Journal of Archaeological Science: Reports 29 (2020) 102065

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Colourants on the wall paintings of a mediæval fortress at the mount Sofeh in Isfahan, central Iran

Parviz Holakooei[a,*], Amir-Hossein Karimy[a], Fariba Saeidi-Anaraki[b], Carmela Vaccaro[c,d], Francesca Sabatini[e], Ilaria Degano[e], Maria Perla Colombini[e]

[a] Department of Art Conservation and Archaeometry, Art University of Isfahan, Isfahan, Iran
[b] Iranian Centre for Archaeological Research (ICAR), Research Institute for Cultural Heritage and Tourism (RICHT), Tehran, Iran
[c] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Ferrara, Italia
[d] Istituto di Scienze dell'Atmosfera e del Clima (ISAC), CNR, Bologna, Italia
[e] Laboratorio SCIBEC, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italia

ARTICLE INFO

Keywords:
Seljuk
Shahdej
Mount Sofeh
Madder red
Raman
XRF
Pigments

ABSTRACT

Colourants on the twelfth century wall paintings excavated at the fortress located on the mount Sofeh in Isfahan, central Iran, were analysed using micro X-ray fluorescence (μ-XRF), micro Raman spectroscopy (μ-Raman) and high-performance liquid chromatography coupled to electrospray ionization quadropole time-of-flight (HPLC-ESI-Q-TOF). The results of the analyses showed that gypsum, atacamite, carbon black, orpiment and ultramarine blue were used as white, green, black, yellow and blue pigments, respectively. Moreover, three red colourants including red lead, red vermilion and madder red were identified in the wall paintings. Furthermore, possible sources for the colourants are discussed.

1. Introduction

Colour has been an important element in Persian arts so that a great deal of research has been employed to identify the colouring agents in Persian artistic production. So far, the research on Persian colourants has been mainly focused on the pigments used in illuminated manuscripts (Anselmi et al., 2015 and references therein) since they are preserved in museums and art collections around the world in a significant number. However, less effort has been spent to characterise colourants on murals and stucco decorations. The few reports published on pigments used for architectural decorations in the Persianate world are related to pre-Islamic wall paintings (Stodulski et al., 1984; Chiari et al., 1993; Appolonia et al., 2008; Simpson et al., 2012; Holakooei et al., 2016), early Islamic pigments (Holakooei and Karimy, 2015a; Holakooei et al., 2018a) and pre-modern Persian art (Holakooei et al., 2018b and references therein). Thus, there is a large lacuna on the history of pigment use and production in Iran during the reign of the Seljuks (1037 – 1194 CE), when arts and crafts developed rapidly, and artworks and objects of common use were produced and circulated widely around the Seljuk empire (Hillenbrand, 1994; Canby et al., 2016) and the first systematic recipes for making pigments appeared (e.g. Teflisi, 12th Century, 1956; Neyshaburi, 1196). Despite the importance of the Seljuk art of painting, only few scientific reports have been published on the identification of the Seljuk pigments in Iran (Karimy and Holakooei, 2015; Holakooei et al., 2018a,b). Thus, a proper study on the colourants used in this period is of great importance for archaeologists and Islamic art historians. The pigments on the murals of a fortress excavated on the mount Sofeh in Isfahan, central Iran, provided an opportunity to depict a clearer image of the use of colourants during this period.

2. Historical background

Stories around an impenetrable fortress, called with mythical names such as Takht-e Rostam (Jaberi-Ansari, 1943, pp. 5 and 51) or Qale-ye Div (Homaii, 2005, p. 116), near Isfahan have attracted scholars to find proper historical explanations for its real name and location. Minasian (1971) has provided the so-far most accepted hypothesis in this regard. He surveyed the ruins of the fortress on the mount Sofeh and collected historical evidence to show that these ruins belong to the famous Seljuk castle named Shahdej, i.e. 'the fortress of Shah.' According to the accounts of Seljuk historians, Malikshah (r. 1072/73 – 92), the Seljuk ruler, selected Dez-kuh (now the mount Sofeh) for erecting this fortress (Ebn-i Athir, 13th century), named later as Shahdej (Ravandi, 12th

* Corresponding author.
E-mail address: p.holakouie@aui.ac.ir (P. Holakooei).

https://doi.org/10.1016/j.jasrep.2019.102065
Received 28 July 2019; Received in revised form 27 October 2019; Accepted 27 October 2019
Available online 12 December 2019
2352-409X/

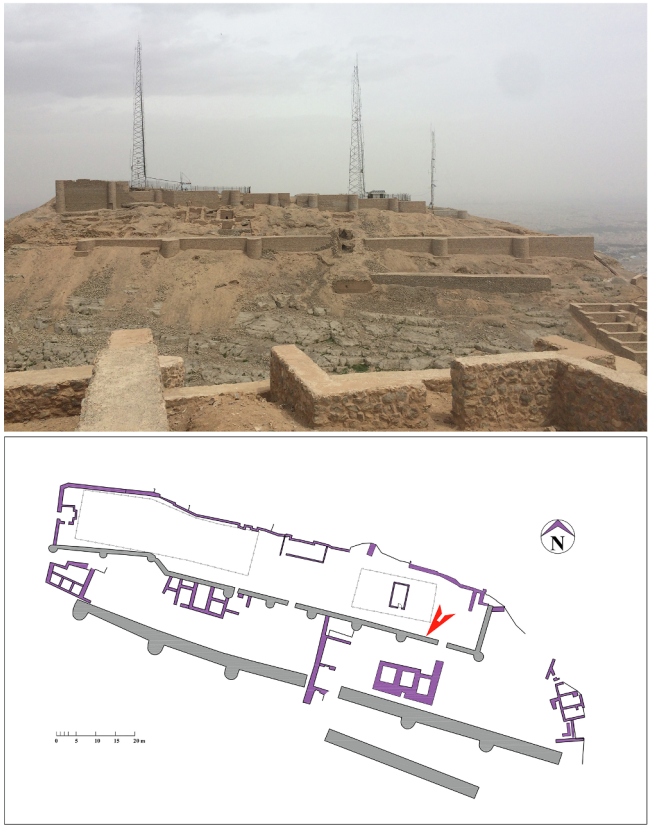

Fig. 1. (top) General view of the northern structures of Shahdej (view from the south) and (bottom) its general plan of architecture. The location of the wall paintings under study is indicated with the red arrow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

century, p. 156). The historic importance of Shahdej was not only due to its formidable fortress, but also to the royal ceremonies and formalities that took place there. Shahdej was also an important place during the short period of the Ismaili occupation (1100–1107 CE) (Ebn-i Athir, 13th century, 431). An evidence for this occupation is a graffiti inscription dated November 1106 CE (Karimian et al., 2009).

During the excavations at the mount Sofeh, which started in 2004 and continued in 2016, various archaeological finds including wall paintings, stucco decorations, potteries, leather objects, glass shards and wooden objects were retrieved from several public structures including a water reservoir, a bathhouse, a leather workshop, storehouses and other buildings (Fig. 1). According to Karimian et al. (2009) and Saeidi-Anaraki (2016), while the fortress itself may have been founded in the pre-Islamic era, the wall paintings (Fig. 2) and the relief stuccos of Shahdej show the stylistic characteristics of the Seljuk art.

3. Experimental

3.1. Samples

Samples were collected from white, black, blue, green, yellow and three shades of red used on the wall paintings with geometric patterns found in the trench B of Shahdej during the first season of excavations (Figs. 1 and 2). While the characterisation of a number of colourants presented in this study was sufficiently addressed by non-invasive micro X-ray fluorescence (μ-XRF) and micro Raman spectroscopy (μ-Raman), the identification of a particular shade of red colour was only achieved through high-performance liquid chromatography coupled with electrospray ionization quadropole time-of-flight (HPLC-ESI-Q-TOF).

Fig. 2. Shahdej wall paintings with geometric patterns.

3.2. X-ray fluorescence

An ARTAX™ 200 (Bruker AXS Microanalysis GmbH, Germany) was used as μ-XRF to qualitatively analyse the pigments. The instrument consisted of an X-ray tube with a Mo target and an SSD Peltier-cooled detector (10 mm^2 active area and resolution of < 155 eV at 10 kcps). The maximum voltage and current of 50 kV and 1500 μA, respectively, were used to excite the secondary fluorescence X-rays. A collimator with a diameter of 1 mm was used to collect the emitted secondary X-rays from a surface area of about 0.79 mm^2 in air.

Also, a quantitative XRF study was conducted on the white ground of the Shahdej wall paintings, gypsum deposits on the mount Sofeh and several other places in Isfahan area using a Unisantis XMF-104 machine equipped with a Kumakhuv polycapillary lens and an XR-100CR Si-PIN detector from Amptek (7 mm^2 active area and resolution of 186 eV for ^{55}Fe at 5.9 keV) operating at 40 kV and 600 μA for 150 s. The quantification was performed through Python multichannel analyser (PyMCA) software package (Solé et al., 2007) based on the fundamental parameters method. It is important to mention that the quality of the quantitative compositional data of the plasters was affected by three major issues. First, the plasters showed a non-uniform distribution of gypsum crystals and other inclusions so that the samples were not sufficiently homogenous. Second, the incident and take-off angles of X-ray were affected by the uneven surface of the samples. Furthermore, the small spot size of the X-ray beam used in the quantitative measurements (*ca.* 80 μm) prevented to have an overall composition from the plasters. To overcome these issues, several measurements were performed on different spots from the plasters where the distribution of particles was uniform and the surface of analysed spots was almost flat. The quantitative data were averaged and reported in Table 1.

Table 1
XRF data on the composition of different gypsum plasters mentioned in this study.

Place	Area	Date	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	SrO	Total
Shahdej castle	Isfahan	12th C.	41.26	0.77	30.31	0.05	0.02	0.85	3.68	76.93
			(0.22)†	(0.18)	(0.36)	(0.02)	(0.01)	(0.05)	(0.31)	
Sofeh mount	Isfahan	Prepared for this study	41.27	0.69	32.53	0.05	0.02	1.39	1.05	77.00
			(1.57)	(0.13)	(1.35)	(0.01)	(0.00)	(0.17)	(1.27)	
Bersiyan mosque	Isfahan	12th C.	34.04	0.98	33.99	0.18	0.05	3.49	2.36	75.09
			(2.19)	(0.21)	(0.30)	(0.13)	(0.03)	(2.26)	(0.53)	
Gar mosque	Isfahan	14th C.	35.31	0.66	26.11	0.08	0.03	2.86	9.31	74.35
			(3.04)	(0.08)	(0.94)	(0.02)	(0.01)	(0.58)	(4.91)	
Haftshouyeh mosque	Isfahan	14th C.	35.63	0.86	31.14	0.45	0.03	3.81	0.54	72.45
			(2.12)	(0.11)	(1.86)	(0.54)	(0.02)	(1.35)	(0.08)	
Ali-Qapu palace	Isfahan	17th C.	38.22	0.98	30.98	0.21	0.03	3.73	1.05	75.20
			(1.96)	(0.20)	(4.05)	(0.21)	(0.01)	(1.15)	(0.17)	
Bethlehem church	Isfahan	17th C.	34.94	0.92	32.30	0.13	0.03	4.33	1.27	73.92
			(1.79)	(0.10)	(1.40)	(0.04)	(0.00)	(0.10)	(0.11)	
David house	Isfahan	17th C.	34.69	1.03	33.33	0.11	0.09	5.18	2.20	76.63
			(3.04)	(0.04)	(0.55)	(0.02)	(0.03)	(1.19)	(1.41)	
Plaster*	Isfahan	Modern	34.79	1.15	33.28	0.05	0.04	3.30	0.96	73.58
			(0.27)	(0.20)	(0.23)	(0.02)	(0.00)	(0.09)	(0.32)	

† Standard deviation of measurements are shown in parenthesis.
* Plaster made from modern plaster of Paris supplied from Isfahan deposits of gypsum.

3.3. Raman spectroscopy

A LabRam HR800 spectrometer (Horiba Jobin Yvon, France) with a focal length of 80 mm was used to acquire Raman scattering signals. A 600 groove/mm grating was used to send the collected signals, which were acquired by an Olympus BXFM microscope and ×100 objective, to a Peltier-cooled CCD detector (1024 × 256 pixels) at −70 °C. The excitation source was a He-Ne laser (632.8 nm line) with a maximum laser power of 20 mW. The maximum laser power was, however, kept at 0.2 mW for the green pigment to avoid pigment degradation under high laser powers. The exposure time was about 15 s with 5 accumulations. The calibration of the spectrometer was performed with silicon at 520 cm^{-1} and the recorded spectra were handled with LabSpec 5 software.

3.4. HPLC-ESI-Q-ToF

3.4.1. Sample treatment

Since the analytical studies on the dark red colour were not conclusive, liquid chromatography was performed to identify this colour. Thus, 6 mg of sample were analysed using a mild extraction method with an EDTA/DMF solution. However, since the extraction was not successful, a stronger treatment based on methanolysis was used. It consists in the following steps: addition of 300 μL of MeOH/HCl (30:1) solution, extraction in ultrasonic bath at 60 °C for 60 min, filtration with PTFE (0.45 μm) filters, evaporation under nitrogen flow, re-dissolution with 200 μL of DMSO and finally injection of 20 μL of the extract in HPLC-ESI-Q-ToF.

3.4.2. HPLC-ESI-Q-ToF

An HPLC 1200 Infinity, coupled with a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector by a Jet Stream ESI interface (Agilent Technologies, USA) was used. The data were processed with Mass Hunter Qualitative Analysis software. Working conditions for the ESI were as follows: drying gas (N_2; purity > 98%), temperature 350 °C, flow 10 L/min; capillary voltage 4.5 KV; nebulizer gas pressure 35 psig; sheath gas (N_2; purity > 98%) temperature 375 °C, flow 11 L/min. High resolution MS and MS/MS acquisition range was set from 100 to 1000 *m/z* in negative mode; nozzle, skimmer and octapole RF voltages were set at acquisition with an MS and MS/MS scan rate of 1.04 spectra/sec.

Liquid chromatographic separation was performed using a Poroshell 120 EC-C18 column (3.0 mm × 75 mm, 2.7 μm particle size) with a Zorbax Eclipse plus C-18 guard column (4.6 mm × 12.5 mm, 5 μm particle size). The injection volume was 20 μL and the flow rate 0.4 mL/min. The separation was achieved at 30 °C using a gradient of formic acid (FA) 0.1% v/v in H_2O (eluent A) and FA 0.1% v/v in CH_3CN (eluent B). The elution program was 15% B for 2.6 min, then to 50% B in 13.0 min, to 70% B in 5.2 min, to 100% B in 0.5 min and then held for 6.7 min. Re-equilibration took 11 min.

4. Results and discussion

4.1. White

The white pigment had been applied thickly (with a thickness of about 2 mm) on a clay-based *intonaco*. As XRF showed, the white pigment is composed of Ca and S with minor to trace occurrence of Si, K, Ti, Mn, Fe and Sr. μ-Raman registered the Raman bands at 413, 493, 671, 1008 and 1134 cm^{-1} confirming the occurrence of gypsum, $CaSO_4{\cdot}2H_2O$, as the white pigment (Berenblut et al., 1971) (Fig. 3a; Table 2).

It is interesting to mention that the gypsum plaster used in historical monuments from Isfahan has a pinkish appearance owing its colour to the red iron oxide content while the gypsum plaster used at Shahdej has an almost white colour. To check if the historical plaster used as white ground layer in the Shahdej wall paintings bears the same amount of Fe as the gypsum plaster used in historical buildings in the Isfahan area, a quantitative XRF examination was conducted on several gypsum plasters occurred in Isfahan and on the white plaster of Shahdej. The historical gypsum plasters were collected from various places in Isfahan dated from the twelfth to the seventeenth century (Table 1). Apart from the historical samples, a modern gypsum plaster originated from the Isfahan gypsum deposits and widely distributed as masonry material in Isfahan was also analysed by XRF. As can be seen in Table 1, the Fe content of the gypsum plaster used in the Isfahan area is markedly higher than the white plaster used in Shahdej. The lower Fe content of this plaster has in fact resulted in its white appearance with respect to the plaster used in Isfahan. In general, the chemistry of the gypsum plaster from Shahdej is significantly different from the historical plasters and the modern plaster which occur in Isfahan (Table 1).

Gypsum deposits in Isfahan area are found in gypsum-enriched soils occurring in alluvial fans, dissected flood plains and piedmont plains from north to the east of Isfahan. These gypsum-enriched soils contain fibrous gypsum crystals distributed in the soil (Toomanian et al., 2001). Thus, significant amounts of Fe, derived from the soil, might be

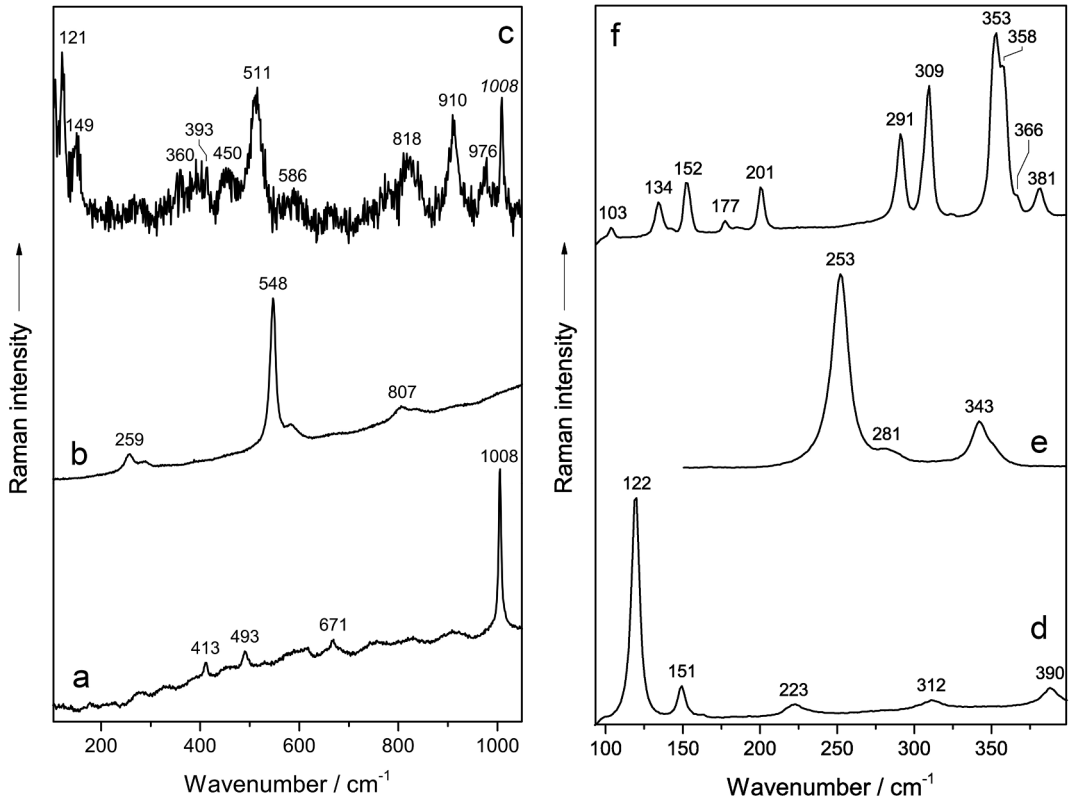

Fig. 3. Raman spectra of (a) white gypsum, (b) ultramarine blue, (c) atacamite (the Raman band at 1008 cm^{-1} shown in *italic* is due to gypsum plaster), (d) red lead, (e) vermilion and (f) orpiment.

detected in the plaster obtained from these deposits. In order to check if the gypsum used in the wall paintings of Shahdej has been supplied from gypsum deposits in the Cretaceous limestone of the mount Sofeh (Sohrabi et al., 2015) or from other areas, a survey was conducted on the mount. During the survey, scattered pure selenite crystals and fibrous gypsum-enriched soil were discovered near the fortress (Fig. 4). A specimen from the gypsum deposits was heated at 180 °C in a muffle kiln for two hours to make a plaster. The specimen was then ground and mixed with water. After setting, an XRF study was conducted on the dried plaster. The chemical composition of the plaster matched with the gypsum white ground of the Shahdej wall paintings and was markedly different from the common gypsum plaster available in Isfahan area (Table 1). On the other hand, as Table 1 shows, the historical and the modern gypsum plasters driven from the gypsum deposits in the Isfahan area demonstrate fairly the same chemical composition and contain significant amounts of Fe which is markedly higher than the Fe content of the gypsum plaster from Shahdej. Altogether, one might suggest that the gypsum deposits on the mount may have been used as the preparatory white layer of the Shahdej wall paintings.

4.2. Blue

μ-XRF demonstrated that the blue colour incorporated Si, S and Ca together with trace and minor quantities of Cl, K, Ti, Mn, Fe and Sr. This composition was in line with that of ultramarine blue, $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$, whose occurrence was confirmed by μ-Raman by the bands at 259, 548, 583, 807 and 1096 cm^{-1} (Burgio and Clark, 2001) (Table 2; Fig. 3b). The minor occurrence of Fe in the blue pigment might be linked with pyrite, FeS_2, which occurs in the natural ultramarine blue (Plesters, 1966). Ultramarine blue has been widely documented to have been used in both Persian wall paintings (Holakooei and Karimy, 2015a,b; Karimy and Holakooei, 2015; Holakooei et al., 2018a,b) and illuminated manuscripts (Bruni et al., 2001; Muralha et al., 2012). Ultramarine blue has also been reported to be mixed with blue smalt in the pre-seventeenth century wall paintings of Masjid-i Jame of Abarqu, Yazd (Holakooei and Karimy, 2015b). The

Table 2
Summary of the μ-XRF and μ-Raman observations.

Colour	μ-XRF*	Raman bands (cm^{-1})†	Pigment
White	**S**, **Ca**, (Si, K, Ti, Mn, Fe, Sr)	413 (w), 493 (w), 671 (w), 1008 (vs), 1134 (w)	Gypsum
Black	S, Ca, (Si, K, Ti, Mn, Fe, Sr)	1330 (vs, br), 1605 (vs, br)	Carbon black
Blue	**Si**, **S**, Ca, (Cl, K, Ti, Mn, Fe, Sr)	259 (w), 548 (vs), 583 (vw), 807 (w), 1096 (m)	Ultramarine blue
Green	S, **Cl**, Ca, **Cu**, (Si, K, Ti, Mn, Fe, Sr, Pb)	121 (s), 149 (w), 360 (w), 393 (w), 450 (w), 511 (vs), 586 (w), 818 (s), 910 (s), 976 (m)	Atacamite
Yellow	**S**, **As**, Ca, (Si, Cl, K, Ti, Mn, Fe, Cu, Sr, Pb)	103 (w), 134 (m), 152 (m), 177 (w), 201 (s), 291 (s), 309 (s), 353 (vs), 358 (sh), 366 (w), 381 (w)	Orpiment
Red	**S**, Ca, **Hg**, **Pb**, (Si, Cl, Ti, Mn, Fe, As, Sr)	253 (vs), 281 (vw), 343 (w)	Vermilion
	S, Ca, (Si, P, Cl, K, Ti, Mn, Fe, Cu, Sr, Pb)	–	Madder red‡
	S, Ca, **Pb**, (Si, Cl, Ti, Mn, Fe, Cu, Sr)	122 (vs), 151 (m), 223 (w), 312 (w), 390 (w), 479 (w), 548 (s)	Red lead

* Colouring agents in bold and trace and minor elements in parentheses.
† vw: very weak; w: weak; m: medium; s: strong; vs: very strong; sh: shoulder; br: braod.
‡ See the text.

Fig. 4. Fibrous gypsum deposits on the mount Sofeh.

methods for preparing and using ultramarine blue is described in mediæval Persian texts (Unknown author, ca. 1447; Mansur, ca. 1454-1478).

4.3. Green

The main elements detected in the green pigment using XRF were Cu and Cl together with S, Ca, Cu, Si, K, Ti, Mn, Fe, Sr and Pb (Table 2) suggesting the use of copper (hydro)oxy chlorides as the green pigment. μ-Raman demonstrated atacamite, $Cu_2Cl(OH)_3$, as the green pigment by assignment of the bands at 121, 149, 360, 393, 450, 511, 586, 818, 910 and 976 cm^{-1} (Frost et al., 2002) (Fig. 3c).

The use of atacamite in historical wall paintings is well-documented. Kossolapov and Kalinina (2007) and Cotte et al. (2008) reported the occurrence of atacamite as green pigment in the wall paintings of Bamiyan, Afghanistan. Atacamite has also been employed as the green pigment in the wall paintings of the Masjid-e Jame of Abraqu (Holakooei and Karimy, 2015a), Pir-i Hamza Sabzpush tomb in Abarqu (Karimy and Holakooei, 2015) and early Islamic paintings in Nishapur (Holakooei et al., 2018a). Atacamite has also been reported as green pigment in two Persian manuscripts dated to the early 16th century CE (Burgio et al., 2008; Muralha et al., 2012). Moreover, Purinton and Watters (1991) listed atacamite in Persian illuminated manuscripts. The usual method for making green atacamite consists of soaking copper filings in dissolved *sal ammoniac*, NH_4Cl (Teflisi, 12th Century, 1956; Unknown author, 1582). The historical recipes for manufacturing green copper pigments in Iran including atacamite are currently being studied by Karimy and Holakooei (forthcoming).

4.4. Reds

Three shades of red occur in the wall paintings at Shahdej; i.e. orange, pinkish and dark reds. As far as the orange/red is concerned, it was composed of Pb as well as minor amounts of S, Ca, Si, Cl, Ti, Mn, Fe, Cu and Sr (Table 2). The Raman bands matched with those of red lead, Pb_3O_4, at 122, 151, 223, 312, 390, 479 and 548 cm^{-1} (Burgio and Clark, 2001) (Fig. 3d). It is well-documented either in historical texts (Porter, 1994) or in recent scientific literature that red lead has been one of the most extensively used red pigments ever used in the old Persian illuminated manuscripts (Bruni et al., 2001; Burgio et al., 2008; Muralha et al., 2012) and wall paintings (Holakooei and Karimy, 2015a; Karimy and Holakooei, forthcoming; Holakooei et al., 2018a,b). Red lead has also been reported as the red pigment in the pre-Islamic Persian paintings of Ghaleh Guri (Holakooei et al., 2016). The historical production of red lead in Iran entailed heating either metallic lead sheets (Teflisi, 12th Century, 1956) or lead white under an oxidising atmosphere (Sadeqi-beg Afshar, ca. 1601).

The main elements in the pinkish shade detected using XRF are Hg and Pb (Table 2). The μ-Raman study on this colour showed the occurrence of red lead mixed with red vermilion, HgS, by assignment of the bands at 253, 281 and 343 cm^{-1} (Burgio and Clark, 2001) (Fig. 3e). The chemistry of the red vermilion may give a hint about its origin. The pinkish shade of red contained minor As content as XRF showed (Table 2). As is known, natural sources of vermilion (cinnabar) in Iran are reported from gold deposits in north-western Iran (Mehrabi et al., 1999; Deliran, 2008), where ore fluids of silica (SiO_2) and barite ($BaSO_4$) are enriched in As and Hg, and precipitated orpiment (As_2S_3) and cinnabar can be found in open spaces (Daliran, 2008). The seventeenth century treatise of Tohfeh-ye Hakim-e Mo'men notes that natural sources of vermilion are always contaminated with gold, copper and mercury (Hoseyni, 1669). Thus, the presence of As in the XRF data of this pigment may be connected with minor orpiment crystals, which are naturally associated with cinnabar. However, the absence of Ba in the composition of the red vermilion (Table 2) points against the use of the natural cinnabar. It is important to mention that some old practices of making red vermilion involve mixing mercury and sulphur with either orpiment or realgar (AsS) (Amoli, ca. 1341, p. 176; Aqili Alavi Shirazi, 1844, p. 48). Thus, the presence of As in the pinkish shade and the absence of Ba in the XRF data of the pinkish shade of red, which is normally associated with cinnabar deposits from Iran, may suggest that it was artificially made.

The first evidence about the use of vermilion in pre-Islamic Persia are reported from the Achaemenid period (550 – 330 BCE) (Stodulski et al., 1984), from the Parthian sites of Nisa (Chiari et al., 1993) and Uruk (Simpson et al., 2012) and the Sasanian site of Ghaleh Guri (Holakooei et al., 2016). Vermilion has also been reported to be a predominant red pigment in Persia over the Islamic period (Purinton and Watters, 1991). Mediæval Persian treatises describe how to obtain artificial vermilion. They explain how to mix equal proportions of mercury and sulphur in a sealed glass jar or an un-fired pottery with a slightly narrow neck and a small hole on top. This procedure involves grinding sulphur with mercury, introducing the ground and blackened product into the glass jar and slightly heating it in a special kiln (Razi, 9–10th Century, 1992, p. 60; Biruni, 11th Century, p. 576; Teflisi, 12th Century, 1956).

The μ-XRF and μ-Raman analyses on dark red areas did not conclude to the identification of this colour. While no legible Raman band due to high fluorescence background could be registered by μ-Raman, the elemental composition of this colour was fairly similar to that of the white pigment (Table 2) suggesting that this paint was mainly made of low *Z* elements. An organic dye is thus the most likely candidate for the preparation of this paint. It is interesting that the XRF spectra featured

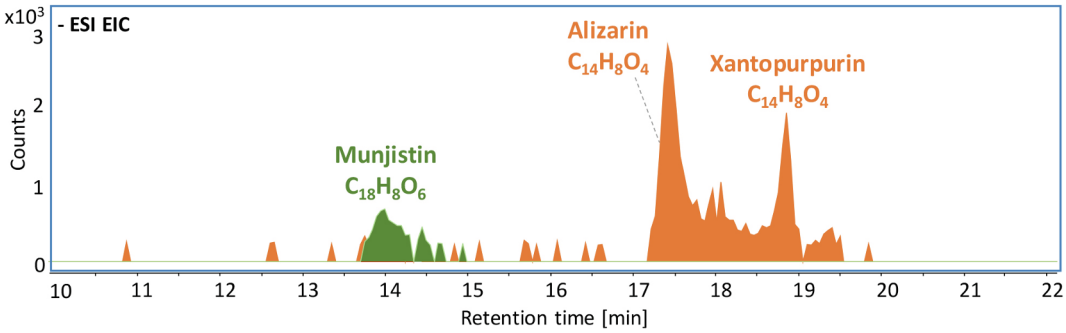

Fig. 5. Extracted Ion Chromatograms acquired by HPLC-ESI-Q-ToF EIC corresponding to the raw formulas $C_{18}H_8O_6$ (green, corresponding to munjistin) and $C_{14}H_8O_4$ (orange, corresponding to both alizarin and xanthopurpurin) from the extract of the sample (negative acquisition mode). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the presence of phosphorus in the composition of the dark red paint (Table 2). It is known that cochineal and madder red, the two main organic dyes used in historical paintings of Iran, incorporate minor quantities of phosphorus in their composition (Kirby et al., 2005). Thus, an ultra-sensitive LC-MS/MS technique was used in order to identify the organic component of the pink colour. The chromatographic profile of the sample highlights the presence of alizarin (m/z = 239.031), xantopurpurin (m/z = 239.031) and traces of munjistin (m/z = 283.002) as shown in the Extract Ion Chromatograms (EIC) (Fig. 5). These species belong to the anthraquinone family and are typical of madder red; in particular, being alizarin the main compound, the use of an alizarin-rich madder lake can be hypothesised, such as that extracted from the roots of *Rubia tinctorum* L (Daniels et al., 2014; Bracci et al., 2019). Scientific studies on freshly dried *Rubia tinctorum* root have showed lucidin primeveroside, ruberythric acid, pseudopurpurin and munjistin from which pseudopurpurin is converted to purpurin, ruberythric acid to alizarin and munjistin to xanthopurpurin in an acidic solution or in water when sufficient enzyme activity is present (Daniels et al., 2014). Although the exact assignment of the original raw material is not straightforward, since modification in the anthraquinone profile can occur as a consequence of particular pre-treatments in the dye production or of ageing, and in spite of the absence of purpurin, the occurrence of alizarin, xantopurpurin and munjistin in the red colour of Shahdej might be related to *Rubia tinctorum* L. *Rubia tinctorum* L is native to the eastern Mediterranean, the Middle East and North Africa and is known to contain more alizarin than pseudopurpurin or purpurin when compared to *Rubia peregrina* L. in which alizarin is often absent or only present in low quantities. Moreover, *Rubia peregrina* L. often contains significant quantities of rubiadin, which is not normally a major component in *Rubia tinctorum* L. (Daniels et al., 2014).

Madder red has been reported to appear first in Egypt during the 18th dynasty (*ca.* 1350 BCE) and was known by the Akkadians in Mesopotamia around 1900 BCE. Several examples of the use of madder red have been reported from Greek, Hellenistic, Roman and Islamic worlds (Cardon, 2007, pp. 119–20; Shahid et al., 2019). However, scientific studies which confirm the occurrence of madder-based colourants in the Iranian world are scant. In a rare report, madder red has been documented to have been found in pre-Islamic Parthian stucco decorations from Uruk (Simpson et al., 2012). Due to the absence of alizarin in the madder colourant used in the Uruk stucco, one can argue that the origin of madder colourant in Shahdej and the Uruk stucco may be different. It is worth-noting that Isfahan was an important place for producing madder red (*runas*) during the seventeenth century in Iran (Ferrier, 1986, p. 447) so that an Armenian merchant from Isfahan became the founder of the madder industry in Avignon, France (Wulff, 1966, p. 190). The madder red produced in Iran was also well-known in the East. Chardin (1711, p. 15) reports that madder red was largely produced in Iran and was widely exported to India in the seventeenth century.

4.5. Yellow

The yellow pigment was composed of S, As and Ca together with minor amounts of Si, Cl, K, Ti, Mn, Fe, Cu, Sr and Pb (Table 2). μ-Raman study registered the bands at 103, 134, 152, 177, 201, 291, 309, 353, 358, 366 and 381 cm^{-1} consistent with yellow orpiment, As_2S_3 (Burgio and Clark, 2001) (Fig. 3f). It is worth-noting that the higher intensity of the band at 353 cm^{-1} with respect to that at 358 cm^{-1} suggests that the yellow orpiment has deteriorated due to light exposure (Vermeulen et al., 2017) and, thus, the colour of the pigment might have changed respect to its original appearance on the walls of the fortress.

Orpiment is one of the most extensively yellow pigments used in the history of Persian painting. Several contributions report the use of this pigment from the pre-Islamic Persian paintings (Kostrov and Sheinina, 1961; Azarpay, 1981; Kossolapov and Kalinina, 2007) and Islamic murals (Burgio et al., 2007) until the fifteenth to seventeenth century Persian illuminated manuscripts (Purinton and Watters, 1991). The natural deposits of orpiment are mostly distributed in north-western Iran and in particular in Zarshuran mines (Mehrabi et al., 1999), where evidence of mining activities have been reported from the pre-Islamic era until the Islamic period, to exploit gold, mercury and orpiment (Momenzadeh et al., 2016). Orpiment deposits have also been reported near Isfahan, in the Muteh gold mining area (Keshavarzi et al., 2012).

4.6. Black

The black colour was used in the graffiti found near the southern wall of the fortress. The chemical composition of the black pigment was identical to that of the white pigment; that is, low Z elements were composing the black pigment (Table 2). The Raman study on this pigment showed two strong broad Raman bands at 1330 and 1605 cm^{-1} (Fig. 6), consistent with carbon black (Jawhari et al., 1995). The absence of P, Ni and V ruled out the occurrence of bone black and bitumen (Filby, 1994). A closer look under the microscope revealed that charred fibres of linen were used as the black pigment (Fig. 6). The historical method of making carbon black from charred fibres (especially paper fibres) has been described in mediæval Persian treatises. In particular, a mixture of gall, burnt paper, soot and Arabic gum has been mentioned for obtaining good quality black ink or *medad* (Tabari, 11th century; Teflisi, 12th century). Using charred paper for pharmaceutical uses in bleeding control has also been mentioned in many of historic Persian books of medicine (e.g. Jorjani, 12th century, 2012; Afshar, 2011, p. 65).

5. Conclusions

Apart from ultramarine blue, atacamite, white gypsum, red lead, orpiment and vermilion, which have been widely reported in the palette of Persian painters, the identification of madder red on the wall

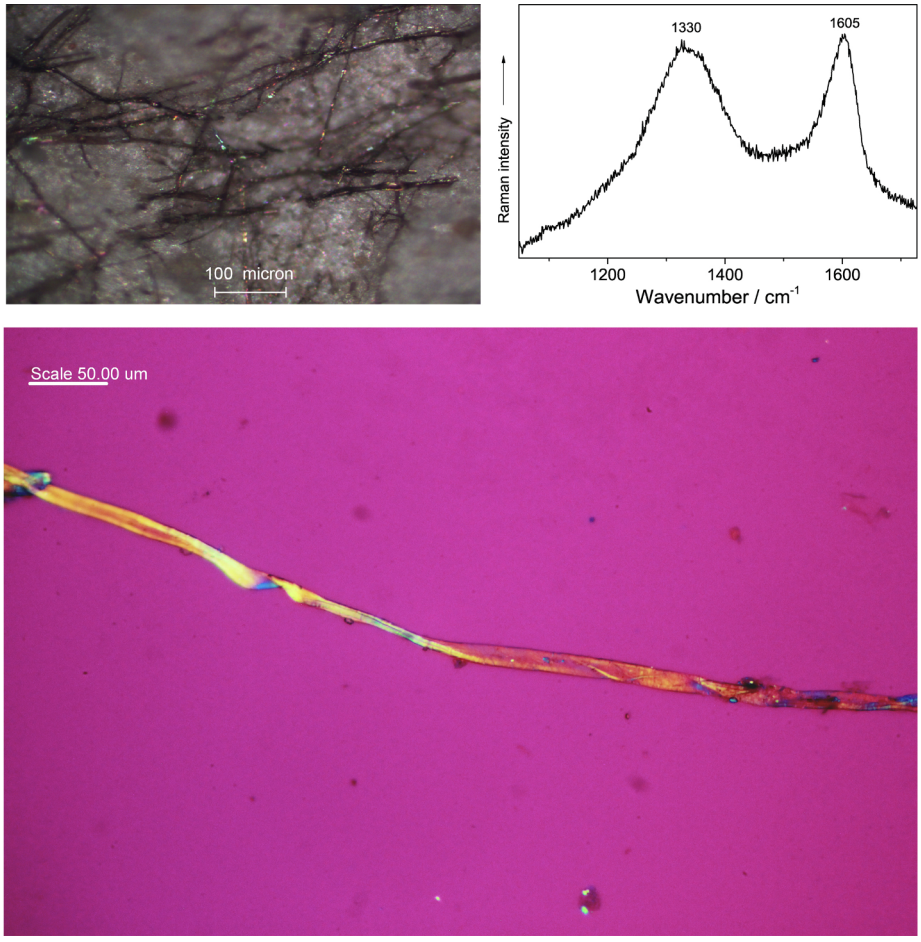

Fig. 6. (*top*, *left*) The black colourant under the Raman microscope and (*top*, *right*) its Raman spectrum. The linen fibre used in the black colour of the Shahdej wall paintings.

paintings of Shahdej was unusual. The unicity of this finding is more striking taking into account the availability of natural deposits of red ochre on the mount Sofeh that are still being used in the works of contemporary Isfahani painters. Moreover, the vibrant madder-red-painted fragments preserved in the archive of Shahdej archaeological finds are fading quickly. Thus, detecting such a vibrant but sensitive colourant on the wall paintings of Shahdej suggests that the building has been demolished shortly after executing the wall paintings. While the pigments have most certainly been imported to the mount for painting, the use of gypsum deposits from the mount Sofeh for whitening the walls and preparing a suitable ground for painting is of significant importance, demonstrating that the fortress was erected with building materials accessible on site. If the white gypsum was supplied from the local sources of gypsum available on the mount, why have the red ochre deposits not been exploited for painting purposes? Perhaps, the painters of Shahdej were looking for particular shades of red different from the red ochre deposits on the mount.

Acknowledgments

The authors would like to thank Dr. Nasim Jafari, from the Reconstruction and Revitalization Office of Isfahan Municipality, and Dr. Ali Shojaee, from the Art University of Isfahan, for his useful comments on the history of the castles around Isfahan and Nazanin Shahidi Marnani for her contribution in the preparation of the architecture site plan from Shahdej. Prof. Ferruccio Carlo Petrucci, from the University of Ferrara, is cordially thanked for providing μ-XRF facility.

References

Afshar, I., 2011. Paper in Iranian Life and Culture. Miras-e Maktoob Publication, Tehran (in Persian).
Amoli, S.M. ca. 1341. Nafayes al-Fonun fi Arayes al-Oyun, Vol. 3, (Mostarhami H, ed. 2002), Tehran: Eslamiyyeh (in Persian).
Anselmi, C., Ricciardi, P., Buti, D., Romani, A., Moretti, P., Beers, K.R., Brunetti, B.G., Miliani, C., Sgamellotti, A., 2015. MOLAB® meets Persia: Non-invasive study of a sixteenth-century illuminated manuscript. Stud. Conserv. 60, S185–S192.
Appolonia, L., Radicati, B., Piccirillo, A., Chatel, V. 2008. La materia e i colori, In: Nisa Partica-ricerche nel complesso monumentale arsacide 1990-2006, Monografie di Mesopotamia IX, ed. Le Lettere, FI, 197-209.
Aqili Alavi Shirazi, M.H., 1844. Makhzan al-Adviyyeh. Bavardaran (in Persian), Tehran.
Azarpay, G., 1981. Sogdian Painting: The Pictorial Epic in Oriental Art. University of California Press, Berkeley.
Berenblut, B.J., Dawson, P., Wilkinson, G.R., 1971. The Raman spectrum of gypsum. Spectrochim. Acta Part A 27, 1849–1863.
Biruni, A.R. 11th Century. Al-Saydaneh fi al-Tebb (Mozaffarzadeh B., tran. 2004) Farhangestan-e Zaban va Adab-e Farsi, Tehran (in Persian).
Bracci, S., Vettori, S., Cantisani, E., Degano, I., Galli, M., 2019. The ancient use of colouring on the marble statues of Hierapolis of Phrygia (Turkey): an integrated multi-analytical approach. Archaeol. Anthropol. Sci. 11, 1611–1619.
Bruni, S., Cariati, F., Casadio, F., Guglielmi, V., 2001. Micro-Raman identification of the palette of a precious XVI century illuminated Persian codex. J. Cult. Herit. 4, 291–296.
Burgio, L., Clark, R.J.H., Muralha, V.S.F., Stanley, T., 2008. Pigment analysis by Raman microscopy of the non-figurative illumination in 16th- to 18th-century Islamic manuscripts. J. Raman Spectrosc. 39, 1482–1493.
Burgio, L., Clark, R.J.H., 2001. Library of FT-raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of raman spectra of pigments with visible excitation. Spectrochim. Acta Part A 57, 1491–1521.
Burgio, L., Clark, R.J.H., Rosser-Owen, M., 2007. Raman analysis of ninth-century Iraqi stuccoes from Samarra. J. Archaeol. Sci. 34, 756–762.
Canby, S.R., Beyazit, D., Rugiadi, M., Peacock, A.C.S., 2016. Court and Cosmos: The Great Age of the Seljuqs. The Metropolitan Museum of Art, New York.
Chardin, J., 1711... Voyages de Monsieur le Chevalier Chardin en Perse et autres Lieux de l'Orient. Tome 2. J.-L. de Lorme, Amsterdam.

Chiari, G., Invernizzi, A., Bertolotto, G., 1993. Investigation and restoration of clay fragmentary statues from Old Nisa, Conferência Internacional Sobre o Estudo e Conservaçao da Arquitectura de Terra (7a). Silves (Portugal), 24 a 29 de Outubro 1993, DGEMN, Lisboa, pp. 228–230.
Cotte, M., Susini, J., Solé, V.A., Taniguchi, Y., Chillida, J., Checroun, E., Walter, Ph., 2008. Applications of synchrotron-based micro-imaging techniques to the chemical analysis of ancient paintings. J. Anal. Atomic Spectrom. 23, 820–828.
Daliran, F., 2008. The carbonate rock-hosted epithermal gold deposit of Agdarreh, Takab geothermal field, NW Iran—hydrothermal alteration and mineralisation. Miner. Depos. 43, 383–404.
Daniels, V., Devièse, T., Hacke, M., Higgitt, C., 2014. Technological insights into madder pigment production in antiquity. Br. Museum Tech. Res. Bull. 8, 3–28.
Ebn-i Athir, 13th century. Al-Kamel fi Tarikh, vol. 10. Dar-e Sader Publication, Beirut (1966).
Ferrier, R., 1986. Trade from the mid-14th century to the end of the Safavid period. In: In: Jackson, P., Lockhart, L. (Eds.), The Cambridge History of Iran Vol. 6 Cambridge University Press, Cambridge.
Filby, R.H. 1994. Origin and Nature of Trace Element Species in Crude Oils, Bitumens and Kerogens, Geological Society, Spec. Pub. V78, 203–219.
Frost, R.L., Martens, W., Kloprogge, J.Th., 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. J. Raman Spectrosc. 33, 801–806.
Hillenbrand, R. ed. 1994. The Art of the Saljuqs in Iran and Anatolia: Proceedings of a Symposium Held in Edinburgh in 1982. Costa Mesa, Calif.: Mazda Publishers.
Holakooei, P., Karimy, A.H., 2015a. Early Islamic pigments used at the Masjid-i Jame of Fahraj, Iran: a possible use of black plattnerite. J. Archaeol. Sci. 54, 217–227.
Holakooei, P., Karimy, A.H., 2015b. 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. Spectrochim. Acta Part A 134, 419–427.
Holakooei, P., de Lapérouse, J.-F., Rugiadi, M., Carò, F., 2018a. Early Islamic pigments at Nishapur, north-eastern Iran: studies on the painted fragments preserved at The Metropolitan Museum of Art. Archaeol. Anthropol. Sci. 10 (1), 175–195.
Holakooei, P., Karimy, A.H., Nafisi, G., 2018b. Lammerite as a degradation product of emerald green: scientific studies on a rural Persian wall painting. Stud. Conserv. 63 (7), 391–402.
Holakooei, P., Karimy, A.H., Hassanpour, A., Oudbashi, O., 2016. Micro-Raman spectroscopy in the identification of wulfenite and vanadinite in a Sasanian painted stucco fragment of the Ghaleh Guri in Ramavand, western Iran. Spectrochim. Acta Part A 169, 169–174.
Homaii, J. 2005. Tarikh-e Esfahan, Vol. 4, Historic Buildings, Huma Publication Center, Tehran (in Persian).
Hoseyni, M.M. 1669. Tohfeh-ye Hakim-e Mo'men. Tehran: Mostafavi Library (in Persian).
Jaberi-Ansari, M.H. 1943. Tarikh-e Esfahan, Mazaheri J. (ed. 2000), Isfahan: Mashal Publication (in Persian).
Jawhari, T., Roid, A., Casado, J., 1995. Raman spectroscopic characterization of some commercially available carbon black materials. Carbon 33, 1561–1565.
Jorjani, E.H.12th century. Zakhire-ye Khwarazmshahi, Qom: Moa'sese-ye Ehyae-ye Tebb-e Tabiei (ed. 2012) (in Persian).
Karimian, H., Ahmadi, A.A., Saeidi-Anaraki, F., 2009. The castle of Shahdej in Isfahan based on archaeological excavation data. J. Literat. Human. Faculty Tehran Univ. 187, 79–110 (in Persian).
Karimy, A.H., Holakooei, P., 2015. Analytical studies leading to the identification of the pigments used in the Pīr-i Hamza Sabzpūsh tomb in Abarqū, Iran: a reappraisal, *Period. Mineral.* **84**, 389–405.
Keshavarzi, B., Moore, F., Rastmanesh, F., Kermani, M., 2012. Arsenic in the Muteh gold mining district, Isfahan, Iran. Environ. Earth Sci. 67 (4), 959–970.
Kirby, J., Spring, M., Higgitt, C., 2005. The Technology of red lake pigment manufacture: study of the dyestuff substrate. Nat. Gallery Tech. Bull. 26, 71–87.
Kossolapov, A., Kalinina, K. 2007. The Scientific Study of Binding Media and Pigments of Mural Paintings from Central Asia, in: K. Yamauchi, Y. Taniguchi, T. Uno, T.B. Kenkyūjo (Eds.), Mural Paintings of the Silk Road Cultural Exchanges between East and West, Archetype publications, London, pp. 89-92.
Kostrov, P.I., Sheinina, E.G., 1961. Restoration of monumental painting on loess plaster using synthetic resins. Stud. Conserv. 6, 90–106.
Mansur, M. ca. 1454-1478. Gowhar-nameh, In: Farhang-e Iranzamin IV, Sutudeh M. (ed. 1956), Tehran: Bahman Publisher, pp. 185–287 (in Persian).
Mehrabi, B., Yardley, B.W.D. and Cann, J.R., 1999. Sediment-hosted disseminated gold mineralisation at Zarshuran, NW Iran, *Miner. Deposita* **34**, 673–696.
Minasian C.O. 1971. Shah Diz of Ismaili Fame, (tr. Serri, A. 2008), Tehran: Asatir Publication (in Persian).
Momenzadeh, M., Nezafati, N., Sarraf, M.R., Shabani, K., 2016. Ancient gold-mercury mining in the takht-e soleyman area northwest Iran. Metalla 22, 147–168.
Muralha, V.S.F., Burgio, L., Clark, R.J.H., 2012. Raman spectroscopy analysis of pigments on 16–17th c Persian manuscripts. Spectrochim. Acta Part A 92, 21–28.
Neyshaburi, M.A. 1196. Javahernameh-ye Nezami, (Afshar. I., Daryagasht, M.R., eds. 2004), Tehran: Miras-e Maktub Press (in Persian).
Plesters, J., 1966. Ultramarine Blue, Natural and Artificial. Stud. Conserv. 11, 62–91.
Porter, Y., 1994. Painters, Paintings, and Books: An Essay on Indo-Persian Technical Literature, 12–19th Centuries. Centre for Human Sciences, Manohar, New Delhi.
Purinton, N., Watters, M., 1991. A study of materials used by medieval Persian painters. J. Am. Inst. Conserv. 30, 125–144.
Ravandi, M.A.S. 12th century. Rahat al-Sodur va Ayat al-Sorur, Eqbal, M. (ed. 2006), Tehran: Asatir Publication (in Persian).
Razi, M.Z. 9-10th Century. Ketab al-Asrar (Shaybani, H.A., tran. ed. 1992), Tehran: Tehran University Press (in Persian).
Saeidi-Anaraki, F., 2016. Report on the second season of excavation at the Shahdej castle, Archive of the ICHTTO Office at Isfahan, Document no. 1449, registered on April 13th, 2019.
Sadeqi-beg Afshar. ca. 1601. Qanun al-Suvar, In: Mayel-Heravi N. (ed. 1993), Ketab-arayi dar Tamaddun-i Eslami (Book Illumination in Islamic Civilization), Islamic Research Centre of Astan-e Qods-e Razavi, Mashhad, pp. 345-354 (in Persian).
Shahid, M., Wertz, J., Degano, I., Aceto, M., Khan, M.I., Quye A. 2019. Analytical methods for determination of anthraquinone dyes in historical textiles: a review, *Anal. Chim. Acta* **1083**, 58-87.
Simpson, J., Ambers, J., Verri, G., Deviese, Th. and Kirby, J. 2012. Painted Parthian Stuccoes from Southern Iraq, In: R. Matthews, J. Curtis (eds.) Proceedings of the 7th International Congress on the Archaeology of the Ancient Near East, Vol. 2, The British Museum and UCL, London, pp. 209-220.
Sohrabi, A., Beygi, S., Nadimi, A., Hajihashemi, M., 2015. The role of regional tectonics in structural caves, Simorgh Cave, Sofeh Mountain (Iran). J. Tethys 3 (2), 114–122.
Solé, V.A., Papillon, E., Cotte, M., Walter, Ph., Susini, J., 2007. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. Spectrochim. Acta Part B 62, 63–68.
Stodulski, L., Farrell, E., Newman, R., 1984. Identification of ancient persian pigments from persepolis and pasargadae. Stud. Conserv. 29, 143–154.
Tabari, M.A. 11th century, Tohfat al-Gharayeb (ed. Matini, J. 2012). Tehran: Ketabkhaneh-ye Muzeh va Majles-e Shora-ye Eslami.
Teflisi, H., 1956. 12th century. Bayan al-Sana'at. In: In: Afshar, I. (Ed.), Farhang-e Iranzamin, vol. 5. Anjoman-e Asar-e Melli-ye Iran Press, Tehran, pp. 298–457.
Toomanian, N., Jalalian, A., Karimian Eghbal, M., 2001. Genesis of gypsum enriched soils in north-west Isfahan Iran. Geoderma 99, 199–224.
Unknown author, ca. 1447. Javaher-nameh, In: Binesh, T. (ed. 1965), Farhang-e Iranzamin XII, Tehran, pp. 273-297 (in Persian).
Unknown author, 1582, Majmuat al-Sanaya, manuscript kept in the Library of Islamic Parliament of Iran, Registration No. 15617 (in Persian).
Vermeulen, M., Sanyova, J., Janssens, K., Nuyts, G., De Meyer, S., De Wael, K., 2017. The darkening of copper- or lead-based pigments explained by a structural modification of natural orpiment: a spectroscopic and electrochemical study. J. Anal. Atomic Spectrom. 32, 1331–1341.
Wulff, H., 1966. The Traditional Craft of Persia. The MIT Press, Cambridge, Mass.