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Natural ultramarine in the Roman context of *Volsinii* (Bolsena, Italy): a multianalytical characterization

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***Abstract* –This study presents a comprehensive analysis of a blue pigment lump discovered near *Volsinii* (modern Bolsena, Italy), employing ED-XRF, micro-Raman spectroscopy, and XRPD techniques. The pigment was conclusively identified as natural lazurite, the primary component of lapis lazuli. ED-XRF analyses, supported by principal component analysis, revealed elemental compositions aligning closely with synthetic ultramarine pigments, yet distinct from Egyptian and Herculaneum blues. Micro-Raman spectroscopy detected characteristic S_3^- radical peaks at 548 cm^{-1}, with additional shoulders at 585 cm^{-1} indicative of natural origin. XRPD confirmed a predominantly lazurite crystalline structure, lacking kaolinite impurities typical of synthetic variants. The presence of such a rare and valuable pigment in a provincial Roman context suggests sophisticated material procurement and artistic practices, challenging prevailing assumptions about pigment distribution in antiquity.**

I. INTRODUCTION

Color in Roman wall painting served not only decorative and aesthetic purposes but also conveyed symbolic and material value. While pigments such as cinnabar and Egyptian blue are relatively well-documented and commonly found, the use of ultramarine blue — extracted from lapis lazuli — still remains an exceptional occurrence [1–4].

Ancient authors such as Pliny the Elder (*Naturalis Historia*) and Vitruvius (*De Architectura*) mention several types of blue pigments known to Roman painters: azurite ($Cu_2(CO_3)_2(OH)_2$), indigo ($C_{16}H_{10}N_2O_2$), Egyptian blue ($CaCuSi_4O_{10}$, also called cuprorivaite), and lapis lazuli $(Na,Ca)_8Al_6Si_6O_{24}(S,SO_4^{2-})_2$. Among these, Egyptian blue was by far the most widespread, manufactured in standardized nodules of 15–20 mm across the Empire. Indigo was mostly used for textiles, and azurite appears occasionally in wall paintings. By contrast, lazurite-based ultramarine was an extremely rare and costly material, usually associated with imported lapis lazuli from Afghanistan.

Due to its rarity, high cost, and long-distance sourcing, ultramarine was traditionally reserved for luxury objects like illuminated manuscripts or elite artworks, with only a very few known applications in Roman mural contexts. Previously documented cases included the Servilia tomb in Rome, a villa in Colchester (UK), and the Roman Villa of Baños de Valdearados in Spain, where it was even used in mixture with yellow pigments to produce green tones [3,5].

This study presents new analytical data from an unusual find near the ancient site of *Volsinii* (modern Bolsena, central Italy), where a lump of blue pigment—originally attributed to Egyptian blue—was recovered during agricultural activity in the locality of Ponticello. Located a few kilometers north of the main urban area, this findspot lies within a historically rich landscape associated with Etruscan and Roman occupation, though still largely unexplored archaeologically. The pigment's proximity to the decorated structures of the public quarter at Poggio Moscini, especially the richly painted *forica*, suggests a possible contextual link with the local fresco production [6,7]. In these murals, dated to ca. 30–40 AD, blue features prominently in mythological scenes set against vibrant monochromatic backgrounds, an unusual choice given the general rarity of blue in Roman mural palettes.

Initial Fiber Optic Reflectance Spectroscopy (FORS) analysis suggested the Ponticello pigment may not be Egyptian blue as first assumed, but rather a mineral consistent with lazurite [8]. This hypothesis has been further tested through a suite of archaeometric techniques, including Energy Dispersive X-ray Fluorescence (ED-XRF), micro-Raman spectroscopy, and X-ray Powder Diffraction (XRPD). This research aimed to provide a comprehensive chemical and mineralogical characterization of the material, with comparison against reference samples: synthetic ultramarine pigments, synthetic Egyptian blue, 'Herculaneum blue', and natural lapis lazuli from Monte Somma (Naples province), one of the closest potential geological sources of lazurite within Italy.

The implications of identifying ultramarine in a provincial Roman context are quite significant. Such a discovery challenges existing assumptions about the circulation and accessibility of prestigious materials in non-urban centers, and raises broader questions concerning trade networks, pigment sourcing, and the social value attributed to color in Roman art. The findings presented here contribute to a growing reevaluation of the complexity of local workshop practices and the mechanisms of artistic production in the Roman provinces.

A. Archaeological and Historical Context

The area around modern Bolsena, corresponding to ancient *Volsinii*, has long been recognized for its Etruscan and Roman heritage. The site of Ponticello, though currently underexplored archaeologically, lies in proximity to the better-known complex at Poggio Moscini—situated outside the urban perimeter of the Roman city of Volsinii— where public structures such as baths, shops, and a latrine (*forica*) richly decorated with wall paintings have been excavated.

The discovery of the pigment lump in the locality of Ponticello raises the possibility that it may have been associated with preparatory phases of fresco production or pigment handling activities, potentially in a peri-urban or rural setting. A more systematic archaeological investigation of the area could shed light on the nature of these activities and provide valuable data on artisanal practices, pigment circulation, and the organization of material production in provincial contexts.

II. MATERIALS AND METHODS

To characterize the blue pigment lump recovered at the Ponticello site, a combination of non-destructive and micro-invasive analytical techniques was employed (Fig.1).

ED-XRF**:** Amptek Mini-X X-ray tube with rhodium anode, 40 kV, 80 µA; acquisition time 300 s; Peltier-cooled Si drift detector; spectra processed with PyMca 5.9.2.

Micro-Raman**:** Renishaw inVia confocal spectrometer; 532 nm (green) and 633 nm (red) lasers, power reduced to 1%; spot size ~1 µm; spectral ranges 100–1850 cm^{-1} (green) and 100–2000 cm^{-1} (red).

XRPD**:** Bruker D8 ADVANCE diffractometer; Mo Kα radiation (λ = 0.71 Å); 40 kV, 30 mA; range 2θ = 5–30°, step 0.02°, acquisition 3 s per step

The goal was to gain a comprehensive understanding of its elemental, mineralogical, and molecular composition, and to compare it with known reference materials, both natural and synthetic[9].

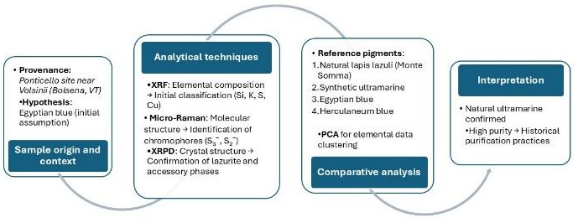
The first step involved portable X-ray fluorescence (XRF) analysis, which allowed for the identification of the main chemical elements present in the pigments. The technique also enabled a broader comparison between the Ponticello lump and several known blue pigments through statistical data treatment, including Principal Component Analysis (PCA), to highlight potential compositional similarities and anomalies.

Micro-Raman spectroscopy was then used to investigate the molecular structure of the chromophores in the sample. Thanks to its high spatial resolution, this technique made it possible to detect and distinguish between mineral phases such as Egyptian blue, lapis lazuli, and synthetic ultramarine. Measurements were conducted under controlled conditions to avoid thermal damage, and two different laser wavelengths were applied to optimize phase identification.

Finally, X-ray powder diffraction (XRPD) was used to confirm the crystalline phases and refine the mineralogical identification. The powdered pigment was analyzed under specific geometric and operational conditions to enhance peak resolution and reliability in phase attribution.

This integrated approach ensured a robust identification of the materials involved and offered the necessary framework to discuss the origin and use of the pigment in relation to Roman painting practices.

Fig. 1. Flowchart of the work



III. RESULTS AND DISCUSSION

The combination of ED-XRF, micro-Raman and XRPD discriminated between the pigment classes analyzed and to characterize the Ponticello sample in detail.

The Ponticello pigment lump exhibited a chemical profile dominated by Si, K and S, the typical markers of lazurite. Minor but significant elements such as Fe, Zn, Mn, Br, Cr and Zr were also detected, a finding consistent with both natural and synthetic ultramarine formulations. When compared with the reference samples, synthetic ultramarines (Poggi and Divolo) clustered closely with Ponticello in PCA space, confirming a shared baseline composition. However, closer inspection revealed differences: the synthetic pigments tended to show higher sulfur contents, the result of controlled industrial synthesis, whereas the Ponticello pigment displayed a slightly different balance of trace elements.

The Monte Somma lapis lazuli sample presented a much more complex chemical fingerprint, enriched in Fe, Ca, K and Sr. These signals reflect the presence of accessory minerals such as calcite, diopside, feldspars and Sr-bearing phases, which are typically co-present in raw lapis lazuli rocks. This heterogeneity sets natural lapis lazuli apart from the chemically more “regular” synthetic ultramarines. By contrast, Egyptian blue was easily identifiable due to its very high copper content, linked to its cuprorivaite structure. Herculaneum blue showed a completely different profile, with high Ca, S and Ba deriving from gypsum and barite additions. The PCA analysis neatly separated the samples into three clusters: ultramarine, Egyptian blue and Herculaneum blue, underlining the diagnostic value of multivariate statistics in archaeometric studies.

Raman spectroscopy provided molecular confirmation of the chromophores. In all ultramarine samples, the symmetric stretching vibration (ν1) of the S_3^- radical appeared prominently at 545–548 cm^{-1}. This is a known diagnostic marker for lazurite. The Ponticello lump, however, exhibited an additional shoulder at 584–586 cm^{-1}, which can be attributed to the presence of S_2^- radicals or to structural disorder within the mineral lattice. This subtle feature, absent in synthetic pigments, was also found in the Monte Somma lapis lazuli and is considered a strong indicator of natural origin.

Other Raman features included the ν2 bending vibration of S_3^- at 257 cm^{-1} and the overtone 1ν1 at 1095 cm^{-1}. Interestingly, peaks at 635 and 970 cm^{-1}, usually linked to wollastonite ($CaSiO_3$) inclusions that sometimes accompany natural pigments, were not observed in the Ponticello spectrum, suggesting that the lump had undergone purification steps to reduce accessory minerals.

The Raman spectrum of “Herculaneum blue” was particularly complex: besides the S_3^- band at ~550 cm^{-1}, it contained intense bands for gypsum (1008 cm^{-1}), calcite (1088 cm^{-1}) and barite (463 and 988 cm^{-1}), along with signals from synthetic organic pigments in the 1590–1620 cm^{-1} region. This composition confirms its modern, composite nature.

Diffraction analysis further clarified the mineralogical distinctions. The Ponticello sample consisted almost entirely of lazurite, with sharp peaks indicating good crystallinity. No traces of kaolinite were observed. This contrasts with the Divolo synthetic ultramarine, where lazurite was accompanied by kaolinite, a by-product of its industrial synthesis pathway (kaolin dehydration followed by sulfurization and redox cycles).

The Monte Somma sample, being a raw lapis lazuli rock, presented a very heterogeneous phase assemble: lazurite, sodalite, diopside, phlogopite, quartz and Sr-rich feldspars. Such mineralogical complexity complicates the diffraction pattern and reflects the natural variability of geological sources.

Taken together, the three techniques converged on the conclusion that the Ponticello lump was a purified natural ultramarine, distinct both from synthetic formulations and from unprocessed lapis lazuli rock.

The implications of these results extend well beyond pigment identification.

First, the analyses show that natural lazurite pigments can be clearly differentiated from synthetic ultramarines and from other Roman blue pigments (Egyptian, Herculaneum blue).

Second, the purified state of the Ponticello pigment suggests deliberate ancient technological processing. As described by later sources such as Cennino Cennini, lapis lazuli could be ground, mixed with waxes and resins, and repeatedly washed in alkaline solutions to separate lazurite grains from unwanted gangue. The Ponticello lump fits this model: it contains nearly pure lazurite, without the quartz, calcite or pyrite inclusions typical of unprocessed lapis lazuli. This strongly points to a workshop product, rather than a raw geological fragment.

Third, the presence of ultramarine in Volsinii, which a provincial but prosperous Roman center, challenges assumptions that such costly pigments were limited to metropolitan contexts like Rome. Ultramarine was extremely expensive in antiquity, sometimes valued higher than gold. Its presence here indicates both the economic resources available locally and the cultural aspirations of patrons who invested in ambitious decorative schemes.

From a trade and provenance perspective, the pigment could have reached Bolsena either through long-distance trade networks connecting to Afghanistan, the classical source of lapis lazuli, or from closer deposits such as Monte Somma in Campania. While provenance cannot be established here, the find would attest the integration of provincial centers into wide exchange systems.

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IV. CONCLUSION

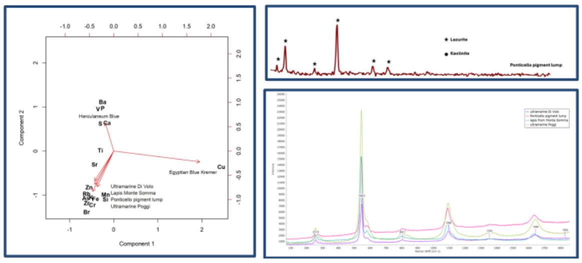
This case study from *Volsinii* contributes to the growing corpus of evidence for the use of ultramarine blue in Roman wall paintings. It challenges the notion that such high-value pigments were restricted to elite metropolitan centers, and highlights the complex interplay of economic, symbolic, and technological factors in Roman art.

This multi-technique investigation demonstrated the diagnostic value of ED-XRF, Micro-Raman, and XRPD in differentiating natural from synthetic ultramarine pigments, as well as other ancient blue pigments. The Ponticello lump, composed of highly pure lazurite, stands in contrast to the raw Monte Somma sample, confirming the use of selective purification in historical pigment preparation. Compositional markers such as Cu for Egyptian blue or Ba for Herculaneum blue proved essential for classification. Raman spectroscopy allowed for the detection of structural impurities and pigment mixtures, while XRPD provided insights into crystalline phases and mineral associations.

These findings not only support pigment attribution and sourcing but also shed light on ancient technological choices and trade dynamics.

In Roman visual culture, the color blue could take on a variety of connotations. In this case, the consistent and extensive use in the mural program of the *forica* at Poggio Moscini—particularly in the lower register of the decoration—suggest the availability of multiple pigment sources and a deliberate chromatic strategy aimed at visual impact, surface coherence, or the differentiation of decorative zones.

Fig. 2. (a) PCA of ED-XRF data comparing chemical composition of Ponticello pigment lump with other synthetic pigments (b) X-ray diffractograms of Ponticello pigment lump (c) Micro-Raman spectra of Ponticello lump, synthetic ultramarine samples, and lapis lazuli from Monte Somma with 532 nm laser excitation



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