Periodico di Mineralogia (2015), 84, 3A (Special Issue), 389-405 DOI: 10.2451/2015PM0020

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on Environment, Archaeometry and Cultural Heritage

Analytical studies leading to the identification of the pigments used in the Pīr-i Hamza Sabzpūsh Tomb in Abarqū, Iran: a reappraisal

Amir-Hossein Karimy* and Parviz Holakooei

Art University of Isfahan, Hakim Nezami St., P.O. Box 1744, Isfahan, Iran
*Corresponding author: *ahkarimy@gmail.com*

Abstract

This paper presents the outcomes of a restoration project started from 2009 and finalized in 2011 at the Pīr-i Hamza Sabzpūsh tomb of Abarqū, central Iran. The project comprised of analytical studies and restoration works on the architectural decorations of the tomb consisting of wall paintings and polychrome stuccoworks. Micro-Raman spectroscopy (μ-Raman) and micro X-ray fluorescence (μ-XRF) analysis were used to compare the chemical and mineralogical composition of the pigments used in the wall paintings and the stuccoworks of the *mihrab*. The results showed that atacamite, huntite and ultramarine were green, white and blue pigments respectively used on both wall paintings and the stuccoworks of the *mihrab*. Furthermore, while red lead was used as red pigment on the *mihrab*, the red pigment of the wall paintings was identified to be red hematite. In addition, the patterns of the wall paintings were delineated with a black paint composed of carbon black. The different trace elements associated with the paints established different sources of supplying pigments used in the decorations. It is also shown that red lead was partially blackened likely due to the action of air pollutants. Moreover, an omitted part of an inscription of the *mihrab* was discovered during restoration works that contributed to re-date the stuccoworks to the second half of the 12th century. Finally, rejecting the current assumptions, which attribute the wall paintings to the 14th century, it was proved that the wall paintings were the first decorations of the tomb created prior to the second half of the 12th century. The current work contains also a corrigendum to our previous study published on the decorations of the tomb.

Key words: wall painting; μ-Raman; μ-XRF; Pīr-i Hamza Sabzpūsh tomb; huntite.

Introduction

Iran Cultural Heritage, Handcrafts and Tourism Organization (ICHHTO) launched a project in 2009 aimed to study and to restore architectural decorations of the Pīr-i Hamza Sabzpūsh tomb in Abarqū, central Iran. This project started in 2009 with analytical studies and finalized in 2011 after extensive restoration works on the decorations. Here, we present the outcomes of our analytical studies (with major emphasis) and restoration works (to a lesser extent) performed on the architectural decorations of the tomb.

The Pīr-i Hamza Sabzpūsh tomb is one of the Persian mausoleums with a dome chamber above a tombstone and a polychrome *mihrab* as the sign of the qibla direction. Although the exterior of the building is simply covered with a rough coat of clay-straw plaster, the interior is fully decorated with wall paintings and stuccoworks. Representing epigraphic and vegetal motifs, the stuccoworks are used to create the *mihrab* and the dado of the tomb (Figure 1). The *mihrab* has two Arabic inscriptions on the top of which one describes who created the *mihrab*. Carved on a gypsum plaster, the text of this inscription is: "The work of Muhammad Ibn-i Ab al-Faraj al-Irāqī, may God have mercy upon him." Another inscription, which contains the date of creating the *mihrab*, was partly vanished, however, clearly indicated that the *mihrab* had been created in the 12th century. The text of the later inscription was "in the Muharram of [the

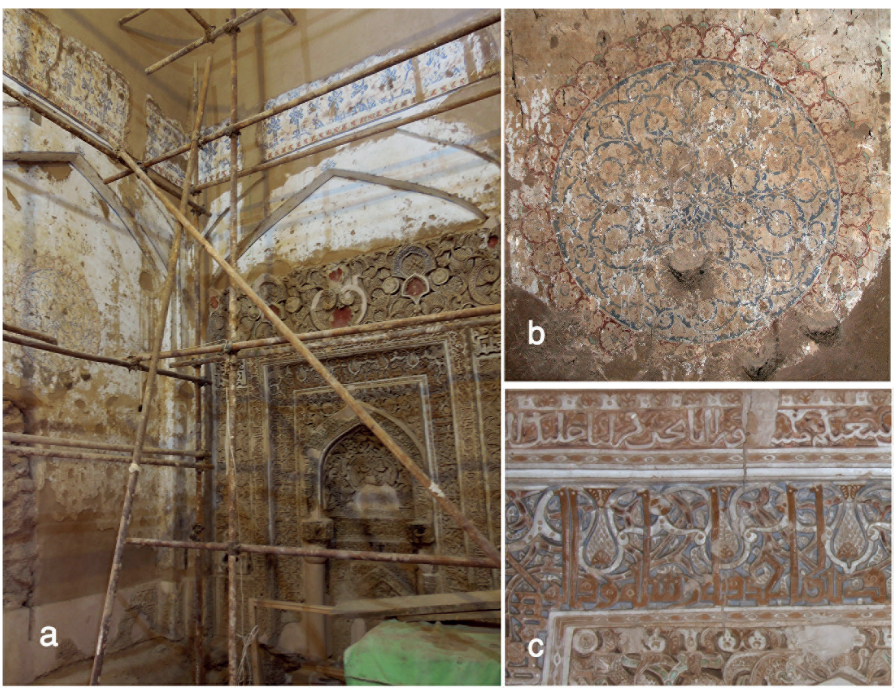

Figure 1. (a) General view of the architectural decorations in the Pīr-i Hamza Sabzpūsh tomb together with (b) the painted medallion on the southern wall of the tomb (c) a detail of the stuccoworks of the polychrome mihrab.

year] five-hundred … (5?? AH / 11?? AD)" from which the ones and the tens of the year were omitted. The colors used on both *mihrab* and wall paintings were red, green, white and blue paints and, in addition, a black shade were observed on the red paint of the *mihrab*.

The Pīr-i Hamza Sabzpūsh tomb has been subject of various studies. First, Godard (1936) studied this tomb in the 1930's and paid a particular attention to the polychrome stucco of the *mihrab* as the most important part of the building. Later on, Afshār (1995) visited the building and attributed the wall paintings to the 14th century. Varjāvand (1977), moreover, noted two distinct phases of decorating the building. He has also quoted the local people's beliefs according to which Azīz al-Dīn Nasafī, a famous Sufi deceased in the 14th century, was buried in this tomb (Varjāvand, 1977). This attribution has been invigorated in the recent decades so that the tomb is known as the Nasafī's tomb. A recent study has also suggested that the building was erected in the first half of the 11th century and two distinct renovation works have been performed in the building; that is, one in the 12th century parallel to the execution date of the *mihrab* and another in the 14th century parallel to the period when the wall paintings were executed (Anisi, 2007). Our previous investigations on the decorations of the tomb have targeted the chemical composition of the pigments used on the *mihrab* and the wall paintings and, further, suggested a hypothesis for the method used for the preparation of gypsum plaster of the stuccoworks (Karimy and Holakooei, 2012).

Several reasons justified a more comprehensive work on the decorations of the tomb of which the identification of the pigments was our priority. An accurate analysis of the pigments of the *mihrab* and the wall paintings could help us to understand whether these pigments were chemically identical or not. It was important because similar chemical composition of the pigments of the *mihrab* and the wall paintings could suggest that the *mihrab* and the wall paintings were created in the same period of time. Further, there was no concrete reason to agree with previous assumptions according to which the stuccoworks were taking precedence over the wall paintings. The current study compares the chemical and mineralogical composition of the pigments used in the wall paintings and the *mihrab* of the tomb and sheds light on the chronological precedence of the decorations at the Pīr-i Hamza Sabzpūsh tomb. To do so, micro-Raman spectroscopy (μ-Raman) and micro X-ray fluorescence (μ-XRF) analysis were used on various paints of both wall paintings and the *mihrab*.

Experimental

Samples

The dome of the Pīr-i Hamza Sabzpūsh tomb is erected on four perpendicular walls on which eight blind arcades are slightly indented. Except the blind arcade where the *mihrab* is placed, each blind arcade was decorated with a painted medallion. It should be mentioned that the decorations on the northern wall of the dome chamber are demolished. Red, green, white and blue colors have been used to paint the medallions. Moreover, there is a blue Kufic inscription that turns around the transition zone of the dome and is delineated delicately with a black line. All the paintings are painted on a thin white ground layer placed on a fine straw clay rendering. There is no layer of lime intonaco and arriccio as regularly can be seen in fresco paintings. Nine samples were collected from the painted medallions and the inscription and also the polychrome *mihrab* as listed in Table 1. As far as the analytical studies on the samples are concerned, they were performed directly on a very tiny amount of the paints. Thus, it was not practically possible to wash the paints or to perform any type of preparation on the samples. We, however, removed the samples from intact parts of the paints where the lowest extent of superficial contaminations was observable.

Table 1. The description of the samples removed from the *mihrab* and the wall paintings of the Pīr-i Hamza Sabzpūsh tomb.

Color	Location	Place of sampling
White	wall paintings	The ground layer of the paintings, the eastern wall
	mihrab	Dividing lines between the inscriptions of the *mihrab*
Green	wall paintings	The medallion on the southern wall, near the *mihrab*
	mihrab	The base of the inscription inside the inner arch
Blue	wall paintings	The lines around the arcade above the *mihrab* on the western wall
	mihrab	The base of the main inscription around the inner part
Red	wall paintings	The medallion on the southern wall, near the *mihrab*
	mihrab	Floral decorations around the main inscription around the inner part
Black	wall paintings	The Kufic inscription on the transition zone of the dome on the south-western angle

μ-XRF

As XRF device, an ARTAX™ 200 (Bruker AXS Microanalysis GmbH, Germany) instrument was used which consisted of an X-ray tube with a Mo target placed at 6° and a Be window. A SSD Peltier-cooled detector was used for detecting the secondary fluorescence X-rays which were emitted under a maximum voltage and current of 25 kV and 1502 μA respectively. The samples were analyzed on a fixed stage and the measurements were performed in air and under helium flow (only for white pigment to detect low atomic weight elements like Mg and Al) for about 120 s while the X-ray beam was irradiated via a collimator with a diameter of 1 mm.

μ-Raman

A LabRam HR800 device from Horiba Jobin Yvon (France) fitted with a Peltier-cooled CCD detector (1024 × 256 pixels) at -70 °C was used in our studies. 50x and 100x objectives coupled with an Olympus BXFM microscope and a 600 groove/mm grating were used to collect and to direct the Raman scattering 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 Laser power was kept below 2 mW for black and green colors in order to lessen the chance of pigment degradation). The calibration of the spectrometer was performed with silicon at 520 cm^{-1} and the exposure time was selected for about 5 to 15 s with 5 accumulations.

Results

Whites

The μ-Raman study on the white paint of the *mihrab* showed the Raman bands at 246, 270, 393 and 1121 cm^{-1} consistent with white huntite [$Mg_3Ca(CO_3)_4$] (Scheetz and White, 1977) and at 220, 246 (common with huntite), 501, 519, 593, 895, 1396, 1463, 1488 and 1629 cm^{-1} derived from mineral whewellite, hydrated calcium oxalate [$Ca(C_2O_4){\cdot}H_2O$] (Frost and Weier, 2004) (Figure 2a). The white paint of the wall paintings, however, exhibited the Raman bands at 243, 251, 272, 279, 316, 390, 724, 879 and 1123 cm^{-1} associated with huntite and at 191, 219, 506, 865, 911, 1055, 1476 and 1630 cm^{-1} attributable to mineral weddellite, calcium oxalate di-hydrate [$Ca(C_2O_4){\cdot}2H_2O$] (Frost et al., 2003) (Figure 2b). On the other hand, while the μ-XRF results showed Mg and Ca as elements composing the white shades of both wall paintings and the *mihrab*, i.e. white huntite, the trace elements associated with the white paints were different. As represented in Figure 2c,d, other than Ca and Mg, minor and trace elements detected in the white of the *mihrab* were Al, Si, K, S, Cl, Fe, Ti, Sr, Cr, Zn, Mn, P and Ba making a difference with that of the wall paintings composed of Al, Si, P, S, Cl, K, Ti, Mn, Fe, Sr, Cr, Zn and Ni (Table 2). In other words, while the white paint of the *mihrab* was basically associated with Ba (Ba was most certainly associated with the gypsum plaster used under the paints because, as will be seen later, Ba was observed in all paints used on the *mihrab*), the white paint of the wall paintings was linked to Ni.

Huntite, as a white mineral, has already been reported to be used as a white pigment in Abarqū (Holakooei and Karimy, 2015a) and in Fahraj (Holakooei and Karimy, 2015b). Deposits of huntite in Abarqū (Eslamizadeh and Samanirad, 2014) can be the main reason of its use as a white pigment in this region. The difference between the trace elements composing the whites of the tomb may suggest that the source of supplying white huntite for painting the walls and the *mihrab* of the tomb is different.

Greens

The green paint of the *mihrab* showed the Raman bands at 354, 410, 453, 514, 814, 846, 904 and 977 cm^{-1} derived from atacamite [$Cu_2(OH)_3Cl$] (Frost et al., 2002) together with the bands at 261, 444, 503, 869, 904 (common with atacamite) and 1262 cm^{-1} attributable to weddellite (Frost et al., 2003), at 492, 623, 670 and 1011 cm^{-1} originated from gypsum (Berenblut et al., 1971) and at 261 (common with weddellite) and 1124 cm^{-1} associated with huntite (Figure 3a). On the other hand, the green paint of the wall paintings showed two main constituents by showing the Raman signals at 217, 264, 362, 455, 510, 588, 823, 913 and 972 cm^{-1} derived from atacamite and at 221, 237, 264 (common with atacamite), 307, 522, 528, 588 (common with atacamite), 655, 913 (common with atacamite), 1472, 1637 and 1659 cm^{-1} attributed to glushinskite (MgC_2O_4) (Frost et al., 2003) (Figure 3b). The results of μ-XRF highlighted the difference between the chemical compositions of the paints (Figure 3c,d). Although both greens showed Cu and Cl as elements responsible for the green color of the paints, the green of the *mihrab* contained traces of Ba, Ni, Zn and Cr which were totally absent in the green of the wall paintings (Table 2).

Atacamite has been mentioned to be a common green pigment in Persian pictorial arts (Purinton and Watters, 1991; Burgio et al., 2008; Muralha et al., 2008) and is interestingly reported as the green pigment in wall paintings of the Masjid-i Jame of Abraqū (Holakooei and Karimy, 2015a). The chemical composition of atacamite in the wall paintings and the *mihrab* makes significantly a distinction between the sources of atacamite in these two paints. Our current studies on green pigments derived from copper shows that the

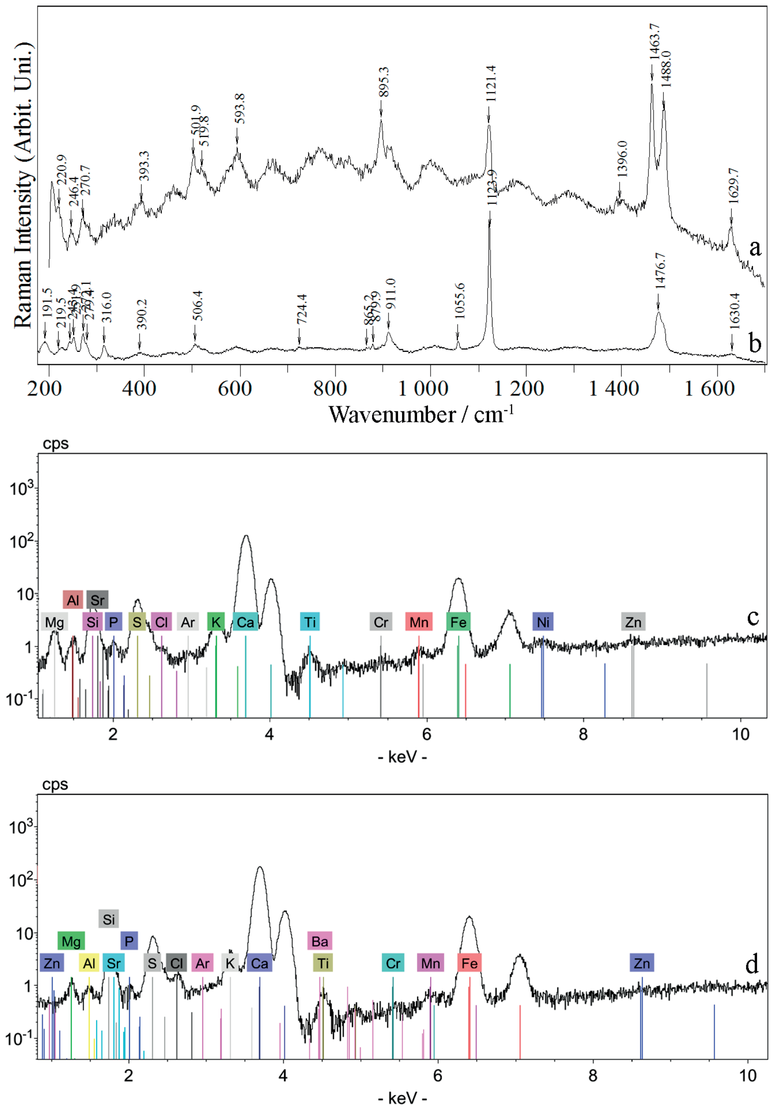

Figure 2. The Raman spectra of the white paint of (a) the *mihrab* and (b) the wall paintings together with the XRF spectra of the white paints of (c) the wall paintings and (d) the *mihrab*.

chemical composition of the green atacamite may be influenced by the chemical composition of the original metallic copper of which the atacamite is made (Karimy and Holakooei, forthcoming). Glushinskite is also reported to be observed in the white paint of the wall paintings of the Masjid-i Jame of Abarqū (Holakooei and Karimy, 2015a), which is placed close to the Pīr-i Hamza Sabzpūsh tomb.

Table 2. Summary of analytical results on the paints used on the wall paintings and the polychrome *mihrab*.

	Paints	μ-XRF[a]	Raman observations			
			Minerals	Raman bands (cm^{-1}) and their relative intensity[e]	Ref.	Fig.
Mihrab	White	(Mg[b], Ca) Ar[c], Al, Si, K, S, Cl, Fe, Ti, Sr, Cr, Zn, Mn, P, Ba[d]	Whewellite	220 (vw), <u>246</u>[f] (vw), 501 (w), 519 (vw), 593 (w), 895 (m), 1396 (vw), 1463 (s), 1488 (s), 1629 (w)	Frost and Weier, 2004	2a
			Huntite	<u>246</u> (vw), 270 (vw), 393 (vw), 1121 (s)	Scheetz and White, 1977	
	Green	(Cu, Cl) Si, Sr, S, Ar, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, Pb, As, Ba	Atacamite	354 (w), 410 (vw), 453 (vw), 514 (s), 814 (w), 846 (vw), <u>904</u> (m), 977 (vw)	Frost, 2002	3a
			Gypsum	492 (w), 623 (vw), 670 (vw), 1011 (s)	Berenblut et al., 1971	
			Huntite	<u>261</u> (vw), 1124 (w)	Scheetz and White, 1977	
			Weddellite	<u>261</u> (vw), 444 (vw), 503 (s), 869 (vw), <u>904</u> (m), 1262 (vw)	Frost et al., 2003	
	Blue	(S, Si) Sr, Cl, Ar, K, Ca, Ti, Mn, Fe, Cr, Cu, Pb, Zn, Ba	Ultramarine blue	258 (w), 546 (vs), 1093 (m)	Osticioli et al., 2009	4a
	Red	(Pb) Sr, S, Cl, K, Ar, Ca, Ti, Cr, Fe, Ni, Cu, Ba	Red lead	219 (w), 312 (w), 389 (w), 476 (w), 547 (vs)	Edwards et al., 1999	5b
	Blackened red	(Pb) Sr, S, Cl, Ar, K, Ca, Ti, Cr, Fe, Ni, Cu, Ba	Plattnerite	387 (w), 419 (vw), 513 (s,br), 540 (sh), 653 (w)	Burgio et al., 2001	6b
Wall paintings	White	(Mg, Ca) Al, Si, P, S, Cl, Ar, K, Ti, Mn, Fe, Sr, Cr, Zn, Ni	Weddelite	191 (w), 219 (vw), 506 (w), 865 (vw), 911 (m), 1055 (w), 1476 (s), 1630 (vw)	Frost et al., 2003	2b
			Huntite	243 (vw), 251 (w), 272 (w), 279 (sh), 316 (w), 390 (vw), 724 (vw), 879 (vw), 1123 (vs)	Scheetz and White, 1977	
	Green	(Cu, Cl) Si, Sr, S, Ar, K, Ti, Mn, Fe, Pb, As	Atacamite	217 (w), <u>264</u> (w), 362 (vw), 455 (vw), 510 (s), <u>588</u> (m), 823 (w), <u>913</u> (m), 972 (w)	Frost et al., 2002	3b
			Glushinskite	221 (w), 237 (w), <u>264</u> (w), 307 (vw), 522 (m), 528 (s), <u>588</u> (m), 655 (vw), <u>913</u> (m), 1472 (vs), 1637 (vw), 1659 (w)	Frost et al., 2003	
	Blue	(Si, S) Sr, Cl, Ar, K, Ca, Ti, Fe, Pb, Zn, Cr, Mn	Ultramarine blue	258 (w), 546 (vs), 1093 (m)	Osticioli et al., 2009	4b
	Red	(Fe) Si, Sr, Cl, Ar, K, Ca, Ti, Mn, Ni, Pb	Hematite	225 (w), 247 (vw), 296 (s), 409 (vs), 610 (m), 657 (m,br)	de Faria et al., 1997	5a
	Black	(Ca, Fe) Ar, K, Ni, Cr, Mn, Zn, Pb, Sr, Cu, S, Cl, Si, Ti	Carbon black	1325 (br), 1594 (br)	Jawhari et al., 1995	7b

[a] Elements contributing as coloring agents in parentheses. The rest of elements are assumed to be associated as minor and trace elements. [b] Mg and Al were observed only when the analysis was performed under the helium flow. [c] Ar was detected in all samples due to analyzing the samples in the air. [d] Ba was observed in all paints of *mihrab* which may suggest that it is associated with the gypsum plaster used as support layer. [e] vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad. [f] Underlined values are common between two constituents of a color.

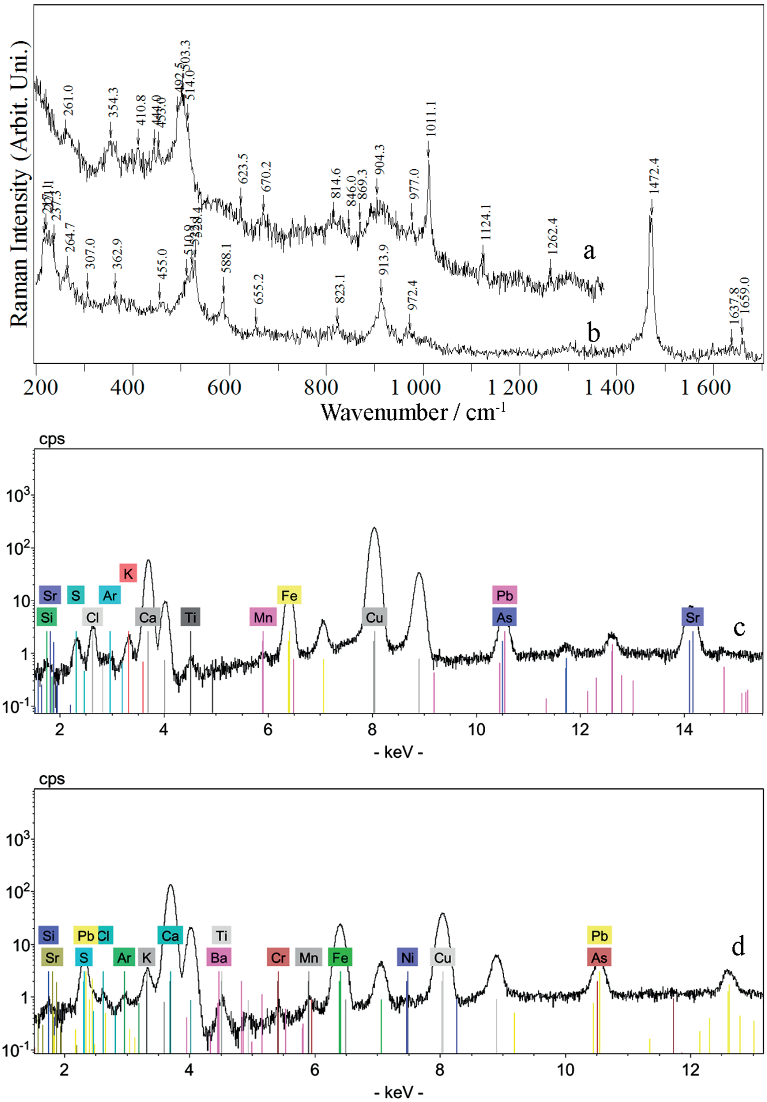

Figure 3. The Raman spectra of the green paint of (a) the *mihrab* and (b) the wall paintings and the XRF spectra of the green paint of (c) the wall paintings and (d) the *mihrab*.

Blues

Blue paints in either *mihrab* or wall paintings exhibited the Raman bands at 258, 546 and 1093 cm^{-1} consistent with ultramarine blue (Osticioli et al., 2009) (Figure 4 a,b). The μ-XRF analysis showed Si, S, Sr, Cl, K, Ca, Ti, Fe, Pb, Zn, Cr and Mn in the chemical composition of both blues of the *mihrab* and the wall paintings.

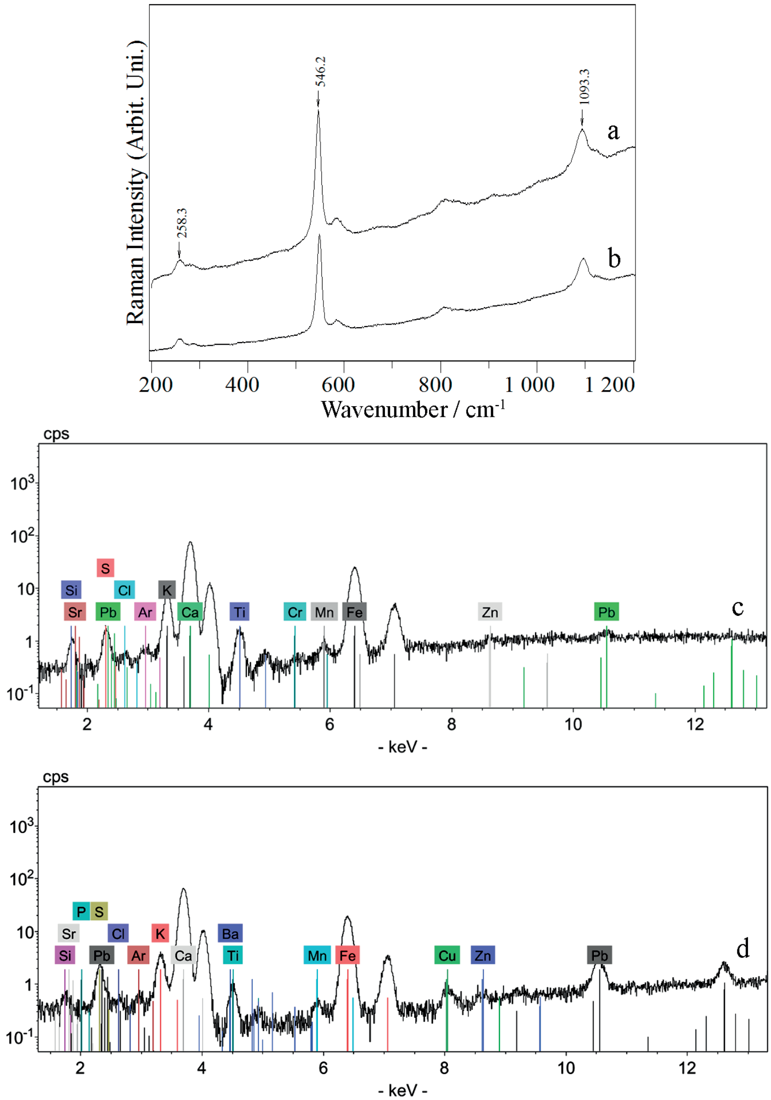

Figure 4. The Raman spectra of ultramarine blue in (a) the *mihrab* and (b) the wall paintings and the XRF spectra of the blue paints of (c) the wall paintings and (d) the *mihrab*.

Nevertheless, the traces of Cu and Ba were detected to be associated with the blue paint of the *mihrab* (Figure 4 c,d) (Table 2) may be derived from the gypsum plaster on which the paints are placed. The use of ultramarine blue in either Persian wall paintings or illuminations is well-documented (Bruni et al., 2001; Muralha et al., 2012).

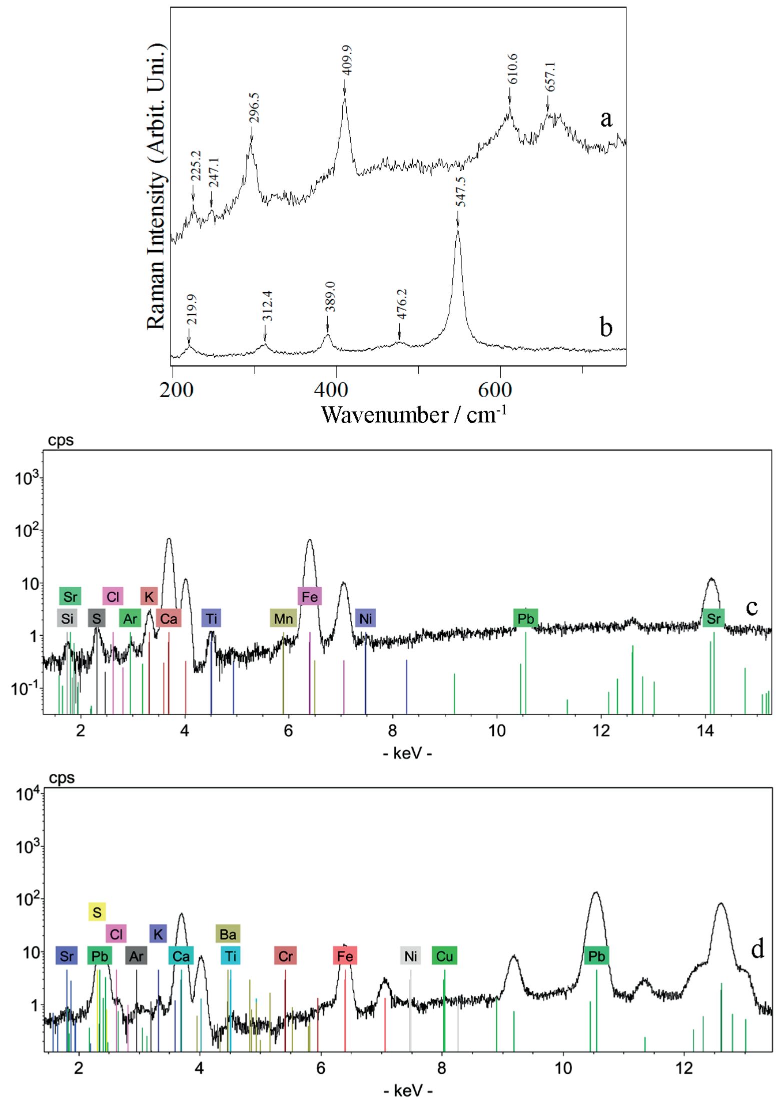

Figure 5. The Raman spectra of the red paints of (a) the wall paintings and (b) the *mihrab*. The XRF spectra of the red paints of the wall paintings and the *mihrab* are represented in (c) and (d) respectively.

Reds

The composition of the red paint in the *mihrab* and the wall paintings was entirely different. While the red of the *mihrab* showed the Raman bands at 219, 312, 389, 476 and 547 cm^{-1} attributable to red lead (Pb_3O_4) (Edwards et al., 1999), the Raman bands centered at 225, 247, 296, 409, 610 and 657 cm^{-1} showed that the red paint of wall paintings was red hematite (de Faria et al., 1997) (Figure 5a,b). Confirming μ-Raman observations, μ-XRF analysis showed Fe as the major component and Si, Sr, Cl, K, Ca, Ti, Mn, Ni and Pb as minor and trace elements composing the red paint of the wall paintings. Moreover, Pb was detected as the main element of the red paint of the *mihrab* with which Sr, S, Cl, K, Ca, Ti, Cr, Fe, Ni, Cu and Ba were linked as minor and trace elements (Figs. 5 c,d) (Table 2).

A dark-brown to black crust could be seen on the red paint of the *mihrab* which was initially assumed to be black soot deposited on the red paint as a result of burning candles near the *mihrab* (Figure 6a) (It is worth-mentioning that pilgrims usually burn candles in holy shrines in Iran and, in fact, the remains of several molten candles, grimes and soot deposited on the walls' tomb were removed in the restorations.) While the μ-XRF analysis of this layer showed no difference with that of the red paint (Figure 6b; Table 2), the Raman bands at 387, 419, 513, 540 and 653 cm^{-1} showed that the black layer was plattnerite (PbO_2) (Burgio et al., 2001) (Figure 6c) most certainly formed due to degrading red lead. It is suggested that the activation of a bacteria like arthrobacter can transform red lead to plattnerite (Petushkova and Lyalikova, 1986). Moreover, Giovannoni et al. (1990) have suggested that, in an alkaline environment of hydrated lime, hydrogen peroxide derived from the metabolism of certain micro-organisms produced by the photo-oxidation can induce lead containing pigments to plattnerite. Gettens and Stout (1966) have also suggested that light, together with moisture, has an important role in blackening red lead. However, the studies of Aze et al. (2007) rejected the influence of light and hydrogen peroxide in darkening red lead and have suggested that the transformation of red lead to plattnerite can be the result of pigment interactions with acidic environment originated from atmospheric pollutants. In the case of the Pīr-i Hamza Sabzpūsh tomb, no alkaline environment is supplied by the plaster which the red lead is placed on as lime is totally absent in the masonry used in building construction. On the other hand, Abarqū city is placed in a very arid zone of Iran (Ghorbani, 2013) and, naturally, the chance of bacterial activity in this condition is unlikely. Moreover, Abarqū is a small city with low concentration of industrial activities producing air pollutants. However, the chance of red lead darkening induced by pollutants was fairly high as pilgrims come to visit the tomb used to burn large number of candles near the *mihrab* of the tomb.

The use of red lead on the *mihrab* was entirely expected as it is reported to be used in Abarqū city on the walls of the Masjid-i Jame of Abarqū (Holakooei and Karimy, 2015a). Red hematite, as a readily available source of red color since antiquity, was also likely to be used on the walls of the tomb. The important point is laid on the fact that the difference in the use of two distinct red pigments on the decorations of a single monument shows how the taste and availability of raw materials can be changed time by time.

Black

A black paint was delicately used to delineate the floral patterns and the Kufic inscription of the wall paintings. According to the μ-XRF analysis, the black paint was mainly composed of Ca and, to a lesser extent, of Fe with which traces of Ni, Cr, Mn, Pb, Sr, Zn, Cu, S, Cl, K, Si, Ti and Ba were associated (Figure 7a). μ-Raman study confirmed the use of carbon black as the pigment of the black paint with two broad Raman bands at 1325 and 1594 cm^{-1} (Jawhari et al., 1995) (Figure 7b). Moreover, no evidence of black magnetite was observed in the black paint to be attributed to Fe detected in the μ-XRF analysis.

Which one was created first: mihrab *or wall paintings?*

As previously mentioned, the tomb was subject of restoration works from 2009. During the restoration works, some evidences were

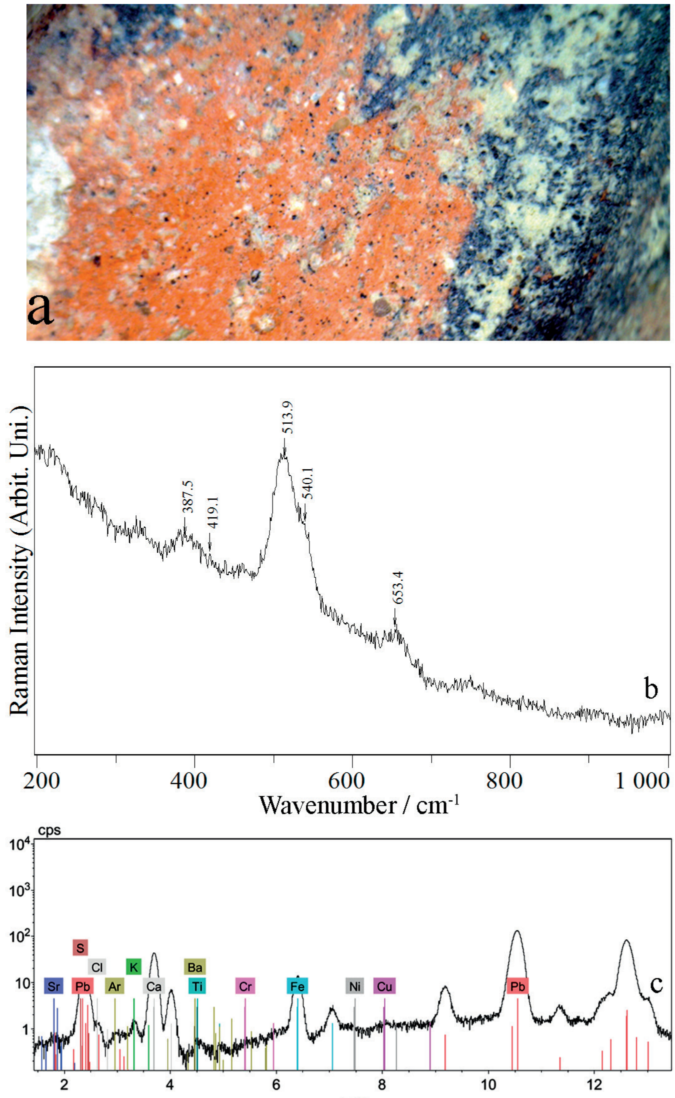

Figure 6. (a) The blackened crust on the red paint together with its (b) Raman and (c) XRF spectra.

found according to which we concluded to new results. First, a piece of the dated inscription of the *mihrab* was found buried in a temporary mud-brick wall placed in the western corner of the southern side of the tomb. This temporary mud-brick wall was most probably added in the 20th century for repairing purposes after the earthquake happened in c. 1931 (Karimy, 2012). Prior to this discovery, Godard (1936), Varjavand (1977) and Afshar (1995) had read

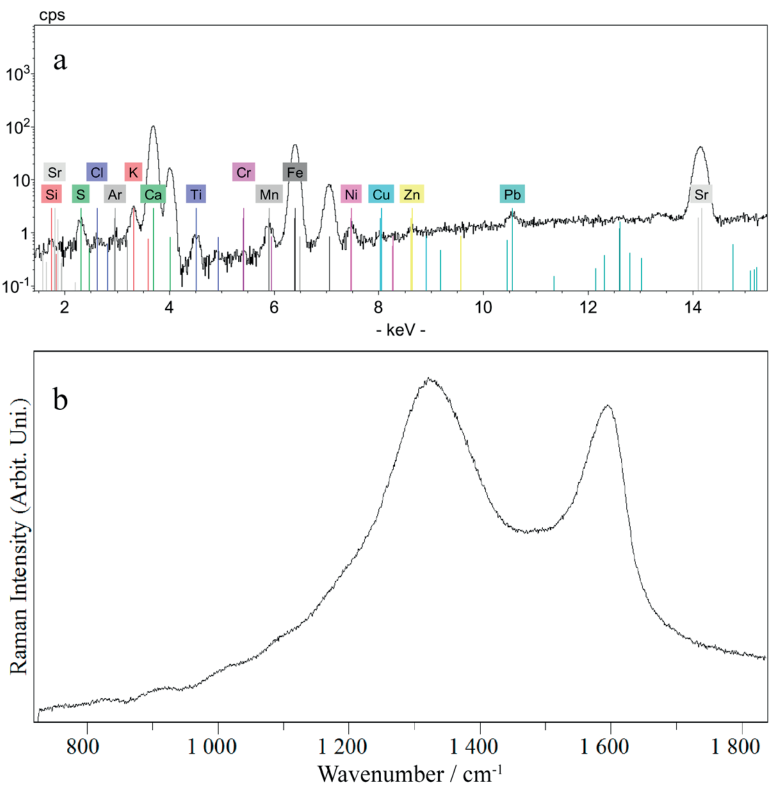

Figure 7. (a) The XRF and (b) the Raman spectra of the black paint of the wall paintings.

this inscription as "Ramadan of [the year] 5?? AH / 11?? AD", "in the Muharram of [the year] 51? AH / 111? or 112? AD" and "in the Muharram of [the year] 5?? AH / 11?? AD" respectively (see Figure 8a from the inscription based on which these assumptions were made). The discovered piece of the inscription, however, contained the Arabic word of *sana*; i.e., year. Studying the calligraphic style of the inscription under a closer look, moreover, showed that the tens of the dated inscription was either "four", "seven" or "nine" (Figure 8b). Therefore, three following dates would be assumed for this inscription: "in the Muharram of the year 54? AH / 114? - 115? AD", "in the Muharram of the year 57? AH / 117? - 118? AD" and "in the Muharram of the year 59? AH / 119? - 120? AD". Therefore, in either case, it could be concluded that the *mihrab* was created in the second half of the 12th century AD.

On the other hand, removing the temporary mud-brick wall, evidences of the white paint layer of the wall paintings were found under the dado stuccos where the western and southern walls cross each other (Figure 9a). Further, remains of the white and blue paints of the wall paintings were found behind the gypsum stuccoworks of the *mihrab* close to its cornice (Figure 9b). Accordingly, it could be concluded that the wall paintings were the first decorative layer of the tomb and made before the second half of the 12th century AD.

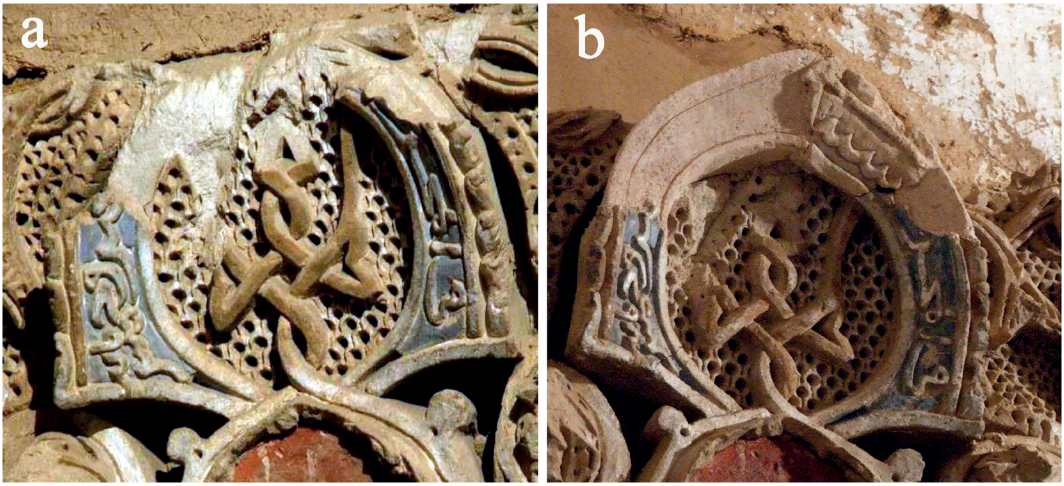

Figure 8. The dated inscription of the *mihrab* (a) prior to and (b) after the restorations.

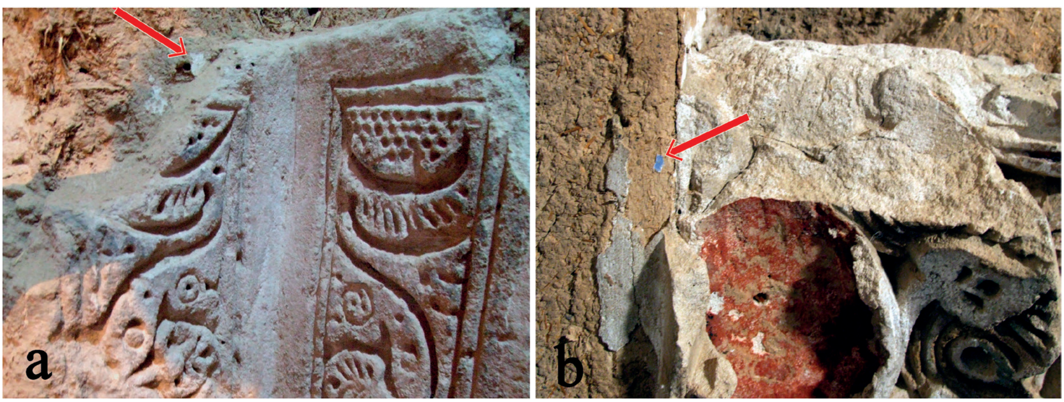

Figure 9. (a) White paint layer discovered under the stuccoworks of the dado and (b) white and blue paint layer under the stuccoworks of the *mihrab* are indicated with a red arrow.

Discussion

According to our analytical studies, atacamite, huntite, carbon black, red hematite, ultramarine blue and red lead were identified in the decorations of the tomb. The fact is that, apart from few examples (Holakooei and Karimy, 2015a), these pigments had not been previously identified by means of analytical methods performed on the pigments used in pre-seventeenth Persia. While the use of ultramarine blue, carbon black, red hematite and red lead is fairly well-documented in the scientific literature available on the Persian historical pigments, white huntite and atacamite are less-reported to be found in Persian wall paintings.

Furthermore, two different palettes were identified to be used in the decorations of the tomb. This showed that the *mihrab* and the walls were not probably decorated in the same period of time. Traces of the wall paintings behind the polychrome *mihrab*, thereafter, supported the idea that the *mihrab* and the wall paintings are not decorated in the same time. In addition, we dated the *mihrab* more accurately to the second half of the 12^{th} century AD. Considering this fact, traces of the white and blue pigments under the stuccoworks of the *mihrab* demonstrated that the wall paintings were created prior to the second half of the 12^{th} century. Our investigations, like previous studies, suggested two phases of creating decorations in the tomb, however, unlike the common assumptions, suggested the second half of the 12^{th} century as the second phase of the intensive decorations in the tomb posterior to an earlier period when the wall painting had been created. This was in contradiction with previous studies which had attributed the wall paintings to the 14^{th} century (Afshār, 1995; Anisi, 2007).

Concerning the natural oxalates observed in our studies, they have already been reported to be observed in works of art (Ruffolo et al., 2010; Ruffolo et al., 2015). The occurrence of weddellite, whewellite and glushinskite in the composition of the white and green paints were of our interest as they have already been reported in the white (Holakooei and Karimy, 2015a; 2015b) and green paints found in central Iran (Holakooei and Karimy, 2015b). Natural oxalates (weddellite, whewellite and glushinskite) identified in this study have been probably resulted from reacting the oxidation products of natural binders and white huntite. In other words, the oxalic acid derived from the degradation of the organic binding media mixed with pigments may have transformed the white huntite to the natural oxalates (Higgitt and White, 2005; Zoppi et al., 2010).

Moreover, the results of the current paper were in contradiction with those we published in our previous study (Karimy and Holakooei, 2012). Conducting energy dispersive X-ray spectrometry (EDS), we had suggested azurite, red hematite, malachite green, lampblack and chalk as blue, red, green, black and white pigments respectively used on the *mihrab* and ultramarine blue, red hematite, chalk and malachite as blue, red, white and green pigments respectively used on the wall paintings. However, according to the current results obtained with more reliable methods of analysis, the quality of the previous results is strongly questioned. We, thus, refer the readers to the current study and suggest ignoring the previous results concerning the identification of the pigment. The rest of the previous results are still confirmed by the authors.

Conclusions

The information provided in this paper contributed to the scant body of literature available on the Persian pigments. In this paper, we also made a reappraisal of our previous study published on the tomb's decorations. Atacamite, huntite, red lead and ultramarine blue were used on the *mihrab* and the wall paintings were painted with ultramarine blue, huntite, atacamite, carbon black and hematite. Moreover, a dark crust of plattnerite, as a degradation product, was identified to be formed on the red lead of the *mihrab*. While the black shade on the *mihrab* was resulted from the degradation of red lead, carbon black was identified to be used on the wall paintings for delineating the floral patterns and the Kufic inscription of the transitional zone of the dome. Calcium and magnesium oxalates were also identified to be mixed with huntite and atacamite. On the other hand, the current study rejected the previous ideas about the precedence of the *mihrab*'s decorations over the wall paintings and suggested that the wall paintings were created prior to the stuccoworks. This work suggested that the tomb undergone the second phase of intensive decorations in the second half of the 12th century when the stuccoworks are created.

Acknowledgments

Prof. Carmela Vaccaro is cordially thanked for her contribution in analytical studies. Majid Olumi and Elaheh Alvandian are especially acknowledged for their contributions in the restoration project. The authors are also grateful to Mohammad-Ali Akrami, as the head of the ICHHTO in Abarqū, and Mohammad Sharbaf, Farshad Moazeni, Hossein Qaraqani and Maliheh Baqaei, as restorers collaborated in the project.

References

Afshar I. (1995) - The Monuments of Yazd. Society of Cultural Works and Celebrated Men & Book House of Yazd, Yazd (in Persian).

Anisi A. (2007) - Early Islamic architecture in Iran (637-1059). Ph.D. Thesis, The University of Edinburgh.

Aze S., Vallet J.M., Pomey M., Baronnet A. and Grauby O. (2007) - Red lead darkening in wall paintings: natural ageing of experimental wall paintings versus artificial ageing tests. *European Journal of Mineralogy*, 19, 883-890.

Berenblut B.J., Dawson P. and Wilkinson G.R. (1971) - The Raman spectrum of gypsum. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 27, 1849-1863.

Bruni S., Cariati F., Casadio F. and Guglielmi V. (2001) - Micro-Raman identification of the palette of a precious XVI century illuminated Persian codex. *Journal of Cultural Heritage*, 4, 291-296.

Burgio L., Clark R.J.H. and Firth S. (2001) - Raman spectroscopy as a means for the identification of plattnerite (PbO_2) of lead pigments and of their degradation products. *Analyst*, 126, 222-227.

Burgio L., Clark R.J.H., Muralha, V.S.F. and Stanley T. (2008) - Pigment analysis by Raman microscopy of the non-figurative illumination in 16th- to 18th-century Islamic manuscripts. *Journal of Raman Spectroscopy*, 39, 1482-1493.

de Faria D.L.A., Venâncio Silva S. and de Oliveira M.T. (1997) - Raman microspectroscopy of some iron oxides and oxyhydroxides. *Journal of Raman Spectroscopy*, 28, 873-878.

Edwards H.G.M., Farwell D.W., Newton E.M. and Perez F.R. (1999) - Minium; FT-Raman non-destructive analysis applied to an historical controversy. *Analyst*, 124, 1323-1326.

Eslamizadeh A. and Samanirad Sh. (2014) - Petrology of ultramafic rocks and Mg-rich carbonate minerals in southeast of Dehshir, Central Iran. *Arabian Journal of Geosciences*, 7, 3675-3682.

Frost R.L. and Weier M.L. (2004) - Thermal treatment of whewellite, a thermal analysis and Raman spectroscopic study. *Thermochimica Acta*, 409, 79-85.

Frost R.L., Jing Y. and Ding Z. (2003) - Raman and FTIR spectroscopy of natural oxalates: Implications for the evidence of life on Mars. *Chinese Science Bulletin*, 48, 1844-1852.

Frost R.L., Martens W., Kloprogge J.Th. and Williams P.A. (2002) - Raman spectroscopy of the basic copper chloride minerals atacamite and paratacamite: implications for the study of copper, brass and bronze objects of archaeological significance. *Journal of Raman Spectroscopy*, 33, 801-806.

Gettens R.J. and Stout G.L. (1966) - Painting Materials: A Short Encyclopedia. Dover Publications, New York.

Ghorbani M. (2013) - The Economic Geology of Iran: Mineral Deposits and Natural Resources. Springer, Dordrecht.

Giovannoni S., Matteini M. and Moles A. (1990) - Studies and developments concerning the problem of altered lead pigments in wall painting. *Studies in Conservation*, 35, 21-25.

Godard A. (1936) - Abarqū, Athar-é Iran I, Paris, 47-74.

Higgitt C. and White R. (2005) - Analyses of paint media: new studies of Italian paintings of the fifteenth and sixteenth centuries. *National Gallery Technical Bulletin*, 26, 88-104.

Holakooei P. and Karimy A.-H. (2015a) - 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 Jame of Abarqu, central Iran. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 134, 419-427.

Holakooei P. and Karimy A.-H. (2015b) - Early Islamic pigments used at the Masjid-i Jame of Fahraj, Iran: A possible use of black plattnerite. *Journal of Archaeological Science*, 54, 217-227.

Jawhari T., Roid A., and Casado J. (1995) - Raman spectroscopic characterization of some commercially available carbon black materials. *Carbon*, 33, 1561-1565.

Karimy A. (2012) - Architectural decorations of Pir-i-Hāmzeh Sābz-Poush's Tomb. Unpublished Conservation and Restoration Report. ICHHTO: Yazd office (in Persian).

Karimy A.H. and Holakooei P. (2012) - Decorations of Pīr-i Hamza Sabzpūš's tomb in Iran. In: Historical Technology, Materials and Conservation: SEM and Microanalysis. (eds.): A. Meek, N. Meeks, A. Mongiatti and C. Cartwright, Archetype Publications, London, 158-160.

Muralha V.S.F., Burgio L. and Clark R.J.H. (2012) - Raman spectroscopy analysis of pigments on 16-17th c. Persian manuscripts. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 92, 21-28.

Osticioli I., Mendes N.F.C., Nevin A., Gil F.P.S.C., Becucci M. and Castellucci E. (2009) - Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 73, 525-531.

Petushkova J.P. and Lyalikova N.N. (1986) - Microbiological degradation of lead-containing pigments in mural paintings. *Studies in Conservation*, 31, 65-69.

Purinton N. and Watters M. (1991) - A Study of materials used by medieval Persian painters. *Journal of American Institute for Conservation*, 30, 125-144.

Ruffolo S.A., La Russa M.F., Barca D., Casoli A., Comite V., Nava G., Crisci G.M., De Francesco A.M. and Miriello D. (2010) - Mineralogical, petrographic and chemical analyses for the study of the canvas "Cristo alla Colonna" from Cosenza, Italy: a case study. *Periodico di Mineralogia, Special Issue,* 79, 71-79.

Ruffolo S.A., Comite V., La Russa M.F., Belfiore C.M., Barca D., Bonazza A., Crisci G.M., Pezzino A. and Sabbioni C. (2015) - An analysis of the black crusts from the Seville Cathedral: A challenge to deepen the understanding of the relationships among microstructure, microchemical features and pollution sources. *Science of the Total Environment*, 502 , 157-166.

Scheetz B.E. and White W.B. (1977) - Vibrational spectra of the alkaline earth double carbonates. *American Mineralogist*, 62, 36-50.

Varjāvand P. (1977) - A Short Traveling in Abarkouh. *Historical Studies Journal*, 5, 176-223 (in Persian).

Zoppi A., Lofrumento C., Mendes N.F.C. and Castellucci E.M. (2010) - Metal oxalates in paints: a Raman investigation on the relative reactivities of different pigments to oxalic acid solutions. *Analytical and Bioanalytical Chemistry*, 397, 841-9.

Submitted, December 2014 - Accepted, May 2015