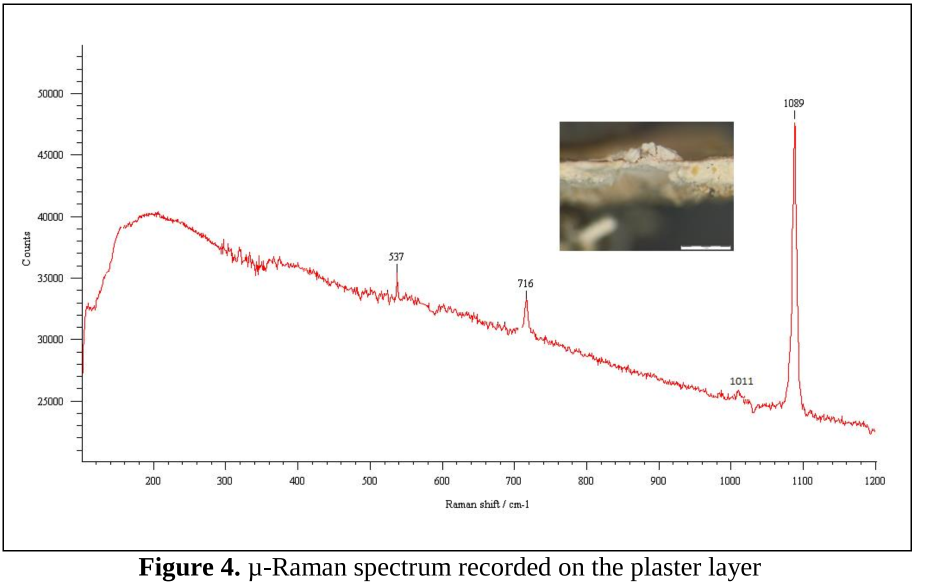

Figure 4. μ-Raman spectrum recorded on the plaster layer (1mW, 10 scans of 20s).

Moreover, the strong band at 149 cm^{-1} is for titanium dioxide (anatase polymorph). Anatase is a rare polymorph occurs as a minor phase in igneous rocks and it widespread in sedimentary rocks [8]. Black grains are observed beneath and on the outer surface of this paint layer. Raman analysis revealed the characteristic bands of carbon black at 1344 and 1585 cm^{-1} (Figure 3b) [9]. The EDX microanalysis of the sample showed high percentage of carbon, and no phosphorus was detected. This suggests that carbon based pigments of vegetable origin were chosen for black areas. A light red tone was obtained by mixing hematite with the lime-binder during the painting process of the murals. The Raman spectrum obtained on the yellow pigment shows bands at 394, 307 and 559 cm^{-1} that can be attributed to goethite (α-FeOOH). The Raman spectrum obtained on the underlying layer (Figure 4) showed clearly a strong characteristic band at 1089 cm^{-1} and another medium one at 716 cm^{-1} that can be associated to calcium carbonates (calcite, $CaCO_3$).

The weak Raman band at 1011 cm^{-1} is probably due to the presence of anhydrite ($CaSO_4$). The transformation of calcium carbonate into phases of calcium sulphate is a well-known phenomenon as the result of multi physico-chemical mechanisms [10].

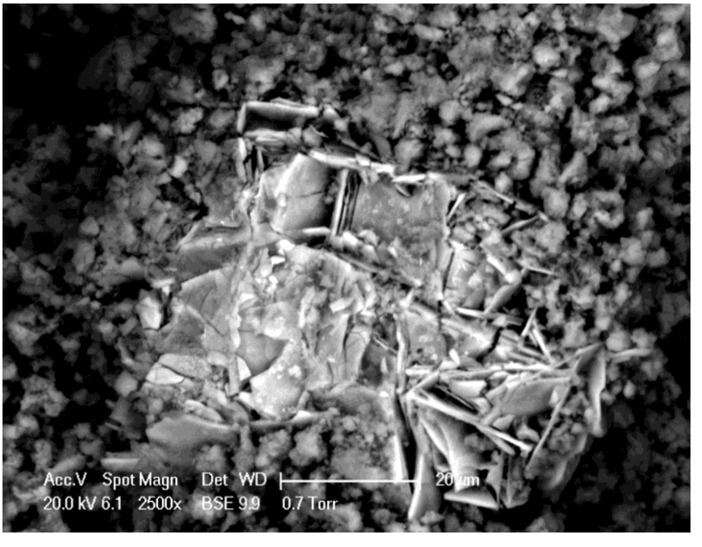

Figure 5. ESEM image of TiO_2 anatase polymorph in the red pigment sample (2500x, scale bar = 20µm).

3.3. ESEM-EDX

Scanning electron microscopy coupled with EDX microanalysis detector was used as a complementary technique to study some samples. A close-up ESEM image obtained on intergrowth grains in the red pigment sample (Figure 5) shows slightly big size light-grey crystals. The microanalysis of these crystals gave titanium (Ti) and iron (Fe) as main elements, together with calcium (Ca), silicon (Si) and aluminium (Al). The Raman analysis of these grains revealed the presence of titanium dioxide (anatase polymorph). The anatase detected in the red pigment samples most likely is a contaminant in the iron deposits. Iron ore deposits in Egypt are located in several locations, such as the Eastern Desert and El-Bahariya oases in the Western Desert [11].

4. Conclusion

In this study, micro-Raman spectroscopy was employed to examine, for the first time, some samples collected from early Christian mural paintings at El-Bagawat cemetery of Egypt. The combined analysis of the samples using Raman microscopy and ESEM-EDX allowed direct identification of the minerals and their chemical composition in the investigated samples. The identified pigments are red ochre, yellow ochre, and carbon black (from a vegetable origin). The analyses showed that the preparation layer consists mainly of calcium carbonate (calcite). Further analyses of another group of painted plasters are in progress in order to build up a Raman-database of the painting materials used in these important murals from the early Christian necropolis in Egypt.

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