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Compositional and Quantitative Microtextural Characterization of Historic Paintings by Micro-X-ray Diffraction and Raman Microscopy

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ABSTRACT: This work shows the benefits of characterizing historic paintings via compositional and microtextural data from micro-X-ray diffraction (μ-XRD) combined with molecular information acquired with Raman microscopy (RM) along depth profiles in paint stratigraphies. The novel approach was applied to identify inorganic and organic components from paintings placed at the 14th century Islamic University—*Madrasah Yusufiyya*—in Granada (Spain), the only Islamic University still standing from the time of Al-Andalus (Islamic Spain). The use of μ-XRD to obtain quantitative microtextural information of crystalline phases provided by two-dimensional diffraction patterns to recognize pigments nature and manufacture, and decay processes in complex paint cross sections, has not been reported yet. A simple *Nasrid* (14th century) palette made of gypsum, vermilion, and azurite mixed with glue was identified in polychromed stuccos. Here also a Christian intervention was found via the use of smalt, barite, hematite, Brunswick green and gold; oil was the binding media employed. On mural paintings and wood ceilings, more complex palettes dated to the 19th century were found, made of gypsum, anhydrite, barite, dolomite, calcite, lead white, hematite, minium, synthetic ultramarine blue, and black carbon. The identified binders were glue, egg yolk, and oil.

Many analytical techniques have been used to study historic paints with the goals of determining palette's manufacture and to enable conservation/restoration interventions. Characterizing historic pigments and binders is a challenging task due to the complex composition of artworks and their artistic and historic value, demanding the use of micro- or nondestructive analytical techniques.[1−3] Moreover, the use of a lone technique is generally insufficient to provide evidence of dating, pigment manufacture, execution technique, retouches, and/or alteration phenomena. Instead, coupling complementary techniques allows us to overcome limitations of each individual technique and increase confidence in the results. Some techniques disclose molecular information as Fourier transform infrared spectroscopy (FTIR) and Raman microscopy (RM), while others identify chemical elements present in inorganic pigments and extenders (X-ray fluorescence, XRF) or detect crystalline phases in samples (X-ray diffraction, XRD).[1,3,5−11] In particular, the use of RM and μ-XRD allows unambiguous identification of organic and inorganic painting materials present in the same sample.[10−12] Thus, while RM identifies amorphous, poorly ordered, and crystalline compounds of small grains thanks to its high spatial resolution (~1 μm), μ-XRD clearly identifies most crystalline phases present in paintings according to their abundance and crystallinity degree.

This paper presents a novel methodology combining μ-XRD and RM to characterize real painting samples at molecular, mineralogical, and microtextural levels to unravel their composition, pigments manufacture, execution technique, and chronology. Other complementary analytical techniques used were gas chromatography−mass spectroscopy (GC−MS), scanning electron microscopy energy-dispersive X-ray spectrometry (SEM-EDX), and optical microscopy (OM). The novelty of this work is the determination of the crystallinity and microtextural characteristics of the crystalline phases composing the samples. These physical properties were determined by analyzing Debye−Scherrer rings recorded on two-dimensional (2D) diffraction patterns collected with in-house μ-XRD equipment.[12−15] The intensity profile along Debye−Scherrer rings was used to estimate sizes and number of grains of the main crystalline phases present in the samples.

In this regard, small crystal sizes may suggest a meticulous pigment manufacture or imply alteration processes. For instance, Cu-based pigments such as malachite ($CuCO_3 \cdot Cu(OH)_2$) when altered into Cu chlorides show smaller crystal sizes.[4] By contrast, gypsum recrystallization in wall ground layers yields an increase in their crystal sizes.[16] Moreover, grain morphology (size and shape) can provide information regarding pigments origin. Thus homogeneous HgS crystal sizes suggest a synthetic pigment (vermilion), as opposed to the natural pigment

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Table 1. Samples Analyzed in the 14th Century Islamic University, Madrasah Yusufiyya, of Granada (Southern Spain)

location	sampling	samples	surface color	pigments in surface	pigments in underlying layers	elements in all layers	binders in all layers
Oratory room (Nasrid period 14th century)	polychromed stucco (14th century)	OR-R-NE	red	V, Gy	Gy	Hg, S, Ca	glue: AL
		OR-BL-E	blue[a]	Sm, B, Gy	V, Gy	Ba, Hg, S, Ca, K, Na, Si, Al	glue: GL oil: Sm
		OR-GR-E	green[a]	B, BG, Gy, C	Gy, C	Ba, Cr, Pb, S, Fe, Ca	glue: GL oil: BG
		OR-GR-NE	green[a]	B, BG, Gy, C	Gy, C	Ba, Cr, Pb, S, Fe, Ca	glue: GL oil: BG
		OR-G-NE	gold[a]	G	Gy, C, Az	Au, Ca, S, Cu	glue + oil: white layer
		OR-R-S	red[a]	H	V, Gy, C	Fe, Hg, Ca, S	glue: GL and V oil: H
	wood ceiling (19th century)	OR-W-S	white	ZW, Gy, C	not present	Zn, Ca, S	oil: white layer
Hall room (16th century)	wall (mural painting, 19th century)	W-R1-N	red	Mi, Anh	Anh, B	Pb, S, Ca, Ba, Fe, Si, K, Al	egg: AL
		W-R2-N	red	Mi, Anh	Gy, Anh, H, B	Ba, Ca, Fe, S, Pb	oil: H egg: GL and M
		W-R3-N	red	H, Mi, Anh, Gy	Gy, Anh, B, Mi	S, Ca, Fe, Pb	egg: AL
		W-R4-N	red	H, Gy, Anh, C	Gy	Fe, Ca, S	glue: AL
	wood ceiling (19th century)	AL-R	red	H, Mi	Anh	Fe, Pb, Ca, Si, S	oil: AL
		AL-W	white	Dol, C, Anh, Gy	H, Ult, Gy, Anh, B	Mg, Ca, S, Ba	egg: AL
Knights room (16th century)	wood ceiling (? century)	C-W1	white	Hy, Cer, C	Hy, Cer, C, Mi	Pb, Ca	oil: AL
		C-W2	white	Hy, Cer, Gy, Mi	Gy, Anh, C, Q	Ca, S, Pb, Si	oil: AL
		C-OC	ochre	Hy, Cer, C, H	Hy, Cer	Pb, Fe, Ca	oil: AL
		C-R1	red	Mi	Gy, Hy, Cer, Anh, C	Pb, Ca, S	oil: AL
		C-R2	red	Mi, C	Gy, C	Pb, Ca, S	oil: AL
		C-BK	black	BC	Cer, Hy, Gy, C	Pb, Ca, S	oil: AL

[a] Christian intervention; pigments identified by μ-XRD and RM; elements identified by SEM-EDX; binders identified by RM and GC−MS. Acronyms for pigments: V = vermilion; Gy = gypsum; C = calcite; B = barite; Sm = smalt; BG = Brunswick green; G = gold; H = hematite; ZW = zinc white; Mi = minium; Anh = anhydrite; Dol = dolomite; Hy = hydrocerussite; Cer = cerussite; BC = black carbon; Az = azurite; Ult = ultramarine; Q = quartz; AL = all layers; GL = ground layer.

cinnabar, which commonly shows heterogeneous HgS crystals. Similar arguments can be used to distinguish between natural and synthetic ultramarine blue.[4,17]

The combined use of μ-XRD and RM to obtain detailed molecular, mineralogical, and microtextural information of crystalline phases provided by 2D diffraction patterns has not been reported in previous studies. Thus, this is the first attempt to use this approach to fully characterize real paint samples, recognize the nature and manufacture of pigments and decay processes, and track historic interventions. The ultimate goal is to draw historic and archeological conclusions to help clarify the confusing chronology of the paintings at the *Madrasah* palace of Granada.[18]

EXPERIMENTAL SECTION

Sampling Site. The Madrasah palace of Granada was built by Yusuf I (of the Nasrid dynasty, 1238−1492 AD) in 1349 AD in the religious and trading center of the ancient Madinat Garnata (Granada, Southern Spain). The original Madrasah Yusufiyya was the first Islamic University of Granada and the only extant Islamic University dating back to the time of Al-Andalus. Soon after the Christian conquest in 1492 AD, the Madrasah became the city council. Since then, the building has undergone numerous reforms including incorporation of new rooms such as "the Hall room" and "the Knight room" and restoration interventions such as that undertaken by the University of Granada. At present, the only original Nasrid room is "the Oratory room"; however, it has undergone several interventions since the 18th century, particularly in 1893.[18] In the 16th century, the Hall room and the Knight room were constructed and decorated, later undergoing further interventions starting in the 18th century.[20] Nevertheless, the full chronology remains unclear.

Painting Samples. Nineteen samples were taken from the monument (Table 1). The sampling procedure was guided by (i) location in the building, (ii) color observed on different substrates (stucco, wood, mural), and (iii) possible historic interventions. Results are organized according to room to facilitate identification of similarities or differences of painting materials and thus enable tracking historic interventions chronologically.[3,4]

Analytical Techniques. Paint stratigraphies were prepared as polished thin sections for analyses. They were first examined using a polarized light microscope in transmitted and reflected light (Olympus BX60) to obtain an overview of the paint layers' disposition, morphology, and color. The system was equipped with a digital camera for microphotography (Olympus DP10). Then a detailed chemical and morphological analysis was performed with a scanning electron microscope SEM Leo 1430VP coupled with an EDX microanalysis (SEM-EDX) INCA 350 version 17 Oxford Instrument. Single-point elemental analyses were registered in every layer of sample stratigraphies. SEM-EDX

working conditions were 500 pA filament current, 20 keV beam energy, and 10 eV/ch resolution.

Micro-X-ray diffraction (μ-XRD) analyses were used to identify crystalline components and for microtextural study. Analyses were performed on paint stratigraphies prepared as double-polished thin sections as described elsewhere.[3] A μ-XRD system developed at the Centre de Recherche et de Restauration des Musées de France at the Louvre Museum was used. The μ-XRD system was equipped with a Cu high-flux, microfocus X-ray tube (Rigaku MSC MicroMax equipped with a Kirkpatrick-Baez mirror). Imaging plates were used as 2D detectors which allow fast data collection (10 min per sample spot) with good angular resolution.[5,12,19] μ-XRD analyses were done in reflection mode with an incidence angle around 10° using a 200 μm collimator for microanalysis. For each sample, a set of analyses was performed across a 1 mm line every 10−50 μm in each paint stratigraphy starting from the sample surface inward. Due to the small thickness of some layers (<10 μm as seen by the OM), the different measurements do not always correspond exactly to individual paint layers. Nevertheless, as demonstrated by Duran and co-workers,[12] useful information of composition evolution along sample depth profiles can be obtained. The FIT2D software was used to transform 2D images into standard one-dimensional (1D) XRD diagrams (2θ scan).[5,12,19] The EVA and/or XPowder software programs were employed to identify crystalline phases using the PDF-2 database (JCPD) from calculated XRD diagrams and to perform quantitative analysis.[20]

Microtextural features of crystalline phases was done by analyzing the concentric Debye−Scherrer rings (2D diffraction patterns) with the software XRD2Dscan.[13,15] Each ring corresponds to a specific set of $\{hkl\}$ crystallographic planes of a particular mineral phase and is formed by reflection spots of all mineral grains illuminated by the X-ray beam that are oriented with a set of $\{hkl\}$ planes to fulfill the Bragg diffraction condition. According to sample characteristics, the rings display particular variations in intensity and continuity. Thus, for a fixed beam size, depending on grain size, the number of grains illuminated is very large for nano- or microcrystalline materials or very small for coarse-grained materials. Also, continuous rings are formed by superposition of many reflections in the case of fine-grained minerals, and broad rings will be obtained when nano- or microcrystalline phases are present. Instead, spotty rings form by isolated reflection spots produced by a reduced number of coarse mineral grains. Additionally, the total number of peaks (TNP) of one ring is a gauge of the number of grains illuminated and of their sizes. Another textural characteristic obtained is the average intensity of peaks (API) along a Debye−Scherrer ring, which is related to the crystal sizes of mineral grains. Indeed, the intensity of these peaks is directly proportional to grain sizes, allowing size quantification.[13,14] Moreover, this technique enables quantification of grain sizes of individual mineral phases that might be present by analyzing rings associated with each mineral.

Raman microscopy analyses were performed with a Renishaw InVia Raman microscope system fitted with a Peltier-cooled CCD detector and a Leica DMLM microscope to identify inorganic and organic compounds present in the paint samples. Samples were excited with a 785 nm diode laser. Spectra were collected with an average resolution of 1 cm^{-1} within the wavenumber range of 200−3000 cm^{-1}. To improve signal/noise ratios, a series of recorded spectra (n = 10) with exposure time of 20 s were collected in each sample spot and averaged. Spectra were taken by placing the samples on the microscope stage and observing them using 20× and 50× objectives. A video camera was employed to identify particular locations in the painting stratigraphies. Precautions were taken to not cause any damage to samples (laser-induced degradation of paintings). Thus, laser power was kept between 0.2 and 20 mW to avoid paint component alteration and to obtain the best spectra.[21] In this work, key Raman bands and main diffraction peaks are given only the first time that a specific paint compound is mentioned in the text. Moreover, elements identified with SEM-EDX from all layers are not mentioned in the text (they confirm μ-XRD and RM results), and readers are referred to Table 1.

Gas chromatography/mass spectroscopy (GC−MS) analyses were done on chip samples to determine the organic binders as described elsewhere.[3]

RESULTS AND DISCUSSION

Oratory Room. Seven samples were studied showing different surface colors, such as red, blue, green, and gold (applied on stucco) and white (used for wood ceiling, Table 1). According to μ-XRD, the red sample OR-R-NE was composed of HgS (main diffraction peaks at 26.5 and 31.2° 2θ; JCPD: 06-0256). Its presence was confirmed by RM analysis thanks to Raman spectra showing key bands at 251 and 343 cm^{-1} (the distinction between cinnabar and vermilion based on μ-XRD textural analysis is explained below). The red color was applied over a ground layer of gypsum ($CaSO_4 \cdot 2H_2O$, key diffraction peaks at 29.2 and 31.2° 2θ; JCPD: 33-0311; and main Raman bands at 418, 497, 628, 1005, and 1140 cm^{-1}). No XRD peaks were detected from the blue sample; instead, a broad band indicated its amorphous nature. RM analysis identified blue smalt via the Raman band at 470 cm^{-1}. Blue smalt is an artificial pigment made of fine to coarsely ground potassium cobalt glass. In Europe, it was used as early as the 15th century up to recent times;[22] thus, this is not an original Nasrid paint layer. This finding was supported by the scarce literature available in this regard claiming that lapis lazuli and azurite were the only blue pigments used in Nasrid polychromes.[3,4,23] In this blue layer, also barite ($BaSO_4$) was identified by both techniques; indeed, Raman spectrum exhibited its key band at 989 cm^{-1}, and the barite XRD pattern showed typical peaks at 28.8 and 42.6° 2θ (JCPD: 24-1035). The barite identified as an extender in this blue layer points to an intervention dated no earlier than the 19th century since barite pigment was introduced in the market in that century.[24] In addition, an irregular layer of HgS was detected under the blue smalt, suggesting that the red layer is originally Nasrid.

The green samples (Table 1) were made of Brunswick green a pigment composed of Prussian blue, chrome yellow, and barite, commercialized in the 19th century.[24] RM analyses identified the main Raman bands of barite, chrome yellow (359, 377, 401, and 840 cm^{-1}), and Prussian blue (275, 530, 2075, 2150, and 2153 cm^{-1}); however, μ-XRD only detected barite. The green layers were applied over a white ground layer made of gypsum and calcite ($CaCO_3$, key diffraction peaks at 29.4 and 47.6° 2θ; JCPD: 05-0586; and key Raman band at 1086 cm^{-1}).

The characterization of the golden sheet (Figure 1a) exemplifies the benefits of our method. Figure 1b shows the OM image of the paint stratigraphy. A golden sheet was applied over a thick white layer, and both lie on top of an irregular blue layer. μ-XRD analyses identified gold (Au) at the surface (key diffraction peaks at 38.3 and 44.5° 2θ; JCPD: 04-0784), gypsum and calcite in the white layer, and azurite grains ($Cu_3(CO_3)_2 \cdot (OH)_2$) in the innermost layer (main diffraction peaks at 25.23° 2θ; JCPD: 11-0682)

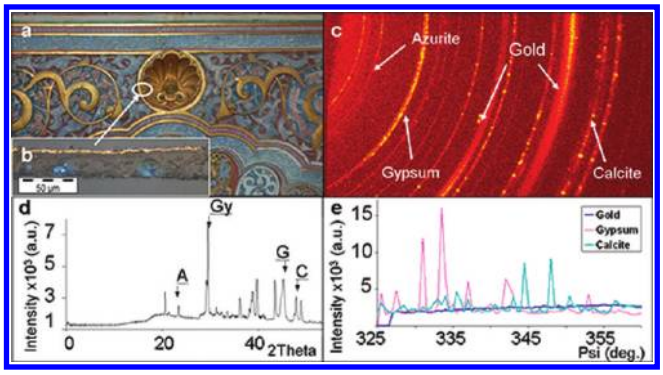

Figure 1. Gold sample from the Oratory room: (a) detail of analyzed area; (b) paint stratigraphy seen by OM (reflected light, crossed Nicols); (c) 2D diffraction pattern of crystalline phases; (d) Two-theta scan calculated from the 2D pattern: azurite (A), gypsum (Gy), gold (G), and calcite (C). (e) Intensity profiles along the main diffraction rings associated with each mineral.

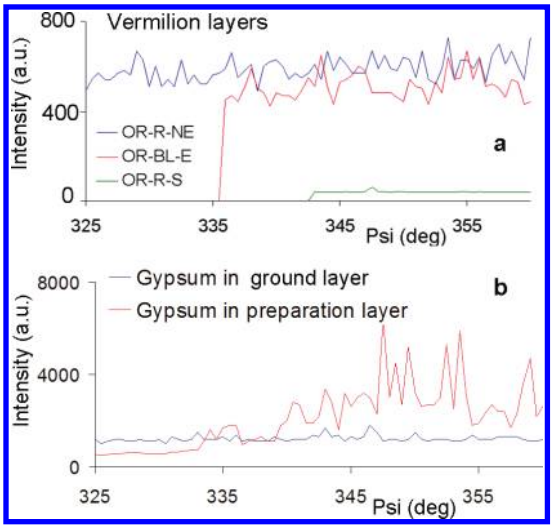

Figure 2. Graphics showing the intensity profile along the strongest diffraction rings of (a) vermilion at 26.5° 2θ corresponding to three layers from the Oratory room samples, and (b) gypsum at 31.2° 2θ from surface and ground layers in all Oratory room samples.

(Figure 1c,d). The detection of gypsum, calcite, and azurite was corroborated by RM analyses via the recognition of their key Raman bands: gypsum and calcite (cited) and azurite at 401 cm^{-1}. In this sample, azurite was believed to be an original Nasrid pigment considering its identification in other early Nasrid polychromes characterized in Granada[3,4,23] and the fact that other layers (gypsum and gold) were applied on top. Thus, the above gilding should be attributed to a later intervention. Although there are not enough data to ascribe this intervention to a particular period, we suggest that it may belong to the 19th century since results in others samples from this room (e.g., OR-BL-E) so suggest.

RM analyses could not detect the presence of gold. Indeed, gold does not have Raman activity due to its crystal symmetry (i.e., face-centered cube). However, gold was identified by μ-XRD due to its abundance. As mentioned above, though our μ-XRD explores a large sample area (~200 μm), to detect a crystalline phase, there must be enough grains of this phase properly oriented to satisfy the Bragg diffraction condition. Thus, the higher the number of crystals, the bigger the probability of satisfying the diffraction condition; so it is difficult to detect scarce and isolated coarse grains with μ-XRD.[15]

The μ-XRD microtextural study revealed the presence of nanocrystalline gold, as suggested by the broad and continuous rings produced by this phase in the 2D diffraction pattern (Figure 1c) and corroborated by 1D XRD diagram (Figure 1d). Additionally, the blue line in Figure 1e shows a low and constant intensity profile along the diffraction rings associated with gold, different from the spotty rings for other mineral phases present in this sample. In particular, the rings attributed to gypsum (Figure 1e) have very strong reflection spots due to the large size of gypsum grains in the ground layer and/or also due to recrystallization events due to alteration processes.[16] The crystal size of these neoformed grains was estimated to be ~40 μm versus the 15 μm size of the unaltered gypsum crystals present in the same layer, as shown by the pink line in Figure 1e (note the sharp gypsum peaks). The rings associated with calcite (Figure 1c,e, green line) showed strong isolated reflection spots, indicating that calcite grains were relatively large (few tens of micrometers). Microtextural analysis was not done on the azurite pigment since, as explained before, only scarce grains were present (which would justify the mentioned historic gilding intervention), and so an estimation of grain size based on μ-XRD could not be achieved.

The OM study of sample OR-R-S revealed two red layers of different hues applied over a coarse white ground layer. The outermost red layer was identified as hematite (Fe_2O_3, key Raman bands at 293, 410, and 616 cm^{-1}) applied over the remains of another red layer identified as HgS. HgS was clearly detected by μ-XRD unlike hematite which showed very weak peaks. The characterization of iron oxide hydroxides using μ-XRD was difficult due to the small amount of these pigments and their low reflecting power compared to the main crystalline phases present in the sample. Another difficulty in identifying hematite is the strong X-ray fluorescence of Fe-bearing minerals when analyzed using Cu radiation.[25] The white ground layer was made of gypsum and calcite according to μ-XRD and RM analyses. The white sample taken from the wood ceiling was composed mostly of zincite (ZnO, with key Raman band at 434 cm^{-1} and diffraction peaks at 31.8 and 36.3° 2θ, JPCD: 05-0664), corresponding to the zinc white pigment. The occurrence of zinc white indicates a 19th century intervention since this pigment was industrially commercialized around 1845.[24] This datum is chronologically compatible with the identification of blue smalt in the polychromed stucco of the Oratory room.

To further demonstrate the benefits of our method, we assessed the microtextural properties of diverse samples from different periods (according to our results). Thus, grain sizes of HgS and gypsum layers were studied analyzing their corresponding 2D diffraction patterns. Results revealed that HgS was very similar in grain size (tens of micrometers) in samples OR-R-NE and OR-BL-E (Figure 2a). On the contrary, grain size of HgS in sample OR-R-S was notably smaller (a few micrometers). In fact, the API data of sample OR-R-S showed lower values (385) than the other two samples (621 and 702), implying smaller crystal size. Moreover, the corresponding averaged TNP data revealed lower number of HgS grains (10) in the OR-R-S sample compared to the other two samples (27 and 25).

Diverse studies conducted in Nasrid palaces in Granada have identified HgS either as cinnabar or vermilion in their polychromed

decoration.[3,4,23] Cinnabar and vermilion are names assigned to HgS of different origin: cinnabar is a natural compound used as pigment since ancient times (China), and vermilion (wet/dry process type) is a synthetic pigment known since the eighth century.[26] No differences in their composition or crystal structure can be recognized, though slight morphological disparities between them may help in its determination, as well as the existence of impurities in natural cinnabar.

Considering our microtextural results, the presence of wet-process vermilion can be excluded in our samples on the basis of the absence of very fine crystals (<1 μm) and even particle size distribution typical of this pigment.[17] Moreover, the wet method is thought to have been known since the late 17th century.[26] On the other hand, cinnabar must be excluded since no impurities were detected with SEM-EDX. Thus it seems that dry-process-type vermilion (introduced to the West by the Arabs in the ninth century) was the pigment used here. Nevertheless, our microtextural study revealed different vermilion grain sizes that may suggest different periods of painting execution. However, microscopic evidence from paint layers in sample OR-R-S suggests that the vermilion layer in this sample is of Nasrid origin similar to the other two samples. Indeed, the hematite layer above the vermilion layer in this sample supports this idea, suggesting that hematite was applied in a later intervention due to the deterioration of the vermilion layer, where only a few grains remain as revealed by OM. We hypothesize that the deterioration of the vermilion layer in this sample may have loosened the biggest crystals.

In the Oratory room, also, gypsum crystal sizes appearing in different layers were studied (see layers in Table 1). Microtextural analyses showed that gypsum grain sizes were notably different depending on the position of the studied layer in the paint stratigraphies (Figure 2b). According to API data, grain sizes were smaller (~10 μm) at the surface layers than in ground layers (~50 μm). In addition, TNP data revealed that gypsum crystals were more abundant in ground layers than in surface layers. Here differences in crystal sizes cannot be ascribed to diverse paint execution periods but rather to the role of the paint layer in the painting structure. Normally, coarse grains are present in ground layers to assist adherence between the substrate and the overlying paint layers. On the contrary, finer-grained pigments are used in surface paint layers to improve paint finish.[24]

Regarding binders, RM analyses identified glue binder (proteinaceous binder) in all layers of sample OR-R-NE, the vermilion layer of sample OR-R-S, and all ground layers of the stucco samples (Table 1) via the detection of a sharp aromatic ring breathing band at 1002 cm^{-1}, the amide III band at 1245 cm^{-1}, and the N−H and C−C (stretching modes) bands of phenylalanine and tyrosine at 1578 cm^{-1} and 1607 cm^{-1}, respectively.[8] Though Raman spectra of protein binders are rather similar, they can be distinguished by differences in band position and relative intensity, particularly of bands near 1000 and 1450 cm^{-1}.[10,27] However, in this work, fluorescence problems did not allow us to discern the type of protein present. Instead, an oil binder was identified in all layers (blue smalt, hematite, green and white) attributed to a Christian intervention (19th century). Oil binders were recognized by RM through the C−H deformation bands of olefinic molecules shown at 1310 cm^{-1} (in-phase methylene twist) and at 1445 cm^{-1} (scissoring mode of methylene $\delta(C_{H_2})$, the cis double bond stretching ν(C=C) band shown at 1660 cm^{-1} and the band at 1747 cm^{-1} (ester stretching ν(C=O)).[28−30] Oil discrimination was not possible due to high fluorescence, which masked other characteristic Raman features. GC−MS further confirmed the presence of oils via the recognition of azelaic acid (A, $C_9H_{16}O_4$, characteristic component of aged oils), palmitic acid (P, $C_{16}H_{32}O_2$), and stearic acid (S, $C_{18}H_{36}O_2$).[31] Quantitative determination of percentage contents of fatty (P and S) acids and dicarboxylic (azelaic and suberic) acids allows discrimination between different types of drying oil (e.g., linseed, walnut, and poppy seed) on the basis of characteristic acid ratios A/P and P/S.[32] Here, however, the nondistinct percentages prevented oil discrimination.

Hall Room. Six samples taken from the wall and the wood ceiling were studied (Table 1). The polychromy of this room is based on white and red (different hues) applied over a white ground layer. The identified red pigments were hematite and minium (Pb_3O_4, key Raman bands at 237, 316, 394, and 550 cm^{-1} and diffraction peaks at 34.1 and 47.6° 2θ; JCPD: 41-1493). Hematite was not detected by μ-XRD for the reason explained above. Synthetic ultramarine blue (a pigment synthesized in 1828) was identified in AL-W sample via the key Raman band at 549 cm^{-1} and distinguished by light microscopy via particle size (very small and even crystal sizes).[26] Instead, it was not detected by μ-XRD due to scarce pigment crystals. All ground layers were made of gypsum and/or anhydrite and/or barite as identified by μ-XRD and RM (Table 1). Both techniques allowed discrimination between the two minerals, that is, gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$). Anhydrite was identified via Raman bands at 422, 503, 615, 681, 1010, and 1128 cm^{-1} and diffraction peaks at 38.8 and 40.8° 2θ (JCPD: 37-1496).

For this room, we present the results of evolution in composition along the depth profile of the white sample AL-W. Figure 3a is an OM view of the sample which consists of five layers. Figure 3b shows the RM analyses of each layer. In layers 1 and 2, dolomite ($CaMg(CO_3)_2$, key Raman bands at 1099 cm^{-1}), anhydrite, and gypsum were identified, while in layer 3, only the latter two were found. Barite, anhydrite, and synthetic ultramarine blue were detected in layer 4 and hematite in layer 5. Figure 3c shows the μ-XRD results. Calcite and dolomite were identified in the surface layer, barite was found in the underlying layers, and gypsum and anhydrite appeared in all layers. Hematite could not be detected.

In the Hall room, the microtextural study was restricted to gypsum and anhydrite crystals present at surface and the ground layers from all samples. The API data suggested that gypsum had smaller grain sizes than anhydrite in both the surface and ground layers (927 and 532 vs 1582 and 714, respectively). However, when analyzing in detail the intensity profile of the two minerals, it was deduced that both had similar grain sizes (ca. 10−20 μm) with the exception of few-larger anhydrite grains (ca. 50 μm in size), which produced some high intensity peaks. Moreover, the averaged TNP data showed a higher number of gypsum grains than anhydrite grains in all layers (42 and 33 vs 26 and 17, respectively). This result suggests that gypsum is the main mineral phase in these layers, as confirmed by XRD quantitative analysis (67% gypsum).

The composition of binders in this room is especially variable. Proteinaceous binders were detected with RM in almost all layers in certain samples (Table 1). Egg yolk was identified through key protein bands at 1360, 1586, and 1603 cm^{-1} (from tryptophan, tyrosine, and phenylalanine aromatic amino acids)[8] and the characteristic carbonyl vibration at 1740 cm^{-1}.[31] Also, RM detected oil

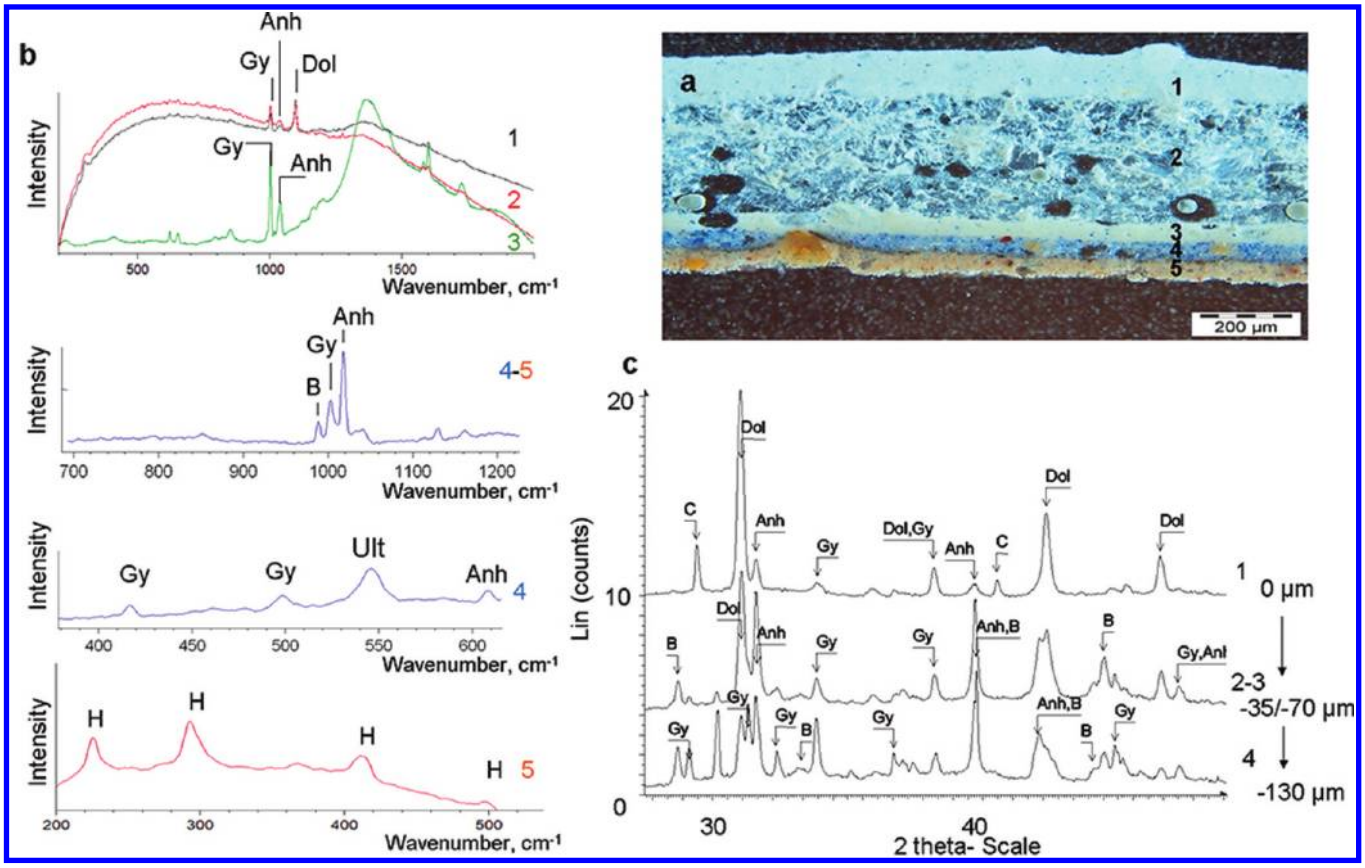

Figure 3. White sample AL-W from the Hall room: (a) paint stratigraphy as seen by OM (reflected light, crossed Nicols); (b) Raman spectra of each layer; (c) diffractogram at 0 (1), 35 and 70 (2−3), and 130 μm (4) from the surface. H = hematite, Anh = anhydrite, Gy = gypsum, Dol = dolomite, B = Barite, Ult = ultramarine, and C = calcite.

in samples W-R2-N and AL-R via the key Raman bands at 1307, 1445, and 1660 cm^{-1} and glue in W-R4-N (key bands above-mentioned). GC−MS results identified linseed oil via recognition of palmitic (P), stearic (S), and azelaic (A) acids (this last characteristic component of aged oils in lesser amount), and by the parameters P/S = 1.8 and A/P = 0.9.[32] In samples where egg yolk was found by RM, the high proportion of palmitic acid detected by GC−MS compared to the other key oil components may indicate the occurrence of egg. In this room, the inconsistent composition of binder and ground layer suggests that diverse historic interventions took place.

Knight Room. Six samples from the wood ceiling showing white, ochre, red, and black color at the surface were studied (Table 1). Results obtained along depth profiles with RM and μ-XRD revealed that the white surface samples were made mainly of lead white (a pigment usually made of hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, and cerussite, $PbCO_3$). Key Raman bands for hydrocerussite were found at 970 and 1051 cm^{-1} and for cerussite at 680, 1051, 1214, and 1330 cm^{-1}. μ-XRD analyses confirmed these minerals; thus hydrocerussite was identified via typical peaks at 34.2 and 40.4° 2θ (JCPD: 13-0131) and cerussite via peaks at 24.8 and 45.1° 2θ (JCPD: 05-0417). Minium was detected by RM and μ-XRD in red samples and in the white C-W2 sample (Table 1). A carbon-based black pigment was identified by RM at the surface of black sample via a wide band at 1590 cm^{-1}. All layers described were applied over ground layers with diverse composition made mostly of gypsum, lead white, and/or lower amounts of anhydrite, minium, calcite, and quartz (Table 1). Quartz was identified with RM via the key band at 467 cm^{-1} and by μ-XRD through the main peaks at 26.7° 2θ (JCPD: 33-1161).

Regarding organic binders, RM analysis identified oil in all layers of all samples (Table 1) by way of key Raman bands at 1310, 1445, 1660, and 1747 cm^{-1}.[29−31] Once again, the type of oils could not be identified with RM due to fluorescence problems. However GC−MS analyses identified suberic, azelaic, palmitic, and stearic acids. The calculated P/S ratio = 1 suggested the presence of linseed oil.[32]

In this room, our method was especially valuable to study the white C-W2 sample. Its mineralogical characterization throughout the paint cross section from surface inward is shown in Figure 4. Strong fluorescence background in the Raman spectrum in the 750−1250 cm^{-1} region hindered the recognition of bands corresponding to gypsum, anhydrite, hydrocerussite, and cerussite. However, their identification by μ-XRD was easier, as seen in the depth profile of Figure 4c. Minium was found together with lead white and small amounts of gypsum at the surface layer, while minium was not found in the intermediate layer. In the ground layer, gypsum, anhydrite, and quartz were identified by μ-XRD.

Here, the microtextural μ-XRD study was restricted to minium crystals from surface layers in the red samples and the surface white layer of C-W2 sample. According to API and TNP values, minium crystal sizes and the number of grains were slightly different for red and white layers. The averaged API values suggested that minium was manufactured similarly in the red

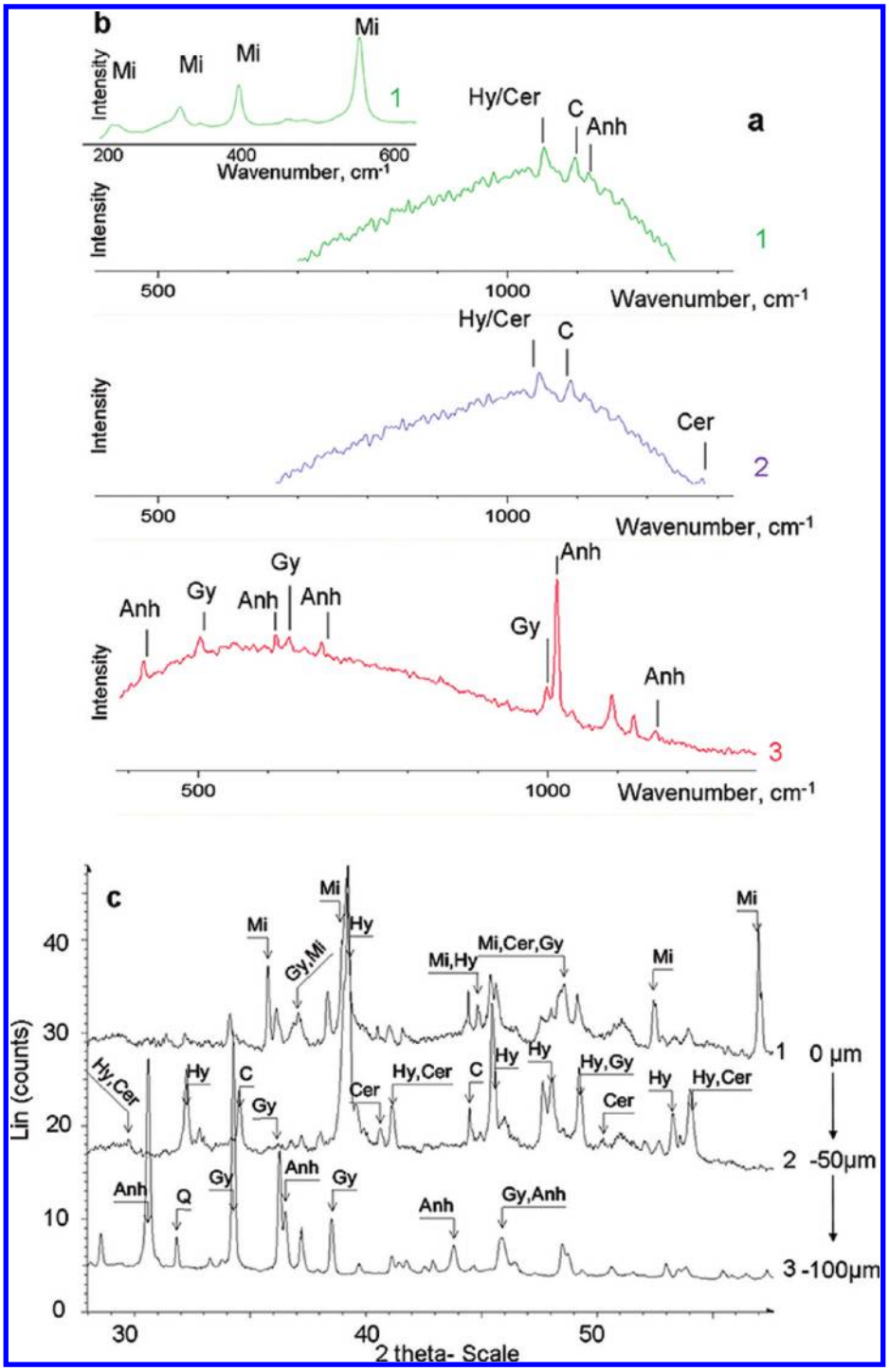

Figure 4. White sample C-W2 from the Knight room: (a) Raman spectra of paint layers 1, 2, and 3 in the 700 to 1300 cm^{-1} range; (b) Raman spectrum of layer 1 in the 200 to 600 cm^{-1} range; (c) diffractograms along the depth profile from the surface inward. See acronyms in Table 1.

samples (1590 and 1987) to obtain crystal sizes around tens of micrometers, versus the minium used in the white sample where the API value (1007) indicated smaller crystal sizes. Averaged TNP data showed a vaguely lower number of minium grains in the red samples (26 and 28) than in the white sample (32). These results suggest that different procedures in paint execution of the red and white samples were employed, most probably due to the color sought rather than different execution periods. In addition, though API and TNP data of minium are similar for both the Knight room and the Hall room (averaged TNP = 26 and API = 1212 for this latter room), a coincident intervention has to be excluded based on the different nature of the binders (egg in the Hall room and oil in the Knight room).

CONCLUSIONS

This study is a part of an ongoing investigation of Hispano-Muslim archeological artifacts[15] and polychromes[3,4] on diverse

substrates (stucco, marble, wood) in Granada (Spain), to clarify historic and artistic issues and to track the technical evolution of Nasrid art. The ultimate goal is to fill gaps in the history of pigments where Islamic pigments and painting techniques have systematically been omitted. In this paper, our novel method based on microtextural μ-XRD information combined with RM analyses allowed identification of inorganic and organic painting components from the 14th century Islamic University, Madrasah Yusufiyya.

The Madrasah Yusufiyya was built in 1349 by the Nasrid ruler Yusuf I, who also built the Comares Palace at the Alhambra.[4] In the only original Nasrid room (Oratory room) still standing in the Madrasah, we found a simple Nasrid palette made of vermilion and azurite to polychrome stucco (named *yesería* by Nasrids). Azurite was also identified in other monuments of Granada from the first period of Nasrid art (1237−1314), for instance the Partal Palace in the Alhambra[4] and the Qubba Dar al-Manjara l-kubra,[23] in contrast to lapis lazuli used during the later Nasrid period in the Alhambra (e.g., in the Lions Palace built by Muhammad V, 1362−1391).

In the Madrasah palace, Christian interventions were also recognized in the Nasrid Oratory room and in other two Christian rooms. Traditionally, historic interventions, forgeries, dating, and chronological uncertainties in paintings have been tackled using pigments as benchmarks.[3,10] However, as demonstrated in this study, information provided by microtextural characteristics of pigments and organic binders was crucial to identify historic interventions. In the Oratory room, Nasrid ground (gypsum) and paint layers (vermilion and azurite) were blended with glue binder, whereas Christian paint layers (smalt, hematite, chrome green, zinc white, and gilding) were mixed with oil binder. Here the identified pigments attest to a 19th century intervention.

Regarding the Christian rooms, in the Hall room, the variable composition of ground layers and binders suggests that diverse historic interventions took place. Here most ground layers were typically prepared using either gypsum or anhydrite, or both, together with barite and egg as binder. To be consistent with our reasoning, we propose that those ground layers containing barite were applied during a 19th century intervention. Other ground layers were prepared either with glue or linseed oil. In the Knight room, all ground layers were mostly made of lead white and gypsum mixed with linseed oil. Here it is difficult to date the polychromy since the pigments used are not indicative of a particular epoch. However, it can be argued that this painting was executed contemporarily with the oil technique painting of the Hall room since linseed oil was identified in both.

Microtextural data such as grain size and amount of crystalline phases present in a dense assemblage, as that usually found in complex paint layers, are not easy to determine with conventional microscopic techniques like OM or SEM. Usually, identification and quantification of a sufficient number of mineral grains require tedious sample preparation and time-consuming image analysis procedures. As shown in this work, our μ-XRD procedure has provided quantitative grain size data and crystal amount of all crystalline phases present in a paint layer in a more efficient, faster, and easier way than using microscopic techniques. In particular, results have shed light on the nature, manufacture, and weathering of pigments. Thus it seems that dry-process-type vermilion was the red pigment used by Nasrids. Though different vermilion grain sizes and quantities were found in the three studied samples, which may suggest different paint execution times, complementary microscopic studies revealed that paint layer deterioration was behind that observation. This fact attests the need to characterize painting samples coupling complementary analytical techniques.

Additionally μ-XRD results disclosed different grain sizes of similar pigments according to the role of the different coats in the paint stratigraphy, for instance, smaller gypsum crystals at the surface than in ground layers. Also, recrystallized gypsum could be identified in ground layers. As well, our method was able to quantify in the same layer the proportion of pigments present and their size. Thus in gypsum and anhydrite-rich surface and ground layers, gypsum was found to be the main pigment, although anhydrite had larger crystal size. Moreover, this method was able to discern different crystal sizes and the amount of minium pigment used by artists to achieve different tonalities at the surface. Our future perspectives in relation with the microtextural information obtained with μ-XRD in real painting samples is to explore its capability as a tool to date historic paintings.

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