Identification of green earth pigments in Coptic wall paintings using ESEM-EDX, FTIR imaging and Visible Reflectance Spectroscopy

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Abstract

The main art form in the Coptic monasteries and churches in Egypt was wall paintings and iconography. In this study, analytical data were gathered on green pigment samples collected from Coptic wall paintings from the monastery of St. Anthony, The Eastern Desert, Red Sea Governorate, Egypt. The samples were analyzed by environmental scanning electron microscopy (ESEM) coupled with an energy dispersive X-ray analysis system (EDX), Imaging with Fourier transform infrared spectroscopy (FTIR imaging) and visible reflectance spectroscopy. The results showed that green earth pigment (terre verte) and mainly the glauconite, was used to produce the green color. In conclusion, some useful information may be obtained from the present study concerning green earth pigments used in Coptic wall paintings.

Keywords:

Coptic wall paintings, monastery of St. Anthony, green earth pigments, ESEM–EDX, FTIR imaging.

Identificação de pigmentos de terra verde em pinturas murais coptas por ESEM-EDX; microscopia de imagem FTIR e Espectroscopia de Reflectância Visível

Resumo

A principal forma de arte dos mosteiros e igrejas coptas no Egito foi a pintura mural de cariz iconográfico. Neste estudo, os dados analíticos foram reunidos em amostras de pigmentos verdes recolhidas de pinturas murais coptas do mosteiro de Santo António, localizado no Deserto Oriental, na província do Mar Vermelho, Egito. As amostras foram analisadas por microscopia electrónica de varrimento ambiental (ESEM) acoplado a um sistema de análise de energia dispersiva de raios-X (EDX), *imaging* por espectroscopia de infravermelho com transformada de Fourier (FTIR *imaging*) e espectroscopia de reflectância visível. Os resultados mostraram que o pigmento terra verde (*terre verte*) e, principalmente a glauconite, foi utilizado para produzir a cor verde. Em conclusão, algumas informações úteis podem ser obtidas a partir do estudo sobre pigmentos de terra verde utilizados em pinturas murais coptas.

Palavras-chave:

Pintura mural copta, Mosteiro de Santo António, pigmentos terra verde, ESEM-EDX, microscopia de imagem FTIR.

Identificación de pigmentos de tierra verde en pinturas murales coptos utilizando ESM-EDX; microscopia de imágenes FTIR y Espectroscopia de Reflectância Visible

Resumen

La pintura mural y la iconografía fué una de las principales formas de arte en los manasterios e iglesias coptos. En este estudio, los datos analíticos se obtuvieron en muestras de pigmentos verdes recogidos de las pinturas murales del monasterio copto de Santo Antonio, ubicado en el Desierto Oriental de la región admnistrativa del Mar Rojo, Egipto. Las muestras se analizaron por microscopía electrónica de barrido ambiental (ESEM) acoplado con un sistema de análisis de energía dispersiva de rayos X (EDX), Imaging con espectroscopia infrarroja con transformada de Fourier (FTIR *imaging*) y la espectroscopía de reflectancia visible. Los resultados mostraron que el pigmento verde tierra (tierra verde) y principalmente la glauconita, se utilizó para producir el color verde. En conclusión, alguna información útil puede obtenerse del presente estudio sobre pigmentos verdes de tierra usados en pinturas murales coptos.

Palabras clave:

Pinturas murales coptos, Monasterio de Santo Antonio, pigmentos de tierra verde, ESEM-EDX, microscopia de imágenes FTIR.

1. Introduction

Christianity was brought to Egypt by St. Mark the Apostle in the mid 1st century, during the reign of the Roman emperor Nero, this era, also known as the 'Coptic Period' (Middleton--Jones 2011). Coptic art displays a mix of native Egyptian and Hellenistic influences. Subjects and symbols were taken from both Greek and Egyptian mythology, sometimes altered to fit Christian beliefs. Persia and Syria also influenced Coptic art, though to a lesser extent, leaving images such as the peacock and the griffin. Coptic art is most well known for its wall-paintings, textiles, icons, metal works. Stylistically, Coptic painting differs from that of Pharaonic one in its emphasis on animal and plant ornamentation; less naturalistic rendering of the human form; simplified outline, color, and detail (Capuani, 2002). Some of the oldest extant Christian art in Egypt can be found in the area of Bagawat in the al-Kharga Oasis in the Western Desert. The paintings in the various chapels and tombs of this region display a notable change from the earlier work in Alexandria, as well as an expansion of the iconographic repertory.

1.1. The monastery of St. Anthony of Egypt (ca. 251–356)

Saint Anthony is a Christian saint who was born to a wealthy family in Lower Egypt around 251 C.E. He was a prominent leader among the Desert Fathers in Egypt. The Monastery of

Saint Anthony is one of the oldest monasteries in the world (Figure 1). It is located in the Eastern Desert of Egypt, 334 km southeast of Cairo. The monastery was established by the followers of Saint Anthony, who is considered to be the first monk. Its origins are due to the 4th century AD when monks began to settle at the foot of Gebel al-Galala al-Qibliya, where their spiritual leader, Anthony, lived. Today the monastery is a large complex surrounded by high walls, with several churches and chapels, a bakery, a lush garden and a spring (Meinardus, 1989; Bolman, 2002).

1.2. Green earth pigments (Terre Verte)

The predominant green pigment used in Roman wall paintings was green earth. It was identified on Roman wall paintings at Pompeii and Dura- Europos. In Egypt, green earth was identified in wall paintings dating back to late 3rd century AD applied on the Pharaonic walls of Luxor temple, Upper Egypt (Marey Mahmoud et al. 2012). In recent publication, Abo El-Yamin et al. (2013) have reported the identification of green earth (mainly of glauconite) in the Coptic wall paintings of El-Bgagwat necropolis at Kharga Oasis. Green earth is described as a clay pigment with a chromogenous element in the clay structure, generally a hydrated aluminosilicate of magnesium, iron and potassium (Genestar and Bonafé, 2004). The primary source minerals for the pigment known as green earth are the dioctahedral micas, celadonite and glauconite (Wainwright et al. 2009). Celadonite and glauconite belong to clayey micas group, consisting of a layer of octahedrally coordinated cations (Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}) sandwiched between two sheets of silicate tetrahedra. Interlayer K^{+} ions hold together the three layers. The chemical formula of celadonite is approximately $K[(Al,Fe^{3+}),(Fe^{2+}, Mg)](AlSi_3,Si_4)O_{10}(OH)_2$ with low aluminium content and a very small replacement of Al for Si in the tetrahedral layer. Glauconite's chemical composition is approximately $(K, Na)(Fe^{3+},Al,Mg)_2(Si, Al)_4O_{10}(OH)_2$, similar to celadonite, but with a great content of aluminium due to a partial substitution of Al^{3+} for Si^{4+} in the tetrahedrally coordinated layer (Aliatis et al. 2008). Microscopically, *terre verte* can often appear as confusing mixture of particles. Particles size is usually 1-30 μm and colours can vary from yellow to green-blue. Crystals are coarse and rounded, most appear as greyish-green, but many characteristic translucent, angular silica particles are usually present.

1.3. Research aims

There are few published data on green earth pigments used in the Coptic age. For this, the present study was devoted to perform a detailed investigation on green pigment samples collected from the wall paintings of the monastery of St. Anthony in the Red Sea Governorate of Egypt. The analysis was carried out by means of ESEM–EDX in order to determine the microstructure and chemical composition and using FTIR imaging for identifying the molecular structure, in addition to measuring the chromatic characteristic of samples by registering the visible reflectance spectra.

2. Analytical methods

2.1. Samples

Due to the serious state of preservation of the wall paintings at the monastery, some detached painted fragments (with approximate dimensions 2x3 to 4x6.5 cm) were carefully chosen for analysis.

2.2. ESEM–EDX analysis

The microstructure of rough and polished cross sections prepared on the samples was analyzed by an environmental scanning electron microscope Philips XL-30 ESEM. This equipment is a field-emission source, offering a wide range of operating conditions, in which specimens can be examined with high chamber pressure environment. 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. EDX data acquisition was obtained through GENESIS 6.x software. Microanalysis of single pigment grains down to 1 µm, as well as of the matrix and the total average of the paint layer were performed. Also, some investigations on polished cross-sections were carried out. Tiny peaces of the samples were embedded in Epoxy resin (EpoFix), cross-sectioned on variable speed silicon carbide papers and DP-lubricant blue for fine and cool polishing, and mounted on glass slides.

2.3. FTIR imaging

FTIR spectra were collected on a Perkin Elmer spectrometer 400 equipped with an ATR (attenuated total reflectance) accessory in the wavenumber range of 4000–650 cm^{-1}, at a spectral resolution of 4 cm^{-1} over 32 scans. It is a contact technique in which the sample is pressed against an ATR crystal which is illuminated by an infrared beam from a spectrometer. The crystal in the ATR accessory is made of germanium with a refractive index of 4.01, which gives excellent spatial resolution and shallow sample penetration, both of which contribute to clear and sharp images. Also, it provides both high spatial resolution and high-quality sample illumination by virtue of a novel (patent pending) design optimization technique. The image was processed using baseline offset correction to compensate for the illumination variations. The crystal image was in fact 300 µm by 300 µm.

2.4. Visible reflectance spectra

Colour measurements can be applied for many purposes: the study of the chromatic effect of the dirt layers covering the painted surface; the determination of the colour palette; and the registration of the characteristic reflectance spectra of pigments and their mixtures (Daniilia et al. 2000). The composition of pigments can be identified depending on the shapes and the peak positions of their reflectance spectrum curves (Wang et al. 2005). The spectroscopic reflectance spectra of the different samples were obtained by a Miniscan® XE Plus spectrophotometer (HunterLab). The reflectance spectra were registered in the visible range (from 400 to 700 nm) over several points for each one of the different sample colours. Chromatic values are expressed as colour coordinates in the CIE L*a*b* colour system (1976) and illuminant D65/10º.

3. Results and discussion

3.1. Microstructure and microanalysis (ESEM–EDX)

The ESEM image obtained on a rough cross-section of the paint layer sample shows slightly thick massive paint layer with aggregates within the layer (Figure 2). The element concentration analysis, performed by the EDX detector, showed the detection of silicon, aluminium, potassium, magnesium, sodium and iron. For more assurance of the chemical composition of the sample, an element distribution EDX map of certain area in the sample was performed (Figure 3). Based on the previous elements found in the sample, we can claim that the green grains in the sample are green earth. Moreover, the absence of copper in the sample excludes the existence of malachite or other Cu-based pigments. The EDX microanalysis of the sample showed a high concentration of aluminium and potassium, and in this case, the existence of sodium in the sample allowed concluding the green earth was specifically of glauconite.

3.2. Results of FTIR imaging

FTIR imaging offers users easy spectroscopic access to “difficult” samples which are hard to analyze by FTIR microspectroscopy in transmission or reflection mode, or which have confusing depth structure. Figure 4 shows FTIR–ATR spectrum of the scanned area of a green paint flake. The 3400–3700 cm^{-1} and 950–1100 cm^{-1} ranges can be used to distinguish different mineralogical species of green earths. Glauconite is characterized by the broad bands in the 1100–944 cm^{-1} region. According to Moretto et al. (2011), celadonite presents one group of four bands well resolved in the region 1110–950 cm^{-1}, with the strongest intensity one at 970–975 cm^{-1}. These bands can be ascribed to a distortion of Si-O bond (972 and 1075 cm^{-1}) and perpendicular to the silicate layer (1105 cm^{-1}). Differently, in the glauconite spectrum the structure of the band characteristic of celadonite is substituted by a large band with broad peaks in the 1000 cm^{-1} region.

3.3. Registration of visible reflectance spectra

Figure 5 shows a visible reflectance spectrum registered on the green pigment sample. The spectrum represented a sharp slope after wavelength higher than 560 nm, in the yellow-green region, and a shoulder near to 485 nm which is characteristic to green earth pigment and specifically, glauconite. The L*a*b* values recorded according to CIE color space (1976) were 65.4, –10.3 and –1.4, respectively. In the spectrum of celadonite, it presents a maximum of reflectance at 522 nm, corresponding to the region green-blue of the colorimetric space L*a*b*, while the glauconite spectrum shows a maximum of reflectance at 569 nm in the yellow-green region, and a shoulder near to 485 nm.

4. Conclusion

The present study emphasizes on green pigments used in wall paintings from the Coptic age. Different analytical methods such as ESEM–EDX, FTIR imaging and visible reflectance spectroscopy were applied to study the samples. The analysis of the green pigment samples from the monastery of St. Anthony, Red Sea Governorate, Egypt has shown the absence of copper in the samples which excludes the existence of malachite, atacamite or other copper-based pigments, and that green earth was used. FTIR imaging and EDX elemental distribution maps ascertained that the green grains are green earth, and specifically of glauconite. Further investigation of pigment samples will provide a clear image of painting materials used in the Coptic age.

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Author's curriculum vitae

Lecturer at the department of conservation, Faculty of Archaeology, Cairo University, Giza, Egypt. A bachelor's degree in Conservation and Restoration of Monuments and Works of Art from the Cairo University and a Master's degree in Conservation of ancient mural paintings from the same university. A doctoral degree from the interdepartmental postgraduate program on Protection, Conservation and Restoration of Cultural Heritage, Faculty of Engineering, Aristotle University of Thessaloniki, Greece.

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FIGURE CAPTIONS:

Figure 1: (Right): General view of St. Anthony's monastery, (Left): Examples of the wall paintings of the monastery.

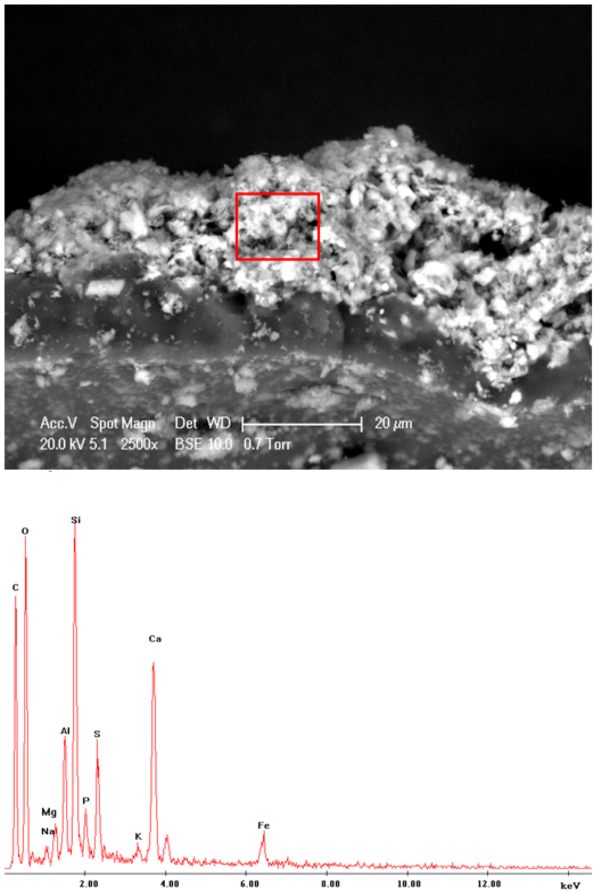

Figure 2: ESEM image and EDX spectrum obtained on rough cross-section of the green paint layer.

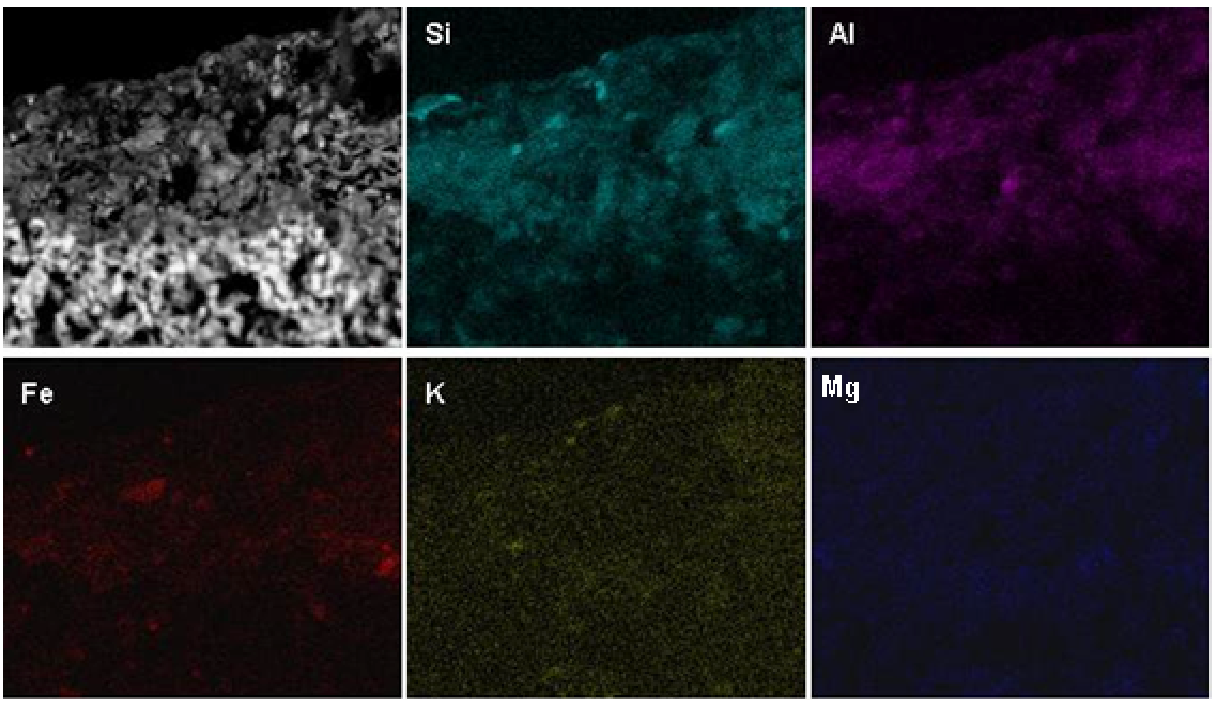

Figure 3: EDX elemental distribution map obtained on a portion of the green paint layer.

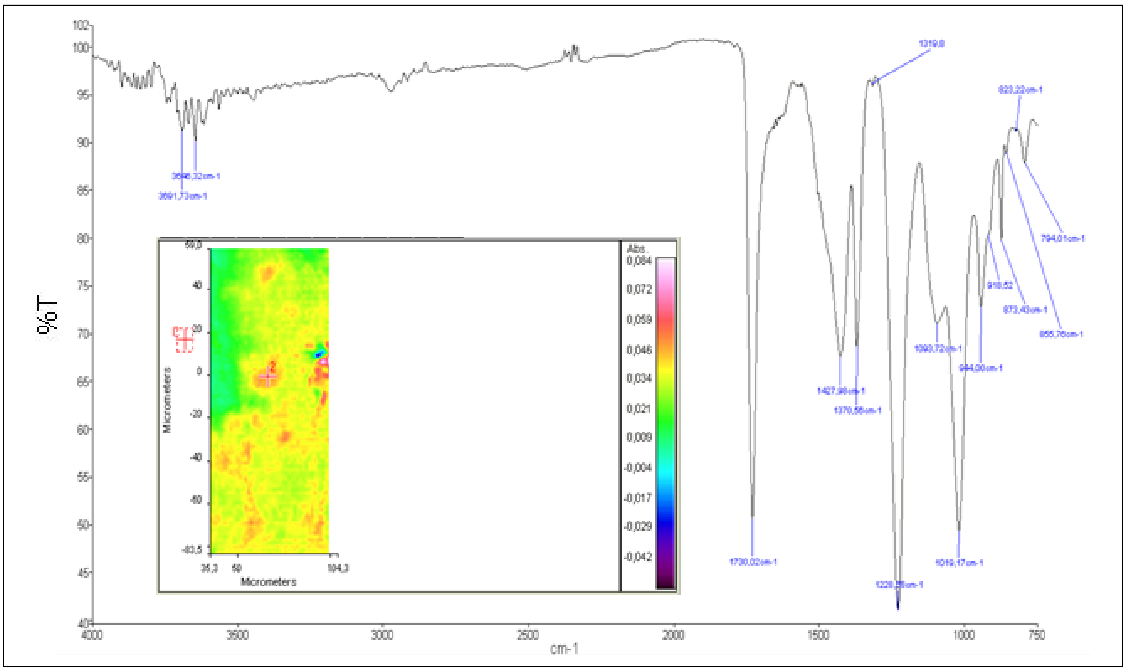

Figure 4: FTIR image and spectrum recorded on the paint layer.

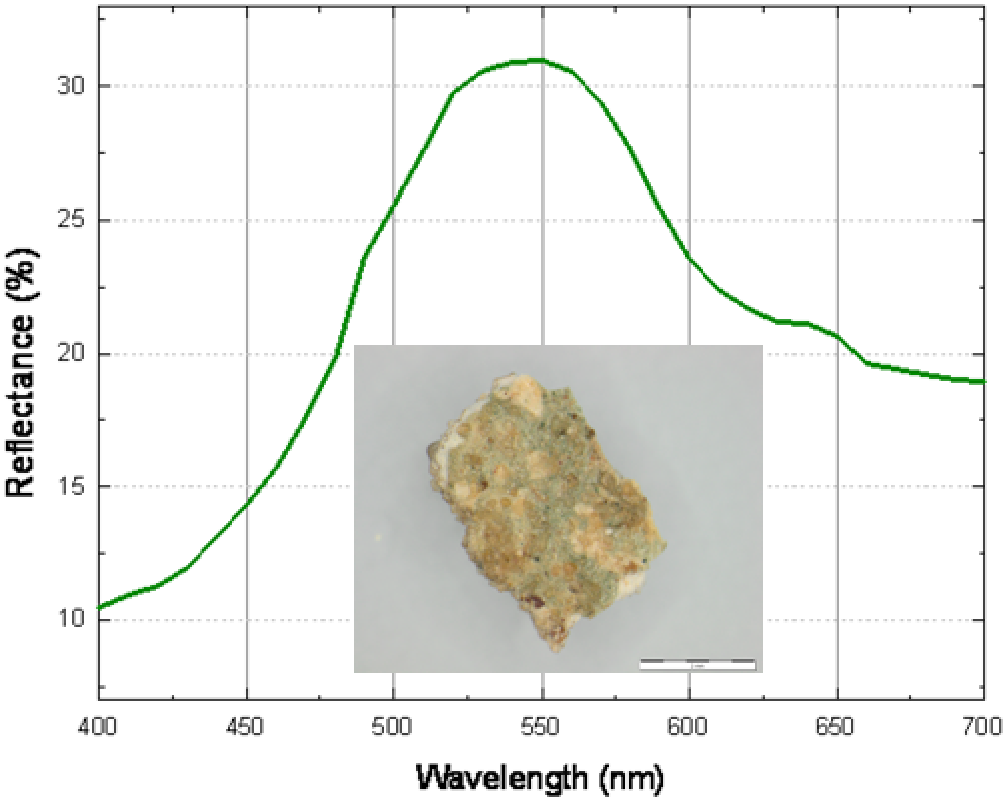

Figure 5: Visible reflectance spectrum obtained on the outer surface of the sample.