

# Decorated plasterwork in the Alhambra investigated by Raman spectroscopy: comparative field and laboratory study<sup>†</sup>

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This work presents the results of the study of plasterwork decorations located on the stalactite vaults of the Hall of the Kings in the Alhambra (Granada, Spain) by means of Raman micro-spectroscopy. Field investigations were carried out *in situ* using a portable Raman spectrometer during a conservation campaign in a completely non-invasive manner. In addition, taking into account the results obtained, a well-directed sampling was carried out to obtain complementary information by means of laboratory studies. Despite several practical problems during the non-invasive field studies (like difficulties for probe positioning and vibrations of the scaffolding), almost all the pigments present in the decorations of the Hall were identified using excitation at 785 nm: cinnabar, minium, carbon black, natural lapis lazuli and synthetic ultramarine blue. In addition, evidence of different degradation mechanisms of the red pigments was obtained *in situ*. On the contrary, the identification of blue-greenish and green pigments had to be performed on microsamples using a Raman microscope with excitation at 514 nm in the laboratory. In samples with blue and green areas, azurite severely degraded to clinoatacamite was identified. These were probably the remains of the oldest blue decorations. In addition, a technique for green decorations consisting on copper chlorides mixed with a small amount of lapis lazuli was identified. Other degradation products, identified in the laboratory regardless of the color of the pigment, were calcium oxalates. Finally, the laboratory studies also enabled the investigation of the stratigraphy of the pictorial layers. In this way, the presence of re-decorations with overlaying layers of pigments even of different colors was revealed. Copyright © 2014 John Wiley & Sons, Ltd.

**Keywords:** plasterwork; portable Raman; pigment degradation; copper hydroxychlorides

## Introduction

This work presents the results of a thorough study of the pigments of the decorated vaults of the Hall of the Kings in the Alhambra (Granada, Spain) using Raman spectroscopy. The Alhambra is the best surviving example of medieval Islamic architecture in Europe and one of the most visited monuments in the world. This complex was built and decorated during the Nasrid period in the 13th–15th centuries. The Alhambra had suffered alterations to the monument's structure and decorations, following the Christian conquer in 1492, as well as the gradual decay occasioned by extended periods of disuse. The most important and generalized restorations took place in the 19th and 20th centuries.

Our study will focus on the ornaments known as *mocarabes* or *muqarnas* that decorate the vaults of many rooms in the Alhambra. This decoration consists of vertical gypsum prisms applied one over another and joined in multiple different arrays resembling the stalactites of a cave. It is one of the most original inventions of Islamic Architecture.<sup>[1]</sup> Usually, in the Alhambra, the white finishing of the gypsum plasterwork of the *mocarabes* is decorated with geometric and vegetable motifs in several colors. They were probably applied using a *secco* painting technique employing an organic binding medium as reported for other Islamic decorations in different monuments.<sup>[2–4]</sup>

For this study, we will combine field investigations using a portable Raman spectrometer to carry out a non-invasive characterization of the decorations with a complementary laboratory study to address those aspects that cannot be fully investigated *in situ*.

In recent years, non-invasive spectroscopic techniques have played an increasingly important role in art conservation. Spectroscopic methods can be used to gain a deep understanding of the material composition of art objects while fully respecting their integrity and value.<sup>[5–7]</sup> Among them, Raman spectroscopy has received special attention. Considerable improvements in detector technology, instrument–computer interfacing, focusing optics and the robustness of air-cooled lasers as excitation sources have led to the development and successful application of a series of portable Raman instruments<sup>[8–10]</sup>.

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Recently, the evolution of this technology and its application in the field of cultural heritage have been reviewed with special focus on the discussion of the advantages and drawbacks of the mobile Raman technique.<sup>[11]</sup> With this work, we will contribute to a further knowledge of the possibilities and limitations of state-of-art Raman portable instrumentation and to demonstrate how a suitable combination of non-invasive investigations with micro-invasive studies can provide a comprehensive understanding of the artwork under study with minimal impact. All the work has been carried in close cooperation with the conservators and with the final aim of providing them with more scientific knowledge to enable the safeguarding of this unique monument. Thus, this work will provide a better understanding of the polychrome decorations of the Alhambra plasterwork, the transformations they have experienced throughout the history and the decay processes affecting them. Our results will be compared with previous studies carried out with a limited number of samples belonging to other spaces of the Alhambra<sup>[12,13]</sup> in order to shed some light on the complex chronology of the decorations of the Alhambra.

## Experimental

### Instruments

The *in situ* studies were carried out with a portable innoRam spectrometer (B&WTEK Inc, Newark, USA) covering a spectral range from 65 to 2565  $\text{cm}^{-1}$  employing a 785 nm excitation laser. The weight of the spectrometer is about 10 kg. It was equipped with a fiber optical probe head attached to a videomicroscope, which was mounted in a tripod motorized in the X–Y–Z axes with remote control. A 20 $\times$  long-distance objective lens was used providing a laser spot size about 85  $\mu\text{m}$  in diameter. A detail of the probe head of the instrument, when working in the Hall of the Kings, is depicted in Fig. 1a.

The laboratory studies started with the examination of the samples under stereozoom. In addition, polished thin cross sections (embedded in epoxy resin) were studied with an Olympus BH-2 petrographical microscope equipped with digital camera.

Raman spectra were recorded on a Renishaw (in Via Reflex) spectrometer equipped with a Peltier-cooled CCD detector. The system, equipped with a Leica microscope with different objectives (5 $\times$ , 20 $\times$ , 50 $\times$  and 100 $\times$ ) to focus the laser on the sample and a color video camera, allowed for positioning of the sample and selection of a specific region for investigation. Two different lasers, a 785 nm diode and a 514 nm ion Ar laser, were available for excitation. The 520.7  $\text{cm}^{-1}$  peak of a silicon standard was

employed for calibration. Both raw samples (without any manipulation) and cross sections were studied.

During the recording of Raman spectra (both in field and in laboratory studies), the laser power was always set to the minimum in order to avoid sample damage (typically 1–3 mW).

Complementary scanning electron microscopy studies and energy dispersive X-ray spectroscopic (EDX) analysis were carried out with a Carl Zeiss field emission scanning electron microscope (FESEM) model SUPRA40VP.

### Description of samples

Samples were carefully taken by the conservator of our team with the aid of a scalpel. The locations were selected on the basis of the real time results provided by the *in situ* investigations and taking into account the previous knowledge about the whole monument. In this way, a good compromise between the selection of representative areas and a minimal impact on the monument was reached.

## Results and discussion

### Non-invasive field studies

The Hall of the Kings consists in a large vestibular room covered with seven vaults, three big squared vaults that alternate with four rectangular ones of smaller size. This space represents a magnificent example of Islamic stalactite vaulting, a self-supporting structure built up of *mocarabes* (see Fig. 1b). The white finishing of these *mocarabes* was decorated with a wide range of colors mainly red, blue, green, black and golden. This Hall has suffered at least two previous interventions during the 19th and 20th centuries to consolidate the structure of the vaults. Structural damage, probably due to the seismic activity of the area,<sup>[14]</sup> was especially relevant in the two small rectangular vaults located at the two opposite sides of the Hall.

Our *in situ* investigation was carried out in close collaboration with the conservators during a recent intervention.<sup>[15]</sup> The portable Raman instrument was carried by hand to the platform located on top of the scaffolding at 12 m of height. A more detailed description of the whole portable equipment including the positioning accessories has been described elsewhere.<sup>[16]</sup> Good quality Raman spectra were obtained during this survey despite working under non-laboratory conditions (e.g. dust, scaffolding, vibrations, daylight, temperature differences). 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* and the vibrations of the scaffolding.



**Figure 1.** *In situ* measurements in the Hall of the Kings: detail of the probe head attached to the videomicroscope (A) and panoramic view of one of the small rectangular vaults (B).

Hence, we succeed in the identification of almost all the pigments of the Hall of the Kings in a non-invasive manner and in real-time cooperation with conservators. Examples of typical Raman spectra obtained from the pigments of the vaults during this *in situ* study are shown in Fig. 2. All the spectra are presented without any baseline correction or smoothing. A spectrum taken from the white finishing layer beside the polychromed motifs is also shown in this figure to facilitate the identification of the bands belonging to the gypsum substrate. Sometimes, gypsum features are present in the spectra of the pigments due to the penetration of the laser through the very thin pictorial layer. No external gypsum depositions that could be attributed to ambient conditions were found.

The main colors that decorate the *mozarabes* of the vaults and other typical Arabic ornaments like *atauriques* (vegetal motifs in relief) are red and blue. Black is mainly used for details like the contours of the drawings and in some geometrical decorations. The best results of the field investigations were obtained from red decorations, where cinnabar and minium were clearly identified. As it can be seen in the Fig. 2, these two strong Raman scatterers provide Raman spectra of extraordinary quality, even working on top of the scaffold with the portable instrument. The position of cinnabar in the decorations of the vaults could indicate that this pigment was originally used by Nasrid artists although it was probably employed also in later redecorations, at least in one of the vaults. On the contrary, minium seemed not to correspond to original decorations. Furthermore, black decorations showed always the Raman signature of carbon, although in this case the Raman spectra were always weak and noisy since very low laser power had to be employed to avoid burning.

Regarding blue color, natural lapis lazuli (with a characteristic luminescence pattern<sup>[17]</sup>) was identified in most of the motifs. In addition, synthetic ultramarine blue (which showed no luminescence bands) was detected only in one of the vaults revealing a much more recent restoration, with motifs of very poor artistic quality.

Although less abundant, there are also some motifs decorated in green color. However, we did not succeed in obtaining good spectra from the green decorations nor from some other decorations showing blue and green areas. This has been reported to occur due to the strong fluorescence emission background which masks completely the Raman signatures as well as absorption of the near infrared light of the laser by green pigments.<sup>[18–20]</sup> In fact, very low laser power had to be used to avoid photodecomposition. For this

reason, the identification of the green and blue-greenish decorations was postponed until the laboratory investigations.

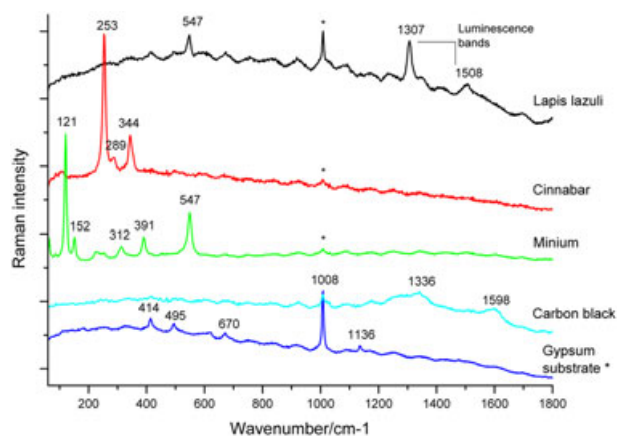
Evidences of the alteration of the red pigments, both cinnabar (HgS) and minium (Pb<sub>3</sub>O<sub>4</sub>), were also found during this survey. A chloride-induced degradation of cinnabar was demonstrated through the identification of calomel (Hg<sub>2</sub>Cl<sub>2</sub>), an intermediate species, with a characteristic Raman band at 164 cm<sup>-1</sup>.<sup>[16,21]</sup> In fact, in many areas, the red color was completely lost and only a greyish tonality remained. Even in these areas, where no red color was appreciable to the naked eye, it was possible to register the characteristic spectra of cinnabar, although very weak.

One of the main advantages of the use of *in situ* non-invasive techniques is that the investigation is not limited by sampling. In this way, more representative results can be obtained and a better knowledge of the spaces of interest as a whole can be achieved. In this study, this was clearly illustrated in the case of minium degradation. Most of the areas decorated with this pigment appeared darkened. With our wide non-invasive investigation, we took many Raman spectra from different locations in the seven vaults of the Hall. Such a wide study would have been impossible by sampling even at micro scale. In this way, we could identify two different alteration processes affecting this pigment (see Fig. 3). One was probably induced by rain water, penetrating into the Hall through the cracks of the vault structure, and led to an initial darkening by the formation of plattnerite (β-PbO<sub>2</sub>). Even when the characteristic Raman bands of this compound were not observed here, we observed an additional feature at 141 cm<sup>-1</sup> in the spectrum of minium. It can be attributed to the formation of minute amounts of the strong scatterer lead monoxide (PbO) due to laser irradiation of plattnerite despite the low power.<sup>[22]</sup> This darkening phase ends into a complete discoloration by transformation into the more stable anglesite (PbSO<sub>4</sub>)<sup>[16]</sup> with characteristic bands at 978, 449 and 438 cm<sup>-1</sup> (see Fig. 3b). This alteration was found in the stalactites (*mozarabes*) of the vaults, in areas with evidence of water leaking through the cracks of the structure.

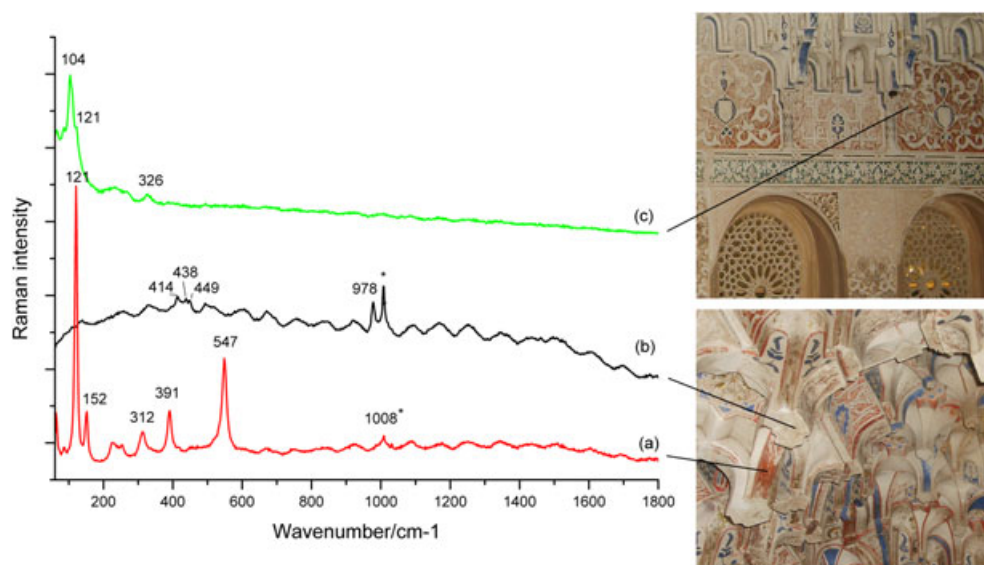
The second kind of alteration was found in other decorations of the walls and it was probably induced by sunlight penetrating from the windows. In this case, the Raman spectra recorded in the altered areas (Fig. 3c) are characterized by a strong band at 104 cm<sup>-1</sup> which do not correspond with any of the documented decay products from minium. The Pb–O system is very complex and includes a number of many different compounds that can be transformed by heating or under light irradiation. Thus, for example plattnerite (β-PbO<sub>2</sub>), the most common degradation product of minium, can be transformed into Pb<sub>3</sub>O<sub>4</sub> and PbO at high temperatures but intermediate species like Pb<sub>12</sub>O<sub>19</sub> and Pb<sub>12</sub>O<sub>17</sub> can be formed at lower temperatures. Such kind of mixed valence Pb oxides could be responsible for the observed Raman features. Previous attempts to characterize any compounds of stoichiometry intermediate between those of PbO<sub>2</sub> and Pb<sub>3</sub>O<sub>4</sub> by Raman spectroscopy did not completely succeed due to difficulties in controlling the decomposition process.<sup>[22]</sup> More investigations are needed to elucidate the nature of this degradation compound.

### Laboratory studies: micro-invasive analysis

Samples of the different colors present in the Hall were analyzed in the laboratory and confirmed the above mentioned results. Thus, most of the effort was dedicated to fill in the gap when the *in situ* studies could not provide sufficient information. That



**Figure 2.** Typical Raman spectra obtained during the *in situ* study employing the portable Raman instrument with 785 nm laser excitation.



**Figure 3.** Characterization of minium degradation performed *in situ*. Raman spectra of (a) unaltered minium, (b) anglesite present in decolored areas of mocarabes and (c) alteration product found in darkened areas of wall decorations. Bands of gypsum substrate are marked with \*.

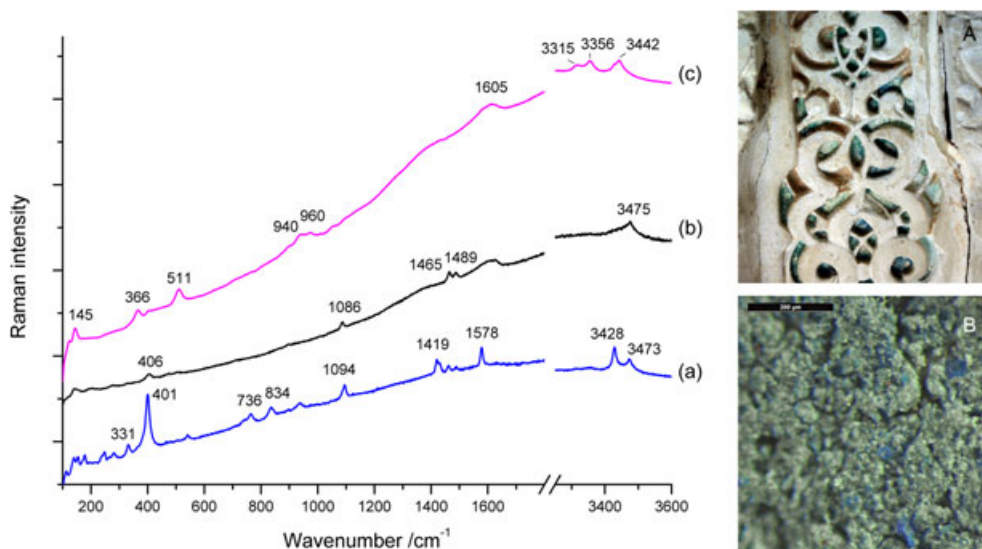
means, (1) for the identification of the pale-blue and green pigments and (2) to gain a deeper knowledge about the stratigraphy of the polychromies to obtain information about possible redecorations and re-paintings.

Regarding the study of samples showing both blue and green areas and completely green samples, the first observations under petrographical microscope revealed always discrete blue crystals surrounded by a poorly crystalline pale green or green-brownish matrix. However, Raman spectroscopy identified two different blue pigments. Therefore, in the samples that macroscopically showed blue and green differentiated areas, the blue crystals were clearly identified as azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ), with characteristic Raman bands at 331, 401, 736, 834, 1094, 1419, 1578, 3428 and  $3473\text{ cm}^{-1}$ . On the contrary, in the samples that macroscopically looked just green, the blue crystals were less abundant and more disperse and they were identified as lapis lazuli crystals (with diagnostic bands at 548s, 1096w and  $1642\text{w cm}^{-1}$ ). It is interesting to point out that using the 785 nm laser in the laboratory it was possible to identify lapis lazuli as natural by means of the characteristic luminescence bands of the impurities (in the same way that in the *in situ* study). In the laboratory, when focusing in the intense blue grains, the band at  $548\text{ cm}^{-1}$ , characteristic of lazurite ( $\text{Na}_3\text{Ca}(\text{Al}_3\text{Si}_3\text{O}_{12})\text{S}$ ), was the most intense; however, if focusing in the close vicinity of the blue grains, the characteristic luminescence bands of the impurities at 1307 and  $1508\text{ cm}^{-1}$  increased.

It is remarkable that the identification of the two blue pigments (azurite and lapis lazuli) was possible employing both the green laser (514 nm) and the near infrared laser at 785 nm, the same used during the *in situ* study, which did not provide useful results on these decorations. In the laboratory study, the higher spatial resolution achieved through the use of objectives with higher magnification (50 $\times$  and 100 $\times$ ) and the absence of vibrations allowed us to focus on these discrete blue crystals and isolate their contribution from the strong and broad fluorescence background of the rest of the pale green matrix. In contrast, in the *in situ* study, the weak Raman signal and the strong fluorescence from the rest of the matrix hindered the recording of any useful Raman spectra.

Even in the laboratory, the recording of Raman spectra from the green areas of all these samples was extremely difficult. Useful spectra were obtained only when using the 514 nm laser with low laser power and prolonged acquisition times. The spectra recorded always presented strong fluorescence backgrounds and weak bands.

In the blue-green samples that contained azurite (see Fig. 4), we also identified calcium oxalate in the form of whewellite and Raman bands typical of copper hydroxychlorides. These features are the characteristic peak at  $511\text{ cm}^{-1}$  that can be attributed to O–Cu–O symmetric stretching accompanied by bands related to Cu–O–H bending in the region from 800 to  $1000\text{ cm}^{-1}$  and those typical of the OH stretching ( $3300\text{--}3450\text{ cm}^{-1}$ ). Copper hydroxychlorides present either as pigments<sup>[23,24]</sup> or as alteration products of copper pigments like azurite<sup>[25–27]</sup> have been identified in several studies on historical paintings using different analytical techniques. The most common copper hydroxychlorides identified include atacamite (orthorhombic  $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), clinoatacamite (monoclinic  $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) and paratacamite (rhombohedral  $(\text{CuM})_2\text{Cl}(\text{OH})_3$ , with M being Ni, Zn or Co). The latter have been sometimes referred as a polymorph of atacamite but in fact it is a different mineral phase. Although the discrimination among different copper hydroxychlorides using Raman spectroscopy is possible,<sup>[28]</sup> it is not straightforward, especially when dealing with historical samples, because mixtures of polymorphs of  $\text{Cu}_2\text{Cl}(\text{OH})_3$  can be formed since there are tiny differences in the free energy between them.<sup>[29]</sup> In addition, as recently pointed out by Bertolotti *et al.*,<sup>[30]</sup> there are several discrepancies in databases and literature data, with studies reporting different spectra for the same mineral species and, on the contrary, similar Raman spectra for different mineral species.<sup>[29,31]</sup> This is not surprising because in the naturally found minerals the members of the atacamite family always occur together. In addition, paratacamite, a separate mineral phase which forms when Ni, Zn or Co replaces some of the Cu, is sometimes confused with clinoatacamite because both have rather similar X-ray powder diffraction patterns. The monoclinic structure of clinoatacamite is easily transformable to a pseudorhombohedral cell approximating that of paratacamite by substitution of part of the Cu ions.<sup>[32,33]</sup> However, in the absence of Ni, Zn or Co cations,

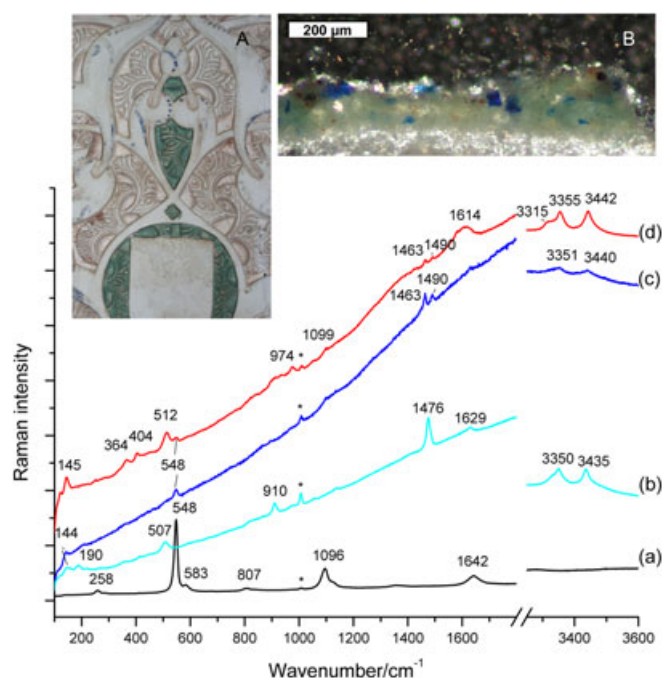


**Figure 4.** Example of decoration with blue and green areas (A) and sample under stereozoom (B) showing blue crystals. Raman spectra obtained of (a) azurite, (b) whewellite and (c) clinoatacamite using laboratory equipment (514 nm excitation). (This figure is available in colour online at [wileyonlinelibrary.com/journal/jrs](http://wileyonlinelibrary.com/journal/jrs).)

the mineral phase more likely to form is clinoatacamite rather than paratacamite. In fact, the Raman spectral features recorded in the samples from the Hall of the Kings with three characteristic bands at 3440, 3348 and 3309  $\text{cm}^{-1}$  together with those at 142, 362, 511, 897, 933 and 967  $\text{cm}^{-1}$  are strongly coincident with those reported for clinoatacamite.<sup>[29,30,34]</sup> Clinoatacamite was probably formed as a result of the degradation of the original azurite pigment in the presence of chloride. According to Frost,<sup>[29]</sup> the presence of clinoatacamite is indicative of an advanced state of degradation of the original azurite pigment because clinoatacamite, the most stable polymorph, is formed the last. Taking into account the locations where these blue-green motifs were found and the experience of the conservator of our team, they were probably the remains of the oldest blue decorations of the Hall.

In the case of completely green samples, apart from the identification of lapis lazuli crystals that was straightforward, the recording of Raman signals from the green areas was extremely difficult in all of them. Typical Raman spectra obtained from these samples are shown in Fig. 5. All the spectra recorded showed very weak Raman features superimposed in a high fluorescence background. Despite this fact, bands typical of copper hydroxychlorides, possibly clinoatacamite, were identified like in the case of the samples containing azurite discussed above. Furthermore, calcium oxalates, both in the form of whewellite and weddellite, were found widespread in all these samples.

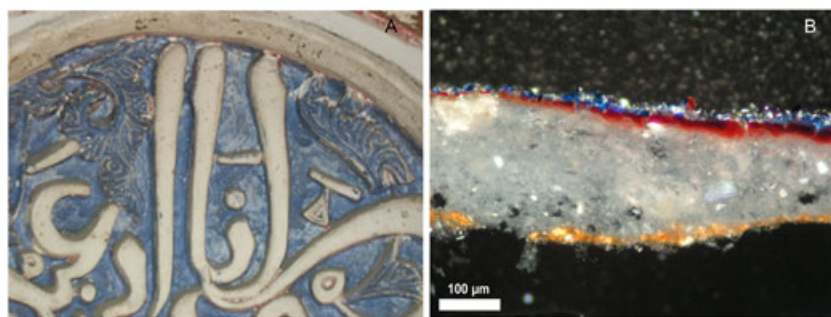
A complementary study of these samples using SEM-EDX corroborated that the pictorial layer was mainly composed of Cu and Cl. Considering that in this cases no traces of azurite were detected the questions that arises is whether the copper hydroxychlorides were original pigments derived from a natural mineral or degradation products. It has been reported that certain verdigris recipes, involving the addition of NaCl or urine, in fact produced a mixture of compounds containing copper hydroxychlorides.<sup>[35,36]</sup> In addition, SEM-EDX revealed also the presence of small amounts of nitrogen and phosphorous. Considering all these findings, our hypothesis is that these samples correspond to redecorations with synthetic copper pigments, prepared with recipes based on the acid attack to copper (like verdigris) but using different additives (like salt, honey or urine) that produced copper hydroxychlorides.<sup>[24,35]</sup> In some cases, a



**Figure 5.** Example of green decoration in relief (A) and thin polished cross section (B) of a sample taken from the green color together with typical Raman spectra (obtained in the laboratory with 514 nm excitation) found in these samples showing (a) lapis lazuli, (b) weddellite, (c) whewellite and (d) clinoatacamite. Bands of gypsum substrate are marked with \*. (This figure is available in colour online at [wileyonlinelibrary.com/journal/jrs](http://wileyonlinelibrary.com/journal/jrs).)

small amount of lapis lazuli was probably added to the pigment in order to improve the chromatic properties. To our knowledge, this is first report of such a pictorial technique. It is also interesting to point out that no malachite has been found in the Hall of the Kings although this one was the only green pigment identified in other spaces of the Alhambra.<sup>[12]</sup>

Finally, to investigate the stratigraphy, thin polished cross sections were studied. In some samples, different overlying pictorial layers were observed what evidenced redecorations. In



**Figure 6.** Detail of an Arabic blue decoration (A) where stratigraphy shows the superposition of two painting layers of different colors over the gypsum substrate (B). (This figure is available in colour online at [wileyonlinelibrary.com/journal/jrs](http://wileyonlinelibrary.com/journal/jrs).)

this way, it was possible to confirm the impression obtained from the *in situ* study about the role of minium and cinnabar in these decorations, since a pictorial layer of minium was found over older cinnabar decorations. Calcium oxalates were also found widespread in the white finishing layer of gypsum just below the pigments. Their presence in most of the decorations of the Hall can be attributed to the degradation of organic compounds used as binders.

Furthermore, sometimes the color of certain motifs was altered in the redecorations. As can be seen in Fig. 6, the pigment lapis lazuli was used to cover a red pictorial layer of cinnabar. The presence of a thin orange layer (a very fine grain clay with small amounts of iron oxides) is very characteristic of the plasterwork of the Nasrid period, when the cast technique was employed to fabricate these decorations.<sup>[13]</sup> After placing the plasterwork pieces on the walls and ceilings, a finishing layer of gypsum was applied providing a uniform white aspect. This layer, constituted by very small crystals of pure gypsum with low porosity, can be considered the preparation layer for the polychromies and it reveals a careful execution. The red pictorial layer (~20 µm) was probably the original Nasrid one as indicated by the presence of the characteristic clay layer. The layer of lapis lazuli used in the redecoration was applied directly over the pictorial layer of cinnabar without any preparation layer to hide the red color. This use of lapis lazuli in redecorations suggests that this pigment was probably not employed in the oldest blue decorations but later, which agrees with our hypothesis of azurite being the oldest blue pigment employed by the Nasrids, and it is also in agreement with previous studies.<sup>[12]</sup>

## Conclusions

The present study highlights the importance of a good compromise between minimal impact and obtaining comprehensive information in cultural heritage investigations. The possibilities and limitations of portable Raman Spectroscopy *in situ* are explored in a case of great complexity that is the stalactite vaults of the Hall of the Kings in the Alhambra. The non-invasive field approach is shown to deal with large works, allowing for simplification and a more representative sampling. Furthermore, it allowed a close cooperation with the conservators providing them with the results in real time. With this approach, we have identified almost all the pigments, except the green ones, and got information about the degradation processes affecting the red pigments. The *in situ* study was complemented by sample analyses in the laboratory taking benefit of higher sensitivity,

higher spatial resolution and the possibility of using different lasers. The identification of the pigments employed in the green decorations as well as several degradation products was achieved in this way. Furthermore, we got information about the stratigraphy of the decorations identifying both minium and lapis lazuli as pigments employed in redecorations.

## Acknowledgements

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