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In situ noninvasive Raman microspectroscopic investigation of polychrome plasterworks in the Alhambra

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A totally non-invasive *in situ* investigation in one of the main halls of the Palace of the Lions in the Alhambra (Granada, Spain) has been carried out. Analyses were made with a fiber-optic portable Raman microspectrometer placed on scaffolding platforms at a height of *ca.* 12 m above the ground level during the period of conservation works. The objects of this study are the decorated plasterworks in the seven vaults of the Hall of the Kings. Together with the results, the different practical problems related to the positioning of the instrumental setup and the influence of the local environment during the analysis are discussed. In general, high quality spectra were obtained despite difficulties for micro-probe head positioning and sometimes the vibrations of the corresponding scaffold. Different typical antiquity pigments have been identified: cinnabar, minium, carbon black and lapis lazuli. Furthermore, the luminescence pattern from lapis lazuli found in most blue decorations has allowed the establishment of the natural origin and provenance of the pigment. Apart from this natural lapis lazuli, synthetic ultramarine blue was also found in one of the vaults showing up a recent restoration. In addition, some degradation products of cinnabar and minium were identified, with the major advantage of providing real-time information to the conservators during their work.

Introduction

In recent decades, several advanced analytical methods have been successfully employed to investigate cultural heritage materials working on either minute bulk samples or cross-sections.[1–4] However, the use of these micro-destructive techniques reveals two main limitations. First, the requirement of sampling that even minimal can be not advisable when dealing with irreplaceable or precious items. Second, even in cases where micro-samples are available the sampling sites may not be totally representative of the entire artwork.

Noninvasive analytical tools and methodologies that can provide a chemical description of cultural heritage materials without any contact with the object are becoming increasingly important due to the capability of studying precious and irreplaceable artworks without compromising their integrity.[5,6] Furthermore, the noninvasive approach permits the examination of the artwork with a virtually limitless number of measurements that can guarantee representativeness.

Over the last decade, Raman spectroscopy has become increasingly used for the study of works of art.[7,8] Most of the research has been carried out in the laboratory working on different kinds of samples: fresco and stucco fragments,[9,10] embedded cross-sections,[11,12] minute pigment grains, objects with small dimensions such as ancient pottery fragments,[13–15] loose leaves of manuscripts[16] and so on. Furthermore, the advances in mobile and portable Raman instrumentation allow bringing analytical equipment from the laboratory to the artwork, rather than the reverse, achieving the benefits of the totally non-invasive approach.[17] However, the use of portable Raman instrumentation *in situ* is not straightforward and many practical problems have already been reported in different situations, far from the ideal conditions of a laboratory environment, like the study of mediaeval wall paintings,[18–20] urban steel sculptures[21] and stained glass windows.[22]

This work presents the results of the *in situ* Raman spectroscopic study of Nasrid decorated plasterworks, situated on the vaults of the Hall of the Kings in the Lions Palace, at the Alhambra. The Alhambra Complex, in Granada, Spain, is the best example of Nasrid art and one of the most important monuments in Spain. Throughout its history, the Alhambra has experienced many transformations, keeping testimonies of each period. It was built and decorated during the Nasrid period in the XIII–XVth centuries. Then it was adapted during the first period of Christian domination in the XVIth century. Neglected for centuries, it was rediscovered in the XIXth century, when the

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most generalized restorations began. This work is aimed at the study of Nasrid plasterwork in one of its most characteristic ornamental elements, the vaults of the Hall of the Kings. The so-called vaults of *mocarabes* or stalactites are self-supporting domes built up with gypsum and a wood supporting structure. In these, vertical prisms applied one over another would be joined in multiple different arrays resembling stalactites of a cave. Nasrid *mocarabes* are usually decorated with a wide range of colors and are unique in western Islam.

Whereas previous studies on Nasrid plasterwork have been limited to fragments or isolated samples[23–25] here a complete study of the different vaults of the Hall of the Kings is approached. Thus, our first contribution to this wide project of restoration is to provide real-time information about the materials present in the plasterwork using portable Raman microspectroscopy. These materials can be either the original materials employed by the Nasrid artists or those used in the several restorations or even degradation products. Hopefully, this information, in combination with the knowledge of the conservator from our team and historical data, will throw light about the original chromatic aspect of the vaults, the techniques employed, the extent of the restorations and the reasons for the degradation of the polychromes.

The Hall of the Kings

The Hall of the Kings is structured around a large vestibular hall, more than 30 meters long. It is covered with seven vaults of *mocarabes* that have been numbered from 1 to 7 starting from the southern side of the Hall. Fig. 1 shows a scheme of the Hall in which three big squared vaults (V2, V4 and V6) alternate with four rectangular ones of smaller size (V1, V3, V5 and V7).

A singular characteristic of these vaults is that each of them is unique thanks to different combinations of vertical prisms of plasterwork applied one over another and joined using a wood structure to form the vault. The Hall has suffered at least two previous interventions during the XIXth and XXth centuries in order to consolidate the structure of the vaults. The seismic activity of the area together with the explosion of a close ammunition store in 1590 damaged the vaults causing cracks through which rainwater penetrated into the hall.

During the first period of Nasrid art, the gypsum plaster was applied and then carved. Afterwards moulds were also used.[26] The plasterworks of the vaults were richly painted in a wide range of colors mainly red, blue, green, golden and black. These polychrome works are in different conservation states depending on the area of each vault. In V1 signs of previous interventions are clearly observed with re-buildings of plaster in many of the *mocarabes* and re-paintings with poor artistic quality. This vault suffered from severe water seepage due to problems of roof covering. V2 also presents a large diagonal crack with partial displacement towards the south-east. Considering the other two big squared vaults, V4 presents a side where the decorations are completely lost whereas in V6 decorations are better preserved. V3 and V5 are the smallest vaults and V7 is the one with higher risk of collapsing. Its polychromy shows a delicate execution but it is almost completely lost in many areas.

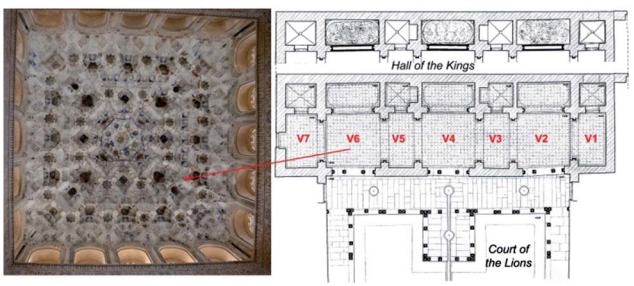

Fig. 1 Floor plan of the Hall of the Kings where the seven vaults are indicated. The photograph corresponds to vault 6.

Instrumentation

A portable innoRam spectrometer (B&W TEK Inc., Newark, USA) provided with a 785 nm excitation laser line and a back thinned two-dimensional CCD detector thermoelectrically cooled at −20 °C was used. The spectral range of the spectrometer is 65–2565 Δ cm^{-1}. It weighs about 10 kg. The spectrometer and laser are connected to a probe head with optical fiber cables (excitation fiber—100 μm; collection fiber—200 μm). The Raman microprobe was attached to a video microscope with an integrated camera and an LED illuminator to allow precision spot sampling. The video microscope with the Raman microprobe was mounted on a tripod, motorised in the *X*–*Y*–*Z* axes with a remote control and a spatial resolution of 1 μm per electrical pulse (Microbeam, Barcelona, Spain). An external camera was used to obtain a macro-image during probe positioning. A 20× long-distance objective lens was used providing a laser spot size about 85 μm in diameter. For the measurements the instrument was carried by hand to top of the platform of the 12 m high scaffold.

The laser power used during the measurements was set to a few milliwatts to prevent pigment photodecomposition. Typical acquisition times were 1 to 10 accumulations with exposition times of 1–5 s each. During this study, more than 300 points have been examined, resulting in *ca.* 500 useful spectra.

Results and discussion

As it has been explained above, the *mocarabes* of the Hall of the Kings are situated on the vaults of the hall. Therefore, to be able to reach the painted areas for the conservation works, scaffoldings were erected for each vault at a height of *ca.* 12 m above the ground level. The Raman instrument as well as its accessories and the positioning equipment were installed on top of these scaffolds for the study (Fig. 2).

Raman measurements in laboratories are usually made in the dark to avoid sunlight perturbations and therefore on-site conditions have reported to experience difficulties in this regard.[17,22] Here we did not observe any strong influence due to sunlight probably because of two different reasons. First, we employed a higher magnification objective (20×) that made the measurements less sensitive to the outside light due to the shorter working distance. Furthermore, the characteristics of the *mocarabe* vaults with their small lattice windows and the cave-like spatial disposition prevented direct sunlight from reaching the measurement areas. In contrast in many cases this constituted an obstacle for the measurements because sometimes the space

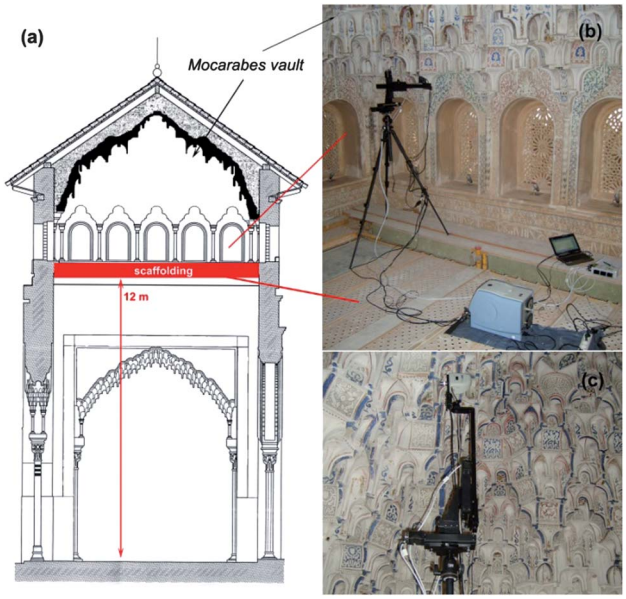

Fig. 2 (a) Vertical section of one vault in the Hall of the Kings. Height of the scaffold is marked as well as the *mocarabes* vault scheme. Raman micro-spectrometer located in vault 4, (b) complete instrument on top of the scaffolding and (c) details of the microscope probe.

between *mocarabes* was so tight that it was very difficult to position the measuring head. This problem was especially important in V3 and V5, these vaults were the narrowest and with lowest ceilings. Here the probe head of the fiber optics was used directly by removing the video microscope and the objective. In addition, for the investigation of some carved motifs the 20× objective focal distance was too short and the decoration inside the relief could not be brought into focus. In these cases a 10× objective with a longer focal distance was employed. Despite all these considerations, we succeeded in obtaining a wide number of Raman spectra of good quality that allow us to identify the materials employed appropriately. In order to show this, all the spectra presented in this work have no pretreatment or smoothing.

Characterization of pigments employed in the decoration of *mocarabes*

Although the main interest of this work is the characterization of the pictorial layers, we also investigated the plasterwork substrate because it can provide information about the execution technique of the building and assembly of the *mocarabes*. We found two different gypsum substrates. One coarse gypsum with abundant calcite impurities and another much more pure gypsum that provided only the spectra of dihydrated calcium sulphate with clear bands[27] at 414, 495, 670, 1009 and 1134 cm^{-1}. Furthermore, in many areas, we found a finishing outer layer with a satin surface. In these spectra the gypsum bands were overlapped with a strong fluorescence background that suggests the use of some organic additives possibly employed to protect gypsum against water.

According to colored decorations in the vaults of the Hall of the Kings, red and blue/green colors are the most common. Furthermore, black color was found in the contours of the drawings and in some geometrical decorations with circles or zig-zag lines.

Carbon black with characteristic broad bands[27] around 1334 and 1594 cm^{-1} was identified in all these motifs (Fig. 3). This is as a generic name for black pigments that are made from the partial burning of natural organic matter, like wood or vegetables. Ivory black or bone black was also a typical black pigment obtained by burning bones. The Raman spectrum is similar, with the signature typical of carbon and a diagnostic band due to phosphate around 960 cm^{-1}. The presence of this pigment cannot be totally disregarded because in some of the spectra a small band can be observed in this region. However, the spectra obtained from black areas are in general of poor quality because the black pigment tends to absorb most of the light in the visible and near infrared regions and the laser power has to be very low in order to avoid burning.

We can state that blue color is the most used in the vaults of the Hall of the Kings especially in the bigger ones, V2, V4 and V6. Most of the spectra retrieved within them presented a band at 548 cm^{-1} characteristic of the symmetric stretching vibration of S_3^- in lazurite ($Na_8[Al_6Si_6O_{24}]S_n$), the mineral responsible for the bright blue color of lapis lazuli[28] (Fig. 4). Furthermore the spectra also showed a strong luminescence background together with several bands, the most intense located at 1306 and 1508 cm^{-1}.

In the spectra registered in different locations the relative intensity of these bands was observed to remain constant, but the overall intensity with respect to the diagnostic lazurite peak varied. This pattern has been observed previously[29] and reported to occur only for natural lapis lazuli and only when a 785 nm laser is used for excitation. The fluorescence of natural minerals is usually due to intrinsic defects in their structure or trapped impurities. Thus, these bands have been attributed to luminescence of diopside ($CaMgSi_2O_6$), a mineral commonly associated with lapis lazuli in nature, containing transition metal dopants. Interestingly, according to Schmidt *et al.*[29] the presence of these characteristic nonlazurite fluorescence/vibronic features not only indicates that a particular ultramarine (lapis lazuli) pigment is derived from a natural source but, more significantly, may be indicative of its particular geological origin. The spectra recorded in the Hall of the Kings have the same fluorescence pattern which

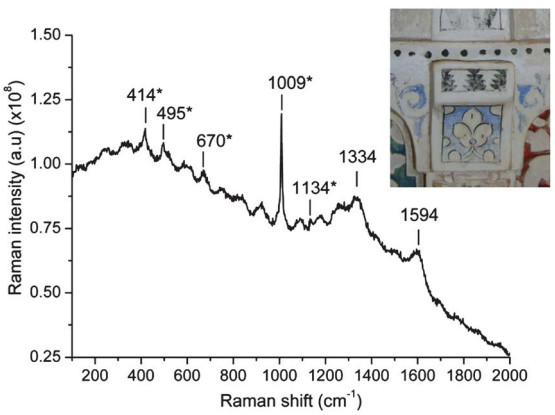

Fig. 3 Raman spectra of carbon black registered in black decorations in V7 of the Hall of the Kings together with the corresponding photograph where linear decorations in black color can be appreciated. Gypsum bands are also observed and marked with *.

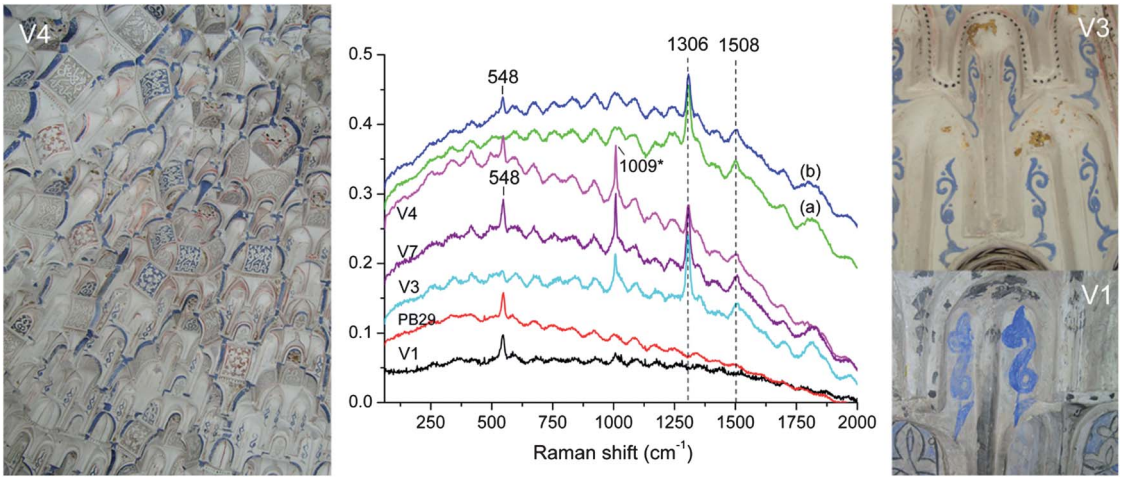

Fig. 4 Photographs of different vaults in the Hall of the Kings with blue decorations. Raman spectra registered in different vaults are accompanied with those of synthetic ultramarine blue PB29, natural lapis lazuli pigment (a) and lapis lazuli rock fragment from Afghanistan (b).

indicates the same geographical origin of the pigment. The lapis lazuli mines in the Badakhshan region of Afghanistan that have been exploited since ancient times are believed to have been the unique source of the lapis lazuli pigments used in Europe during the Middle Ages. As can be seen in Fig. 4, the Raman spectrum of a natural lapis lazuli sample from Afghanistan shows a luminescence pattern identical to the pigments of the Hall of the Kings, which confirms the geographical origin of the pigment.

In fact, the Afghan lapis lazuli is found in veins in which calcite and dolomite are intimately associated with silicates such as diopside.[30] Because of the remote geographic origin and the costly method by which the pigment is extracted from the stone this blue pigment has been one of the most costly and precious of the artist materials equaling and sometimes exceeding the price of gold. Here this pigment is profusely used for the decoration of the vaults which reflects the importance of this Palace and this Hall. It is interesting to point out that in some motifs found in V1 the characteristic spectrum of lazurite without the luminescence bands was observed indicating a synthetic origin of the pigment. Since artificial ultramarine, similar in chemical composition to lazurite,[28] was first synthesized in 1828 these motifs must be attributed to a restoration carried out no early than the end of the XIXth century. In fact, in contrast with the delicate execution of other decorations of the hall, the painting technique in these motifs is much clumsier.

Green decorations are not abundant in the vaults of the Hall of the Kings and did not show a Raman spectrum of sufficient quality. The same happened for some areas with pale blue-greenish decorations. This might be due to the fact that the available excitation line at 785 nm is strongly absorbed by green pigments and therefore the laser power must be reduced for these investigations to prevent photodecomposition. Furthermore, scaffolding vibrations made the use of measurement times longer than a few minutes difficult. In addition, in many cases a strong fluorescence background probably due to an organic binder was observed. For these reasons no useful information was obtained about green and bluish-green pigments and micro-samples were collected for their analysis in the laboratory with a different laser.

Red is also a very common color in the decoration of *mocarabes* vaults and two pigments were used to provide this color. Cinnabar (HgS) was clearly identified due to its strong Raman scattering with characteristic bands[31] located at 251, 284 and 340 cm^{-1}. Decorations with cinnabar were found frequently in the edges of the motifs, applied with a delicate and precise technique. It was also found hidden under layers of lime that were removed during the on-going conservation works. In contrast, minium (Pb_2O_3) with characteristic bands[31] at 121, 150, 221, 312, 390 and 548 cm^{-1} was found in the most exposed ornaments and frequently the color appeared darkened showing even a dark-brown tone. Furthermore, some motifs include decoration using both red pigments.

Investigation of pigment alterations

Once the main pigments have been identified we have also paid attention to the origin of the different chromatic alterations that can be appreciated. Blue decorations identified as lapis lazuli do not appear altered which is consistent with its already known stability.[32] However, there are some regions where the color has almost disappeared probably due to water leaking or degradation of binders. The most intense chromatic changes are observed in red decorations, which in many places showed a dark red-brown color. In these darkened areas different alteration products were identified. Most of the spectra registered corresponded to minium but with additional features at 141 and 978 cm^{-1} (see Fig. 5).

The latter band can be attributed to anglesite, $PbSO_4$. The formation of anglesite from minium has been reported to occur in acidic media due to a disproportionation process giving rise to both lead dioxide (in the form of plattnerite β-PbO_2) and Pb(II) ions.[33] Pb(II) forms anglesite in a medium rich in sulphate like gypsum. The darkened colour must then be attributed to the black plattnerite formed, although the characteristic Raman bands of this compound were not observed here. The reason is that plattnerite is a very weak Raman scatterer and degrades under laser exposure even at a low power. In fact, the band at 141 cm^{-1} can be attributed to the formation of minute amounts of the strong scatterer lead monoxide (PbO) due to laser irradiation of plattnerite.[34] It is also interesting to note that besides dark-brown areas of altered minium we also observed other areas

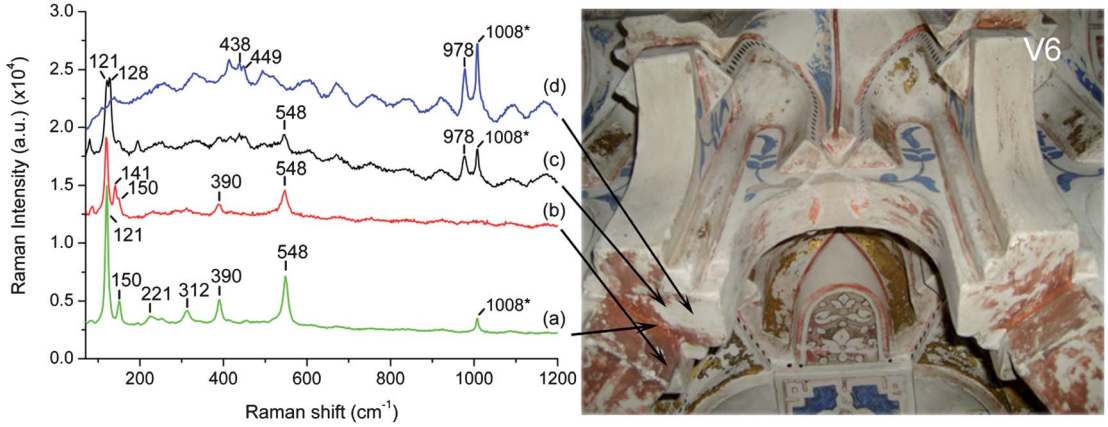

Fig. 5 Image of red decorations in V6 where degradation of minium can be observed. Raman spectra correspond to (a) unaltered minium, (b) altered minium showing the band at 141 cm^{-1}, (c) altered minium where anglesite can be detected, and (d) anglesite with no remnants of minium.

where the brown color was practically lost. Only anglesite was identified in these areas of dirty white color together with the Raman signatures of the gypsum substrate. Since lead dioxide is a strong oxidizing agent, it slowly transforms into the more stable anglesite, which is white. Thus, the alteration of minium initially produces darkening but ends with the total loss of the color.

Darkening phase:

$$\text{Red lead } (Pb_3O_4) \rightarrow \text{plattnerite } (PbO_2) + \text{anglesite } (PbSO_4)$$

Decoloring phase:

$$\text{Plattnerite } (PbO_2) \rightarrow \text{anglesite } (PbSO_4)$$

Curiously, a different alteration of minium has also been detected. In Fig. 6 where a typical Nasrid decoration of vegetal ornaments in relief (*ataurique*) is depicted, we can see the pigment in different stages of conservation producing different colors, from bright red on the bottom to dark-brown on top. The spectra registered on the bottom of the decoration correspond clearly to red lead (Fig. 6a). However, moving up to the red-brown areas of the motif, a new Raman band developing at 104 cm^{-1} can be observed and in the more darkened areas of the top, the bands of minium are totally lost (Fig. 6c). This material could not be identified but potential candidates are mixed crystals of lead oxides. The very strong band at 104 cm^{-1} could be assigned to a Pb–Pb stretching vibration similar to that occurring in Pb_3O_4. In these cases, the formation of anglesite was not detected.

Another common observation was the presence of motifs in white with a grayish background color. It gave the impression of being grey remaining of a color already lost. The collection of good spectra in these motifs was not straightforward and in many cases, only gypsum bands of the substrate on a fluorescence background were retrieved. Nevertheless, the characteristic spectrum of cinnabar could also be clearly identified in the grey areas despite a low intensity. Sometimes also remnants of red color were observed, and when focusing on the red particles very good quality spectra of cinnabar were obtained. In some of the cinnabar spectra obtained an additional band at 164 cm^{-1} was identified.

This band can be assigned to calomel $(HgCl)_2$ and it was also detected in blackened areas of red decorations of cinnabar (Fig. 7). Cinnabar blackening is a well-known phenomenon but its causes and mechanism are not fully understood. This alteration process was already observed since antiquity, and even Vitruvius described the change of the bright red of cinnabar

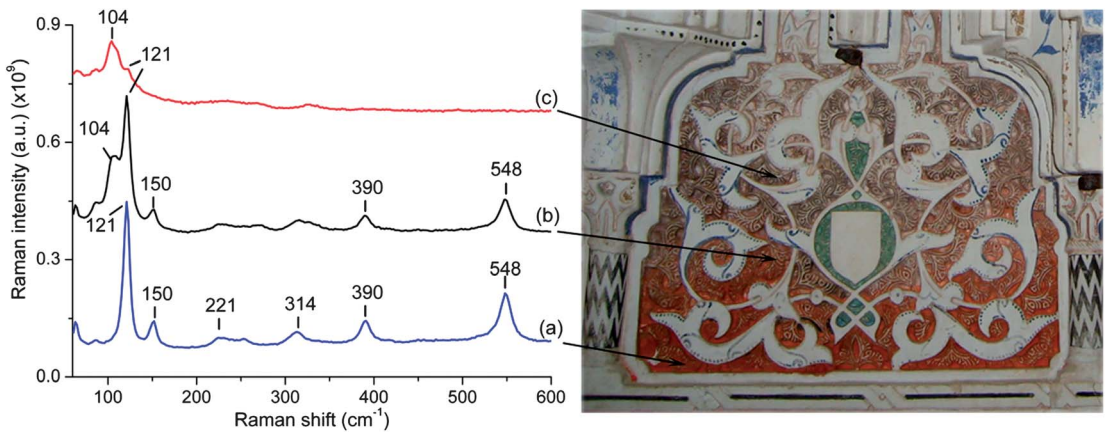

Fig. 6 Different stages of minium degradation observed in a red colored *ataurique* in V4. Raman spectra correspond to the points located in the relief from (a) unaltered minium to (c) completely altered minium.

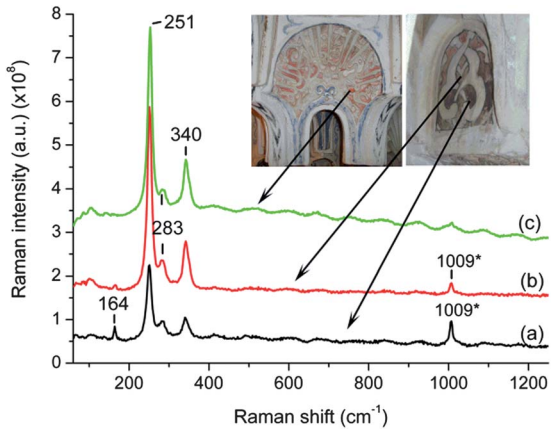

Fig. 7 Cinnabar alteration to calomel. Photographs represent red colored decoration in (a) a good state of conservation and (b) completely degraded where the red color is only a remnant. Raman spectra correspond to these points in V2 and V3 respectively.

when exposed to light.[35] Different studies on both easel paintings[36,37] and wall paintings[38] together with laboratory tests and artificially aged samples[39] using different analytical techniques have shed some light on the problem. In all the cases the presence of different Cl–Hg and Hg–S–Cl compounds was identified, whereas in contrast to the classical hypothesis, no black metacinnabar was found in any of the studies. Chlorine was always involved in the blackening phenomenon either as a catalyst of the photodegradation of cinnabar in a humid environment to produce Hg(0) and S(0) or to react with Hg(0) or HgS to produce Hg–Cl compounds. However, there is no total agreement about the identity of the species responsible for the black color. Keune and Boon[37] attributed the blackening to the deposition of elementary mercury nanoparticles on the surface of the remaining cinnabar, whereas according to Cotte *et al.*[38] other Hg–S–Cl containing compounds could contribute to the dark color. In our case, the observation of the degraded areas at different stages indicates that after an initial darkening of the surface the degradation evolves through the grey color to a progressive lightening. In all the cases only the white compound calomel $(HgCl)_2$ was identified whereas no $HgCl_2$ was detected in agreement with the observations for Pompeian cinnabar paintings.[38]

A major question arising at this point is the origin of the chloride ions. Natural impurities of cinnabar have been reported to be enough to induce photodegradation of the pigment.[40] However, in those areas where calomel is detected the amount of chloride is hard to explain from an original cinnabar source alone. External sources of chloride like environmental pollution have been suggested as explanation for cinnabar degradation in previous studies.[36–38] This can be a plausible explanation especially for geographical locations close to the sea, due to the marine aerosol. However, considering the location of the Alhambra in Granada such sources of chloride ions are not very probable. Another possibility would be the binder employed. This origin would also be supported by the fact that there are also many areas in the vaults where cinnabar has suffered no degradation. Further studies on the stratigraphy of micro-samples from areas suffering different extent of degradation together with complementary analytical techniques will probably help to clarify the origin of the chloride ions as well as the influence of the painting technique on the degradation of cinnabar.

Conclusions

This work has demonstrated the suitability of the portable spectrometer and positioning accessories to obtain good quality Raman spectra when operating under non-laboratory conditions (*e.g.* dust, scaffolding, vibrations, daylight, and temperature differences), as occurring during this survey. The main practical problems encountered had been related to lack of space for probe positioning due to the typical stalactite like disposition of the *mocarabes*. Vibrations of the scaffolding also made the recording of spectra from weak Raman scatterers like the green pigments difficult. Most pigments have been identified in real time, thus assisting conservators during their work in a highly valuable way. Providing the spectrometer with an additional 514 nm laser would probably help in the identification of blue and green pigments although the risk of suffering from fluorescence interfering effects with this excitation wavelength is higher. Despite these difficulties, the survey was continuously implemented during the conservation works, providing real time information to the multidisciplinary team of professionals in charge of the restoration.

Concerning the investigation of the Hall of the Kings, we can conclude that red areas were painted with cinnabar and minium. The position of cinnabar could indicate that this pigment was originally used by Nasrid artists although it was also used in restorations. In contrast, minium seems not to correspond to original decorations. Both red colors showed a darkening due to degradation products some of which have been identified by Raman spectroscopy (anglesite and calomel). Black decorations showed always the Raman signature of carbon. The blue pigment identified was natural Afghan lapis lazuli. Synthetic ultramarine blue was detected only in V1 revealing a recent restoration.

Acknowledgements

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