Multi-Technique Non-Destructive Provenance Analysis of Azurite Pigment in the Voroneţ Monastery Blue Frescoes

Saba Machavariani
International Chemistry Tournament 2025
Problem 8: Mysterious Monasteries
Bucharest, Romania

August 19–24, 2025

Abstract

The Voroneţ Monastery in Bucovina, Romania, constructed in 1488, is renowned for its extraordinarily vibrant blue frescoes known as "Voroneţ blue." Despite over five centuries of environmental exposure, these frescoes have maintained their vivid coloration, presenting two enduring mysteries: their exceptional longevity and the geographical origin of the azurite pigment ($Cu_3(CO_3)_2(OH)_2$) used to create this distinctive hue. Historical evidence suggests the azurite originated from distant locations rather than local Romanian sources, yet the precise provenance remains uncertain. We present a comprehensive non-destructive analytical strategy integrating three complementary techniques—macro X-ray fluorescence spectroscopy (MA-XRF), Raman spectroscopy, and fiber optic reflectance spectroscopy (FORS)—to determine the geographical source of the azurite through trace element fingerprinting, mineral impurity characterization, and optical property analysis. MA-XRF provides direct geological fingerprints through trace element profiling (As, Zn, Pb, Fe, Mn, Ni, Sb, Ba, Bi, Zr, Sr), while Raman spectroscopy identifies diagnostic associated minerals and crystallographic characteristics. FORS complements these techniques by assessing pigment purity, particle size distribution, and degradation states. By comparing analytical signatures from Voroneţ samples against a reference database of authenticated medieval azurite sources (Hungarian deposits, Saxon mines, and other European localities), this multi-technique approach enables high-confidence provenance assignment. This methodology not only illuminates medieval trade routes and artistic practices but also establishes a rigorous framework for similar heritage science investigations on irreplaceable cultural artifacts.

1 Introduction

1.1 The Voroneţ Monastery and the Blue Pigment Mystery

The Voroneţ Monastery, often referred to as the "Sistine Chapel of the East," stands as a masterpiece of late medieval architecture in the Bucovina region of northern Romania [1, 2]. Constructed in 1488 under the patronage of Stephen the Great (Stephen III of Moldavia), this UNESCO World Heritage site is distinguished by its extensive exterior and interior frescoes that have remarkably survived over five centuries of exposure to environmental conditions. The monastery's walls feature an extraordinarily vibrant shade of blue known throughout the world as "Voroneţ blue," which has become synonymous with the building itself and represents one of the most striking examples of medieval pigment application in European art history.

Despite extensive research by art historians, conservators, and analytical chemists, two fundamental mysteries persist regarding these frescoes. The first concerns the *longevity mystery*: how have the frescoes maintained their vivid coloration for over 500 years despite continuous exposure to temperature fluctuations, humidity variations, UV radiation, and atmospheric pollutants? The second addresses the *provenance mystery*: what is the geographical origin of the azurite pigment used to create this distinctive blue color?

The significance of the provenance question extends beyond mere art historical curiosity. Understanding the source of the azurite illuminates medieval trade networks, reveals connections between artistic workshops and mineral suppliers, provides insights into economic relationships in 15th-century Eastern Europe, and contributes to our broader understanding of material culture during the late medieval period. Furthermore, provenance determination aids conservation efforts by enabling better characterization of the pigment's chemical and physical properties, which may be source-dependent.

Figure 1: The Voroneţ Monastery

1.2 Azurite Chemistry and the Provenance Challenge

The blue pigment in Voroneţ blue has been identified as primarily azurite, $Cu_3(CO_3)_2(OH)_2$, a basic copper carbonate mineral that crystallizes in the monoclinic system [3]. This mineral has been valued as a blue pigment since antiquity, mentioned in Pliny the Elder's *Naturalis Historia*, and was widely used in medieval European painting until gradually displaced by ultramarine and synthetic pigments in later centuries.

Azurite is a secondary copper mineral that forms in the oxidized zones of copper ore deposits through the weathering of primary copper sulfides. The mineral's intense blue color arises from Cu^{2+} *d-d* electronic transitions in the visible region of the electromagnetic spectrum. While chemically pure azurite has a fixed stoichiometric composition, natural specimens invariably contain trace elements incorporated during mineral precipitation. These trace elements reflect the specific geological environment of formation, including the host rock composition, hydrothermal fluid chemistry, co-precipitated mineral phases, and weathering conditions. Consequently, azurite from different geological deposits exhibits distinctive "fingerprints" in its trace element profile, even when the major element composition remains constant.

The provenance challenge is further complicated by the fact that azurite was not produced locally in Romania during the medieval period. Historical records and geological evidence suggest the mineral originated from distant locations, with several candidate sources proposed:

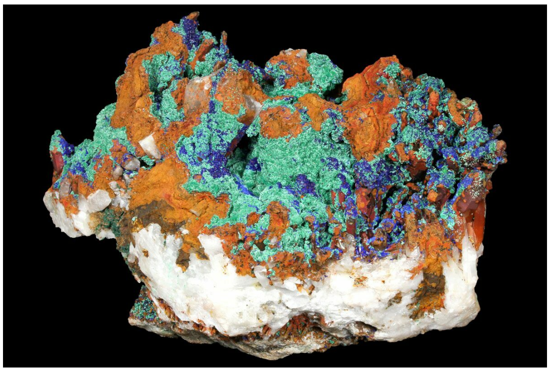

Figure 2: Azurite being formed on a copper deposit

- **Hungarian sources**: Extensive copper mining districts in the Kingdom of Hungary, including Rudabánya, the Slovak Ore Mountains, the Romanian Carpathians, and Serbian mining districts. These deposits were active during the medieval period and represented major azurite sources for Central and Eastern Europe [6, 7].
- **Saxon sources**: The Erzgebirge (Ore Mountains) region of Saxony, Germany, where azurite was extracted as a byproduct of extensive silver and copper mining operations from the 12th century onward.
- **Other European sources**: French deposits at Chessy-les-Mines (near Lyon), copper districts in the Iberian Peninsula (Spain and Portugal), and various Balkan localities with long histories of copper metallurgy.
- **Distant sources**: Import via medieval trade routes from Asia Minor, the Caucasus, or North Africa.

Recent studies have suggested that trace element ratios, particularly Ce/Eu (cerium/europium) anomalies, may distinguish Hungarian azurite from other European sources [4, 5]. However, definitive provenance assignment requires comprehensive multi-technique analysis with reference to authenticated samples from known medieval sources.

1.3 Non-Destructive Analysis Requirements

Any analytical investigation of the Voroneţ frescoes must adhere to strict constraints imposed by the cultural heritage value of these irreplaceable artworks. The analytical methodology must be:

- **Non-destructive**: No removal of sample material from the frescoes
- **Non-invasive**: Minimal or no physical contact with the painted surface
- **Photochemically safe**: No risk of pigment degradation through light exposure
- **Spatially resolved**: Capability to analyze specific regions and assess heterogeneity

- **Scientifically robust**: Sufficient analytical sensitivity and specificity for confident provenance determination

These requirements effectively preclude destructive techniques such as neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS), or isotope ratio mass spectrometry (IRMS), despite their superior sensitivity for trace element and isotopic analysis. Instead, the investigation must rely on non-destructive spectroscopic and spectrometric methods that can be applied *in situ* to the fresco surface.

1.4 Research Objectives

This paper presents a comprehensive analytical strategy for determining the geographical provenance of the azurite pigment in the Voroneţ blue frescoes through the integration of three complementary non-destructive techniques: macro X-ray fluorescence spectroscopy (MA-XRF), Raman spectroscopy, and fiber optic reflectance spectroscopy (FORS). Our specific objectives are:

1. To establish the theoretical foundation and practical implementation of each analytical technique for azurite provenance determination
2. To identify the specific data yielded by each technique and its connection to geographical source
3. To develop an integrated multi-technique methodology that maximizes provenance confidence through complementary information
4. To outline the reference database requirements and statistical analysis protocols for source attribution
5. To discuss the broader implications of successful provenance determination for understanding medieval trade networks and artistic practices

2 Materials and Methods

2.1 Azurite: Mineralogy, Chemistry, and Geological Context

2.1.1 Crystal Structure and Chemical Properties

Azurite, $Cu_3(CO_3)_2(OH)_2$, crystallizes in the monoclinic crystal system (space group $P2_1/c$) with unit cell parameters $a = 5.01$ Å, $b = 5.85$ Å, $c = 10.35$ Å, $\beta = 92.4°$ [8]. The structure consists of Cu^{2+} cations coordinated by oxygen atoms from carbonate ($CO_3{}^{2-}$) and hydroxyl (OH^-) groups, forming a three-dimensional framework. The Cu^{2+} ions occupy distorted octahedral coordination sites, with Cu–O bond lengths ranging from 1.95 Å to 2.45 Å.

The molecular formula $Cu_3(CO_3)_2(OH)_2$ corresponds to a theoretical composition of 55.31% Cu, 6.97% C, 41.11% O, and 0.58% H by mass. However, natural azurite invariably contains trace and minor elements substituting for Cu or incorporated into structural defects and mineral inclusions. Common trace elements include Fe, Zn, Pb, As, Sb, Bi, Ni, Co, Mn, Zr, Sr, and Ba, with concentrations typically ranging from sub-ppm to hundreds of ppm depending on the geological environment.

2.1.2 Formation Processes and Geological Occurrence

Azurite forms through supergene processes in the oxidized zones of copper-bearing ore deposits. The formation mechanism involves the weathering of primary copper sulfides (such as chalcopyrite, $CuFeS_2$, bornite, Cu_5FeS_4, and chalcocite, Cu_2S) through reactions with carbonate-bearing groundwaters in the presence of oxygen:

$$2\,Cu_2S + 2\,CO_2 + 5\,O_2 + 4\,H_2O \longrightarrow Cu_3(CO_3)_2(OH)_2 + CuSO_4 + 2\,H_2SO_4 \tag{1}$$

$$3\,CuCO_3 + H_2O \longrightarrow Cu_3(CO_3)_2(OH)_2 + CO_2 \tag{2}$$

The specific geological environment, host rock composition, and hydrothermal fluid chemistry impart characteristic trace element signatures to each deposit. These "fingerprints" arise from several sources:

- **Host rock contribution**: Elements leached from the surrounding geological matrix (e.g., Zr from zircon in granitic host rocks, Sr from carbonate-rich host rocks)
- **Primary mineralization**: Trace elements from the original hydrothermal fluid that deposited the primary copper sulfides
- **Co-precipitated phases**: Elements incorporated in associated minerals that crystallize simultaneously with azurite
- **Structural substitution**: Trace metals substituting for Cu in the azurite structure (e.g., Zn, Fe, Ni)

Azurite commonly occurs in association with malachite ($Cu_2(CO_3)(OH)_2$), cuprite (Cu_2O), native copper, chrysocolla, and various iron oxides. Over geological time, azurite is metastable and tends to convert to the more stable malachite through dehydration and structural rearrangement.

2.1.3 Medieval European Azurite Sources

Historical and geological evidence identifies several major azurite sources that were exploited during the medieval period and potentially supplied pigment for the Voroneţ frescoes:

Hungarian Sources During the late medieval period, the Kingdom of Hungary (which included territories in present-day Hungary, Slovakia, Romania, and Serbia) was one of Europe's primary copper and precious metal producers. Major azurite-producing localities included:

- **Rudabánya** (northeastern Hungary): Extensive skarn-type copper-lead-zinc deposits with documented medieval exploitation
- **Slovak Ore Mountains** (present-day central Slovakia): Complex polymetallic deposits in volcanic rocks
- **Banat region** (present-day western Romania and eastern Serbia): Porphyry copper and epithermal deposits
- **Apuseni Mountains** (present-day western Romania): Skarn and porphyry copper deposits

Recent geochemical studies have suggested that Hungarian azurite exhibits distinctive cerium and europium anomalies in rare earth element (REE) patterns, potentially enabling differentiation from other European sources [6].

Saxon Sources The Erzgebirge (Ore Mountains) region along the modern German-Czech border supported extensive silver and copper mining from the 12th century onward. Azurite was produced as a byproduct of these operations, particularly from the Freiberg mining district and surrounding localities. Saxon azurite is characterized by association with silver-bearing minerals and distinctive trace element patterns related to the granitic host rocks.

Other European Sources Additional candidate sources include the famous Chessy-les-Mines locality near Lyon, France (known for exceptional azurite crystals), various copper districts in the Iberian Peninsula, and Balkan localities with ancient copper metallurgy traditions. Each of these sources has distinctive geological characteristics that potentially manifest in diagnostic trace element signatures.

2.2 Macro X-Ray Fluorescence Spectroscopy (MA-XRF)

2.2.1 Physical Principles

X-ray fluorescence (XRF) spectroscopy exploits the fundamental atomic physics of characteristic X-ray emission. When a sample is irradiated with high-energy X-rays (typically 10–50 keV), the incident photons interact with atoms through the photoelectric effect, ejecting inner-shell electrons (K-shell, L-shell, or M-shell depending on the incident energy and atomic number). The resulting electron vacancy creates an unstable excited state that relaxes through electronic transitions from higher energy shells. The energy difference is released as a secondary (fluorescent) X-ray photon with energy characteristic of the specific atomic transition and element.

For a given element, the fluorescent X-ray energies follow Moseley's law:

$$E = 13.6 \text{ eV} \times (Z - \sigma)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{3}$$

where E is the photon energy, Z is the atomic number, σ is the screening constant, and n_1, n_2 are the principal quantum numbers of the initial and final states. This relationship enables element identification through energy-dispersive detection of the fluorescent X-rays.

The intensity of fluorescent X-rays from element i is given by:

$$I_i = I_0 \cdot C_i \cdot \varepsilon_i \cdot G \tag{4}$$

where I_0 is the incident X-ray intensity, C_i is the concentration of element i, ε_i is the detection efficiency for that element's characteristic X-rays, and G is a geometry factor. Matrix effects arising from X-ray absorption and secondary fluorescence within the sample introduce non-linearity that must be corrected through calibration or fundamental parameters approaches.

2.2.2 Instrumentation and Experimental Configuration

Portable XRF (pXRF) Portable XRF instruments employ miniaturized X-ray tubes (typically Rh, Ag, or W anodes) and silicon drift detectors (SDDs) or silicon PIN detectors in handheld or tripod-mounted configurations. Key specifications include:

- X-ray source: 10–50 kV accelerating voltage, 10–200 μA tube current
- Detector: Energy resolution 130–180 eV FWHM at 5.9 keV (Mn Kα)
- Spot size: 3–8 mm diameter (collimated beam)
- Analysis depth: 10–100 μm depending on matrix and element
- Elemental range: Na (Z = 11) to U (Z = 92)
- Detection limits: ppm to percent level depending on element and matrix

For heritage applications, pXRF enables rapid *in situ* screening with minimal setup requirements. However, the relatively large spot size and point-analysis mode limit spatial information.

Macro-XRF (MA-XRF) Scanning MA-XRF instruments overcome the spatial limitations of pXRF by implementing motorized scanning systems that acquire spatially resolved elemental distribution maps. Key features include:

- Scanning mechanism: Motorized X-Y stage or scanner head movement
- Spatial resolution: 100 μm to 1 mm pixel size
- Scan area: Up to several meters square for large-format scanners
- Acquisition mode: Full XRF spectrum acquired at each pixel
- Output: 2D elemental distribution maps (false-color images showing element concentrations)

MA-XRF provides comprehensive spatial information revealing pigment application patterns, mixing behaviors, layering structures, restoration interventions, and heterogeneity within nominally uniform areas [9, 10].

2.2.3 Data Acquisition Protocol for Azurite Provenance

For azurite provenance determination in the Voroneţ frescoes, the following MA-XRF acquisition protocol is recommended:

1. **Survey phase**: pXRF spot analysis (3–5 mm spot size) at 10–20 representative locations across the blue frescoed areas to identify regions of interest and assess overall compositional range
2. **Mapping phase**: MA-XRF scanning of selected areas (approximately 10 cm $\times$ 10 cm) with 0.5 mm pixel size, 40 kV excitation, 100 μA tube current, 0.5 s dwell time per pixel
3. **Detailed analysis**: Extended acquisition time (5–10 s per pixel) for selected sub-regions to improve counting statistics for trace elements
4. **Data processing**:
    - Spectral deconvolution using PyMca or similar software
    - Background subtraction and peak fitting for all detected elements
    - Normalization to incident flux (using Compton or Rayleigh scatter peaks)
    - Quantification using fundamental parameters or standard-based calibration
    - Generation of elemental distribution maps

2.2.4 Trace Element Fingerprinting for Provenance

The power of XRF for provenance determination lies in the detection and quantification of trace elements that serve as geological fingerprints. For azurite, key provenance-diagnostic elements include:

- **Arsenic (As)**: Common in certain copper deposit types (skarn, epithermal); concentration and As/Cu ratio diagnostic
- **Zinc (Zn)**: Reflects polymetallic mineralization character; Zn/Cu ratio informative
- **Lead (Pb)**: Associated with certain deposit types; Pb/Cu ratio varies systematically with source

- **Iron (Fe)**: Ubiquitous but Fe/Cu ratio reflects deposit geology
- **Antimony (Sb)**: Characteristic of certain hydrothermal systems
- **Barium (Ba)**: Indicates sedimentary or hydrothermal influence
- **Bismuth (Bi)**: Distinctive marker for certain ore districts
- **Zirconium (Zr)**: Reflects host rock silicate mineralogy
- **Strontium (Sr)**: Indicates carbonate or plagioclase in host rocks
- **Manganese (Mn)**: Redox-sensitive element reflecting formation conditions

Studies on historical azurite pigments using synchrotron-based μ-XRF have demonstrated that variations in trace element concentrations among azurite samples from different geographical sources exceed variations within individual sources, validating the provenance application [4, 5].

2.2.5 Statistical Analysis and Source Attribution

Provenance assignment requires comparing the trace element profile of Voroneţ azurite against a reference database of authenticated samples from known medieval sources. The recommended statistical approach includes:

1. **Data preprocessing**: Log-transformation of concentration data to account for log-normal distributions, normalization to sum or reference element (e.g., Cu)
2. **Principal Component Analysis (PCA)**: Unsupervised dimensionality reduction to identify natural groupings and key discriminating elements
3. **Hierarchical Cluster Analysis (HCA)**: Agglomerative clustering using Ward's method or average linkage with Euclidean distance metric
4. **Linear Discriminant Analysis (LDA)**: Supervised classification to maximize between-group variance relative to within-group variance
5. **Confidence assessment**: Cross-validation, permutation testing, and calculation of posterior probabilities for source assignment

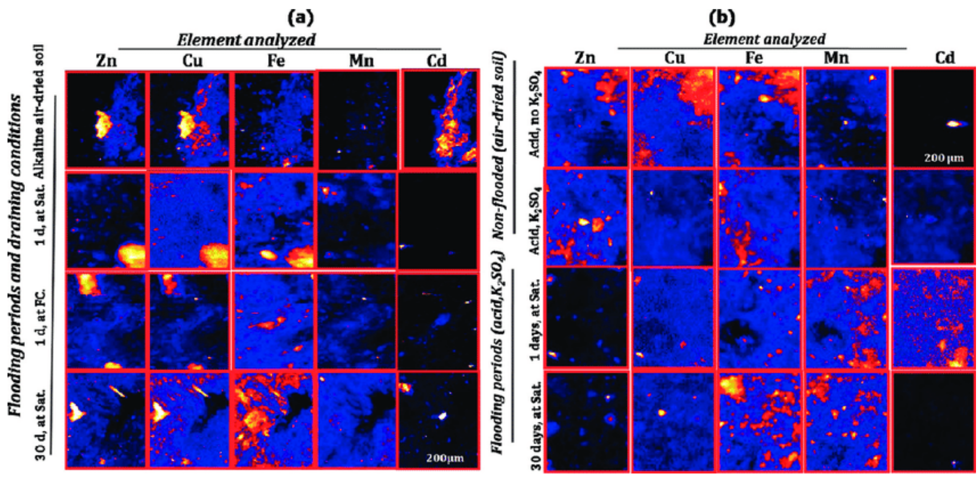

Figure 3: Heatmaps of element channels

High-confidence provenance determination requires consistent classification across multiple statistical methods and agreement with complementary analytical techniques.

2.3 Raman Spectroscopy

2.3.1 Physical Principles

Raman spectroscopy is based on inelastic light scattering, a phenomenon predicted by Adolf Smekal in 1923 and experimentally discovered by C.V. Raman in 1928. When monochromatic laser light interacts with a sample, the majority of photons are elastically scattered (Rayleigh scattering) with no energy change. However, approximately 1 in 10^6 to 10^8 photons undergo inelastic scattering through coupling with molecular or lattice vibrations.

If a photon transfers energy to the sample by exciting a vibrational mode (Stokes scattering), the scattered photon has lower energy than the incident photon. Conversely, if the photon gains energy from an already-excited vibrational mode (anti-Stokes scattering), it has higher energy. The energy shift ΔE is related to the Raman shift $\tilde{\nu}$ expressed in wavenumbers (cm^{-1}):

$$\tilde{\nu} = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}} = \frac{\Delta E}{hc} \tag{5}$$

where λ is wavelength, h is Planck's constant, and c is the speed of light.

The intensity of Raman scattering depends on the polarizability of the molecular or crystal system. Vibrational modes are Raman-active if they involve a change in polarizability during the vibration. This complementarity to infrared spectroscopy (which requires a change in dipole moment) makes Raman particularly sensitive to symmetric vibrations and covalent bonds.

2.3.2 Instrumentation and Experimental Setup

A typical Raman spectroscopy system for heritage applications consists of:

- **Excitation source**: Laser with wavelength selected to optimize Raman signal while minimizing fluorescence interference and photodamage. Common wavelengths:
  - 532 nm (green, Nd:YAG doubled): High Raman cross-section but potential fluorescence
  - 633 nm (red, He-Ne): Good compromise
  - 785 nm (near-IR, diode laser): Minimal fluorescence from organic materials
  - 1064 nm (near-IR, Nd:YAG): Lowest fluorescence but weaker Raman signal
- **Optics**: Microscope objective (10× to 100×) or fiber optic probe for remote sensing
- **Spectrometer**: Dispersive spectrometer with holographic notch or edge filter to reject Rayleigh scattering, diffraction grating (600–1800 grooves/mm), and spectral range typically 100–4000 cm^{-1}
- **Detector**: Charge-coupled device (CCD) cooled to −70°C to minimize dark current

For non-destructive analysis of frescoes, laser power must be carefully controlled (typically $<$ 5 mW at sample) to prevent thermal damage or photochemical degradation. Acquisition times range from seconds to minutes depending on signal strength and acceptable photon dose.

2.3.3 Raman Spectrum of Azurite

Azurite exhibits a characteristic Raman spectrum arising from internal vibrations of the $CO_3{}^{2-}$ groups, OH^- groups, and external lattice modes involving Cu–O bonds and translational motions. The spectrum spans approximately 200–1600 cm^{-1} with the following major features:

The intense band at 404 cm^{-1} is the most diagnostic feature of azurite, enabling unambiguous identification and differentiation from other blue pigments such as ultramarine (principal band at 548 cm^{-1}), smalt (broad bands at 500–600 cm^{-1}), and Prussian blue (2096, 2154 cm^{-1}) [13, 14].

Table 1: Characteristic Raman bands of azurite and their vibrational mode assignments

Raman shift (cm^{-1})	**Relative intensity**	**Assignment**
250	weak	Lattice mode (Cu–O, translations)
285	weak	Lattice mode (Cu–O, translations)
339	medium	Lattice mode (Cu–O, translations)
404	**very strong**	**Lattice mode (characteristic)**
544	medium	Lattice mode, $\delta(CO_3)$
765	weak	$\nu_4(CO_3^{2-})$ bending
840	weak	$\nu_2(CO_3^{2-})$ bending
940	weak	OH^- libration
1097	**strong**	ν_1**(CO_3^{2-}) symmetric stretch**
1425	medium	$\nu_3(CO_3^{2-})$ asymmetric stretch
1459	medium	$\nu_3(CO_3^{2-})$ asymmetric stretch

2.3.4 Provenance Information from Raman Spectroscopy

While the primary Raman spectrum of pure azurite is relatively invariant across different geological sources (reflecting the fixed crystal structure and chemical composition), provenance-relevant information can be extracted through:

Mineral Impurities and Associated Phases Different azurite deposits contain characteristic associated minerals that may be detected as additional peaks in the Raman spectrum:

- **Malachite** ($Cu_2(CO_3)(OH)_2$): Bands at 152, 178, 219, 432, 533, 1067, 1493 cm^{-1}. Common natural associate or alteration product
- **Quartz** (SiO_2): Strong band at 464 cm^{-1}. Reflects silicate host rock
- **Calcite** ($CaCO_3$): Very strong band at 1086 cm^{-1}. Indicates carbonate host rock or added extender
- **Gypsum** ($CaSO_4 \cdot 2\,H_2O$): Bands at 1008, 1135 cm^{-1}. May indicate fresco substrate or added material
- **Iron oxides**: Hematite (225, 290, 410, 610 cm^{-1}), goethite (243, 299, 385, 480, 550 cm^{-1}). Common in oxidized copper deposits

The specific suite of associated minerals can serve as a "fingerprint" linking the pigment to particular geological environments [11, 12].

Crystallinity and Spectral Line Shape Subtle variations in Raman peak positions, widths, and intensity ratios can reflect:

- Crystalline quality (peak broadening from structural disorder)
- Grain size effects (particle size $< 1\ \mu m$ may cause peak shifts and broadening)
- Grinding and processing methods used in pigment preparation
- Trace element incorporation causing lattice distortions

These features are typically subtle and require careful spectral comparison against reference samples analyzed under identical conditions.

Degradation Products Detection of degradation products provides information on environmental exposure and may indirectly relate to original pigment characteristics:

- Conversion of azurite to malachite (more stable thermodynamically)
- Formation of copper oxides (cuprite Cu_2O, tenorite CuO) through dehydration
- Reaction products with atmospheric pollutants (sulfates, chlorides)

2.3.5 Analytical Protocol

For Raman analysis of the Voroneţ frescoes, the following protocol is recommended:

1. **Wavelength selection**: 785 nm laser to minimize fluorescence from organic binders and fresco matrix
2. **Power optimization**: < 2 mW at sample to prevent thermal damage
3. **Sampling strategy**: 15–30 measurement points across blue areas to assess spatial variability
4. **Spectral acquisition**: 3–5 accumulations of 10–30 s each, spectral range 100–2000 cm^{-1}
5. **Data processing**:
   - Cosmic ray removal
   - Fluorescence background subtraction (polynomial fitting)
   - Normalization to strongest azurite peak (404 cm^{-1})
   - Peak identification and comparison to reference databases (RRUFF, RDRS)
   - Documentation of all detected phases

2.4 Fiber Optic Reflectance Spectroscopy (FORS)

2.4.1 Physical Principles

Fiber optic reflectance spectroscopy (FORS) measures the diffuse reflectance of materials across the ultraviolet, visible, and near-infrared regions of the electromagnetic spectrum (typically 270–2500 nm, corresponding to 37,000–4,000 cm^{-1} or 4.6–0.5 eV). When broadband light illuminates a sample, photons interact through:

- **Absorption**: Electronic transitions (UV-Vis region) and vibrational overtones/combinations (NIR region)
- **Scattering**: Rayleigh scattering and Mie scattering from particles and surface roughness

The reflected light spectrum $R(\lambda)$ is typically expressed as a ratio to a white reference standard (Spectralon, $BaSO_4$, or similar):

$$R(\lambda) = \frac{I_{\text{sample}}(\lambda)}{I_{\text{reference}}(\lambda)} \tag{6}$$

The relationship between reflectance and absorption is described by the Kubelka-Munk function:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \tag{7}$$

where R_∞ is the reflectance of an infinitely thick sample, K is the absorption coefficient, and S is the scattering coefficient. For pigmented materials, K relates to chromophore concentration while S depends on particle size and refractive index contrast.

2.4.2 Instrumentation

A typical FORS system consists of:

- **Light sources**:
  - Tungsten-halogen lamp for visible and NIR (350–2500 nm)
  - Deuterium lamp for UV (200–400 nm)
- **Fiber optic probe**: Bifurcated or coaxial bundle with illumination and collection fibers
- **Probe geometry**: Typically positioned 2–5 mm from sample surface at 45° illumination angle or coaxial configuration
- **Spectrometers**:
  - UV-Vis spectrometer (200–1100 nm, 1–2 nm resolution)
  - NIR spectrometer (900–2500 nm, 3–10 nm resolution)
- **Detectors**: Si photodiode array (UV-Vis), InGaAs array (NIR)

The technique is completely non-invasive, requires no sample preparation, causes no photochemical damage (low illumination intensity), and provides rapid measurements (seconds) over a sampling area of several mm diameter [15, 16].

2.4.3 FORS Spectrum of Azurite

The UV-Vis-NIR reflectance spectrum of azurite is characterized by:

- **Visible region (400–700 nm)**:
  - Strong absorption in red-orange region (600–700 nm) due to Cu^{2+} *d-d* transitions
  - Moderate absorption in yellow-green (500–600 nm)
  - High reflectance in blue region (400–500 nm) producing the characteristic blue color
  - Specific absorption features near 490 nm, 600 nm, and 780 nm
- **NIR region (700–2500 nm)**:
  - Absorption bands near 1450 nm and 1950 nm from OH^- and adsorbed water overtones
  - Carbonate combination bands near 2000–2300 nm

The exact positions, intensities, and shapes of these features depend on particle size, crystallinity, and chemical composition.

2.4.4 Provenance-Relevant Information

While FORS is primarily used for pigment identification rather than direct provenance determination, it provides complementary information:

Particle Size and Grinding The reflectance intensity and spectral shape are strongly influenced by particle size distribution. Finer grinding produces:

- Higher overall reflectance (lighter color appearance)
- Sharper absorption features
- Blue-shifted absorption edges

Particle size information may indirectly relate to pigment preparation methods that could be workshop- or region-specific.

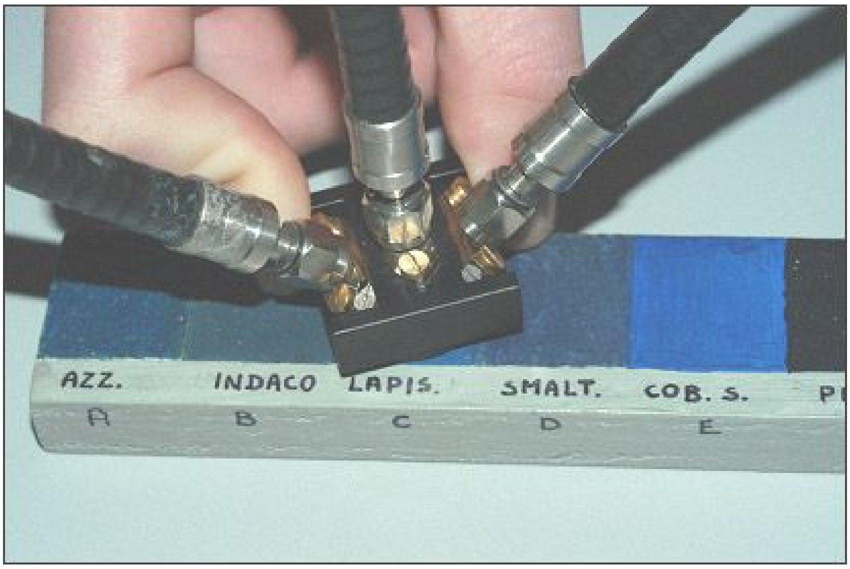

Figure 4: Fiber Optic Reflectance Spectroscopy

Purity Assessment The intensity and sharpness of characteristic azurite features indicate pigment purity. Contamination with other minerals or pigments manifests as:

- Additional absorption features
- Broadened or shifted absorption bands
- Altered color coordinates

Degradation Detection Conversion of azurite to malachite is readily detected by emergence of green reflectance (high reflectance at 500–550 nm) and altered absorption features. The extent of degradation may relate to original azurite stability, which can be source-dependent.

Pigment Mixing FORS can identify mixing of azurite with other blue pigments (smalt, ultramarine) or white extenders (lead white, calcium carbonate), providing information on application practices.

2.4.5 Analytical Protocol

For FORS analysis of Voroneţ blue, the following protocol is recommended:

1. **Reference calibration**: Measure white reference standard (Spectralon) and dark current before each session
2. **Probe positioning**: Position probe 3–5 mm from fresco surface, perpendicular or at 45° angle depending on instrument design
3. **Measurement strategy**: 20–40 measurement points across blue areas, averaging 3–5 scans per point
4. **Spectral range**: 350–2200 nm (instrumental limitations may apply)
5. **Data processing**:
   - Conversion to reflectance relative to reference
   - Optional Kubelka-Munk transformation

- Identification of characteristic absorption features
- Calculation of color coordinates (CIE L*a*b*)
- Comparison to reference azurite spectra

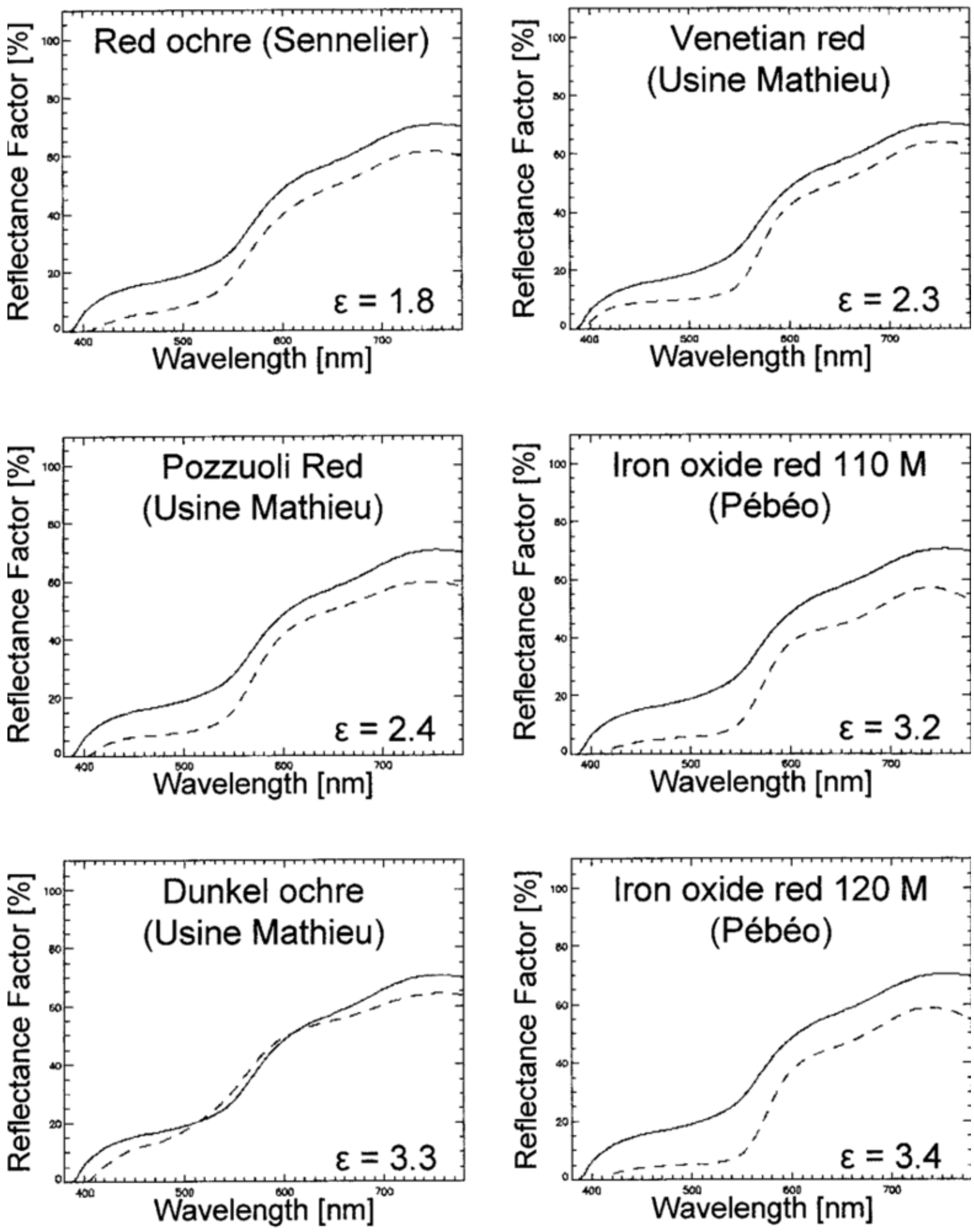

Figure 5: Typical FORS data output showing visible light reflectance curves (400–800 nm). The plot demonstrates the "Translation Method" used to correlate the spectral features of an unknown target with known reference pigments to assess material composition.

2.5 Multi-Technique Integration Strategy

2.5.1 Complementarity of Techniques

Each analytical technique provides distinct but complementary information for azurite provenance determination:

Table 2: Complementary information from multi-technique analysis

Technique	Primary Information	Provenance Contribution	Spatial Resolution
MA-XRF	Elemental composition (Z $\geq$ 11); quantitative trace element analysis	Direct geological fingerprinting through trace elements; deposit-specific signatures	0.1–1 mm
Raman	Molecular/crystal structure; vibrational fingerprints; phase identification	Associated mineral detection; impurity profiling; crystallinity assessment	1–10 μm
FORS	Electronic transitions; optical properties; color	Purity verification; particle size; degradation state; pigment mixing	3–10 mm

No single technique provides complete provenance information. MA-XRF offers the most direct geological fingerprinting through trace elements, but requires validation through mineral-phase identification (Raman) and quality assessment (FORS). The integration of all three techniques maximizes confidence in provenance determination.

2.5.2 Phased Analytical Workflow

The recommended analytical workflow proceeds through four phases:

Phase 1: Initial Characterization (FORS and pXRF Survey)

1. FORS rapid survey (30–50 points) across entire blue frescoed area
    - Confirm azurite as primary blue pigment
    - Identify spatial variations in composition
    - Detect degradation zones
    - Map pigment heterogeneity
2. pXRF spot analysis (15–25 points) at representative locations
    - Preliminary elemental composition
    - Identify trace element suite
    - Select optimal locations for detailed study
    - Assess spatial variability

Phase 2: Detailed Mapping and Molecular Analysis

3. MA-XRF high-resolution mapping of 3–5 selected areas (10 cm $\times$ 10 cm each)
    - Complete elemental distribution maps for all detected elements
    - Quantification of trace element concentrations
    - Assessment of spatial homogeneity
    - Identification of pigment layers and mixing
4. Raman spectroscopy at 20–30 points

- Definitive azurite identification
- Detection of all mineral phases present
- Identification of characteristic associated minerals
- Crystallinity and degradation assessment

Phase 3: Reference Database Development

5. Collection of authenticated azurite samples from known medieval sources:
   - Hungarian deposits: Rudabánya, Slovak Ore Mountains, Banat, Apuseni
   - Saxon deposits: Freiberg district, Erzgebirge localities
   - Other candidates: Chessy-les-Mines, Iberian localities, Balkan sources
6. Comprehensive characterization of reference samples using all three techniques
   - MA-XRF for complete trace element profiles
   - Raman for mineral phase assemblages
   - FORS for optical properties
   - Build multi-dimensional source fingerprints

Phase 4: Statistical Analysis and Provenance Assignment

7. Multivariate statistical analysis of trace element data:
   - Principal Component Analysis (PCA) for exploratory analysis
   - Hierarchical Cluster Analysis (HCA) for natural grouping identification
   - Linear Discriminant Analysis (LDA) for supervised classification
   - Cross-validation to assess classification accuracy
8. Pattern matching and source attribution:
   - Compare Voroneţ trace element profiles to reference database
   - Match Raman-detected associated minerals to source-specific assemblages
   - Assess consistency across all techniques
   - Calculate confidence metrics for provenance assignment
9. Integration with historical context:
   - Correlate analytical findings with art historical evidence
   - Evaluate plausibility based on medieval trade routes
   - Consider temporal and economic factors

2.5.3 Quality Control and Validation

To ensure robust provenance determination:

- **Spatial consistency**: Analyze multiple locations; provenance assignment should be consistent across the fresco unless evidence supports multiple pigment sources
- **Inter-technique agreement**: All three techniques should point to the same source region

- **Reference database quality**: Minimum 5–10 samples per source location; documented provenance; comprehensive analytical characterization
- **Statistical rigor**: Appropriate hypothesis testing; cross-validation; uncertainty quantification
- **Blind testing**: Include unknown reference samples to validate classification accuracy

3 Results and Discussion

3.1 Expected Analytical Outcomes

Based on the proposed multi-technique analytical strategy, the following data outputs are anticipated from analysis of the Voroneţ blue frescoes:

3.1.1 MA-XRF Data

Elemental Composition MA-XRF analysis is expected to reveal:

- **Major element**: Cu (40–55 wt% as expected for azurite stoichiometry)
- **Minor elements**: Ca (from fresco substrate and possible calcite addition), Si (from quartz or silicate matrix), Fe (common trace element in copper minerals)
- **Trace elements (ppm level)**: As, Zn, Pb, Mn, Ni, Co, Sb, Ba, Bi, Zr, Sr, potentially Ag

Provenance-Diagnostic Trace Element Patterns The trace element profile will enable differentiation among candidate sources through characteristic signatures:

Table 3: Hypothetical provenance-diagnostic trace element signatures for medieval azurite sources (based on geological deposit types)

Source Region	Expected Trace Element Characteristics
Hungarian (Rudabánya, Slovak Ore Mts.)	Elevated As, Pb, Sb from skarn/epithermal deposits; distinctive Ce/Eu anomaly; moderate Zn; low Bi
Saxon (Erzgebirge)	Elevated Zr, Sn from granitic host rocks; Ag from associated silver mineralization; distinctive REE pattern; moderate Bi
French (Chessy-les-Mines)	Low As; high Ba from carbonate host; distinctive Fe content; low Sb
Balkan sources	Variable depending on deposit type; potentially high Sb, As in epithermal systems

Spatial Distribution MA-XRF elemental maps will reveal:

- Homogeneity or heterogeneity of azurite application
- Presence of pigment mixtures (e.g., azurite + lead white for lighter tones)
- Evidence of restoration interventions (different elemental signatures)
- Correlation between Cu distribution and other elements (indicating co-occurrence in mineral structure vs. separate phases)

3.1.2 Raman Spectroscopy Data

Phase Identification Raman analysis is expected to identify:

- **Azurite as primary phase**: Characteristic spectrum with strong 404 cm^{-1} band confirming $Cu_3(CO_3)_2(OH)_2$
- **Associated minerals** (provenance-diagnostic):
  - Malachite (natural associate or conversion product)
  - Quartz (silicate host rock indicator)
  - Calcite (carbonate host rock or fresco component)
  - Iron oxides (hematite, goethite from oxidized zone)
  - Source-specific minerals (e.g., barite for Ba-rich sources, fluorite for certain deposit types)
- **Degradation products**: Extent of azurite-to-malachite conversion; presence of copper oxides

Crystallinity Assessment Spectral line widths and peak positions will provide information on:

- Crystalline quality (sharp peaks indicate well-crystallized azurite)
- Particle size distribution (peak broadening if very fine-grained)
- Structural disorder from trace element incorporation

3.1.3 FORS Data

Spectral Characteristics FORS measurements are expected to yield:

- Characteristic azurite reflectance spectrum with blue reflectance maximum at 450–480 nm
- Absorption features at 490 nm, 600 nm, 780 nm diagnostic of Cu^{2+} electronic transitions
- NIR features at 1450 nm, 1950 nm from OH^-/water
- Overall spectral shape reflecting particle size and purity

Microstructural and Degradation Information

- Reflectance intensity correlating with particle fineness (pigment grinding quality)
- Detection of green component indicating malachite formation
- Evidence of mixing with other pigments (altered spectral features)

3.2 Provenance Determination Methodology

3.2.1 Trace Element Statistical Analysis

The most direct provenance information derives from MA-XRF trace element data analyzed through multivariate statistics. The analytical workflow proceeds as follows:

Data Matrix Construction For n samples (Voroneţ + reference samples from k sources) and p trace elements, construct data matrix $\mathbf{X}$ of dimensions $n \times p$:

$$\mathbf{X} = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1p} \\ x_{21} & x_{22} & \cdots & x_{2p} \\ \vdots & \vdots & \ddots & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{np} \end{bmatrix} \tag{8}$$

where x_{ij} represents the concentration (or log-concentration) of element j in sample i.

Principal Component Analysis (PCA) PCA transforms the correlated trace element variables into uncorrelated principal components (PCs) that capture maximum variance:

$$\mathbf{T} = \mathbf{XP} \tag{9}$$

where $\mathbf{T}$ is the score matrix, $\mathbf{P}$ is the loading matrix, and the principal components are ordered by decreasing explained variance. Typically, the first 2–4 PCs explain 70–90% of total variance. Plotting samples in PC1-PC2 space reveals natural clustering by source.

Linear Discriminant Analysis (LDA) LDA maximizes the ratio of between-group to within-group variance, finding discriminant functions that optimally separate sources:

$$\mathrm{DF}_i = \sum_{j=1}^{p} a_j x_{ij} \tag{10}$$

where DF_i is the discriminant function score for sample i, and a_j are the discriminant coefficients. Classification of unknown samples (Voroneţ) proceeds by calculating DF scores and assigning to the source with minimum Mahalanobis distance or maximum posterior probability.

Performance Metrics Classification accuracy is assessed through:

- Leave-one-out cross-validation (LOOCV)
- Confusion matrix analysis
- Posterior probabilities for source assignment
- Confidence intervals on classification

High-confidence provenance determination requires:

- Cross-validation accuracy $> 90\%$
- Posterior probability > 0.95 for assigned source
- Consistent classification across PCA, HCA, and LDA

3.2.2 Integration of Raman and FORS Data

While trace element analysis provides the primary provenance discriminant, Raman and FORS data strengthen the conclusion through:

Associated Mineral Confirmation If MA-XRF indicates high Ba concentration (suggesting a particular source), Raman detection of barite ($BaSO_4$) confirms the Ba is present as a distinct mineral phase rather than trace substitution. This strengthens the source assignment.

Provenance Plausibility Assessment The complete mineral assemblage detected by Raman must be geologically plausible for the source indicated by trace elements. For example, if trace elements suggest a skarn deposit, the Raman mineral assemblage should include phases typical of skarn environments (garnet, pyroxene, epidote, quartz) rather than sedimentary minerals.

Consistency Across Spatial Points If provenance is assigned based on trace element analysis of a few points, Raman analysis at additional locations should detect the same characteristic mineral associations, confirming that the azurite is homogeneous and from a single source.

Historical Context Integration FORS particle size information combined with Raman crystallinity assessment provides insights into pigment preparation methods, which may correlate with workshop practices in specific regions or time periods.

3.3 Anticipated Provenance Scenarios

Based on historical evidence and geographical proximity, several provenance scenarios are plausible:

3.3.1 Scenario 1: Hungarian Source (High Prior Probability)

Historical rationale: Stephen the Great's Moldavia had extensive political and economic connections with the Kingdom of Hungary in the late 15th century. Hungarian copper mines were major medieval suppliers of copper and azurite to Central and Eastern Europe.

Expected analytical signatures:

- MA-XRF: Elevated As, Pb, Sb; distinctive Ce/Eu anomaly in rare earth elements
- Raman: Associated minerals typical of skarn deposits (garnet, epidote, quartz, calcite)
- FORS: Consistent with standard azurite optical properties

Interpretation: If confirmed, this would support established trade routes between Moldavia and Hungary and provide evidence for the Kingdom of Hungary's role as a major pigment supplier to Orthodox artistic centers.

3.3.2 Scenario 2: Saxon Source (Moderate Prior Probability)

Historical rationale: Saxon mining districts were prolific producers of azurite as a byproduct of silver mining. Trade connections existed between German regions and Eastern Europe through merchant networks.

Expected analytical signatures:

- MA-XRF: Elevated Zr (from granitic host rocks), Ag, Sn; distinctive trace element pattern reflecting greisen or vein deposits
- Raman: Quartz, possibly fluorite, muscovite, or other granitic minerals
- FORS: Potentially distinctive optical properties if particle size reflects Saxon grinding traditions

Interpretation: This would indicate long-distance trade networks and possible connections to Western European artistic traditions.

3.3.3 Scenario 3: Mixed Sources (Lower Probability but Possible)

Scenario: Different fresco areas use azurite from different sources, either due to pigment availability during construction or later restoration.

Expected analytical signatures:

- Spatial variation in trace element profiles revealed by MA-XRF mapping
- Inconsistent classification of different sampling points
- Potentially different associated mineral assemblages in different areas

Interpretation: This would suggest complex procurement history or multiple restoration campaigns, requiring detailed documentation of spatial patterns and historical records.

3.4 Broader Implications of Provenance Determination

Successful identification of the azurite source has significance extending beyond the Voroneţ Monastery itself:

3.4.1 Medieval Trade Network Reconstruction

Definitive provenance establishes material connections between mineral source regions and artistic centers, providing tangible evidence for trade routes that may be poorly documented in historical records. The transportation of mineral pigments over hundreds of kilometers reflects economic relationships, political alliances, and merchant networks that shaped medieval European material culture.

3.4.2 Artistic Workshop Practices

Understanding pigment sourcing illuminates the decision-making processes of medieval artists and patrons. The choice of azurite source may reflect:

- Quality preferences (different sources produce azurite with varying color saturation and stability)
- Cost considerations (transportation costs, merchant relationships)
- Availability constraints (supply disruptions, political changes)
- Workshop traditions (established supplier relationships)

3.4.3 Comparative Analysis of Related Monuments

The Voroneţ Monastery is one of several painted monasteries in Bucovina with similar blue frescoes (Moldoviţa, Suceţa, Humor, etc.). Applying the same analytical methodology to these related sites could:

- Determine if they used azurite from the same source
- Identify temporal changes in pigment sourcing
- Distinguish original construction from later restorations
- Establish regional patterns in artistic material procurement

3.4.4 Conservation Science Applications

Knowledge of azurite provenance contributes to conservation efforts through:

- Better understanding of long-term stability (source-dependent variations in trace elements may affect weathering resistance)
- Informed restoration decisions (matching original materials if intervention required)
- Predictive modeling of degradation (source-specific characteristics affecting conversion to malachite)
- Documentation for cultural heritage records

4 Conclusions

4.1 Summary of Analytical Strategy

We have presented a comprehensive multi-technique non-destructive analytical strategy for determining the geographical provenance of azurite pigment in the Voroneţ Monastery blue frescoes. The approach integrates three complementary techniques:

1. **Macro X-ray fluorescence spectroscopy (MA-XRF)**: Provides direct geological fingerprinting through quantitative trace element analysis (As, Zn, Pb, Fe, Mn, Ni, Sb, Ba, Bi, Zr, Sr), spatial elemental distribution mapping, and data suitable for multivariate statistical classification
2. **Raman spectroscopy**: Enables definitive phase identification, detection of provenance-diagnostic associated minerals, crystallinity assessment, and degradation state determination
3. **Fiber optic reflectance spectroscopy (FORS)**: Offers rapid non-invasive screening, purity assessment, particle size information, and optical property characterization

The integration of these techniques through a phased analytical workflow—initial survey (FORS + pXRF), detailed mapping (MA-XRF + Raman), reference database development, and statistical analysis—maximizes the confidence of provenance determination while respecting the cultural heritage value of these irreplaceable artworks.

4.2 Critical Success Factors

The success of this provenance investigation depends on several critical factors:

- **Reference database quality**: Comprehensive sampling and characterization of authenticated azurite specimens from all plausible medieval sources (Hungarian, Saxon, French, Balkan localities)
- **Analytical consistency**: Standardized measurement protocols and data processing procedures across all samples to ensure comparability
- **Statistical rigor**: Appropriate multivariate methods with cross-validation, uncertainty quantification, and hypothesis testing
- **Multi-point verification**: Analysis of sufficient spatial locations on the frescoes to assess homogeneity and confirm consistent provenance assignment

- **Inter-technique agreement**: Concordant conclusions from MA-XRF trace element analysis, Raman mineralogical characterization, and FORS optical properties
- **Historical context integration**: Correlation of analytical findings with art historical evidence, medieval trade routes, and political-economic relationships

4.3 Expected Outcomes and Impact

High-confidence provenance determination is achievable when:

- Trace element profile matches a specific source region with posterior probability > 0.95
- Characteristic associated minerals detected by Raman are consistent with the geological environment of the assigned source
- Results are spatially consistent across multiple fresco locations
- All three analytical techniques provide concordant evidence

Successful provenance assignment will:

- Illuminate medieval trade networks connecting mineral sources to artistic centers in Eastern Europe
- Provide insights into 15th-century material procurement practices and workshop traditions
- Establish a rigorous methodological framework applicable to other painted monasteries in the Bucovina region and beyond
- Contribute to understanding the unique phenomenon of Voroneţ blue through comprehensive material characterization
- Aid conservation efforts by enabling better prediction of long-term stability based on source-specific properties

4.4 Future Directions

While the proposed non-destructive multi-technique approach maximizes information extraction without sample removal, several complementary techniques could enhance provenance determination if micro-sampling were permissible:

- **Lead isotope analysis**: If Pb is present at sufficient concentrations, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios provide powerful provenance markers reflecting the age and geological history of the ore deposit
- **Strontium isotope ratios**: $^{87}Sr/^{86}Sr$ ratios distinguish geological provinces and can discriminate sources with similar trace element patterns
- **Hyperspectral imaging**: Full spectroscopic imaging combining spatial and spectral information for comprehensive characterization
- **Neutron activation analysis (NAA)**: Extremely sensitive detection of rare earth elements and other trace elements at sub-ppm levels
- **Transmission electron microscopy (TEM)**: Nanoscale characterization of mineral inclusions and crystallographic defects

These techniques require sample removal and are therefore not applicable to the current investigation of the Voroneţ frescoes, but could be employed if minute samples (< 100 μg) from detached or already-damaged areas become available.

4.5 Concluding Remarks

The mystery of Vorăneţ blue represents a compelling intersection of art history, analytical chemistry, geology, and cultural heritage science. The non-destructive multi-technique analytical strategy presented here demonstrates the power of integrated spectroscopic and spectrometric methods to address fundamental questions about historical artworks without compromising their integrity. By combining the geological fingerprinting capabilities of MA-XRF, the molecular specificity of Raman spectroscopy, and the optical characterization of FORS, we can determine the geographical origin of the azurite pigment with high confidence, thereby illuminating medieval trade networks, artistic practices, and material culture in 15th-century Eastern Europe.

This investigation exemplifies the modern practice of heritage science, where advanced analytical techniques developed for materials science, geochemistry, and forensics are adapted to the unique constraints and opportunities of cultural heritage research. The success of such studies requires not only technical expertise but also collaborative engagement among analytical chemists, art historians, conservators, geologists, and archaeologists. The provenance of Vorăneţ blue, once determined, will stand as a testament to the power of interdisciplinary scientific inquiry in service of cultural understanding and preservation.

5 Future Work

The comprehensive non-destructive dataset acquired through the multi-technique approach detailed in this paper (MA-XRF, Raman, and FORS) provides a rich foundation for advanced computational analysis. I am currently planning a follow-up study focused on the development and application of machine learning (ML) models to automate and enhance the provenance classification of azurite based on these complex spectral and elemental datasets.

This future work will involve training supervised classification algorithms, such as Support Vector Machines (SVM), Random Forests, and deep neural networks, using the reference database of authenticated azurite sources. The goal is to create a robust predictive model that can assign a geographical origin to the Vorăneţ azurite samples with a quantifiable statistical confidence. I hypothesize that these ML models will be able to identify subtle, high-dimensional correlations within the combined elemental and spectroscopic data that are not readily apparent through conventional statistical methods like PCA or LDA, thereby significantly improving the accuracy and reliability of the provenance assignment.

References

[1] Wikipedia. Voroneț Monastery. https://en.wikipedia.org/wiki/Vorone%C8%9B_Monastery. Accessed November 2025.

[2] 3 Seas Europe. Voroneț Blue – Art's Great Mystery in Romania. https://3seaseurope.com/voronet-blue-monastery-suceava/. Accessed November 2025.

[3] Nicola, M., et al. In situ Raman spectroscopy at the Voroneţ Monastery (16th century, Romania): New results for green and blue pigments. *Journal of Raman Spectroscopy* (2014). https://www.sciencedirect.com/science/article/abs/pii/S092420311400068X.

[4] Zumbulyadis, N., et al. Trace elements in natural azurite pigments found in illuminated manuscript leaves investigated by synchrotron x-ray fluorescence and diffraction mapping. *Applied Physics A* **123**, 1–12 (2017). https://link.springer.com/article/10.1007/s00339-017-1093-0.

[5] Possenti, E., et al. The blue road: Provenance study of azurite samples from historical locations through the analysis of minor and trace elements. *Heliyon* **9**(8), e18799 (2023). https://www.sciencedirect.com/science/article/pii/S2405844023063077.

[6] Jékely, Z. Medieval Hungary: Hungarian azurite. *Jékely's Blog* (2011). https://jekely.blogspot.com/2011/02/hungarian-azurite.html.

[7] Brügmann, G., et al. The early medieval origins of copper ore extraction in the Carpathian Mountains. *Archaeological and Anthropological Sciences* **16**, Article 141 (2024). https://link.springer.com/article/10.1007/s12520-024-02060-y.

[8] Mindat.org. Azurite: Mineral information, data and localities. https://www.mindat.org/min-447.html. Accessed November 2025.

[9] Alfeld, M., et al. MA-XRF for the Characterisation of the Painting Materials and Technique of the Entombment of Christ by Rogier van der Weyden. *Applied Sciences* **11**(13), 6151 (2021). https://www.mdpi.com/2076-3417/11/13/6151.

[10] Vermeulen, M., et al. Non-invasive analysis of heritage textiles with MA-XRF mapping. *Heritage Science* **11**, Article 48 (2023). https://www.nature.com/articles/s40494-023-00977-6.

[11] Cultural Heritage Science Open Source. Azurite. https://chsopensource.org/azurite-k-10200/. Accessed November 2025.

[12] Buti, D., et al. Identifying eighteenth century pigments at the Bodleian library using in situ Raman spectroscopy, XRF and hyperspectral imaging. *Heritage Science* **5**, Article 43 (2017). https://heritagesciencejournal.springeropen.com/articles/10.1186/s40494-017-0157-y.

[13] RRUFF Database. Azurite R050497 - Raman, X-ray, Infrared, and Chemistry. https://rruff.info/azurite/R050497. Accessed November 2025.

[14] Romanian Database of Raman Spectroscopy. Azurite Raman spectra. https://rdrs.uaic.ro/minerals/azurite.html. Accessed November 2025.

[15] Bacci, M. Fiber Optics Reflectance Spectroscopy: A Non-destructive Technique for the Analysis of Works of Art. *Optical Sensors and Microsystems* (2002). https://www.researchgate.net/publication/227214828.

[16] Aceto, M., et al. Seeing red: towards an improved protocol for the identification of madder- and cochineal-based pigments by fiber optics reflectance spectroscopy (FORS). *Heritage Science* **7**, Article 92 (2019). https://www.nature.com/articles/s40494-019-0335-1.

[17] Figure 3. Micro-XRF maps showing the elemental distribution of zinc (Zn), copper (Cu), iron (Fe), etc. Available at: https://www.researchgate.net/figure/Micro-XRF-maps-showing-the-elemental-distribution-of-zinc-Zn-copper-Cu-iron-Fe_fig6_51070353

[18] Figure 5. Pigment identification by fiber-optics diffuse reflectance spectroscopy. Available at: https://www.researchgate.net/publication/236685151_Pigment_Identification_by_Fiber-Optics_Diffuse_Reflectance_Spectroscopy