ANALYSIS OF NASRID POLYCHROME CARPENTRY AT THE HALL OF THE MEXUAR PALACE, ALHAMBRA COMPLEX (GRANADA, SPAIN), COMBINING MICROSCOPIC, CHROMATOGRAPHIC AND SPECTROSCOPIC METHODS*†

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The pigments, binders and execution techniques used by the Nasrids (1238–1492) to polychrome carpentry in the Hall of the Mexuar Palace at the Alhambra (Granada, Spain) were studied using optical microscopy, scanning electron microscopy with EDX analysis, selective staining techniques and gas chromatography – mass spectrometry. This pioneering investigation presents the first results of a research project devoted to filling gaps in the knowledge of Nasrid art, traditionally approached by stylistic studies. Moreover, it is essential for the polychromy conservation of the studied artworks, and will help to clarify historical and painting uncertainties in the Alhambra monument. The palette consists of a limited range of colours: white (lead-base pigment), red (cinnabar and red lead), blue (lapis lazuli), black (carbon-based) and false gold (golden tin). Tempera grassa was the painting technique identified. Two types of grounds were used: (i) gypsum in calligraphy decoration for the false gold technique, and (ii) synthetic minium in geometric drawings in carpentry. Organic insulating layers of linseed oil were used between paint strata. Artists applied synthetic minium to protect the wood (Juglans regia and conifer) against attack by xylophages. To lighten the surface darkened by this ground layer, powdered tin was added to achieve a metallic lustre.

KEYWORDS: ALHAMBRA, ISLAMIC, AL-ANDALUS, PIGMENTS, BINDERS, CARPENTRY, SEM–EDX, GC–MS, OPTICAL MICROSCOPY

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THE ARCHAEOMETRIC QUESTION

The Alhambra monument is a palatial citadel built over three centuries, with extensive undocumented reuse and redecoration of woodwork among palaces (Velasco-Gómez 1993). One of the main challenges for experts is to date, or ascribe to a particular Nasrid period, non-contextual and other woodwork of uncertain chronology. Yet scientific publications on composition and painting techniques used by the Nasrids to polychrome carpentry in the Alhambra are sparse (Cardell *et al.* 2004).

To shed light on this issue, this pioneering research focused on scientific analysis of some of the oldest preserved polychromed carpentry in the Alhambra (dated from the period of Ismail I, 1314–25), originally situated in the Hall of the Mexuar, part of the lost Mexuar Palace, and currently housed in the Alhambra Museum. A comparative study of these data (a potential benchmark for further archaeological investigations) is presented with in- and out-of-context polychromed pieces located in this same room, which was profoundly transformed by both Muslim and Christian monarchs. Thus, the final goals of the work are: (1) to characterize the painting materials and techniques of Nasrid polychrome carpentry in the Hall of the Mexuar, (2) to use this information as a reference point to date further polychromed woodwork from the Alhambra, (3) to help to establish the diachronic evolution of the painting materials and techniques applied throughout the Nasrid period, and (4) to provide conservators with scientific knowledge to enable the safeguarding of this unique monument.

INTRODUCTION

The Alhambra and Generalife represents the grandest and finest example of Islamic art and architecture from the Middle Ages still standing in the Western world. The Alhambra was a fortified palatial city (Fig. 1), whose construction started in the 11th century and ended when the Catholic kings conquered Granada in 1492. The Nasrid dynasty established its official residence here, and their reign represented the zenith of Islamic culture in Europe. At present, only a small part of the original palaces and some vestiges of the *medina* (city) remain. The Nasrid palaces today include part of the Partal Palace (Muhammad III, 1302–9), the Hall of the Mexuar (part of the Mexuar Palace, Ismail I, 1314–25), the Comares Palace (Yusuf I, 1333–54) and the Lions Palace (Muhammad V, 1362–91).

Internal decorations represent the most attractive aspects of the Alhambra, and numerous books are available regarding the art, history and architecture (Barrucand and Bednorz 1992; Cid-Acedo 2000), yet scientific studies on Nasrid painting materials and techniques are limited (Capitán-Vallvey *et al.* 1993; Cardell *et al.* 2004; Cardell and Navarrete 2006). In the Alhambra, the basic technique for surface decoration was to use dado tiling at the bottom of the wall and to cover the upper part with carved stucco. Mural paintings are scarce, and woodwork is limited to ceilings, doors or architectural elements. Carpentry attained new heights of magnificence during Nasrid times. Woodwork was made in two forms: (i) incising the wood with geometric, vegetal drawings and epigraphic inscriptions (designs combining symbolism with beauty); and (ii) marquetry (*taracea*). Flat tables were also used in ceilings. Irrespective of its structural or decorative function, carpentry was polychromed with vivid colours to produce an astonishing mixture of shapes, colours and textures (Fig. 2). The polychromy was carefully performed even in unreachable areas (ceilings) and colours were distributed in symmetrical patterns (Fig. 3). Unfortunately, much of the polychromy is today either lost, discoloured or obscured by a dusty film.

Figure 1   *A general view of the Alhambra monument complex erected on the Sabika hill, overlooking the city of Granada.*

EXPERIMENTAL PROCEDURE

Sampling

Sampling was carried out in the Hall of the Mexuar Palace, the Nasrid council room (Fig. 2). This room has undergone many alterations, particularly during the times of the Christian monarchs, who installed their chapel here and changed its design. The original entrance to the Hall of the Mexuar is difficult to identify (López-López and Orihuela 1992). The current small entrance is a later introduction; its doorway and decorations were brought from elsewhere, unfortunately not documented. As a result, original Nasrid polychromed carpentry is scarce in this area; however, its scientific analysis is crucial, since it will serve as a benchmark for future investigations. Avoiding the post-Nasrid intervention woodwork, a total of seven samples representing 14 different colours—exhibited at the surface—were taken from three wooden pieces (table, lintel and ceiling) considered to be original Nasrid by experts from the Alhambra Museum. The following colours were studied: four whites, one orange–red, four reds, two blues (dark and light), two blacks and one metallic grey (Table 1 and Fig. 4).

Instrumentation

In this work, the information obtained by combining microscopic, chromatographic and X-ray emission spectroscopy (XES) methods was effective in recognizing painting materials, pigment manufacture and distinct microtextural painting characteristics that can be indicative
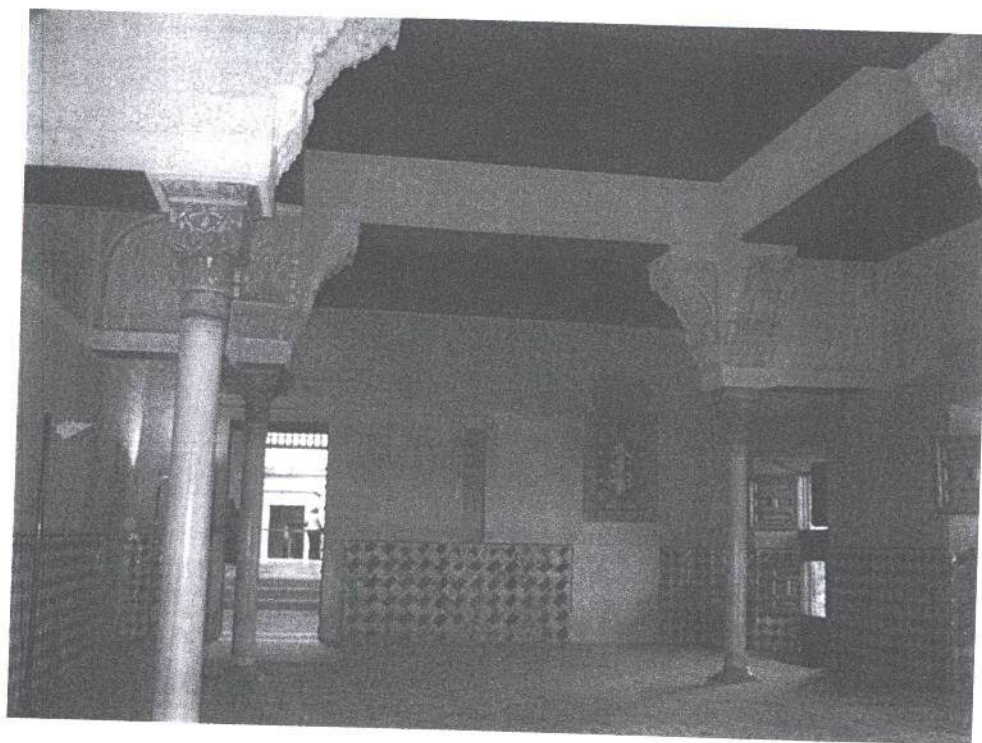
Figure 2 *A view of the Hall of the Mexuar Palace in the Alhambra.*

of particular artistic periods, thus resolving archaeological questions (Scott 2001; Sever Škapin *et al.* 2007).

A stereomicroscope (Olympus SZH10) was used to examine the overall polychrome structure and conservation state. Then, polished thin sections were prepared to allow the study of paint cross-sections and wood identification. Pigment composition, texture, manufacture, polychrome microstructure, deterioration and wood substratum were examined by polarized light microscopy (PLM) in transmitted and reflected light (Olympus BX60), equipped with digital microphotography (Olympus DP10).

The chemical composition of the pigments was identified with a SEM Leo 1430VP (VP-SEM) scanning electron microscope, coupled with an EDX microanalysis Inca 350 version 17 Oxford Instrument, which allows identification of elements with low atomic numbers, including carbon. Images were done in backscattered electron (BSE) and secondary electron (SE) modes. These modes are complementary, since SE provides information on the texture and structure while BSE identifies elemental composition. Single-point analyses and X-ray maps were acquired. The SEM–EDX working conditions were 500 pA filament current, 20 keV beam energy, and 10 eV/ch resolution for pinpoint analyses, and 1 nA filament current and 20 eV/ch resolution for map acquisition. High-resolution maps (1024 × 768 pixels) were obtained in selected areas with 500 frames and a dwell time of 10 ms (16-h acquisition). To ascertain the nature of the pigments, mineral maps were compiled from elemental distribution maps by applying the *Phasemap* tool implemented in the Inca 350 version used in this work. This software allowed identification of mineralogical phases using ternary element plots of specific pixel information
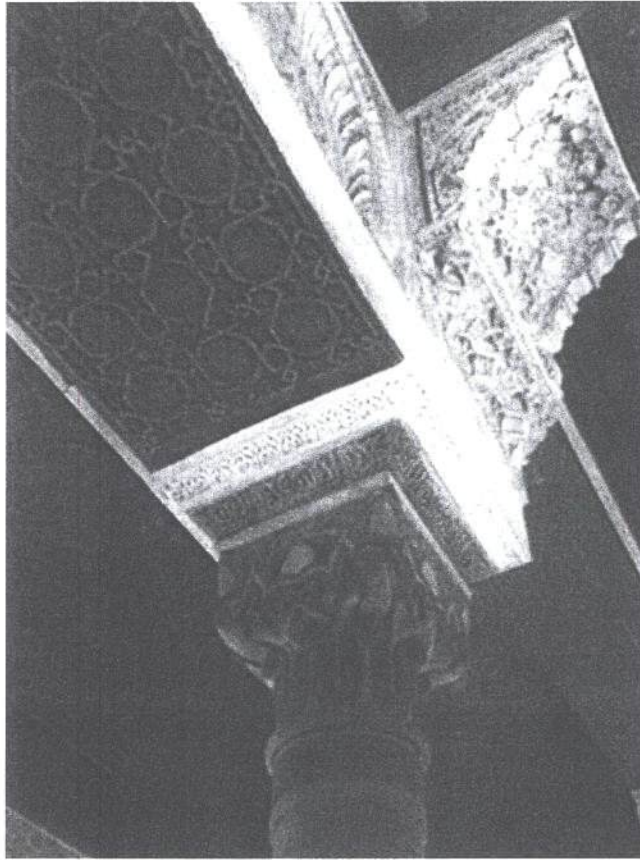
Figure 3 *A detail of the carved polychrome carpentry found in the ceiling between the columns in the Mexuar Hall.*

from montaged X-ray maps of the whole paint cross-sections. This technique particularly highlights the location and morphology of the pigments in the paint stratigraphy.

In the Alhambra from 1923 until recently, carpentry was treated with a mixture of linseed oil, turpentine and beeswax to protect it against deterioration (Torres-Balbás 1965). This complicates recognition of the original binders used by the Nasrids. Thus, analysis of the original binders was first performed using staining tests, and then GC/MS was used to ascertain their nature more precisely (Marinach *et al.* 2004; Andreotti *et al.* 2006).

Staining tests are one of the oldest techniques that have been used for the identification of paint media (Johnson and Packard 1971). We are aware that colour tests are generally considered with suspicion because of their poor selectivity. Nonetheless, it is a convenient preliminary procedure to localize binders within the painting stratigraphy. In fact, these sensitive micro-tests on thin sections constitute a convenient method to determine the medium of a paint layer in a situation where global analysis techniques cannot be applied (Ionescu *et al.* 2004; Fiorin and Vigato 2007). Two reagents (powder dyes, Kremer Pigments GmbH & Co. KG) were used: Fuchsine S for proteinaceous compounds and Sudan Black B for glycerolipid materials. First, samples were tinted with Fuchsine S, which coloured whole egg (yolk and glair) and
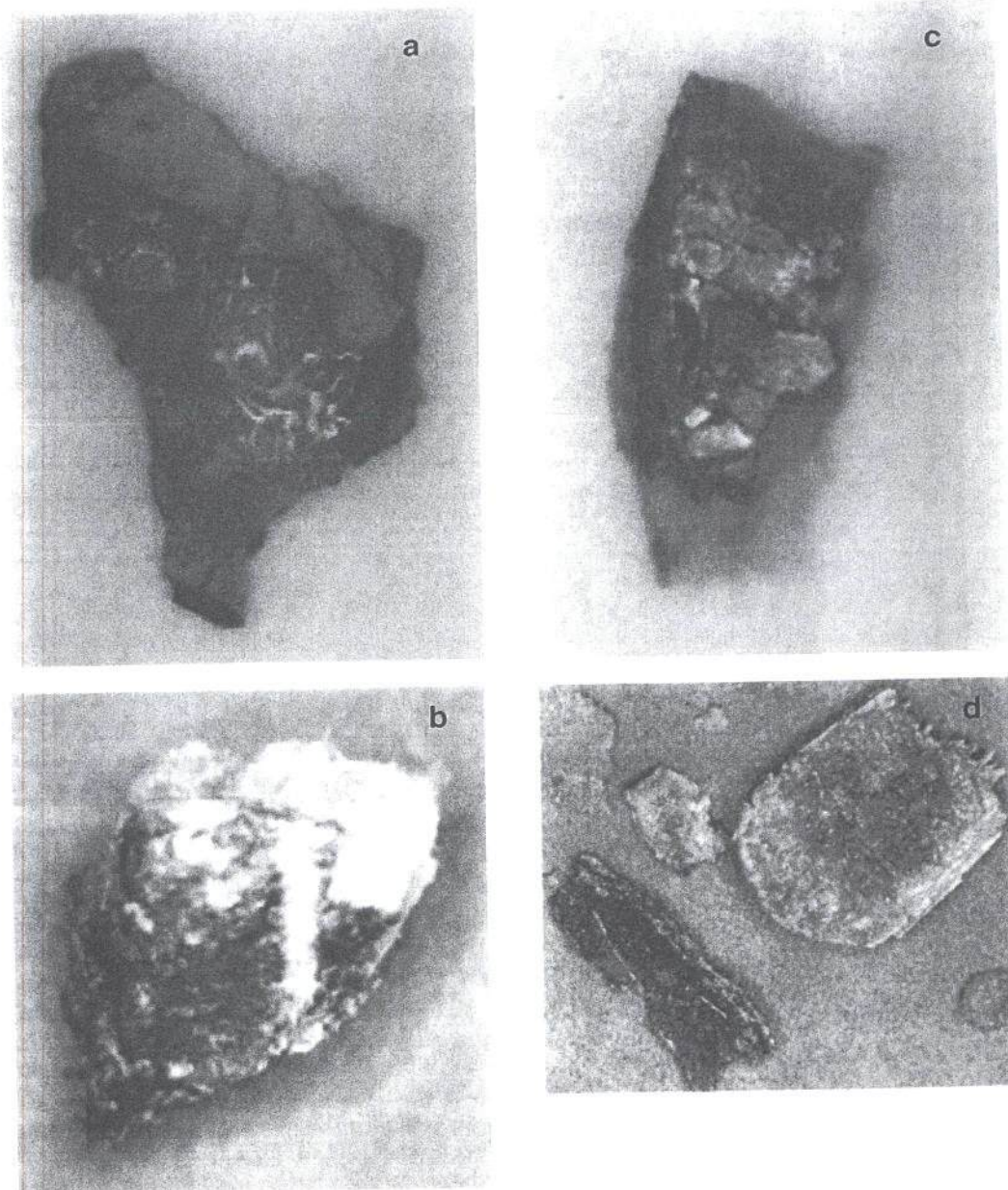
Figure 4   Stereomicroscope photographs of the polychrome samples: (a) sample LMx1, taken from the lintel of the Mexuar's original gate; (b) sample LMx2, taken from the same lintel; (c) sample NCT, taken from a non-context, flat inscribed table; (d) samples CMx1 (dark blue) and CMx2 (light blue), from an alfarje placed in the ceiling. Magnifications 6×.

Table 1 *Samples analysed in the Hall of the Mexuar Palace, Alhambra monument*

Woodwork	Sample	Surface colour	Elements identified in surface layer	Pigments	Underlying layers*	Binder identified with GC/MS	Wood
Lintel original gate† (carved piece)	LMx1	White‡	Pb, Ca	Pb carbonate-based	Organic, Pb carbonate-based organic + HgS	Linseed oil + diterpenic resin	Conifer
Lintel original gate†	LMx2	Black	C	Black carbon	Red lead	—	Conifer
		Red	Pb, Hg, S Sn	Red lead + cinnabar Sn powder			
Lintel original gate†	LMx3	Orange-red	Pb	Red lead	Red lead	—	Conifer
		Red	Pb, Hg, S	Red lead + cinnabar			
Lintel original gate†	LMx4	White	Pb	Pb carbonate-based	Red lead + cinnabar, red lead + chloride salt	Linseed oil	Conifer
Non-context table (flat piece)	NCT	Metallic	Sn	Sn leaf	Ca sulphate-based	Linseed oil + diterpenic resin	?
Flat ceiling (*alfarje*) (carved piece)	CMx1	Dark blue	Na, Al, Si, S, K, Ca	Lapis	Red lead	Egg yolk + walnut oil	*Juglans regia*
		White	Pb	Pb carbonate-based			
		Red	Pb, Hg, S	Red lead + cinnabar			
Flat ceiling (*alfarje*)	CMx2	Light blue	Na, Al, Si, S, K, Ca, Pb	Lapis + white lead	Red lead	Linseed oil + beeswax	*Juglans regia*
		Black	C	Black carbon			
		Red	Hg, S, Pb	Red lead + cinnabar		Linseed oil + beeswax	*Juglans regia*
		White		Pb carbonate-based			

* Starting from below the surface paint layer and going towards the inside of the paint cross-section.
† Housed in the Alhambra Museum.
‡ Non-original Nasrid.
—, Not analysed.

casein pink and animal glue dark red. One gram of the dyestuff was dissolved in 1 litre of distilled water. After a 10 min immersion in this solution, the paint cross-sections were washed with tap water. Next, the same cross-sections were covered with Sudan Black B to demonstrate the existence of lipids (main components of fatty binders) in layers that turned blue or black. The staining reagent was prepared as a 60% solution of ethanol, and after 30 min immersion in the solution the sections were rinsed with 60% ethanol. The paint cross-sections were photographed with PLM subsequent to each test.

GC/MS analyses were carried out using a Platform II mass spectrometer (Micromass Instruments, UK) coupled to a Carlo Erba 8060 gas chromatograph (Thermo Instruments, USA). Chromatographic separations were achieved on a fused-silica capillary column (HP-5MS), with a stationary phase of 5% phenyl – 95% methylpolysiloxane (30 m $\times$ 0.25 mm I.D. and 0.25 μm film thickness). The chromatographic conditions for the analysis were as follows: injector temperature = 250°C; transfer line temperature = 250°C; oven temperature = 120°C (2 min); 5°C per minute to 300°C, then isothermal for 20 min. The carrier gas was helium, at a flow rate of 1.2 ml min^{-1}. Samples were injected in splitless mode. Mass spectra were performed in total ion monitoring mode (mass range 50–450 m/z) and ions were generated by electron impact ionization (70 eV). The source temperature was 210°C. A MassLynx v.4.0 data system was used for data acquisition and processing, and the peak area (TIC) data were used to obtain peak area percentage values. Prior to the GC/MS analysis, solid amounts of paint samples (~5 mg) were introduced in a microvial. Each sample was treated with 0.2 M methanolic solution of Meth Prep II (Alltech, USA) and benzene in a sonic bath at 55–60°C for 45 min (Romero-Noguera *et al.* in press).

RESULTS AND DISCUSSION

The lintel of the original gate

This is a table housed in the Alhambra Museum (ref. no. 2229), considered to be one of the oldest preserved polychrome woodworks in the Alhambra (possibly from the period of Ismail I, 1314–25). It has a red background and a geometric drawing consisting of eight-bow knots with white (LMx1 and LMx4) and red (LMx2, LMx3) colours outlined in black (LMx2) (Table 1 and Figs 4 (a) and 4 (b)). The paint cross-sections examination by PLM in transmitted light under crossed polars (TL–CP) shows that the ground layer (~65 μm thickness) is made of a well-mixed mass of irregularly shaped orange–red and white grains, ranging from <10 μm to 50 μm in thickness (Fig. 5 (a)). The rough surface of these crystals and their variable (high-) reflectivity grades (Fig. 5 (b)) are better observed in reflected light under uncrossed polars (RL–UP). In this image scarce irregularly shaped grains, displaying low reflectivity and variable crystal size (10–30 μm in diameter) are observed. Since all particles are closely combined both amongst themselves and also with the binder, their optical properties are generally difficult to recognize.

An in-depth study of the paint stratigraphies was performed via VP–SEM. In addition to pinpoint analyses, in sample LMx4 elemental maps were acquired of the paint cross-section. Single-point analysis of the ground layer reveals the presence of lead (Pb) in both the orange–red and the white grains that form the matrix (Figs 5 (c) and 5 (d)). Silicon (Si) was detected in some of the largest particles (Fig. 5 (e)), which suggests the presence of quartz (SiO$_2$), most likely added as an extender to give more body to the layer. Additionally, tin (Sn) was identified in the finest particles (~5 μm in size) dispersed in the matrix (Fig. 5 (f)). These particles, which
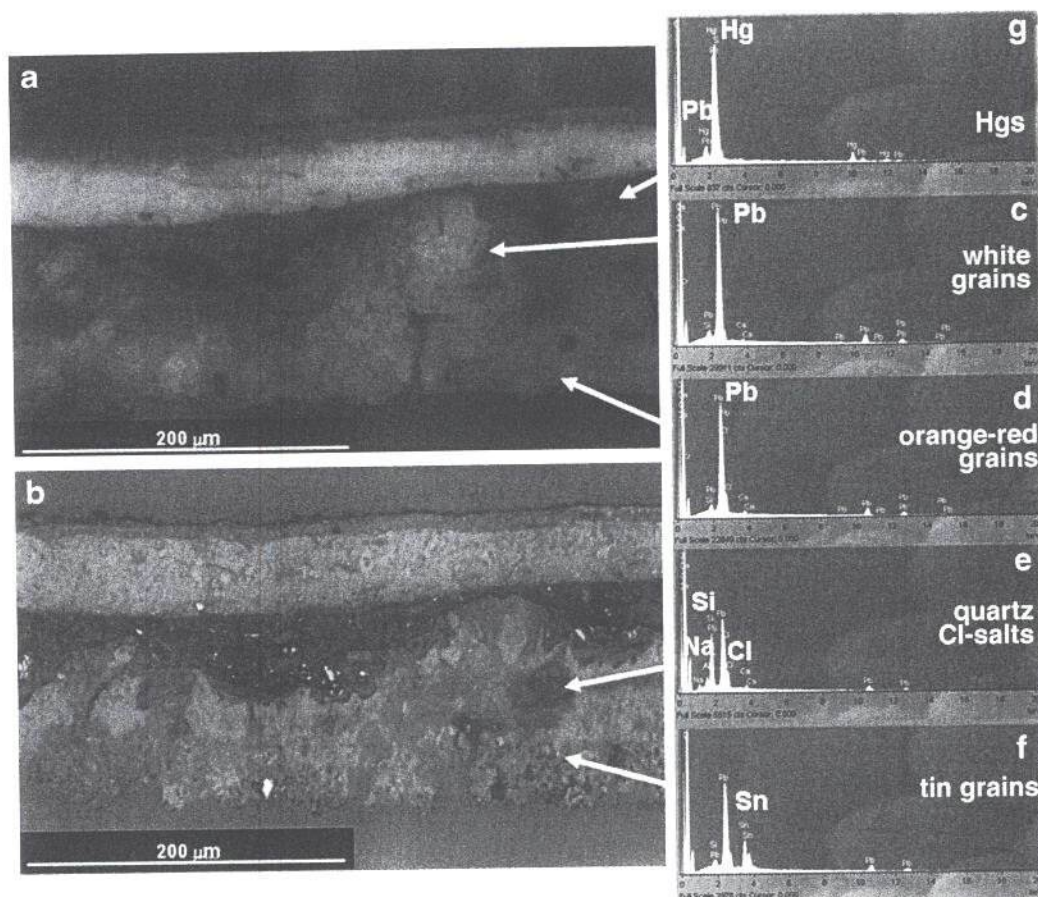
Figure 5   *Photomicrographs showing the cross-section of sample LMx4: (a) tinted with Fuchsine S under TL–CP; (b) under RL–UP. From the inside out, the layer sequence is as follows: red lead base layer, vivid red layer made of cinnabar and white lead layer at the surface. SEM–EDX spectra of (c) white grains, (d) orange–red grains, (e) quartz particles and chloride-based salts, (f) tin grains and (g) red grains.*

were not easily observed with PLM due to their small crystal size, are clearly identified with SEM–EDX as shown by the elemental map for tin (Fig. 6 (b)). The SEM–EDX study revealed clearly that the unaltered tin particles are too abundant to represent impurities. The fact that dispersed tin dots were also detected in red ground and paint layers on different woodwork in the Alhambra palaces (Cardell *et al.* 2004) suggests the hypothesis that powdered tin was intentionally added to confer metallic highlights to the surface of paintings. This is consistent with the Nasrid artists' use of tin glaze to give ceramic a metallic lustre (Jenkins 1983). The metallic overglaze is called *loza dorada*, Spanish for 'golden pottery'. Powdered metals such as gold, silver and tin mixed with other colour pigments to make them intentionally lighter or to achieve a metallic shine have been widely used by different cultures throughout history (Damiani *et al.* 2003; Civici *et al.* 2005, Van Loon *et al.* 2006).

The SEM–EDX study also detected in the ground layer scarce crystals made of chloride (Cl) and sodium (Na) and chloride and lead (Fig. 5 (e)). These were interpreted as sodium
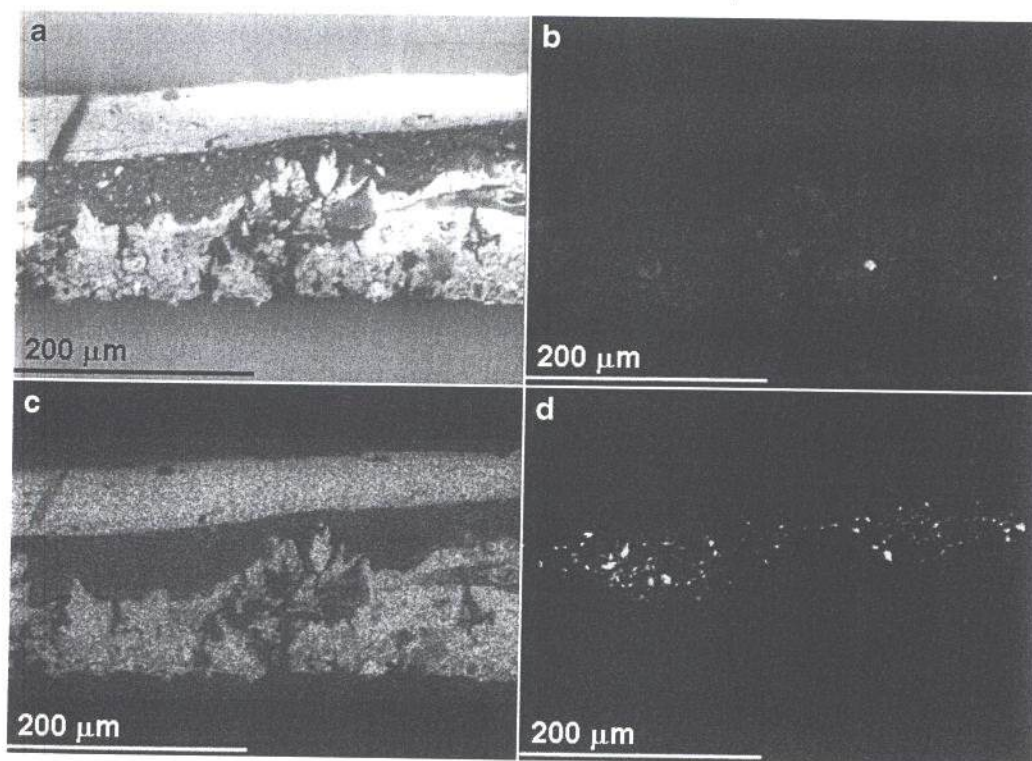
Figure 6   *Elemental maps in the paint cross-section of sample LMx4 for the following elements: (a) a SEM secondary electron image; (b) Sn (tin); (c) Pb (lead); (d) Hg (mercury).*

chloride and lead chloride salts, resulting from the chemical reaction between saline solutions and the Pb-based ground layer. Similar alteration products were identified in red lead-based layers in the polychromed stuccos in the Lions Palace (Cardell and Navarrete 2006), as well as in mural paintings and canvas from elsewhere (Winter 1981; Ordoñez and Twilley 1998; Van den Berg 2002; Cardell and Rodríguez-Gordillo 2003). A rigorous study of alteration products is beyond the scope of this paper, and will be presented elsewhere.

During the conventional SEM study of the matrix, the in-depth examination of the X-ray emission spectra of Pb in the orange–red particles and in the white particles revealed interesting spectral features. The spectroscopic characterization of both Pb-based pigments allowed their differentiation. It was systematically observed that the Pb Mγ spectral line was more intense in the orange–red grains than in the white grains, when intensities were normalized to Pb Mα–Mβ peaks (Fig. 7). The Pb Mγ line corresponds to a transition from a valence shell, contrary to the Pb Mα and Mβ spectral lines, which correspond to electronic transitions between atomic core-levels. Electronic transitions from valence orbitals depend on the Pb chemical environment, and therefore on the nature of the chemical bonds between Pb and the surrounding anions. These electronic properties are different for lead oxides—as is the case of our red grains, which should correspond to natural/synthetic minium (Pb$_3$O$_4$)—and for lead salts; for example, lead carbonates, namely cerussite (PbCO$_3$) or hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$). Minium is an intermediate band-gap semiconductor, whereas cerussite and hydrocerussite are
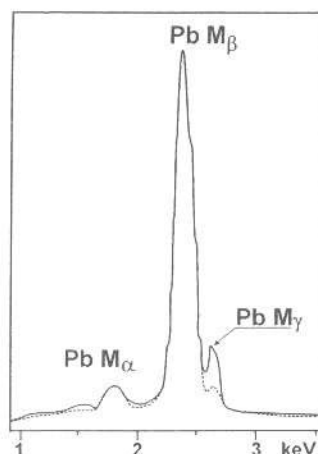
Figure 7 *X-ray emission spectra of Pb for the orange–red and white pigments from the ground layer, showing the Pb Mα, Mβ and Mγ spectral lines normalized to the intensity of the Pb Mα–Mβ peak. Note that the Pb Mγ spectral line is more intense in the red pigment (solid line) than in the white pigment.*

insulators. It is known that reduction of the band gap is accompanied by high electronic neutrality of the atoms (Harrison 1989). The increase of free atom behaviour for Pb atoms, probably as result of the decrease of the fraction of Pb $6s$-character in the Pb-O bonds, is responsible for the higher intensity observed for the Pb Mγ spectral line in the oxide compared to the carbonate. Therefore, it is proposed that the finding of the Pb Mγ spectral line can be used as a feasible diagnostic method to discriminate among red (oxides) or white (carbonates) Pb-based pigments, which further highlights the benefits of applying scanning X-ray fluorescence analysis in the study of artworks (Scott 2001).

In spite of this, the identity of the white Pb-based compound could not be ascertained from the analytical measurements conducted in this study. However, the likely possibility is that lead white, a pigment often found as a mixture of cerussite and hydrocerussite (Palet 2002; Durán *et al.* 2008), is present in the ground layer.

Regarding the orange–red grains, the study with PLM suggests that the ground layer is principally made of a mixture of red lead (Pb_3O_4), orange lead—chemically similar to red lead, but obtained when roasted red lead is produced under insufficient heat from white lead (Palet 2002)—and white lead in lesser amounts. In fact, the layer morphology and textural characteristics of these minerals observed under TL–CP support the hypothesis that, rather than being a layer mainly composed of red lead with scarce white lead pigments added, it seems to be made of improperly manufactured red lead , since a non-homogeneous stratum is seen with shapeless orange, red and white grains (Figs 5 (a) and 5 (b)). It is known that red lead is produced by heating white lead in the presence of air. When red lead is produced under insufficient heat, red–orange oxide forms and white grains can remain embedded in the matrix (Palet 2002). Moreover, this observation supports the premise that synthetic red lead was used, as opposed to natural minium.

On the other hand, intense fissuring affecting the ground layer has caused bowls and detachment visible with PLM and also to the naked eye. We suggest that the use of red lead in this layer, a pigment considered too reactive to be reliable for use in art, is crucial in the deterioration process of the polychromy.

Above, there is a vivid red layer (LMx3) of around 45 μm thickness (Fig. 5 (a)). Here, grains of different red hues in close combination are observed under TL–CP, making it difficult to identify their optical properties. The pigment morphology is better discerned in RL–UP, where angular particles with a broad grain size distribution (<5–30 μm) are seen (Fig. 5 (b)). Pinpoint SEM analysis identified Hg (mercury), Pb and S (sulphur), which suggests the occurrence of mercury sulphide and red lead (Fig. 5 (g)). The elemental distribution maps for Pb and Hg are illustrated in Figures 6 (c) and 6 (d), which reveal the very low amount of Pb in this paint layer. The map for Pb was acquired by choosing the $L\alpha$ line instead of the $M\alpha$ line due to the peak overlapping with the S $K\alpha$ line.

Throughout history, expensive cinnabar/vermilion has frequently been adulterated with cheaper but visually comparable pigments, usually with red lead (Palet 2002; Eastaugh *et al.* 2004a). In the Alhambra, the combination of mercury sulphide and red lead was also found in red layers covering the lacework stucco (Cardell and Navarrete 2006). Although this mixture could be attributed to cost saving, the fact that extremely expensive pigments such as lapis lazuli and gold were widely used to decorate the interior of the Alhambra palaces seems to invalidate this supposition (Cardell *et al.* 2004). More probable is the hypothesis that red lead was added as a siccative – to improve the drying process, since cinnabar/vermillion has poor drying properties. This is further supported by the low amount of red lead detected in the HgS-based layer, and thus this indicates that we are most probably not dealing with an adulterated cinnabar/vermillion pigment.

Regarding the synthetic or natural origin of the mercury sulphide—in other words, artificial vermilion (wet/dry-process type) or natural cinnabar, respectively—the presence of wet-process vermilion can be excluded in our red layer on the basis of the absence of very fine crystals (<1 μm), bacterioid shapes and an even particle size distribution typical of this pigment (Eastaugh *et al.* 2004b). In addition, the wet method is thought to have been known since the late 17th century (Eastaugh *et al.* 2004a). Thus it seems that either cinnabar or dry-process type vermillion was the pigment used here. These two pigments are very difficult to distinguish optically (Eastaugh *et al.* 2004b), although here the use of cinnabar could be inferred from the impurities detected with SEM–EDX in the red layer. Figure 8 shows the elaborated false-colour mineral map for quartz, calcite ($CaCO_3$) and cinnabar, which allows examination of the grain distribution of these minerals, and two total spectra constructed using all the spectra included in two selected windows of the red layer. In addition to Hg, the identified elements were Ca, Si, Al, Mg and Na, which are indicative of calcite, quartz and clay minerals (sheet hydrous aluminium silicates).

It is not unrealistic to consider that expensive cinnabar was used to polychrome carpentry in the Alhambra, considering that very costly pigments such as lapis lazuli and gold were widely employed by the Nasrid artists to decorate the lacework stucco (Cardell and Navarrete 2006). It should be noted—since it is spatially relevant—that the largest cinnabar deposit in Europe was Almadén in Spain, near Granada, already mined during Roman times (Damiani *et al.* 2003; Eastaugh *et al.* 2004a).

With relation to the lead oxide found in this layer, a synthetic origin could be inferred considering that artificial red lead was identified in the underlying ground layer. On the other hand, the SEM–EDX analysis of this red layer revealed the occurrence of isolated, small particles (<10 μm in diameter) identified as tin (Sn). Therefore, it seems that powdered tin was also added to this red paint layer to increase the final luminosity of the polychromy.

Next, the white (LMx1 and LMx4) and black colours (LMx2) were applied according to the decorative design. The homogeneous, well-preserved white pictorial layers (~75 μm thick)
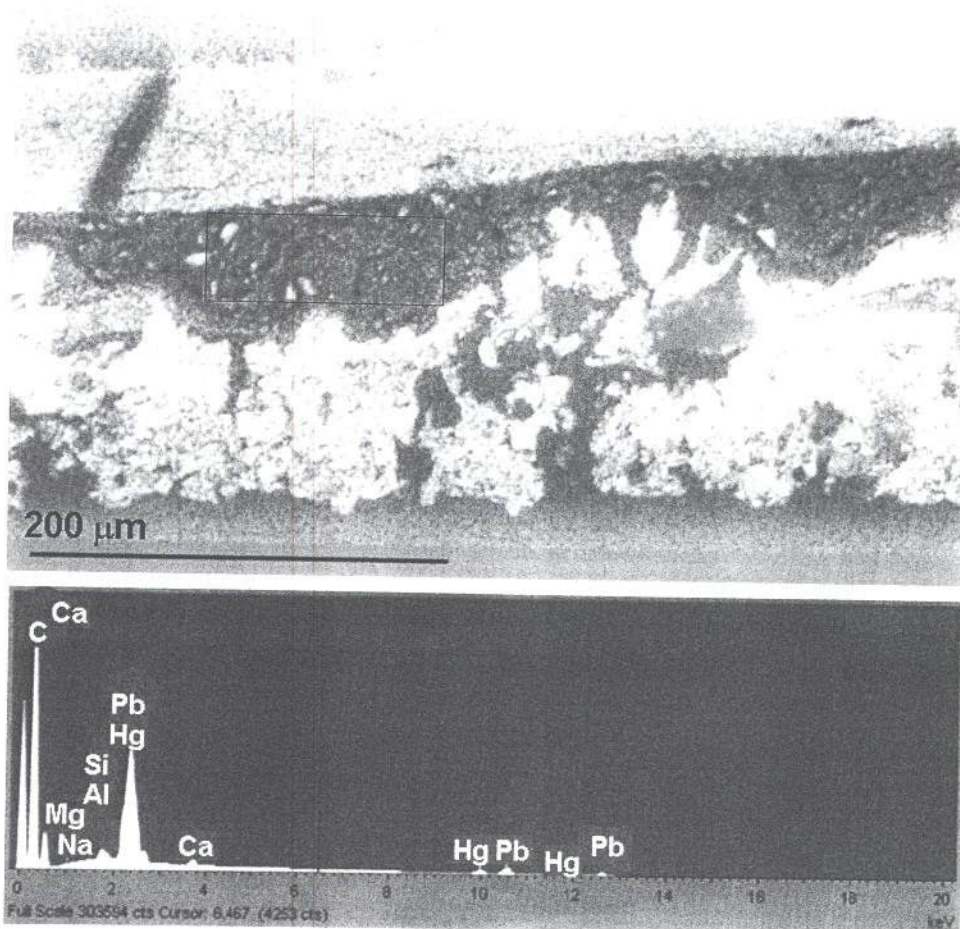
Figure 8   *A false-colour mineral map elaborated from SEM–EDX elemental mappings in the paint stratigraphy of sample LMx4. Red represents quartz, green represents calcite and blue represents cinnabar. The lower part shows the total spectrum of the selected area exhibited in the map.*

show an intense and warm white colour under TL–CP, distinctive of the white lead pigment when mixed with an oil binder (Fig. 5 (a)). The identification of the white pigment with PLM is difficult due to the high packing density of the particles, which additionally are closely mixed with the binder. Nonetheless, in RL–UP, crystals of variable sizes (5–30 μm) are observed exhibiting angular, shard-like habits (Fig. 5 (b)). Lead was the element identified by SEM–EDX, which attests to the presence of a white Pb-based pigment, although the exact composition could not be established with the analytical techniques used in this work. The white paint layer (Fig. 5) is in a good state of conservation, with no signs of pigment dissolution, aggregate formation or darkening. Figure 9 shows the mineral distribution map of the LMx4 paint cross-section, where the false colours were selected in such a way as to reproduce the original paint stratigraphy most realistically. Due to *INCA Phasemap* software limitations, only distributions of four minerals can be displayed at one time. Thus in the elaborated map the ground layer made of red lead exhibits an orange colour, showing dispersed coarse blue
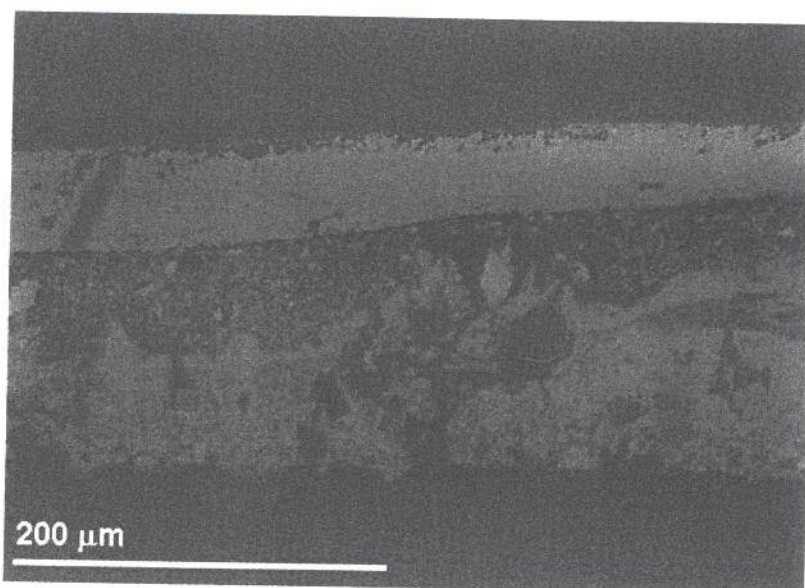
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Figure 9 *A false-colour mineral map of the LMx4 sample paint cross-section based on SEM–EDX elemental mappings. Orange represents red lead, blue represents quartz, green represents a white Pb-based pigment, and bright red represents cinnabar.*

grains that attest to quartz, and smaller green grains that correspond to white Pb-based pigment. Next appears the cinnabar-based layer in vivid red, with scarce blue grains of quartz. At the top there is the white Pb-based paint layer, which shows as a green colour on the map.

Regarding the black colour (LMx2), the PLM study revealed a non-uniform, very thin (<10 μm) layer of intense black colour in TL–CP, made up of finely dispersed particles about 5 μm in size, displaying low reflectivity in RL–UP. The SEM microanalysis identified only C, pointing to the presence of black carbon, since no other element was detected. The absence of phosphorus (P), calcium (Ca) and iron (Fe) excludes the use of bone ash and mineral black pigments, while the lack of vegetal structures indicates that vine black was not employed.

As far as the binders are concerned, the chromatogram of sample LMx4 identified palmitic ($C_{16} H_{32} O_2$) and stearic ($C_{18} H_{36} O_2$) acids—esters of saturated fatty acids—azelaic ($C_9 H_{16} O_4$) acid—characteristic component of aged oils—and suberic acid ($C_8 H_{14} O_4$) in lesser amounts (Fig. 10). The quantitative determination of the percentage content of fatty (palmitic and stearic) acids and dicarboxylic (suberic and azelaic) acids allows discrimination between different types of drying oil (linseed, walnut and poppy seed) on the basis of characteristic parameters: acid ratios A/P (azelaic/palmitic) and P/S (palmitic/stearic) (Mills and White 1994; Andreotti *et al.* 2006). For sample LMx4, the following values were obtained: P/S = 1.6 and A/P = 1.6, which is consistent with the presence of linseed oil, whereas the amount of suberic acid suggests that cooked oil (*oglio cotto*) was used. These results should be interpreted with caution—particularly the A/P index, since the azelaic content varies with ageing and interaction with pigments (Mills and White 1994). Additionally, dehydroabietic and 7-oxodehydroabietic acids were identified in sample LMx1, suggesting the presence of diterpenic resin (Andreotti *et al.* 2006).
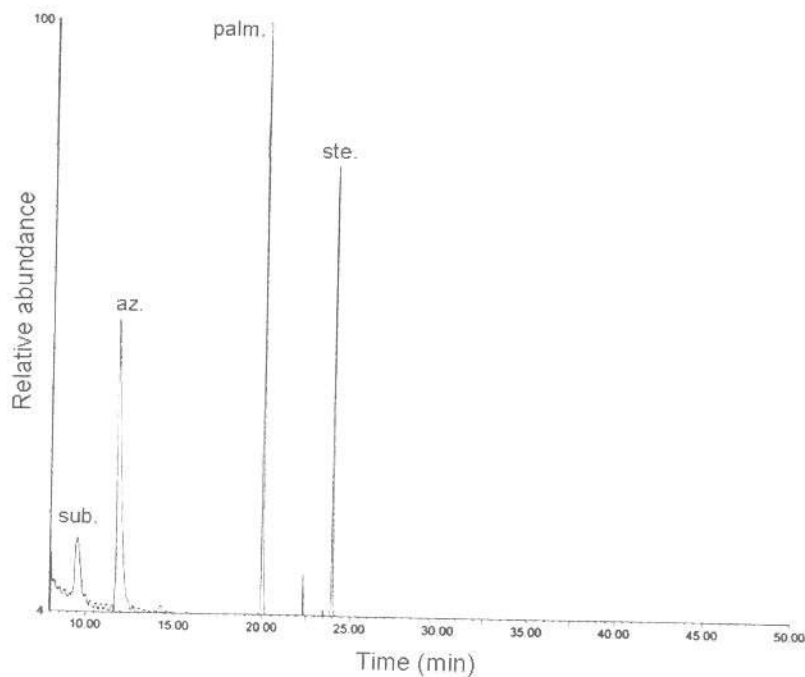
Figure 10 *A chromatogram of sample LMx4. The organic components identified are suberic acid (sub.), azelaic acid (az.), palmitic acid (palm.) and stearic acid (ste.).*

The test with Sudan Black B in all the samples suggests the occurrence of fatty components in the outer layer of the paint cross-sections, thus supporting the belief that they correspond to the refresher paintings initiated in 1923. Tinctures with Fuchsine S show the presence of proteinaceous materials in the preparation, and also in the red and white pictorial layers above, as observed in Fig. 5 (a). The pale pink colour observed leads us to hypothesize that the painting technique used was based on a mixture of drying oil and egg to form *tempera grassa* (Colombini *et al.* 1999).

Wood identification was performed by means of the anatomical structure of the transverse cutting observed in the cross-sections. Conifer wood was recognized, but the species could not be identified. PLM examination revealed that the polychromy was applied on a wood surface that does not correspond to the traditional tangential wood cut.

Inscribed tablet

This is a non-context table hidden by the flat ceiling (*alfarje*) located in the north-west of the Mexuar Hall, and uncovered during the 1995 restoration. Visual inspection shows that it is a flat table with very scarce polychromy, made of metallic cursive calligraphy with a gold lustre over a white ground layer (Table 1 and Fig. 4 (c)). Examination of the paint cross-section with PLM in TL–CP revealed the presence of a homogeneous white ground around 185 μm thick, having a bimodal particle-size distribution; it is composed mainly of even and finely ground crystals (size ~10 μm) and fewer coarser grains (>30 μm). The non-uniform distribution of the binder in this layer is better observed in RL–CP.

The SEM–EDX analyses identified Ca and S in the finest grains and Si in the largest ones, which were interpreted as a calcium sulphate-based pigment and quartz, respectively. In this work, the precise composition of the calcium sulphate could not be established. In fact, one form of calcium sulphate or another (i.e., gypsum, $CaSO_4·2H_2O$, anhydrite, $CaSO_4$ or hemi-hydrite, $CaSO_4·0.5H_2O$) could be present, as frequently occurs in the gesso grounds of paintings and gilded objects from Mediterranean countries, notably Italy and Spain (Khandekar and Schilling 2001). Quartz should correspond to an extender. Also, with PLM dissolution phenomena were observed in the matrix, which favours the coalescence of pores up to 200 μm in diameter, leading to the detachment of the polychrome from the wooden substrate.

A non-uniform bright metallic leaf of around 10 μm thickness follows, with severe physical and chemical alteration, as observed in RL–UP. A dull brownish–buff-coloured coat was seen under RL–CP, as well as intense fissures forming flakes and detachment. SEM–EDX identified the leaf to be formed by tin, and covered by an organic layer of chestnut tone under TL–CP. This technical procedure resembles the Spanish decorative technique called *corladura*, which consists of a varnish applied on a polished piece of silver, to confer a golden lustre (García and Ruiz 1996). In Spain, the *corladura* was one of the painting techniques used throughout the 16th and 17th centuries to decorate wooden sculptures and altarpieces (Calvo-Manuel 1997). Furthermore, the varnish protected the underlying leaf from deterioration. Tin leaf has been identified in diverse polychrome woodworks in the Alhambra (Cardell *et al.* 2004) and also as the underlying layer of gold sheets; both metals were used in the Nasrid gilding technique to decorate the lacework stucco (Cardell and Navarrete 2006). In contrast to the function that tin leaf plays in such gilding, here the tin sheet clearly contributes to the final paint appearance (texture and colour) of polychromed carpentry. In the literature, references were not found concerning the used of false gold on carpentry by medieval Muslims in Al-Andalus (711–1492). On the contrary, false gold is widely found in Christian ornamental implements and altarpieces in the 16th, 17th and 18th centuries, in the cultural heritage of Andalusia (González-López 2002; Durán *et al.* 2008). Contemporaneous uses of golden tin (i.e., tin gilded artificially with varnish) similar to the one found in our gilded woodwork are those from Giotto's frescoes (1267–1337) in Padua (Italy) and in Siena (Italy) during the first half of the 14th century (Tintori 1982).

The GC/MS analysis identified suberic, azelaic, palmitic and stearic acids which, together with the parameters P/S = 1.8 and A/P = 1.6, suggest the occurrence of linseed oil. Additionally, the identification of dehydroabietic and 7-oxodehydroabietic acids attests to the occurrence of diterpenic resin. The identification of the binders with Fuchsine S suggested the occurrence of animal glue in the gypsum ground. The tincture with Sudan Black B did not offer reliable results.

Ceiling

The woodwork studied is a carved piece used only for artistic and symbolic purposes (*capialzado*), situated among the E columns in the Mexuar Hall (Fig. 3). The table displays a reddish-orange background with geometric decoration polychromed in white, dark blue (CMx1) and light blue (CMx2), highlighted in black (Table 1 and Fig. 4 (d)).

PLM examination in TL–CP revealed a reddish-orange ground layer ranging from 150 μm (CMx1) to 50 μm (CMx2), similar to that described in the samples of the lintel, containing white and red shapeless grains (Fig. 11 (a)). Therefore, and considering that the SEM–EDX analyses identified Pb in all the grains, it can be inferred that this layer is made of incomplete
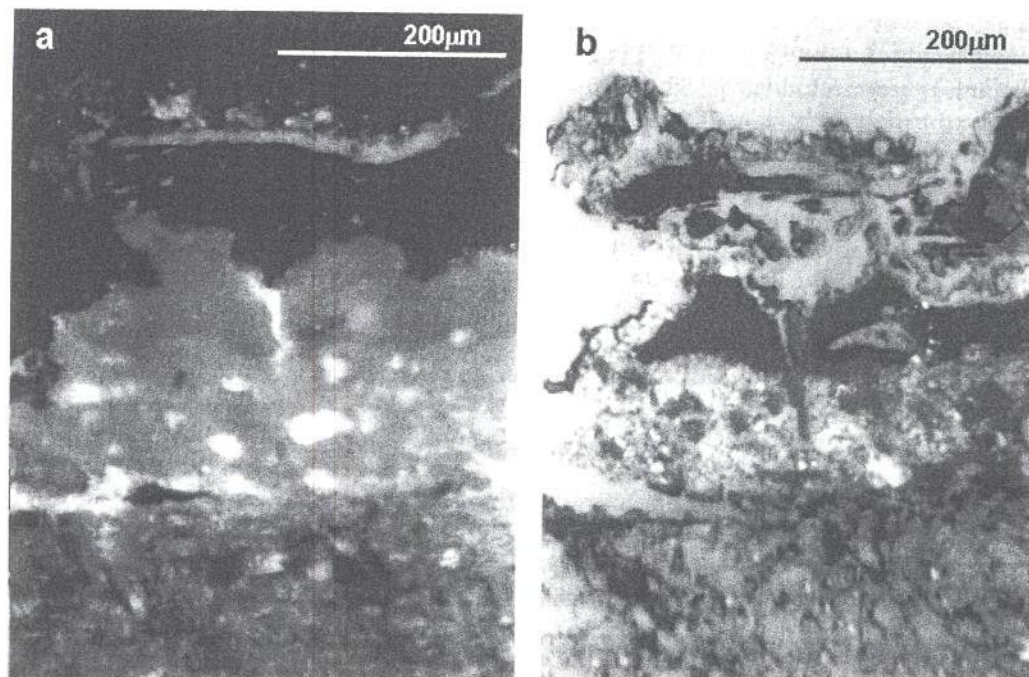
Figure 11 *Photomicrographs showing the stratigraphic section of sample CMx1: (a) under TL–CP; (b) under TL–UP. From the inside out, the layer sequence is as follows: red lead ground, red layer made of cinnabar and red lead, organic layer, white lead layer and lapis lazuli layer at the surface.*

roasted lead oxide; consequently, orange oxide has formed and white grains still remain in the mass. In contrast to the ground layer of the lintel, here the PLM study showed the occurrence of some well-defined white Pb-based crystals (once again, the lead speciation could not be established), in addition to the shapeless white grains embedded in the matrix. This suggests that a white Pb-based pigment was intentionally added to brighten the colour. This is a distinct painting characteristic compared to the polychromed lintel, and while it might be attributed to the artists' technical skill, it could also be indicative of a particular Nasrid period. Additional polychromy samples are being analysed to draw reliable conclusions in this regard.

In Andalusia, an oral source refers to the use of minium as a protective coat against the attack of insect xylophages. Because of its great durability in oil, red–orange lead was used as an anti-corrosive paint and for priming wood (Eastaugh *et al.* 2004a). Recently, minium has been identified as priming in the polychromed sculptures of Alonso Cano (Granada, 1601–67), considered to be one the best painters in the Spanish Baroque. It appears that the Nasrid artists already knew of the protective properties of minium; otherwise, it is difficult to justify the use of this dark base, which clearly reduces the final brightness of the surface colours. Then, to counteract the effects of this dark preparation, the artists added metal powders to the paint layers to attain luminosity.

Above the ground layer, a vivid red layer under TL–CP of around 50 μm thickness was applied (Fig. 11 (a)). The SEM–EDX analysis identified Hg, Pb and S. Thus this layer is considered to have a comparable composition to the similar red layer of the polychromed lintel; that is, a cinnabar-based layer containing red lead pigment. Both this layer and the underlying

ground are crossed by perpendicular fissures, leading to the formation of bowls and detachment from the wood substrate (Fig. 11 (a)). Minium is not an appropriate pigment to be used in priming, because it dries quickly in oil, which could explain the severe physical alteration of the red base layer leading to detachment from the support.

Then, in CMx1 there follows an organic layer (Fig. 11 (b)), lacking in CMx2, made of linseed oil, as revealed by GC/MS analysis through the identification of suberic, azelaic, palmitic and stearic acids, in proportions corresponding to P/S = 1.8 and A/P = 0.3. Often in the studied samples, PLM examination revealed the occurrence of similar organic layers above the red preparation but also between painting layers. Such layers are considered to be insulating coats between paint strata. In *tempera* techniques, as is the case studied here, insulated organic layers are usually applied between painting layers to avoid the binders of the above layers dissolving or mixing with the analogous organic component included in the underlying layers.

This layer was covered by white, dark blue, light blue or black layers, according to the painting design. In CMx1 (Fig. 11 (a)), a homogeneous layer of around 10 μm thickness, exhibiting an intense white colour under TL–CP, was applied upon the organic layer. SEM microanalysis mainly identified Pb and C, attesting to the presence of a Pb-based carbonate pigment such as white lead. Then, the dark blue layer appears. Using PLM and SEM-EDX, the blue pigment was identified to be lapis lazuli ($3Na_2O_3 \cdot Al_2O_3 \cdot 6SiO_2 \cdot Na_2S$), which is composed mostly of the blue silicate mineral lazurite. The elements identified by SEM-EDX in the blue crystals were Na, Al, Si, S, Cl and Ca. Coarse crystals containing Si attributed to quartz (extender) were also detected. In the paint cross-section a non-uniform 40 μm-thick layer made of isotropic crystals of varying size (5–20 μm), angular shapes and deep brilliant blue colours was observed, suggesting a natural origin for the lapis. This result is consistent with the finding of natural lapis in the polychromed stucco in the Mexuar Hall (Cardell and Navarrete 2006).

In CMx2 above the red layer, different colours are seen at the surface. PLM examination in TL–CP revealed the occurrence of a bright white layer applied in two coats totalling 50 μm thickness and affected by vertical fissures. SEM–EDX analysis detected Pb and C, suggesting that a white Pb-based carbonate pigment—for example, white lead—was used. Regarding the black layer, the study with PLM showed that it is an inconsistent coating made of scarce black crystals of around 5 μm in size. The analysis with SEM only identified C, suggesting that black carbon was used, since no other elements, such as P, Ca and Fe, indicative of bone ash and mineral black, were detected. The light blue layer observed in TL–CP is of around 30 μm thickness, and is made by a close mixture of white pigments together with deep-blue isotropic grains. The SEM–EDX analyses identified Pb in the white grains and Na, Al, Si, S, Cl and Ca in the blue isotropic grains, which can be interpreted as a white Pb-based carbonate pigment and lapis lazuli, respectively. The varying sizes (5–20 μm) of the blue pigment areas exhibiting angular shapes lead us to infer that natural lapis was used.

The results of the GC/MS performed on the red layer of sample CMx1 revealed the occurrence of suberic, azelaic, palmitic and stearic acids, in proportions corresponding to A/P = 0.7 and P/S = 1.9, suggesting that cooked linseed oil was used. The oleaginous character of the result could be ascribed to the occurrence of an insulating layer applied between the red and the white layers (Fig. 11 (b)). Following the layered sequence of the stratigraphy, the paint stratum that appears over the red layer should have a certain fatty nature to adhere properly to the underlying layer. The GC/SM analysis of these white and blue strata is consistent with this statement. The chromatogram shows peaks corresponding to azelaic, palmitic and stearic

acids, which indicate the presence of a drying oil. The high palmitic acid content, compared to the other two peaks, suggests the occurrence of yolk. The values of the characteristic ratios $A/P = 0.1$ and $P/S = 3.3$ point to the presence of walnut oil. This kind of oil was preferentially mixed with blue pigments, rather than linseed oil, since the latter turns blue pigments green (Mallégol *et al.* 2001). For both samples, the chromatogram of the top layer reveals the occurrence of linseed oil along with beeswax [fatty acids C22–28 (even carbon numbers) were detected, together with a sequence of straight-chain saturated hydrocarbons, C25–31 (odd carbon numbers)], suggesting that these correspond to the mentioned refreshers. Concerning the wood, PLM examination reveals that walnut (*Juglans regia*) was used.

CONCLUSIONS

The following conclusions can be drawn from the preliminary results obtained in diverse polychromed woodwork from the Hall of the Mexuar (the only remaining part of the Mexuar Palace of Ismail I, 1314–25) at the Alhambra.

Two painting techniques were recognized according to the decorative design: (i) for geometric and vegetal drawings, a dark ground layer of synthetic minium (applied for wood protection) was covered by the diverse-coloured painting layers chosen as a result of artistic considerations; (ii) for epigraphs, only false gold made of varnished tin leaf over a ground layer based on calcium sulphate was found.

Two palettes were identified in the carpentry with geometric drawings. The simpler palette—consisting of white (lead-based pigment), red (cinnabar and red lead) and black (carbon) applied on conifer wood—was identified in the lintel of the original gate, considered to be one of the oldest preserved polychrome woodworks in the Alhambra, possibly from the period of Ismail I. The second, more ample palette, consisting of a similar range of colours but also blue (lapis lazuli) applied on walnut (*Juglans regia*) wood, appears in the flat ceiling (*alfarje*).

In the polychrome carpentry no stylistic differences are evident to the naked eye; thus only an in-depth analytical and microtextural characterization of the paintings reveals distinctions either in the painting materials used or in the execution techniques. In the studied polychromes, only slight differences were found in the elaboration of the red ground layer, the presence/absence of a blue colour and the type of wood used (conifer in the lintel and *Juglans regia* in the ceiling). More polychrome woodwork from different palaces in the Alhambra complex are currently under study to identify distinctive epochal characteristics.

Simple or combined rich pigments were used to achieve different tonalities. Thus for red, a mixture of cinnabar and red lead was used; and for blue, lapis lazuli was used alone or in combination with a pigment based on white lead. Powdered tin was added to the red ground layer to brighten the final painting effect.

Organic insulating layers were applied between painting strata to avoid disturbance of the binders of the lower layer during the application of upper layers with similar organic components.

This research will help to track the technical evolution of Nasrid polychromy on carpentry in the Alhambra. Moreover, it adds knowledge concerning the ascendants of such polychromy, as well as the Nasrid legacy for later Spanish styles—particularly in the *mudejar* style (i.e., the Iberian architecture and decorative style, mainly in Aragon and Castile in the 12th and 16th centuries, which was strongly influenced by Moorish taste and workmanship).

Finally, with this work we would like fill gaps in the history of pigments, where Islamic pigments and painting techniques have systematically been omitted.

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