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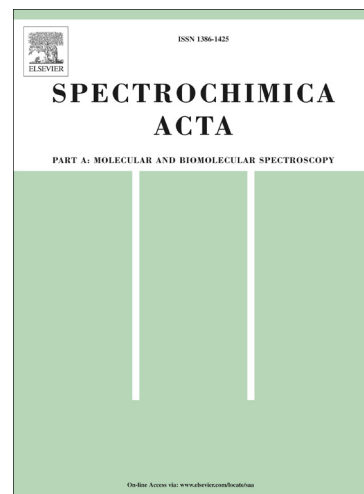
PII: S1386-1425(14)01022-1  
DOI: <http://dx.doi.org/10.1016/j.saa.2014.06.123>  
Reference: SAA 12382

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 23 April 2014  
Revised Date: 12 June 2014  
Accepted Date: 22 June 2014

Please cite this article as: P. Holakooei, A-H. Karimy, Micro-Raman spectroscopy and X-ray fluorescence spectrometry on the characterization of the Persian pigments used in the pre-seventeenth century wall paintings of Masjid-i Jāme of Abarqū, central Iran, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2014), doi: <http://dx.doi.org/10.1016/j.saa.2014.06.123>

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Title page

**Micro-Raman spectroscopy and X-ray fluorescence spectrometry on the characterization of the Persian pigments used in the pre-seventeenth century wall paintings of Masjid-i Jāme of Abarqū, central Iran**

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## Micro-Raman spectroscopy and X-ray fluorescence spectrometry on the characterization of the Persian pigments used in the pre-seventeenth century wall paintings of Masjid-i Jāme of Abarqū, central Iran

### Abstract

The pigments used in the wall paintings of the Masjid-i Jāme of Abarqū, central Iran, as less-known pigments used in the history of Persian painting, were investigated with micro-Raman spectroscopy, micro X-ray fluorescence (micro-XRF), scanning electron microscopy (SEM), and polarised light microscopy (PLM). The results showed that the green, red, and blue pigments were atacamite, red lead, and smalt mixed with natural ultramarine blue respectively applied on a white substrate composed of white huntite. Moreover, the blue smalt was identified to be used on the white huntite and under the paint layer in order to delineate the design of the wall paintings and to act as a rough sketch for the subsequent use of the other pigments. Glushinskite, as a less-reported mineral in historical wall paintings, was identified by micro-Raman spectroscopy and hypothesised to be associated with the degradation of the white huntite binder. Furthermore, micro-Raman spectroscopy studies surprisingly revealed the mineral woodhouseite sparsely mixed with the green pigment. This paper strongly suggests micro-Raman spectroscopy for identifying archaeological pigments and for diagnosing their deterioration products. Conducting scientific methods of analysis, the pigments identified in this study are reported for the first time to be used in Persian wall paintings.

**Key words:** micro-Raman spectroscopy, micro-XRF, huntite, smalt, atacamite, wall painting, Masjid-i Jāme of Abarqū

### 1. Introduction

The boom of executing both figurative and floral wall paintings in Persia is reported from the 17th century AD onwards [1]. While the post-seventeenth century Persian wall paintings have been either aesthetically or scientifically studied, the scientific data published on the wall paintings created prior to the 17th century in Iran is scant. Our information about the pigments used before the 17th century AD in Iran is limited to those studies performed on pre-seventeenth century illuminated manuscripts [2,3], the analytical studies performed by Purniton and Watters [4], and some historical texts of which Gulistan-i Hunar (early 17th century) [5] and Qānūn-us-Suvar (ca. 1601 AD) [6] are the most important ones. Created long before the seventeenth century AD, the wall paintings of Masjid-i Jāme of Abarqū belong to an era when wall paintings were not still widespread in Persia and painting techniques were evolving to flourish in the subsequent centuries [1].

Abarqū city, located on 31.13° N, 53.28° W, in 150 km of south-west Yazd, central Iran, hosts one of the oldest mosques erected in Iran. The great mosque of the city, Masjid-i Jāme of Abarqū, has always been subjected to the renovation from the seventh century [7] until the twelfth [8] towards the

fourteenth centuries under the Mongol domination [9]. Although the mosque has followed a quite clear historical line of evolution, the wall paintings of the mosque are not clearly dated yet. These paintings can be artistically compared with those fourteenth century paintings reported by Lentz [10], where a dark blue pigment in creating the painting's composition represents the same artistic style.

Despite the importance of the pre-seventeenth century wall paintings in Iran, these paintings have received less attention in terms of materials and pigments. Although some analytical studies are published on the pre-seventeenth Persian pigments used in illuminated manuscripts, the pigments used in the pre-seventeenth century Persian wall paintings are not scientifically studied. The current paper presents an analytical study conducted on the pigments used in the wall paintings executed prior to the seventeenth century in Iran using micro-Raman spectroscopy, micro X-ray fluorescence (micro-XRF), X-ray maps of scanning electron microscopy (SEM) and polarised light microscopy (PLM).

## 2. Experimental

### 2.1 Samples

The wall paintings of Masjid-i Jāme of Abraqu exhibit floral and arabesque patterns. The colours used in the wall paintings comprise of white, green, red and two shades of blue (Fig. 1a). The paintings were not previously restored and the pigments were to be considered as the authentic ones. Among the pigments, the red and green were scarcely used on the walls (Fig. 1b). However, the extensive use of the white and blue pigments predominately manifested a monochrome blue design on a white substrate. The blue colour, on the other hand, consisted of two shades: a pale blue on which a darker shade of blue was applied. Under a closer observation, it could be recognised that the pale shade was used only to delineate a general sketch of the wall paintings which was then covered by the darker shade in order to make the general sketch more visible (Fig. 1c).

### 2.2 Optical microscopy

An Alltion BK-POLT (China) polarized light microscope (PLM) was used to observe the optical properties of the pigments under the plane and crossed polarised lights. The microscope was fitted with a Canon EOS Kiss x4 digital camera while the photos were acquired with DSLR Remote Pro software and the captured photos were processed in TSView software. The pigments were immersed in glycerin with a refractive index of 1.47 in order to enhance the visualization of the pigments.

### 2.3 Micro-XRF analyses

A portable ARTAX<sup>TM</sup> 200 of Bruker AXS Microanalysis GmbH was used as the XRF spectrometer which was consisted of an X-ray tube with a Mo target placed at 6° and a beryllium window. A SSD Peltier-cooled detector (10 mm<sup>2</sup> active area and resolution of <155 eV at 10 kcps) was used for detecting the secondary fluorescence X-rays which were emitted under a maximum voltage and

current of 50 kV and 1000  $\mu\text{A}$  respectively. The samples were analysed on a fixed stage and the measurements were performed in air for about 120 s while the X-ray beam was irradiated via a collimator with a diameter of 0.65 mm.

#### 2.4 Micro-Raman spectroscopy

The micro-Raman spectroscope which was used in our studies was a LabRam HR800 spectrometer with a focal length of 80 mm from Horiba Jobin Yvon, France, fitted with an air-cooled CCD detector (1024  $\times$  256 pixels) at  $-70$  °C. An Olympus BAXFM microscope and 50x and 100x objectives were used to collect the Raman scattering signals and a 600 groove/mm grating was used to send the collected signals to the detector. The excitation source was a He-Ne laser (632.8 nm line) with a maximum laser power of 20 mW. The exposure time was varied from 5 to 15 s with 5 accumulations. The calibration of the spectrometer was performed with silicon at  $520\text{ cm}^{-1}$  and the recorded spectra were handled with LabSpec 5 software.

#### 2.5 Scanning electron microscopy (SEM) and X-ray mapping

A tiny sample from the red colour was coated with gold and observed by a TESCAN scanning electron microscope under 15 kV accelerating voltage and with about 24 mm working distance. SEM was used to acquire back-scattered micrographs and X-ray maps from the outermost surface of the red pigment. As the red pigment was used on the blue pigment, an X-ray map could be useful to have an idea about the distribution of the composing elements of the red pigment on the blue pigment. Moreover, the X-ray map could be helping us to observe the distribution of the low atomic weight alkaline and alkaline earth elements (Na and Mg) which could not be detected by micro-XRF in air.

### 3. Results and discussion

#### 3.1 White pigment

The pigments used in the mural paintings consisted of blue, red, and green, which were performed on a white substrate. The micro-XRF analysis of the white pigment showed calcium as the main constituent of the pigment while sulphur and iron were detected as minor elements in the composition (Fig. 2a). More interestingly, the Raman spectrum of the white pigment showed the Raman bands at 704, 726, 744, 880, and  $1123\text{ cm}^{-1}$  which are assigned to the mineral huntite [11], together with the Raman bands at 413, 495, 618, and  $1008\text{ cm}^{-1}$  attributable to gypsum [12] and 529, 587, 672, 917, and  $1472\text{ cm}^{-1}$  associated with glushinskite [13] (Table 1), which is not subjected to any thermal event [14] (Fig. 2b).

Apart from gypsum, which was most certainly introduced from the gypsum rendered walls under the wall paintings, the presence of both huntite and glushinskite could be of interest as they have been less reported to be used in the architectural paintings found in Iran. The only example of the use of huntite

as a pigment in Iran is reported to be in Husaynīyān House, Yazd, 150 km in north-east Abarqū, which was interestingly mixed by glushinskite [15]. Huntite, which is a double carbonate of magnesium and calcium ( $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ ), was identified in 1953 [16] and soon after was reported to be used in objects of art and archaeology from the antiquity in dynastic Egypt [17-19], in the Roman era [20,21], until the modern times in the aboriginal Australian rock arts [22] as a white pigment. As a mineral, huntite is also reported to be occurred in various zones of Iran including southern coast of the Persian Gulf [23], eastern [24] and central Iran, Yazd, and particularly in Abarqū [25], where it is called '*gil-i sifid*', *i.e.* white mud [26]. The evidences of the use of huntite for painting walls can also be found in the descriptions of historical texts of painting materials. There are some historical Persian treatises which mention clearly the term '*gil-i sifid*' for describing a white pigment for whitening walls of buildings [27,28]. It should be mentioned that the absence of magnesium in the micro-XRF spectrum is resulted from its low atomic weight and analysing the sample in the air instead of helium flow.

Concerning the presence of glushinskite, magnesium oxalate ( $\text{MgC}_2\text{O}_4$ ), in the white pigment, it can be noted that this mineral has probably been formed as a result of juxtaposing natural binders and white huntite [29]. The formation of oxalic acid, derived from the organic binding media mixed with pigments, can chemically transform the chemical and mineralogical composition of pigments to the natural oxalates [30,31]. In other words, glushinskite is likely derived from the gradual oxidative degradation of an organic material as binder (especially proteinaceous materials) probably via micro-organisms [32] and its reaction with the magnesium-containing pigment, *i.e.* huntite. The formation of natural oxalates can also be the result of the formation of oxalic acid derived from the lichens' growth [33,34] and other micro-organisms on the surface of the works of art [35]. However, as no trace of fungi hyphae and lichens' growth was found on the paintings' surfaces, it was more relevant to attribute the oxalate formation to the binder mixed with the white huntite. Surprisingly, glushinskite is reported to be used as a white pigment in the paintings of the Church of San Fiorenzo in Piedmont, Italy [36]. However, one cannot exclude that the mineral huntite could be originally associated with glushinskite prior to quarrying and use as a pigment. This hypothesis needs to be accompanied with more scientific data for approval.

### 3.2 Green pigment

As the micro-XRF spectrum of the green pigment shows (Fig. 3a), the green pigment was mainly consisted of Cu, Cl, S, and Ca, together with the traces of Fe, K, Sr, Pb and Sn. The micro-Raman investigations revealed more interesting results (Fig. 3b). The Raman bands registered at 410, 455, 510, 588, 822, 909, 972, and 990  $\text{cm}^{-1}$  are to be attributed to atacamite, a green basic copper chloride ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) [37]. Moreover, a sharp band centred at 1027  $\text{cm}^{-1}$ , together with two Raman bands at 990 (also observed for the green atacamite) and 1003  $\text{cm}^{-1}$ , a weak band at about 1170  $\text{cm}^{-1}$ , multiple weak Raman bands at 590, 630, and 655  $\text{cm}^{-1}$ , can be assigned to the mineral woodhouseite

( $\text{CaAl}_3(\text{PO}_4, \text{SO}_4)_2(\text{OH})_6$ ) [38] (Table 1). As a hypothesis, the presence of sulphur in the composition of the green pigment (Fig. 3a) can be associated with this mineral. Nevertheless, it remained unclear for us what constituent of the green colour was associated with woodhouseite. It should be mentioned that woodhouseite was only observed scarcely in the green sample and the majority of the Raman spectra acquired from the green pigment showed the presence of glushinskite mixed with atacamite. Higgitt and White [32] report oxalates are usually found in historical copper green pigments.

The use of atacamite in historical wall paintings is fairly well-documented. For instance, Kossolapov and Kalinina [39] and Cotte *et al.* [40] report atacamite as the green pigment used in the wall paintings of Bamiyan, Afghanistan. The use of atacamite as a green pigment is not only limited to mural paintings. Using micro-Raman spectroscopy, Burgio *et al.* [41] and Muralha *et al.* [42] have identified atacamite as a green pigment used in two Persian manuscripts dated to the early sixteenth century AD. Moreover, Purinton and Watters [4] list atacamite as a green pigment used in Persian illuminated manuscripts.

### 3.3 Blue pigment

Under the plane polarised light, two types of blue pigment were observed (Fig. 4a). More abundantly, a glassy, transparent and pale blue pigment with various particle sizes from 10 to 30  $\mu\text{m}$  and another blue pigment, with a sporadic occurrence and denser hue, with about 50  $\mu\text{m}$  in diameter, could be recognised under the transmitted light of PLM. The micro-Raman spectroscopy study on the blue pigment with denser hue showed the Raman bands at 257, 545, and 1092  $\text{cm}^{-1}$  consistent with the Raman bands of ultramarine blue [43] (Fig. 4b). The transparent and glassy blue, which exhibited conchoidal fractures under the polarised light, however, showed a very pronounced fluorescence signal under Laser beam so that no Raman signal could be observed. Although micro-Raman spectroscopy did not show any result, the results of micro-XRF analysis on the light blue pigment were conclusive (Fig. 4c). The presence of Si, K, and Co in the composition of the blue pigment showed that the pale blue pigment had a glassy lattice in which  $\text{Co}^{2+}$  had yielded a blue shade. Other elements detected in the micro-XRF analysis can be attributed to the glassy matrix of the blue smalt either as flux (*i.e.* Pb and Ca) or colouring agent (*i.e.* Fe and Cu) (Table 1). As a result, it can be assumed that the second type of blue with a lighter hue and a glassy appearance was smalt. More interestingly, the blue smalt showed traces of As in the composition which can contribute to the provenance study of the pigment (see below). Confirming the micro-XRF results, the optical properties of this blue pigment were consistent with the optical characteristics of blue smalt under polarised light microscope [44].

It is well-studied that the Co ores in Iran are mainly consisted of cobaltite ( $\text{CoAsS}$ ), erythrite ( $\text{Co}_3(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})$ ), and asbolane ( $(\text{Ni}, \text{Co})_{2-x}\text{Mn}^{4+}(\text{O}, \text{OH})_4 \cdot n\text{H}_2\text{O}$ ) [45]. These ores are found in near Kāshān, Qamsar, and have been used since the medieval times for making blue glazes derived from

Co [46]. Considering this fact, the presence of As in the composition of the blue pigment can be associated with either cobaltite or erythrite minerals found in Qamsar. Moreover, there are some medieval texts which have documented the use and the methods of purifying the Co ores of Qamsar for the preparation of blue smalt [47,48]. On the other hand, the absence of bismuth in the composition of the blue pigment could be considered as another evidence of the local provenance for the blue smalt as bismuth is reported to be sometimes associated with the blue smalt pigments found in Europe and India [49].

Scientific approaches have documented the use of blue smalt in Persian illuminated manuscripts. For instance, Newman [50] reports smalt in two 18th century Persian illuminated manuscripts in the Brooklyn museum and in an eighteenth century Persian oil painting. The use of blue smalt is not only limited to the area under the Persian influence but it is also reported to be used in the neighbour cultures like those eighteenth century Indian miniatures found in Bundi [49]. The only example of the use of smalt in the paintings created before the 18th century in the lands under Persian influence is reported to be in a fifteenth century Armenian illuminated bible found in Khizan (now in Turkey) [51].

As far as the ultramarine blue constituent of the blue pigment is concerned, it could be natural ultramarine as the particle size of the pigment was fairly large (about 50  $\mu\text{m}$ ) (Fig. 4a). As generally accepted, the artificial ultramarine can be finer in size with 0.5 to 5  $\mu\text{m}$ , up to 30  $\mu\text{m}$  in diameter [52], which is not consistent with the blue ultramarine particle size observed in this study. The particle size of natural ultramarine, nonetheless, is much variable and can be much larger in size (up to 80  $\mu\text{m}$ ) in comparison with artificial ultramarine [43]. The use of natural ultramarine in the pictorial arts found in Iran is well-recorded [4,5,6,42,53] and its methods of the preparation and use is well-documented in medieval Persian texts [47,54].

### 3.4 Red pigment

Under the Raman microscope, the red pigment appeared to be applied on a blue pigment which was itself applied on the white huntite substrate (Fig. 5a). Under the crossed polarised light, moreover, a glassy and an isotropic nature were identified for the blue pigment whilst the red pigment was observed dispersed in the white huntite (Fig. 5b). While no Raman band was registered for the blue pigment as a result of a high fluorescence signal, the red pigments showed the Raman bands at 222, 309, 385, 474, and 544  $\text{cm}^{-1}$  attributable to red lead ( $\text{Pb}_3\text{O}_4$ ) [55] (Fig. 5c). The micro-XRF analysis revealed the presence of Pb, Si, Co, and As together with the traces of Ca, Sr, S, K, and Fe in the composition of the red pigment (Fig. 5d) (Table 1). The X-ray map derived from SEM back-scattered imaging showed the elemental distribution of the red colour (Fig. 6) according to which the red particles were rich in Pb and, on the other hand, the blue pigment was revealed to be formed from Co, Si, and Na. In the SEM X-ray map (Fig. 6), the distribution of Ca and Mg can also be observed which are associated with the white huntite used as the white substrate of the wall paintings. As far as it can



be deduced from the optical microscopy observations, SEM X-ray map, micro-Raman study and micro-XRF analysis, the red pigment was red lead which was applied on blue smalt. Under a closer look at the paintings, it seemed that the blue smalt was practically used to delineate the general foliage patterns of the wall paintings. Concerning the history of the use of red lead in Iran, it is well-documented either in historical texts [4,27,56] or in recent scientific literature [41,42,53] that red lead has been one of the most popular red pigments ever used in the old Persian pictorial arts.

#### 4. Conclusions

This paper presented the results of the scientific investigations on one example of not well-studied pre-seventeenth century wall paintings found in today's Iran. Red lead, white huntite, atacamite green, blue smalt and natural ultramarine were used in these paintings. The current study also showed some less-known angles of the history of Persian wall paintings. For instance, huntite was reported for the first time to be used in Persian mural paintings. Moreover, the identification of glushinskite, which was hypothesised to be associated with reacting white huntite with oxalic acid derived from an organic binder, was achieved by invasive micro-Raman spectroscopy. Further, woodhouseite was reported for the first time to be detected in a wall painting by conducting micro-Raman spectroscopy on only a tiny sample. As a general result, micro-Raman spectroscopy was found a very useful tool for identifying historical pigments and for diagnosing their deterioration products.

#### Acknowledgments

The authors express their gratitude to Prof. Carmela Vaccaro for providing micro-Raman spectroscopy and micro-XRF analysis systems. Majid Olumi, Elaheh Alvandian and Mohammad-Ali Akrami in the Cultural Heritage Organization of Yazd Province are cordially acknowledged for providing the opportunity of working on both the wall-paintings and the mosque. The comments of two anonymous reviewers helped us to improve the quality of paper. They are cordially acknowledged.

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**Figure Captions**

**Fig. 1** (a) Various colours, (b) the dominance of blue and white pigments and (c) the application of two shades of blue in the mural paintings of Majid-i Jāme of Abarqū

**Fig. 2** (a) XRF spectrum and (b) Raman spectrum of the white pigment representing huntite, gypsum and glushinskite in the composition

**Fig. 3** (a) XRF spectrum and (b) Raman spectrum of the green pigment attributable to atacamite and woodhouseite.

**Fig. 4** (a) Plane polarised light image of the blue shade, (b) its XRF spectrum and (c) Raman spectrum of natural ultramarine blue in the composition of the blue colour

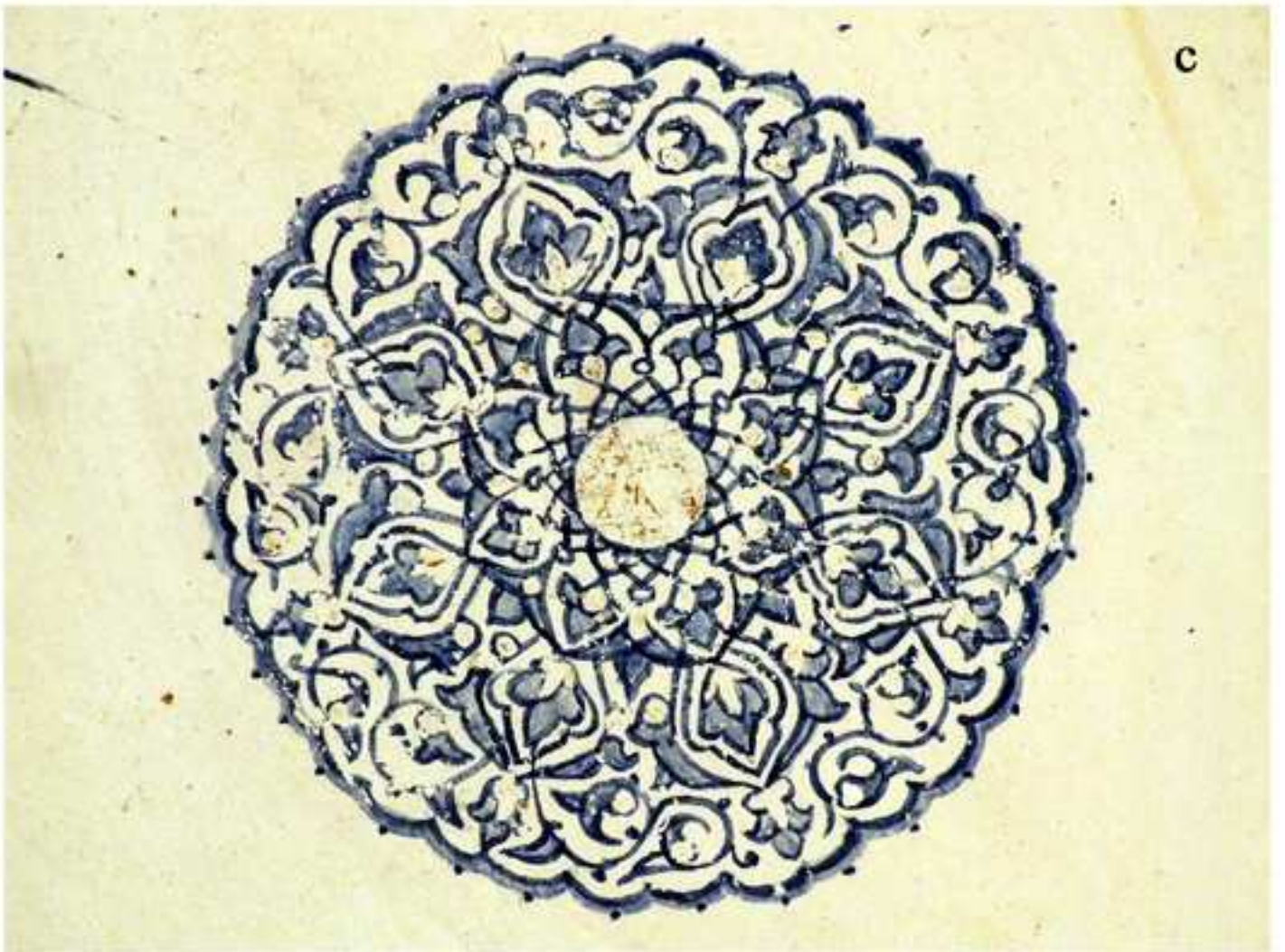
**Fig. 5** (a) The mixture of red and blue pigments in the red shade, (b) crossed polarised light image of the red colour (note that the red lead is observed together with white huntite and blue smalt), (c) Raman spectrum of the red pigment and (d) XRF spectrum acquired from the red pigment

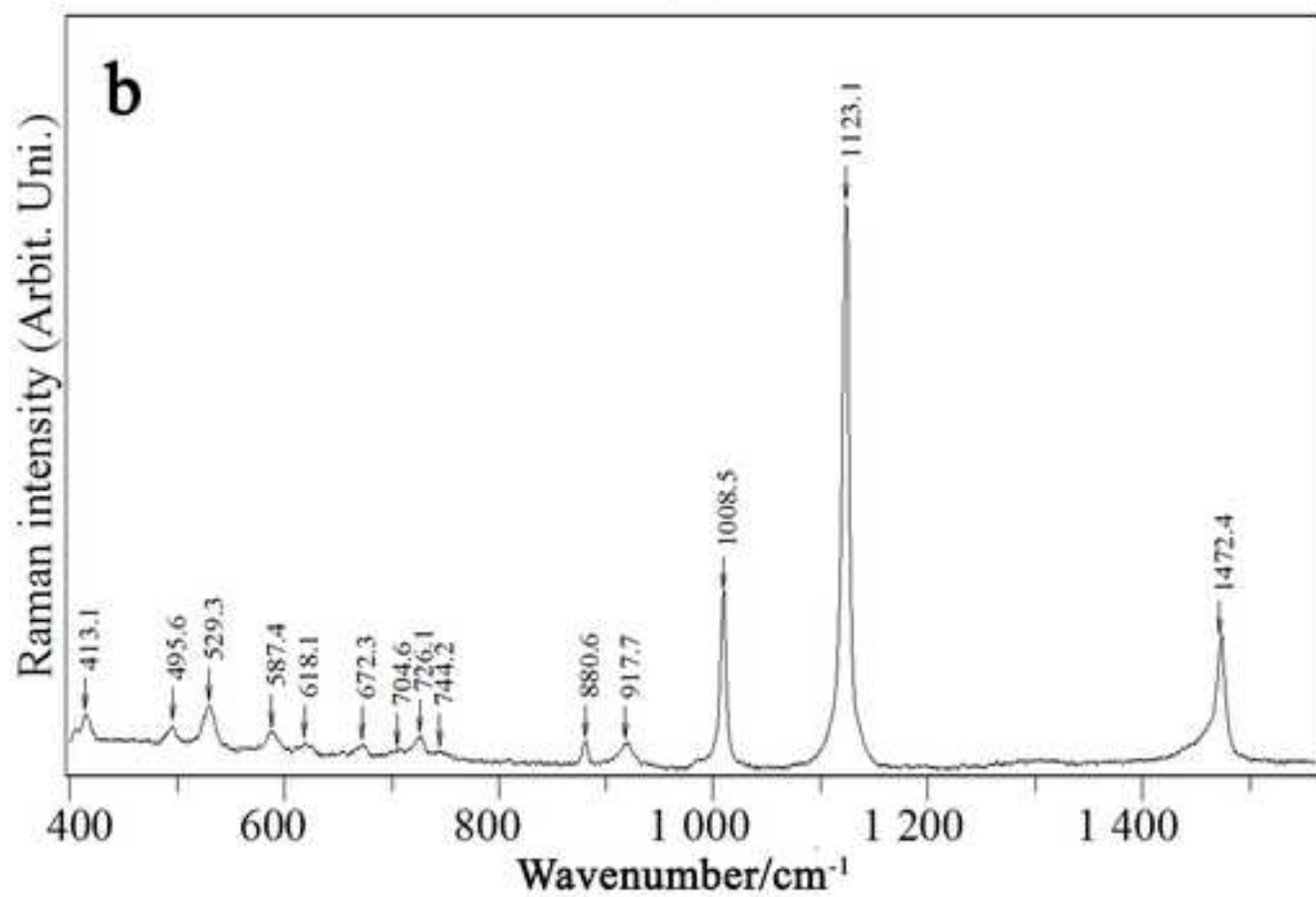
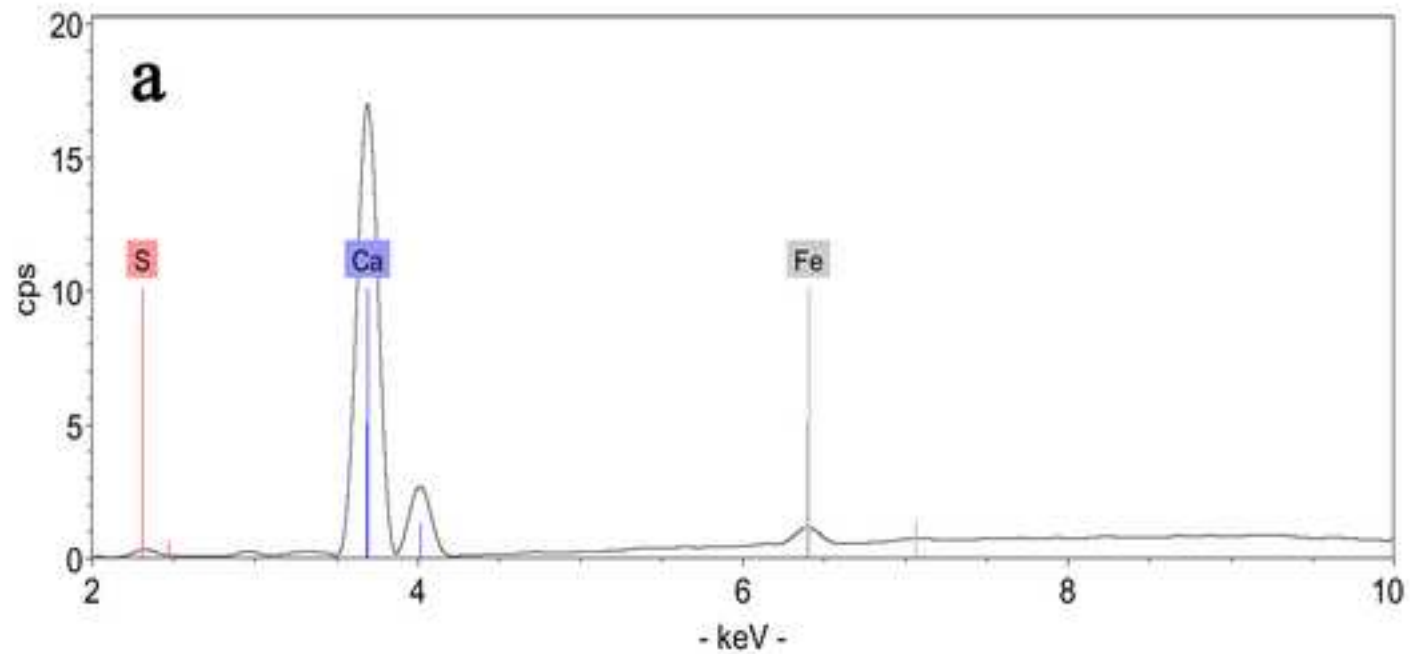
**Fig. 6** PLM image of the red lead on blue smalt (*top left*) and the SEM back-scattered micrograph of the same area (*top middle and right*) together with the SEM X-ray map acquired from red lead on top of the blue smalt.

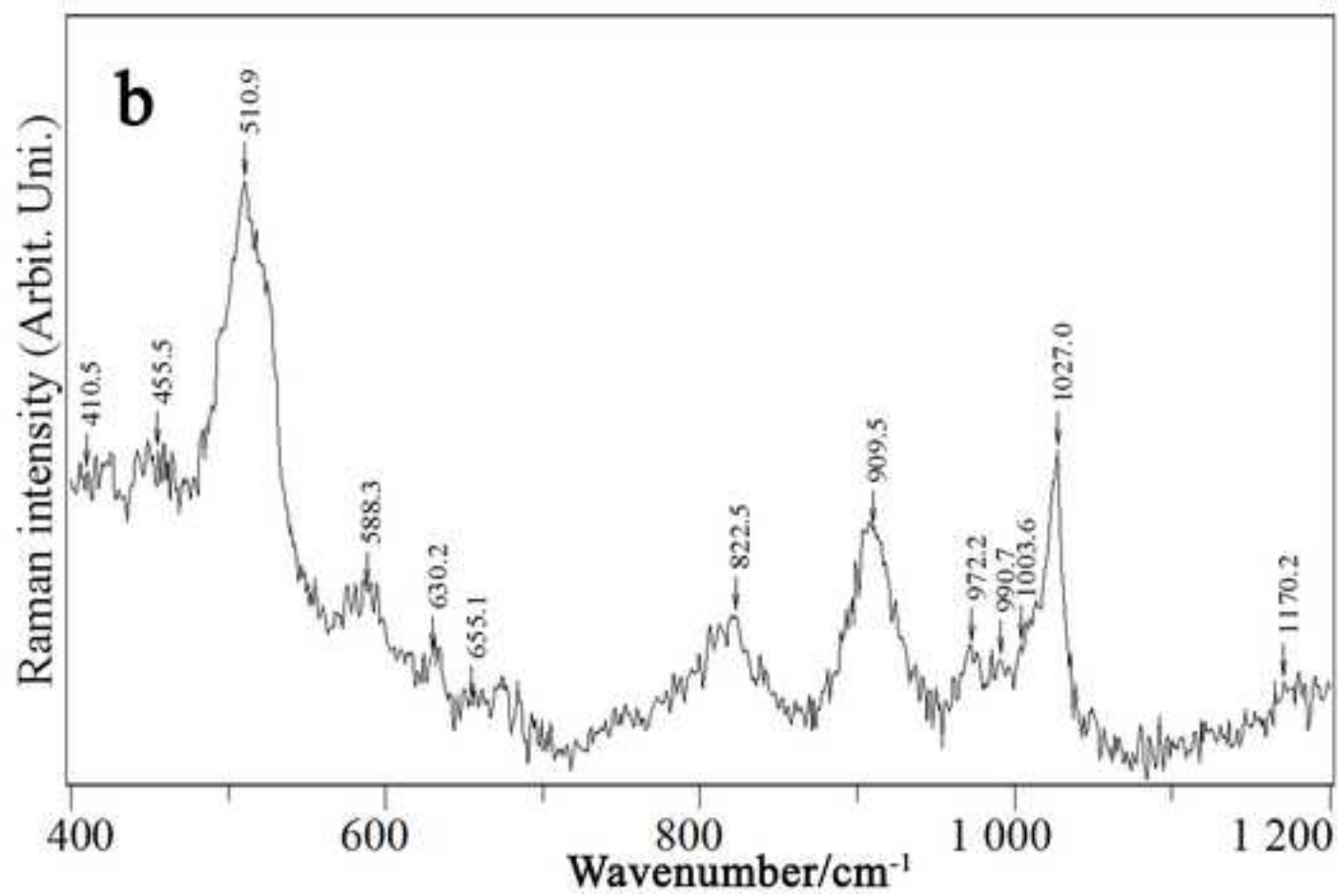
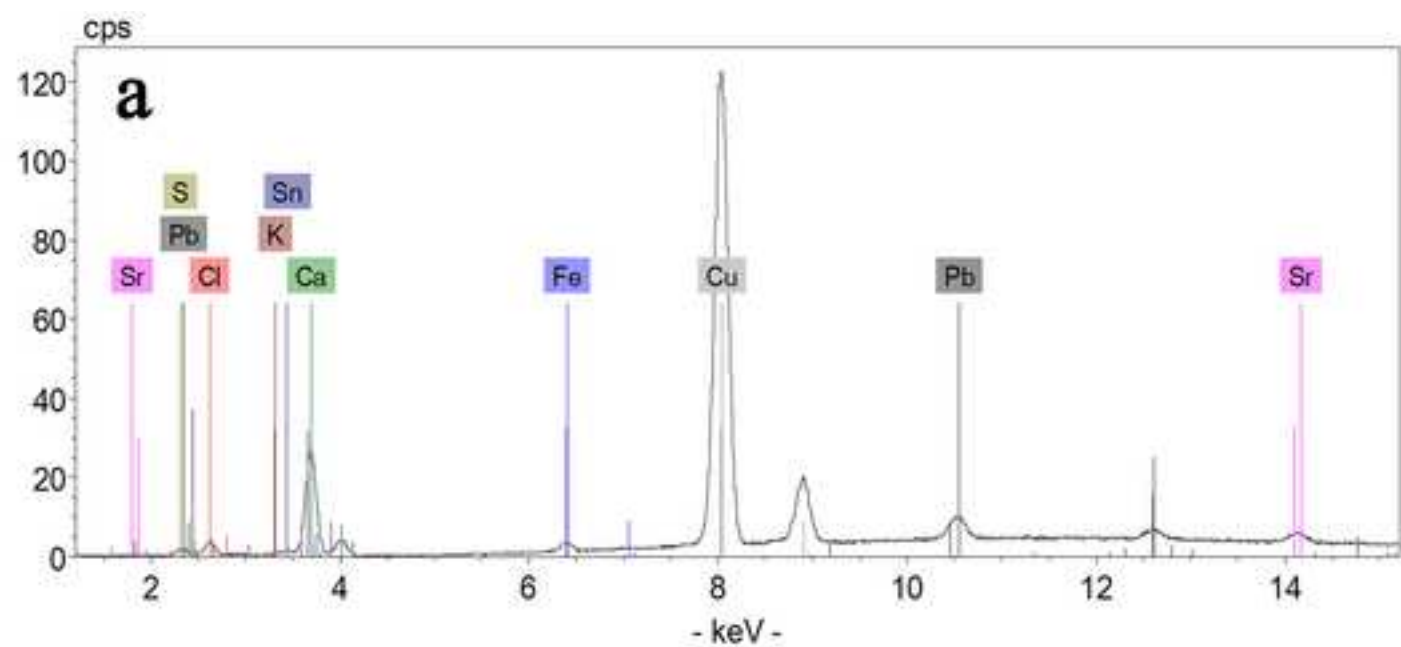
**Table captions**

**Table 1** Summary of analytical studies on various colours of the wall paintings

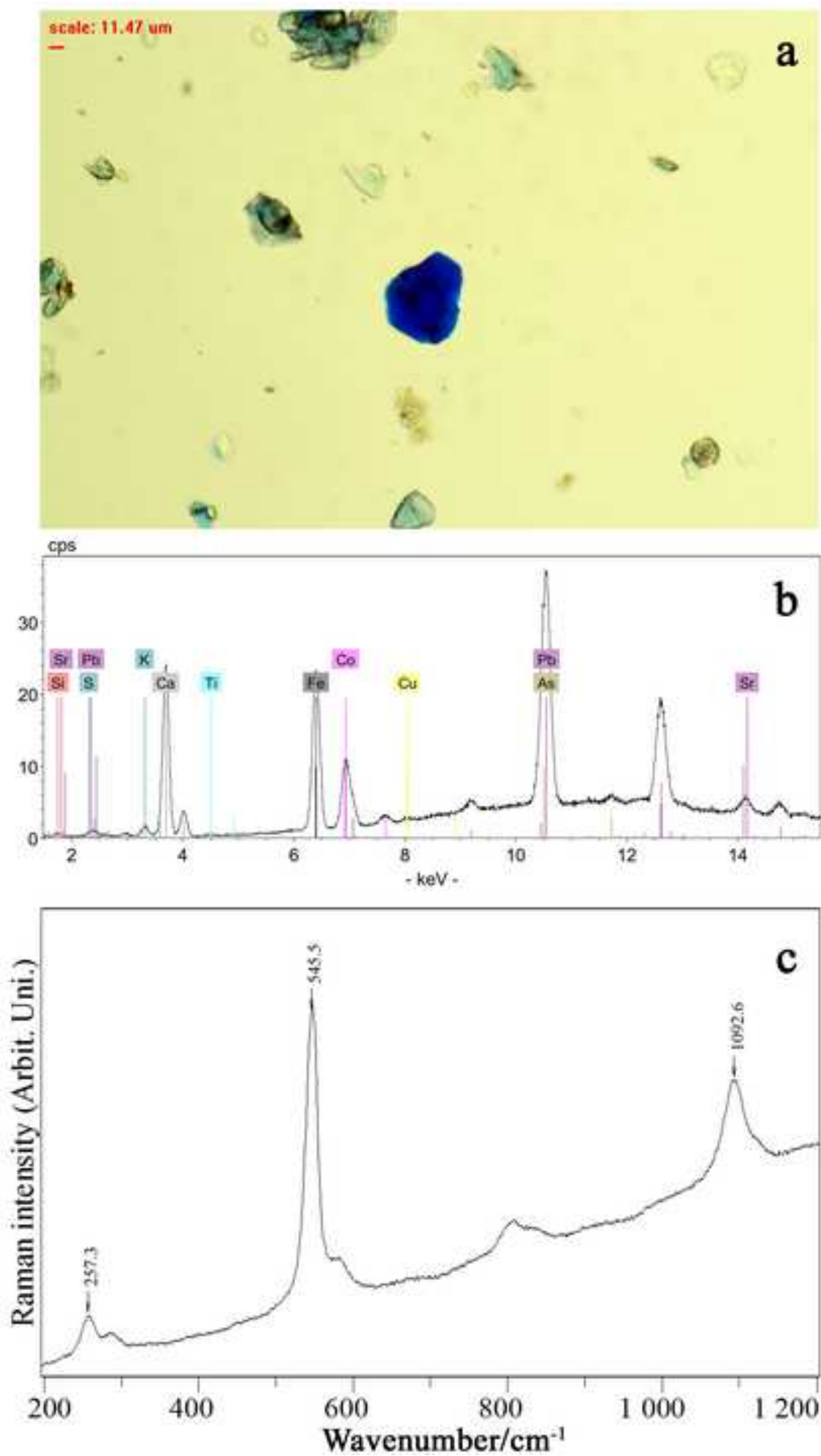


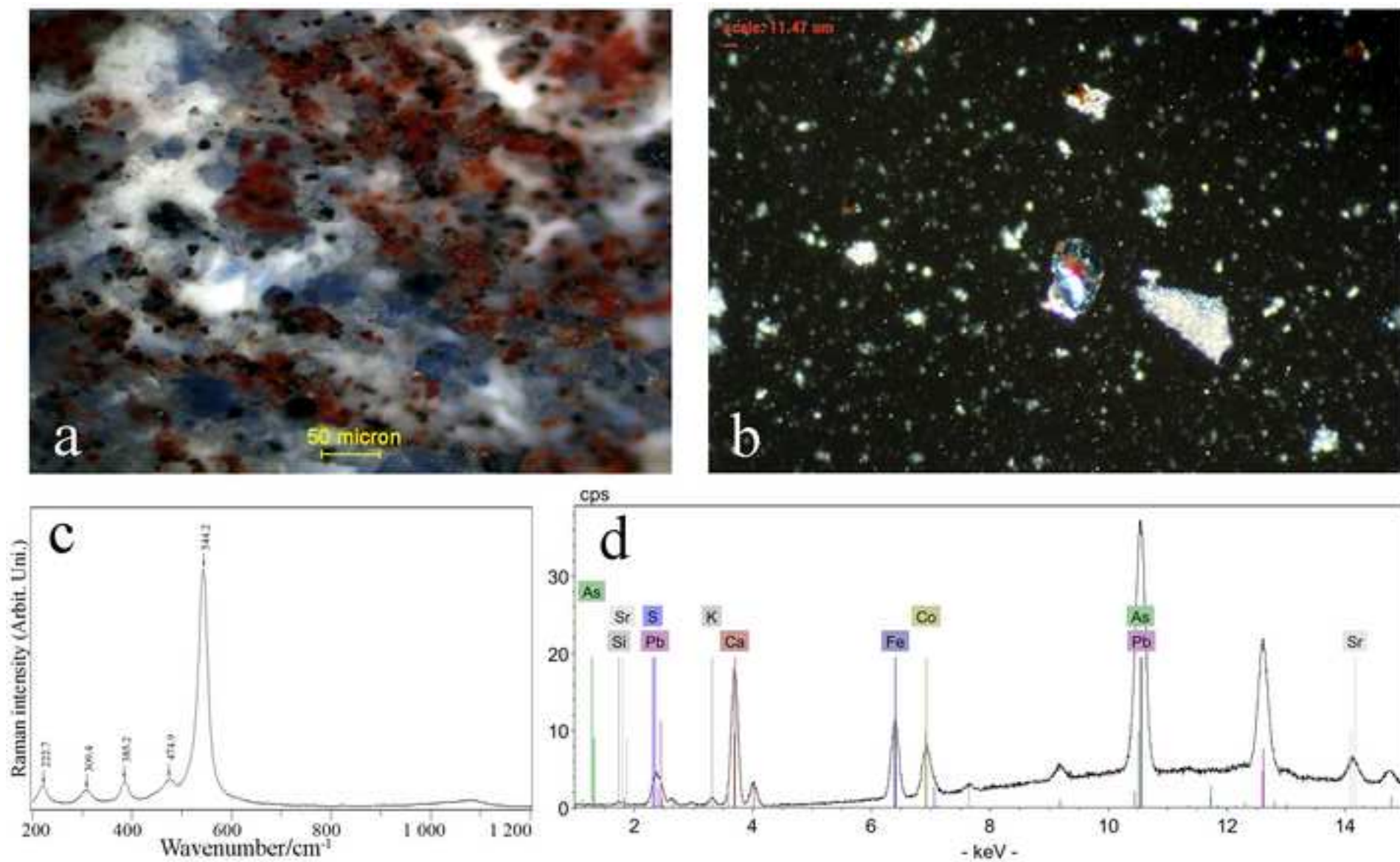


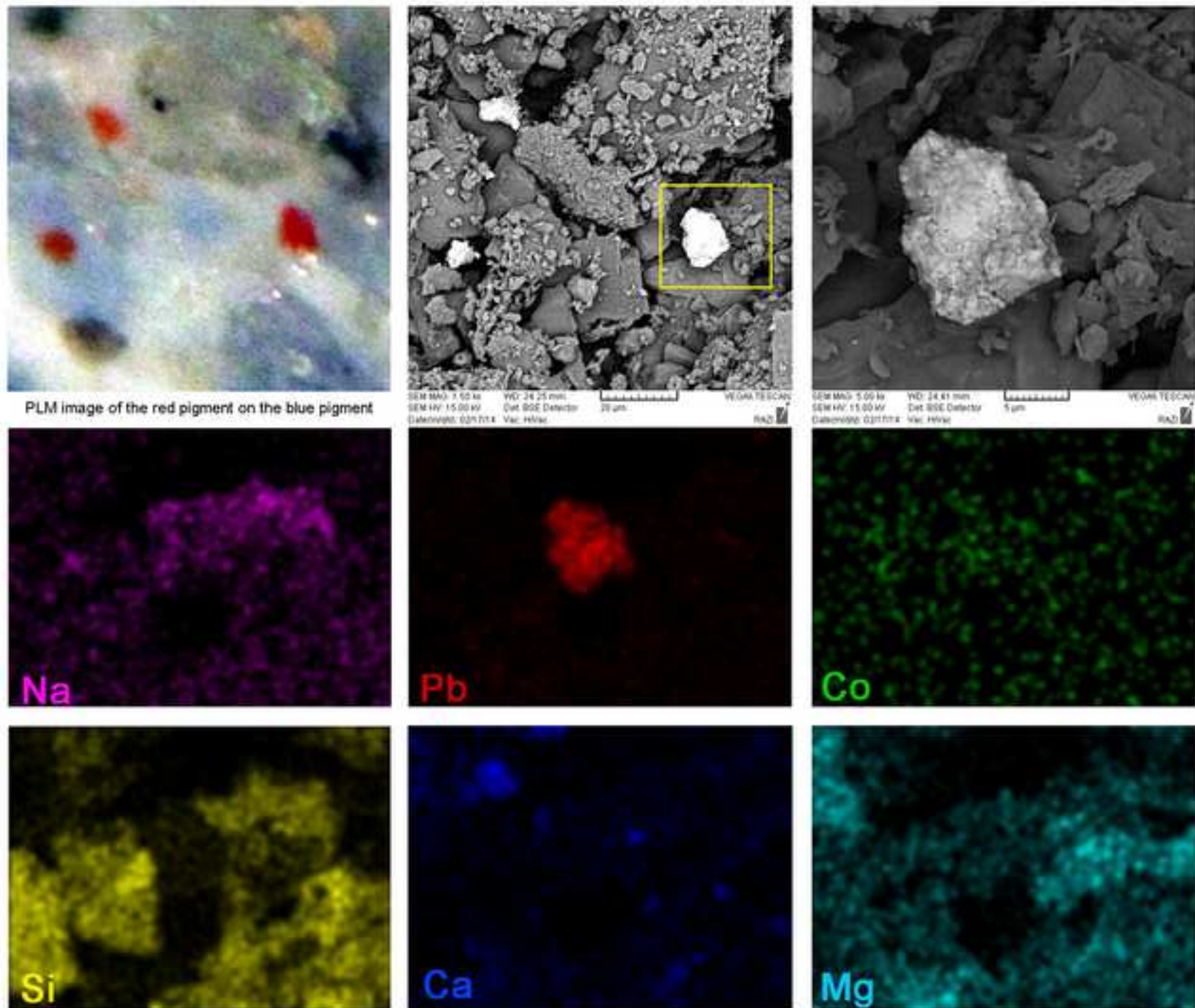














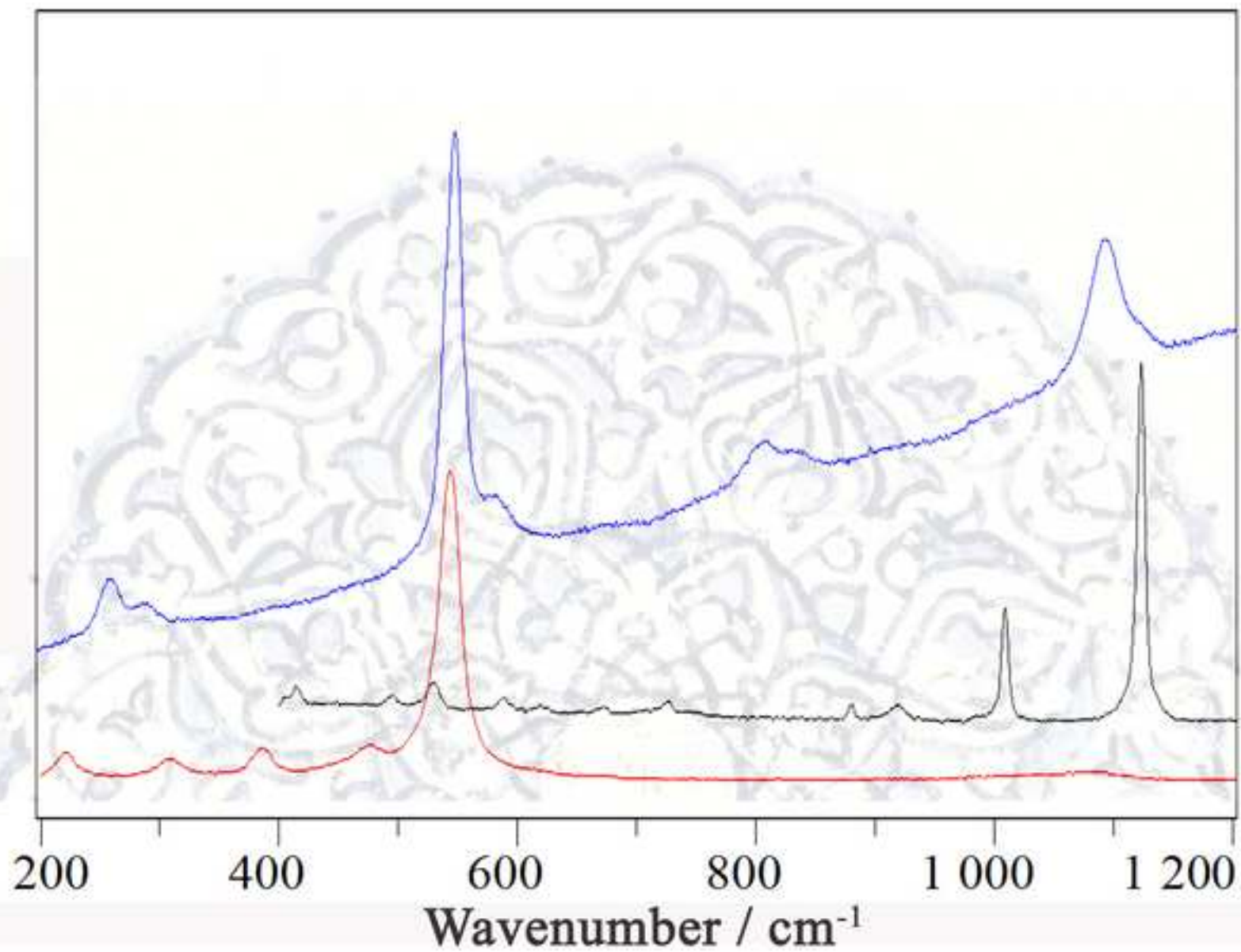


Table 1 Summary of analytical studies on the various colours of the wall paintings

Colours	pXRF	Raman Observations				
	Elements*	Phase detected	Raman bands (cm <sup>-1</sup> )	Band assignment	Relative band intensity**	Reference
White	Ca (S, Fe)	Huntite	704	$\nu_4^i(\text{CO}_3)^{2-}$	vw	[11]
			726	$\nu_4(\text{CO}_3)^{2-}$	w	
			744	$\nu_4^m(\text{CO}_3)^{2-}$	vw	
			880	$\nu_2(\text{CO}_3)^{2-}$	w	
			1123	$\nu_1(\text{CO}_3)^{2-}$	vs	
		Gypsum	413	$\nu_2(\text{SO}_4)^{2-}$	vw	[12]
			495	$\nu_2(\text{SO}_4)^{2-}$	m	
			618	$\nu_4(\text{SO}_4)^{2-}$	w	
			1008	$\nu_1(\text{SO}_4)^{2-}$	vs	
		Glushinskite	529	ring deform + $\delta_{(\text{O}-\text{C}=\text{O})}$	w	[13]
			587	water libration	vw	
			672	$\delta_{(\text{O}-\text{C}=\text{O})} + \nu_{(\text{M}-\text{O})}$	w	
			917	$\nu_{\text{s}(\text{C}-\text{C})} + \delta_{(\text{O}-\text{C}=\text{O})}$	w	
1472	$\nu_{\text{s}(\text{C}-\text{O})} + \nu_{(\text{C}-\text{C})}$	vs				
Green	Cu, Cl, S, Ca, (K, Sr, Fe, Pb, Sn)	Atacamite	410	CuCl stretching	vw	[37]
			455	CuO stretching	vw	
			510	CuO stretching	vs	
			588	CuO stretching	w	
			822	Hydroxyl deformation	m	
			909	Hydroxyl deformation	s	
			972	Hydroxyl deformation	m	
			990	Hydroxyl deformation	vw	
			Woodhouseite	590	$\nu_4(\text{SO}_4)^{2-}$ bending	
		630		$\nu_4(\text{SO}_4)^{2-}$ bending	w	
		655		$\nu_4(\text{SO}_4)^{2-}$ bending	vw	
		990		$\nu_1(\text{PO}_4)^{3-}$ symmetric stretching	vw	
		1003		$\nu_1(\text{PO}_4)^{3-}$ symmetric stretching	sh	
		1027		$\nu_1(\text{SO}_4)^{2-}$ symmetric stretching	vs	
		1170	$\nu_3(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-}$ antisymmetric stretching	w		
Blue	Si, S, K, Ca, Co, (Ti, Sr, Fe, Cu, Pb, As)	Smalt	n.o.***	-	-	
		Ultramarine Blue	257	$\delta(\text{S}_3^-)$	w	[43]
			545	$\nu_1(\text{S}_3^-)$	vs	
1092	$3\nu_1(\text{S}_3^-)$	m				
Red	Pb, Ca, (Sr, Fe, S, Si, K, Co, As)	Red Lead	222	$\delta(\text{O}-\text{Pb}-\text{O})$	w	[55]
			309	?	mw	
			385	?	w	
			474	?	vw	
			544	$\nu(\text{PbO})$	vs	

\* minor and trace elements in parentheses

\*\* vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder  
\*\*\* not observed

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**Highlights**

- Micro-Raman spectroscopy is a useful tool for identifying artists' pigments
- Smalt is one of blue pigments used in Persian wall paintings
- Huntite is one of the most popular pigments used as a white pigment in Persian wall paintings
- Natural oxalates can be associated with historical pigments as deterioration products