Mediterranean Archaeology and Archaeometry 2024, 24(1), 1244 ISSN:2241-8121

https://www.maajournal.com/

Research Article

Methodology for the Identification of Roman Pictorial Workshops: Application to the Second Style Sets of the *Municipium Augusta Bilbilis* (Calatayud, Saragossa, Spain)

Lara Íñiguez Berrozpe ^{1*}, Daniel Cosano Hidalgo ¹, Arnaud Coutelas ³, Carmen Guiral Pelegrín ⁴, José Rafael Ruíz Arrebola ⁵

¹ Doctor, Faculty of Philosophy and Letters, Universidad de Zaragoza, Zaragoza, Spain

² Doctor, Department of Organic Chemistry, University of Cordoba, Cordoba, Spain

³ Doctor, Société de portage salarial DTalents consulting, Archéologie et Philologie d'Orient et d'Occident (AOROC)-Université PSL (Paris), Paris, France

⁴ Doctor, Faculty of Geography and History, Universidad Nacional de Educación a Distancia (UNED), Madrid, Spain

⁵ Doctor, Department of Organic Chemistry, University of Cordoba, Cordoba, Spain

* Corresponding Author: <u>laraib@unizar.es</u>

Citation: Íñiguez Berrozpe, L., Cosano Hidalgo, D., Coutelas A., Guiral Pelegrín C., & Ruíz Arrebola J. R. (2024). Methodology for the Identification of Roman Pictorial Workshops: Application to the Second Style Sets of the *Municipium Augusta Bilbilis* (Calatayud, Saragossa, Spain). *Mediterranean Archaeology and Archaeometry*, *24*(1), 154-179. <u>10.5281/zenodo.10893845</u>

ARTICLE INFOABSTRACTReceived: 06 Nov 2023
Accepted: 26 Jan 2024In this study we present the results of an interdisciplinary analysis applied to four pictoric sets from
three domus (Domus 1, Domus 2 –belonging to Insula I- and House of the Lararium) of the roman
site of Municipium Augusta Bilbilis (Calatayud, Spain). The main objective is to find out if the
analytical techniques applied to the pigments (archaeometry) and the study of the mortars (petrology)
allow us to find our own craft recipes and there-fore conclude that these decorations were made by the
same workshop. The aim is also to establish a working methodology to identify this type of workshop
beyond the traditional one based on the observation of certain iconographic or technical aspects. The

four pictoric sets fall stylistically within the so-called II style and all of them come from representation

Keywords: Archaeometry, Petrology, Pigments, Mortar, Celadonite.

rooms within the three most important dwellings in this town.

INTRODUCTION

The Roman city of *Bilbilis* (Calatayud, Zaragoza, Spain), located at the confluence of three rivers, the Jálón, the Ribota and the Jiloca, controlled the pass towards the Ebro, the Levantine coast and the Meseta, providing the city with a privileged strategic position. If this was considered an advantage, less advantageous was the difficult terrain that the Romans and before them the Celtiberians had to deal with. This decisively conditioned the layout of the city, which adapted to the steep slopes of the area by being built on terraces. This settlement of Celtiberian origin was elevated to the status of *municipium* in the time of Augustus and given the name Augusta. This can be considered a consequence of having previously been granted the *ius italicum*—this occurring around the middle of the first century BC, as indicated by numismatic finds—as well as having the advantage of including Italic settlers among its inhabitants.

This first period of the city is archaeologically established by the construction of private buildings, specifically *Domus* 1 and 2 (both belonging to *Insula* I) and the House of the Lararium (previously known in historiography as the House of the Nymphaeum), since the public buildings we know today were erected when the city obtained the aforementioned status, culminating during the reign of Tiberius (Figure 1).

There are four sets of paintings dated to the first phase of the life of these dwellings: one from the exedra (H.7) of *Domus* 1, one that decorated the *cubiculum* (H.14) of *Domus* 2, one that decorated the *tablinum* (11) of the House of the Lararium, and one found in the *torcularium* (20) and possibly belonging to the *cubiculum* (12) of the same house. All of them have been the subject of stylistic studies, thanks to which it has been possible to classify



them as Second Style (Íñiguez Berrozpe, C. Guiral Pelegrín, Sáenz Preciado, & Martín-Bueno, 2022)¹, although they belong, in principle, to different phases, or at least one of them does, as we will see below. Two of them, the set from the exedra (H.7) of *Domus* 1 and the one that decorated the *tablinum* (11) of the House of the Lararium, have also been the subject of archaeometric analysis (Cerrato, Íñiguez, Cosano, Guiral, & Ruiz, 2021), leading to the conclusion that they were made by the same workshop of craftsmen. In this article, we have decided to extend the study to include the other two sets mentioned above and to complement the archaeometric analyses of the pigments with petrographic analyses of the mortars of the four decorations.



Figure 1. Archaeological site of Bilbilis

ARCHAEOLOGICAL CONTEXT

As we will explain throughout this study, it is essential to know the archaeological context of the selected samples in order to reach results that allow us to establish historical conclusions. Therefore, the objective of this section is to explain the characteristics of the *Domus* as well as its chronology in order to justify the selection of samples and establish comparisons between them.

Insula I

This *Insula* is made up of three *domus*, which have very particular characteristics designed to overcome the difficult terrain of the site at *Bilbilis*. It was built on two terraces, rising as a three-level construction, so that the lowest level, where the taverns were located, was on the first terrace and the next two on the second. It was also surrounded by three streets; the commercial space located on the lowest level opened onto one of them. On the upper floor there was a back street, and running perpendicular to it as a ramp was the third street, connecting the two terraces.

From a chronological point of view, the study of the ceramic material extracted provides a date of around the middle of the first century BC for its construction. Initially, it was considered that the three *domus* had been in use until the middle of the first century AD, a chronology supported by the absence of Hispanic *terra sigillata*, although the use of the *tabernae* extended into the third century. The latest research, however, has made it

¹ There is another Second Style set restored from a few fragments found in a fill between walls 3 and 4 of the *postcaenium*, dated to the Augustan period. These materials were mixed among the earth from the rubble of buildings that had already been destroyed (Guiral Pelegrín & Martín-Bueno, 1996). We have not included it in the present study because it is now lost.

possible to reconsider this assumption as regards *Domus* 3, since part of the pictorial material exhumed dates to the second half of the first century AD. In any case, its end is linked to two factors: the structural problems it faced due to being built directly on the bedrock without this being reworked—with the exception of the southern enclosure on which the third *domus* was built—and the great pressures exerted by the terraces.

Domus 2 and the Decoration of the Cubiculum (H.14)

Domus 2 has an Italic layout and a double entrance. The main entrance led to the main floor and was via a staircase attached to the southeast side. The second entrance was located in the rear street on the second terrace. It was accessed by a staircase leading from the atrium (H.1).

The house thus has three documented floors: on the upper floor there is a testudinate *atrium* (H.1) around which the rest of the rooms are distributed. Identified among these are the *tablinum* (H.2), the *culina* (H.3), and the *triclinum* (H.4). The *cubicula* were probably located in the eastern area of this third floor; the pictorial decoration of one of them (H.14), exhumed in the storeroom (6-7) on the second floor, has been recovered, as will be seen below. On the first floor at street level are the taverns (T.9 and T.10), which are longer than those in *Domus* 1. Their layout, paving and pictorial decoration allow us to identify them with two cubicles preceded by an antechamber that have a clear relationship with the neighbouring tavern (Martín-Bueno & Sáenz Preciado, 2002; Beltrán Lloris, 2003; Uribe Agudo, 2004, 2015; Martín-Bueno, Lope Martínez, Sáenz Preciado, & Uribe Agudo, 2007; Guiral Pelerín & Íñiguez Berrozpe, 2012) (Figure 2).



Figure 2. Plan of Domus 2 (Insula I) (Uribe Agudo, 2015)

To focus on the decoration of the cubicle (H.14) (Figure 3)—which was found in a fragmentary state in storeroom H.6 on the lower floor—the reconstruction allows us to configure a cubicle with a square layout; the first two thirds correspond to the antechamber, and the remaining third to the alcove, separated by stucco pilasters crowned with capitals. This division is also marked in the roof, which is flat in the antechamber and vaulted in the alcove.

The plinth is divided into compartments that imitate marble slabs with white veins on a green, yellow, and brown background. In the middle area there is a succession of monochrome panels—green, cinnabar red, yellow— and others imitating alabaster. The upper part of the panel is an emulation of marble blocks on a red background,

arranged in headers and stretchers. Both these and the panels in the middle section have the characteristic bichrome framing fillets of the Second Style. Afterwards, a band, which emulates a wooden strip, leads to the epistyle framed by cornices (Lope, 2007; Martín-Bueno et al., 2007; Sáenz Preciado et al., 2018; Guiral Pelegrín, Iñiguez Berrozpe, Sáenz Preciado, & Martín-Bueno, 2018).

The rock imitations in the middle and upper parts of the wall are worth analysing, given their uniqueness. In the panels of the middle part, only slabs with imitations of the so-called "fiorito" alabaster are recognizable. These have a special characteristic: the presence of small red or blue oval motifs that we do not find in the reference Campanian examples (Barker & Perna, 2018, Figure 3), but which are repeated in the paintings of the Maison aux Deux Alcôves (XVIII) at *Glanum*. It was this peculiar characteristic that raised the possibility that the two decorations were made by the same workshop, which worked in the Gallic city between 50-30 BC (Barbet, 2007).

As regards the upper area, we can identify the representation of onyxes (both the so-called *cotognino* and the banded variant) (Barker & Perna, 2018, Figure 2), alabaster, *marmor numidicum*, and other rocks that we cannot define. This invention of marbles is also noted in the paintings of high-status houses, such as the House of Augustus on the Palatine Hill in Rome, or the *Casa di Obellius Firmus* or the Villa of the Mysteries in Pompeii. There are many imaginary marbles depicted in Roman paintings, which seem to be inspired by *lumachella* or so-called peacock's eyes, but some of them are the fruit of the painters' imagination (Mulliez, 2014).



Figure 3. Decoration of the Cubiculum (H.14) of Domus 2. Paintings on Display in Calatayud Museum

Another special feature of the paintings from *Bilbilis* is the upper part of the wall, where the blocks are not arranged in the usual headers and stretchers in which the lines of union between the blocks are clearly marked, but are placed on the red background without any connection between them. This same arrangement is found, among others, in the paintings in the rooms in front of the Sanctuary of Cybele at *Lugdunum* (Lyons), which are dated to around 43 BC, the year the colony was founded. In these paintings we find the same chromatic range, plain blocks of green, burgundy, and yellow, and others with imitations of marble and alabaster (Desbat & Caparros, 2007).

Stylistically², and in view of the similarities between the paintings from *Glanum*, dated to 50-30 BC, and those from *Lugdunum*, dated to 43 BC, the paintings from *Bilbilis* are preliminarily taken to fall within this chronological framework, pending the archaeometric results presented in this study.

Domus 1 and the Decoration of the Exedra (H.7)

Domus 1, with its Italic layout and orthogonal appearance, had three entrances, one of which led directly to the main floor with a porticoed courtyard (H.2) through the *vestibulum* (H.1). Around it we have identified

 $^{^{2}}$ In this pictorial set as well as in the following ones, some parallels will be cited to justify the stylistic study and thus endorse the chronology.

various rooms, such as the *cella ostiaria* (H.3), a *triclinum* (H.5) that is quite irregular in its layout, the *tablinum* (H.4) and a *cubiculum* (H.6). Room H.7 was initially also interpreted as a *cubiculum*, but the results obtained from the study of the decorative fragments, added to the fact that the wall separating the room from the porticoed courtyard was not found at the time of excavation, have established the hypothesis that in fact it is an exedra. The house is completed by a set of taverns (T. 10-13) on the ground floor, which were later unified to form a single establishment, possibly a *popina*. The most noteworthy aspect of this *domus* is the alteration it underwent for the installation of a *balneum* (H.8), an occurrence that García-Entero (2005) dates to the change of era. This was a time that was used to renovate, at least decoratively, most of the house (Martín-Bueno & Sáenz Preciado, 2002; Lloris, 2003; Uribe Agudo, 2004, 2009, 2015; Martín-Bueno, Sáenz Preciado & Sevilla Conde, 2007; Guiral Pelegrín & Íniguez Berrozpe, 2012; Íniguez Berrozpe, Guiral Pelegrín, Sáenz Preciado, & Martín-Bueno, 2020) (Figure 4).



Figure 4. Plan of Domus 1 (Insula I) (Uribe Agudo, 2015)

The pictorial fragments to which we refer (Figure 5), found in the taverns (T.12 and T.13), possibly decorated room H.7 and were thrown to the lower level, perhaps by individuals who lived among the ruins of *Bilbilis* when the city had already been abandoned. This was an action that undoubtedly had the purpose of searching for and taking advantage of the building material of the house (Sáenz Preciado, Martín-Bueno, & García Francés, 2019). The complex was found in a very fragmentary state, with only part of the plinth remaining. After the process of restoration, it was found that this area of the wall would have been decorated with *velaria*, as in the *tablinum* (11) of the House of the Lararium, painted in beige on a black background. The passage to the middle area is through yellow compartments framed on the inside by bichrome fillets and separated from each other by red bands.

Two cornices (type 4 and 14 of the total of 52 types documented in *Domus* 1) with a long horizontal band and projecting listel characteristic of the mouldings that accompany the paintings of the First and Second Styles (Riemenschneider, 1986: Figures. I-XXV), and the fragments of six columns with polygonal shafts made of stucco (Íñiguez Berrozpe et al., 2020), are also related to this group and therefore to the room in question.



Figure 5. Decoration of the Possible Exedra (H.7) of Domus 1

The House of the Lararium

The House of the Lararium is located in the central area of the city, and although it was presumably divided into several floors, only the main floor has survived. It has a typical Italic layout, arranged around a large testudinate *atrium* (16) to which the rest of the rooms opened: the *tablinum* (11), *triclinium* (4) and two *cubicula* (1 and 12). The most significant room is the one identified as the *sacrarium* (13), inside which the remains of a stucco lararium were found (Íñiguez Berrozpe, 2016). The living structure is flanked by service areas: on the eastern side, a storage area, and on the western side, a space interpreted as a *torcularium* (20), used for winemaking. The structure has two construction phases, the first dating from the second half of the first century BC and the second from the Flavian period, when the aforementioned *sacrarium* and the rooms for artisanal use related to the dwelling were built. The building was abandoned in the second century AD (Sáenz Preciado et al., 2018). All the rooms in the dwelling area were painted, documenting a wide compositional and ornamental repertoire from the Second, Third and Fourth Styles, which corresponds to the evolution of the structure (Figure 6).



Figure 6. Plan of the House of the Lararium (Uribe Agudo, 2015)

The Decoration of the Tablinum (11)

The room was paved with a white terrazzo floor, as was the atrium, and the separation was marked by a line of red tesserae. The pictorial decoration is partially preserved in situ on the eastern wall; the paintings on the northern and western walls were found collapsed on the paving.

The decoration of the north wall (Figure 7) is articulated by a black plinth, decorated with curtains hanging from loops located under the separation bands of the middle zone, from which golden ribbons emerge that are brought together in the centre by a trapezoid-headed nail. The middle zone consists of five panels—green, blue, purple, blue and green—framed on the inside by black and white fillets that attempt to emulate the illumination by creating the relief characteristic of orthostats. These panels are separated from each other by wide black bands, decorated with thin stems ornamented with miniaturist motifs. In the two central bands, the stems clearly imitate a thyrsus, and five bifolia are inserted along it. In the side bands the decoration is more complex, with two opposing stems separated by a star-shaped motif; both are decorated with bifolia and rhomboid motifs and end with a quadripetal flower surrounded by eight dots. At the top, rectangular compartments alternate with square compartments on the blue ones, and a green compartment on the central purple panel. The black squares are decorated with a quadripetal flower bordered by four bifolia. The rectangles, of which only the green and purple have survived, are decorated differently: in the former, two opposing stems are separated by a quadrupedal flower and bounded at the ends by star-shaped motifs; in the purple compartment, the opposing stems are separated by a star-shaped flower.



Figure 7. Decoration of the N Wall of the Tablinum (11)

Only three panels have survived from the western wall, which shows the same development and composition. Behind this middle zone is the upper zone, with a white background and no decoration (Figure 8). This area ends with a stucco cornice with a long listel in its middle part. This is characteristic of the Republican period, as explained in the description of the cornices of *Domus* 1.

In the second half of the first century AD, part of the eastern wall was altered during the construction of the *sacrarium*. This renovation led to the production of new paintings that imitated the previous ones, although the painters had already forgotten the function of the bichrome of the interior framing fillets and painted them white (Guiral Pelegrín et al., 2018; Guiral Pelegrín, Iñiguez Berrozpe, Sáenz Preciado, & Martín-Bueno, 2020).



Figure 8. Decoration of the W Wall of the Tablinum (11)

The compositional structure is among the simplest documented in Roman painting, with an alternation of wide panels and separating bands decorated with very simple plant motifs of a marked miniaturist nature. The upper compartments are clearly derived from the rigging with marble imitations, characteristic of the paintings of the First and Second Styles, as analysed in the *cubiculum* of *Domus* 2. The miniaturist ornamentation of these compartments, very similar to that of the bands between the middle panels, also confirms that this is the last phase of the Second Style, as they are closely related to those decorating pilasters, bands or upper compartments

of other paintings from Rome and Campania in this period. Among other items, we might cite the pilasters in cubicle 7 of the House of Fabius Rufus (VI Ins. Occ. 40) in Pompeii. Similarly, in various rooms of the Villa della Farnesina there is also a series of plant friezes that bear certain similarities to those under analysis (Mariette & Bragantini, 1982).

Whatever the case, the most interesting area from a decorative point of view is the plinth, as this has very similar draperies to those in room H.7 in *Domus* 1.

The (Possible) Decoration of the Cubiculum (12)

In the space (20) identified as a *torcularium*, several pictorial assemblages were found as part of its fill, including the one we present here, which is currently under study.

We have fragments from all four walls of the room, including the one where the entrance door was located. By piecing the fragments together like a jigsaw puzzle, we were able to determine the total width of one of them, which would have been 2.74 m, coinciding exactly with the measurement of the east-facing wall of the *cubiculum* (12) of this *Domus*. It is thus very likely that this set originally decorated this room and was later used as rubble material for work on the *torcularium* (20).

In general, the ensemble would have a black plinth and, on the side walls of the room, a middle area made up of white, green, and red panels, some of which were decorated with theatrical masks suspended in the manner of an *oscillum*. The upper area would be the most ornate. This would also be divided by panels in the same colours as the middle area and decorated on the inside with Egyptian motifs and kraters (on a white background), fictitious architecture (on a red background), and hanging *infuelae* accompanied by plant motifs (on a green background). This upper area also features interpanels with a black or blue background decorated with the beginning of a metal candelabrum, crowned by a caryatid or a krater depending on the model, which, crossing the middle area and separating the different middle panels, rests on its base at the beginning of the plinth (Figure 9).

There are also painted columns with Egyptian capitals which, judging by their position on the wall and their development from the highest part of the wall to the beginning of the plinth, seem to articulate not only the decoration but also the room itself. We have explained the same phenomenon for the *cubiculum* of *Domus* 2.



Figure 9. Decoration of the Upper Area of the Cubiculum (12)? Found in the Torcularium (20)

The wall we consider to be the one at the back of the room would have the same plinth, but in this case the middle section has two white panels flanking a central aedicule with a red background and limited by slender columns with Egyptian capitals that go beyond the middle section and reach the upper one. Inside, there are two small, standing figures, one male and one female, identified as the matron and the *pater familias*, within a double fillet perhaps in the form of a frame. The upper area is also divided into three panels: a burgundy-red one decorated with fine architecture, jugs and small figures, a green one decorated with the aforementioned suspended *infulae*and, in between, a white one with the imitation of a *pinax* on which is painted the portrait we have interpreted as representing their young daughter.

In addition to presenting the same chromatic palette as those already described, this set has the characteristic bichrome fillets of the Second Style and its own Egyptian-style decoration, which became popular, above all, from the last quarter of the first century BC, when the candelabra characteristic of the following style also began to appear (Barbet, 1985). However, we have sought to support this hypothesis with the analyses presented below.

In summary, on the basis of the stylistic study alone, we have three sets—the one from the exedra (H.7) of *Domus* 1, and the sets from the *tablinum* (11) and the *cubiculum* (12) (?) of the House of the Lararium—dated to the last quarter of the first century BC and thus the last years of the Second Style, as well as a further one also from this stylistic period but from a slightly earlier time, around 40 BC, from the *cubiculum* (H.14) of *Domus* 2.

The archaeometric analyses carried out on the pigments from the exedra (H. 7) of *Domus* 1 and from the *tablinum* (11) of the House of the Lararium confirmed that they were made by the same workshop (Cerrato et al., 2021). The stylistic similarity, but also the visible technical similarity, made it necessary to extend the study to include the set that possibly decorated the *cubiculum* (12) of the House of the Lararium. Finally, given the chronological proximity of these three sets and the one from the *cubiculum* (H.14) of *Domus* 2, as well as their similarity in terms of the chromatic palette used, we decided to add the latter to the analysis.

METHODOLOGY

Sampling Protocol

As already stated in our previous study (Cerrato et al., 2021), there is a series of maxims that must be followed in venturing an analysis that, as in the present case, aims to answer a series of questions in order to reconstruct a historical reality. First, the researcher must choose assemblages belonging to the same chronological period and to the same type of dwelling. It is well known that Roman mural painting served to create a hierarchy of rooms; i.e. the same workshop could work in several houses in the same city or in several rooms in the same house but not use the same colors or even the same composition for the same pigment, since the compositional scheme, the iconography, and of course the selection of colours clearly depended on the representativeness of the dwelling (Guiral Pelegrín, 2014). In our case, all the decorations under analysis correspond to rooms either for representation (exedra and *tablinum*) or for receiving guests but in a more restricted way (cubicles), all of them belonging to two of the most important dwellings in the city.

Another of the premises that must be respected when taking samples, especially in comparing decorations that we suspect were made by the same workshop, is to choose fragments whose position is known within the painted wall. In this respect, it is also important to know whether they decorate large surfaces or whether they are restricted to small decorative motifs, a factor particularly important for high-cost colours. Analysis of the pigments used to decorate large surfaces may reveal the use of other, base colours to reduce the cost of particularly expensive ones, or this practice may be used for technical or aesthetic reasons, for example, to give a particular shade or shine to the final result. The colours used for small decorative motifs will always be placed on top of other base colours, as these ornaments will have been painted last. Moreover, the sampling of the latter can determine whether there was a change of technique for their application, as large surfaces were usually applied in fresco, whereas small decorative motifs, being laid out when the surface was already dry, could also have been done with other techniques such as tempera.

In our case, after a visual analysis revealing that in several assemblages of presumably similar chronology the same background colours were repeated for some of the large surfaces (plinth/middle zone and/or upper zone), we selected a series of fragments of each pigment to determine whether they did indeed have the same composition. We also selected a series of samples with decorative motifs to determine whether, as mentioned above, there was a change in technique.

For the petrographic analyses, samples were chosen that preserved all the layers of mortar. It should be remembered that petrographic analyses had not been carried out on any of the four assemblages, but archaeometric pigment analyses had been carried out on the assemblages from the *tablinum* (11) and the exedra (H.7). Accordingly, the colours already analysed in the previous study are not present in Table 1, which is laid out below.³ However, neither of these two sets has decorative elements that could have been produced in tempera, unlike those from *cubiculum* H.14 and *cubiculum* 12. Finally, although there are more colours in some of the sets, we have only taken samples of those that can be compared, i.e. those that were repeated on the large surfaces of some of the other sets:

³ The analyses were performed by the same laboratory that carried out the analyses for the present study. In any case, we will return to the results obtained for comparison.

Acronym	Source	Type of sample	
PIG-LAR-H20-1	House of the Lararium, <i>Torcularium</i> (20)*.	White pigment	
PIG-LAR-H20-2	House of the Lararium, <i>Torcularium</i> (20)*.	Green pigment	
PIG-LAR-H20-3	House of the Lararium, <i>Torcularium</i> (20)*.	Burgundy-red pigment	
PIG-LAR-H20-4	House of the Lararium, <i>Torcularium</i> (20)*.	White pigment with an orange undercoat	
PIG-LAR-H20-5	House of the Lararium, <i>Torcularium</i> (20)*.	Decorative element	
PIG-DOM2-14-1	Domus 2 Cubiculum (H.14)	Yellow pigment	
PIG-DOM2-14-2	Domus 2 Cubiculum (H.14)	Green pigment	
PIG-DOM2-14-3	Domus 2 Cubiculum (H.14)	Burgundy-red pigment	
PIG-DOM2-14-4	Domus 2 Cubiculum (H.14)	Decorative element	
MOR-DOM1-H7	Domus 1 Exedra (H.7)	Mortar	
MOR-LAR-H20	House of the Lararium, <i>Torcularium</i> (20)*.	Mortar	
MOR-LAR-TAB	House of the Lararium, <i>Tablinum</i> (11)	Mortar	
MOR-DOM2-14	Domus 2 Cubiculum (H.14)	Mortar	

Table 1. Samples Taken from the Second Style Assemblages for Analysis of Mortars, Decorative Elements, and

* Possibly belonging to the *cubiculum* (12), but found in the *torcularium* (20), so we refer to it by this provenance.

Analytical Techniques for Pigments

The fragments were initially examined under an optical microscope to distinguish layers, examine their microscopic properties, and select appropriate areas for spectroscopic analysis. Micro-Raman spectroscopy (μ -Raman) was used here to elucidate the chemical nature of the pigments. Also, ultraviolet-visible (UV-Vis) and Fourier transform-infrared (FT-IR) spectroscopies allowed us to determine the pictorial technique used by identifying the residues after methanol extraction.

Raman Spectroscopy

Raman spectra of the specimens were recorded using a Renishaw inVia Raman microscope, which was equipped with a Leica microscope fitted with multiple lenses, also used for optical microscopy observations. Additionally, the setup included monochromators, filters, and a CCD detector. Calibration was performed using a silicon standard sample as a reference (520 cm⁻¹). Spectra were generated by exciting the samples with green laser light (532 nm) within the wavenumber range of 140-1700 cm⁻¹. The laser had a maximum output power of 100 mW at the source. To prevent thermal decomposition, laser powers between 5 and 0.2 mW at the source were typically employed. The acquisition time and number of accumulations per spectrum varied according to spectral acquisition conditions, which were always selected to maximize the signal-to-noise ratio. All spectral processing tasks, including baseline correction and smoothing, were conducted using Renishaw's Wire 3.4 software. Spectrum assignment involved a comparison with descriptions in databases, followed by a precise assignment of different Raman bands by comparing them with spectra described in the literature.

Binder Extraction and Analysis

To identify the possible organic matter used to make the tempera paints on the decorative elements of fragments PIG-LAR-H2O-5 and PIG-DOM2-14-4, first a transesterification process was carried out, followed by GC-MS analysis. This is the procedure usually followed in the study of fats in archaeological materials and works of art. In all cases, treatment of the sample prior to GC-MS analysis requires hydrolysis followed by derivatization of the fatty acids to increase their volatility, in order to convert them into methyl esters (FAMEs). To this end, we followed the method described by Manzano, Rodriguez-Simón, Navas, Checa-Moreno, Romero-Gámez, and

Capitan-Vallvey (2011). About 15 mg of samples were taken from the areas of the decorative elements and placed in a microvial. They were then treated with 15 μ L of a 0.2 M methanolic solution of m-(trifluoromethyl) phenyltrimethylammonium hydroxide, TFTMAH, and 200 μ L of toluene, to prepare the FAMEs by transesterification of the triglycerides present. The mixture was sonicated for 30 minutes and then centrifuged at 3000 rpm for 5 minutes. The supernatant liquid was analysed by GC-MS.

To identify the presence of protein residues, the procedure described by Casoli and Santoro (2012) was followed. In 10 mL of methanol 10 mg of sample were suspended. Then, 100 µg of heptadecanoic acid, 100 µg of norleucine, and 10 µg of norvaline were added. After complete evaporation of the methanol, the residues were dissolved in 6 N hydrochloric acid (2 mL) and hydrolysed in a screw-capped vial for five hours at 100 °C under nitrogen atmosphere. After complete evaporation, the hydrolysed residues were esterified using 3 ml of 2 N HCl in isopropanol at 90 °C for one hour. After cooling, the solvent was evaporated under reduced pressure, and the residue was dissolved in 0.2 ml dichloromethane and derivatized with 0.2 mL trifluoroacetic anhydride at 60 °C for one hour. After cooling, the solvent was evaporated again under reduced pressure, and the paint sample residue was dissolved in 0.2 ml dichloromethane for gas chromatographic analysis.

Finally, a study by ultraviolet-visible spectroscopy (UV-Vis) and Fourier transform infrared spectroscopy (FT-IR) was also carried out. Samples scraped from the paint layer (10-15 mg) were analysed in KBr pellets by FT-IR spectroscopy. The extraction protocol was as follows: 10-15 mg of powdered sample scraped from the paint layer were placed in a glass flask containing 10 mL of methanol and sonicated for four hours. The methanol was then separated from the solid by filtration, and this methanolic extract was analysed by UV-Vis spectroscopy. In cases where this extract yielded a UV-Vis spectrum compatible with the presence of organic matter, the methanol was evaporated, and the resulting residue was analysed by FT-IR spectroscopy in the form of KBr pellets. FT-IR spectra were recorded over the wavenumber range 400-4000 cm⁻¹ on a FT-MIR Nicolet Magna IR 500 spectrophotometer. UV-Vis spectroscopy analysis was performed using a Suzi 455 instrument equipped with a tungsten lamp and a silicon photodiode detector in the range 190-400 nm.

Analytical Techniques for Mortars: Petrography

The analysis of the mortars was approached in accordance with the principles of the "petroarchaeology of lime mortars". So-called "petroarchaeological" studies consider ancient lime mortars to be the products of lore and incorporate both archaeological data and the results of the optical petrographic analysis of the materials. In the early 2000s a first synthesis was presented that specifically addressed this question in mainly Gallo-Roman wall paintings (Coutelas, 2003, 2007). Since then, numerous results have made it possible to reconstruct not only a chain of operations for lime mortar but, more broadly, a technical sequence that identifies the parameters and relationships that influence the final composition of the material or render (Coutelas, 2011).

The method developed by Elsen (2006), Pavia and Caro (2008), Coutelas et al. (2009), and Pecchioni, Fratini, and Cantisani (2014) starts with observations made with the naked eye and a diamond magnifying glass (approximately x10 magnification). The samples are then prepared in thin slices. The fragments are impregnated with resin, then cut with small saws, glued to a glass slide, then thinned to 30 µm and polished. They can then be observed under an optical microscope, specifically a transmission polarizing microscope with a magnification of up to about x200.

RESULTS AND DISCUSSION

Study of Pigments

Green

The fragments PIG-DOM2-14-2 and PIG-LAR-H2O-2 show this colour on their surface. Since ancient times, one of the most common raw materials used to obtain green paints has been so-called green earth, mainly due to its availability and stability. In the past, the pigments were obtained from mining. The most famous deposits of green earth were found near Verona, Italy, as well as in Tyrol, Bohemia, Saxony, Poland, Hungary, France, Cyprus, and England (Rafalska-Lasocha, Kaszowska, Lasocha, & Dziembaj, 2010). Green earths have always been considered to consist mainly of two types of minerals from the mica family: celadonite and glauconite. The two minerals differ in their composition, morphology, and crystalline order (Rafalska-Lasocha et al., 2010; Tóth et al., 2010). The chemical composition of celadonite is approximately K[(Al,Fe³⁺),(Fe²⁺,Mg)](AlSi₃,Si₄)O₁₀(OH)₂, with a low aluminium content and a very small exchange of Al³⁺ for Si⁴⁺ in the tetrahedral layer. Common impurities are crystals of pyrite, haematite, goethite, and other iron oxides. The chemical composition of glauconite, (K,Na),(Fe³⁺,Al,Mg)₂(Si,Al)₄O₁₀(OH)₂, is similar to that of celadonite, but differs in the aluminium content, which in glauconite is high due to partial substitution of Al³⁺ for Si⁴⁺ in the tetrahedrally coordinated layer. Impurities of

calcite, pyrite and gypsum are frequent in glauconite (Grisson, 1986). Apart from these differences in composition, celadonite is characterized by a bluish-green colour, due to the presence of Fe cations²⁺, whereas glauconite has a yellowish colour due to the presence of iron only in the +3 oxidation state (Moretto, Orsega, & Mazzocchin, 2011). Celadonite occurs as a relatively pure substance that, in small quantities, is found in vesicular cavities or fractures in volcanic rocks. Glauconite is a mineral of lower purity but is more abundant and more widely distributed geographically. Optical microscopy of the two fragments shows the presence of blue particles along with the green ones 4(Figure 10).



Figure 10. Optical Microphotographs of Fragments PIG-DOM2-14-2 (a) and PIG-LAR-H20-2 (b)

Their chemical similarity makes it difficult to differentiate between these two minerals. In recent years, the most widely used technique for the unequivocal identification of each of them has been Raman spectroscopy. Figure 11 shows the Raman spectra obtained in the green-coloured area of these two fragments. There is a clear difference between them, which is none other than the presence of a very intense signal at 1008 cm⁻¹. Together with the signals at 1134, 701, 494 and 415 cm⁻¹, this certifies the presence of gypsum, CaSO₄·2H₂O. The two spectra present a signal at 1086 cm⁻¹, indicative of calcite, CaCO₃. Also in both, common bands are observed around 275, 320, 395, 415, 545 and 701 cm⁻¹, which can be assigned to the green earth pigment. To differentiate between glauconite and celadonite, several spectral zones must be considered. The zone between 140-300 cm⁻¹ is where the internal vibrations of the MO₆ octahedra appear, where M is the interlamellar metal cation. In the 300-800 cm⁻¹ region, the bands that appear are due to the vibrations of the SiO₄ tetrahedra, this region being where glauconite and celadonite can be differentiated, as both minerals present a band below 600 cm⁻¹, assignable to the stress vibrations of the SiO₄ units, which normally appear above 590 cm⁻¹ in glauconite whereas in celadonite they appear at a lower wavenumber, around 545 cm⁻¹ (Perez-Rodriguez, Jimenez de Haro, Siguenza, Martinez-Blanes, 2015; Wang, Alsmeyer, & McCreery, 1990). In our spectra this band appears at 544 cm⁻¹ in PIG-DOM2-14-2 and at 547 cm⁻¹ in PIG-LAR-H2O-2, so the green earth used to obtain this green colour was celadonite. Resonance phenomena in the case of celadonite can have a significant influence on the spectrum. As described by Ospitali, Bersani, Di Lonardo, and Lottici (2008), laser excitation with argon ions causes the bands at 459 and 960 cm⁻¹ (which in our spectra appear at 457-458 and 955-956 cm⁻¹) to be more intense, whereas, higher excitation wavelengths, the band at 394 cm⁻¹ (in our case at 394 and 397 cm⁻¹) is more intense than the previous ones. The green laser used in this work is of a slightly longer wavelength (532 nm) than the one used by Ospitali et al. (2008) (514 nm), and the bands mentioned appear with a medium-low intensity and there is practically no variation in the wavenumber of each of the signals. These authors also confirm that when the wavelength increases, there is a decrease in the wavenumbers of the band that appears above 545 cm⁻¹ (for example, when changing the excitation from 514 to 780 nm, the change is from 548 to 538 cm⁻¹), perhaps due to changes in intensity in an unresolved doublet.

In our previous study (Cerrato et al., 2021), the green sample from the *tablinum* (11)—the other assemblage that also presents this colour in one of the panels (sample named LAR-04)—pointed to the use of glauconite for the manufacture of the green. In view of this, these analyses were repeated, and this time they did indeed indicate the use of celadonite also in the *tablinum* (11).⁵ The green colour from glauconite is not usually used to cover large surfaces, but rather as separating bands and small ornaments. The reason is to be found in its texture, which is difficult to apply and has problems relating to uniformity of adherence. Moreover, the use of green pigment for

⁵ The sample was also analysed by the laboratory of Jorge Villar at the University of Burgos, who noted the use of celadonite for the green of the *tablinum* (11), prompting a repeat analysis. Jorge Villar's study will be the subject of a forthcoming publication focusing on the green and blue colors from the *Bilbilis* site.

large surfaces was not common (Santoro, 2007). Groetembril and Sanyova(2021) have noted the use of green on large surfaces in Gaul, but the green used in these cases comes from celadonite. Presumably, the explanation for this is the obvious technical advantage—if we compare its properties with those of glauconite—but it has also been found that it is always linked to elite contexts, given its rarity and the relative difficulty of obtaining it. Bearing in mind the type of rooms from which the present samples come, this hypothesis could be supported by our assemblages.



Figure 11. Raman Spectra of Fragments PIG-DOM2-14-2 (a) and PIG-LAR-H20-2 (b)

We also carried out a Raman spectroscopic study of the blue particles observed in the two fragments. The spectra obtained (Figure 12 shows that of the fragment PIG-DOM2-14-2) shows an intense band at 428 cm⁻¹, together with another intense band at 1085 cm⁻¹. The presence of these two bands, together with others of lower intensity at 987, 787, 569 and 475 cm⁻¹, suggests the use of Egyptian blue (Pagès-Camagna, Colinart, & Coupry, 1999), which was also present in the sample from the *tablinum* (11) (Cerrato et al., 2021).



Figure 12. Raman Spectrum of the Blue Particles of Fragment PIG-DOM2-14-2

Yellow

Fragment PIG-DOM2-14-1 is yellow in colour. Yellow is a very common colour in Roman wall paintings. In the overwhelming majority of cases, this colour was obtained from the pigment called yellow ochre, which mainly consists of goethite, an iron oxyhydroxide with the formula α-FeOOH (Hradil, Grygar, Hradilová, & Bezdička, 2003). According to Mayer (1990), yellow ochre is a clay with different yellowish shades and has been used as a pigment since prehistoric times. Raman spectroscopy indisputably reveals the use of this pigment in a painting (Legodi & de Waal, 2007). The Raman spectrum of fragment PIG-DOM2-14-1 is shown in Figure 13. According to the literature, goethite presents a Raman spectrum with bands at 243, 299, 385, 479, 550, 685 and 993 cm⁻¹, whose exact position varies by ± 5 cm⁻¹ (De Faria, Venâncio Silva, & de Oliveira, 1997), although in many cases not all these bands can be discerned. In the spectrum of Figure 13, the bands at 299, 385 and 553 cm⁻¹ clearly indicate that the yellow pigment used was goethite-based. In addition, the spectrum shows a very intense signal at 463 cm⁻ ¹, which, together with the signal that appears at 206 cm⁻¹, suggests the presence of silica (quartz, α -SiO₂) (Liang, Miranda, & Scandolo, 2006), as also occurred in the fragment already analysed (Cerrato et al., 2021) from the exedra (H.7) (sample named DOM-03 in that study). Furthermore, we can also certify the presence of calcium carbonate (calcite, CaCO₃) (signals at 1085 and 281 cm⁻¹) (Sun, Wu, Cheng, Zhang, & Frost, 2004). Silica occurs naturally mixed with goethite, so its presence could be explained by this (Froment, Tournié, & Colomban, 2008), although the detection of calcite could also indicate that these signals come from the mortar on which the priming was carried out. Another possibility is that the calcite is present due to the application of the yellow ochre using a fresco technique.



Figure 13. Raman Spectrum of Fragment PIG-DOM2-14-1

White

The Raman spectra of the white colour of fragments PIG-LAR-H2O-1 and PIG-LAR-H2O-4 are shown in Figure 14. From these spectra we established that this white colour is due to calcium carbonate (CaCO₃) in its calcite phase. Both spectra are dominated by an intense, sharp band centred at 1085 cm⁻¹, with other bands of lower intensity at 711, 279 and 153 cm⁻¹ that can be unequivocally assigned to calcite (Sun et al., 2004). What may be more complex to establish is which pigment was actually used to obtain this white colour. Quicklime (calcium oxide, CaO), slaked lime [calcium hydroxide, Ca(OH)₂] or limestone (calcium carbonate, CaCO₃) have been used as white pigments since ancient times. However, it seems plausible that, as the surfaces painted in this colour were large, the painting technique used would have been fresco, which generally involves the use of slaked lime. In this way, calcium hydroxide is transformed into calcium carbonate by the action of atmospheric carbon dioxide.



Figure 14. Raman Spectra of Fragments PIG-LAR-H2O-1 (a) and PIG-LAR-H2O-4 (b)

Red

Red appears in fragments PIG-LAR-H2O-3 and PIG-DOM2-14-3. Under the optical microscope of the Raman spectrometer, both fragments reveal this red colour mixed with black particles. The Raman spectroscopic study was carried out on both the red and the black particles. The Raman spectra obtained for the red areas are similar, with the same number of bands, the only difference being the resolution and very slight variations in the wavenumbers (Figure 15). Both spectra are dominated by an intense band around 1330 cm⁻¹. The presence of this band, together with others of lower intensity at Raman shifts of approximately 226, 246, 293, 410, 507, 613 and 667 cm⁻¹, indicates that this red colour was obtained from haematite (α -Fe₂O₃) (De Faria et al., 1997)]. In addition, in both spectra there is a signal at 1085 cm⁻¹ of calcium carbonate (calcite), as mentioned above, making a fresco technique plausible for the application of these red pigments. For the black particles, the Raman spectrum obtained is shown in Figure 16. It is noteworthy that, together with the bands corresponding to haematite and calcium carbonate (whose wavenumber values are similar to those described above), a low intensity band is also observed at 1008 cm⁻¹, assignable to calcium sulphate. However, the highest intensity bands in the spectrum are those that appear at 1324 and 1597 cm⁻¹, which can be assigned to carbon in the graphite phase (Coccato, Jehlicka, Moens, & Vandenabeele, 2015). The former overlaps with the most intense part of the haematite spectrum appearing at 1330 cm⁻¹. Therefore, these results indicate that this red colour, whose hue is burgundy, has been achieved by a mixture of haematite and charcoal. The same results were observed for the pigment of the same shade from the *tablinum* (11) studied previously (Cerrato et al., 2021, sample named LAR-05).



Figure 15. Raman Spectra of the Red Pigmented Area of Fragments PIG-LAR-H2O-3 (a) and PIG-DOM2-14-3 (b)



Figure 16. Raman Spectrum of the Black Particles of Fragment PIG-DOM2-14-3

Orange

In fragment PIG-LAR-H2O-4 there is an orange coloration covered by a white layer, which, as mentioned in "White" section, corresponds to calcium carbonate. The orange pigmentation zone yields a Raman spectrum (Figure 17) with a series of signals (bands at 549, 480, 391, 312 and 225 cm⁻¹) characteristic of *minium*, also known as red lead (Pb_3O_4), as we have already seen in the sample from the *tablinum* (11) (Cerrato et al., 2021, sample named LAR-O3 in that study). In both cases, it does not seem to be a sublayer that extends uniformly across the whole panel, but rather an arrangement in the form of "spots". This is a *unicum* with no parallel in Roman mural painting and whose purpose is not yet known: perhaps it had a technical purpose, such as trying to protect the pictorial layer by acting as an insulator, or perhaps it was more of an aesthetic issue, i.e. giving the

main layer a certain tonality. Curiously, this workshop also used red lead as an undercoat for certain decorative motifs, something we have observed in the ensemble possibly from the *cubiculum* (12).



Figure 17. Raman Spectrum of the Orange Area of Fragment PIG-LAR-H20-4

Study of Binders

After performing the derivatization tests for fats and proteins described in "Binder Extraction and Analysis" section of this work, the chromatographic analyses were found to be negative in all cases, so although we could not completely rule out the presence of these binders, we were unable to detect them. Nevertheless, we did not give up in our search for the presence of organic matter in samples PIG-LAR-H2O-5 and PIG-DOM2-14-4, proceeding to perform a direct extraction using methanol in accordance with the procedure described in the "Methodology" section. Once the sonication was performed and the methanolic extract was separated, this was subjected to UV-Vis spectroscopy analysis. The spectra obtained, shown in Figure 18, show an intense absorption at 202 nm, together with a shoulder above 220-240 nm, indicating the presence of organic matter dissolved in the methanol.



Figure 18. UV-Vis Spectra of the Methanolic Extract of the Decorative Elements from Fragments PIG-LAR-H20-5 and PIG-DOM2-14-4

To try to identify the nature of this organic matter, the methanol was evaporated, and the remaining residue was analysed by FT-IR spectroscopy using KBr pellets. Thus, methanol was evaporated under reduced pressure, and 50 mg of potassium bromide was added to the remaining residue to make a pellet which was subsequently analysed by FT-IR spectroscopy. The spectra for the residues after the removal of methanol for fragments PIG-LAR-H20-5 and PIG-DOM2-14-4 are shown in Figure 19. The presence of relatively intense bands in the region below 3000 cm⁻¹ reflects the presence of organic matter. By contrast, the absence of a signal above 1740 cm⁻¹, typical of the ester bonds of fats, allows us to rule out their presence. In the 3100-3600 region, a broad and intense band appears, and the two bands that normally appear as shoulders in this region due to the N-H tensions

of the peptide bonds in proteins are not observed. We can thus also rule out the presence of this type of component.

However, both UV-Vis and FT-IR spectra indicate the presence of organic matter. A third possibility is the presence of carboxylates from the saponification of fat that may have been used originally. This saponification, which occurs in alkaline media, involves the cleavage of the ester bonds of the fat releasing glycerol and the corresponding salts of the fatty acids. The FT-IR spectra of these salts are characterized by the presence of relatively intense bands below 3000 cm⁻¹, assignable to stresses in the C-H bonds of the salt's hydrocarbon chains, together with bands of lower intensity in the 1400-1600 cm⁻¹ region, originating from the C=O stresses of the carboxylate groups, the C-C stresses, and the deformations of the C-H bonds of the hydrocarbon chains. Likewise, in the 1000-1200 cm⁻¹ zone, stresses of the C-O bonds of the carboxylate groups appear. A fat could thus plausibly have been used as a binder in the decorative elements of fragments PIG-LAR-H20-5 and PIG-DOM2-14-4. Whatever the case, the fact that they show a similar spectrum could mean that the binder used in the two cases was of the same nature, and we would therefore be witnessing the same handmade "recipe" in two different paints.



Figure 19. FT-IR Spectra of the Residue Samples from the Methanol Extraction of the Decorative Elements from Fragments PIG-LAR-H20-5 and PIG-DOM2-14-4

Study of Mortars or Substrates⁶

Normally, the study of Roman mural painting is associated with the study of the mortar that covers the wall and supports the painting. In general, as Vitruvius established (On Architecture, VII 3, 6), Roman mortar consisted of lime and sand. In his treatise on the subject, Vitruvius described how obtaining a high-quality mortar involved mixing one part lime and three parts sand, or two parts lime and five parts sand, depending on the quality of the latter. To make mortar, the process began with the firing of carbonate rocks or other material that served as a source of calcium carbonate, such as marble or mollusc shells, in a kiln at a temperature of over 800 °C. The thermal decomposition of the calcium carbonate contained in these materials transformed it into carbon dioxide gas and calcium oxide. The latter remained as a white residue after cooling, called quicklime. When fresh, quicklime reacts vigorously with water to form slaked lime. If an excess of water is added, we obtain a paste with partially dissolved calcium hydroxide. When exposed to air, in a process known as setting, the paste dries out and absorbs atmospheric carbon dioxide, transforming it into a hard calcium carbonate crust, which cracks very easily. To prevent this cracking, aggregate, usually silica-rich sand, was added to the lime paste. During the setting process, the sand formed a rigid framework. In the hollows of this framework, the lime particles were located, which, on contracting, provided additional compaction to the mortar, but without cracking. When the mortar dried, the process of carbonation and hardening began by reaction with atmospheric carbon dioxide.

Identification of Raw Materials

It is never easy to identify which rock may have been used as limestone. However, since the work of Frizot (1975), we know that the limestone used was as pure as possible, which coincides with the precepts of ancient

⁶ The "support" is understood to be all the layers of mortar that make up the painted render. The pigment layer is called the "paint layer" or Cp. The finishing layer, or *intonaco*, is known as layer (a). The following layers, from the surface down, are called "1st preparatory layer (b)", "2nd preparatory layer (c)", etc. (Table 2).

authors such as Cato (De Agricultura. XXXVIII), who recommended the whitest and hardest stones. All recent works confirm the use, at least, of air lime. This is the case here. The mortar matrix always has the appearance of a recrystallized aerial lime, which is very light brown under non-analysed polarized light (LPNA) and slightly birefringent and bluish under polarized and analysed light (LPA) (Figure 20).



Figure 20. Unanalysed Polarized Light Micrographs (LPNA, left) and Analysed Polarized Light Micrographs (LPA, right) of Sample MOR-DOM1-H7. A and B belong to the Finishing Layer (a); C and D belong to the Preparatory Layer (b)

The original limestone could not be identified, as none of the observed nodules consisted of a "badly baked" limestone with potentially recognizable characteristics. The documented limestone remains are often fine and not true nodules. Be this as it may, as has already been proven for other mortars from *Bilbilis*, the material used probably comes from the local Miocene limestones, more specifically from the compact limestone banks that still exist in the area today, in any case ruling out the sandstone, marl, and gypsum formations of the region.

Table 2 and Figure 21 show the stratigraphy of the mortar layers and their composition.

Mortar laver	Thickness (mm)	Matrix (lime)	Lime/aggregate ratio	Aggregates	Grain size
MOR- DOM1-H7 (a)	2	air lime	1:2	3/4 quartz, 1/4 limestone, calcite, schist	100-800 µm
MOR- DOM1-H7 (b)	19	air lime	1:3	3/4 quartz, 1/4 limestone, flint, schist	< 2 mm, mainly 50- 800 μm
MOR-LAR- H20 (a)	5	air lime	1:2 to 1:3	1/2 quartz, 1/2 limestone, calcite	50-800 µm
MOR-LAR- H20 (b)	15	air lime	1:3 to 1:4	3/6 quartz, 2/6 limestone, 1/6 schist	< 3 mm, mainly 50- 800 μm
MOR-LAR- TAB (a)	5.5	air lime	1:3	80% calcite, 10% limestone, 10% quartz	75-200 μm, some 1 mm
MOR-LAR- TAB (b)	10	air lime	1:3	1/2 quartz, 1/4 calcite and limestone, 1/4 schist	50-300 μm,
MOR-LAR- TAB (c)	10	air lime	1:3 to 1:4	3/4 quartz, 1/4 other	75-200 μm or 400-500 μm
MOR-LAR- TAB (d)	8	air lime	1:3	3/4 quartz, 1/4 other	50-150 μm, some 600 μm
MOR- DOM2-14 (a)	0.5	air lime	2:1?	3/4 quartz, 1/4 calcite	About 75 μm
MOR- DOM2-14 (b)	4.5	air lime	1:3	3/4 quartz, 1/4 other	50-400 μm, some 1 mm
MOR- DOM2-14 (c)	14.5	air lime	1:3 to 1:4	3/4 quartz, 1/4 other	100-400 μm, some 1- 2 mm



 Table 2. Composition of the Mortar Layers of each of the Samples Analysed

Figure 21. Stratigraphy and Composition of the Mortar Layers of Each of the Samples

Analysis

The analyses carried out show the two coatings MOR-DOM1-H7 and MOR-LAR-H20 have many similarities. Their total thickness is about 2 cm.⁷ Both consist of two layers of mortar: a thin finishing layer covering a thick

⁷ In other parts of the group found in the *torcularium* (20) and probably belonging to the *cubiculum* (12) of the House of the

preparatory layer. And for both layers predominantly quartz sand is always used, i.e. the local natural sand, without any specific treatment, even for the finishing layer. There are, however, some small differences: the MOR-LAR-H2O sample is richer in aggregate, whereas MOR-DOM1-H7 has a proportionally higher quartz content, which suggests that it is of slightly higher quality. To this we should add the particularity found in the previous study for this sample, which was observed thanks to X-ray diffraction and Raman spectroscopy (Cerrato et al., 2021; sample named DOM-01 in that study): the existence of a very thin layer of gypsum (5 μ m) prior to the pictorial layer. It should be remembered that of the ensemble from which this fragment comes, only the black plinth with *velaria* has survived. The presence of this charcoal-based colour, with the problems it posed for fresco application, is what would explain the use of this layer, at least in this area of the wall, as the plaster sets more quickly and gives greater plasticity.

As we can see in Figure 21, the mortar of sample MOR-DOM2-14 is very similar to the previous ones, especially that of MOR-LAR-H20, the only difference being the addition of a finishing layer with a little quartz enriched with some calcite crystals. This is particularly important as this sample corresponds to the only assemblage that could be of a slightly earlier chronology than the rest, as we have seen in the section on the "Archaeological Context".

In comparison, the MOR-LAR-TAB plaster is much more complex, comprising four layers (Figure 21). Preparatory layers 3 and 4 (Table 2: c & d) are of lime mortar rich in quartz sand, with secondary layers of schist and limestone. These two layers are reminiscent of the two preparatory layers of the MOR-DOM2-14 render. The first preparatory layer (Table 2: b) again has a mortar mainly of quartz sand and lime, but richer in limestone fragments and calcite crystals. Finally, the finishing layer (Table 2: a) is notable for its great thickness (0.5 cm) and abundant aggregate composed almost entirely of calcite crystals. It is therefore a quality render, which has benefited from very special care.

CONCLUSION

The present study has focused on several pictorial ensembles that can be included in the Second Style. This increases the list of known Hispanic decorations of this style, making *Bilbilis*, together with the sites of *Celsa* (Velilla de Ebro, Zaragoza) and *Emporiae* (Ampurias, Gerona), one of the benchmark sites for the study of painting from this period.

As we have seen throughout this article, analyses of the mortars and pigments show that they were made according to the same artisan recipe, so it is plausible that the same workshop of craftsmen made the four decorations. The craftsmen probably came from Italy, given their extraordinary technical knowledge of the support and pigments, although they also had their own recipes. These include the use of an orange pigment as an undercoat in some of the middle panels, as can be seen in the sets from the *tablinum* (11) and the *cubiculum* (12)⁸. Another characteristic feature is the use of charcoal to darken the red, something also found in the two sets mentioned above.

A very interesting aspect is the use of green from celadonite in the middle panels of the assemblages from the *cubiculum* (H.14), the *tablinum* (11), and the *cubiculum* (12). In all cases, moreover, it has been mixed with Egyptian blue. This is an imported pigment that is more adherent than the glauconite pigment, but more difficult to obtain. As S. Groetembril (2021) points out, its use is thus linked to elite contexts, as in our case, given the character of the rooms studied. As noted above, large green surfaces are rare in Roman painting—there are very few examples in Pompeii (Santoro, 2007)—but the use of the pigment was nonetheless constant. This does not, therefore, reflect chronological criteria or regional fashions. In Gaul it was used in sites located on important road axes. The set from Rue des Farges in Lyons, dated to around 30-20 BC like our sets, and where the use of green from celadonite can be seen, shows that this pigment was already present on the trade routes of the first century BC.

All the colours were applied in fresco, using technical solutions for those with poorer adherence. In this context, it should be remembered that a thin layer of plaster was used to help fix the black pigment on the plinth of the exedra ensemble (H.7). In the decorations where decorative motifs were arranged—the assemblages from the *cubiculum* (H.14) and the *torcularium* (20)/*cubiculum* (12)—they were applied in tempera. It is possible that grease was used as a binder, although it has not been possible to identify which one. In any case, the fact that the samples show a similar spectrum could mean that the binder used in the two cases was of the same nature, and we would therefore be witnessing the same handmade "recipe" in two different paintings.

Lararium, the thickness of the mortar has been found to be much greater, exceeding 7 cm. This occurs mainly in the wall that we consider to be the one facing east, which is a load-bearing wall.

⁸ A fragment from *Celsa* with the same technical characteristics has also been analysed, so this workshop may have been itinerant, or at least its technical characteristics travelled.

The petrographic analysis leaves no doubt that the same recipe was used to create the mortar layers of the assemblages from the exedra (H.7), the *cubiculum* (H.14), and the *cubiculum* (12). The composition of these layers also occurs in the mortar from the *tablinum* (11), but this was enriched with two more layers of a different composition. This solution may have been adopted to solve a technical problem.

In summary, we have three decorations—the exedra (H.7), the *cubiculum* (12), and the *tablinum* (11)—whose style dates chronologically to around 30–20 BC. However, examination of the assemblage from the *cubiculum* (H.14) produced a date of around 40 BC. Our analysis of pigments and mortars leads us to believe that in reality they were all made by the same workshop—a workshop that possibly also worked at *Celsa*, as a fragment with an orange undercoat on white pigment was also found at this site—and that its repertoire included "more conservative" compositions along with others of a more avant-garde style.

Whatever the case, we cannot conclude this study without briefly addressing the term "craftsmen's workshop" or *officina*, understood as a group of individuals in charge of pictorial and stucco decorations. Although it is now an accepted concept, it has traditionally given rise to much discussion in the scientific literature (Guiral Pelegrín, 2014)⁹. These debates have mainly focused not only on the term "workshop" itself or on the individual role that each craftsman would have—with analyses carried out mainly on the basis of written sources such as the Edict of Diocletian or archaeological sources such as the Sens Stele—but also on the configuration of the group itself. The complexity of the execution of the decorative work, which required exceptional coordination between the *tectores* who applied the plaster and the *pictores* in charge of applying the background colours to the fresco, as well as of the decorative elements—sometimes using different techniques for the latter, as we have seen—brings to mind perfectly configured organizational structures. However, authors such as Allison (1995) argue that there must have been great mobility among craftsmen, with groups created for a specific job, but with no further links between individuals. Certainly, in Roman mural painting, no two walls are alike, which seems to support the thesis put forward by this author. It should not be forgotten, however, that the choice of the final design for the decoration of a room was up to the client.

None of the walls presented here is the same. Some elements, such as the *velaria* on the plinths of the *tablinum* (11) of the House of the Lararium and the exedra (H.7) of *Domus* 1, do have a similar design. However, it is the technique used in arranging the pigments, preparing the mortars, and laying out the decorative elements that have revealed certain particularities that seem to indicate that the same hands were responsible for the four decorations. Beyond analysing repetitions of iconographic elements whose similarity may simply be due to the transmission of models, an issue on which there is heated debate, archaeometry and petrography thus prove to be essential tools in shedding light on these questions.

AUTHOR CONTRIBUTIONS

L. Íñiguez coordinated the work and was also in charge, together with C. Guiral, of the stylistic study of the pictorial sets. A. Coutelas was in charge of the petrographic study; and D. Cosano and J.R. Ruíz carried out the archaeometric study.

ACKNOWLEDGEMENTS

This work was made possible by the Palarq Project: "Pinturas romanas del II estilo del Municipium Augusta Bilbilis (Calatayud, Zaragoza): estudio arqueométrico de morteros, pigmentos y técnicas pictóricas", as well as grant RYC2021-030958-I, funded by MCIN/AEI/10.13039/501100011033, and the European Union "NextGenerationEU"/PRTR. It was carried out as part of a research project directed by C. Guiral: Tectoria et pigmenta; and Estudio analítico y arqueológico de los pigmentos y morteros de las pinturas del cuadrante NE de Hispania (s. II a.C.-s. VI d.C.) (HAR2017-84732-P). Part of the research was made possible by a stay at the Deutsches Archäologisches Institut in Rome. We would like to thank the directors of the Bilbilis site, Manuel Martín-Bueno and Carlos Sáenz Preciado, for their kindness and willingness to allow the study of these pieces. The authors would also like to acknowledge the use of the Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza. D.C. acknowledges the FEDER funds for the Programa Operativo Fondo Social Europeo (FSE) de Andalucía 2014-2020 (DOC_01376).

⁹ See this publication for a bibliographic compilation on this issue.

REFERENCES

Allison, P. (1995). Painter-workshops" or "decorators' teams". MededRom, 54, 98-109.

Barbet, A. (2007, February). L'évidence d'un atelier de peintres itinérants. In *Villas, maisons, sanctuaires et tombeaux tardo-républicains: Découvertes et relectures récentes. Actes du colloque international de Saint-Romain-en-Gal en l'honneur d'Anna Gallina Zevi (*pp. 8-10). Roma, Italy: Quasar.

Barker, S., & Perna, S. (2018). Imitation alabaster: Varieties and symbolism in Roman painting. In Y. Dubois, & U. Niffeler (Eds.), *Pictores per provincias II-Status quaestionis (Lausanne, del 12 al 16 septiembre 2016), ANTIQUA 55, Veröffentlichung der Archäologie Schweiz, Basel* (pp. 405-412). Retrieved from http://hdl.handle.net/2072/450487

Casoli, A., & Santoro, S. (2012). Organic materials in the wall paintings in Pompei: A case study of Insula del Centenario. *Chemistry Central Journal*, *6*, 1-10.

Cerrato, E. J., Íñiguez, L., Cosano, D., Guiral, C., & Ruiz, J. R. (2021). Multi-analytical identification of a painting workshop at the Roman archaeological site of Bilbilis (Saragossa, Spain). *Journal of Archaeological Science: Reports*, *38*, 103108.

Coccato, A., Jehlicka, J., Moens, L., & Vandenabeele, P. (2015). Raman spectroscopy for the investigation of carbon-based black pigments. *Journal of Raman Spectroscopy*, *46*, 1003-1015.

Coutelas, A. (2003). Pétroarchéologie du mortier de chaux gallo-romain. Essai de reconstitution et d'interprétation des chaînes opératoires: Du matériau au métier antique [Petro-archaeology of Gallo-Roman lime mortar. Attempt to reconstruction and interpretation of the "chaînes opératoires": From material to ancient craftsmanship] (Doctoral dissertation). Available from Portail HAL theses database. (tel-00528508)

Coutelas, A. (2007). Les mortiers de support des peintures murales de Gaule romaine: Première synthèse. *Circulación de temas y sestemas decorativos en la pintura mural antigua*, 505-507.

Coutelas, A. (2011). The selection and use of lime mortars on the building sites of Roman Gaul. *Commentationes Humanarum Litterarum*, *128*, 139-151.

Coutelas, A., Büttner, S., Oberlin, C., Palazzo-Bertholon, B., Prigent, D., & Sumera, F. (2009). *Le mortier de chaux*. Paris, France: Éditions Errance.

De Faria, D. L. A., Venâncio Silva, S., & de Oliveira, M. T. (1997). Raman microspectroscopy of some iron oxides and oxyhydroxides. *Journal of Raman Spectroscopy*, *28*(11), 873-878.

Desbat, A., & Caparros, Th. (2007). Peintures di II^e style à Lugdunum. In B. Perrier (Ed.), *Villas, maisons, sanctuaires et tombeaux tardo-républicains: Découvertes et relectures récentes: Actes du colloque international de Saint-Romain-en-Gal en l'honneur d'Anna Gallina Zevi: Vienne, Saint-Roman-en-Gal, 8-10 février 2007* (pp. 221-233). Roma, Italy: Quasar.

Elsen, J. (2006). Microscopy of historic mortars-A review. Cement and Concrete Research, 36(8), 1416-1424.

Frizot, M. (1975). *Mortiers et enduits peints antiques: Étude technique et archéologique (Vol. 4)*. Retrieved from http://pascal-francis.inist.fr/vibad/index.php?action=getRecordDetail&idt=13035193

Froment, F., Tournié, A., & Colomban, P. (2008). Raman identification of natural red to yellow pigments: Ochre and iron-containing ores. *Journal of Raman Spectroscopy*, *39*(5), 560-568.

García-Entero, V. (2005). *Los "Balnea" domésticos-ámbito rural y urbano-en la Hispania romana* (Vol. 37). Madrid, Spain: Editorial CSIC-CSIC Press.

Grisson, C. A. (1986). Green earth. In R. L. Feller (Ed.), *Artists' pigments: A handbook of their history and characteristics* (pp. 141-167). Washington, DC: National Gallery of Art; London, UK: National Gallery of Art.

Groetembril, S., & Sanyova, J. (2021). Les décors à champ vert en Gaule: État de la recherche et apport des analyses. In *Cavalieri and Tomassini 2021, La peinture murale Antique: méthodes et apports d'une aproche technique* (pp. 161-171). Rome, Italy: Quasar.

Guiral Pelegrín, C. (2014). Painted decoration in Roman Hispania: Craftsmen and workshops. In M. Bustamante, & D. Bernal (Eds.), *Artífices idóneos: Artesanos, talleres y manufacturas en Hispania* (pp. 105-125). Madrid, Spain: Instituto de arqueología de Mérdia.

Guiral Pelegrín, C., & Martín-Bueno, M. A. (1996). *Bilbilis I: Decoración pictórica y estucos ornamentals*. Zaragoza, Spain: Institución "Fernando el Católico".

Guiral Pelegrín, C., Iñiguez Berrozpe, L., Sáenz Preciado, C., & Martín-Bueno, M. (2018). El segundo estilo en la

Casa del Larario de Bilbilis (Zaragoza, España). In *Pictores per provincias II—Status quaestionis. Actes du 13^e Colloque de l'AIPMA* (pp. 685-692). Retrieved from https://www.researchgate.net/publication/327405036_El_segundo_estilo_en_la_Casa_del_Larario_de_Bilbili s_Zaragoza_Espana

Guiral Pelegrín, C., Iñiguez Berrozpe, L., Sáenz Preciado, C., & Martín-Bueno, M. (2020). Un atelier de peintres d'époque tardo-républicaine à Bilbilis (Calatayud, Espagne). In J. Boislève, & F. Monier (Eds.), *Peintures et stucs d'époque romaine. Études toichographologiques, actes du 30^e colloque de l'AFPMA* (pp. 231-244). Bordeaux, France: Ausonius.

Guiral Pelerín, C., & Íñiguez Berrozpe, L. M. (2012). Alta et versicolor Bilbilis. *Salduie: Estudios de prehistoria y arqueología*, (11-12), 275-298.

Hradil, D., Grygar, T., Hradilová, J., & Bezdička, P. (2003). Clay and iron oxide pigments in the history of painting. *Applied clay science*, *22*(5), 223-236.

Íñiguez Berrozpe, L. (2016). Análisis del aparato decorativo del sacrarium hallado en la Casa del Larario de Bilbilis (Calatayud, Zaragoza) [Analysis of the decorative apparatus of the sacrarium found in the Casa del Larario de Bilbilis (Calatayud, Zaragoza)]. *Archivo Español de Arqueología*, *89*, 95-116.

Íñiguez Berrozpe, L. (2020). Novedades en el estudio de la pintura mural romana del cuadrante nororiental de la península Ibérica. In *La pintura romana en Hispania: Del estudio de campo a su puesta en valor* (pp. 35-49). Corunna, Spain: Servicio de Publicaciones.

Íñiguez Berrozpe, L., Guiral Pelegrín, C., Sáenz Preciado, C., & Martín-Bueno, M. (2020). La decoración pictórica y en estuco de la Domus 1 (Insula I) de Bilbilis (Calatayud, Zaragoza) [The pictoric and stucco decoration of the Domus 1 (Insula I) of Bilbilis (Calatayud, Zaragoza)]. In *III Congreso de Arqueología y Patrimonio Aragonés* (pp. 207-215). Aragon, Spain: Colegio Oficial de Doctores y Licenciados en Filosofía y Letras y en Ciencias de Aragón.

Íñiguez Berrozpe, L., C. Guiral Pelegrín, Sáenz Preciado, & Martín-Bueno, M. (2022). La pintura romana en Aragón: el II estilo en el Municipium Augusta Bilbilis. In *IV Congreso de Arqueología y Patrimonio Aragonés* (pp. 217-230) Aragon, Spain: Colegio Oficial de Doctores y Licenciados en Filosofía y Letras y en Ciencias de Aragón.

Legodi, M. A., & de Waal, D. (2007). The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste. *Dyes and Pigments*, *74*(1), 161-168.

Liang, Y., Miranda, C. R., & Scandolo, S. (2006). Infrared and Raman spectra of silica polymorphs from an ab initio parametrized polarizable force field. *The Journal of Chemical Physics*, *125*(19), 194524.

Beltrán Lloris, M. (2003). La casa hispanorromana. Modelos. *Bolskan: Revista de arqueología del Instituto de Estudios Altoaragoneses*, (20), 13-66.

Manzano, E., Rodriguez-Simón, L. R., Navas, N., Checa-Moreno, R., Romero-Gámez, M., & Capitan-Vallvey, L. F. (2011). Study of the GC-MS determination of the palmitic—Stearic acid ratio for the characterisation of drying oil in painting: La Encarnación by Alonso Cano as a case study. *Talanta*, *84*(4), 1148-1154.

Mariette, R., & Bragantini, I. (1982). *Museo Nazionale Romano. Le Pitture II.1: Le decorazioni della villa romana della Farnesina.* Roma, Italy: De Luca.

Martín-Bueno, M., & Sáenz Preciado, J. C. (2002). La Insula I de Bilbilis (Calatayud, Zaragoza). Salduie, (2), 127-158.

Martín-Bueno, M., Lope Martínez, J., Sáenz Preciado, C., & Uribe Agudo, P. (2007, February). La Domus 2 del Barrio de las Termas de Bilbilis: La decoración del II estilo pompeyano. In *Villas, maisons, sanctuaires et tombeaux tardo-républicains: Découvertes et relectures récentes. Actes du Colloque Internacional de Saint-Romain-en-Gal en l'honneur d'Anna Gallina Zevi (pp. 235-271). Rome, Italy: Quasar.*

Martín-Bueno, M., Sáenz Preciado, C., & Sevilla Conde, A. (2007). Barrio de las Termas (Insula I): Bilbilis (Calatayud-Zaragoza). Campaña 2007. *Salduie*, (7), 249-258.

Mayer, R. (1990). Collins dictionary of arts terms and techniques. London, UK: Harper Collins.

Moretto, L. M., Orsega, E. F., & Mazzocchin, G. A. (2011). Spectroscopic methods for the analysis of celadonite and glauconite in Roman green wall paintings. *Journal of Cultural Heritage*, *12*(4), 384-391.

Mulliez, M. (2014). Le luxe de l'imitation. Les trompe-l'oeil de la fin de la République romaine, mémoire des artisans de la couleur. Napoli, Italy: Publications du Centre Jean Bérard.

Ospitali, F., Bersani, D., Di Lonardo, G., & Lottici, P. P. (2008). 'Green earths': vibrational and elemental characterization of glauconites, celadonites and historical pigments. *Journal of Raman Spectroscopy*, 39(8),

1066-1073.

Pagès-Camagna, S., Colinart, S., & Coupry, C. (1999). Fabrication processes of archaeological Egyptian blue and green pigments enlightened by Raman microscopy and scanning electron microscopy. *Journal of Raman Spectroscopy*, *30*(4), 313-317.

Pavia, S. A. R. A., & Caro, S. (2008). An investigation of Roman mortar technology through the petrographic analysis of archaeological material. *Construction and Building Materials*, *22*(8), 1807-1811.

Pecchioni, E., Fratini, F., & Cantisani, E. (2014). I constituenti delle malte [The components of the mortars]. In *Atlante delle malte antiche in sezione sottile al microscopio ottico* (pp. 9-22). Firenze, Italy: Nardini Editore.

Perez-Rodriguez, J. L., Jimenez de Haro, M. C., Siguenza, B. Martinez-Blanes, J. M. (2015). Green pigments of Roman mural paintings from Seville Alcazar. *Applied Clay Science*, *116–117*, 211–219.

Rafalska-Lasocha, A., Kaszowska, Z., Lasocha, W., & Dziembaj, R. (2010). X-ray powder diffraction investigation of green earth pigments. *Powder Diffraction*, *25*(1), 38-45.

Riemenschneider, U. (1986). *Pompejanische Stuckgesimse des Dritten und Vierten Stils*. Frankfurt am Main: Peter Lang GmbH.

Sáenz Preciado, J. C., Martín-Bueno, M. A., Bonilla Santander, O., Guiral Pelegrín, C., García Villalba, C., Íñiguez, L., & Pérez Aranda, M. (2018). La casa del Larario de Bilbilis (Calatayud, Zaragoza) [Lararium's house from Bilbilis (Calatayud, Zaragoza)]. In *Actas: 9 y 10 de noviembre de 2017* (pp. 243-253). Zaragoza, Spain: Colegio Oficial de Doctores y Licenciados en Filosofía y Letras y en Ciencias de Aragón.

Sáenz Preciado, J. C., Martín-Bueno, M., & García Francés, E. (2019). *Bílbilis desde la Tardoantigüedad hasta el Medioevo*. Calatayud, Spain: Centro de Estudios Bilbilitanos.

Santoro, S. (2007). Intorno a una parete verde al Museo di Trier: alcune riflessioni sulla monocromía nella pittura romana. In *IX Congreso international pour la Peinture Murale Antique AIPMA* (pp. 153-164). Retrieved from https://hdl.handle.net/11381/2302190

Sun, J., Wu, Z., Cheng, H., Zhang, Z., & Frost, R. L. (2014). A Raman spectroscopic comparison of calcite and dolomite. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *117*, 158-162.

Tóth, E., Weiszburg, T. G., Jeffries, T., Williams, C. T., Bartha, A., Bertalan, É., & Cora, I. (2010). Submicroscopic accessory minerals overprinting clay mineral REE patterns (celadonite–glauconite group examples). *Chemical Geology*, *269*(3-4), 312-328.

Uribe Agudo, P. (2004). Arquitectura doméstica en Bilbilis: La domus I. Salduie, (4), 191-220.

Uribe Agudo, P. (2009). Los fenómenos de imitación en las viviendas urbanas romanas en el Nordeste de la Península Ibérica [The Roman urban household: imitation phenomena in the Northeast of the Iberian Peninsula]. *Espacio, Tiempo y Forma, Serie II Historia Antigua, 22, 7*1-81.

Uribe Agudo, P. (2015). La arquitectura doméstica urbana en el valle medio del Ebro (siglos II a.C.-III p.C.). Bordeaux, France: Aquitaine.

Wang, Y., Alsmeyer, D. C., & McCreery, R. L. (1990). Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra. *Chemistry of Materials*, *2*, 557-563.