

Article

Mural Paintings Characterisation Using X-ray Fluorescence and Raman Spectroscopy—A Case Study: Nossa Senhora das Neves Chapel, Vilar de Perdizes, Galicia—North Portugal Euroregion

David M. Freire-Lista ^{1,2,*} , Ezequiel Vázquez ³ , Pablo Barreiro Castro ⁴ , Eunice Salavessa ⁵ ,
Maria do Rosário Costa ^{1,6} , Rafael Moreira ⁷ and Ana J. López ⁸ 

- ¹ Department of Geology, Universidade de Trás-os-Montes e Alto Douro (UDAT), Quinta de Prados, 5001-801 Vila Real, Portugal; rosariomc@utad.pt
 - ² Centro de Geociências da Universidade de Coimbra, Universidade de Coimbra—Polo II, 3030-790 Coimbra, Portugal
 - ³ Unidade de Espectroscopia IR-Raman, Edifício CACTUS, Campus VIDA, Rede de Infraestruturas de Apoio à Investigação e ao Desenvolvimento Tecnológico (RIAIDT), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain; ezequiel.vazquez@usc.es
 - ⁴ Centro de Investigación en Tecnologías, Energía y Procesos Industriales, Novos Materiais Group, Dpto. de Física Aplicada, Escola de Enxeñaría Industrial, Universidade de Vigo, 36310 Vigo, Spain; pbarreiro@uvigo.gal
 - ⁵ Departamento de Ciências Florestais e Arquitectura Paisagista, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal; eunicesalavessa@sapo.pt
 - ⁶ GeoBioTec Geobiociencias, Geotecnologias e Geoengenharia Research Centre, Campus de Santiago, 3810-193 Aveiro, Portugal
 - ⁷ CHAM Centro de Humanidades, Faculdade de Ciências Sociais e Humanas, Universidade Nova de Lisboa, 1099-085 Lisboa, Portugal; rfdmoreira@gmail.com
 - ⁸ Laboratorio de Aplicacións Industriais do Láser, Campus Industrial de Ferrol, Universidade da Coruña, 15471 Ferrol, Spain; ana.xesus.lopez@udc.es
- * Correspondence: davidfreire@utad.pt



Citation: Freire-Lista, D.M.; Vázquez, E.; Barreiro Castro, P.; Salavessa, E.; Costa, M.d.R.; Moreira, R.; López, A.J. Mural Paintings Characterisation Using X-ray Fluorescence and Raman Spectroscopy—A Case Study: Nossa Senhora das Neves Chapel, Vilar de Perdizes, Galicia—North Portugal Euroregion. *Heritage* **2023**, *6*, 7277–7292. <https://doi.org/10.3390/heritage6120382>

Academic Editor: Vittoria Guglielmi

Received: 30 September 2023
Revised: 13 November 2023
Accepted: 14 November 2023
Published: 21 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: Sixteenth-century mural paintings of Nossa Senhora das Neves in Vilar de Perdizes (Galicia—North Portugal Euroregion) were analysed. An iconographic study has allowed us to understand the meaning of the seven scenes that constitute the mural painting. X-ray fluorescence (XRF) and Raman spectroscopies determined the compounds used in this mural painting, both in the original and in later repaintings. The black paint was bone black. Hydroxyapatite characteristic bands and those of the associated phosphates have been identified. White lime was used as white paint. Lepidocrocite and goethite were used to make yellows, and hematite was used to make red shades. Cinnabar has been used for a later red repaint. Carbon-based compounds and rutile were used to create different tonalities by darkening or lightening colours. It is of great significance to obtain accurate and reliable mural painting information through scientific means, since preservation, restoration, and repainting without detailed information can be harmful to mural paintings.

Keywords: pigment; frescoes; hydroxyapatite; lepidocrocite; cinnabar; Trás-os-Montes

1. Introduction

Studies on mural painting evaluations [1–3] must be carried out to ensure understanding not only to the scientific community but also to all the population of the importance of their iconographies, which keep historical memory alive and attract cultural tourism. Historical mural paintings are a legacy that must be preserved and studied to create a historical narrative that is attractive to the public. They are a record of the history of each region that contains them [4]. Historical mural paintings exist in a wide variety of built heritages. They are found in prehistoric rock art [5], archaeological sites [6], ancient tombs [7], churches [8], monasteries [9], and temples [10].

There are many mural paintings in Portuguese historical buildings [11–14]. Nossa Senhora das Neves Chapel is an excellent example of the rich heritage of mural paintings in rural villages in northern Portugal. This chapel is in União das Freguesias de Vilar de Perdizes e Meixide, a parish of Montalegre municipality, district of Vila Real (Euroregion Galicia—North Portugal) (N 41°51'18.573"; O 7°37'52.578"). This village is on a Jacobean route, and it had a pilgrim's hospital. This border region between Spain and Portugal has a valuable heritage built in stone that must be catalogued and studied to promote its cultural and tourist attractiveness associated with heritage stones [15,16]. In this sense, the main objective of the IACOBUS program is to promote cooperation in the Galicia—North Portugal Euroregion. Nossa Senhora das Neves Chapel has mural paintings attributed to so-called Marão mural painting workshops from the 16th century. Mural paintings from other churches in the Vila Real district are also attributed to the Marão workshops of the 15th and 16th centuries. The following churches, among others, have examples of mural paintings: Santa Marinha, Vila Marim, 15th and 16th centuries [17]; Santa Maria, Covas do Barroso, 15th and 16th centuries; Nossa Senhora da Azinheira, Outeiro Seco, 16th century [18]; São João Baptista, Cimo de Vila da Castanheira, 16th century; Santa Leocadia, Chaves, 16th century; São Miguel, Três Minas, 16th century; Nossa Senhora de Guadalupe, Mouços, 16th century, [19]; São Brás Chapel, Vila Real, 16th century; São Tiago, Folhadela, 15th and 16th centuries, [20]. The appreciation of these mural paintings will mean a revitalisation of this area with a low population density and a need to attract cultural tourism.

The study of mural paintings is a complex process in which various scientific areas must participate to consider the type of mortars, pigments, and aggregates [21], painting techniques [22,23], additives [24], decay [25,26], conservation treatments [27], biodeterioration [28], and iconography. Different analytical techniques are used for mural painting characterisation: petrographic microscopy [29]; Fourier-transform infrared spectroscopy (FT-IR) [30]; X-ray diffraction (XRD) [31]; laser-induced breakdown spectroscopy (LIBS) [32]; Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray analysis (EDX) (SEM-EDX) [33], and X-ray fluorescence (XRF) [34]. All these, among other techniques, have been extensively used in the study of ancient artworks.

This work aims to interpret the meaning of the mural paintings of Nossa Senhora das Neves Chapel and characterise their paint compounds using XRF and Raman spectroscopies. XRF enables the recognition of pigment and additive classes containing characteristic elements with a detectable atomic weight, but it cannot distinguish differences within the same chemical class, nor can it clearly characterise pigment mixtures [34,35]. Raman spectroscopy [36,37] has proven to be the standard technique, in its portable and contactless version, capable of achieving information from a large selection of ancient pigments. It has shown reasonable efficacy in identifying and differentiating pigments with similar compositions.

2. Materials and Methods

Nossa Senhora das Neves Chapel has a rectangular plan with a gable roof. It has double-leaf walls, and it is built with dressed granite ashlar with little decoration. The main façade faces northwest, and its central door has a lowered arch. This façade has two lateral pilasters with a moulded base and capital, crowned by the bell tower topped with a Latin cross. Above the door is an oculus with a simple moulding. The façade is finished with a simple cornice and two pyramidal pinnacles on both sides. The side façades are blind and end in a cornice, and the rear ones in a gable.

The chapel's interior is a single nave and preserves mural paintings which represents an altarpiece, with an inscription from 1571 on the back wall and a painted altar immediately in front of the mural paintings. Approximately the lower third of these mural paintings have been lost, and only the upper two thirds remain. This painted wall has a setback in the centre. In this way, the sides protrude from the sunken central plane, where an altar could be embedded. This central setback ends in a semi-dome at the top (Figure 1).

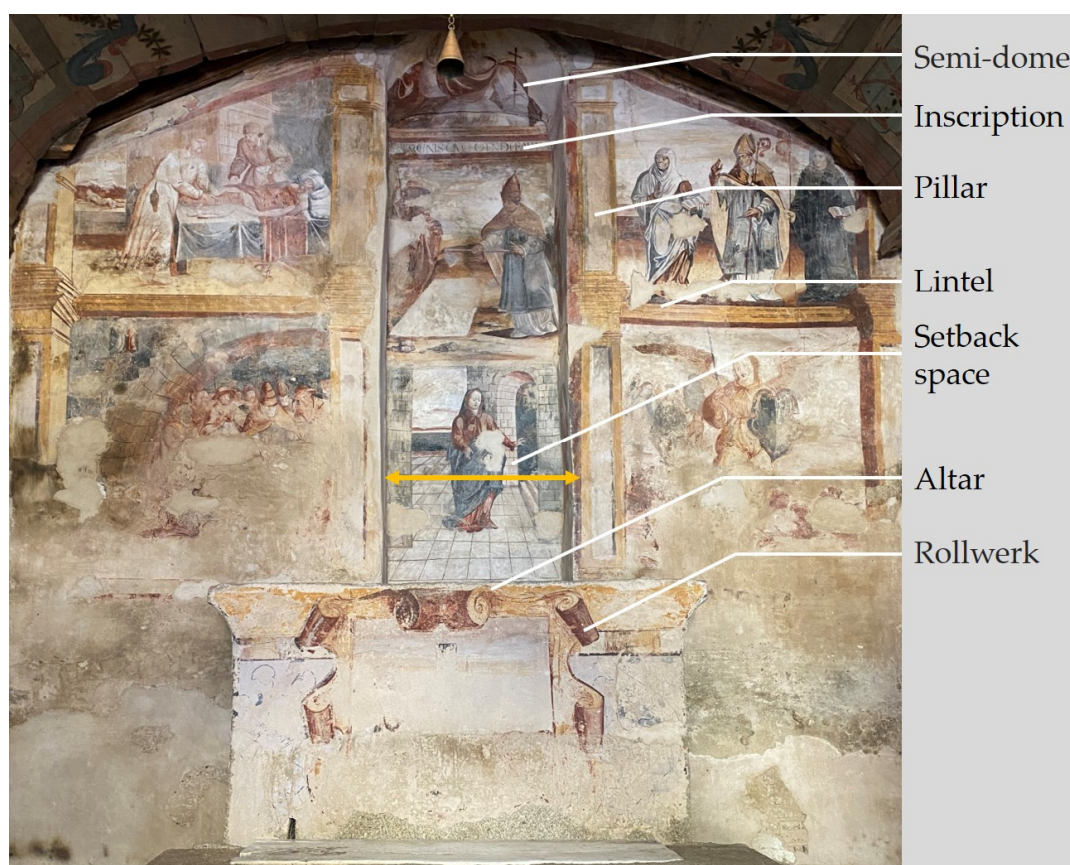


Figure 1. General view of the mural paintings preserved in Nossa Senhora das Neves Chapel. Orange arrow indicates the setback space.

After a historic, stylistic, and iconographic analysis of the mural paintings of Nossa Senhora das Neves Chapel, four main colours, grey, white, yellow and red, were selected to measure their different tonalities. Figure 2 shows the seven panels of the main preserved mural paintings, the location of the measurements carried out with the portable Raman equipment (circles), and the location of the samples used for confocal Raman microscope analysis (squares) and XRF.



Figure 2. Location of the analysed colours with portable i-Raman (circles) and detached areas of sampling (squares) in Nossa Senhora das Neves Chapel mural paintings. G = grey, W = white, Y = yellow, and R = red.

The measurements of the four colours have been made at the points where the paintings were best preserved (Table 1 and Figure 2). The analysis of the samples has been

carried out using a portable Raman model i-Raman—BWS415-785S from B&W Tek. It was excited by a laser at 785 nm wavelength with a maximum power of 300 mW, adjustable from 1% to 100% power. Both the excitation signal and the detection Raman signal were guided by optical fibre from a head that can be used manually or attached to a microscope objective. In this case, the manual head has been used. The Raman spectra have been taken with a resolution of 5 cm^{-1} in a spectral range of $175\text{--}3200\text{ cm}^{-1}$. The results of i-Raman spectroscopy were obtained through several readings on the painting surface of 17 measurement points from the mural paintings (Figure 2).

Table 1. Location of colours measured with portable i-Raman spectroscopy in the mural paintings of Nossa Senhora das Neves Chapel.

Colour	Sample	Location	Panel Number
Grey	G1	Our Lady of the Snows veil	Panel 5
	G2	Grey of the open space in the door	Panel 5
	G3	Tiles cement joint	Panel 5
	G4	Lintel inscription, letter D	Between panel 6 and 7
	G5	Lintel inscription, letter F	Between panel 6 and 7
White	W1	Robe of woman holding a book	Panel 4
	W2	Book page held by a woman	Panel 4
	W3	Bishop's chasuble	Panel 4
	W4	God the Father's clothing	Panel 7
	W5	God the Father's clothing	Panel 7
Yellow	Y1	Centre-right lintel capital	Between panel 4 and 6
	Y2	Ground	Panel 6
Red	R1	Skirt of Our Lady of the Snows	Panel 5
	R2	Our Lady of the Snows top of dress	Panel 5
	R3	Centre-right pillar	Between panel 1 and 5
	R4	Centre-right pillar	Between panel 1 and 5
	R5	Red robe of God the Father	Panel 7

Small chips were sampled in places where the painted mortar was detached (Archangel Saint Michael with a shield and sword scene). These samples are represented by squares (Figure 2, panel 1). Two measurements in each coloured sample (G: grey, W: white, Y: yellow, and R: red) were recorded with a WITec confocal Raman microscope model Alpha 300R, with a 532 nm laser and a power between 0.4 and 1.3 mW between 0.5 and 1 s integration time and between 50 and 100 accumulations, using a $50 \times$ LD objective.

Micro X-ray fluorescence measurements were performed on the same coloured samples (G, W, Y, and R) using an M4 Tornado system from Bruker, equipped with an Rh anode X-ray tube coupled to a polycapillary lens that enables a spot-size analysis of $25\text{ }\mu\text{m}$ diameter at the sample and an SDD detector with a resolution of 142 eV for Mn-K α energy. The tube operated at a voltage of 40 kV and a current of 500 μA , with a step of $25\text{ }\mu\text{m}$ and an acquisition time of 75 ms per pixel in a vacuum scanning atmosphere.

3. Results

3.1. Mural Painting Iconographic Interpretation

The mural paintings have a structure representing false architecture in perspective. This structure is defined by two painted pillars on each side of the protruding plane. They support a lintel on each side. The pillars and lintels are painted yellow, with some planes represented in red to highlight perspective (Figures 1–3). Two rectangles are defined on the lower sides and two irregular quadrilaterals on the upper part (the upper side adapts to the gable roof). The recessed, sunken plane, like an aedicule in the central panel, is divided by two lintels. This central panel has two lower rectangles and an upper semi-dome that adapts to the vertex of the roof. The sides of this setback space are also painted, although the left side is very deteriorated. In this way, the wall is painted in two planes, and it is

divided into seven panels, arranged as windows (four sides and three central). On these panels, figurative scenes are painted in perspective that simulate “opening” the real world to the supernatural through miracles such as visions. The Latin phrase written in black capital letters on the upper central lintel (VIRGINIS.QVOQVE.IN.DIE. MIRAC.VLVM. NIVIS) means “In the day the Virgin performed the snow miracle”. This phrase underlines the duality between the natural and divine worlds.



Figure 3. Scenes of the seven panels from the mural paintings of Nossa Senhora das Neves Chapel. (1): Archangel Saint Michael with shield and sword. (2): Looking at hell. (3): Miracle. (4): Blessing. (5): Patroness: Nossa Senhora das Neves (Our Lady of the Snows). (6): Foundation of Santa Maria Maggiore Basilica. (7): God the Father.

The front of the altar also preserves the upper two thirds painted and presents a rectangle wrapped in a yellow moulding with six red rollwerkes. An inscription, now missing, possibly existed inside the rectangle (Figure 1).

The iconographic reading direction of the lower scenes on the sides is from right to left, and they represent the supernatural world. It belongs to the most valuable area, the one that really matters: saving the soul. The iconographic reading direction of the upper scenes is the opposite. They represent scenes of earthly or mundane life; they are from the realm of what is valuable, although less than the soul: human body health. The sunken central plane, behind the altar, has an autonomous reading from bottom to top and represents the Roman Catholic Church. Seven pictorial scenes are described following the correct iconographic reading direction (Figure 3):

1. Archangel Saint Michael with shield and sword: Two angels are painted in the background; they are arranging the souls of the dead in Hell. Archangel Saint Michael's tunic is painted in different shades of yellow and red. The shield and sword are painted in grey tonalities. The background is painted in yellow, white, and grey shades (Figure 3 (1)).

2. Hell: under a large arch built with stone ashlar, important figures of the time (pope, cardinal, and other men) are looking at a pit below where the souls are, and to the left you climb a staircase in which, at the top, are those saved from damnation. The characters' clothing is painted in yellow and red shades; the stone ashlar arch is painted with grey tonalities, the joint mortar with black, and the sky with grey tonalities (Figure 3 (2)).

3. Miracle: domestic scene inside a room where a sick man lies in a bed. He is assisted by two doctors. Other beds are visible in the background. It could be the hospital for pilgrims to Santiago de Compostela that is close to the chapel. The sheets are painted in grey tonalities, the blanket in red tonalities, the doctors' robes in white, yellow, and red tonalities, and the floor in yellow tonalities (Figure 3 (3)).

4. Blessing: A bishop blesses a woman who has her back turned to him, holding a book in her hand, assisted by a monk with a staff and holding a book. Saint Benedict,

founder of the Benedictine hermits, is dressed in a black cloak. The bishop's cape and miter are painted in yellow tonalities, the chasuble in grey tonalities, and the alb in white. The woman's tunic is painted in red tonalities and her veil in white tonalities. Saint Benedict's cloak is painted in black tonalities, the ground in yellow tonalities, and the sky in white and grey tonalities (Figure 3 (4)).

5. Patroness: Nossa Senhora das Neves (Our Lady of the Snows) (Salus Populis Romanis) is inside a room pointing to the ascending staircase of Salvation, following the stone arch. The Virgin's dress is painted in red tonalities. There are some areas repainted in brighter red tonalities. Her veil is painted in grey tonalities. These colours are repeated in the architectural setting in which the Virgin is (Figure 3 (5)).

6. Basilica of Santa Maria Maggiore foundation: Pope Liberius (352–366) blessed the stones of Mount Esquiline covered with miraculous snow with a wand in the year 352, thus founding the Basilica of Santa Maria Maggiore in Rome, or Our Lady of the Snows. Pope Liberius' clothing has white, grey, red, and yellow tonalities. The floor has the same tonalities, and the sky is painted in white and grey tonalities (Figure 3 (6)).

7. God the Father: God the Father blesses everything with his raised right hand, holding a cloth with a square white stone in his left hand and a cross in his left arm. God the Father's is in the upper semi-dome. His robe is painted in white tonalities, his cape in red tonalities, and the sky in white and yellow tonalities (Figure 3 (7)).

3.2. Micro X-ray Fluorescence Mapping

Micro X-ray fluorescence mapping of coloured samples showed that Ca and P are present in all samples. Mn and Fe are the most prominent elements in the grey-coloured sample (G). Ca, P, and Al are the most outstanding elements in the white-coloured sample (W). Fe, Mn, and Ti are the most outstanding in the yellow-coloured sample (Y), and Fe and Mn are the most outstanding in the red-coloured sample (R) (Figure 4).

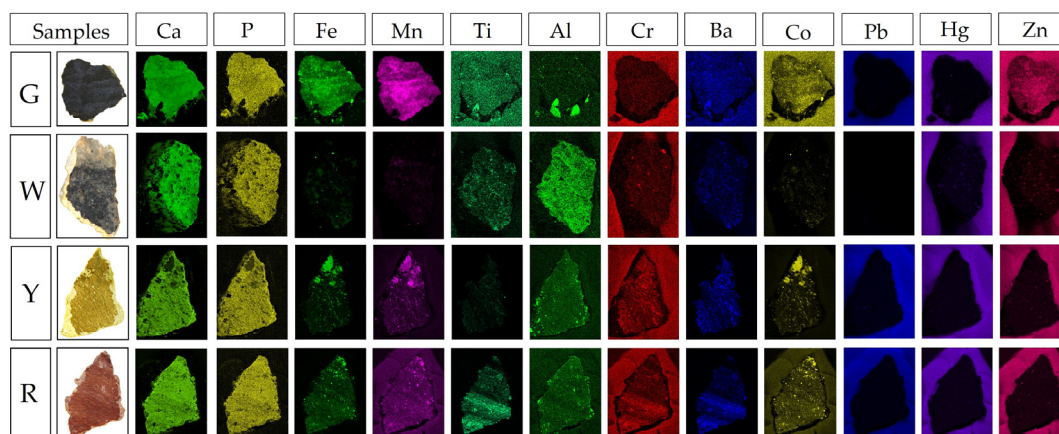


Figure 4. XRF mapping of the coloured samples (G = grey, W = white, Y = yellow, and R = red) of Nossa Senhora das Neves Chapel.

3.3. Portable *i*-Raman

The identified compounds of each colour by the *i*-Raman spectrum are as follows.

3.3.1. Grey

Five Raman spectra (Figure 5) have been obtained from the greyish samples analysed in the Nossa Senhora das Neves Chapel mural paintings. The same compounds have been detected with greater or lesser intensity: Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) has Raman bands at ca. 445, 578, 959, and 1068 cm^{-1} [38]. Carbon-based compounds (CB) have two broad bands at ca. 1300 and 1600 cm^{-1} , which are associated with carbon hybridisation [39]. Manganese oxides have Raman bands at ca. 330, 435, and 635 cm^{-1} [40].

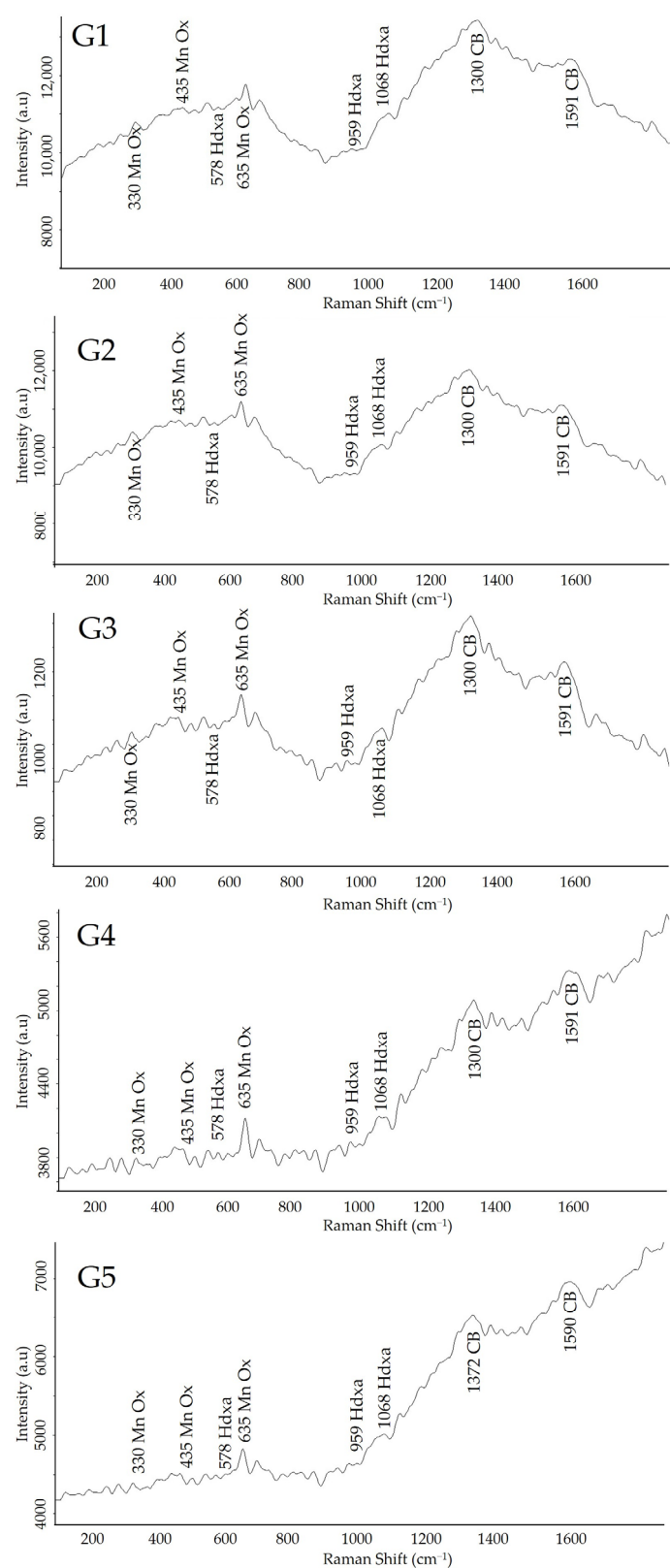


Figure 5. Raman spectra obtained with the portable equipment i-Raman (B&W Tek) of measurements made in greyish paintings (G1–G5) from Nossa Senhora das Neves Chapel. Labels: CB = carbon-based compounds; Hdxa = hydroxyapatite; Mn Ox = manganese oxides.

3.3.2. White

The compounds that have been identified by portable i-Raman analysis of the five white measured areas are shown in Figure 6.

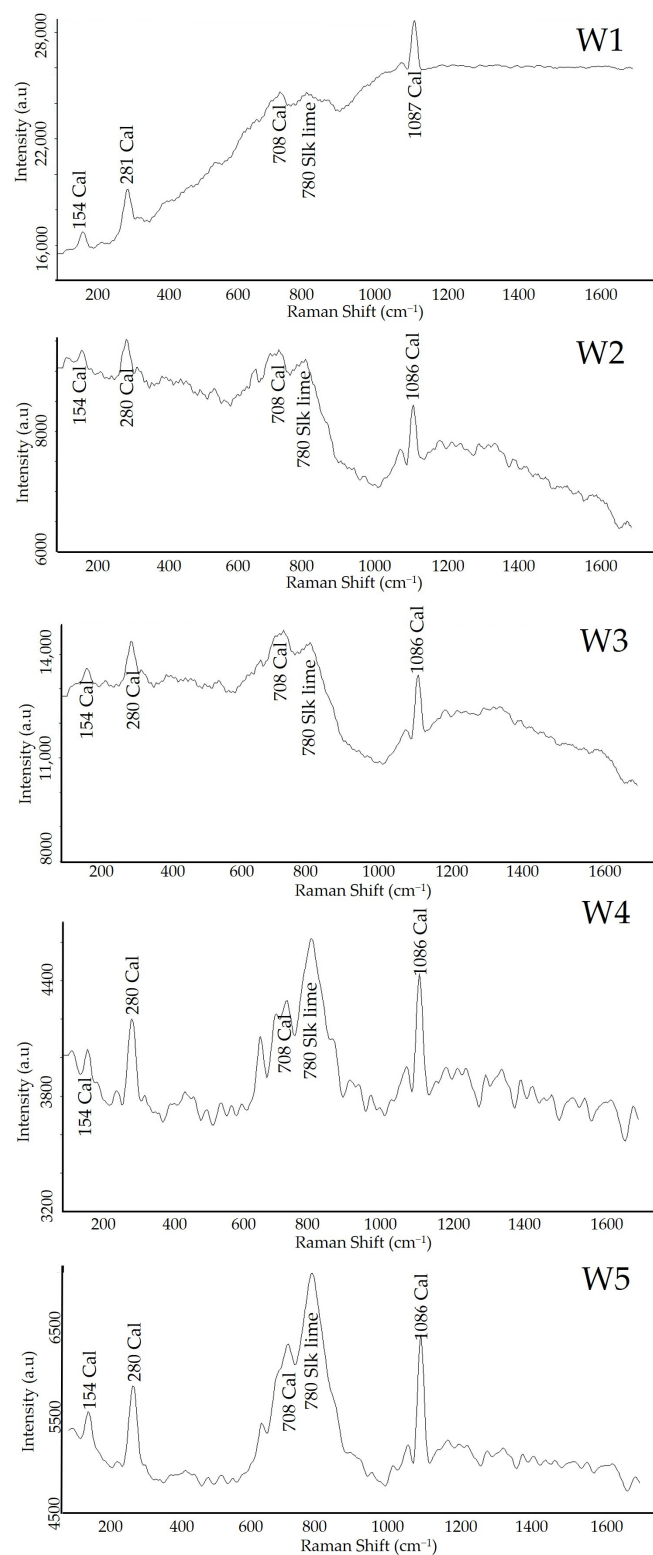


Figure 6. Raman spectra obtained with the portable equipment i-Raman (B&W Tek) of measurements made in whitish paintings (W1-W5) from Nossa Senhora das Neves Chapel. Labels: Cal = calcite; Slk lime = slaked lime.

Calcite (CaCO_3) has Raman bands at ca. 153, 282, 711, and 1088 cm^{-1} [41]. A band at 780 cm^{-1} has also been identified that can be attributed to hydrated calcium oxide-hydroxide [42,43].

3.3.3. Yellow

The following compounds have been obtained from the analysis of the two yellow measured areas with portable i-Raman (Figure 7).

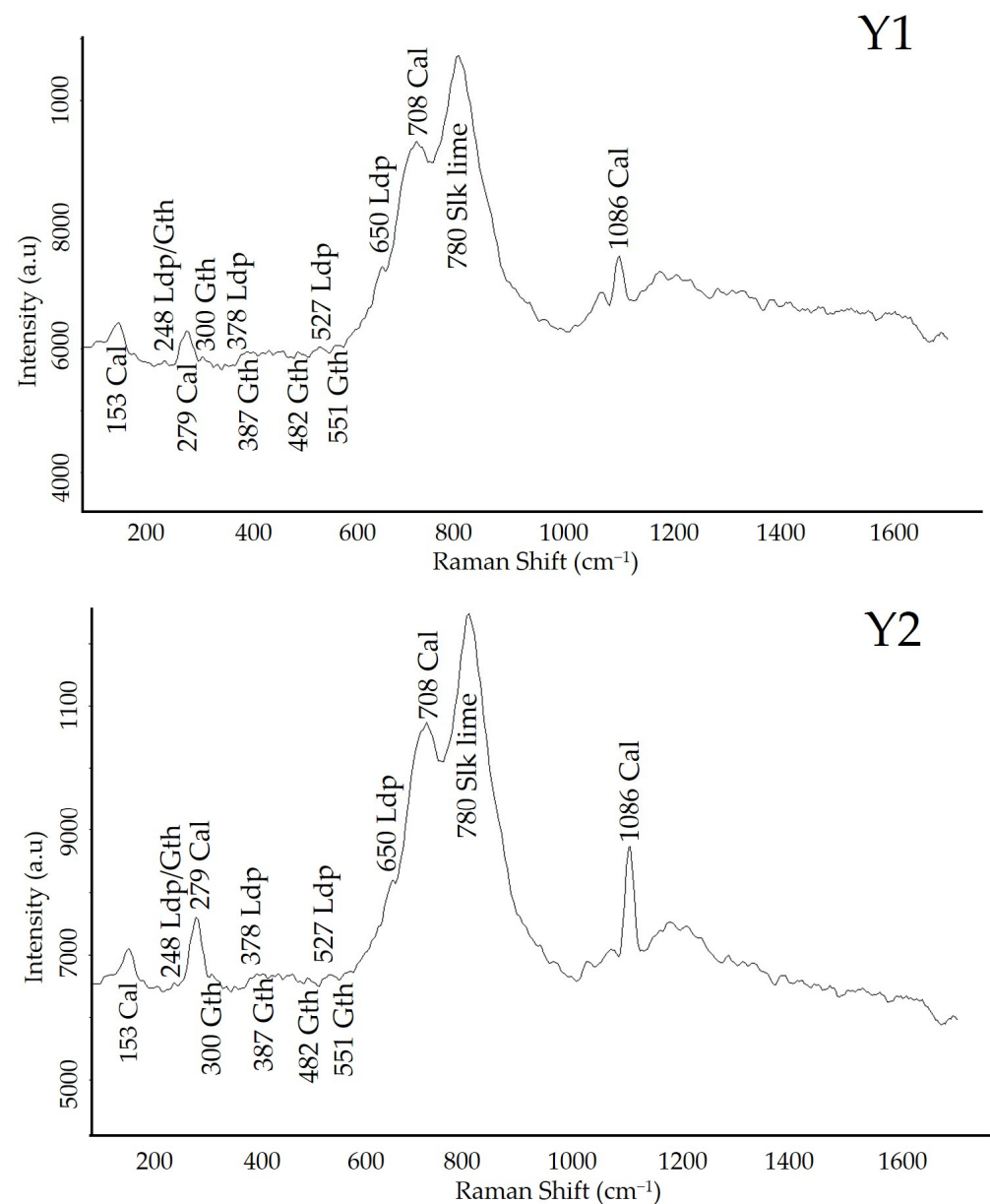


Figure 7. Raman spectra obtained with the portable equipment i-Raman (B&W Tek) of yellowish measurements (Y1 and Y2) of Nossa Senhora das Neves Chapel mural paintings. Labels: Cal = calcite; Gth = goethite; Ldp = lepidocrocite; Slk lime = slaked lime.

Lepidocrocite ($\gamma\text{-Fe}^{3+}\text{O}(\text{OH})$) has characteristic Raman bands at ca. 248, 378, 528, and 650 cm^{-1} [44]. Goethite (FeO_2H) has characteristic Raman bands at ca. 243, 300, 388, 481, and 551 cm^{-1} [44]. Calcite and hydrated calcium oxide-hydroxide (slaked lime) have also been identified.

3.3.4. Red

Two red pigments have been detected by portable i-Raman spectroscopy (Figure 8). Sample R1 contains cinnabar, and the other samples (R2, R3, R4, and R5) contain hematite.

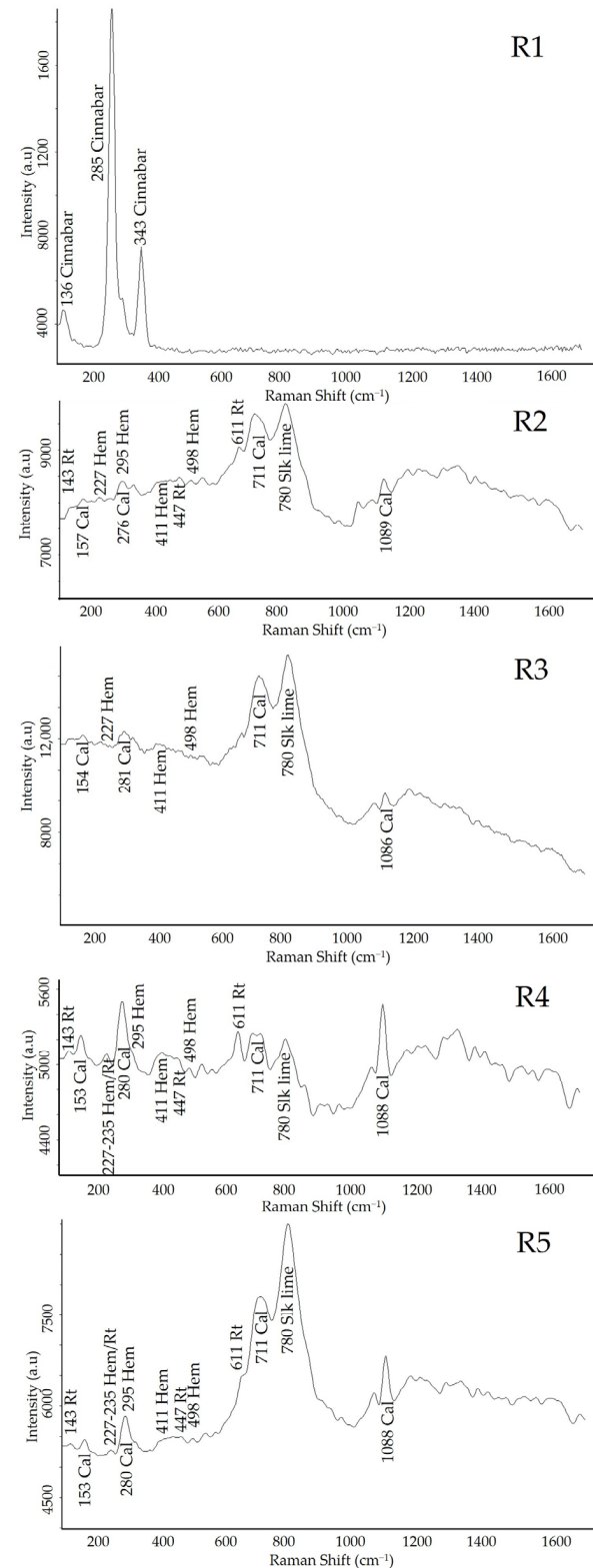


Figure 8. Raman spectra obtained with the portable equipment i-Raman (B&W Tek) of reddish measurements (R1-R5) in Nossa Senhora das Neves Chapel mural paintings. Labels: Cal = calcite; Hem = hematite; Rt = rutile; Slk lime = slaked lime.

Cinnabar (HgS) has characteristic Raman bands at ca. 253, 282, and 343 cm^{-1} [45]. Hematite (Fe_2O_3) has its Raman bands at ca. 227, 295, 411, and 498 cm^{-1} [45,46]. The typical Raman bands of the rutile (TiO_2) phase appear at ca. 143, 235, 447, and 612 cm^{-1} [47]. Slaked lime has also been detected.

3.4. Confocal Raman Microscope

The WITec confocal Raman microscope spectra of the two measurements of each colour sample (G = grey, W = white, Y = yellow, and R = red) are shown in Figure 9.

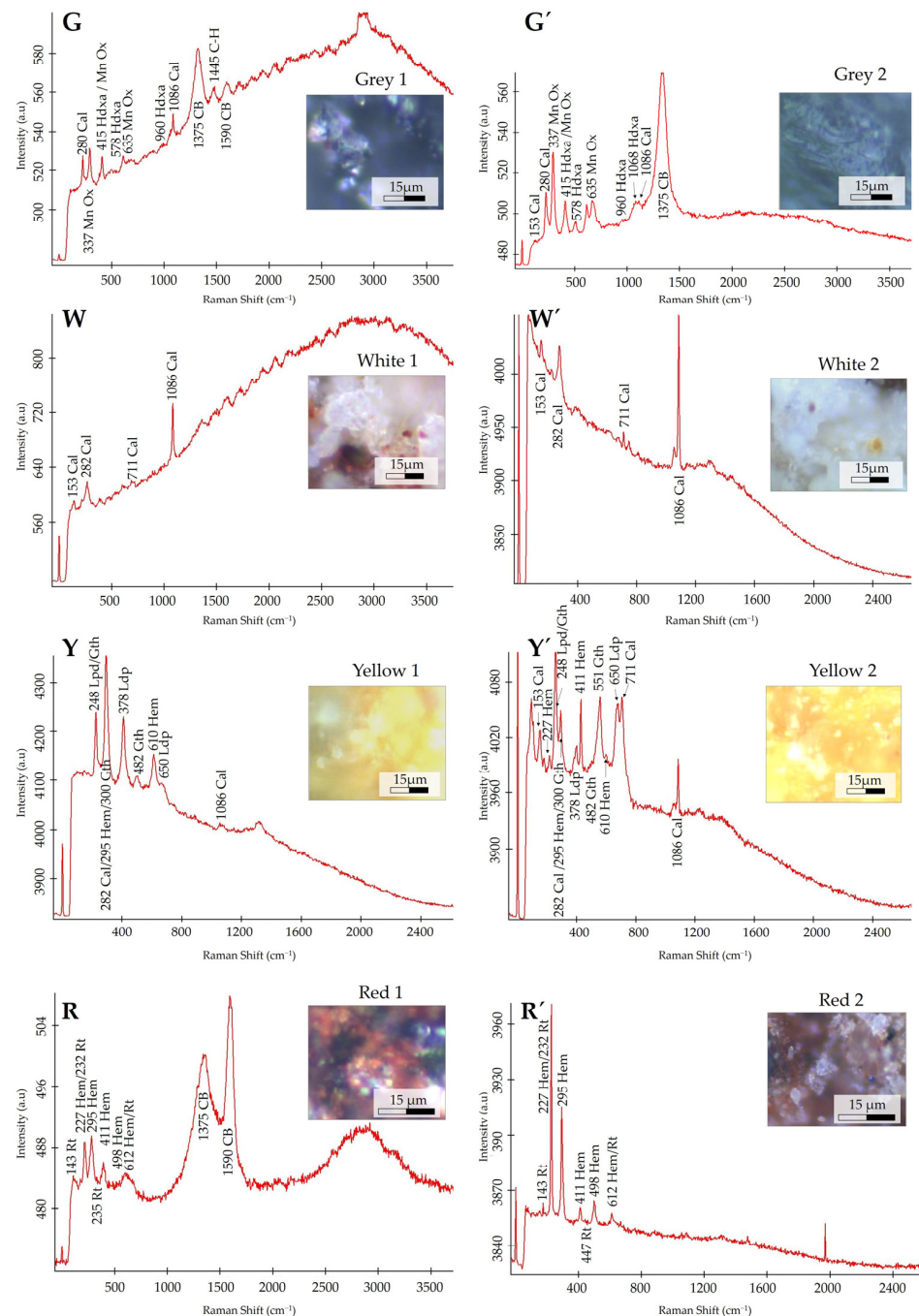


Figure 9. Raman spectra obtained with WITec confocal Raman microscope of grey samples (G,G'); white (W,W'); yellow (Y,Y'), and red (R,R'). Labels: CB = carbon-based compounds; Cal = calcite; Hem = hematite; Hdxa = hydroxyapatite; Gth = goethite; Ldp = lepidocrocite; Mn Ox = manganese oxides; Rt = rutile.

In general, WITec confocal Raman microscope spectra are better defined than the bands recorded with portable i-Raman. Nonetheless, the bands obtained with each piece of equipment are basically the same: Sample G (grey) has characteristic bands of hydroxyapatite, carbon-based compounds, and manganese oxides. Sample W (white) has characteristic bands of white lime. Sample Y (yellow) has characteristic bands of lepidocrocite, goethite, hematite, and calcite. Sample R (red) has characteristic bands of hematite, rutile, and carbon-based compounds.

4. Discussion

Nossa Senhora das Neves mural paintings have a limited colour palette; four colours are repeated in the seven panels. Colours fundamentally belong to the range of greys, whites, yellows (ochres and browns), and reds (reds and maroons). Reddish, yellows, ochres, and brown tonalities are the most frequent colours used in Trás-os-Montes mural paintings due to the existence of several iron mines in the region. Heating yellow goethite powder to obtain the red of hematite requires only 260–280° C. Therefore, the mural paintings of Nossa Senhora das Neves Chapel have predominantly yellow and red colours.

The spectra obtained with the portable i-Raman equipment were noisier and more difficult to interpret than the spectra obtained with the WITec confocal Raman microscope (model Alpha 300R). Despite the intense fluorescence bands that mask the portable i-Raman signal, an assignment of the bands in the spectra of the mural paintings has been performed.

G samples (greys) are “Bone black” paint. It is generally obtained by burning bones that contain hydroxyapatite ($\text{Ca}_5(\text{OH})(\text{PO}_4)_3$). XRF results indicated it contains phosphorus and calcium, which are part of the hydroxyapatite component of bone tissue [21,48]. These data were corroborated the Raman spectra, where broad bands of carbon-based compounds (CB) are at ca. 1300 and ca. 1600 cm^{-1} . Raman results indicated the presence of poorly organised carbonaceous materials in these portions of G paint. Representative spectra (Figure 5) are characterised by a broad band in the first-order Raman spectrum around 1300 cm^{-1} . This band is a consequence of structural disorder and is commonly assigned to the C single-bond C vibration for sp^3 hybridisation. The G-type band, characteristic of carbon sp^2 hybridisation and assignable to the E_{2g} (C single-bond C) stretching in aromatic structures, is observed at around 1590 cm^{-1} . These two bands unequivocally characterise carbon-based compounds. In addition, a band associated with the stretching of the phosphate ion $[\text{PO}_4]^{3-}$ at ca. 960 cm^{-1} was detected. It corresponds to a rather modified bone-derived hydroxyapatite. As reported [49,50], in bone black, the collagen forms a coke that is intimately mixed with hydroxyapatite, which consequently could be considered a clue for its identification. Moreover, the characteristic band of the phosphate group at ca. 960 cm^{-1} (originating from the remains of the bone minerals apatite of hydroxyapatite) seems to indicate that bone black or ivory black was present [48,51]. As stated above, the Raman spectrum of a protein is characterised by amide I (1600–1690 cm^{-1}) and amide III (1230–1300 cm^{-1}) vibrations of bone back. A strong broad band at ca. 1454 cm^{-1} corresponds to modes of CH_2 and CH_3 bending [52].

The presence of Ca in the FXR mapping and calcite in most of the Raman spectra indicates that the mortar on which it has been painted is a lime mortar. W samples (whites) are “White lime”. It is produced from limestone by heating calcium carbonate (800–900 °C). Therefore, it may present a greyer or more yellowish hue depending on the amount of impurities present in the limestone. It has been used for millennia as pigments or primers. When white lime is mixed with pigments in the fresco technique, the reaction with atmospheric carbon dioxide goes to completion, thereby binding the pigments, and the calcium hydroxide reacts with protein to form protein lime white compounds that enclose the pigments.

It is worth noting that the spectrums of Figures 6–8 presented a broad band at ca. 780 cm^{-1} assigned to hydrated calcium oxide-hydroxide ($\text{Ca}(\text{OH})_2$) when excited with near-infrared radiation [42,43]. This band, together with the bands at ca. 282, 711 and 1086 cm^{-1} of calcium carbonate, can be related to the use of the so-called limewash or

slaked lime [53,54] that was used by artists in the preparation of the wall for pigment application [55]. It appears from ancient texts that the “limewash” putty had two functions: one associated with its application to a variety of substrate surfaces to provide a type of smooth “plaster” coating, and the other for the adhesion of the applied pigments in mural paintings [42]. It could have originated from the surprising conversion of lime to calcium carbonate, which can be a very slow process [56].

Y samples (yellows) (Figure 7) have lepidocrocite and goethite. Lepidocrocite has a red, yellowish brown, or blackish brown colour. Lepidocrocite, although less common, has the same origins as goethite, and they often occur together. The i-Raman spectrum shows a slaked lime band. Sample Y, analysed with the WITec confocal Raman microscope, presents characteristic bands of hematite, since this yellow has red tones.

Hematite is the main chromophore mineral of the R samples (reds) (Figures 8 and 9 R,R'). Iron oxide powders have been known since pre-historic cave paintings as a source of pigments [57]. The elements found by analysing the coloured samples and endorsed by data obtained from XRF may suggest the presence of a natural earth containing iron oxides, kaolin, silicates, and titanium oxides. The presence of titanium in the R samples with Al, Si, and Ca may be an indication that the pigment is natural because titanium is easily carried by minerals in the form of rutile (TiO_2) [11]. Rutile has been identified in the Raman spectra of the red samples (Figures 8 and 9 R,R'). Carbon-based compounds have also been identified in the Raman spectra obtained with the WITec confocal Raman microscope (Figure 9 R). The width and morphology of CB bands between ca. 1300 and 1600 cm^{-1} , in addition to the lack of a band ca. 2720 cm^{-1} and a small band at ca. 513 cm^{-1} (Figure 9 G) that can be attributed to the S-S vibrational band, indicate that it is amorphous carbon of possible organic origin [58,59]. Although it must be considered that the spectral range between 500 and 1000 cm^{-1} tends to be noisy due to fluorescence, making protein discrimination difficult [52].

Cinnabar was only detected in the R1 i-Raman spectrum because it has not been possible to extract a sample of this red colour. It is found in the intense red of a repainting on the bottom of the dress of Nossa Senhora das Neves (Figure 2 (5)). Prolonged light exposure and moisture are responsible for the chemical alteration of cinnabar to metacinnabar, turning it darker [60].

5. Conclusions

Iconographic interpretation of mural paintings contributes to the understanding of rural life in the Galicia—North Portugal Euroregion at the end of the Middle Ages.

To stimulate the Euroregion's cultural tourism, it is necessary to create a historical narrative, and the iconographic meaning of Nossa Senhora das Neves Chapel mural paintings was discovered with this work.

The lower-side scene iconographic reading direction is from right to left. They represent the supernatural world. These scenes indicate to the parishioners that they must save their souls.

The upper-side scene iconographic reading direction is from left to right. They represent mundane life. These scenes indicate to the parishioners that they must take care of their bodies.

The sunken central scenes have an independent reading from bottom to top. Nossa Senhora das Neves is below God the Father, who is blessing the world.

The WITec confocal Raman microscope spectra were better defined than the bands recorded with the portable i-Raman. The joint use of XRF and Raman spectroscopies has allowed us to identify the components of the mural paintings of Nossa Senhora das Neves Chapel. The colours found in the specimens were typical of the palette of the Galicia—North Portugal Euroregion at the end of the Middle Ages. In all cases, XRF and Raman spectroscopies have allowed us to unequivocally identify the chemical composition of these colours: The black paint was bone black; the white paint was white lime; the yellow pigments were goethite and lepidocrocite; and the red pigment was hematite. White lime,

rutile, and carbon-based compounds have been used to create different tonalities. Cinnabar has been used for a later red repaint.

It is of great significance to obtain accurate and reliable pigment information through scientific means, since preservation, restoration, and repainting without detailed information can be harmful to the mural paintings.

Author Contributions: Conceptualisation, D.M.F.-L.; methodology, D.M.F.-L., E.V. and P.B.C.; validation, D.M.F.-L., E.V., P.B.C., E.S. and A.J.L.; formal analysis, E.V. and P.B.C.; investigation, D.M.F.-L., M.d.R.C. and E.S.; resources, D.M.F.-L., E.V. and P.B.C.; data curation, E.V. and P.B.C.; writing—original draft preparation, D.M.F.-L.; writing—review and editing, D.M.F.-L.; visualisation, D.M.F.-L., E.V., P.B.C., E.S. and A.J.L.; formal analysis, E.V. and P.B.C.; supervision, D.M.F.-L.; project administration, D.M.F.-L.; funding acquisition, D.M.F.-L., E.V., P.B.C. and A.J.L.; Iconographic interpretation, R.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financed with national funds through FCT -FUNDAÇÃO PARA A CIÊNCIA E A TECNOLOGIA, I.P. of Portugal, under the projects with the references CEECIND/03568/2017, (UIDB/00073/2020), and (UIDP/00073/2020) projects of the I, D unit Geosciences Centre (CGEO) of Coimbra University (Portugal). Ezequiel Vázquez and Ana J. López were beneficiaries of a scientific stay financed by Erasmus+, HERDADE Consortium (2021-1-ES01-KA130-HED-000007519). Pablo Barreiro Castro and D.M. Freire-Lista were beneficiaries of a scientific stay in University of Trás-os-Montes e Alto Douro (UTAD) and A Coruña University (UC), respectively, financed by the IACOBUS program.

Data Availability Statement: Data are contained within the article.

Acknowledgments: This work has been completed within the framework of a research stay at the Paleoeconomy and Subsistence of Preindustrial Societies research group, Institute of History, Centre for Human and Social Sciences (CCHS-CSIC), Madrid, Spain. My most sincere thanks to Alberto Núñez Cardezo of Unidade de Análise Estrutural de Servizos de Apoio á Investigación (SAI), Universidade da Coruña for the XRF analyses.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Hernanz, A.; Bratu, I.; Marutoiu, O.F.; Gavira-Vallejo, J.M.; Edwards, H.G.M. Micro-Raman spectroscopic investigation of external wall paintings from St. Dumitru's Church, Suceava. Romania. *Anal. Bioanal. Chem.* **2008**, *392*, 263–268. [\[CrossRef\]](#)
- Li, Y.; Wang, F.; Ma, J.; He, K.; Zhang, M. Study on the pigments of Chinese architectural colored drawings in the Altar of Agriculture (Beijing, China) by portable Raman spectroscopy and ED-XRF spectrometers. *Vib. Spectrosc.* **2021**, *116*, 103291. [\[CrossRef\]](#)
- Marrocchino, E.; Telloli, C.; Paletta, M.G.; Leis, M.; Vaccaro, C. The mural paintings of the cloister in the Certosa di Calci, Pisa. *J. Archaeol. Sci.* **2022**, *43*, 103461. [\[CrossRef\]](#)
- Tsantini, E.; Minami, T.; Takahashi, K.; Cau Ontiveros, M.Á. Analysis of sulphur isotopes to identify the origin of cinnabar in the Roman wall paintings from Badalona (Spain). *J. Archaeol. Sci.* **2018**, *18*, 300–307. [\[CrossRef\]](#)
- Lofrumento, C.; Ricci, M.; Bachechi, L.; De Feo, D.; Castelluccio, M. The first spectroscopic analysis of Ethiopian prehistoric rock painting. *J. Raman Spectrosc.* **2012**, *43*, 809–816. [\[CrossRef\]](#)
- Veneranda, M.; Prieto-Taboada, N.; Fdez-Ortiz de Vallejuelo, S.; Maguregui, M.; Morillas, H.; Marcaida, I.; Castro, K.; Garcia-Diego, F.J.; Osanna, M.; Madariaga, J.M. In-situ multi-analytical approach to analyze and compare the degradation pathways jeopardizing two murals exposed to different environments (Ariadne House, Pompeii, Italy). *Spectrochim. Acta Part A* **2018**, *203*, 201–209. [\[CrossRef\]](#)
- Liu, Z.; Yang, R.; Wang, W.; Xu, W.; Zhang, M. Multi-analytical approach to the mural painting from an ancient tomb of Ming Dynasty in Jiyuan. China: Characterization of materials and techniques. *Spectrochim. Acta Part A* **2022**, *279*, 121419. [\[CrossRef\]](#)
- Priego, E.; Herráez, J.; Denia, J.L.; Navarro, P. Technical study for restoration of mural paintings through the transfer of a photographic image to the vault of a church. *J. Cult. Heritage*. **2022**, *58*, 112–121. [\[CrossRef\]](#)
- Buzgar, N.; Buzatu, A.; Apopei, A.I.; Cotiugă, V. In situ Raman spectroscopy at the Voroneț Monastery (16th century, Romania): New results for green and blue pigments. *Vib. Spectrosc.* **2014**, *72*, 142–148. [\[CrossRef\]](#)
- He, J.; Zhou, W.; Hu, D.; Liu, S.; Otero, J.; Rodríguez-Navarro, C. A multi-analytical approach for the characterization of materials, manufacturing process and damage mechanisms of wall paintings in Samye Temple, Tibet. *Dyes Pigm.* **2022**, *207*, 110704. [\[CrossRef\]](#)
- Gil, M.; Carvalho, M.L.; Seruya, A.; Ribeiro, I.; Queralt, I.; Candeias, A.E.; Mirao, J. Limewashing paintings in Alentejo urban heritage: Pigment characterization and differentiation by WDXRF and XRD. *Appl. Phys. A Mater. Sci. Process.* **2007**, *90*, 49–54. [\[CrossRef\]](#)

12. Gil, M.; Manso, M.; Pessanha, S.; Manhita, A.; Cardoso, A.; Nunes, M.; Relvas, C.; Monteiro, P.; Pereira, C.; Mirão, J.; et al. Old masters under the microscope. Technical and material comparison of a 17th c. mural and panel painting assigned to José de Escovar in Southern Portugal. *Microchem. J.* **2020**, *153*, 104396. [\[CrossRef\]](#)
13. Salavessa, E.; Candeias, A.; Mirão, J.; Sousa, L.M.O.; Duarte, N.; Jalali, S.; Salgueiro, J. 19th century coloured stuccos and plasters from Grilos' Church (Oporto, Portugal): Materials and techniques employed. *Color Res. Appl.* **2016**, *41*, 246–251. [\[CrossRef\]](#)
14. Rosado, T.; Silva, M.; Dias, L.; Candeias, A.; Gil, M.; Mirão, J.; Pestana, J.; Caldeira, A.T. Microorganisms and the integrated conservation-intervention process of the renaissance mural paintings from Casas Pintadas in Évora—Know to act, act to preserve. *J. King Saud Univ. Sci.* **2017**, *29*, 478–486. [\[CrossRef\]](#)
15. Freire-Lista, D.M.; Vidal Gonçalves, G.; Vazquez, P. Weathering Detection of Granite from Three Asynchronous Historical Quarries of Sabrosa Municipality (North Portugal). *J. Cult. Heritage.* **2022**, *58*, 199–208. [\[CrossRef\]](#)
16. Freire-Lista, D.M.; Becerra Becerra, J.E.; Simões de Abreu, M. The historical quarry of Pena (Vila Real, north of Portugal): Associated cultural heritage and reuse as a geotourism resource. *Resour. Policy.* **2022**, *75*, 102528. [\[CrossRef\]](#)
17. Campos, B.; Marco, A.; Freire-Lista, D.M.; Durão, N.; Silvestre-Albero, J.; Silva, E.F.; Vieira, E.; Pintado, M.; Moreira, P.R. Rare Biogeochemical Phenomenon Associated to Manganese Patinas on Mural Painting and Granite Ashlars. *Coatings.* **2021**, *11*, 917. [\[CrossRef\]](#)
18. Lourenço, P.B.; Roque, J.A. Simplified indexes for the seismic vulnerability of ancient masonry buildings. *Constr. Build. Mater.* **2006**, *20*, 200–208. [\[CrossRef\]](#)
19. Freire-Lista, D.M.; Campos, B.B.; Moreira, P.; Ramil, A.; Lopez Díaz, A. Building Granite Characterisation, Construction Phases, Mason's Marks and Glyptography of Nossa Senhora de Guadalupe Church, Mouços e Lamares, Galicia-North Portugal Euroregion. *Geoheritage.* **2023**, *15*, 24. [\[CrossRef\]](#)
20. Freire-Lista, D.M.; Campos, B.B.; Costa, R.; Sanjurjo-Sánchez, J. Main building granite of São Tiago de Folhadela Parish Church (North of Portugal). Petrography, glyptography, construction phases and decay by pyrite oxidation. *Constr. Build. Mater.* **2022**, *350*, 128904. [\[CrossRef\]](#)
21. Dal Fovo, A.; Mazzinghi, A.; Omarini, S.; Pampaloni, E.; Ruberto, C.; Striova, J.; Fontana, R. Non-invasive mapping methods for pigments analysis of Roman mural paintings. *J. Cult. Heritage* **2020**, *43*, 311–318. [\[CrossRef\]](#)
22. Oriols, N.; Salvadó, N.; Pradell, T.; Jiménez, N.; Juanhuix, J.; Buti, S. The three-tone system in Sant Climent de Taüll wall paintings: An imprint of medieval treatises. *J. Cult. Heritage.* **2023**, *62*, 114–123. [\[CrossRef\]](#)
23. Pérez-Diez, S.; Caruso, F.; Frine Nardini, E.; Stollenwerk, M.; Maguregui, M. Secco painting technique revealed in non-restored Pompeian murals by analytical and imaging techniques. *Microchem. J.* **2023**, *194*, 109365. [\[CrossRef\]](#)
24. Oriols, N.; Salvadó, N.; Pradell, T.; Buti, S. Amorphous calcium carbonate (ACC) in fresco mural paintings. *Microchem. J.* **2020**, *154*, 104567. [\[CrossRef\]](#)
25. Costantini, I.; Aramendia, J.; Tomasini, E.; Castro, K.; Madariaga, J.M.; Arana, G. Detection of unexpected copper sulfate decay compounds on late Gothic mural paintings: Assessing the threat of environmental impact. *Microchem. J.* **2021**, *169*, 106542. [\[CrossRef\]](#)
26. Ortega-Ramírez, J.; Bano, M.; Villa Alvarado, L.A.; Medellín Martínez, D.; Rivero-Chong, R.; Motolinía-Temol, C.L. High-resolution 3-D GPR applied in the diagnostic of the detachment and cracks in pre-Hispanic mural paintings at “Templo Rojo”, Cacaxtla, Tlaxcala, Mexico. *J. Cult. Heritage.* **2021**, *50*, 61–72. [\[CrossRef\]](#)
27. Isola, D.; Bartoli, F.; Casanova Municchia, A.; Ju Lee, H.; Hye Jeong, S.; Chung, Y.J.; Caneva, G. Green biocides for the conservation of hypogeal mural paintings raised from Western and Eastern traditions: Evaluation of interference on pigments and substrata and multifactor parameters affecting their activity. *J. Cult. Heritage.* **2023**, *61*, 116–126. [\[CrossRef\]](#)
28. Caneva, G.; Bartoli, F.; Fontani, M.; Mazzeschi, D.; Visca, P. Changes in biodeterioration patterns of mural paintings: Multi-temporal mapping for a preventive conservation strategy in the Crypt of the Original Sin (Matera, Italy). *J. Cult. Heritage.* **2019**, *40*, 59–68. [\[CrossRef\]](#)
29. Tomasini, E.; Costantini, I.; Careaga, V.; Rua Landa, C.; Castro, K.; Madariaga, J.M.; Maier, M.; Siracusano, G. Identification of pigments and binders of a 17th century mural painting (Bolivia). New report on pigments associated with Andean minerals. *J. Cult. Heritage.* **2023**, *62*, 206–216. [\[CrossRef\]](#)
30. Akyuz, S.; Akyuz, T.; Basaran, S.; Kocabas, I.; Gulec, A.; Cesmeli, H.; Ucar, B. FT-IR and EDXRF analysis of wall paintings of ancient Ainos Hagia Sophia Church. *J. Mol. Struct.* **2009**, *924–926*, 400–403. [\[CrossRef\]](#)
31. Crupi, V.; Allodi, V.; Bottari, C.; D'Amico, F.; Galli, G.; Gessini, A.; La Russa, M.F.; Longo, F.; Majolino, D.; Mariotto, G.; et al. Spectroscopic investigation of Roman decorated plasters by combining FT-IR, micro-Raman and UV-Raman analyses. *Vib. Spectrosc.* **2016**, *83*, 78–84. [\[CrossRef\]](#)
32. Lazic, V.; Fantoni, R.; Falzone, S.; Gioia, C.; Loreti, E.M. Stratigraphic characterization of ancient Roman frescos by laser induced breakdown spectroscopy and importance of a proper choice of the normalizing lines. *Spectrochim. Acta Part B.* **2020**, *168*, 105853. [\[CrossRef\]](#)
33. Daniilia, S.; Minopoulou, E.; Demosthenous, F.D.; Karagiannis, G. A comparative study of wall paintings at the Cypriot monastery of Christ Antiphonitis: One artist or two. *J. Archaeol. Sci.* **2008**, *35*, 1695–1707. [\[CrossRef\]](#)
34. Cerrato, E.J.; Cosano, D.; Esquivel, D.; Otero, R.; Jiménez-Sanchidrián, C.; Ruiz, J.R. A multi analytical study of a wall painting in the Satyr domus in Córdoba, Spain. *Spectrochim. Acta Part A.* **2020**, *232*, 118148. [\[CrossRef\]](#)
35. Almaviva, S.; Fantoni, R.; Colao, F.; Piuja, A.; Bisconti, F.; Fiochi Nicolai, V.; Romani, M.; Cascioli, S.; Bellagamba, S. LIF/Raman/XRF non-invasive microanalysis of frescoes from St. Alexander catacombs in Rome. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2018**, *201*, 207–215. [\[CrossRef\]](#)

36. Fico, D.; Pennetta, A.; Rella, G.; Savino, A.; Terlizzi, V.; De Benedetto, G.E. A combined analytical approach applied to medieval wall paintings from Puglia (Italy): The study of painting techniques and its conservation state. *J. Raman Spectrosc.* **2016**, *47*, 321–328. [\[CrossRef\]](#)
37. Ziemann, M.A.; Madariaga, J.M. Applications of Raman spectroscopy in art and archaeology. *J. Raman Spectrosc.* **2020**, *52*, 137–142. [\[CrossRef\]](#)
38. Nosenko, V.V.; Yaremko, A.M.; Dzhan, V.M.; Vorona, I.P.; Romanyuk, Y.A.; Zatovsky, I.V. Nature of some features in Raman spectra of hydroxyapatite-containing materials. *J. Raman Spectrosc.* **2016**, *47*, 726–730. [\[CrossRef\]](#)
39. Bonnat, G.F.; Desimone, P.M.; Martínez, G.A.; Mazzanti, D.L. Raman spectroscopy study of ca 12,000 yrs cal BP lithic artifacts adhesions from archaeological sites in the Pampas region, Argentina. *J. Archaeol. Sci. Rep.* **2021**, *38*, 103101. [\[CrossRef\]](#)
40. Bernardini, S.; Bellatreccia, F.; Casanova Municchia, A.; Della Ventura, G.; Sodo, A. Raman spectra of natural manganese oxides. *J. Raman Spectrosc.* **2019**, *50*, 873–888. [\[CrossRef\]](#)
41. Gunasekaran, S.; Anbalagan, G.; Pandi, S. Raman and infrared spectra of carbonates of calcite structure. *J. Raman Spectrosc.* **2006**, *37*, 892–899. [\[CrossRef\]](#)
42. Edwards, H.G.M.; Middleton, P.S.; Jorge Villar, S.E.; de Faria, D.L.A. Romano-British wall-paintings II: Raman spectroscopic analysis of two villa sites at Nether Heyford, Northants. *Anal. Chim. Acta.* **2003**, *448*, 211–221. [\[CrossRef\]](#)
43. Guglielmi, V.; Andreoli, M.; Comite, V.; Baroni, A.; Fermo, P. The combined use of SEM-EDX, Raman, ATR-FTIR and visible reflectance techniques for the characterisation of Roman wall painting pigments from Monte d'Oro area (Rome): An insight into red, yellow and pink shades. *Environ. Sci. Pollut. Res.* **2022**, *29*, 29419–29437. [\[CrossRef\]](#)
44. Edwards, H.G.M. Analytical Raman spectroscopic discrimination between yellow pigments of the Renaissance. *Spectrochim. Acta Part A* **2011**, *80*, 14–20. [\[CrossRef\]](#)
45. Botticelli, M.; Maras, A.; Candeias, A. μ -Raman as a fundamental tool in the origin of natural or synthetic cinnabar: Preliminary data. *J. Raman Spectrosc.* **2019**, *51*, 1470–1479. [\[CrossRef\]](#)
46. Argote, D.L.; Torres, G.; Hernández-Padrón, G.; Ortega, V.; López-García, P.A.; Castaño, V.M. Cinnabar, hematite and gypsum presence in mural paintings in Teotihuacan, Mexico. *J. Archaeol. Sci. Rep.* **2020**, *32*, 102375. [\[CrossRef\]](#)
47. Gao, Q.; Wu, X.; Fan, Y.; Zhou, X. Low temperature synthesis and characterization of rutile TiO_2 -coated mica-titania pigments. *Dyes Pigm.* **2012**, *95*, 534–539. [\[CrossRef\]](#)
48. Tang, W.; Xu, W.; Zhong, M.; Zhang, Z. Slightly doped hydroxyapatite pigments of subtractive color with high near-infrared reflectance. *J. Solid State Chem.* **2023**, *322*, 123947. [\[CrossRef\]](#)
49. Daveri, A.; Malagodi, M.; Vagnini, M. The bone black pigment identification by noninvasive, in situ infrared reflection spectroscopy. *J. Anal. Methods Chem.* **2018**, *1–8*, 6595643. [\[CrossRef\]](#)
50. Sauer, G.R.; Zunic, W.B.; Durig, J.R.; Wuthier, R.E. Fourier transform Raman spectroscopy of synthetic and biological calcium phosphates. *Calcif. Tissue Int.* **1994**, *54*, 414–420. [\[CrossRef\]](#)
51. Tomasini, E.; Siracusano, G.; Maier, M.S. Spectroscopic, morphological and chemical characterization of historic pigments based on carbon. Paths for the identification of an artistic pigment. *Microchem. J.* **2012**, *102*, 28–37. [\[CrossRef\]](#)
52. Bordes, L.; Prinsloo, L.; Fullagar, R.; Sutikna, T.; Hayes, E.; Jatmiko, R.; Wahyu Saptomo, E.; Tocheri, M.; Roberts, R. Viability of Raman microscopy to identify micro-residues related to tool-use and modern contaminants on prehistoric stone artefacts. *J. Raman Spectrosc.* **2017**, *48*, 1212–1221. [\[CrossRef\]](#)
53. Edwards, H.G.M.; Farwell, D.W.; de Faria, D.L.A.; Rozenberg, S. Raman spectroscopic study of red pigment and fresco fragments from King Herod's Palace at Jericho. *J. Raman Spectrosc.* **1999**, *30*, 361–366. [\[CrossRef\]](#)
54. Edwards, H.G.M.; Farwell, D.W.; de Faria, D.L.A.; Monteiro, A.M.F.; Afonso, M.C.; De Blasis, P.; Eggers, S. Raman spectroscopic study of 3000-year-old human skeletal remains from a sambaqui, Santa Catarina, Brazil. *J. Raman Spectrosc.* **2001**, *32*, 17–22. [\[CrossRef\]](#)
55. Schmid, T.; Dariz, P. Shedding light onto the spectra of lime: Raman and luminescence bands of CaO , Ca(OH)_2 and CaCO_3 . *J. Raman Spectrosc.* **2015**, *46*, 141–146. [\[CrossRef\]](#)
56. Edwards, H.G.M.; Farwell, D.W. The conservational heritage of wall paintings and buildings: An FT-Raman spectroscopic study of prehistoric, Roman, mediaeval and Renaissance lime substrates and mortars. *J. Raman Spectrosc.* **2008**, *39*, 985–992. [\[CrossRef\]](#)
57. Iriarte, M.; Hernanz, A.; Gavira-Vallejo, J.M.; Alcolea-González, J.; de Balbín-Behrmann, R. μ -Raman spectroscopy of prehistoric paintings from the El Reno cave (Valdesotos, Guadalajara, Spain). *J. Archaeol. Sci. Rep.* **2017**, *14*, 454–460. [\[CrossRef\]](#)
58. Escribano, R.; Sloan, J.J.; Siddique, N.; Sze, N.; Dudev, T. Raman spectroscopy of carbon-containing particles. *Vib. Spectrosc.* **2001**, *26*, 179–186. [\[CrossRef\]](#)
59. Tomasini, E.P.; Halac, E.B.; Reinoso, M.; Di Liscia, E.J.; Maier, M.S. Micro-Raman spectroscopy of carbon-based black pigments. *J. Raman Spectrosc.* **2012**, *43*, 1671–1675. [\[CrossRef\]](#)
60. Neiman, M.K.; Balonis, M.; Kakoulli, I. Cinnabar alteration in archaeological wall paintings: An experimental and theoretical approach. *Appl. Phys.* **2015**, *121*, 915–938. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.