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In situ Raman spectroscopic study of marble capitals in the Alhambra monumental ensemble

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Abstract The marble capitals of five different sites in the Alhambra complex (Granada, Spain), namely the Mexuar, the Hall of the Abencerrages, the Hall of the Kings, the Court of the Myrtles and the Court of the Main Canal, have been investigated. The decoration of the capitals exhibits mainly blue, red, black and gilding motifs with different states of conservation. The work has been carried out in situ by means of a portable Raman micro-spectrometer with an excitation laser of 785 nm. In addition to preserving the artwork with a non-invasive study, the on-site investigation gives a more representative knowledge of the art objects because the measurements are not limited to the samples that can be taken (few and small). The obtained Raman spectra were of good quality despite challenging adverse conditions out of the laboratory. Cinnabar, minium, carbon black, natural lapis lazuli and azurite were the main pigments found. Synthetic ultramarine blue was also detected in a capital as a result of a modern restoration. Degradation products as tin oxide in the gildings and weddellite in the preparation layers were also identified. All the results together with a careful visual inspection can be combined to elucidate the different execution techniques employed to apply the pigments on the marble substrate of the capitals in the Nasrid and Christian periods.

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1 Introduction

In conservation science, the investigation of the physical–chemical condition of artworks can be very useful not only to diagnose the actual state of the materials but also to elucidate the deterioration causes and mechanisms, as well as the existence of previous interventions. In this sense, it is essential to carry out extensive scientific investigations based on chemical analysis to better know about the execution technologies, the raw materials employed, their degradation processes and the extension of undocumented restorations, as well as the kind of materials employed [1].

In the last years, the development of non-invasive and non-destructive analytical techniques has been the main focus in cultural heritage investigations. The use of mobile or portable systems for the characterization of materials in non-invasive manner is a precious tool, particularly when dealing with architectural heritage [2, 3]. It can be very useful to formulate initial hypotheses that can then be verified through other kinds of analysis carried out on micro-samples [4–6]. The use of non-destructive techniques such as Raman spectroscopy, X-ray fluorescence, X-ray diffraction, diffuse reflectance infrared spectroscopy or digital microscopy with visible and infrared illumination for working in situ is increasing [5, 7–10] in the investigations of different types of artwork as mural, manuscript, decorated glasses, plasterworks, pottery, wood or silk [11–17]. In addition to the main advantage of not damaging the artwork, working in situ allows a more complete understanding of the work under study and its environment than working with isolated samples in the laboratory. Furthermore, information can be obtained in real time. Thus, it is possible to make decisions based on the results at the moment and according to that gradually modify the study. Raman spectroscopy is one of the best suited techniques for performing this kind of studies. With the development of robust portable Raman spectrometers with no moving parts and increasingly sensitive CCD detectors, the interest on this technique for in situ investigations has increased extraordinarily [18, 19].

The research presented here is devoted to the study of the decorated capitals in several spaces in the Alhambra monumental ensemble using a portable Raman instrument. The Alhambra complex (Granada, Spain), included in the World Heritage since 1984, is one of most famous examples of Islamic art overall, and it is certainly the culmination of medieval Islamic culture in the Iberian Peninsula. Its construction began in the thirteenth century under the reign of the Nasrid dynasty. The Alhambra was a courtly city, conceived and built to serve the royal court of the Nasrid Kingdom, which became the last Islamic sultanate on the Iberian Peninsula. It is a characteristic example of the Islamic architecture, where highly ornate interior spaces, particularly in the palatial zone, contrast with the plain walls of the exterior fortress. In the case of the marble capitals, object of our study, they were richly decorated with vivid colours and gildings.

It is interesting to point out that, in general, scientific studies on decorated marble items are scarce in the literature. Most of them are referred to marble provenance, degradation processes and explanation of different natural colours or composition [20–24]. Only few papers report about decorated marble [25, 26]. This can be explained by the fact that original polychromies in ancient Roman and Greek marble sculpture have largely been lost in burial. Thus, when they were rediscovered during Renaissance their white monochromatic appearance gave rise to new, modern canons of sculpture characterized by an emphasis on form and with little consideration of colour. Furthermore, painting on marble surfaces is technically more complex than painting on materials such as plaster, lime, cloth or wood because it is a very smooth and slippery surface. In contrast to marble, many investigations can be found about the pigments employed in artworks made with other types of stones [27, 28] such as alabaster [29, 30] or in wall paintings such as stuccoes [31, 32].

2 Experimental

2.1 Instrumentation for the in situ study

To carry out the in situ study, a portable Raman spectrometer innoRam (B&W TEK Inc., Newark, USA) was used (Fig. 1). This spectrometer is equipped with an excitation near-infrared laser of 785 nm, a 5-metre-long fibre optic probe and a CCD detector thermoelectrically cooled to −20 °C. The Raman shift range is from 65 to 2565 cm^{-1}. The probe was coupled to a video microscope sampling system with a long focal distance objective (20×). The integrated camera allowed for precision Raman sampling through camera monitoring of the laser beam and the sample image details. The video microscope head was attached to an extensible bar placed in an accessory motorized in the *X*–*Y*–*Z* axes with remote control, which was mounted on a tripod. This allowed for the positioning and the focusing of the laser beam on the surface of the artwork even reaching areas of interest up to 3 metres height.

Fig. 1 Portable Raman spectrometer working in situ in the Mexuar. Capital Mexuar B

For spectra acquisition, laser power was limited to a few milliwatts to avoid any damage to the materials. Other instrumental parameters, such as exposition time and number of accumulations, were optimized for each measurement depending on the sensitivity of the signal, fluorescence effects, etc. Typical acquisition conditions were 30 mW of laser power, 10 s of exposition time and 5 accumulations.

2.2 Complementary study of samples in the laboratory

Eight micro-samples (≤1 mm long) were taken from the studied capitals to analyse them in the laboratory. The morphology of the samples was studied using a Leica M205C stereomicroscope equipped with a Leica DFC450C digital camera. Raman spectra were registered using a

Renishaw inVia Raman Confocal Microscope. This spectrometer is provided with two excitation lasers, one green (514 nm) and one near-infrared (785 nm). Four objectives (5×, 20×, 50× or 100×) are also available.

2.3 Description of the sites of study

Marble columns with decorated capitals can be found in different locations in the Alhambra complex. For this study, the capitals of six columns located in five different sites have been selected (see Fig. 2). Three of the columns are located inside halls, two are outside in courtyards, and one is located semi-outside, in the limit between the hall and the courtyard. A brief description of the different sites, namely the Mexuar, the Hall of the Abencerrages, the Court of the Myrtles, the Court of the Main Canal and the Hall of the Kings, is given below.

2.3.1 Mexuar

This was the place where the Surah or Counsel of Ministers met and the hall where the Sultan dispensed justice. Its construction is attributed to Isma'il (1314–1325) and has undergone many alterations and modifications. The most important took place in the sixteenth century, after the Christian conquer of the city. The Catholic Kings ordered intense changes in this space adding an upper floor and transforming it into a chapel. Here, we have studied two of the capitals of the original marble columns that have been preserved. One is located northwest of the hall, under the choir railing (Mexuar A), and the other southwest (Mexuar B). Both capitals show polychrome decoration in blue, red and black colours.

2.3.2 Hall of the Abencerrages

It was a residential area situated in the Palace of the Lions, at the south end of the famous Court of the Lions. It has a square ground floor design with a central marble fountain flanked by two alcoves that are framed by double arches. The capital of the column situated in the middle of the arch of the east bedroom was studied. This capital is exquisitely decorated in different colours with a lot of details carved in the marble. Some remains of gilding can be also observed.

2.3.3 Court of the Myrtles

This area is the central part of the Palace of Comares. The name of this courtyard comes from the bushes which are on the longer sides of the central pond. This court features two porticoed galleries at the sides. The column studied is situated in the south gallery. The capital shows stalactites motifs decorated in blue and black. Curiously, small black drawings of human faces, flowers and animals can also be found in this capital.

2.3.4 Hall of the Kings

This hall was a place of rest and conversation, and it was also used for the reception and festive representations. It is divided into seven areas, three square room separated by rectangular sections. The marble columns are located in a semi-outside area open to the Court of the Lions. Most of the columns of this area were sanded in a restoration in the nineteenth century to eliminate the remnants of the pigments of the original decoration in order to give them a cleaner aspect. The decoration was only preserved in two capitals in the whole area of the Hall of the Kings and the Court of the Lions. The one situated in the west of the square central room was studied.

2.3.5 Court of the Main Canal

It is a long and narrow court in the Palace of Generalife. It has arcaded pavilions on the sides. The capital under study was located in the west side of the south pavilion. It shows a pale blue-greenish decoration.

3 Results and discussion

The in situ study in the Alhambra complex was performed on the five sites described above. Many different challenges were encountered during the analyses, depending on the specific experimental circumstances, which hampered

Fig. 2 Capitals studied in the different spaces in the Alhambra: **a**, **b** Mexuar, **c** the Hall of the Abencerrages, **d** the Court of the Myrtles, **e** the Hall of the Kings and **f** the Court of the Main Canal (Generalife)

the investigations. Before reporting the results, we would like to describe the main obstacles that can be found when working in the field in conditions that are very different to laboratory or even museum studies. Here, all the studies were carried out in spaces open to the public and thus, sometimes the flash of the cameras of the visitors interfered with the measurements and the pass of large groups of tourists caused vibration of the focusing optics. Furthermore, other difficulties also ensued from working during public exhibition time. Visitors were naturally curious about our work, and therefore, the members of our team had to provide them with information about the investigations and to be very careful to prevent visitors from touching the equipment or approaching the laser beam during the measurements.

The most challenging working conditions were found when working in the exterior and, particularly, in the Court of the Myrtles. The measurements were taken on the north and west sides of the capital, which was located completely outside. Daylight was a big problem since the Raman effect is very weak and background radiation from sunlight interfered with the spectra. This problem was partially solved by attaching a cover of dark foam to prevent the sunlight from reaching the objective aperture. Nevertheless, the spectra obtained in exterior locations were always of less quality than those recorded in the darker interior halls. Furthermore, the height of the capitals of the columns in this court was around 3 metres; consequently, the tripod and the extensible bar had to be completely extended and any wind, even very light, moved the equipment bringing the optics out of focus. Despite all these difficulties, spectra of reasonable good quality were obtained allowing the identification of different pigments and degradation products. To confirm some results, we also took small samples in selected locations for further analysis in the laboratory.

3.1 Pigments identified

A summary of the pigments identified in the different sites of study is presented in Table 1. Figure 3 shows typical Raman spectra of all these pigments registered in situ.

Mercury sulphide (HgS) was identified in all the red decorations by the bands at 255 and 344 cm^{-1}. The Raman spectra of this pigment are very intense, which allowed its easy identification during the study. However, it was not possible to distinguish between the synthetic (vermillion) and natural (cinnabar) origin of it [33]. Even if impurities from the natural mineral were present, the extraordinary intensity of the Raman bands of the HgS with this laser would hinder their observation. In the capital Mexuar B, another red-orange pigment was found showing Raman bands at 121, 150, 312, 391, 550 cm^{-1} that can be attributed to minium (Pb_3O_4) in a well-preserved state. This

Table 1 Summary of the pigments identified in the different sites of study

Location	Colour	Pigment	Raman bands (cm^{-1})
Mexuar capital A	Blue	Lapis lazuli	548, 1307, 1557, 1818
	Clear blue	Azurite	142, 176, 248, 283, 331, 401, 765, 839, 1096, 1428, 1580
	Black	Carbon black	1323, 1592
	Red	Cinnabar	255, 344
Mexuar capital B	Blue	Lapis lazuli	548, 1307, 1557, 1818
		Synthetic ultramarine blue	548
	Red	Cinnabar	255, 344
	Orange	Minium	121, 150, 312, 391, 550
	Reddish-orange	Cinnabar and minium mixed	121, 150, 312, 391, 550
			255, 344
Hall of the Abencerrages	Blue	Lapis lazuli	548, 1307, 1557, 1818
	Black	Carbon black	1323, 1592
	Red	Cinnabar	255, 344
Court of the Myrtles	Blue	Lapis lazuli	548, 1307, 1557, 1818
	Black	Carbon black	1323, 1592
Hall of the Kings	Blue	Lapis lazuli	548, 1307, 1557, 1818
	Black	Carbon black	1323, 1592
Court of the Main Canal	Clear blue	Azurite	142, 176, 248, 283, 331, 401, 765, 839, 1096, 1428, 1580
	Black	Carbon black	1323, 1592

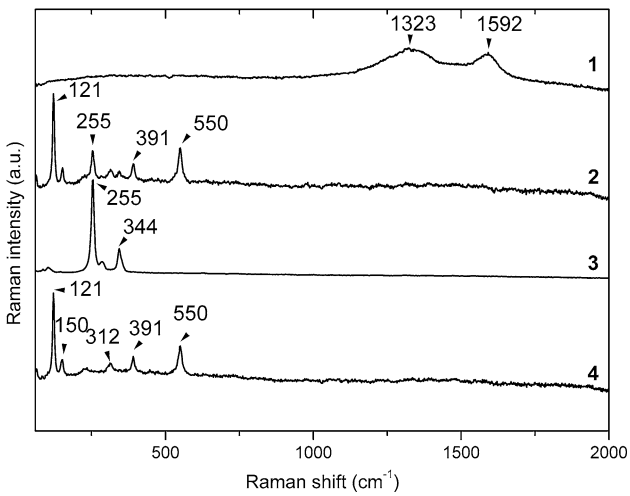

Fig. 3 Typical Raman spectra of the pigments registered during the in situ study: (*1*) amorphous carbon, (*2*) mixture of cinnabar/vermillion and minium, (*3*) cinnabar/vermillion and (*4*) minium

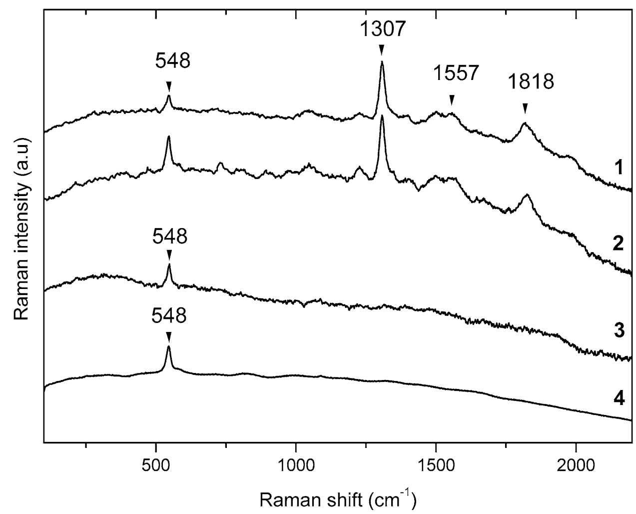

Fig. 4 Raman spectra collected in situ in the Alhambra, Mexuar A (*1*) and Mexuar B (*3*). Spectra of commercial pigments of lapis lazuli (*2*) and synthetic ultramarine blue (*4*)

pigment appeared sometimes mixed with HgS in this capital to provide a lighter tonality of reddish-orange colour [19].

Black colour was also found in most of the studied capitals in the form of black lines, points, contour lines and in the drawings of flowers, animals and faces of Court of the Myrtles. The in situ study allowed the observation of the characteristic Raman broad bands centred at ca. 1350 and 1580 cm^{-1} typical of amorphous carbon [34].

As can be seen in the images shown in Fig. 2, blue decorations are the most abundant in the studied capitals. The precious blue pigment ultramarine obtained from lapis lazuli rock was found in all the capitals except in the Court of the Main Canal. Additionally, synthetic ultramarine blue (synthetic lazurite, first prepared in the nineteenth century) was found only in one of the capitals of the Mexuar (Mexuar B). This place was object of a documented intervention involving chromatic reintegration in the second half of the twentieth century. Figure 4 shows the comparison between the Raman spectra recorded during the in situ study and those of commercial pigments of natural lapis lazuli and synthetic lazurite. When using the 785-nm excitation laser, natural lapis lazuli exhibits additional luminescence bands forming a complex pattern, with main bands at around 1300, 1550 and 1810 cm^{-1}, due to the impurities of the rock. However, the Raman spectra of synthetic lazurite do not present these luminescence patterns. This fact enables the distinction between both pigments [13, 35].

Furthermore, in the capital of the Court of the Main Canal a different blue tonality was found. It was a lighter blue colour with a greenish hue. In addition, in the capital

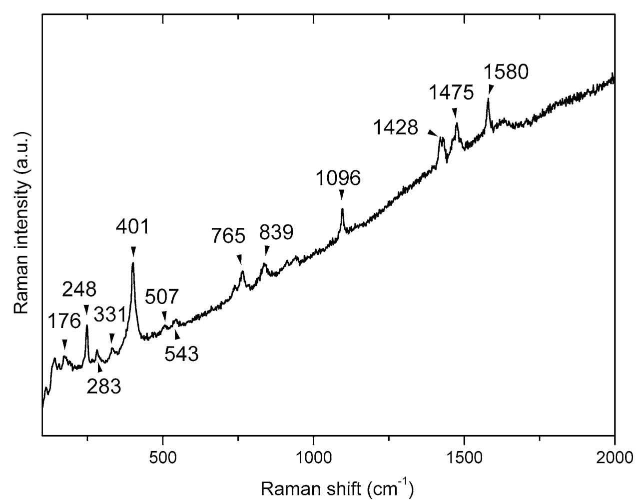

Fig. 5 Raman spectrum collected using the 514-nm excitation laser in the sample of the Court of the Main Canal where azurite was identified as the blue pigment

Mexuar A, remnants of another blue decoration were noticed lying over a deeper pictorial layer. Unfortunately, the pigment responsible for these colours could not be identified during the in situ studies using the portable instrument. The spectra recorded in these areas had no characteristic Raman features. In order to identify the pigment, selected samples were analysed in the laboratory. Azurite ($2CuCO_3{\cdot}Cu(OH)_2$) with its characteristic band due to the vibration of Cu–O at 401 cm^{-1} and other bands at 142, 176, 248, 283, 331, 401, 765, 839, 1096, 1428 and 1580 cm^{-1} was easily identified in these samples when using the 514-nm excitation laser [36] (Fig. 5).

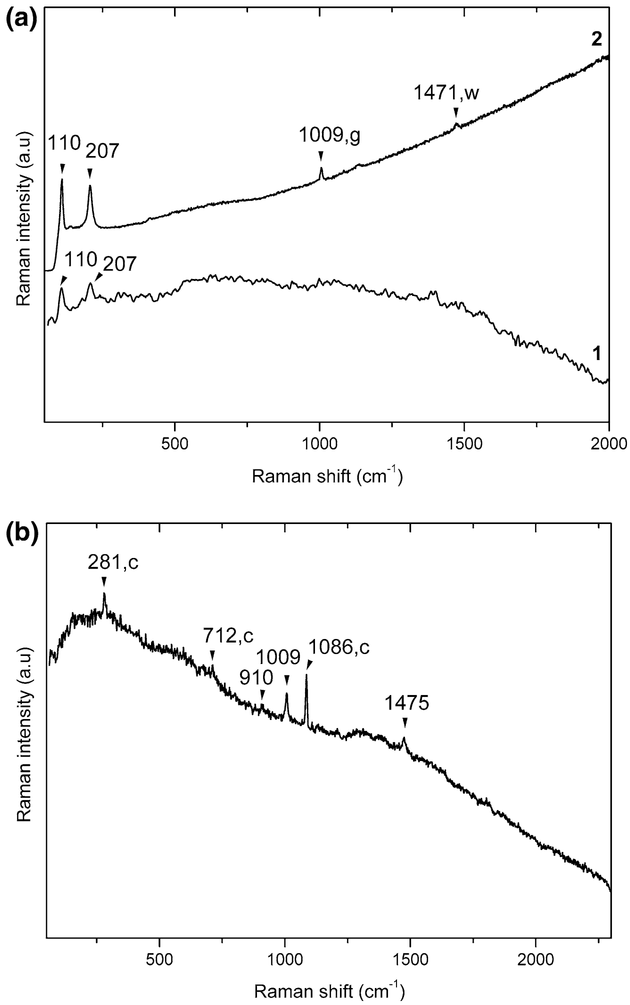

Fig. 6 Raman spectra of degradation products found in the capitals of the Alhambra. **a** Tin monoxide found in the gildings of the Hall of the Abencerrages, (*1*) spectrum recorded in situ and (*2*) in the laboratory. Bands of gypsum, g, and weddellite, w, can also be observed. **b** Calcium oxalate in the form of weddellite accompanied with the bands of the marble substrate typical of calcite, c

3.2 Degradation products

During the in situ study, the presence of several degradation products has been detected (Fig. 6). In addition, a few complementary studies in the laboratory provided spectra with better signal-to-noise ratio and aided in their identification.

Tin monoxide (SnO) with typical Raman bands at 110 and 207 cm^{-1} (Fig. 6a) was found in dark areas in the gildings of the Hall of the Abencerrages. In fact, it was the unique compound that could be identified in these decorations with Raman spectroscopy working in situ. Similar findings were described in a previous work on gilded plasterwork in the Hall of the Kings [37]. These gildings were composed of two different metal layers, one over another. A thick tin layer was employed to make easier the application of very thin gold foils. The oxidation of tin destroyed the gildings and gave them the dark colour due to the formation of SnO.

Calcium oxalate in the form of weddellite (CaC_2O_4·$2H_2O$) was found in the capitals of the Hall of the Kings, the Court of the Myrtles, the Hall of the Abencerrages and the Court of the Main Canal. The characteristic band of weddellite at 1475 cm^{-1} due to the stretching vibration mode of the COO^- is shown in Fig. 6b [24]. Weddellite has also a characteristic band at 910 cm^{-1} that can also be observed in the spectra although it is practically within the spectral noise. These bands appeared always associated with the spectrum of gypsum (main band around 1009 cm^{-1}) and here also with the spectral features of the marble substrate (281, 712 and 1086 cm^{-1}). The origin of this degradation compound is not completely clear, but it could be the result of the biodegradation of the organic binder used to fix the polychromies in a Ca-rich environment.

3.3 Execution techniques

Particular attention was paid during the study to gain information about the execution techniques of these polychrome works on marble. This was achieved by combining the information about the materials obtained from Raman spectra with a careful visual inspection of the decorations. Especially interesting were those areas where the deterioration of the most external painting layers could provide insight into the presence of priming layers over the underlying marble substrate.

In some cases, the presence of a preparation layer between the marble substrate and the pigment was imperceptible to the naked eye. Nevertheless, in areas where the pictorial layer was very thin, the Raman spectra showed the characteristic band of gypsum at 1009 cm^{-1} together with the features of the marble substrate (with the strongest band of calcite located at 1086 cm^{-1}) as shown in Fig. 7. Thus, it seems that the pigments were applied above a very thin preparation layer of gypsum. Weddellite was also frequently found together with gypsum in these cases, revealing the presence of an organic binder to fix the preparation on the substrate.

This execution technique was found in almost all the locations, particularly on those capitals with more details in their decoration, except in the two capitals of the Mexuar and in the Court of the Main Canal in the Generalife. In these two locations, the pigments seemed to have been applied directly above the marble without any preparation layer or this is extremely subtle. No clear Raman signals from gypsum were detected in these spectra (see Fig. 7), although the bands of marble were clearly observable, revealing that the pictorial layer was extremely thin. Of

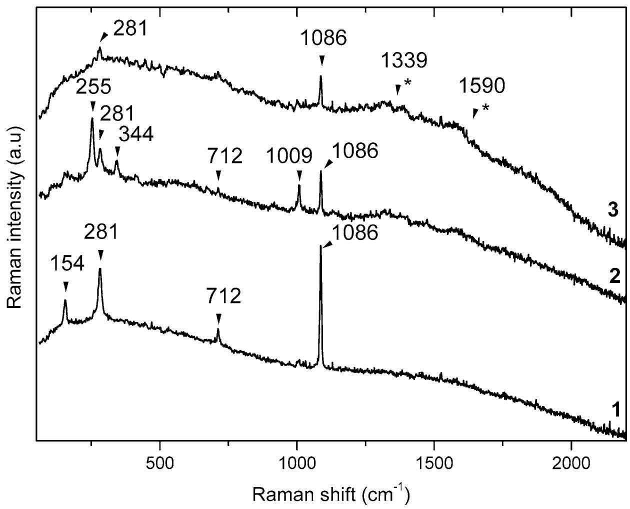

Fig. 7 Raman spectra of (*1*) marble substrate without pictorial layer, (*2*) pictorial layer of cinnabar/vermillion showing the bands of the gypsum preparation layer and the marble substrate and (*3*) extremely thin pictorial layer of carbon black (marked with *) where spectral features of the marble substrate are clear

course, it must be also taken into account that marble is a metamorphic rock formed from limestone through a process of recrystallization due to heat or pressure. This gives it a dense crystalline structure that, apart from making possible its polished surface, leads to a very strong Raman signal.

Finally, it is interesting to highlight that in the capital Mexuar A, the remains of a very thick preparation layer of gypsum were found over the already painted marble (see Fig. 8). This layer seems to have been applied to hide the original Nasrid decoration. However, this overlying pictorial layer is nowadays almost completely detached, revealing the underlying original decoration. Probably, this redecoration was part of the complete transformation of the Mexuar carried out after the Christian conquer. In this Christian redecoration, much less delicate in its execution than the Nasrid one, we could not find lapis lazuli or cinnabar/vermillion during the in situ study. Only very fragmented rests of it are still preserved, but in the laboratory, it was possible to identify a different gilding technique, based on the application of a red bole (preliminarily identified as red ochre) and gold. Additionally, azurite was later employed for repainting the gilding areas in blue colour.

4 Conclusions

The use of a portable Raman micro-spectrometer allowed for a non-invasive study of the pigments which are decorating the capitals in different locations in the Alhambra. It is remarkable that this study was successful in places open to the public during exhibition times and working both inside halls and in exterior courtyards. Typical Nasrid pigments were identified, namely cinnabar/vermillion, carbon black, minium, lapis lazuli and azurite. The use of a portable spectrometer equipped with a laser of 785 nm as excitation source is especially useful for the distinction between lapis lazuli and synthetic ultramarine blue allowing the easy identification of modern restorations and redecorations. Furthermore, degradation products as tin monoxide and weddellite were found. More exhaustive studies in the laboratory using different analytical techniques, including SEM–EDS and micro-XRD for a better characterization of the different layers and estimation of their thickness, are needed to completely elucidate the execution techniques. Nevertheless, the findings of the in situ study have provided an interesting preliminary insight into this topic. In the Nasrid period, the pigments were found either applied directly above the marble without any preparation layer or over a very thin preparation layer of gypsum in the case of decorations with more elaborated drawings and motifs. The Christian redecoration in the Mexuar was characterized by a thick gypsum layer to hide the original Nasrid polychromy.

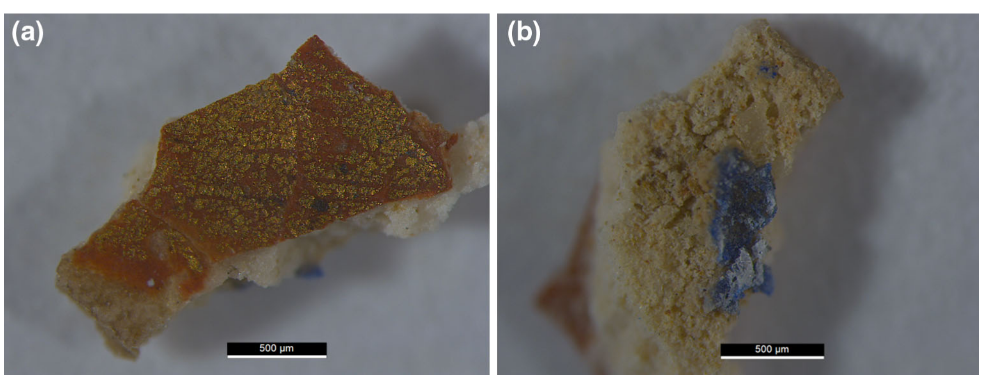

Fig. 8 Images under stereomicroscope of the **a** obverse and **b** reverse sides of a sample from Mexuar (capital A). It can be observed the thick gypsum preparation layer over the Nasrid original *blue* to introduce the *red* and gilded redecoration

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