Byzantine wall paintings from Mani (Greece): microanalytical investigation of pigments and plasters

Anno Hein · Ioannis Karatasios · Dionysis Mourelatos

Abstract The present case study concerns the technology of Byzantine wall paintings from the Mani Peninsula, Greece. An assemblage of 12 Byzantine churches, constructed in the tenth to fifteenth century, was included in an initial analytical survey. Two random samples of wall paintings were taken in each monument in order to study their micro stratigraphy and the composition of pigment and plaster layers. Polished sections were fabricated for examination with optical microscopy and scanning electron microscopy (SEM). Furthermore, selected samples were powdered and analysed with Fourier-transformed infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The analytical results achieved in this case study provided general conclusions concerning painting techniques for wall paintings in a rather provincial area of the Byzantine Empire. The palette comprised mainly earthen pigments like ochres and carbon black but occasionally also other pigments like cinnabar, minium and ultramarine. In view of future studies, a portable X-ray fluorescence analysis (XRF) set-up was tested.

Keywords Wall painting · Pigments · Lime plaster · SEM-EDS · FTIR · XRD

Introduction

The present study was carried out in the framework of a survey concerning the technology of wall paintings of Byzantine churches in Mani, a peninsula, located in Southeast Peloponnese (Greece). This survey was of special importance for understanding the development of wall paintings in the Byzantine era, since written sources, in general, offer only ambiguous information about painting techniques [1]. Furthermore, much of the hitherto scientific research on Byzantine wall paintings has been focused on metropolitan monuments [2]. In this context, the churches of Mani provided an interesting case study because Mani was a remote and rather rural province of the Byzantine Empire. Nevertheless, a large assemblage of Byzantine monuments is still relatively well preserved, presenting construction phases from different historical periods, particularly from the tenth to fifteenth century. Furthermore, the monuments are located in a relatively small area and some of the wall paintings were presumably created by the same artists or workshops.

A number of questions were raised at the beginning of this research, concerning mainly the technical development of specific artistic workshops during the Byzantine era. A specific issue was to which extent painters working in provincial monuments were following instructions from the known painter’s manuals or guide-books [3, 4]. The objectives of the analytical study, therefore, were the examination of the technological diversity of Byzantine wall paintings of the region and the investigation of potential regional peculiarities. The results were expected to provide conclusions concerning the technological level in comparison to metropolitan monuments of the same period and to
complement the art historic research on the Byzantine monuments in Mani [5]. A representative number of monuments were selected, in each of which random samples were taken. The analytical approach was focussed on the identification of pigments and the investigation of the micro stratigraphy of the wall paintings. Therefore, a series of standard analytical techniques was applied, in terms of comprehensive chemical and mineralogical examination. In the present paper, the results of the case study will be summarised and assessed, aiming to provide a valuable background for future studies.

**Sampling**

In order to examine the stratigraphy of paint layers applied on the plaster, it was necessary to take small samples from the wall paintings. Twelve churches were selected for sampling (Fig. 1), representing the construction period from the tenth to fifteenth century. From each of these churches, two random samples were collected (Table 1). The selected monuments were expected to provide some conclusions in terms of the above mentioned questions. Three of the churches, Aghios Philippos, Aghios Nikitas and Aghios Panteleimon, have been attributed on stylistic reasons to a particular workshop of the late tenth century [5]. On the other hand, monuments of the second half of the thirteenth century and the first half of fourteenth century represented a broad range in the terms of the level of artistic practise.

In order to minimise the damage, the areas selected for sampling belonged either to the paintings’ background or, rather, to peripheral parts. Nevertheless, it was attempted to sample a sufficient variety of colours. The samples were moulded in epoxy resin, grinded and polished, in order to produce cross sections for examination under polarising and scanning electron microscope. Additionally, representative fragments of some selected samples were powdered in order to be studied for their mineralogical composition.

**Experimental**

**Optical microscopy**

The initial samples were studied under the stereomicroscope in order to describe their surface structure and colour impression. Furthermore, the polished sections were examined under the polarising microscope. This examina-
tion was mainly focussed on the stratigraphy and thickness of paint layers and preparatory layers. Another aspect was the microstructure of plaster and paint layers, in terms of characteristics such as coherence, inclusions, porosity or size of pigments.

Scanning electron microscopy

After the examination under the polarising microscope the sections were carbon-coated and were examined under a FEI, Quanta Inspect D8334 scanning electron microscope, coupled with an energy-dispersive X-ray spectrometer (SEM-EDS), in order to determine the chemical composition of pigments, binding medium and plaster layers. The beam voltage for the quantitative determination of element was set to 25 kV, in order to obtain better excitation of the low-energy- and low-concentration compounds. Finally, the distribution of the elements (mapping) in cross sections was determined by simultaneous acquisition of X-ray data from each pixel of the secondary electron (SE) image areas.

Fourier-transformed infrared spectroscopy

In order to complement the chemical analysis by SEM-EDS concerning the identification of pigments, selected paint layers were analysed by Fourier-transformed infrared spectroscopy (FTIR). The FTIR analysis was performed in a Bruker, Equinox 55/S spectrometer. Transmittance spectra were collected in the region of 4,000 to 400 cm\(^{-1}\), with 4 cm\(^{-1}\) resolution. The samples were mixed with KBr and scanned 40 times, in order to reduce the signal to noise ratio.

X-ray diffraction

For the examination of the mineralogical composition of the plaster, selected samples were powdered and examined with X-ray powder diffraction (XRD). The samples were analysed in a Siemens D-500 Diffractometer, using the Cu-K\(_{\alpha}\) radiation (\(\lambda=1.5406\) Å) with a graphite monochromator in the diffraction beam, at 1.2 kW (40 kV, 30 mA). Spectra were collected in the range of 2–60° 2\(\theta\), with a step size of 0.03°/s.

Energy-dispersive X-ray fluorescence analysis

In order to assess the feasibility of non-destructive in situ analysis of pigments several samples were examined with energy-dispersive X-ray fluorescence analysis (EDXRF). The used portable set-up consists of an X-ray tube with Ag-anode, which was operated at 20 kV for the present measurements, and of an Amptek XR 100CR Si PIN
Results and discussion

The adherence of the paint layers to the preparatory layer indicated that the ‘al fresco’ technique was applied for the construction of the wall paintings. According to the ‘al fresco’ technique, the pigments are mixed with plain water or lime water (calcium hydroxide super-saturated solution) and then they are applied on damp lime-based plaster [2]. In contrast, the ‘al secco’ technique is used for painting on dry plaster with pigments mixed with different types of organic binders.

In most cases, the used pigments were soil-based materials, ochre but also fine clay without particularly high iron oxide content. For dark colours, usually powdered charcoal was used. Only in a few cases the use of other types of pigments was confirmed. The preparatory layer of the wall paintings consisted of a thin lime mortar layer. The coherence of this layer ranged from a very compact with pores size below 50 μm to a loose microstructure with a considerable amount of micro-cracks. In many cases, particles of non-hydrated lime (CaO) were identified, which were indicative for a local and pressing production.

The high magnesium concentrations in some of the samples were noticeable, particularly at the surfaces. This could be due to the use of dolomitic plaster as binder or due to the use of magnesium rich pigments. There was also the possibility that the wall paintings were covered at some point with a different, i.e. more dolomitic, plaster.

a. Elemental composition of pigment layers

Ochre

The majority of the collected samples presented colours in a spectrum from yellowish brown to orange red.

![Polished sections of various samples: a CH09_S2: red ochre sample from the Church Aghios Sergios kai Bakchos. b CH12_S1: red ochre sample with carbon black top layer from the Church Aghios Nikolaos at Platsa. c CH02_S2: cinnabar top layer from the Monastery of Faneromeni. d CH07_S1: minium layer from the Church Ai-Strategos. e CH10_S2: ultramarine paint layer from the Church Aghios Philippos. f CH07_S2: green paint layer from the Church Ai-Strategos](image-url)
The paint layers consisted usually of ochre mixed with lime, the colour of which depended on the presence of iron hydroxides and oxides [7]. A typical example of red ochre with a high content of hematite is presented in Fig. 2a. The dark red sample CH09_S2 was collected from the North wall of the Church Aghios Sergios kai Bakchos at Kita. The section indicated two layers, an orange red layer L1 of c. 80 μm, and a surface layer L2 of c. 20 μm (Table 2). According to SEM-EDS the Fe₂O₃ concentration in Layer L1 was above 10% with comparably low concentrations of silicon and aluminium. Therefore, it can be assumed that in this case, a high-quality red ochre or sinopia was used, in contrast to other paintings created rather with iron rich clay. In Table 3, the chemical compositions of four different red orange paint layers are presented, demonstrating the variety of ochre used in Mani.

**Carbon black** Black or dark bluish colours were achieved in most cases with carbon black, i.e. lime mixed with powdered charcoal. A typical example was a dark fragment collected from the bema of the Church Aghios Nikolaos at Platsa, CH12_S1. The polished section (Fig. 2b) showed three distinct layers, a light-orange preparatory layer L1 (c. 100 μm), an orange red layer L2 (c. 80 μm) and on top, a white layer mixed with black pigments L3 (c. 100 μm). In the top layer, also some occasional green inclusions were visible, which will be referred to later. Apart from distinct black layers, charcoal was apparently also used mixed with ochre in order to produce dark red colours (Table 2).

**Cinnabar** In the Monastery Faneromenis in Frangoulwianika, a bright red sample CH02_S2 was collected from the bema. The section (Fig. 2c) indicated two paint layers, one orange red layer L1 of c. 80 μm and a second discontinuous rather thin red layer L2 on top (c. 10 μm). The SEM examination showed in back-scattered mode a concentration of an element with high atomic number in the top layer (Fig. 3). According to the SEM-EDS analysis, Layer L1 consisted of lime mixed with red ochre, while layer L2 presented high concentrations of mercury and sulphur, a clear indication for cinnabar (HgS) [2]. Sparse cinnabar particles assumedly as contamination were detected also in the second sample from the Monastery Faneromenis. Furthermore, the red ochre in the above-presented Sample CH09_S2 was apparently mixed with a small portion of cinnabar.

**Minium** An orange red sample with a black streak CH07_S1 was collected from the bema in the Church of Ai-Strategos Boularion. The streak appeared in the polished

---

Table 2 Summary of the analytical results: The groups in the last column correspond to the plaster types described in the text

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stratigraphy</th>
<th>Identified pigments</th>
<th>Plaster composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01_S1</td>
<td>Two layers: L1 red / L2 light brown</td>
<td>L1: red ochre, L2: brown ochre, lime</td>
<td>Group 4</td>
</tr>
<tr>
<td>CH01_S2</td>
<td>One light brown layer</td>
<td>L1: yellow ochre</td>
<td></td>
</tr>
<tr>
<td>CH02_S1</td>
<td>One red layer with dark crust</td>
<td>L1: ochre and charcoal, sparse cinnabar</td>
<td>Group 2 (Fig. 6)</td>
</tr>
<tr>
<td>CH02_S2</td>
<td>Two red layers (Fig. 2c)</td>
<td>L1: red ochre, L2: cinnabar</td>
<td></td>
</tr>
<tr>
<td>CH03_S1</td>
<td>Two layers: L1 red / L2 light brown</td>
<td>L1: red ochre, L2: brown ochre</td>
<td>Group 1</td>
</tr>
<tr>
<td>CH03_S2</td>
<td>Two layers: L1 red / L2 brown</td>
<td>L1: red ochre, L2: brown ochre (Table 2)</td>
<td></td>
</tr>
<tr>
<td>CH04_S1</td>
<td>Two layers: L1 red / L2 light brown</td>
<td>L1: red ochre, L2: yellow ochre</td>
<td>Group 1</td>
</tr>
<tr>
<td>CH04_S2</td>
<td>One dark red layer</td>
<td>L1: red ochre with charcoal</td>
<td></td>
</tr>
<tr>
<td>CH05_S1</td>
<td>Two layers: L1 orange/ L2 light brown</td>
<td>L1: yellow ochre, L2: yellow ochre</td>
<td>Group 3 (Fig. 6)</td>
</tr>
<tr>
<td>CH05_S2</td>
<td>One thin dark layer</td>
<td>L1: charcoal</td>
<td></td>
</tr>
<tr>
<td>CH06_S1</td>
<td>Two layers: L1 red / L2 brown</td>
<td>L1: red ochre, L2: brown ochre</td>
<td>Group 5</td>
</tr>
<tr>
<td>CH06_S2</td>
<td>Two layers: L1 red / L2 light brown</td>
<td>L1: ochre, L2: yellow ochre</td>
<td></td>
</tr>
<tr>
<td>CH07_S1</td>
<td>Three layers: L1 red/ L2 dark red/ L3 white (Fig. 2d)</td>
<td>L1: ochre, L2: minium (Fig. 3)</td>
<td>Group 2</td>
</tr>
<tr>
<td>CH07_S2</td>
<td>Two layers: L1 red orange/ L2 green (Fig. 2f)</td>
<td>L1: red ochre, L2: amphiboles or serpentine (Table 4)</td>
<td></td>
</tr>
<tr>
<td>CH08_S1</td>
<td>Two layers: L1 red / L2 yellowish white</td>
<td>L1: red ochre , L2: lime</td>
<td>Group 2</td>
</tr>
<tr>
<td>CH08_S2</td>
<td>Two layers: L1 red / L2 yellowish white</td>
<td>L1: red ochre, L2: brown ochre, lime</td>
<td></td>
</tr>
<tr>
<td>CH09_S1</td>
<td>Dark red layer with occasional white crust</td>
<td>L1: red ochre, charcoal</td>
<td>Group 1</td>
</tr>
<tr>
<td>CH09_S2</td>
<td>Bright red layer with yellowish white crust (Fig. 2a)</td>
<td>L1: clay, sporadic cinnabar, L2 yellow ochre (Table 2)</td>
<td></td>
</tr>
<tr>
<td>CH10_S1</td>
<td>One red layer</td>
<td>L1: red ochre (Table 2)</td>
<td>Group 1</td>
</tr>
<tr>
<td>CH10_S2</td>
<td>Three layers: L1 white/ L2 blue/ L3 green (Fig. 2c)</td>
<td>L1: lime plaster, L2: ultramarine (Fig. 4, Table 3)</td>
<td></td>
</tr>
<tr>
<td>CH11_S1</td>
<td>One red layer</td>
<td>L1: red ochre (Table 2)</td>
<td>Group 2 (Fig. 6)</td>
</tr>
<tr>
<td>CH11_S2</td>
<td>One dark layer with occasional red pigments</td>
<td>L1: red ochre with occasional ochre</td>
<td></td>
</tr>
<tr>
<td>CH12_S1</td>
<td>Two layers: L1 dark red/ L2 bluish green (Fig. 2b)</td>
<td>L1: ochre/fine clay, L2: charcoal, green earth (Table 4)</td>
<td>Group 1</td>
</tr>
<tr>
<td>CH12_S2</td>
<td>Two layers: L1 red/L2 bluish white</td>
<td>L1: red ochre, L2 lime mixed with charcoal</td>
<td></td>
</tr>
</tbody>
</table>
section as a dark red layer of up to c. 60 μm laying on an orange red layer of c. 100 μm (Fig. 2d). The surface was additionally covered with a thin white layer (<30 μm). According to SEM-EDS examination the red layer consisted of a red earth or clay mixed with lime. The dark red layer appeared to consist mainly of a lead sulphate. It seemed, however, questionable, whether the present state of the wall painting represented the originally used pigments. Assumedly, the lead sulphide is an alteration product of minium (Pb₃O₄), which interacted over time with moisture and atmospheric pollutants [8]. Cennini already remarked concerning red lead that ‘...if you use it on the wall it soon turns black ...’ [3].

Ultramarine blue In the Church Aghios Philippus in Korokoyannika, a bright blue sample CH10_S2 was collected from the background of a wall painting at the south wall. The section of the sample (Fig. 2e) showed a discontinuous thin blue paint layer (c. 30 μm) on a preparatory layer (c. 120 μm). In some areas, the surface was covered with a greenish yellow layer. In this case, the SEM examination in back-scattered mode did not indicate any elements with high atomic number in the paint layer. Instead, element maps indicated increased concentrations of sodium and sulphur (Fig. 4). This was confirmed by SEM-EDS analysis (Table 3). The yellow surface layer L3 presented an even higher sulphur concentration and a high chlorine content while sodium was again clearly decreased compared to Layer L2. The preparatory layer showed the same composition as the plaster. The chemical composition of Layer L2 was an indication for the use of lapis lazuli (ultramarine) mixed with lime binder, the main mineral component of which is lazurite [9]. The surface layer L3 assumedly was the result of an alteration due to interaction with the atmospheric environment, as also the sulphur concentration in the other layers was higher than expected.

Green In the Church of Ai-Strategos Boularion, a dark greenish sample CH07_S2 was collected, related to the second construction phase. The section showed two paint layers, one orange layer (c. 60 μm) and one greenish layer (c. 80 μm; Fig. 2f). Apart from these two layers, in some areas, the surface was covered with a thin third layer (c 20 μm), giving a white to opaque impression. The pigments in both paint layers appeared to be soil-based according to the SEM-EDS examination. The analysis indicated rather high magnesium concentrations, particularly in the green layer. However, assuming a typical green earth pigment on the basis of celadonite or glauconite, the potassium concentration appeared too low [7, 9]. Instead, the use of an amphibole, such as actinolite, or serpentine as pigment could be considered in this case. Green pigments
with higher potassium concentration, resembling the composition of typical green earth were found in the above-presented Sample CH12_S1 (Table 3).

b. Chemical and mineralogical composition of pigments and binders

**Red pigments** The FTIR spectrum of the red ochre sample from Aghios Sergios kai Bakchos (Fig. 2a) presented a band of strong peaks at 1,143 cm$^{-1}$ and 1,020 cm$^{-1}$, and a peak at 1,107 cm$^{-1}$ (Fig. 5: CH09_S2), which are assigned to $S_2O_3^{2-}$ [10] and $SO_4^{2-}$, respectively [11]. The above bands are indicative for the presence of cinnabar (HgS) and comply with SEM-EDS results. The spectrum also presents an infrared absorption band at 1,384 cm$^{-1}$, typical for the degradation products of sodium and potassium nitrates [12].

The peaks between 400 and 750 cm$^{-1}$ are indicative for the presence of red ochres [13] and are apparent in all red pigments (Fig. 5: CH08_S1). The peaks at 466 and 532 cm$^{-1}$ are attributed to the presence of iron oxide (Fe$_2$O$_3$), while the shoulder at 1,166 cm$^{-1}$, the double peak at 798 and 775 cm$^{-1}$ and the single peaks at 694 and 510 cm$^{-1}$ (small shoulder) are indicative for the presence of red ochre and quartz [13]. The main peaks for both quartz and red ochre in the range of 1,080 to 1,100 cm$^{-1}$ are hidden in the bands of cinnabar.

**Blue pigments** The FTIR analysis of the blue sample from the Church Aghios Philippos (Fig. 5: CH10_S2) presented a spectrum of low degree of resolution for blue chromophores. However, this is something already emerged in FTIR analysis of blue pigments [14]. The evaluation of the spectrum revealed the presence of four peaks at 924, 1,030, 1,085 and 1,153 cm$^{-1}$, which are indicative for the presence of lapis lazuli [15]. Moreover, the presence of a weak peak at 540 cm$^{-1}$, which increases its intensity in the first derivative plot, is also characteristic for the stretching vibration of the S-S bond and therefore the presence of ultramarine [14, 16]. The ability of FTIR to identify sulphate compounds is of great importance for wall paintings surveys and highlights the complimentary character of IR with other portable spectroscopic techniques, such as LIBS and EDXRF, since they appear limitations for the identification of sulphur and light elements in air atmosphere.
Green and black pigments In the case of green earths (Fig. 5: CH07_S2), FTIR spectra present only the characteristic bands of aluminosilicates (Si–O–Al) at 457, 635 and 1,010 cm$^{-1}$ [17]. Other typical absorption bands of green earths are hidden below calcite peaks. Similarly, in the case of dark blue–black pigments, the absorption bands of calcite and hydromagnesite covers any potential peaks from carbon charcoal or bone black.
Binders and surface layers. In all spectra, infrared absorptions at 1,425–30 cm\(^{-1}\), 873–7 cm\(^{-1}\) and 710–5 cm\(^{-1}\) were assigned to the presence of calcite [12, 18]. There are also some characteristic peaks of sulphates (600 cm\(^{-1}\), 670 cm\(^{-1}\), 1,115 cm\(^{-1}\), 1,620–5 cm\(^{-1}\), 1,685–90 cm\(^{-1}\)), which are indicative for the presence of calcium sulphate hydrate, while the wide and weak peak at the range of 1,420–1,480 cm\(^{-1}\) is mainly attributed to the presence of hydromagnesite (Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)-4(H\(_2\)O)) [19]. The presence of hydromagnesite is clearly seen in the case of the crust form the surface of wall paintings in Ai-Stratigos Boularion church (Fig. 5: CH07_Crust).

c. Mineralogical composition of plaster layers

According to the stratigraphy of wall paintings and especially to the number of preparatory mortar layers, they can be divided to the following groups:

- Group 1 (churches 3, 4, 9, 10 and 12): one single preparatory layer of 0.5–1.5 cm, which consists of lime mixed with small amount of soil material. Lime lumps (non-hydrated CaO) are present within their mass and along with the large amount of meso-macro pores attribute to the mortars a moderate compactness and strength.

- Group 2 (churches 2, 7, 8 and 11): the wall paintings consist of two layers. The superficial is a thin (1–3 mm) lime layer, applied to a thicker and less compact mortar layer. The latter contains considerable amount of both animal and plant fibres, while it presents a microstructure similar to those of group 1. The coherence of the external thin layer ranges from very compact with pores size below 50 \(\mu\)m to moderate, with a considerable amount of micro-cracks. In many cases, particles of lime lumps are identified, which are indicative for a local and pressing production of the lime.

- Group 3 (church 5): the preparatory mortar for the paint layer consists of lime mixed with about 50–60 % (w/w) ceramic fragments (aggregates), in the range of 200 \(\mu\)m–2 mm. The mortar presents a compact microstructure and contains a small amount of micro-cracks. Finally, plant fibres are present in their mass.

- Group 4 (church 1): the wall paintings of Agia Paraskevi at Dirou are fabricated on a thin lime layer, mixed with plant fibres and small amount of soil material.

- Group 5 (church 6): one single layer of 0.5–1.0 cm thickness consisted of lime mixed with thin aggregates. The preparatory layer of Agios Nikitas at Kypoula (CH 06) contains about 35–50% (w/w) angular crushed limestone aggregates, in the range of 100–500 \(\mu\)m.

The binding material of all mortars is hydrated lime, resulting in the formation of calcite through carbonation. In the diffraction patterns (Fig. 6) it is shown that the addition of soil or ceramic aggregates did not result in the formation of any hydraulic compounds within their setting products. Also, the absence of dolomite or magnesite from the binding material indicates that the amounts of magnesium (Mg) identified in EDX should be attributed to the dissolution and migration of potential external Mg-rich depositions. The analysis of the crust formations on many wall paintings revealed that these are consisted primary of Hydromagnesite (Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)-4(H\(_2\)O)), calcite (CaCO\(_3\)) and small amounts of gypsum (CaSO\(_4\)\(_2\)H\(_2\)O). The presence of gypsum, which is also evident in FTIR spectra, should be regarded as a deterioration product of calcite. Consequently, hydromagnesite should have been resulted from the degradation of a magnesian, due to increased humidity and wetting/drying cycles [20]. Hydromagnesite is more soluble than calcite and therefore it is easily dissolved and diffused within the mortar mass. The latter phenomenon may partially explain the detection of magnesium concentrations in the preparatory paint layers.

The above observation indicates that the wall paintings of all churches included in this study were covered at some point (most probably at the same time period) with a surface layer of magnesian lime. This is a quite interesting result, since dolomitic or magnesian limes do not very often appear in the Greek area, while their use is usually related to the mineralogy and geology of the raw materials available at different sites [21].

d. Portable EDXRF: feasibility test

The experiments with the portable EDXRF indicated a sufficient application of the instrument concerning the identification of the majority of the pigments, even with purely qualitative evaluation of the spectra. Particularly
pigments like cinnabar and minium could be clearly identified, due to their elemental components with high atomic numbers. Concerning the lighter elements, such as silicon (Z = 14) and below, however, the detection is affected by the X-ray absorption in air. This appeared to be critical in view of the used earthen pigments with main components as sodium, magnesium, aluminium and silicon. Pigments like ultramarine and green earth are rather difficult to identify with the present set-up. Therefore, it is questionable if a portable EDXRF can substitute completely the sampling of micro fragments and their examination in the laboratory. There is, however, the potential to overcome the problems at least to some extent by modifying the set-up, for example by optimising the spectrum of the X-ray tube, by using another type of detector, such as a silicon drift detector, or by applying helium flow during the measurement [22]. Nevertheless, even the present set-up can be used complementary during sampling in order to examine a larger number of areas and in order to make decisions about the areas to be sampled.

Conclusions

This case study can be considered as an initial survey of construction and painting techniques applied in churches in the Mani Peninsula. The sampled areas were selected more or less on a random basis. Nevertheless, the achieved analytical results allow for basic conclusions. A relatively high level of artistic techniques in a remote and rather rural area of the Byzantine Empire was demonstrated. The identified pigments indicated a typical Byzantine palette maybe with the exception of the green earth pigments used. At least to some extent, precious pigments were used similarly to the metropolitan monuments. Local peculiarities concerned mainly the raw materials used for preparatory layer and lime binder. However, it became clear that a larger number of samples will allow for more specific results and answers, concerning the questions initially raised.

As for the applied spectroscopic techniques, the characterisation of natural earth pigments is not a straightforward issue, especially when the pigments are mixed with calcium hydroxide (lime water) as a binding medium or they are applied on a lime substrate, as in al fresco technique. FTIR analysis basically confirmed the results achieved by SEM-EDS spectroscopy. In comparison to diffraction analysis and EDXRF, however, FTIR offers advantages in terms of the identification of hydrated or low-crystallinity phases, such as hydromagnesite, and the detection of sulphates (e.g. gypsum). Therefore, FTIR allows for distinguishing different types of ochres, such as aluminosilicate-based and sulphate ochres, and thus, it expands the applicability of spectroscopic techniques to the study of materials used in cultural heritage.

In view of a successive study of Byzantine wall paintings from Mani, the supplemental application of portable non-destructive techniques appears to be reasonable, in order to include a larger number of samples. A broader analytical basis would be expected to allow for additional conclusions, in terms of specific workshops and in terms of use of pigments in different parts of the church.

Acknowledgements

The analytical work was part of a project on Byzantine wall paintings coordinated by M. Panayotidi and S. Kalopissi-Verti at the University of Athens, which has been funded by EPEAK II/ PYTHAGORAS II. The measurements with the portable XRF were carried out at the TEI of Athens in collaboration with I. Sianoudis.

References