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Wall Paintings from The Roman City of Volubilis in Morocco: XRF, Raman and FTIR-ATR Analyses

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Abstract. The work is an in-depth investigation of painting remains from the roman city of Volubilis in Morocco, classified World Heritage. Raman and ATR-FTIR structural and XRF elemental spectroscopies were crossed to decrypt the pigments adopted by roman craftsmen in the south Mediterranean region. Red-ochre alone or in admixture with cinnabar was used in brown-red paintings, while yellow ochre, green earth and Egyptian blue pigments were used to achieve yellow, green and blue ones. All pigments highlighted had been commonly used in the roman world, among which some ones continue until the medieval period in Morocco. In addition to documenting built heritage in Morocco, the results provide a helpful background for archaeologists interested in Roman sites around the Mediterranean space.

Introduction

The scientific community has devoted increasing efforts to the investigation of roman wall paintings owing to the widespread presence of the Roman empire [1–6]. In the case of Roman sites in Morocco, archaeometric investigations are very rare; to our knowledge the unique study on painting remains is the one carried out by Gliozzo and al. [7]. Painting analysis provides background supporting conservators, restorators and archeologists.

The Volubilis Roman site in Morocco dates back to the 3rd C. BC [8]; founded initially as a headquarters to control the north of Africa, in the 8th C it became the starting point of Islamisation by Idriss 1st who took refuge in Walila (ancient Volubilis) [9]. Exhibiting exceptional remains (forum, baths, capitol, shopping streets, basilica, etc.), the city of Volubilis was listed as World Heritage by UNESCO in two times: a first part in 1997 and all the 42 hectares in 2008. It is one of the most attracting architectural Roman sites in the south Mediterranean region.

The present on-going experimental work aims exploring a set of eighty wall painting fragments sampled during recent archaeological excavations of Volubilis remains. To achieve the purpose of characterizing painted plasters, different analytical techniques have been combined: elementary compositions were determined by X-ray fluorescence spectrometry (XRF), while coloring phases were identified by crossing micro-Raman and infrared vibrational spectrometries with optical reflectance and X-ray diffraction (XRD) analyses [10–12]. This investigation, which is the first fairly depth one on Roman paintings, is part of a large research program taking aim of the

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establishment of a scientific documentation on ancient architectural heritage of Morocco [13]. The results we present here relate to a sub-set of five representative painting fragments; only XRF, Raman and ATR-FTIR results are reported.

Materials and methods

Materials

Eighty wall paintings fragments sampled in the site of Volubilis have been studied; we will show the results relative to only five representative ones. All samples are stored at the reserve of the INSAP in Rabat.

The five samples are denoted VER6, VER9, VEJ, VEV7 and VEB1 (fig.1); they are selected to show all the colours present in the corpus: brown-red, yellow, green and blue. Their sizes vary from 1 cm x 1,5 cm to 3,5 cm x 4,5 cm, with thicknesses ranging between 1 and 3 cm.

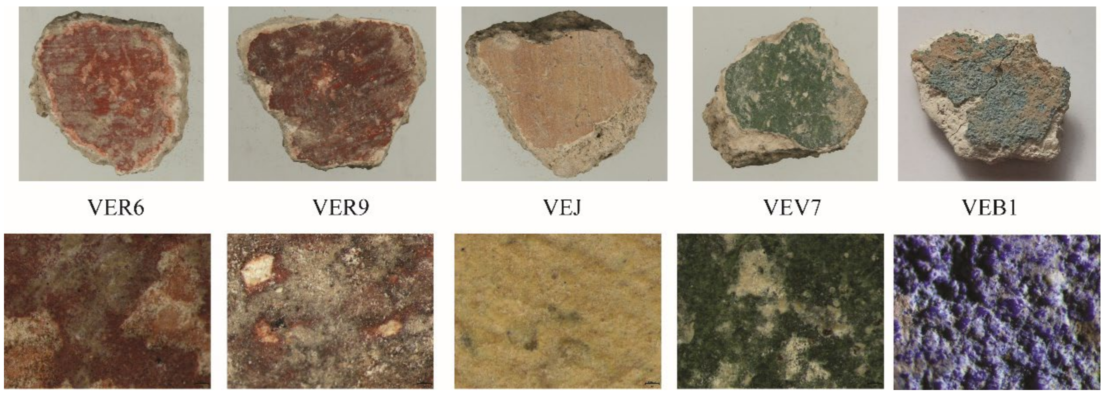

Fig. 1. Photos of the representative samples

Techniques

As a first step, the painting fragments were examined visually by means of a stereomicroscope ZEISS SteREO Discovery V8. The colours were measured as a*, b* and L* chromatic coordinates, using a portable Konica Minolta CM-700d colorimeter piloted by SpectraMagicTMNX; the illuminant is the D65 one and the observer set at 10 °.

The XRF elemental analyses were carried using the handheld portable analyzer S1 Titan from Brucker, based on Rh target/50 kV X-ray tube. The instrument was used in the conditions of its original factory energy calibration, and the acquisition time adopted was 2 × 30 s.

Two spectrometers with two different laser excitation wavelengths were used in Raman analysis; the first one is a Renishaw RM1000 spectrometer equipped with a laser (He-Ne) emitting at 632.8 nm and coupled to a Leica DMLM microscope with 4 objectives (x5, x20, x50, x100). The second one is a HR800 Jobin-Yvon Horiba spectrometer equipped with an ionized Argon Laser providing 458 and 514 nm excitations, and coupled to an Olympus microscope equipped with lenses (x5, x10, x50 and x100). The equipment was adjusted to obtain a power ranging from 70 µW to 4 mW.

The ATR-FTIR spectra were collected, in the range of 4000–400 cm^{-1} at a spectral resolution of 2 cm^{-1}, by means of a Vertex 70 spectrometer (Bruker) equipped with a diamond crystal using a single reflection ATR-Golden Gate accessory (Specac) and managed by the OPUS software. Less than 1 mg of sample powder was pressed on the surface of the crystal.

Mineral phases were identified using Raman and Infrared databases [14,15], and also by means of comparison with published works cited later.

Results and discussion

Brown-red

Samples VER6 et VER9 show brown-red colour with different hues, the corresponding chromatic coordinates a* and b* are positive (fig. 2), with mean values of sample VER6 (a* ≈ 24 and b* ≈ 23) higher than those of sample VER9 (a* ≈ 17 and b* ≈ 14); the lightness ones are medium increasing from L*≈46 for VER9 to L*≈58 for VER6. These chromatic coordinates are practically similar to those reported for red painted plasters from Roman sites [11,16].

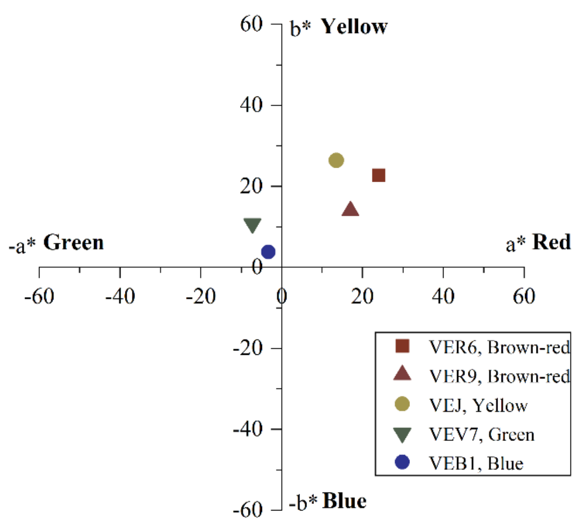

Fig. 2. Chromatic coordinates represented in the Lab space.

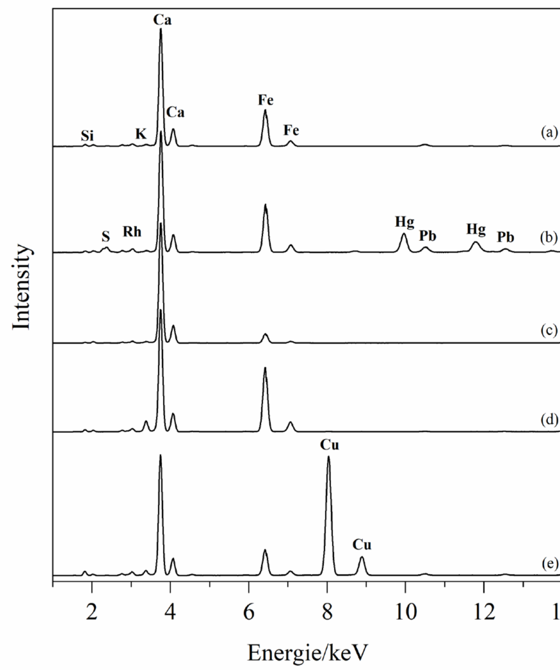

Fig. 3. XRF spectra of samples: (a) VER9, (b) VER6, (c) VEJ, (d) VEV7 and (e) VEB1.

The XRF spectra collected on brown-red areas of VER9 and VER6 samples (fig. 3-a,b) reveal iron (Fe) as a main element with, in the case of the sample VER6, some amount of mercury (Hg) and sulfur (S); in both fragments Calcium (Ca) is the main element. Traces elements such as Si, K and Pb were also detected. To identify the coloring phases, Raman and Infrared spectra were measured. The Raman lines observed on fragment VER9 and located at 222, 242, 290, 405, 608 and 1317 cm^{-1} (fig. 4A-a) are characteristic of hematite (Fe_2O_3) [14], while bands emerging at 250, 283 and 340 cm^{-1} in the case fragment VER6 (fig. 4A-b) are those of Cinnabar (HgS) [14]. The Infrared measurements further the vibrational analyses; hence in both samples the presence of hematite is confirmed by the bands observed at 465 and 527 cm^{-1} (fig. 4B-a,b) [15]. In concordance with the XRF spectra, calcite is also emerging at 217, 285, 711, 870 and 1401 cm^{-1} vibrational frequencies [15]. The non-appearance of cinnabar on these infrared spectra may be explained by the facts that this inorganic red pigment does not absorb in the region 400-4000 cm^{-1} at one hand [17,18], and probably also because of its high refractive index [19].

Other components such as clays in the form of kaolinite, emerging at 1008 and 1030 cm^{-1}, as well as Quartz (SiO_2) in small quantities appearing at 797, 778 cm^{-1} and 695 cm^{-1} [15] are also observed.

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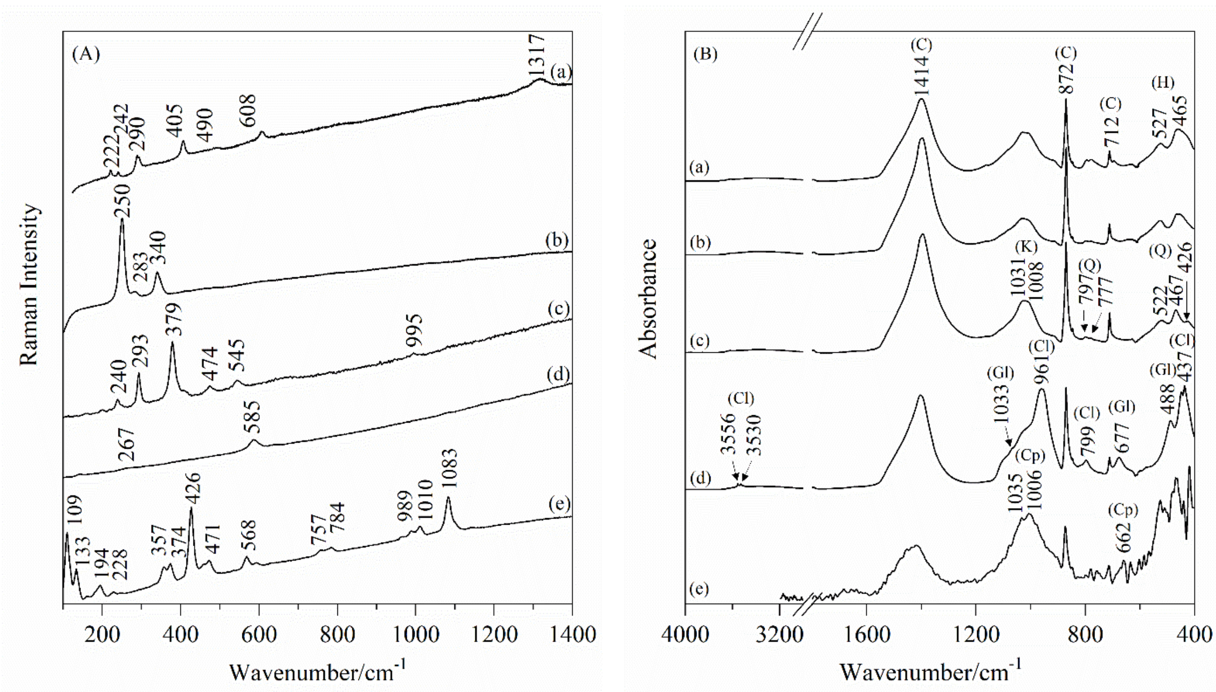

Fig. 4. (A) Raman and (B) ATR-FTIR spectra of samples: (a) VER9, (b) VER6, (c) VEJ, (d) VEV7 and (e) VEB1. (H: hematite, Cn: Cinnabar, Gl: Glauconite, Cl: Celadonite, Cp: Cuprorivaite, C: Calcite, Q: Quartz and K : kaolinite).

The correlation of all the previous results, indicating a coexistence of hematite with clays (possibly in the form of kaolinite [$Al_2Si_2O_5(OH)_4$]), leads to consider red ochre as the main pigment used to prepare the red-brown color. In the case of sample VER6, this pigment is mixed with cinnabar. The silica or quartz observed may be associated with iron oxide or contamination by the mortar layer, they may also relate to impurities present on the surface of the fragments due to their underground burial. Calcite is likely origination from the preparatory layer during the painting process or even while the powder sampling.

The red ochre was widely used by Roman artists in ancient mural paintings [5,20]**.** In some cases, it used to be mixed with cinnabar, a very expensive mineral whose use dates back to the antiquity [19]; primary cinnabar mines were in Spain [16]. The practice of pigment Admixtures was fairly common in Roman and medieval times as an economic necessity, especially for wall paintings [20,21].

Yellow colour

The chromatic coordinates mean values obtained on the yellow area of fragment VEJ are: a*≈ 13,5 for a*, 26,5 for b* and 70 for the lightness L* (fig. 2). They are characteristic of yellow shades and similar to those already reported in the case of other sites [1,16]. The corresponding XRF elemental composition (fig. 3,c) is similar to those revealed by the brown red fragments (fig. 3-a,b). However, the relative low content of iron (Fe) leads to the assumption that the yellow pigment used is an iron-based one such as goethite. This assumption is confirmed by the structural Raman analysis recorded on the yellow area, showing lines at spectra at 240, 293, 379, 474 and 545 cm^{-1} (fig. 4A-c) characteristic of goethite ((α-FeO(OH)) [14]. The complementary infrared analysis of VEJ doesn't show any goethite signal probably a very low amount of this pigment was used to achieve the yellow color. Similarly to the case of brown-red areas, calcite and quartz are also identified on the infrared spectrum. Consequently, the main pigment used is yellow ochre in the form of goethite which was widely used in Roman times [5,20]**.**

Green colour

Regarding the green area of fragment VEV7, the chromatic coordinate values are ≈ -7,21 for a* and ≈ 2,7 for b* quietly consistent with the green shade. The measured lightness L*≈ 54 is also in concordance with the observed clarity of the green painting layer (fig. 2). The elementary analysis of this green colour revealed by XRF measurements (fig. 3-d) shows a high content of iron (Fe) with some amount of K and Si, in addition to the commonly observed high content of calcium (Ca). This indicates the use of an iron-based green pigment. The Raman spectra recorded on this green area (fig. 4A-d) exhibits a low intensity band around 267 cm^{-1} along with another signal at 585 cm^{-1}, attributable respectively to glauconite $[(K,Na)(Fe^{3+}, Al, Mg)_2(Si,Al)_4O_{10}(OH)_2]$ and to celadonite $[K[(Al, Fe^{3+}), (Fe^{2+},Mg)](AlSi_3, Si_4)O_{10}(OH)_2]$ which are minerals forming the green earth pigment and responsible of the observed green color [22,23].

The high intensity bands at 437 and 961 cm^{-1} observed on the ATR-FTIR spectrum, measured on a micro-sample taken on the same green zone (fig. 4B-d), are those of celadonite; the lower intensity and less resolved ones located around 488, 677 and 1033 cm^{-1} correspond to glauconite [15,22]. Calcite characteristic bands are also observed. Green earth pigments are composed of several minerals whose proportions vary depending on the ore deposit; the most abundant ones are glauconite and celadonite [23]. Consequently, the green colours were obtained by the use of green earth pigments that have been identified in painted plasters dating back to the Roman period [5,20]**.** During Antiquity, the Romans especially employed these green earth pigments when painting in fresco where the pigments are impregnated on a freshly spread moist lime plaster, technique well known to fix the colours on the wall [23].

Blue colour
The chromatic coordinates mean values corresponding to the blue area of fragment VEB1 are: a* ≈ -3,7, b* ≈ 2,7 and L*≈ 67. The corresponding point on the Lab diagram seems very close to the achromatic region because of the low value of the yellow/blue coordinate b* (fig. 2). The XRF elementary composition measured on this blue paint revealed a high content of copper (Cu) along with other relatively low amount elements such as iron (Fe), silicon (Si) and lead (Pb) (fig. 3,e), indicating thus the use of a copper-based blue pigment. The structural Raman analysis carried out on the same zones (fig. 4A-e) revealed signals at 109, 426 and 1083 cm^{-1} characteristic of Egyptian blue ((cuprorivaite, $CaCuSi_4O_{10}$), besides other bands of different intensities located at 133, 194, 228, 357, 374, 471, 568, 592, 757, 784, 989 and 1010 cm^{-1} [16,24]. The Infrared measurements of micro-sample from this blue pictorial layer corroborate the use of Egyptian blue by its bands observed at 662, 1006 and 1035 cm^{-1} (fig. 4B-e) [5,25]. This pigment has also been identified in wall paintings from the Roman site of Thamusida in Morocco [7]; it was commonly used in several Roman sites in Spain and Italy [2,26].

Conclusion

In the course of the establishment of a scientific documentation on architectural heritage sites in Morocco, a set of eighty wall painting fragments from the Roman city of Volubilis have been investigated by means of different analyses combining elemental XRF and structural Raman with ATR-FTIR techniques, supported by other ones.

Here, are presented the results relative to a sub-set of five representative painting samples exhibiting a large palette of colours ranging between red-brown, yellow, green and blue. All pigments used have identified. Hence, brown-red paintings had been achieved by using either red-ochre alone or in admixture with cinnabar, yellow ochre was used for yellow, green earth for green and Egyptian blue for blue. This palette represents the typical one commonly used in the roman world.

On the insight of the on-going CH scientific documentation results, it seems that in Morocco, the use of red ochre and cinnabar had been maintained until the medieval period for brown-red shades, while malachite replaced green earth for green colours and azurite or lazurite replaced Egyptian blue for blue ones.

Going deeper into the investigation, stratigraphic analysis and cross-section examinations are in progress; they are focusing on the painting techniques adopted throughout Roman and medieval periods in Morocco.

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