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An extensive colour palette in Roman villas in Burgos, Northern Spain: a Raman spectroscopic analysis

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Abstract Seventy-five specimens from thirty fragments of Roman villa wall-paintings from sites in Burgos Castilla y Leon, Spain, have been analysed by Raman spectroscopy. This is the first time that a Raman spectroscopic study of Roman wall-paintings from Spain has been reported. The extensive range of tonalities and colour compositions contrasts with the results found in other provinces of the Roman Empire, for example Romano-British villas. Calcite, aragonite, haematite, *caput mortuum*, cinnabar, limonite, goethite, cuprorivaite, lazurite, green earth, carbon and verdigris have been found as pigments. Some mineral mixtures with different tonalities have been made using different strategies to those more usually found. Of particular interest is the assignment of the Tarna mine for the origin of the cinnabar used for obtaining the red colour in some specimens analysed here. The wide range of colours, tonalities and minerals found in some of the sites studied in this work is suggestive of a high social status for the community.

Keywords Raman spectroscopy · Roman villa · Pigment · Wall-painting · Mineral

Introduction

Raman spectroscopy is a valuable technique in the study of pigments used in art-works for several reasons [1–4]. It provides molecular information, it has the ability to characterise polymorphous and isomorphous phases,

especially in the low wavenumber region where metal-oxide and metal-sulphur spectral signatures are critical for their unambiguous identification [5–8]. In addition, the possibility of non-destructively analysing macro- and micro-samples using no chemical or mechanical treatment has made Raman spectroscopy a technique of choice in the field of archaeological art [9–16]. The information obtained from Raman spectra contributes to historical, social, political and economic knowledge and it has an additional benefit for the scientific preservation and restoration of deteriorating art-work and heritage.

Several Raman spectroscopic studies have been carried out on Roman wall-paintings from the United Kingdom [19, 20] and the Ukraine [21]. Italian Roman pigments have been extensively studied using various techniques [17, 18] (including FTIR, SEM, XRD, Mossbauer spectroscopy, atomic absorption spectroscopy) illustrating a wide range of pigments and mixtures but, hitherto, only FTIR, SEM and XRD analyses have been reported for Spanish [22–24] analogues, and no Raman spectroscopic study from the Roman wall-paintings in Spain has been carried out before.

In the Kertch site, in Ukraine, a Raman spectroscopic study [21] has shown that cuprorivaite, carbon and minium were used as pigments in the wall-paintings of the tomb. The study of the pigments was carried out from micro-samples extracted from two walls. The palette from the sites in the United Kingdom shows a rather poor range of pigments, with carbon, calcite, haematite, limonite, cuprorivaite, green earth and *caput mortuum*, as well as very simple mixtures (for example, in order to darken or lighten colours, carbon or calcite, respectively, were added in admixtures with the main pigment). It was rather surprising to find the highly-prized *caput mortuum* in this context. In the Romano-British villa samples, the Raman analyses were completely non-destructive and the wall-painting fragments were directly analysed without removing any particle.

In the different analyses made on the Roman wall-paintings from Spain, calcite, haematite, goethite, cin-

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Fig. 1 Situation of the villas in the Burgos province studied in this work

nabar, cuprorivaite, iron oxides, carbon and malachite were found, and some interesting and unusual mixtures of pigments have been reported; however, in these cases the destruction of small amounts of sample has been necessary in order to collect the data.

We present here the first Raman spectroscopic study of an extensive collection of Romano wall-painting specimens from northern Spain. These non-destructive analyses of wall-painting fragments from seven Roman villas sited in Burgos indicate some interesting results in regard to the number and quality of pigments used, and unusual mixtures of them. These results contain significant differences to the results obtained from the study of Romano-British villas, which were also sited at the fringe of the Roman Empire in the first century A.D.

Experimental

Specimens

Seven excavation sites of different Roman villas near Burgos (Fig. 1), Castilla y Leon, Spain, have provided specimens of wall-paintings which are noteworthy for their extensive range of tonalities and colour compositions (Table 1). These comprise

- Four fragments from the Roman villa in Salinas de Rosio, excavated between 1972 and 1977.
- Seven fragments from the Sasamon site excavated in 1971.
- Five fragments from the Valdeande site, in Ciella, excavated in 1990.
- One fragment from a Roman villa in San Martín de Losa, excavated between 1989 and 1991.
- One fragment from a Roman villa in the Cardeñajimeno site.
- Eight fragments from a Roman villa in Baños de Valdearados, excavated in 1994.
- Four fragments from “casa numero 1” from the Roman City of Clunia.

Several fragments show geometric signatures and parts of humans, as shown in Figs. 2 and 3.

It has been estimated that the ages of these Roman villas cover 200 years, from the first century B.C. to the first century A.D., except for villa number 1 in the Clunia Site, for which the excavations have determined successive remodelings of the house between the first century and the fourth century A.D.

Spectroscopy

A Renishaw inVia Raman microscope with a dedicated Leica DMLM microscope was utilised to achieve spec-

Table 1 The number of fragments, the colours found and the pigments used at each site studied in the present work

Site	Number of fragments	Colours found ^a	Pigments used
Salinas de Rosio	4	Purple (2); Light red (1); White (2)	<i>Caput mortuum</i> ; Haematite; Calcite
Sasamon	7	Red in different tonalities (4); White (3); Black (2); Grey (1); Brown (1)	Haematite; Calcite; Carbon
Ciella	5	Green in different tonalities (4); Brown (2); Yellow (2); White (2); Black (5)	Calcite; Aragonite; Carbon; Green earth; Limonite
San Martín de Losa	1	Red (1)	Haematite; Calcite
Cardeñajimeno	1	White (1); Grey (1)	Calcite; Carbon
Baños de Valdearados	8	Brown in different tonalities (4); Beige in different tonalities (3); Green in different tonalities (2); Red in different tonalities (5); Yellow in different tonalities (2); Grey (1); Black (5); White (7)	Lazurite; Green earth; Verdigris; Limonite; Goethite; Haematite; Cinnabar; Calcite; Carbon
Clunia	4	Red in different tonalities (3); Brown (1); Yellow (1); Blue (1); White (2); Grey (1); Black (3)	Cuprorivaite; Haematite; Goethite; Limonite; Calcite; Carbon



Fig. 2 Fragment of a Roman wall-painting from the Baños de Valdearados site. Several tonalities of brown are visible in the hair drawing

tra; the objective lenses used were 50 \times and 20 \times with 785 and 514 nm laser excitation wavelengths. 20 to 60 accumulations at 10 s exposure time were typically used to improve the signal-to-noise ratios. The laser power used ranged between 0.2 and 50 mW to avoid damage to the sample and mineral changes caused by thermal heating in the laser beam.

Several samples have been analysed by FT-Raman spectroscopy using a Bruker IFS66 spectrometer with FRA 106 Raman module attachment and dedicated microscope using a Nd³⁺/YAG laser at 1,064 nm laser excitation wavelength. Typically, 4,000 scans were accumulated to improve the signal-to-noise ratio with a laser power from 10 to 20 mW.



Fig. 3 Fragment of green, white and black geometric lines in a sample from the Baños de Valdearados site

Red colours

Different tonalities of the red colour, from light to dark, appear in 16 specimens. Haematite, with Raman bands at 610, 494, 409, 295 and 225 cm⁻¹, is the most common pigment used to obtain the red colour. Light tonalities have been achieved by mixing haematite with calcite (1,086, 712, 281, 156 cm⁻¹); the addition of carbon (bands at 1,600 and 1,320 cm⁻¹) has been used to make a darker colour.

A bright red colour is noted in one of the samples (Fig. 2) from Baños de Valdearados; the spectrum has bands at 253, 284 and 342 cm⁻¹ characteristic of cinnabar. A spectrum collected from a relatively large (approximately 100 μ m) cinnabar crystal (Fig. 4) shows a weak band at 1,084 cm⁻¹ (Fig. 5) characteristic of calcite. As the analysis has been achieved with the microscope imaging into the single crystal, we can conclude that the signature at 1,084 cm⁻¹ is an impurity within the crystal, which is hence connected with the origin of the mineral.

There were two cinnabar mines in the Spanish region of the Roman Empire, one sited in the North, in Tarna (Leon) and the more important mine of Almaden, sited in the South, near Ciudad Real. In Tarna, the cinnabar is found associated with sedimentary carbonate stone, whereas in Almaden it is with quartz. The band at 1,084 cm⁻¹, characteristic of calcium carbonate, indicates that the source of cinnabar in this wall painting was Tarna, which is close to the villa site at Baños de Valdearados.

A purple colour appears in the Salinas de Rosio samples. The spectra achieved show that only very pure haematite is present, with bands at 225, 245, 293, 388 (shoulder), 409, 496 and 611 cm⁻¹ (Fig. 6). The presence of the 245 cm⁻¹ band, the purity of the pigment in this dark red specimen (which has not been mixed with any

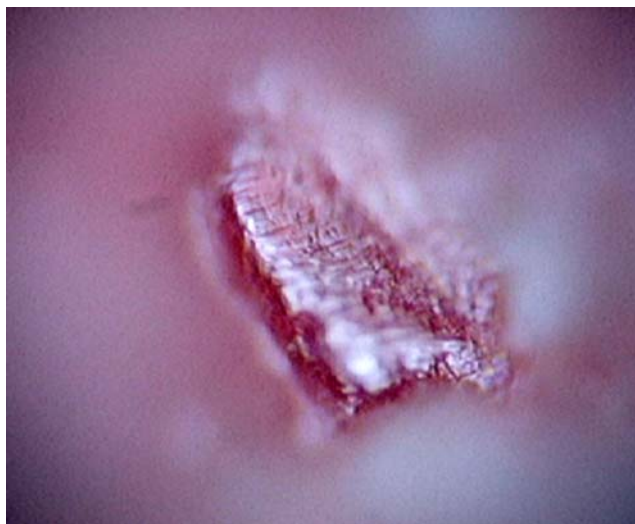


Fig. 4 Microphotograph of a cinnabar crystal found in a red specimen in the "human head" from the Baños de Valdearados site

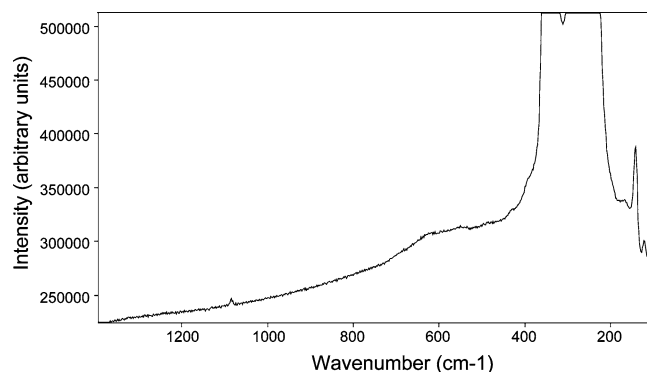


Fig. 5 Raman spectrum of one single cinnabar crystal from a red specimen from the Baños de Valdearados site (Fig. 4). The very weak signature at $1,084\text{ cm}^{-1}$ is characteristic of calcium carbonate and indicates that the mineral source is probably the Tarna mine

other mineral), and the very fine grain size are indicative that the very expensive and desirable *caput mortuum* pigment was used at this site.

Brown colour

Brown colours (from dark to light brown) appear in three samples (Baños de Valdearados, Ciella and Clunia). In the Ciella and Clunia samples, the brown colour was obtained by mixing limonite ($553, 481, 392, 299$ and 247 cm^{-1}), calcite and carbon.

Samples from Baños de Valdearados are more complex in their palette. The range of tonalities extends from dark to light brown; here the brown colour pigment shows Raman bands of haematite, carbon, calcite (small amount), cinnabar and goethite ($552, 479, 385$ and 300 cm^{-1}). In the spectra collected from the pigment coloured medium brown, haematite, cinnabar and limonite have been used as pigments, but in the light brown colour haematite and limonite were mixed but with no traces of cinnabar; furthermore, the signature of calcite has a stronger relative intensity in these tonalities than in the dark brown colour, which means that it has been used in a larger proportion, whereas the carbon

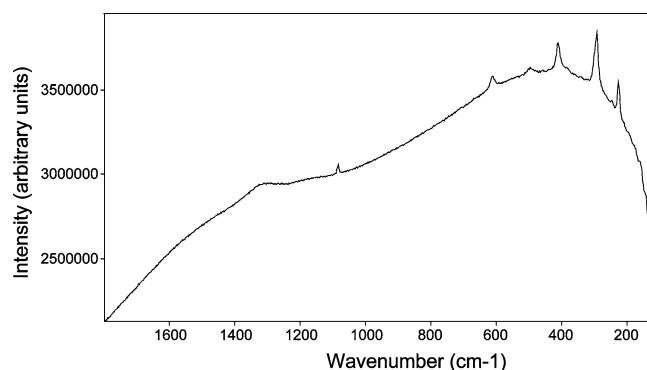


Fig. 6 Raman spectrum of *caput mortuum* collected from a specimen from the Salinas de Rosio site

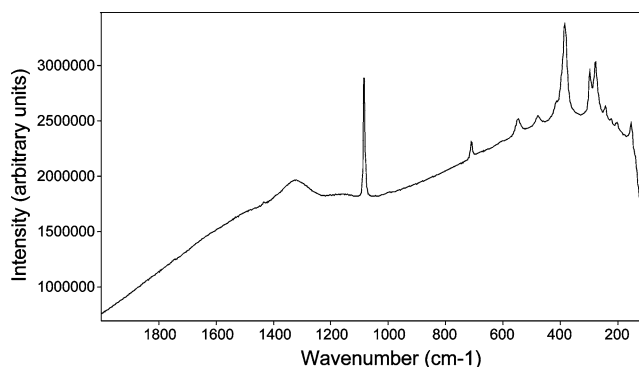


Fig. 7 Raman spectrum of a yellow specimen from the city of Clunia, showing the characteristic bands of goethite and calcite

bands appear with a weaker relative intensity in the specimen of medium brown colour and they are absent altogether in the spectra collected from specimens of the light brown colour.

Although cinnabar was a very expensive and much admired pigment in Roman times and was normally used in a pure form for the red colour because of its bright tonality, the amount of cinnabar that appears in the brown colour in these samples is rather unusual and suggestive that the painter used this pigment with the intention of obtaining a particular tonality, and that its presence as a contaminant or impurity is unlikely.

Yellow colour

A yellow colour is present in all three of the sites studied here, namely Baños de Valdearados, Clunia and Ciella. Limonite and goethite (Fig. 7) are the pigments used in Clunia in admixture with calcite. In the Ciella site, four samples show a yellow colour, which was obtained by mixing limonite and calcite, but carbon has also been added to achieve a brownish-yellow colour found at this site.

Two samples have a yellow colour in the Baños de Valdearados site. Limonite is the main pigment used, but a band at 142 cm^{-1} appears in several spectra obtained from one specimen (Fig. 8). This is a

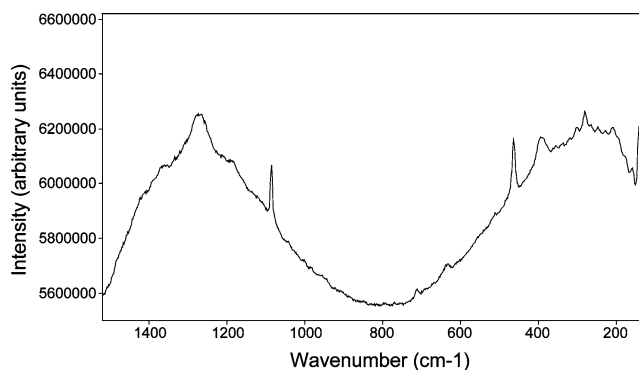


Fig. 8 Raman spectrum of a yellow specimen from Baños de Valdearados. Signatures of limonite, calcite and quartz are visible

characteristic band of the polymorphs of lead oxide litharge (red) or massicot (yellow); as the other main Raman bands of these minerals are close to the calcite and limonite bands they are not identified here unambiguously, but the colour suggests that massicot was probably the mineral used. A signature at 463 cm^{-1} in one spectrum is indicative of quartz; this mineral was commonly used in antiquity to aid the fine grinding of the earth pigments.

Beige colour

This colour appears only at the Baños de Valdearados site. Two different samples have been analysed with different results. Only haematite and calcite appear in one of the specimens, but goethite, haematite, calcite and a small amount of cinnabar have been found in the second sample. The artist's wish to obtain a particular tonality probably accounts for the use of different mixtures to achieve the beige colour.

Although some isolated cinnabar particles have been found in the yellow colour of the Baños de Valdearados site, their disposition suggests that they were probably a contaminant; however, in contrast, the quantity of cinnabar found in the beige colour at this site is indicative that it has been used definitively to provide the colour needed.

Blue colour

Only one sample, from the Clunia site, has a blue colour. The spectrum observed gives bands at $1,084, 1,013, 988, 787, 569, 429, 376$ and 230 cm^{-1} characteristic of cuprorivaite (Egyptian blue). A signature of quartz at 462 cm^{-1} also appears with medium intensity (Fig. 9).

Green colour

Samples from Baños de Valdearados and Ciella have green colours. Bands at $1,134, 1,085, 959, 701, 550, 458,$

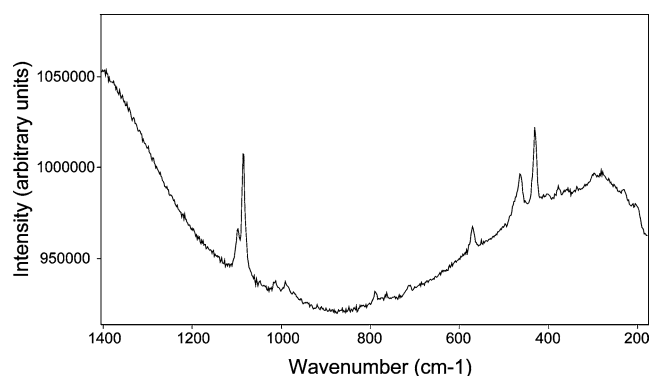


Fig. 9 Raman spectrum of a blue sample from the Clunia site. Bands of cuprorivaite and quartz are visible

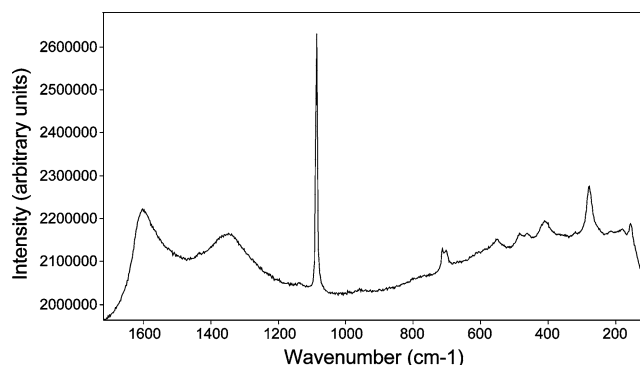


Fig. 10 Raman spectrum of a sample from the Baños de Valdearados site. Green earth and carbon were used in admixtures to obtain the green colour

$397, 318, 275, 216$ and 180 cm^{-1} have been assigned to green earth (*terre verte*), usually mixed with carbon, in the Ciella site (Figs. 3 and 10).

In the Baños de Valdearados site different strategies has been adopted to obtain the green colour. The Raman spectrum of one of the samples shows the characteristic bands of green earth (*terre verte*) and carbon. The second sample in this site seems to be a mixture of lazurite, which gives a band at 542 cm^{-1} in the Raman spectrum, with limonite (397 cm^{-1}); we assign the bands centred at $1,594, 1,489, 1,458, 1,347, 1,224, 1,192, 1,083, 966, 834, 585$ and 537 cm^{-1} to a variety of verdigris (basic copper(II) acetate) (Fig. 11). Because of the different manufacturing processes involved in its synthesis, some changes in structure and composition of the verdigris can be expected with consequent changes in the Raman spectra.

White colour

Calcite is the pigment commonly used to obtain the white colour. However, samples from Ciella show signatures at $1084, 702, 205\text{ cm}^{-1}$, characteristic of aragonite, the marine version calcium carbonate (Fig. 12).

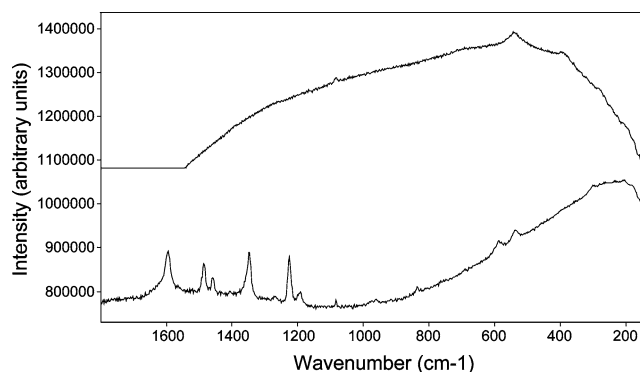


Fig. 11 Raman spectra of a green sample from the Ciella site. In the upper spectrum, bands of lazurite and limonite are present; in the lower spectrum, bands assignable to verdigris are identifiable

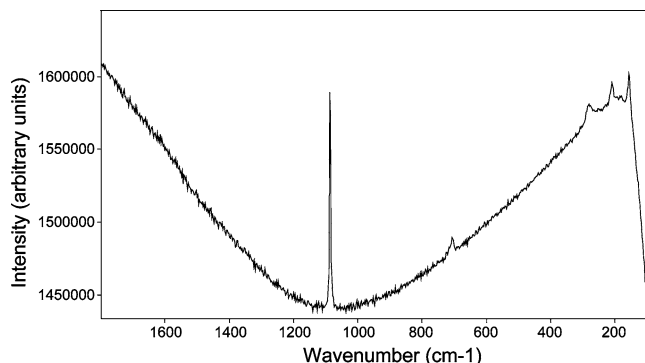


Fig. 12 Raman spectrum of a white sample from the Ciella site showing calcite and aragonite bands

This mineral appears with calcite in the white samples at Ciella and is possibly also present in very small amounts in the green colour observed at this site.

Grey colour

Carbon and calcite mixed in different proportions are the pigments used to obtain the grey colours of different tonalities.

Black colour

The Raman spectra obtained for the black pigment show that carbon was the only pigment used. Absence of a band at 960 cm^{-1} indicates that the carbon was obtained from a vegetable origin rather than bone black obtained from the incineration of bones or ivory.

FT-Raman spectroscopy

Spectra collected using the FT-Raman spectrometer with $1,064\text{ nm}$ excitation show a broad band centred at 780 cm^{-1} (Fig. 13) and assigned to limewash putty. This

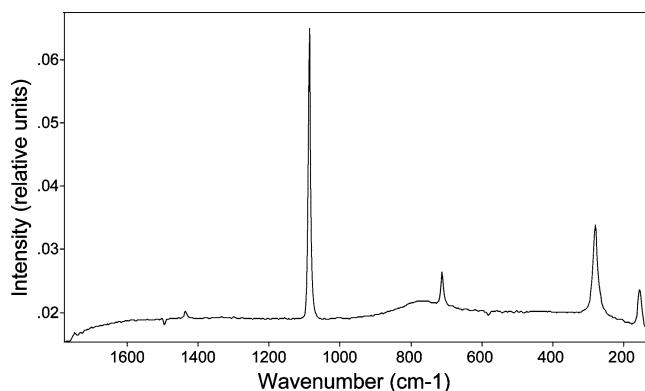


Fig. 13 FT-Raman spectrum of a white sample showing the broad band at 780 cm^{-1} from limewash putty used to prepare the substrate walls for painting

compound is characteristic of the Roman fresco technique and was used to prepare the wall before the application of pigment; it is typical of the wall-painting procedures operating during in this period.

Conclusions

Twelve different pigments have been found, either in a pure form or in admixtures in different proportions of two or more compounds: cinnabar, haematite, *caput mortuum*, limonite, goethite, cuprorivaite, lazurite, green earth, calcite, aragonite, carbon and verdigris.

A wide palette of pigments have been used to obtain the different colours in the Roman wall-paintings from the Burgos provincial sites in Northern Spain and this contrasts strongly with a much more limited variety found in the Romano-British provinces. It is remarkable that expensive pigments, such as cinnabar, *caput mortuum* and lazurite, even in admixture with other minerals, were found extensively at the Burgos sites, which is perhaps indicative of the high social status and wealth of the settlements there.

To darken or lighten a colour, particularly yellow and red, carbon and calcite respectively have been used in admixtures with the appropriate pigments.

It is interesting to note here the presence of haematite and the expensive pigments cinnabar and *caput mortuum* in the red tonalities, whereas cinnabar has been found in only one Romano-British villa fragment [20]. This can be related to the sourcing of suitable mineral pigments in Roman Spain.

The discovery of the calcite impurity in a single crystal of cinnabar in a red specimen sample means that the painter used the natural mineral and not the manufactured form of vermilion, which has the same composition and structure; furthermore, it confirms the Tarna mines in Northern Spain as the likely origin of the cinnabar, instead of the more important and well-known Almaden mine in Southern Spain. The local mineral source seems to have been preferred for the villas studied here.

The brown colours show a deliberate and selected admixture of minerals (haematite, cinnabar, limonite, goethite, carbon, calcite) in different proportions to obtain the desired tonality, which contrasts strikingly with the results obtained from our previous studies of Roman wall-paintings that indicate the sole presence of ochre in admixture with carbon.

It is interesting that the green colours seen in the Burgos sites were obtained in two very different ways; the mixture of the very expensive blue pigment lazurite with limonite (yellow) and verdigris (green) is rather unusual. In antiquity, lazurite was only used sparingly in private villas because of its price, and it is remarkable for its presence here in the same villa where cinnabar was also widely used. This is strongly suggestive of a well-endowed and wealthy region. The alternative use of green earth, *terre verte*, also found in these sites, is more common in Roman wall-paintings.

The adoption of different strategies to achieve the colour palette used in the Burgos villa sites is strongly suggestive of the presence of several ateliers of painters who clearly had preferences for different methods of producing their colour tones.

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