The Painted Cities of Vesuvius:  
Pigments, Application, and Conservation of Roman Wall Paintings from the Bay of Naples

Master’s Thesis

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Alison M. Crandall

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Dedication

For

Ann O. Koloski-Ostrow

whose tireless, exuberant passion inspired me to study the ancient world;
in whom an out-of-place small-town student found a mentor, teacher, and friend;
and who gave life and purpose to this project.
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ABSTRACT

The Painted Cities of Vesuvius: Pigments, Application, and Conservation of Roman Wall Paintings from the Bay of Naples

A thesis presented to the Department of Classical Studies and MA Program in Ancient Greek and Roman Studies

Graduate School of Arts and Sciences
Brandeis University
Waltham, Massachusetts

By Alison M. Crandall

Wall paintings decorated the majority of space in both Roman households and public buildings, depicting everything from the objects and scenes of daily life to vibrant vignettes of mythology, and there is no better corpus of preserved images than those found in the colorful Roman towns and villas on the Bay of Naples, buried and preserved by the 79 CE eruption of Mount Vesuvius. Today, these sites attract millions of visitors every year, simultaneously capturing the imagination of the world and endangering the remains of the day frozen in time. To properly address this, further study must be done into the materials that compose these walls, from the base levels of cement and plaster to the pigment adorning them in order to better understand the art form and how to protect it.

This study begins with the general construction of walls, their plaster-layer preparation, and the sources for pigments and their subsequent application. Then, conservation approaches and techniques are described and examined. This project also incorporates scientific...
methodology into a case study of fragments of wall painting from the region from private collections, including portable X-Ray Fluorescence (pXRF), Fourier (FT-IR), and Gas Chromatography-Mass Spectrometry (GC-MS), to extrapolate details about their composition and production.

The case study shows a variety of material from the Bay of Naples and demonstrates the complexity of finding a standardized and effective way of protecting these sites as part of the world's cultural heritage. More research is required to determine the next course of action and it must be done carefully, but it is, in some ways, a race against time.
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Chapter 1: Introduction to a Problem

Wall paintings decorated large swaths of space in Roman households and public buildings, depicting everything from the everyday objects of daily life to vibrant scenes of mythology, and the plants and minerals used as pigments in creating these images are as diverse as the subject matters themselves. Several ancient sources describe the colors and outline the sources of these materials, and by using modern scientific equipment, particular pigments within ancient walls may be studied and identified to examine the provenance of materials at specific sites and the relative expense of the decoration. Proper analysis of the materials used in ancient times may aid in their modern preservation and protection from the elements that fade and otherwise destroy the decorations in cultural heritage sites like Pompeii and Herculaneum, and this study seeks to contribute to the research and development of solutions for future application.

The first instance of painting in ancient times remains debatable to this day, as archaeology discovers continuously older cave paintings and other markers of civilization. Even in antiquity, cultures did not share a single answer. In his work the *Naturalis Historia*, Pliny the Elder discusses this, starting with the Egyptian's claim to have invented painting six thousand years prior to his contemporary time, though his belief lies in Greek origin stories from Sicyon or Corinth.¹ Regardless of where painting started as an art, he suggests the common origin began

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with the tracing of shadows, slowly progressing to monochrome sketches of life, and then with colors added from crushed ceramic materials, though by the time the Greeks achieved such pigmentation, he claims that painting had been perfected in Italy by the predecessors of Rome, known by such decorations as in the Temple of Ardea, which “antedate the foundation of Rome.” Though the environmental conditions have changed in the subsequent millennia, he describes the paintings to have “survived... as if newly painted,” despite being open to the sky, and the fact calls his first claim into question, for even in antiquity, measures had to be taken to prevent the fading of wall-adorning art.

This concern with understanding and preserving of the wall art indicates a certain prominence of the form in the daily lives of the Roman people. Every day, Romans were exposed to many forms of art – statues, reliefs, mosaics, and wall-paintings, among others, sometimes free-standing and otherwise incorporated into architecture, all of which had a specific purpose and meaning, whether functional, political, entertaining, or symbolic.

The ancient Roman people upheld a distinct separation of public and private space, from the temples and cult spaces that served their gods to the interiors of their homes. Public space was used for conveying, and the art in those places was bold and colorful to capture attention and make impressions. When possible, private space was decorated lavishly to a similar effect - to exhibit the kind of decadent wealth the Roman civilization is remembered for. Temples were well-adorned as a type of tribute, giving prestige to the god or goddess 'housed' inside. Similarly, private houses of the well-off Roman citizens were covered in decorations. Walls in poorer

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2 The predecessors of Rome being the native Italics, like the Villanovan and Etruscan civilizations.
3 Pliny the Elder. *Natural History: A Selection*, 35.16-35.17, 325.
4 Pliny the Elder. *Natural History: A Selection*, 35.17, 325.
households and functional areas like the kitchen, however, often went undecorated to spare expense.

The art that served the public had specific intentions - social, political, and propagandistic in nature. Although these decorations employ many of the same techniques and materials than the Romans incorporated into their private homes, the pigments adorning the monuments of the Roman world have been exposed to more damage, and in many cases, have been wiped away to near invisibility. Generally, the art of public spaces incorporated the depth and texture of sculpture, and so the image still remains, as long as it has not been dismantled or changed by other activity. The study of these monuments and the colorants that once adorned them is more of a cosmetic curiosity – helping to reimagine the colorful sight of the ancient Roman city streets in their former lives, both fascinating and important, but in most cases, not as immediately concerning.

Graffiti and programmata might lie between the public and private life of the Romans, sometimes incorporating pigment painted across the external walls of buildings in place of etched-in commentary. The study of graffiti, which consists primarily of words, deserves a scientific examination, but requires a more literary approach which needs more consideration and space beyond the scope of this project, particularly for the politically-involved programmata announcements, endorsements, and defamations scrawled across street-lining walls.

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6 Other activity includes actions like conventional acid washing used by archaeologists to remove dirt.
7 For an example, see Figure 1, which shows house IX.11.3 on the Via dell'Abbondanza has a complex scrawl of red programmata.
This study focuses on the art of the private sphere of Roman life, specifically the wall decoration of the wealthier houses and villas. The wall art in these spaces are primarily for personal enjoyment, though they also serve the prestige and intrigue of their owners. Not many houses have had their images studied as a whole, but in some cases, it seems plausible that they may be related to more than the simple preference.\textsuperscript{8} Every image and possibly even the color was likely chosen by the patron, to be seen every day by the family, and to impress their guests and clients alike.

Both functional and symbolic, the Roman atrium house stood at the center of the ideal private domestic situation, obtainable only by the wealthy and elite Roman population. The

\textsuperscript{8} The Room of the Cupids in the Pompeian “House of the Vettii,” for example, is said to be a reflection of the owner's or owners' businesses, one panel of which can be seen in Figure 2.
*domus* remained an iconic feature of traditional Rome in the social, architectural, and topographical spheres, late into (and presumably after) the Severan age. Unfortunately, no ruins of second century CE atrium houses survive in Rome itself, but documentation does exist,⁹ as do the comparisons of better preserved and later unoccupied sites, like those buried on the Bay of Naples. Despite disasters and developing technology, the basic concepts of the traditional house form remained relatively constant, a tribute to its deep-rooted tradition.

Although the Romans claimed to be descendants of Trojan survivors, they did not deny their roots from the native Italians. The open-ceiling form of the *domus'* atrium echoes the mud and thatch huts of the Villanovans¹⁰ and is reminiscent of the early Greek *megaron*.¹¹ Both forerunners incorporated posts or columns (respectively) to support the roof around the opening to allow smoke from the hearth to escape. The Romans adapted this to the *impluvium* (an opening in the ceiling) and *compluvium* (a shallow basin in the floor) combination to collect and store rainwater, though the *tetra-style atrium* would later be replaced with the column-less Tuscan style. A later Roman, Terentius Varro, suggested that “the Romans derived the atrium, the word and the convention, from the Etruscan town of Atria.”¹² Regardless, the adoption and continuation of the style attests to the eclectic and traditional-mindedness of Roman civilization, back to the rumored home of Romulus, the mythological founder of Rome, with its post markings.¹³ The concept of the atrium became the cornerstone of the *domus*, simultaneously the heart of Roman origins and domestic life.

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⁹ This evidence is partially in the form of the fragmentary Forma Urbis, or Marble Plan of Rome.
¹⁰ “...simple rectangular or oval huts made of a wooden-post frame and wickerwork sides daubed with mud. The roof was pitched, and often covered an entrance porch at one end,” (J. E. Stambaugh, *The Ancient Roman City*. Baltimore and London: Johns Hopkins University Press, 1988, p 161-162.)
What was the appeal of such a building to attract the wealthy? The Roman atrium house was built like a one-family medieval castle, and as the forerunner, probably inspired the latter. The structure of an atrium house can be described in typically terms, but every house had its own shape and space constraints and was tailored to fit the specific location and owner. The exterior walls of a Roman house were thick and tall to prevent unwelcome guests from entering. A *domus* had, “at most, only a few small windows in their outside walls... This made them quieter and cooler in the bustle of town life, as well as less open to burglary and other dangers of urban civilization.”\(^1^4\) A strong wooden or brass door opened into the *fauces* (an entrance hall, but in literal translation, the “throat” of the house), which led directly to the atrium, flanked by two rooms closed-off from the house, external shops. “...even the more prestigious buildings were often fronted by shops.”\(^1^5\) In the atrium is the *impluvium* opening over the *compluvium* pool that rests over the water-storing cistern. Normally, *cubicula*, the bedrooms of the house, were doored or curtained rooms off the atrium, but as housing developed and Romans were forced to build upward for lack of horizontal space, bedrooms relocated to the second floor, and their doors yielded to flat decoration or other types of rooms. In earlier *domi*, across the atrium from the entrance, aligned on axis was the *tablinum*, the head-of-household's business room. Beyond this lay the private realms of the house, the later incorporated walled garden, either partially or completely surrounded by a colonnade,\(^1^6\) known as the *peristyle* garden. Most rooms looking out onto the garden would be *triclinia*, or dining rooms, to entertain the family and guests alike.\(^1^7\)


\(^{15}\) Roman Domestic Buildings, 24.

\(^{16}\) These gardens were called “peristyle,” indicating that the columned walkway surrounded it on four sides. Lisa C. Nevett, Domestic Space in Classical Antiquity. (Cambridge: Cambridge University Press, 2010), 92.

With its own kitchen for moderate countertop cooking and a healthy supply in stock, or its own stable and garden, a Roman house could easily sustain itself for a short time.

But what is the significance of this arrangement? The owners intended a *domus* to be a place of business, and of displaying wealth as well as their private residence. The atrium could be described as “a semipublic waiting room, its doors usually left open to the street [during the day], [and] it welcomed guests and contained the finest tokens of the family's prestige.” A stark line is drawn, however, between the more public and private spheres of the home, giving glimpses but never allowing a person direct access to a room unless invited. Past the *tablinum*, “was a more intimate area into which only higher-status associates would have been invited to stroll in the porticoes or dine in decorated triclinia along its sides.”

And almost every wall of the *domus* would be covered in decoration, painted on directly instead of hung, usually as *frescos*. These wall paintings came in many forms and colors, of almost any imaginable subject manner to suit the preference of the *domus'* owner. Sometimes these appear to simply be following the stylistic fashion of the time, and other times, they show scenes of specific mythology or industry, which appear to be conveying a message or something important to the family. Whether these were placed intentionally to be seen by friends and clients or simply made to please the owner is impossible to confirm without further evidence of who these owners were, but the study of the images remains a facet of scholarly fascination, particularly in the cities around the Bay of Naples – the 'painted cities' of Vesuvius, which has the best preserved samples.

Located in the region of Campania, the shin of modern Italy's boot, the Bay of Naples

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18 Stambaugh, *The Ancient Roman City*, 162.
spans between the Cape Misenum in the northwest, named for Misenus, a character in Virgil's *Aeneid*, and the Sorrentine Peninsula to the south. The bay is dotted by the islands of Procida, Ischia, and Capri, leading out toward the Tyrrhenian Sea. Campania has the typical Mediterranean climate, attracting vacationing emperors since the first century CE. The bay has a higher than normal seismic risk in the region, due to the proximity of the volcanic Mount Vesuvius, which looms in the middle of the bay's interior. The volcanic activity has contributed to its fertile soil and subsequent agricultural industry, with a history reaching back into the Roman times.

Before the Romans, the Bay of Naples was settled by the native Italics. Towns like Pompeii and Herculaneum were built by the Oscan tribes, like the Samnites. In the first century BC, these towns were defeated and colonized by the Roman Republic through the course of the Samnite Wars. There was a strong Greek presence in the region, centered in Neapolis, until the towns were Romanized, with the amenities and buildings diagnostic of every Roman settlement.

Being an agricultural area, the towns never achieved fame like that of larger cities except in their death, but the remote beauty of the region attracted the attention of the wealthiest of Romans. These Romans had residences within the towns and elaborate villas in the surrounding foothills. The villas served as vacation get-aways, as well as agricultural bases, for growing, storing, and processing goods like the wine and olive oil that Italy is still known for.

After the pyroclastic eruption in 79 CE, this region was buried and the old cities eventually forgotten, allowing them to be preserved at the specific moment in time. Though adventurers of the first century CE returned to reclaim their treasures, many were unsuccessful, and the pursuit abandoned. Renaissance artists explored some too, though mostly stayed to
search the ceilings of the *Domus Aurea* and similar ruins in Rome.

Like the ancient Romans who spent their money and reputation on these images and the Renaissance artists who drew inspiration from glimpses of the buried ruins, the modern tourist and academic alike should be aware and involved in preserving these wall paintings. Today, the sites on the Bay of Naples attract millions of visitors every year, simultaneously capturing the imagination of the world and endangering the remains of the day frozen in time, a diorama of the past. To properly address this, further study must be done into the materials that compose these walls, from the base levels of cement and plaster to the pigment adorning them in order to better understand the art form and how to protect it. This study does not seek to criticize or otherwise propose a solution to this problem of preserving the wall paintings of the ancient world, the Roman empire, or specific sites like Pompeii, rather, it is intended to provide an introduction to the art form, the complexity of materials used, and concerns in identifying and protecting such wall paintings.
Chapter 2: Materials and Technology of Roman Walls and Their Decoration

2.1 Beneath the Surface: A Holistic Approach

With the recent collapses of buildings in the ancient city of Pompeii, a renewed awareness of the deteriorating situation has come to the general public. In response, experts have begun to study the materials used holistically to conserve and protect the site. But this response, while effective, is incident-specific and therefore both expensive and inefficient. A more permanent and uniform solution must be developed, and this catalog of material and technological summary, as described by the Romans themselves, is the first step to understanding the pigments incorporated into the lives and spaces of the Romans on the Bay of Naples. Using this information in conjunction with more modern scientific study and methodology may lead to such a solution in the future.

In addition to understanding the pigments used to decorate the space, the very structure supporting the images must be studied in order to approach a proper solution. As seen in the collapsed houses, protecting the paintings in situ means little if the structure itself crumbles. The walls built in Roman times, particularly those more structurally sound than those built of mud-brick and straw like those that caused the city of Rome to be subject to leveling fires like that of

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64 CE,\textsuperscript{22} survive well to this day, particularly those in abandoned/buried sites or otherwise built-into modern cities. The Bay of Naples, in particular, is home to some of the best-preserved Roman buildings, asphyxiated and supported by meters of pumice or the mud of pyroclastic flow. This lack of exposure is why many of the wall paintings still stand and exist today, though since the excavations of the early nineteenth century, the open-air conditions have contributed to the structural failure of many of these buildings, particularly those that have been neglected for lack of monetary support. This is just one of many reasons calling for an appropriate holistic solution to the preservation of ancient sites, such that the cultural heritage may survive and educate future generations.

2.2 Discussion of Ancient References

Pliny the Elder, or Gaius Plinius Secundus, a Roman Equestrian of the first century of the modern era (23-79 CE) lived as a career military man and author. As an apparently well-travelled naturalist, his most notable work is arguably the 	extit{Naturalis Historia}, or 	extit{Natural History}, wherein he lists and describes aspects of the natural world, lending words to catalog the thought and science contemporary to what was arguably the height of the Roman empire. Though his accounts can occasionally be exaggerated or fanciful, likely due to the transfer of second or third-hand information, he accurately portrays many plant and animal species, mining and manufacturing processes, and natural phenomena. In many chapters of 	extit{Naturalis Historia}, he describes things that may be used for pigment, ranging from the usual plants and minerals to several animal and insect species as well. In later chapters, he brings these facts together to

\textsuperscript{22} Vitruvius calls these lower-quality walls “wattled,” and describes them as “conducive to great calamity.” Vitruvius, 	extit{De Architectura}, 2.8, http://penelope.uchicago.edu/Thayer/E/Roman/Texts/Vitruvius/2*.html
describe their use in artwork, particularly that which decorated domestic spaces: frescoes.

Marcus Vitruvius Pollio, or simply Vitruvius, as he is commonly known in the modern era, was a Roman author, architect, and engineer during the earlier part of the first century BCE. He was and still is primarily known for his multi-volume work on the architecture of Rome, *De Architectura*. Though most of this literature is focused on practical principles and descriptions of building materials, machines, and structures. In *De Architectura*, he famously asserted that a structure should be constructed with and possess “strength, utility, and beauty,” which explains his concern and handling of the materials used to decorate finished buildings in the Roman Empire. Vitruvius also goes to great lengths to describe a proper method of preparing walls prior to decoration, to increase their durability and resistance to fading.

These two sources have facts reliable for initial study, though each had their own agenda, and caution should be applied, particularly in that the names and places mentioned within their descriptions of these materials may not always be consistent with the modern day. Moreover, the accounts may not be completely comprehensive or infallible in describing the properties, as they might be known to more advanced science and analyses.

Pigment came from numerous sources of every kind in antiquity and from every corner of the Mediterranean. Following his discussion of the general history of painting as an art, Pliny describes the basic colors, separating them into bright colors and dark colors, natural and artificial. According to Pliny, the bright colors (prior to any sort of mixing) are “bright red, rich blue, vermilion, green, indigo and bright purple. The rest are dark.” He continues to explain that “brown, red ochre, ruddle, white chalk, white marl, Melian white, and bright yellow” are the

\[\text{Pliny the Elder. Natural History: A Selection, 35.30, 327.}\]
\[\text{Ibid.}\]
natural colors, whereas “yellow ochre, burnt white lead, realgar, vermilion, Syrian red, and black” are the most common of the artificial colors. Vitruvius, in *De Architectura*, also describes the colors used for wall paintings, along with their ancient sources or manufacturing processes. Compared with Pliny's brief discussion of the basic colors of the Roman palette, Vitruvius focuses on the historical use of the materials, detailing other colors in the ancient spectrum.

### 2.3 From the Ground Up

#### 2.3.1 Building Walls

The ancient Romans applied colors to the wall with great care, though the exact technique varied with the locale and quality of the decoration. In Roman times, engineers and builders applied a number of building techniques and materials, which were combined and altered depending on purpose and expense. In the time of the Julio-Claudian emperors and the early Flavian Imperial dynasty, the material of choice was a combination of brick and Roman cement, though the exact construction of walls depends on the cost to the owner and when the house was built. Pompeii, being a small town from the time before the Romans, was made with a lesser quality than the richer residences of those who settled into the uncovered areas of Herculaneum. The second book of Vitruvius' work on architecture begins with describing the materials used in construction, after a historical review of how and why most buildings utilize four walls and a roof.

The first material outlined is brick, which required a particular kind of clay without many

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27 Ibid.
28 Vitruvius. *De Architectura, Book 7.*
30 Vitruvius, *De Architectura*, 2.3-2.8.
inclusions, as Vitruvius describes it “earth of a red or white chalky, or strong sandy nature. These sorts of earth are ductile and cohesive, and not .. heavy...”\textsuperscript{31} Bricks were made in the spring and autumn to avoid shrinkage and cracking due to the heat. The best materials are those that have had thorough amounts of time to dry, for when plaster is laid onto wet brick, they shrink over time and separate from the plaster. Since the plaster is comparatively thin and fragile, it breaks, sometimes causing the wall itself to fail as well.\textsuperscript{32} Vitruvius describes different kinds of bricks, which are classified by size, though he also mentions a type made of porous material which is water-resistant and buoyant, like pumice, which he remarks are great for building.\textsuperscript{33}

Next, he discusses buildings of “rubble work,”\textsuperscript{34} these structures utilize sand and gravel, from sand pits or rivers, if necessary. Sea sand may also be used, but he warns that it is slow to dry and cannot be used for vaulting or plaster, since the salt destroys the plaster and may crack. Material from the sand pits is viable, though it must not be allowed to dry out for a long time before use, and is best in mortar. The river sand is the best for making the plaster as hard as cement, when tempered with beaters.\textsuperscript{35}

Lime, which is “burnt either from white stone or flint,”\textsuperscript{36} is of a stronger texture for building walls, but is also porous and good for plastering. It is slaked for making mortar with pit sand, where “three parts of sand are mixed with one of lime,”\textsuperscript{37} though river and sea sand may also be used, in “...two parts of sand... to one of lime...”\textsuperscript{38} and tempered with “potsherds ground

\begin{itemize}
\item \textsuperscript{31} Vitruvius, \textit{De Architectura}, 2.3.
\item \textsuperscript{32} Ibid.
\item \textsuperscript{33} Ibid.
\item \textsuperscript{34} Vitruvius, \textit{De Architectura}, 2.4.
\item \textsuperscript{35} Ibid.
\item \textsuperscript{36} Vitruvius, \textit{De Architectura}, 2.5.
\item \textsuperscript{37} Ibid.
\item \textsuperscript{38} Ibid.
\end{itemize}
and passed through a sieve, in the proportion of one third part.”

This limestone mortar is water-resistant, once the initial setting has occurred – in fact, after setting, water causes the pores to fill with a gel-like material, increasing the strength of the structure. If water gets into it before it sets, however, it may simply melt away. The hydraulic cement utilized by the Romans is similar to this, though it requires the use of sand from the “neighborhood of Mount Vesuvius,” near Baiae. Unlike the pit and river sand, the use of the volcanic ash type of sand (with pumice) allows the lime to harden even under water. This final type of cement is now more commonly known as *pozzolanic*, and after the end of the Roman period its durability and strength had not been matched until the 1800's Portland cement. To this day, scholars still debate the exact composition of the Roman building material and marvel at what the ancient peoples were able to achieve with it.

At the time of Vitruvius' writing, *opus reticulatum* was the prevailing method for facing walls, since it was the most visually appealing. Vitruvius explains that the form is liable to split, so the older, rougher-looking *incertum* was stronger. Both, he remarks, should use the smallest stones available. Using soft and porous stones may soak up the wetness in the mortar, allowing for a greater cementing power at first, but after a time the lack of moisture will lead to the lime separating out of the cement and separating from the facing stones, making the work unsound. To circumvent this issue, Vitruvius recommends that walls should be built two feet thick of “red stone, or of brick or common flint,” and bound together “with iron crams run with lead...

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39 Ibid.
40 Ibid.
41 Vitruvius, *De Architectura*, 2.6.
42 Vitruvius, *De Architectura*, 2.8.
preserving the middle space or cavity.”\textsuperscript{43} Here, he discusses the Greek methods, which avoid this problem by using smooth, hard stone, which cannot absorb the moisture and simultaneously isolates the mortar between two faces of stone, preserving it.\textsuperscript{44} Vitruvius suggests the most durable and common way to achieve a similar effect during the Roman period was to use brick on either face, with rubble and mortar between.\textsuperscript{45}

The Roman cities and villas along the Bay of Naples incorporated and mixed these styles of construction, which is especially apparent in the areas where the plaster and other facings have fallen away.\textsuperscript{46} The earthquake of 62 CE left the area in a state of reconstruction, and some of this stylistic fusion can be traced to the repairs begun during that time.

\footnotesize
\textsuperscript{43} Ibid.
\textsuperscript{44} Ibid.
\textsuperscript{45} Ibid.
\textsuperscript{46} Redecorating efforts can be seen in several places, but is most apparent in the atrium of the Villa at Oplontis (Figure 3), where one layer of plaster has crumbled off the wall, revealing the depiction of traditional atrium doors on another.
2.3.2 Preparing the Plaster

The first step of painting a wall consisted of creating a plaster layer that adhered to the wall, which usually meant modifying the wall itself. The rough surface of bricks eased this process, though signs of additional keying or pecking have also been observed. Keying often occurred in crossed or “herring-bone” patterning that a Roman artisan would score or imprint either directly into a wall or on a render coat, whereas pecking was primarily used in the process of redecoration and utilized holes hammered into a surface (either the wall itself or an older layer of plaster) to roughen the exterior. After this preparation, the plaster could be applied, usually in
several coats.\textsuperscript{47}

Vitruvius suggests using lime of the highest quality, properly slaked to a uniform consistency to avoid a blistering of the plaster, which can break and destroy the smoothness of the stucco.\textsuperscript{48} In total, he recommends a six-layered plaster, with three coats of sand and three coats of marble-dust. The first coat should be rough, and the second layer, sand, should be added while the first is drying, and brushed length and height-wise across the wall. When this is dry, the second coat should be added, then a third. After this, a coat of marble-dust should be added. The second coat of marble should be added during drying, well-worked and rubbed down, before the final coat, which should be of final material. After beating and smoothing, this technique “throws out the colors mixed therein with great brilliancy,”\textsuperscript{49} and with polishing, can be reflective.\textsuperscript{50}

Not all Romans followed this Vitruvian standard, either due to expense or practicality. Vitruvius himself acknowledges the variation, but warns that such frescoes are easily broken and not as bright in appearance.\textsuperscript{51} The layering technique relied on precision and increasingly fine inclusions, from the base coat containing sand, gravel, and pottery fragments to a layer of smoothed and polished, almost pure slaked lime to produce the solidification and shine that Roman frescoes are known for.\textsuperscript{52}

The ancient Romans added the colored pigments to this plaster treatment before the last coat dried, which Vitruvius explains as a method to keep frescoes from fading, even when washed. “The lime being deprived of its moisture in the kiln, and having become porous and dry, readily imbibes whatever is placed on it... and when dry, the whole seems composed of one body

\textsuperscript{47} Ling, “Technique,” in \textit{Roman Painting}, 198-220.
\textsuperscript{48} Vitruvius, \textit{De Architectura}, 7.2.
\textsuperscript{49} Vitruvius, \textit{De Architectura}, 7.3
\textsuperscript{50} Ibid.
\textsuperscript{51} Vitruvius, \textit{De Architectura}, 7.3
\textsuperscript{52} Pye, “Wall Painting in the Roman Empire,” 24-27.
of the same quality.”\textsuperscript{53} Though both Vitruvius and Pliny provide some insight into the preparation of pigments, not every material has a particular adhesive described, since the wet plaster itself would provide the primary adhesion for dry pigments, though these would also presumably be mixed with water\textsuperscript{54} to ease application. Once the wall had dried, pigment could still be added, though it would need to be mixed with either a lime-solution or another adhesive, such as egg.\textsuperscript{55}

### 2.4 Catalog of Pigments by Color

#### 2.4.1 White Pigments

The Romans obtained white from several sources, though chalk provided the cheapest and most accessible form of the color. White chalk was also known as \textit{paraetonium}, and according to Pliny, it is taken primarily from Crete and Cyrene.\textsuperscript{56} Natural chalk is abundant, so this may indicate a quality or mining preference. Another type of white pigment called Marl, or \textit{Melinum}, was found on the island of Melos,\textsuperscript{57} in the form of a lime (calcium carbonate) clay. The last type of white detailed by Pliny is burnt white lead, or \textit{cassiteros}, as it was known to the Greeks. According to a legend referenced by Pliny, they obtained it on islands in the Atlantic Ocean, though he states that Lusitania and Gallaecia have deposits of the material in sandy, black surface strata.\textsuperscript{58} He later suggests the same material was “discovered by accident when some was burnt in jars in a fire at Piraeus,” and he notes that it was used for shadows in paintings,\textsuperscript{59} a

\textsuperscript{53} Ibid.  
\textsuperscript{54} Ibid.  
\textsuperscript{55} The use of egg as an adhesive is also known as \textit{tempura}, though pigments added in addition after the initial fresco had dried would be considered \textit{a secco}. Some walls were made \textit{a secco} intentionally and entirely, but those should be examined separately to determine what binder was used.  
\textsuperscript{56} Pliny the Elder, \textit{Natural History: A Selection}, 35.36, 327.  
\textsuperscript{57} Pliny the Elder, \textit{Natural History: A Selection}, 35.37, 328.  
\textsuperscript{58} Vitruvius, \textit{De Architectura}, 7.7.  
\textsuperscript{59} Pliny the Elder, \textit{Natural History: A Selection}, 34.156, 321.
procedure that Vitruvius verifies the Rhodians preformed. “The Rhodians place, in the bottoms of large vessels, a layer of twigs, over which they pour vinegar, and on the twigs they lay masses of lead. The vessels are covered, to prevent evaporation; and when, after a certain time, they are opened, the masses are found changed into white lead.”

The Temple of Venus in Pompeii utilizes the calcite form of white paints selectively in the samples analyzed, generally as a background. The temple was destroyed by the massive earthquake of 62 C.E. Following this disaster, the Temple of Isis was reconstructed and embellished by a wealthy freedman in the name of his six-year-old son, Numerius Popidius Celsinus, who was awarded a seat on the senate, as his father had probably hoped, in return. Similarly, the reconstruction effort of the Temple of Venus indicates a certain significance to the cult and therefore to its decoration, so the choice of chalk for white does not necessarily depict simply a “cheaper” alternative to the lead.

2.4.2 Black Pigments

Pliny considers black, or atramentum, an artificial pigment, though “it can come from [the] earth in two ways,” either “like brine” or by use of sulphur-colored earth. Pliny notes that painters went so far as to dig up charred grave remains to obtain the pigment. Artificially produced from the soot of burnt resin or pitch, the highest quality was said to be derived from pine-wood. The next step of manufacture required the soot to be exposed to sunlight, and then mixed with glue. Vitruvius repeats this information, though he refers to the glue as size. He also

60 Vitruvius, De Architectura. 7.11.
63 Pliny the Elder, Natural History: A Selection, 35.41, 328.
64 Pliny the Elder, Natural History: A Selection, 35.41-35.43, 328.
describes a similar black color, “made by drying and burning lees of wine in a furnace, and
grinding the result with size... The better the wine whose lees are used, the better will be the
black color; which will, in such case, approach the color of indigo,”65 a fact, which, the ancient
Romans undoubtably utilized, since a bluish color would be considerably more difficult and
expensive to produce through normal channels, either through trade or manufacture.

Scientific studies have identified forms of carbon-black in Roman wall paintings,
sometimes in the presence of calcite, which may have either functioned to lighten the color or
otherwise as a lime-wash binder. Microtextural studies can separate the black pigments made
with charred bone by the presence of phosphorus and metal oxides from that made when fuels
(coal, wood, oil, etc) undergo combustion (are burnt), by the particulate matter66 and chemical
structure of carbon.67

2.4.3 Purple Pigments

Vitruvius spends two chapters of book seven describing the ways to obtain purple dye.68
The first is that of “marine shells,” from the murex snail, which is gathered and broken into small
pieces. The dye “oozes out like tears, and is drained into mortars and ground,”69 which Vitruvius
notes is called ostrum. The color dries fast due to the marine salt and is prepared with honey.70

He also describes how the color varies according to the sun exposure and locale, where that from

65 Vitruvius, De Architectura, 7.10.
66 Particulate matter refers to material in the smallest size possible that is still within macro-scale, or is otherwise
visible.
68 Please note that dyes and pigments are inherently different – dyes are generally in liquid form and do not require
a binder to be used as a colorant, whereas pigments need a binder like the wet plaster of a fresco, to affix it to
the wall.
69 Vitruvius, De Architectura, 7.13.
70 Ibid.
Pontus and Galatia is brown, those south and west have a paler yield, Rhodes and southern
countries produce a red dye, and in equinoctial regions east and west is violet. Pliny also
discusses the manufacture of this dye from murex in his discussion of sea creatures, noting that
the purple is obtained from within a vein of the snail and boiled with water to dilute it. If exposed
to sunlight, the color oxidizes and turns the color of indigo blue. Which was utilized in the
Roman east – specifically the Levant. The color it is known for and was generally produced is
the royal, or Tyrian purple, making it one of the most expensive dyes in antiquity for both wall-
paintings and textiles.

Vitruvius’ discussion also covers other ways of creating purple pigments. One way is to
tinge chalk with madder-root and hysginum-colored material. Attic ochre, a yellow pigment,
can also create a purple color when heated and quenched by vinegar, and in the same way Attic
ochre can be synthesized, purple can be obtained from vaccinium, or bilberries, mixed with
milk. Science has identified that in certain circumstances, purple could be obtained by mixing
Egyptian blue with cinnabar, as in a house on the Caelian hill, as well as other frescoes from
Pompeii.

2.4.4 Blue Pigments

Vitruvius states that Alexandria manufactured blue first, then Vestorius at Pozzuoli. To

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71 Ibid.
Sometimes ancient peoples mimicked tapestries of the color by painting their walls with dye mixed with other
pigments.
73 Madder is generally known as a reddish pigment, whereas hysginum is defined as a scarlet-purple dye.
74 Vitruvius, *De Architectura*, 7.11.
76 The house is below the Basilica of SS John and Paul, dating from between the first and fourth century C.E.
Paola Fermo, Andrea Piazzalunga, Mariette de Vox, Martina Andreoli. “A Multi-Analytical Approach for the
Study of the Pigments Used in the Wall Paintings from a Building Complex of the Caelian Hill (Rome),”
make it, “sand is ground with flowers of sulphur, till the mixture is as fine as flour, to which coarse filings of Cyprian copper are added, so as to make a paste when moistened with water.”

This paste could then be rolled out and dried before heating in a furnace to acquire the blue color. Pure sulphur naturally takes on a yellow color, whereas copper is a bluish color in hydroxide form, which would naturally make a greenish hue, but the furnace would heat and burn off the sulphur as a gas. Indigo, according to Vitruvius, was named for its region of obtainment, India. The Greeks imitate it using Selinusian chalk mixed with glass, which they call ὑαλος. Imported lapis lazuli mined in the region of present-day Afghanistan provided a rich, but fairly expensive version of a blue color, though azurite was also more readily available.

The ancient Egyptians synthesized blue pigment called Egyptian blue (also caeruleus), using a calcium copper tetrasilicate (analogous to cuprorivaite) mixed with calcium carbonate as a binder, with glass and occasionally tin inclusions. The presence of tin suggests that the color may have used bronze in its manufacturing process, since copper-tin smelting was one of the main ways to produce bronze in the Mediterranean region. In ancient times the popularity of Egyptian blue caused the technique to spread all the way to China by means of the Silk Road, which suggests that the Romans of Italy had also adopted the same process.

### 2.4.5 Green Pigments

77 Vitruvius, *De Architectura*, 7.11.
78 Ibid.
79 Vitruvius, *De Architectura*, 7.9.
Vitruvius mentions a greek chalk that is found in many places, though he remarks that the best comes from Smyrna, known for its association with Theodotus, who discovered it. He also discusses a pigment referenced as verdigrease, or aeruca, which is obtained in the same way as white lead, by using plates of copper. The Romans also obtained green from chrysocolla, or malachite, a mineral ranging from blue to green in color, comes from Macedonia, generally in the vicinity of copper mines, as Vitruvius mentions. For those who cannot afford chrysocolla, blue can be mixed with “herb weld to obtain a brilliant green.”

The green earth colors vary from emerald to pale and encompass several types of minerals including calcite, aragonite, quartz, and celadonite or glauconite. Celadonite, also known as creta viridis, was found in Cyprus and Spain and glauconite are green ferromagnesian silicate minerals similar to mica. Additional deposits of this material would have been available in Campania due to geological deposits of celadonite from weathered basaltic rocks and marine sediments with glauconite. Both celadonite and glauconite occur in the painting from Pompeii of Bacchus standing beside a lush Vesuvius, topped with trees. Other green earth mineral categories are smectites, chlorites, serpentinaes, and pyroxenes, as well as certain oxidations of copper, though green could also be manufactured by combining Egyptian blue with a yellow

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84 Vitruvius, De Architectura, 7.7  
85 Vitruvius, De Architectura, 7.12.  
86 Malachite and chrysocolla, by modern standards, are different minerals. Malachite often occurs nearby or with azurite and/or chrysocolla, but chrysocolla is thought to be a mixture of copper hydroxide (spertiniete) and chalcedony.  
87 Vitruvius, De Architectura, 7.9.  
91 This image can be found in the House of the Centenary (IX.8.6) and is referenced often for its depiction of Mt. Vesuvius in the background.
ochre (goethite). The availability of green shades allow for increasingly detailed and realistic views of nature that lend to scenes like that in the House of the Golden Bracelet.

2.4.6 Yellow Pigments

According to Pliny, the most renowned painters used yellow from Attica. Burnt yellow, or Attic Ochre, according to Vitruvius, is often used in stucco, and can be obtained by boiling dried violets and squeezing out the liquid. Then they mixed the liquid with Eretrian earth, which produced the yellow color when ground. Vitruvius mentions a yellow-orange mineral known as orpiment, obtained from Pontus. Archaeological studies have identified two other types of yellow pigments. Yellow ochre, composed of goethite, probably derived from iron oxide hydroxides, was generally understood as a lesser quality version of Attic ochre, though of a

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93 See Figure 4, which is an image of the aforementioned House of the Golden Bracelet's fresco, displayed at the Museum of Science's exhibition on Pompeii.
94 Pliny the Elder, Natural History: A Selection, 35.50, 328.
95 Vitruvius, De Architectura, 7.11.
97 Vitruvius, De Architectura, 7.7
similar shade. Goethite, according to studies, comprises the type of yellow wall that reacted with the heat and gases during the eruption of Mount Vesuvius, forming hematite to appear red.

Yellow-brown glass also occurs in some wall-paintings, like those in the Temple of Venus, the composition of which matches that of trachyandesitic-phonotephritic glasses from Somma-Vesuvius, derived from a natural volcanic glass, ground to produce a yellow pigment.

2.4.7 Red Pigments

The “best painters” in Pliny's pigment discussion also used the brown-red ochre from Sinope, though the only other red pigment he mentions in the Natural Histories is cinnabar. Pliny describes two types of red that he labels as cinnabar, mercuric sulphide (HgS) and red lead, both of which were found in silver mines.

Theophrasus wrote that an Athenian named Callias discovered the former type of cinnabar in Athens, though it could also be found in Colchian territory and east of the Ephesus. Workers ground the sand and washed it to obtain the color, which as The Romans, Pliny notes, imported most of their cinnabar from Spain (Sisapo in Baetica), rather than Greece, Carmania, or Ethiopia. He remarks that although the reason has been lost to time, Verrus lists authors who said that Romans decorated the statue of Jupiter on holidays with cinnabar, as well as the faces of men in triumphal processions, perhaps giving further cultural significance to the value and rarity of the material, which was fixed as seventy sesterces per pound. Scientific studies have

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99 Ibid.  
100 Ibid.  
101 Pliny the Elder, Natural History: A Selection, 35.50, 328.  
102 Pliny the Elder, Natural History: A Selection, 33.111-33.122, 303-304.  
103 The former being the mineral form of Cinnabar, mercury sulphide (HgS), which appears a red-orange color, also known as Vermillion.  
104 Pliny the Elder, Natural History: A Selection, 33.113-4, 303-304.  
105 Pliny the Elder, Natural History: A Selection, 33.111, 303.  
106 Pliny the Elder, Natural History: A Selection, 33.113-4, 303-304.
identified this color in the Temple of Venus at Pompeii as well, and the small concentration suggests that only small amounts of the pigment were required to produce bright red paintings, another testament to the economic and cultural value of the mineral.

The red lead type of cinnabar, in addition to silver mines, could also be obtained from lead mines, produced by smelting rock with metal veins. To polish it, Pliny describes that workers wore masks of bladder-skin to avoid breathing the dust indicating that they knew its toxicological effects. Pliny attributes this type of cinnabar to the lettering in scrolls, inscriptions on walls, and on tombs. According to Vitruvius, the best red lead, also known as minium, like many pigments, may be acquired in Pontus, near the river Hypanis, though it is also found between the borders of Magnesia and Ephesus, though a better quality red lead may also be made out of roasted white lead.

Red ochre, according the Vitruvius, can be found in many places, but Sinope (Pontus), Egypt, Spain (Balearic Islands), and Lemnos have the best. According to scientific studies, red ochre, composed primarily of hematite, was generally used without much alteration to the actual ground pigment, though artists often mixed it with other pigments to obtain desired hues.

Although it is a variation of cinnabar, Vitruvius also describes vermilion, a pigment from the Cilbian fields (an area near Ephesus) at length in a discussion of quicksilver, because the “manner of procuring and preparing it is very curious.” Prior to processing, the clod of earth containing vermilion is known as anthrax, “wherein are veins resembling iron, but of a red color,

108 Pliny the Elder, Natural History: A Selection, 33.122, 304.
109 Vitruvius, De Architectura, 7.9.
110 Vitruvius, De Architectura, 7.7
111 Vitruvius, De Architectura, 7.12.
113 Vitruvius, De Architectura, 7.8-7.9.
and having a red dust round them.”  

Vitruvius, *De Architectura*, 7.8.

115 Ibid.

116 Ibid.

117 Ibid.

118 Chalk is a form of calcium carbonate, described as white chalk by Pliny.


119 Ibid.
variation in quality, in comparison to material like cinnabar. Colors like blue and green would have been more expensive and harder to access in general, since the sources are so few and far from the center of the Roman world. These are used generally for smaller details, though not exclusively, since blue may occasionally be found as background and rarely green as well. Green is generally used in first-style to imitate serpentine-infused marble or otherwise in garden scenes, but not usually as a background or for large effects. Though some variation occurs between the Pompeiiian Styles of wall painting, these denominations are focused on layout and not pigment.

![House of the Orchard's garden-painted oecus. Photo Credit: Robert Caudill.](image)

120 For example, the House of the Venus in the Shell uses a starkly blue background, as does the House of the Orchard's oecus (Figure 5). The green in first style walls may been seen in the Samnite House in Herculaneum (green earth; Figure 6)) as well as in the House of the Sallust and House of the Faun, in Pompeii.
Figure 6: First Style Wall in the Samnite House. Photo Credit: Robert Caudill
2.5.2 A Brief Review of Pompeian Styles

One of the earliest excavators of Pompeii, August Mau, identified and described the four apparent stylistic movements, which are based almost completely on design, rather than the color, since those remained generally consistent throughout. Though there are signs of variation and blending between them, it is convention that most walls in the Roman empire from this time period are referred to by these terms.

The First Style, also known as Masonry Style, exists to simulate the use of colored marble blocks stacked in ashlar masonry, like that used in monumental architecture, which were too costly to import for use in the majority of residential buildings (Figure 6). This is the earliest style, of which the origins are uncertain, but similar work has been found in Aegean buildings like in the fourth century BCE Athenian agora. Literary evidence suggests that houses in the Roman countryside were being decorated in this fashion by 310 BCE. The First Style employed a range of colors to produce the effect of imported marbles from across the Mediterranean – though the coloring is not consistent in its use, sometimes within the same wall. Ling mentions the use of white, black, purple, green, yellow, and red in his examples, which correspond to Travertine or Greek marble, granite or gabbro, porphyry, Cipollino or serpentine, Numidian yellow, and red granite.

This style soon began employing the use of columns and other architectural features to break up the orthostates and other “stones.” Such detail-work would lead to the Second Style as it became more elaborate and began to incorporate figures and architectural landscape scenes.

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122 Ling, “The First Style,” in Roman Painting, 12-22.
123 Ibid.
124 Ibid.
onto the panels.\footnote{Ibid.}

The Second Style emerged in the first century BCE in Pompeii, during the time it became a colony of Rome. Ling splits it into phases, wherein the first phase puts dimension into the First Style, then slowly opens the wall into “windows,” with imaginary rooms beyond the actual room.\footnote{Ling, “The Second Style,” in \textit{Roman Painting}, 23-51.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.jpg}
\caption{Villa of the Mysteries, early Second Style. Photo Credit: Robert Caudill.}
\end{figure}

The transition between First and Second Styles into the first/architectural phase, can be seen in Figures 7 and 8.
The second phase returned the focus to within the room, closing off the windows thrown open to imagined architecture to enhance the forms of the walls themselves. This manifests as either strips of wall resembling the First Style of “stone” panels, flattened with some designs or scenes, and separated by depth-inventing columns and garlands or as exaggerated windows to colonnades and statuary. Soon, the separating columns became thinner and stretched, supporting more figures, objects, and floral motifs, while losing the Second Style depth.

127 Ibid. See Figure 9 for this transition.
Ornamental pattern-work loses emphasis, and central frames begin to dominate the designs.\textsuperscript{128} The color here is primarily red, black, and white, though colors similar to that in the First Style are also incorporated, usually for the details. In the more elaborate architectural windows, blue was also used to portray the sky.

The Third Style came into existence co-existing with the Second. Though more conservative Romans like Vitruvius lamented this “impossible” distortion of architectural features adorned with monsters and other unsavory images,\textsuperscript{129} it soon became a popular fashion

\textsuperscript{128} Ibid.
\textsuperscript{129} Vitruvius, \textit{De Architectura}, 7.5.
through the middle of the first century CE. 130 The “chief characteristic of the Third Style is that it rejected illusionism in favor of surface effects and fastidious ornament,” 131 in other words, it traded the windows and depth for scenes and figures with delicate artistic candelabra and columns (Figure 10). Egyptianizing images also begin to gain popularity in this style. The colors in Third Style become more elaborate, and end up making the architectural scenes more pattern-like than realistic. Yellow gains prominence in this style, used instead of and in greater quantity alongside the primary red, white, and black.

The Fourth Style is the last to be implemented in Pompeii and the Roman cities and villas on the Bay of Naples prior to the eruption of Mount Vesuvius, which lends to it being the most abundant in representation, as well as the most eclectic. 132 This style combines the depth and

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130 Ling, “The Third Style,” in Roman Painting, 52-70.
131 Ibid.
132 Ling, “The Fourth Style,” in Roman Painting, 71-100.
perspective scenery windows of the Second Style with the fantastic and “flimsy” architecture of the Third. Ling comments that the Fourth Style is the most “populated” in Pompeii, on account of the figures that appear outside of scenic boxes.

The color in the Fourth Style employs a single background color, over which panels of other backgrounds are placed, generally of the red, black, white, or yellow, though there are some exceptions, such as the early Fourth Style oecus in the House of the Menander at Pompeii, which is primarily green (Figure 12).

133 Ibid.

Figure 11: House of the Tragic Poet, Fourth Style. Photo Credit: Robert Caudill.
There are decoration types that both combine and transcend the Pompeiian Styles in both the Bay of Naples and the Roman world outside Campania. Movements of mythological and historical scenes, landscapes, portraits, and still-life art, as well as elaborate, lush green gardens (Figures 4 and 5) decorate some houses, indicate a certain preference outside the “fashion.” The colors in these range to suit the subject matter, though they tend to have more of the rare or
expensive colors, for they were the particularly impressive and smaller pieces of walls. These likely were less widely available by “wall-paper book” type selection or possibly from another book altogether. After the eruption in 79 CE, other stylistic movements continued to adapt and mature in other regions of the empire too, but these are less preserved.
A major problem for cultural heritage sites and archaeology as an academic field is the preservation of excavated materials. For every object found in the field, the material composition and site environment must be recorded and analyzed to provide the best treatment plan for preservation. Generally, factors like moisture, salts, and atmospheric pollution, among many others, have been identified as responsible for the deterioration of Roman wall paintings, though biological agencies, like fungi\textsuperscript{134} or other plant and animal species native to the environment surrounding an archaeological site, also pose a threat to the endurance of a wall painting. The unfortunate truth of the matter is that all these factors together are responsible for the alteration of materials at a chemical level, contributing to a failure in structure and eventual collapse, fading, or chipping away, advanced by carelessness in general human interaction, including, but not limited to: flash photography, touching, and dislodging pieces of this material to take with them as souvenirs\textsuperscript{135}.

Most damage has occurred since the unearthing of these sites in the eighteenth and nineteenth-century excavations, rather than in antiquity, though once color changes have occurred, it is difficult if not impossible to reverse it. Therefore, most damage must be prevented before it happens. Some damage occurred in antiquity, however, some by general wear-and-tear.


situations or simply by the impossible-to-avoid exposure to light. The ancient Romans knew this would damage the walls, as evidenced by Vitruvius' remarks in his discussion of vermilion, that “in open places, such as peristylia or exedrae, and similar situations whereto the rays of the sun and moon penetrate, the brilliancy of the color is destroyed by contact with them, and it becomes black.”\textsuperscript{136} The conservation methods applied to Roman wall paintings have ranged depending on era and intention,\textsuperscript{137} allowing for unpredictable biological and chemical effects. Vitruvius gives steps to an ancient technique, again in his discussion of vermilion in final coats of plastering:

...when the wall is colored and dry, rub it with a hard brush charged with Punic wax melted and tempered with oil: then, with live coals in an iron pan, the wall should be thoroughly heated, so as to melt the wax and make it lie even, and then rubbed with a candle and clean cloth, as they do marble statues. This practice is called καῦσις by the Greeks.\textsuperscript{138}

He continues by describing that the wax prevents the fading caused by exposure to the sun and moon.\textsuperscript{139} Punic Wax (partially saponified beeswax)\textsuperscript{140} was used as a sealant in antiquity, and reapplied in the early days of excavation to make the walls appear more vibrant,\textsuperscript{141} and the addition of these organics may have contributed to the modern growth of fungi and bacteria that damage the painting.

The growth of fungi is also propagated by conditions in the excavated city, thousands of

\textsuperscript{136} Vitruvius, \textit{De Architectura}, 7.9.
\textsuperscript{138} Vitruvius, \textit{De Architectura}, 7.9.
\textsuperscript{139} Ibid.
\textsuperscript{140} Hermann Kuhn, “Punic Wax,” \textit{Studies in Conservation}, 8, No. 3 (1963), 112-113.
Maguregui, “Thermodynamic and Spectroscopic Speciation to Explain the Blackening Process of Hematite Formed by Atmospheric SO\textsubscript{2} Impact,” 3319-3326.
years later. Particularly in the rainy season, mold growth is accentuated by the high relative humidity, but this may occur in any season with the proper nutrition and temperature. The Bay of Naples is prime for this condition, since the temperature is generally within the 20—35°C range and the nutrition required for fungal growth is inherently present in the pigments and organic binder. Pigments like limonite, hematite, and malachite, however, inhibit this sort of activity. But how do spores arrive at the site to begin with? The answer lies within the human population, since spores may reach the surface of otherwise protected paintings via the site visitors. Environmental pollution also contributes to fungal growth with the emission of hydrocarbons from nearby oil refineries and cellulose pulp plants, which may leave a layer of organic residue that the microorganisms may feed on.

Once grown, the fungus can cause the deterioration of the wall painting, which can manifest in several conditions: where the pigment loses its substrate and simply flakes away, craters, or blisters. Some species of fungus may also excrete enzymes capable of penetrating through the pigment and into the cementitious material, causing larger-scale structural failures. Certain secretions may also chemically react with the pigment, causing staining via the production of new pigments or even chemical reactions, wherein new minerals like whewellite and wedellite or salts are formed.

To control the fungal growth on wall-paintings the conditions which promote the growth of fungus must either be avoided or the species present must be removed. Research suggests that ventilation and climate control may help circumvent most growth by preventing the buildup of surface moisture, but these are factors that are too complex and costly for large, open-area sites.

143 Ibid.
144 Ibid.
like Pompeii. Hydrophobic material coatings have been suggested, but often avoided, since it may be counterproductive when the moisture is from the substrate itself. Epoxy resins were also considered to act as a dampness proof coating for walls. The majority of situations, however, are addressed once the growth has already begun, and is a challenge for conservators. Biocides (fungicides) are generally employed by injection, spray, or brushing, but sometimes these are ineffective and may produce negative side-effects, particularly if any portion of infected area is missed during treatment.\textsuperscript{145}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{House_of_the_Relief_of_Telephus_Herculaneum.jpg}
\caption{House of the Relief of Telephus, Herculaneum. Photo Credit: Robert Caudill.}
\end{figure}

\textsuperscript{145} Ibid.
Figure 14: House of the Menander. Photo Credit: Robert Caudill.
In the sites in the shadow of Mount Vesuvius, some colors used for wall paintings reacted to the gases present during the eruption of the volcanic mountain. Walls in Pompeii and Herculaneum, known for their bright “Pompeian red,” changed from their original yellow color during the eruption in a dehydration reaction\(^\text{146}\) (Figures 13 and 14). A study by Italy’s National Institute of Optics suggests that although currently “246 walls perceived as red, and 57 as yellow... the numbers must have been, respectively, 165 and 138.”\(^\text{147}\) Such color changes may not only change the way viewers perceive a painting, but also how academics and experts interpret it. The alteration of color, particularly in “tides,” can obscure and smudge important details in a mythological scene that may hinder its interpretation, in addition to the difficulties imposed by irreparable fading and environmental damage.

Some areas painted with cinnabar also underwent some physiochemical alterations. In this case, the red blackens (Figure 15), likely due to the presence of halogens in the volcanic gases, though it may also have been supplied by the nearby ancient shoreline or from the Punic Wax treatment which the Romans commonly prepared with seawater.\(^\text{148}\)

The Punic wax is prepared in the following manner: yellow [bees] wax is first blanched in the open air, after which it is boiled in water from the open sea, with the addition of some nitre. The flower of the wax, or, in other words, the whitest part of it, is then skimmed off with spoons, and poured into a vessel containing a little cold water. After this, it is again boiled in sea-water by itself, which done, the vessel is left to cool. When this operation has been three times repeated, the wax is left in the open air upon a mat of rushes, to dry in the light of the sun...\(^\text{149}\)

In either case, the chlorine acts either as a catalyst of the photochemical reaction or in the

\(^{146}\) A dehydration reaction of yellow ochre \((\text{Fe}_2\text{O}_3, n\text{H}_2\text{O})\) to red ochre \((\text{Fe}_2\text{O}_3)\) may have been initiated by the sheer heat of the pyroclastic mud flows. See Figures 13 and 14.


\(^{149}\) Pliny the Elder, Natural History: A Selection, 21.49.
formation of mercury-chloride compounds. Unfortunately, the effects of these chemical changes are irreversible, but the progression of fading and other changes can be prevented.

In the early days of excavation, other than polishing surfaces with beeswax, some restorations were attempted. Most of these utilized organic binders like egg or animal glue to reaffix or “touch up” areas of certain frescoes. Though well-intentioned, more recent scientific study discovered that modified areas tend to correlate to places where the pictorial surface is now flaking.

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150 Cotte, “Blackening of Pompeian Cinnabar Paintings: X-Ray Microspectroscopy Analysis,” 7490. Photochemical reactions also require light, so this process may be more explicative of the after-excavation damage. It is represented by the reaction: HgS → Hg + S; where the sulfur is released into the atmosphere.

Some houses were covered with ceramic roofs in the 1950s,\textsuperscript{152} which limits the pigment from being washed away by precipitation or by fading in direct sunlight. In the 1970s, some paintings were protected with transparent polycarbonate sheets or glass boxes. Microclimate analyses of these boxes show that they produce an unfavorable green-house effect that causes higher temperatures and humidity to be trapped within. In the House of Ariadne in Pompeii, some of these coverings were replaced by “undulating opaque red roof sheets made of fiber cement with a thickness of about 6 mm.”\textsuperscript{153}

In other cases, neglect to monitor the atmospheric conditions of these sites has allowed the wall paintings and their pigments to deteriorate. Hematite, a red color used on Pompeiian walls, like cinnabar, has blackened in the modern day due to traces of magnetite in the pigment that reacts with atmospheric sulfur dioxide.\textsuperscript{154} Gypsum forms from the calcite in the mortar during this process, only serving to make the painting more susceptible to rain damage and the washing away of pigment binder.\textsuperscript{155} Wherever calcium carbonate occurs in the plaster (where chalk may have been used or deposited), it may react with the sulfuric acid in the atmosphere, transforming it into more gypsum. And where a roof has not been added to a house, this expedites the loss of image.

Other issues include the pigeon population of the sites. The pigeon droppings are acidic enough to literally bleach the pigment. Furthermore, they have a habit of pecking at the

\textsuperscript{152} Merello, “Evaluation of Corrective Measures Implemented for the Preventive Conservation of Fresco Paintings,” 87-98.
\textsuperscript{153} Ibid.
\textsuperscript{155} Maguregui, “Thermodynamic and Spectroscopic Speciation to Explain the Blackening Process of Hematite Formed by Atmospheric SO\textsubscript{2} Impact: The Case of Marcus Lucretius House (Pompeii),” 3319-3326.
carbonized wood of doors and furniture found in Herculaneum. Both issues are being controlled by simply employing hawks to scare them away, rather than with a technological solution.\textsuperscript{156}

In a renewed effort to preserve Pompeii and the surrounding sites, in the past two years, the frescoes of the Villa of the Mysteries have been cleaned and conserved in a multi-million dollar project.\textsuperscript{157} This conservation effort utilized a full repertoire of analyses and introduced careful repairs to maintain the site. Conservators studied the walls beneath the paintings using a combination of ultrasounds, thermography, and radar to monitor the decay and inject mortar where necessary.\textsuperscript{158} Changes in the frescoes were also noted with these techniques, and after thorough documentation, they were cleaned using lasers, which removes the grime quickly and effectively without altering the pigments.\textsuperscript{159}

Modern preventive conservation uses scientific analysis and microclimate studies to make tailored solutions for each individual painting, a process which, although moderately successful, is labor-intensive and time-consuming, requiring several years of data collection before implementation, and many studies acknowledge the need for further study and better, more long-term solutions.\textsuperscript{160} The ideal solution would be larger in scale, adaptable for micro-climate conditions, but standardized and inexpensive enough to be implemented on a larger scale.


\textsuperscript{157} Lobell, “Saving the Villa of the Mysteries.”
\textsuperscript{158} Ibid.
\textsuperscript{159} Ibid.
\textsuperscript{160} Merello, “Evaluation of Corrective Measures Implemented for the Preventive Conservation of Fresco Paintings,” 87-98.
Chapter 4: Case Study of Wall Painting Fragments

Figure 16: The four fragments of the case study. Photo Credit: Author.
4.1 Introduction

To accompany the working catalog of pigments and discuss their use in context, several fragments of wall paintings were analyzed by scientific methodology. This was done to determine the pigments used on them and glean information about the technology used to create them, leading to an understanding of the materials, as well as characterize the context which they may have come from through a discussion of relative quality and apparent expense.

The pieces chosen for this study (Figure 16) were primarily constricted by availability. Even fragmentary wall paintings are not – and should not - be allowed to be taken from sites without permission and proper accommodation. These fragments were obtained before the formal regulations of modern antiquities laws, and though little documentation if any support their provenance, they are all most certainly Roman and likely from the Bay of Naples. Those from Jennifer Stern's private collection were taken by a family in the 1930s, and have changed hands several times through the dealers in the art market.161 The secondary consideration was given to the purpose of this study – the identification and characterization of pigments and their backing for use in the conservation efforts of the sites on the Bay of Naples buried in the 79 CE eruption of Mount Vesuvius. With this, the widest range of color was selected, with consideration of the sample size required for each analytical technique.

4.2 Methodology

The study began with an optical analysis and scan of the object under ultraviolet (UV) light with a Mineral Light Lamp UVGL-55, Multiband UV-254 366 NM. This is the least

161 Though further investigation is needed, the current documentation suggests the original owners were the Swiss Jaeger family, who took the pieces from Pompeii.
technologically involved of the scientific trials used to characterize the materials of the fragment, but possibly the most important. A visual observation may inform and influence the subsequent studies to obtain the most relevant data with the highest efficiency. Studying the objects under blacklight helps identify several features – layers, details that have been faded or obscured, differences in the pigments and other materials, and potential restorations.\textsuperscript{162}

Using a Bruker Tracer III-SD Portable XRF (pXRF), the surface's metallic composition was revealed, lending to the analysis and identification of the source material.\textsuperscript{163} With enough sample points, an XRF analysis may also reveal faded details or images on the fragment, if they exist,\textsuperscript{164} though this study was limited in the attempt to simply identify each visible pigment with the portable XRF device, rather than the full-size machine, which may scan artifacts and artworks. Since this analysis gives elemental results, limited to those larger than potassium (K) there is little to no differentiation between smaller elements that would make up metallic ligands, and therefore distinguish between similar mineralogical formations, like that between different iron oxidation states (hematite vs yellow ochre, for example) or between copper-based minerals like lapis lazuli (lazurite) and azurite. The XRF analysis is based solely on an internal, sample-specific measurement of elemental abundance, which may fail to distinguish between details and comparative samples. By comparing the paints to that of the analyzed base material and the

\textsuperscript{162} For additional images for each fragment and a summary of upcoming results, see the Lab Reports in Appendix A.
ratios of elements between samples, however, background noise and wall components can be factored out, allowing for the identification of unusual or key metallic elements.\textsuperscript{165}

An Attenuated Total Reflection (ATR) - Fourier Transform Infrared Spectroscopy (FT-IR) study was conducted using a Nicolet – IR 200, FT-IR machine with a diamond crystal to help decrease the uncertainty of the XRF analysis by illuminating the molecular structures of the pigments, the technique requires small samples to be scraped from the object to be placed directly onto the instrument.\textsuperscript{166} The direct analysis removes the need to dissolve and/or derivatize a sample in order to get clean readings, which is a step in developing a cost-effective portable device for direct use in archaeological contexts. The FT-IR functions by measuring how much a specific sample absorbs light in the visible and ultraviolet range (UV-Vis), which is characteristic of particular molecules, depending on their structure and intramolecular movement frequencies. The FT-IR cannot distinguish all pigments, however, due to limitations in the wavelength detection ranges, especially in the “lower” (400-600 nm) range.

Finally, using the remaining sample taken for the FT-IR analysis, a Gas Chromatography-Mass Spectrometry sample was made of each color analyzed, as well as the plaster layers.\textsuperscript{167} These were extracted using the ARCHEM protocol for organic residues\textsuperscript{168} and analyzed with an Agilent 7890A GC with a HP-5MS column and a 5975C VL MSD Triple Axis Detector over a 28 minute method. The GC-MS allows for an identification of any organic/plant-based pigments or

\textsuperscript{165} For resulting pXRF spectra and a table summarizing the numerical data, see Appendix B.
\textsuperscript{166} Due to the limitations of available equipment, samples were scraped off the edges to preserve the integrity of the fragments and may include plaster.
\textsuperscript{167} See Appendix C for FT-IR Absorbance Spectra.
\textsuperscript{168} More details about the ARCHEM method can be found in the article about the Tel Kabri wine cellar analysis (below), among others.

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components. This is of particular interest in the more colorful of plaster layers, which may indicate an inclusion of madder dye. Further study of madder dye may illuminate other beneficial effects, though it is most likely to be a luxurious cosmetic addition.

4.3 Fragment Studies

4.3.1 CLARC Fragment (Anonymous Donor, Private Collection Loan)

The fragment exists as an irregular shape, probably knocked off the wall and shattered in antiquity, from the eruption of Mount Vesuvius in 79 C.E. or during one of the earthquakes prior to the disaster. The paint layer is mounted on a creamy, almost pink colored plaster, over a single, somewhat thick layer of deep grey cement with smaller, rocky inclusions. The “top” of the piece is a tan-yellow, with darker, brown and yellow stripes. In this yellow field, a lighter-colored (white) triangle points upward. Several black spots of uncertain material dot this area, though they could not be sampled by any method due to their size and location. The next stripe is a brown-gold, with a curved, fang-like projection to the right, accompanying five curved projections of the tan color, slightly embossed with lighter paints. Below this, the fragment is painted in a gradient of swaths from red to pink. In the pink field, darker red points act as shadows to the gold projections. The darker region of red hosts the yellow projections and hints at a similar feature that continues on an adjoining fragment. A lighter region of the red indicates scraping damage, from the ancient disaster or potentially excavation. Fading indicates potential brush strokes to proceed laterally across the length of each color. Although the features are unidentifiable, it is possible that the yellow is part of some architectural shape or border, suggesting that it is from a later style.
Screening of the piece on loan to the CLARC determined the sample sites of varying color to be large enough for detection, though the accuracy of reading smaller points was inhibited by the pXRF device's safety procedures. Yellow-tan, the brown and yellow stripes, the white triangle, yellow projection, gold projection, red (upper and lower), red projection, and pink were sampled by pXRF in addition to the cement and plaster layers. Not all of these could be sampled for FT-IR analysis in order to protect the integrity of the piece, but the primary colors: yellow-tan, the yellow stripe, gold, red, and pink were analyzed by both FT-IR and GC-MS.

Calcium (Ca) and iron (Fe) were the primary elements of every sample, where lighter colors generally had a higher abundance of calcium. The cement layer had high levels of calcium, with negligible sulfur, suggesting that the base material was lime, rather than gypsum, and perhaps pozzolana-type cement, on account of the higher aluminum (Al) and silicon (Si) content.

The lighter colors appear to share a common ferrous base. The tan-yellow color, despite a large inclusion of copper, appears to be a type of yellow ochre or mixed orpiment. The stripe also indicates this, though the detector may have missed the intended analysis spot or confused signals between the two colors (yellow and brown). If the two colors combined produced the results, this speaks to the nature of the yellow as well, since the yellow could be a mixture of pigments. The white triangle has the least diagnostic results, potentially as a result of instrument bumping or otherwise obscured due to degradation over time and blending with the tan-yellow. It is composed of calcium, which would allow for an interpretation of chalk (calcium carbonate), though the amount of lead may allow for white lead, it has the most significant amount of strontium, potentially indicating celestite, a white mineral. The gold-brown appears to be a raw
umber (combination of iron and manganese oxides), though it may also be a sienna (MnO, Fe(III)) derivative, based on the presence of manganese (Mn) and higher iron content. Lead (Pb) and zinc (Zn) are also notable in the gold-brown sample.

Initially, three types of red seem to have composed the painting. The upper red point appears faded, and so it was sampled separately. It has high lead and iron readings, possibly indicating a red lead and hematite mix. The lower red sample is compositionally identical, and both have a trace amount of mercury (Hg). It may also be interpreted as a blending between the red lead and cinnabar from the pink sample. The pink sample is cinnabar (HgS) lightened with a white lead or calcium-base, as indicated by its relatively high abundances of both mercury and sulfur.

A closer look at the painting and further research led to another explanation of the red pigments. An isotope study of lead in cinnabar from Roman wall paintings observes that most samples of cinnabar contained at least trace amounts of lead and occasionally iron.\textsuperscript{169} The presence of iron in the sample could indicate an undercoat of some kind to prevent the blackening of the pigment, which does not appear to be a problem on this section of the piece, though it may explain the dark spots in the red, which appears to be painted over the same pink color. It is interesting to note that the faded section (with the most blackened spots) appears to have a yellow undercoat as well, in which case, the blackening may be attributed to the yellow ochre. Yellow ochre may have transformed into hematite during the eruption to create the darker red color and further, blackened due to the formation of magnetite, caused by a reaction with calcite (which may explain the red gradient's lower calcium content).\textsuperscript{170} Without careful sampling

\textsuperscript{170} Maguregui, “Thermodynamic and Spectroscopic Speciation to Explain the Blackening Process of Hematite Formed by Atmospheric SO\textsubscript{2} Impact,” 3319-3326.

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of the black spots and further analyses, such a reaction remains conjecture, but cannot be
discounted, and therefore, it is possible that the red section is not naturally red ochre (hematite),
but was once a combination of cinnabar and yellow ochre. This does not explain why the angled
projection remains yellow, except to further the argument for a mixture of pigments and an
undercoat of paint throughout the fragment.

Assuming accurate analysis, the wall painting this belonged to would have had
significant value in antiquity, particularly if the colors represented on this fragment continued for
any significant length of wall-space. The cinnabar, in particular, has a fixed price of seventy
sesterces per pound to protect the price from inflation.\(^\text{171}\) The smoothed quality of the pigments
suggest this piece was from a more wealthy establishment, likely a villa outside the walls of the
Roman towns of the Bay of Naples. These villas belonged to the wealthiest of Romans and
usually housed some sort of agricultural activity, like wine-pressing,\(^\text{172}\) wherein the patron's
clients would be exposed to greater displays of wealth than the cities could house. Furthermore,
many villas were built with multiple, large triclinia for parties, and this fragment of the
decoration, no matter how obscure, shows the care and quality put into every detail of the wall
painting in these spaces.

Its preservation speaks of the way it was handled, in antiquity and in the modern day.
Despite the light scraping damage, the pigments are still vibrant and almost creamy, though the
lines between them remain straight and crisp in comparison to the other fragments, which are
encrusted with dirt and possible products of chemical reaction. This suggests that the CLARC
fragment was not exposed to the same amount of light in its original location, and therefore it did

\(^{171}\) Pliny the Elder, *Natural History: A Selection*, 303-304.
\(^{172}\) The Villa of the Mysteries, for example, has the remains of a room used for wine-pressing and features a
reconstruction of the actual press.
not fade, nor was it protected with a wax coating that may have otherwise promoted fungal growth and distortion. The piece is likely from higher up on a wall or in a more interior room, and therefore unaffected by the eruption's debris.

4.3.2 Architectural Fragment (Jennifer Stern, Private Collection Loan)

This fragment is also irregular in shape, though the image on it distinguishes it from the others. The paint layer is mounted on thick layer of grey-white cement and a creamier plaster. At closer look, there seems to be three layers here, obscured in a gradient between the bottom of the cement and the plaster layer. This middle layer seems a little whiter than the plaster and bottom, which has several large granule size inclusions, and smoothed-out groves on the reverse face, mostly in-line with the painted column. These are likely part of the herring-bone plaster patterning to affix the fresco to the wall.

The painting is composed of a single shade of blue and two reds, light and dark, all covered with an encrustation. The blue is particularly affected – dulled beneath the rough texture, which is possibly indicative of surface reaction. The reds appear more vibrant and smooth. The primary color of the apparent column is the lighter, pinkish red, which appears to be painted over a creamier base. The dark red is painted directly over both of these, used for detail to create the shadowing separation between pieces of the capital. The column itself is simple, possibly Doric or Tuscan, though the piece may show the foot of the column, rather than the capital. There is a distinct separation between this image and the blue background, in the form of another dark red stripe, that may be another shadow, though the encrustation makes this boundary more pronounced.
All the major colors here were sampled for all parts of the analysis. For the pXRF tests, two readings were taken from each color to account for the distortion by encrustation, which is particularly significant on the blue pigment. The cement and plaster were sampled in addition to the dark red, light and almost pink red, and sky blue.

Again, the cement and plaster layers were primarily made of calcium and iron, though this seemed to vary depending on where the sample point was taken. On the ridge of the cement, there was a stronger reading for both elements. Though samples points are only relatively comparable, again the plaster had more calcium than iron. The cement here, however, did not have an elevated level of aluminosilicates or sulfur, suggesting that the material was the older, lime mortar technique.

Both reds in the column exhibited the mercury and sulfur indicative of cinnabar. The darker red seems to have been tempered by hematite, and both have some inclusion of lead, which again may be a natural trace element found with the cinnabar and unseparated during processing.

The blue that offset the architectural image suggests sky and has the color to match. It is primarily composed of a copper silicate, which is not initially identifiable. With the FT-IR analysis and database comparison, this proved to be azurite, the less expensive of the mineral blues, though still considerable in comparison to locally-synthesized Pompeiiian or Egyptian blue. This is not uncommon, however, since the blue here may be part of a larger background that may have continued for a significant amount of space. The sheer use of blue suggests wealth for any length of image, regardless of the source material, since most of the mineralogical

sources of the color must be imported from the far eastern reaches of the Roman empire, near present-day Afghanistan. There are no traces of green, but the possibility remains for this fragment to be a clear corner of a garden or mythological scene, since blue generally accompanies naturalistic images, such as water or sky.  

The condition of the cinnabar red suggests that the Architectural Fragment, like the CLARC fragment, was housed indoors and away from direct sunlight. Though the exact textural quality of the fragment is obscured by the layer of dirt and encrustation, no cinnabar blackening is visible. This piece has been affected by some sort of reaction at the surface level, particularly on the blue-painted region of the fragment. Although some crust material may be partially explained by the untampered nature of the collection and lack of thorough museum-quality cleaning, the rough surface of the blue region is likely due to the composition of the backing material, which may have formed gypsum at the surface in reaction with the atmosphere and ambient moisture before it was taken out of its context and placed into a private collection. Since the blue area appears raised, it is particularly affected by this chemical change, suggesting that a component of the pigment may have contributed to it. Though the FT-IR analysis suggests the pigment is azurite blue ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), the azurite may be oxidized under certain conditions to form malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) which ranges from deep to chalky green, but owing to the lighter-blue color of the raised area, further oxidation may have occurred to produce spertiniite ($\text{Cu}($OH$)_{2}$$), which is theorized to be a part of chrysocolla ($\text{Cu},\text{Al}_{2}\text{H}_2\text{Si}_2\text{O}_5($OH$)_{4}\cdot n\text{H}_2\text{O}$). The trace elements indicated by pXRF may support this blend with indications of higher aluminum.

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174 For an example of each, as mentioned earlier, the House of Venus in the Shell's namesake is surrounded by a large expanse of blue. The House of the Golden Bracelet's garden sports a similar backdrop.

175 Water helps to drive the reaction from azurite to malachite:

$$2 \text{Cu}_3(\text{CO}_3)_2(\text{OH})_2 + \text{H}_2\text{O} \rightarrow 3 \text{Cu}_2(\text{CO}_3)(\text{OH})_2 + \text{CO}_2$$
and silicon content than the red region, though these minerals often occur together naturally.

4.3.3 Stripes Fragment (Jennifer Stern, Private Collection Loan)

The stripes fragment is primarily triangular in shape, and like the previous columnar fragment, this piece is thick, consisting of grey-white cement layers with a creamier plaster layer beneath the pigment. The backing appears to be in four layers here, where the plaster sits atop two off-white layers of cement, almost identical, but separated by lines, indicating an intentional smoothing process. The bottom cement is more creamy brown, with larger inclusions, mostly white, like chalk. This layer preserves one ridge, a patterning again like the previous fragment, to affix it to the wall, which runs perpendicular to the painted stripes. This seems to suggest the plaster was supported with a cross-hatching pattern on the wall, since the stripes are likely the edge of or between panels from what could be any Pompeiiian style, with the end colors constituting the background color. The fact that the final backing layer appears to be of a different material may suggest that it was part of a later repair, or otherwise an intentionally chosen material.

The pigment stripes include a large swath of peach or mixed yellow, followed by a black or darker blue, and a deep red, over which a small portion of sky-colored blue is painted at the tip of the fragment. This piece is also covered in encrustation, though of a lighter nature than that on the Architectural Fragment. Here too, the blue is particularly effected, though less texturized. All the colors seem to have been painted in the same direction with crisp lines between the colors.

Again, all the colors of the striped fragment were sampled, including the cement and
plaster layers – peach, black, red, and blue. The visible red stripe was too small to access for FT-IR sampling, though it appears to be an undercoat for the blue.

The cementitious material of the Stripes Fragment, though it contains more silicon, is still likely lime mortar, due to the lack of aluminum. A further analysis of the different layers of material might clarify this, but by the brown hue of the ridged base of the fragment in comparison to the grey-white between it and the plaster, this bottom layer of cement may be composed with river sand, since higher amounts of silicon generally correspond to material found nearby bodies of water, and the sodium (Na) is not concentrated enough to suggest Mediterranean salt.

Of these colors, the peach was the most difficult to identify, and requires further investigation. Under FT-IR scrutiny, it appears to be a muddled Naples Yellow, though the pXRF could not make any further conclusion, possibly due to red underpainting. The peach is a standard mixture of each element examined, primarily calcium, iron, and a slightly elevated copper, though this is not inherently diagnostic. The black, which has a dark blue or purple hue, did not have a lot of copper or iron. GC-MS analysis did not detect any specific organics in the sample, but the FT-IR scan matched database examples for bone black. Further examination of the pigment for traces of light elements may confirm this further. Bone black was produced by charring bones, usually of animals. This was a rather inexpensive, but generic way to produce a rich, dark color. The red stripe and underpainting had a slightly elevated amount of mercury, though not as strongly as the other cinnabar samples. It also had a small amount of lead, but the main component of this color is the iron, which indicates hematite or red ochre. The blue, which sits atop it, had the same elevation in iron content, though it also had more copper and silicon,
like the azurite from the previous fragment. The FT-IR does not match the background color of the Architectural Fragment, however, and loosely matches database examples for Egyptian Blue. Both the red and blue had a larger trace amount of arsenic (As).

Due to where this fragment is broken, it is hard to tell what the stripes or borders actually composed on a wall, and therefore, it is difficult to get a sense of its context. It seems to be the edge of panels, likely Third or Fourth Style, on account of the larger use of yellow. The underpainting of the dark red is interesting in this case, since both the black and blue colors were added to it without blending. The upper half of the black appears to be painted over the yellow as well. The use of undercoat-layers of pigment on this fragment explains why the 'Naples Yellow' is more of a peachy hue, as well as the difference in the black. It is possible that the multi-coat style was used in order to straighten the lines between the colors or purposefully achieve the difference in color as more of a 'wash' than a traditional fresco.

**4.3.4 Floral Motif Fragment (Jennifer Stern, Private Collection Loan)**

Smaller than the other two from the Jennifer Stern Collection, this fragment is almost rectangular, and much thinner, as if it were separated from the majority of its cement backing. The plaster layer is creamy and almost pink, though the color may be influenced by its pigment decoration. The cement remaining is also a warmer color than the last two examples, though it appears mostly grey. It has several granule inclusions, some pink, others almost black. It is rough, though there appears to be a streak of resin or glue, possibly from an undocumented repair from the initial owners.

The deep red backdrop paint here is worn down, as if scraped, following the contour of
the floral motif across the shorter diagonal of the fragment. The plant detail is a light and almost chalky green, painted translucently across the red. It has extended leaves or fronds, darker and wider on one side of the image than the other. The center is worn away on one side, and encrusted on the other, though the wear may be from an attempt to remove this. The red area has no encrustation, and on account of the scraping-like wear that exposes the plaster beneath the pigment, suggesting that it has possibly been cleaned. It still retains some areas of glossy sheen in the places where the paint is thickest.

In the Floral Motif Fragment, the back was sampled twice for pXRF analysis, once in an area with rough grey cement, and the other in a place that may have been more plaster-based material. A strip of glue in this region suggests that the rest of the plaster had been removed along with the wall fragment, but probably came loose until it fell away completely. Though a non-professional likely glued it, the fix was only temporary and the wall backing was likely lost or discarded. The plaster appears a bit more creamy pink than the other two, though not to the same extent as the CLARC fragment. The colors were sampled several times to attempt to account for variations in gloss and texture, since the green pigment is heavily encrusted.

The red on the Floral Motif Fragment is simply iron-based, indicating red ochre. The green color was harder to identify, possibly because of the encrustation. It had a relatively high level of iron, though this may be a false reading on account of the red, which the green seems to have been painted over as a second layer, thin and possibly with binder. The green had a small reading of arsenic, but this is non-diagnostic. The FT-IR data was generally inconclusive and requires more examination, but it appears similar to celadonite or malachite. The grey-green shade of the color suggests it should be celadonite.
This fragment is a good example of the 'average' domus wall painting in the Bay of Naples, with the red which the painted cities of Vesuvius are known for. The green floral motif is likely a garland or small offshoot of one,176 indicating the Third or Fourth Style of wall painting. Images like this were meant to imitate the real thing, usually nearby the peristyle garden, where the real counterparts would normally hang. Presumably, these were hung around the Roman house to counteract the smell from the street, latrines, and any animals in the residence. The pigment quality is well-preserved, and suggests a thick, glossy application, potentially tempered with wax. Like the blue in the Architectural Fragment, the green of the Floral Motif is heavily encrusted, as if it reacted at the surface, specifically at that color. Although the red appears unaffected, this may be on account of a substance like Pliny's Punic Wax, which may have caused the metallic component in the green pigment to recombine and form by-products. The mechanism at which this occurred cannot be determined without further study of the mass in general.

4.4 General Discussion and Future Study

The four fragments in this study unintentionally represent a survey of wall qualities from the highest quality decoration of an elite's villa to that of the 'average' wealthy Roman domus on the Bay of Naples. Though the fragments are not diagnostic in their images or colors in order to give a larger or more specific sense of the walls they belonged to, the complexity of their pigments lends to the understanding that the study and preservation of these wall paintings is not a simple matter.

176 Like in the Villa at Boscoreale, where the garland is particularly full, small offshoots compose the length of the image, rather than a single strand of leaves.
XRF was the most valuable tool in this analysis, since in most cases, it identified a
elevation in a specific element or a presence of a trace element that could be considered
diagnostic. When this failed, the FT-IR could usually clarify at least a potential match, although
the FT-IR alone could not have identified these pigments, though this ambiguity may have been
exasperated by the exclusion of the low (400-600 nm) wavelength range. Despite the availability
of good database comparisons, every condition changes the result enough to make analysis
difficult. In many cases, the FT-IR spectra of the standards only matched parts of the samples,
which indicates that the samples certainly included some of the plaster layer and perhaps
materials from coatings and/or underpainting that obscured the intended analyte. Generally, FT-
IR is paired with Raman Spectroscopy, since some pigments can only be identified by one
technique and not the other.

The GC-MS analysis produced no viable results of organic pigments for any of the
fragments. This may suggest that they are all mineral based and therefore not necessarily in the
detection range of the instrument, which requires samples to be volatilized.177 If there are
undetected organic components present, it clarifies that the ARCHEM organic residue analysis
(ORA) method is not directly applicable to the study of dyes and pigments within a cementitious
matrix. This is somewhat established, since there has been little to no success in extracting
organic residues from stone, glass, or similarly textured vessels. Other chemical methods have
extracted pigment from wall paintings for analysis, but these usually require more extensive
chemical workup using solutions and equipment that are not readily available to the average
archaeologist,178 especially in the field. Further analytical development is required to continue

177 Some heavier metallic compounds cannot evaporate even at the max temperature of the oven, which would
inhibit detection.
this research. No madder dye was detected in the plaster layer of the CLARC fragment, which has a rosy appearance indicative of the dye, though this too, may be an issue with the volatilization of the plaster-bound colorant.

In addition to the development of an appropriate extraction method for dye and pigment analysis by GC-MS, other techniques are available that would further the study of these fragments, as well as others. Raman spectroscopy, though unavailable for this particular analysis, is the method generally paired with FT-IR for the identification of pigments. Raman, like GC-MS can “fingerprint” a molecule, though Raman analyzes the molecule-specific vibrations and intramolecular movement (frequency), instead of molecular weight. It provides data similar to that of the FT-IR, though it is used complementarily because Raman measures the energy of this activity instead of the UV-Visual absorbance, which may be used together to distinguish compounds that may only be identifiable by one of the two techniques (such as vermilion). Raman may also be used in conjunction with a microscope, allowing for the accurate identification of specific samples.

A thin-section analysis would be able to reveal more details about the technology involved in creating the paintings that these fragments belonged to, however, such a technique is considerably more invasive and destructive, requiring a slice to be taken from the sample and ground down in preparation of a thin-section slide. This would provide more details about the different compositions of the cement layers and their “firing technique” (or lack thereof, in this case, though it may illuminate technological issues like drying times).
Chapter 5: Conclusion

This study, though in no measure comprehensive or final, should lend to future research and preservation efforts of archaeological sites, with particular interest in the sites on the Bay of Naples like Pompeii and Herculaneum, both of which are invaluable to the cultural history of the entire world, as well as modern understanding of daily life in ancient Roman times. With proper analysis and preservation, they could survive to function as time capsules for future study, but without proper awareness, these sites may be easily be lost to the decay of several millennia.

Due to the private ownership of the particular fragments described in the case study, they have been greatly preserved by their exclusion from the elements which they may have been exposed to in situ at sites on the Bay of Naples. Like museums, well-cared-for private collections serve to protect these samples for viewing, and though they are not accessible to the general public, small pieces like these are invaluable to the study of wall paintings in a more original state, allowing for the identification and thorough characterization of the materials in hopes for the invention and implementation of a viable, long-term solution for all the wall paintings decorating the painted cities of Vesuvius.
APPENDIX A:

Lab Reports

CLARC Fragment
Architectural Fragment
Stripes Fragment
Floral Motif Fragment
Title: Fragment of Wall Painting

On Loan From: Anonymous Donor to CLARC

Provenience/Provenance: a Villa on the Bay of Naples

Size (at greatest length x width x depth): 9.2 x 5.7 x 2.2 cm

Shape: Irregular

Painting Description: Fine, with several undercoats

Backing Description: Dark, porous grey cement with volcanic inclusions, possibly pozzalonic

Colors: Yellow-tan, Yellow, Brown, Gold, White/Cream, Red, Pink

Condition: No encrustation, light fading/scraping (likely from falling off original wall)

Analyses:
  UV: all
  pXRF: all
  FT-IR: Plaster, Yellow-Tan, Yellow Stripe, Gold, Red, Pink
  GC-MS: Plaster, Yellow-Tan, Yellow Stripe, Gold, Red, Pink
Results Summary:

Figure 17: Image of CLARC Fragment with sample numbers (Table 1). Photo Credit: Author.

<table>
<thead>
<tr>
<th>XRF Element</th>
<th>Cement</th>
<th>Plaster</th>
<th>Yellow-Tan (1)</th>
<th>White Triangle (2)</th>
<th>Gold Projection (3)</th>
<th>Red (4)</th>
<th>Red Projection (5)</th>
<th>Prk (6)</th>
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<td>167</td>
<td>725</td>
<td>401</td>
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<td>409</td>
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<td>331618</td>
<td>460571</td>
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</tr>
</tbody>
</table>

FT-IR Spectra Match: NA
Used as "standard": Orpiment
Red Lead does not show on FTIR: NA
Cinnabar does not show on FTIR: NA

GC-MS Results: NA

Final Interpretation: Pozzolanic Cement
No Madder Dye?
Yellow Ochre
Mixed, possibly Celestite
Raw Limber?
Red Ochre
Red Lead Mix
Cinnabar Mix
Cinnabar with white lead
Figure 18: Image of CLARC Fragment with scale. Photo Credit: Author.
Figure 19: Image of CLARC Fragment backing. Photo Credit: Author.

Figure 20: Image of CLARC Fragment layers. Photo Credit: Author.

Figure 21: Image of CLARC Fragment layers, angled. Photo Credit: Author.

Figure 22: Image of CLARC Fragment during pXRF analysis. Photo Credit: Author.
Figure 23: Blacklight analysis of the CLARC Fragment, pigments. Photo Credit: Author.

Figure 24: Blacklight analysis of the CLARC Fragment, layers. Photo Credit: Author.

Figure 25: Blacklight analysis of the CLARC Fragment, backing. Photo Credit: Author.
Title: Architectural Fragment

On Loan From: Jennifer Stern, Private Collection

Provenience/Provenance: Obtained from the Bay of Naples in the 1930s by the Jaeger(?) Family, sold by dealers on the art market thereafter

Size (at greatest length x width x depth): 11.5 x 7.3 x 3.8 cm

Shape: Irregular v-shape

Painting Description: Smooth

Backing Description: Thick, grey-white cement with large inclusions, herring-bone pattern grooves

Colors: Dark Red, Light Red, Blue

Condition: Heavy encrustation on the blue pigment; mild on the red

Analyses:
  UV: all
  pXRF: all
  FT-IR: Dark Red, Light Red, Blue
  GC-MS: Dark Red, Light Red, Blue
Figure 26: Image of Architectural Fragment with sample numbers (Table 2). Photo Credit: Author.

<table>
<thead>
<tr>
<th>XRF Element</th>
<th>Cement</th>
<th>Cement B - Ridge</th>
<th>Plaster</th>
<th>Dark Red (1)</th>
<th>Light Red (2)</th>
<th>Blue (3)</th>
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<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>FT-IR Spectra Match</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Cinnabar/Red Lead does not show on FTIR</td>
<td>Cinnabar/Red Lead does not show on FTIR</td>
<td>Azurite</td>
</tr>
<tr>
<td>GC-MS Results</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Final Interpretation</td>
<td>Lime Cement</td>
<td>Lime Cement, different</td>
<td>Nb Madder Dye</td>
<td>Cinnabar, possibly with Red Lead and/or Ochre</td>
<td>Cinnabar, possibly with Red Lead</td>
<td>Azurite</td>
</tr>
</tbody>
</table>
Additional Images:

Figure 27: Image of Architectural Fragment with scale. Photo Credit: Author.
Figure 28: Image of Architectural Fragment, backing. Photo Credit: Author.

Figure 29: Image of Architectural Fragment, layers. Photo Credit: Author.
Figure 30: Blacklight analysis of Architectural Fragment, pigment. Photo Credit: Author.

Figure 31: Blacklight analysis of Architectural Fragment, backing. Photo Credit: Author.

Figure 32: Blacklight analysis of Architectural Fragment, layers. Photo Credit: Author.
**Stripes Fragment**

Title: Stripes Fragment

On Loan From: Jennifer Stern, Private Collection

Provenience/Provenance: Obtained from the Bay of Naples in the 1930s by the Jaeger(?) Family, sold by dealers on the art market thereafter

Size (at greatest length x width x depth): 8.8 x 6.9 x 4.0 cm

Shape: Irregular triangle

Painting Description: Slightly grainy

Backing Description: Thick, grey-white cement; brown-grey cement; both with inclusions, evidence of ridges

Colors: Peach, Black, Dark Red, Blue

Condition: No encrustation or fading, except in blue pigment

Analyses:

UV: all
pXRF: all
FT-IR: Peach, Black Blue
GC-MS: Peach, Black, Blue
Figure 33: Image of Stripes Fragment, with sample numbers (Table 3).

<table>
<thead>
<tr>
<th>XRF Element</th>
<th>Cement</th>
<th>Plaster</th>
<th>Peach (1)</th>
<th>Black (2)</th>
<th>Red Stripe (3)</th>
<th>Blue (4)</th>
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<td>78756</td>
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<td>1</td>
<td>1</td>
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</tbody>
</table>

FT-IR Spectra
- Match: NA
- GC-MS Results: NA
- Final Interpretation: Lime Cement

Egyptian Blue
Additional Images:

Figure 34: Image of Stripes Fragment with scale. Photo Credit: Author.
Figure 35: Image of Stripes Fragment, backing. Photo Credit: Author.

Figure 36: Image of Stripes Fragment, layers. Photo Credit: Author.
Figure 37: Blacklight analysis of Stripes Fragment, pigments. Photo Credit: Author.

Figure 38: Blacklight analysis of Stripes Fragment, backing. Photo Credit: Author.
Floral Motif Fragment

Title: Floral Motif Fragment

On Loan From: Jennifer Stern, Private Collection

Provenience/Provenance: Obtained from the Bay of Naples in the 1930s by the Jaeger(?) Family, sold by dealers on the art market thereafter

Size (at greatest length x width x depth): 7.5 x 6.0 x 1.1 cm

Shape: Irregular rectangular

Painting Description: Arched, green overpainting

Backing Description: Thin layer of grey-pink cement with inclusions, evidence of glue

Colors: Red, Green

Condition: Encrustation on green pigment, some missing; scraping in red pigment

Analyses:
UV: all
pXRF: all
FT-IR: Red, Green
GC-MS: Red, Green
Figure 39: Image of Floral Motif Fragment, with sample numbers (Table 4). Photo Credit: Author.

<table>
<thead>
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<th>XRF Element</th>
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<th>Red (1)</th>
<th>Green (2)</th>
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</table>

FT-IR Spectra Match: NA, NA, Ultramarine Red?, Celadonite or Malachite

GC-MS Results: NA, NA, -

Final Interpretation: Not enough data, No Madder Dye, Red Ochre, Celadonite or Malachite
Additional Images:

*Figure 40: Image of Floral Motif Fragment, with scale. Photo Credit: Author.*
Figure 41: Image of Floral Motif Fragment, backing. Photo Credit: Author.

Figure 42: Image of Floral Motif Fragment, layers. Photo Credit: Author.
Figure 43: Blacklight analysis of Floral Motif Fragment, pigments. Photo Credit: Author.
APPENDIX B:

*pXRF Spectra and Raw Data*

CLARC Fragment Samples

Architectural Fragment Samples

Stripes Fragment Samples

Floral Motif Fragment Samples

*pXRF Sample Summary*
CLARC Fragment

Cement

Plaster
Pink
Architectural Fragment

Cement

Cement B – Ridge
Stripes Fragment

Back – Cement

Side – Plaster?
Blue

Red Stripe

102
<table>
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<tr>
<th>pXRF Sample Summary</th>
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<tbody>
<tr>
<td><strong>CLABR Loan</strong></td>
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<td>Gold Projection</td>
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<td></td>
</tr>
<tr>
<td>Red Upper</td>
</tr>
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<td></td>
</tr>
<tr>
<td>Red Lower</td>
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<td></td>
</tr>
<tr>
<td>Red Projection</td>
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<td>Pink</td>
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<td>JS Loan - Stripes</td>
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<td>JS Loan - Column</td>
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</table>

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</thead>
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</tr>
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<td><strong>Cement B - Ridge</strong></td>
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<tr>
<td><strong>Side</strong></td>
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<td></td>
</tr>
<tr>
<td><strong>Plaster</strong></td>
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<tr>
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<td><strong>Dark Red</strong></td>
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<td></td>
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<td><strong>Dark Red B</strong></td>
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</tr>
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<td><strong>Light Red</strong></td>
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<tr>
<td></td>
</tr>
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</tbody>
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APPENDIX C:

FT-IR Spectra

CLARC Fragment Samples

Architectural Fragment Samples

Stripes Fragment Samples

Floral Motif Fragment Samples
CLARC Fragment

Plaster
Gold
Red
Architectural Fragment

Light Red

![Graph Image](image-url)
Dark Red
Blue
Stripes Fragment

Peach
Blue
Floral Motif Fragment

Red
APPENDIX D:

GCMS Spectra

CLARC Fragment Samples
Architectural Fragment Samples
Stripes Fragment Samples
Floral Motif Fragment Samples
Madder Dye Standard Samples
CLARC Fragment

Plaster

Yellow-Tan

124
Yellow Stripe

Gold
Architectural Fragment

Light Red

[Graph showing the abundance over time for Light Red]

Dark Red

[Graph showing the abundance over time for Dark Red]
Stripes Fragment

Peach

Black

129
Blue
Madder Dye Standards

Rubia *Tinctoria* (root powder)

Rubia *Frondosa* (root pieces)
BIBLIOGRAPHY


