

REVIEW ARTICLE

From blue to green: A review of the use and alteration of azurite pigment in cultural heritage

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Abstract

Azurite is a key blue pigment in historic art, with well-studied physical and chemical properties; however, a comprehensive synthesis that connects analytical characterization, degradation processes, and provenance studies across diverse contexts remains lacking. This review addresses this critical gap by providing an interdisciplinary synthesis of current research on azurite, a prominent blue pigment extensively used in historical artworks and cultural heritage artifacts. Based on a comprehensive survey of scholarly literature, the article consolidates findings on the pigment's physical, chemical, optical, and mineralogical properties as examined through diverse analytical techniques. Studies employing methods such as X-ray diffraction, Raman spectroscopy, and infrared (IR) spectroscopy are critically evaluated to highlight how azurite has been identified, characterized, and differentiated from related copper-based pigments. Particular emphasis is placed on the influence of particle size—categorized as coarse, medium, and fine—on optical performance and visual appearance in artworks. The review also addresses degradation phenomena, notably azurite's transformation into malachite and cupric oxide under thermal and environmental stress, with implications for pigment stability and material authenticity. Case studies, including notable examples such as the Tomb of Murongzhi, are discussed to illustrate real-world applications of these techniques in heritage science. In addition, the identification of mineral inclusions and impurities is examined in the context of geological provenance and sourcing studies. While the Tomb of Murongzhi is cited as a key example, this review considers the use and transformation of azurite across a range of cultural and geographic contexts.

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Citation: Ali AA, Singh MR.
From blue to green: A review
of the use and alteration of
azurite pigment in cultural
heritage. *Arts & Communication*.
2026;4(1):025220048.
doi: 10.36922/AC025220048

Received: May 28, 2025

Revised: July 11, 2025

Accepted: July 28, 2025

Published online: August 13, 2025

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Keywords: Azurite pigment; Historical colorants; Cultural heritage conservation; Pigment degradation; Analytical characterization; Mineralogical provenance

1. Introduction

Azurite, a stunning copper carbonate hydroxide mineral, has been celebrated since antiquity for its vibrant blue hue. Its discovery in the tomb of Murongzhi, dating back to the Tang dynasty (691 AD), vividly demonstrates the prominence of valuable mineral

pigments in elite burial practices.¹ The use of azurite, often alongside malachite (a striking green pigment), highlights both the luxurious material culture and the artistic mastery of the Tuyuhun people. It also reflects their extensive connections to broader Eurasian trade and cultural networks via the Silk Road. These findings firmly establish azurite not only as a prominent pigment but also as a significant indicator of transcontinental exchange. Its widespread historical use across civilizations, including Ancient Egypt and regions of Central Asia, underscores its importance in cultural interaction.^{2,3}

Azurite, with the chemical formula $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, is renowned for its deep blue to violet-blue color, reminiscent of azure evening skies seen above deserts and winter landscapes.^{4,5} The molecular structure of azurite, shown in Figure 1, reveals a layered arrangement of copper ions (Cu^{2+}) coordinated with carbonate and hydroxide groups, which contribute to its distinctive optical and stability characteristics. Although not widely abundant, azurite's captivating blue hue has drawn human attention for millennia. Historically, it has been utilized across various cultures not only as a copper ore but also as a pigment, gemstone, and ornamental stone—a versatility that endures to this day. This distinctive mineral, with its unique properties, remains valued for both its aesthetic appeal and practical applications.

Lucas and Harris⁶ suggest that azurite may have been utilized as a paint pigment as early as Egypt's Fourth Dynasty. However, its application in Egypt and the classical world appears limited, likely due to the availability of the synthetic copper pigment Egyptian blue (copper calcium silicate). In contrast, azurite became the primary blue pigment in European art throughout the Middle Ages, the Renaissance, and beyond (Figure 2A-C), despite the greater fame of the more exotic and costly ultramarine. In 15th- and 16th-century European easel painting, natural azurite was frequently employed as an underlayer for ultramarine,

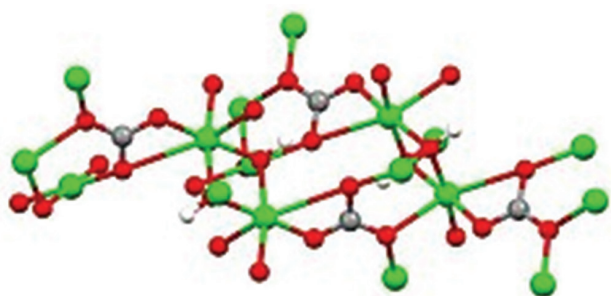


Figure 1. Chemical structure of azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) adapted from standard crystallographic data. Color code: red = O, green = Cu, gray = C, white = H.
Source: RRUFF database ([https://www.wikiwand.com/en/article/Copper\(II\)_hydroxide](https://www.wikiwand.com/en/article/Copper(II)_hydroxide)).

enhancing the depth and brilliance of blue hues. Giotto used azurite to render the blue robes of the apostles in his early 14th-century work *Pentecost* (1310–1318 AD). The central panel's sky in Hubert and Jan van Eyck's *Adoration of the Lamb* ("Ghent Altarpiece," 1425–1432 AD) was also painted with azurite, which has since aged to a greenish hue due to the pigment's chemical transformation. Piero della Francesca's *The Baptism of Christ* (after 1437 AD) features a luminous sky achieved using azurite in egg tempera, showcasing the pigment's versatility and brilliance. The pigment's rich color was especially well-suited for conveying the sanctity and significance of the figures. In *Christ Taking Leave of His Mother* (1520 AD), Albrecht Altdorfer employed azurite for both garments and the sky, demonstrating the pigment's expressive power in conveying depth and emotion. Azurite was extensively used in tempera paintings during the Middle Ages, particularly when ultramarine (derived from lapis lazuli) was unavailable or prohibitively expensive. Ultramarine was highly prized for its vivid blue hue, was sourced exclusively from Afghanistan, making it one of the most expensive pigments of the time. In contrast, azurite, found more abundantly in Europe, offered a more affordable alternative.⁷ In illuminated manuscripts and panel paintings, artists frequently used azurite for blue areas, particularly underpaintings, reserving ultramarine for highlights or significant figures to emphasize divinity and importance. For instance, in a 15th-century *Book of Hours*, azurite was used as a base layer, with ultramarine applied on top to achieve a richer blue, balancing both cost and visual impact.⁷ This strategic use of azurite allowed artists to manage resources effectively while still achieving the desired aesthetic, making it a staple of medieval tempera painting.

Evidence indicates that Hungary served as the principal source of azurite in Europe until the mid-17th century, when Turkish conquest disrupted its supply.^{8,9} This is partially substantiated by reports identifying Hungary as a present-day source of azurite.^{4,10} Other potential historical sources include Chessy, near Lyon in France, and Sardinia, both of which remain known azurite localities today. In the Far East, azurite held a prominent place as the primary blue pigment in traditional paintings. It was extensively used in wall paintings during China's Sung and Ming dynasties, particularly in Central China, and found significant application in Japanese art.¹¹ While azurite was traditionally employed in Japanese art, particularly during the Heian and Kamakura periods, its use in "Ukiyo-e" prints was largely supplanted by the introduction of Prussian blue (known in Japan as "bero-ai") in the early 19th century. This synthetic pigment offered a more vibrant and lightfast blue, leading to its widespread adoption in the "Aizuri-e" (blue printed pictures) style of "Ukiyo-e."¹¹

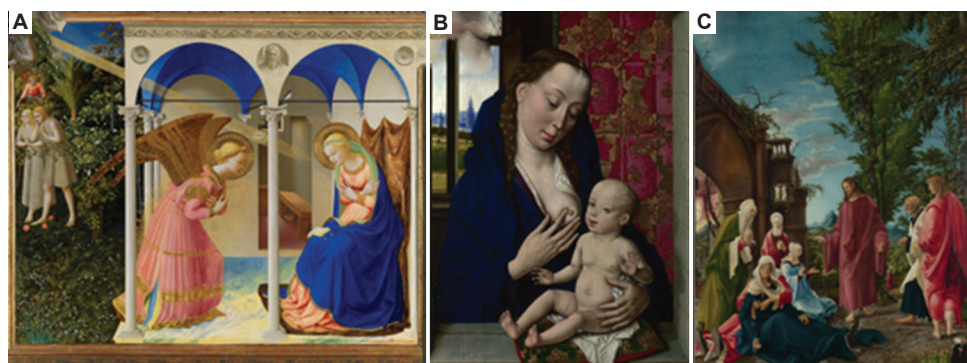


Figure 2. Examples of azurite use in European art. (A) Giotto's *Pentecost* (1310–1318 AD), fresco, Basilica of Saint Francis of Assisi, Italy. (B) *Adoration of the Lamb* by Jan and Hubert van Eyck (1432 AD), oil on panel, "Ghent Altarpiece," Saint Bavo's Cathedral, Belgium. (C) *The Baptism of Christ* by Piero della Francesca (after 1437 AD), egg tempera on panel, National Gallery, London. Mediums: fresco and egg tempera; dimensions vary. Images shown for educational and illustrative purposes.⁸ <https://www.museodelprado.es>, accessed on July 28, 2025. ©Madrid, "Museo Nacional del Prado."

Figure 3A and B shows Japanese paintings in which azurite was used as a colorant. In the Americas, azurite was used to a lesser extent by pre-Columbian Indigenous peoples in the Southwest and later in Spanish Mission Church paintings.¹² According to Kühn,¹³ the use of natural azurite in European easel painting largely declined by around 1800 AD, with most occurrences predating the last quarter of the 17th century. The invention of Prussian blue in the early 18th century appears to have significantly displaced azurite as a favored pigment in European art.

This review aims to synthesize interdisciplinary research on azurite pigments, with a focus on their historical use, physicochemical properties, degradation mechanisms, analytical characterization, and provenance. It seeks to provide a comprehensive resource for scholars, conservators, and materials scientists engaged in the study and preservation of cultural heritage. By integrating scientific findings with case-based insights, this review offers both a foundational overview and a forward-looking perspective on azurite's role in heritage conservation.

2. Geological occurrence

Azurite, a mineral commonly found in the upper oxidized zones of copper ore deposits worldwide, serves as a natural pigment when ground into a fine powder (Figure 4). In nature, azurite is often associated with malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$), a green basic copper carbonate that is even more abundant.^{4,14}

Azurite is a secondary mineral typically formed when carbon-dioxide-rich waters infiltrate the earth and interact with subsurface copper ores. The carbonic acid in these waters dissolves small amounts of copper, which are then carried until the water encounters a different geochemical environment. This new environment—marked by changes in water chemistry, temperature, or evaporation—can

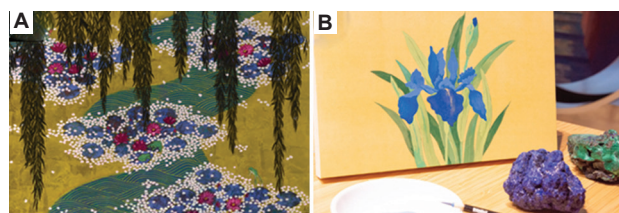


Figure 3. Use of azurite in traditional Japanese painting. (A) *Fugen Bosatsu on an Elephant*, 14th century, hanging scroll, mineral pigments on silk, Nezu Museum, Tokyo. (B) Blue landscape scene, attributed to the Edo period, ink and mineral pigments on paper. Mediums: hanging scroll and printed paper; approximate dimensions: (A) 120 × 50 cm, (B) 40 × 30 cm.¹⁴ <https://www.pinterest.com/pin>, accessed on July 28, 2025. ©Madrid, "Museo Nacional del Prado." ©2025 Pinterest.

prompt the formation of azurite. With prolonged favorable conditions, substantial accumulations of azurite can develop, as has occurred in various locations worldwide. Azurite typically precipitates within pore spaces, fractures, and cavities of subsurface rock, where it commonly forms massive or nodular deposits. In rare instances, azurite can develop as stalactites or botryoidal structures. Well-formed monoclinic crystals are less frequently encountered and only emerge when azurite precipitates freely within a fracture or cavity, undisturbed by later crystallization or geological movements. Malachite, another copper carbonate mineral, forms under conditions similar to those of azurite. These minerals frequently occur together in the same deposits and are often intergrown, creating a material known as azurmalachite. When of high quality, azurmalachite serves as an attractive material for lapidary work.

3. Preparation

Preparing azurite pigment involves selecting high-quality lumps, which are then ground, washed, levigated, and sieved. The pigment's color varies with particle size—coarsely ground azurite yields a deep blue, while finer

grinding results in a lighter tone. In recent times, Japanese producers have refined this process by creating three grades of azurite pigment—coarse, medium, and fine.

4. Physical properties

Azurite is best identified by its distinctive deep blue color. It is a relatively soft mineral, with a Mohs hardness of 3.5–4, and contains copper, which contributes to its blue hue. With a specific gravity of 3.7–3.9, azurite is unusually dense for a non-metallic mineral. As a carbonate, it reacts with dilute hydrochloric acid, creating mild effervescence and producing a light blue solution. When streaked on unglazed porcelain, azurite leaves a light blue mark.

Historically, preparing azurite pigment involved a multistage process to refine the mineral and enhance its chromatic qualities. The raw mineral was first broken into coarse fragments, then subjected to repeated grinding using a mortar and pestle. After grinding, the material was thoroughly washed to remove clay and lighter impurities. This was followed by levigation—a process in which suspended azurite particles were allowed to settle in water, separating coarser particles from finer ones. The levigated

material was dried and sieved to produce pigments of different grades, with particle size directly influencing color intensity.^{13,15} In certain traditions, the pigment was bound with animal or hide glue during preparation to improve adherence. Some recipes also recommend aging the pigment before final use to enhance tone and stability.^{13,15}

5. Particle characteristics

Because azurite pigment is produced by grinding, its particles exhibit a broken and fractured appearance with characteristic conchoidal fractures (Figure 5A–C). These images illustrate the fracture surfaces of azurite, which are significant for both mineral identification and understanding the pigment's behavior in artworks. Without thorough sieving, particle sizes remain irregular, with larger particles often ranging from 20 to 30 μm . Due to azurite's natural association with malachite and cuprite, scattered particles of these minerals are frequently present as impurities, which can significantly impact the color of an azurite paint film. Azurite has a specific gravity of 3.77 and a Mohs hardness of 3.5–4. Particle size distributions in azurite layers from Early Netherlandish paintings were analyzed by De Boer.¹⁶

6. Optical properties

In transmitted light, coarse azurite particles appear deep blue, while finer particles exhibit a pale blue hue. Unlike ultramarine, which possesses a purplish undertone, azurite displays a greenish undertone. Larger azurite particles exhibit high relief and dark edges, particularly when mounted in a medium of lower refractive index, such as Canada balsam or Aroclor. Azurite is classified as a monoclinic crystal and is characterized by moderate to high refractive qualities, as well as strong birefringence. It is biaxial positive, with refractive indices of $\alpha = 1.730$, $\beta = 1.758$, and $\gamma = 1.838$.

7. Chemical properties

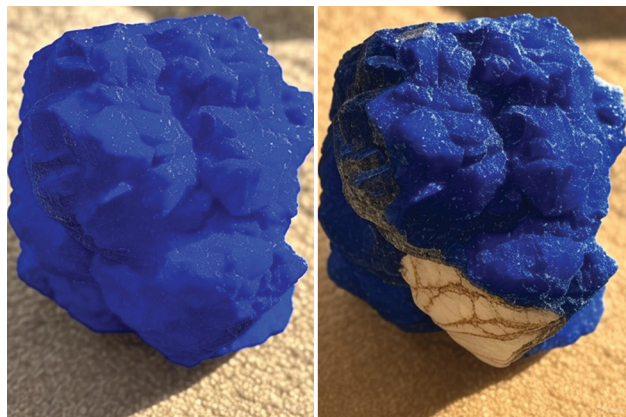


Figure 4. Azurite as a natural blue pigment sourced from copper ore deposits.¹⁵ <https://www.dakotamatrix.com>, accessed on July 28, 2025. Credit to ©Dakota Matrix Minerals, Inc.,

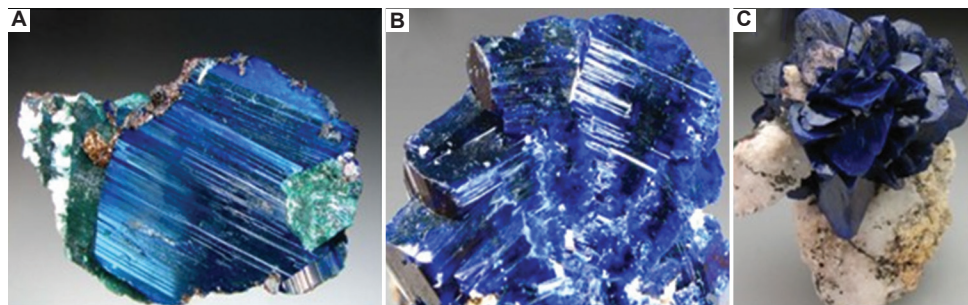


Figure 5. (A–C) Morphological characteristics of ground azurite pigment particles showing conchoidal fractures.¹⁶ <https://www.dakotamatrix.com>, accessed on July 28, 2025. © 2025 Dakota Matrix Minerals, Inc.,

Azurite is stable under light and atmospheric conditions. When heated to approximately 300°C or higher, it releases water and carbon dioxide, leaving a black residue due to the formation of cupric oxide.¹⁷ While azurite is unaffected by cold alkalis, it turns black when warmed with them. It also readily decomposes in the presence of dilute mineral acids, producing carbon dioxide gas. However, when azurite particles are embedded in an organic medium or present in small quantities, they may dissolve without a noticeable release of gas.

Azurite is a monoclinic copper carbonate hydroxide, with a deep blue hue resulting from Cu^{2+} ion d-d transitions. It has a Mohs hardness of 3.5–4, a specific gravity of ~3.7–3.9, perfect cleavage on [011], and a vitreous to dull luster. The mineral is transparent to translucent and commonly forms tabular or prismatic crystals. These properties, including its tendency to alter to malachite under humid or acidic conditions, are well documented in the mineralogical literature.^{18,19}

7.1. Permanence

Although azurite is a carbonate and thus sensitive to acids, it demonstrates considerable permanence when used in oil and tempera media. Azurite may transform into malachite, cupric oxide, or paratacamite, depending on humidity, heat, and exposure to alkaline or sulfurous environments (Figure 6).

However, it tends to darken when exposed to sulfur fumes, particularly in mural paintings.²⁰ Azurite can also turn green over time due to alteration into malachite, as observed in Cimabue's frescoes on the ceiling of the Upper Church of St. Francis in Assisi.²¹ In rare cases, azurite may transform into the basic copper chloride mineral paratacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) under specific environmental conditions.⁹ The pigment remains unaffected by light.

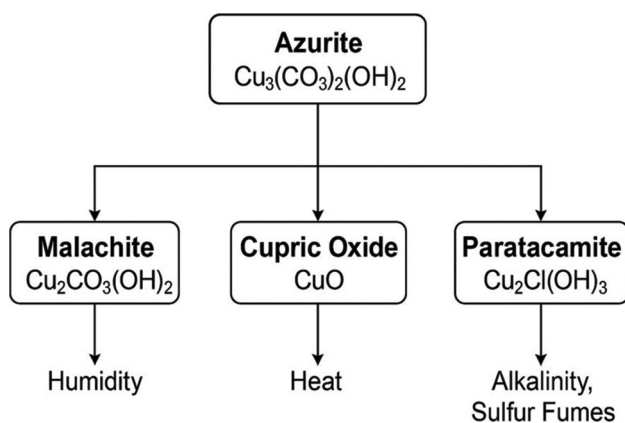


Figure 6. Schematic representation of azurite degradation pathways under environmental stress. Image created by the authors.

According to Selim Augusti,²¹ nearly every medieval Italian church containing azurite mural paintings shows signs of transformation into malachite. Similar transformations have also been reported in mural paintings in Romania.^{22,23}

In many oil-based easel paintings, thick layers of azurite have developed a greenish or very dark, almost black appearance, particularly when the pigment is used alone without mixing with others.⁵ A notable example of this discoloration is found in *St. Margaret* (no. 1930) by Zurbarán, specifically in the saint's blue cloak, at the National Gallery in London.²⁴ The exact cause of this color change remains unclear, and transformation into malachite does not appear to be the primary explanation. It may partly result from darkening of the oil medium in thick, coarse-textured paint layers, despite the known siccative and antioxidant effects of copper pigments on oil films. Another possible cause is the formation of a thin surface layer of black cupric oxide (tenorite) on azurite particles through various hypothesized mechanisms. Recent studies have confirmed the conversion of azurite to cupric oxide in alkaline environments, such as those found on excavated polychrome sculpture.²⁵ In addition, thickly applied azurite paint is often prone to wrinkling and fissuring, although the pigment itself may remain well-preserved beneath the surface.

8. Historical use of azurite pigment

The use of azurite as a blue pigment spans millennia and continents. From Egyptian faience and Chinese tomb murals to medieval European manuscripts and Renaissance panel paintings, azurite has been one of the most prized minerals for its intense hue and relative abundance. Its application methods and aesthetic effects varied by region, reflecting distinct cultural preferences and technological approaches. Azurite was widely used as a pigment in China but is rarely found in Indian paintings. Nonetheless, it is likely that azurite occurs naturally alongside copper ores in India, raising the question of whether it could have been collected for producing natural azurite pigment. A synthetic version, known as blue verditer, has also been produced, though it lacks the durability of the natural mineral.²⁶ Azurite was ground into a pigment for blue paint as early as ancient Egypt,¹⁵ and its use expanded significantly over time. By the Middle Ages and Renaissance, it had become the most important blue pigment in Europe. Much of the azurite used during this period was sourced from mines in France.

Producing pigment from azurite was an expensive process in the Middle Ages, as mining was challenging, transportation was slow, and grinding and processing required significant effort.²⁷ Starting in the 18th century, azurite pigment was gradually replaced by synthetic

alternatives like Prussian blue and blue verditer. These man-made pigments offered standardized, uniform properties, making them more predictable and consistent in application, as well as more economical to produce. Numerous medieval paintings created before the introduction of Prussian blue show signs of blue pigment deterioration.²⁸ Over time, and with exposure to light and atmospheric conditions, azurite gradually weathers into green malachite. This transformation is a key reason synthetic pigments have replaced azurite. Although azurite pigment and paints remain available today, they are primarily used by artists interested in historical painting techniques.²⁹

9. Characterization

In a comprehensive scientific analysis of artifacts excavated from the tomb of Murongzhi, situated along the historic Silk Road in China, azurite emerged as a prominent mineral pigment utilized in decorative artwork. This study employed advanced multi-analytical techniques, including Raman spectroscopy and X-ray diffraction (XRD), to accurately determine the composition and authenticity of the pigments found on murals, pottery, lacquered wood, and textiles.¹

X-ray diffraction is an ideal tool for identifying and confirming the presence of azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) in pigment samples. XRD analysis is based on the unique diffraction patterns produced when X-rays interact with the azurite crystal lattice, allowing for precise mineral identification. Pigment samples are finely ground to ensure homogeneous, fine-grained particles. Care is taken to avoid environmental contamination or transformations, particularly conditions that could lead to azurite's conversion into malachite or cupric oxide. Azurite's monoclinic crystal structure produces a characteristic XRD pattern with distinctive peaks that serve as "fingerprints" for the mineral. The XRD data provided strong support for the identification of azurite from the Tomb of Murongzhi. Notable diffraction peaks were detected at 2θ values of 17.5, 17.58, 24.72, 34.26, 40.66, and 49.26, which align well with the crystalline structure characteristic of azurite (Figure 7). These findings confirm that azurite is a prominent component in the surface layer of blue-painted artifacts from the site, highlighting its cultural and analytical significance.¹ By comparing the sample's XRD pattern with reference patterns from databases such as the International Centre for Diffraction Data or the Inorganic Crystal Structure Database, azurite can be accurately identified and distinguished from other copper-based carbonates such as malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$). Malachite has an orthorhombic structure and produces a distinct set of XRD peaks, allowing researchers to identify and quantify

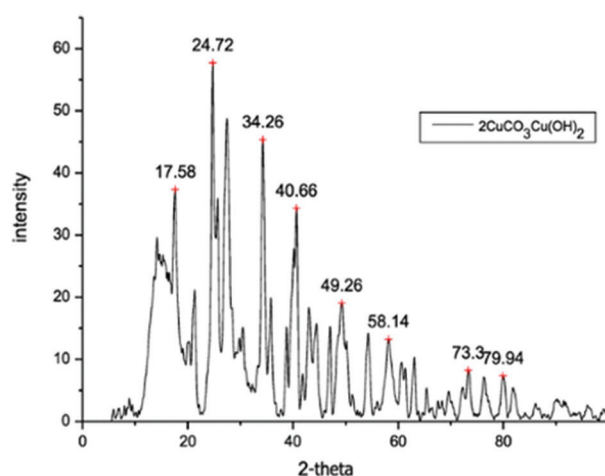


Figure 7. X-ray diffraction pattern of azurite showing characteristic crystalline peaks. Reprinted with permission from Wei *et al.*¹ Copyright © 2023, American Chemical Society.

each mineral phase. XRD can also assess the purity of azurite by detecting additional phases such as malachite or cupric oxide that may have formed as alteration products. This analysis helps identify samples that have undergone weathering or degradation over time, as azurite gradually converts to malachite under environmental exposure. The presence of cupric oxide peaks may also indicate exposure to heat or alkaline conditions. Such data are crucial for developing conservation strategies and understanding the original materials used by artists across different historical and cultural contexts.

Brown *et al.*³⁰ explored the thermal decomposition of azurite using *in situ* X-ray thermodiffraction techniques, tracking the pigment's phase transitions and analyzing the effects of heating up to 220°C, which can lead to the formation of tenorite (CuO). This research is significant for understanding azurite's stability in conservation efforts, particularly under various environmental conditions. Hiley *et al.*³¹ demonstrated a high-resolution, non-invasive XRD approach suitable for azurite and other historical pigments. Their study shows the application of XRD in detailed phase analysis and crystallographic data acquisition for cultural heritage pigments. Frost *et al.*³² examined azurite's thermal decomposition stages and the transformation to malachite under specific conditions. Their study provides insight into azurite's structural changes over time, which can help in understanding its alteration in art and archeological artifacts exposed to natural aging.

Raman spectroscopy is a powerful tool for characterizing azurite, a copper carbonate hydroxide mineral widely used as a pigment in historical artwork. Raman spectroscopy offers several advantages for analyzing azurite, including

its non-destructive nature, the ability to detect subtle structural and compositional differences, and its capability to work *in situ* on artifacts and paintings without causing damage. Azurite exhibits distinctive Raman peaks, typically observed around 400–1,600 cm^{-1} . These peaks correspond to the vibrational modes of the carbonate and hydroxide groups in the crystal structure. The primary Raman bands for azurite include those associated with the symmetric stretching and bending modes of the carbon trioxide (CO_3) groups, as well as bands corresponding to the Cu-O and Cu-OH bonds.^{32,33} These peaks allow for reliable identification of azurite and differentiation from other blue pigments such as ultramarine or synthetic blue pigments.

Raman spectroscopy is particularly useful in conservation science because it can detect transformation products, such as malachite, which sometimes forms due to azurite's gradual weathering or alteration under environmental conditions. This is relevant for preserving historical artifacts, as Raman analysis can track the degradation processes that occur in azurite-containing artworks over time. Studies have noted that exposure to light, humidity, and air pollutants can induce azurite's gradual conversion to malachite, identifiable through changes in the Raman spectra. Moreover, Raman microscopy, combined with XRD and other analytical methods, enhances the understanding of azurite's composition and stability within complex paint layers.

Aru *et al.*³⁴ conducted Raman microscopy analysis on 19 natural azurite specimens sourced from historically significant mining regions across Europe and beyond. Their findings revealed a consistent pattern of mineral impurities, with hematite ($\alpha\text{-Fe}_2\text{O}_3$) being the most prevalent impurity, identified in 14 of the samples. Noteworthy specimens included BM 59247 from Moldova, BM 91434 from Oravicza, Krasso (Hungary), and BM 91438 from Falkenstein, Schwaz, Tyrol (Austria). Goethite ($\alpha\text{-FeO}(\text{OH})$) was identified in 13 samples, including BM 91440 from Moldova, Krasso (Hungary), BM 91432 from Zellerfeld, Harz (Germany), and BM 1964 R7046 from Gwennap, Cornwall (United Kingdom). Malachite ($\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$), another prevalent impurity, was present in 11 samples, including BM 91436 from Falkenstein (Austria), BM 1955.214 from Garrigill, Cumberland (United Kingdom), and BM 91442 from Chessy, Lyon (France). Cuprite (Cu_2O) was found in seven samples, such as BM 91440 (Hungary), BM 59258B from Barnaul, Tomsk (Siberia), and BM 91444 from Molina de Aragón, New Castile (Spain).

Less common impurities included anatase and rutile (TiO_2), quartz (SiO_2), calcite (CaCO_3), cerussite (PbCO_3), cinnabar (HgS), rhodochrosite (MnCO_3), and amorphous carbon, many of which are associated with host rock

matrices or environmental contamination. Rare minerals such as jarosite and beudantite were found in only two samples each but may serve as provenance markers if consistently detected in future studies. Contrary to earlier assumptions, tenorite (CuO) was not detected, and many of the orange-brown and black inclusions were identified as goethite or hematite rather than copper oxides. These findings suggest that the impurity phases commonly observed in museum azurite pigments are a result of natural geological processes rather than artistic manipulation.³⁴ The Raman spectra of blue pigments from the Tomb of Murongzhi clearly revealed distinctive peaks at 248, 398, 767, and 831 cm^{-1} (Figure 8). These peaks align perfectly with the established spectral signatures of azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$), definitively confirming its presence as a blue pigment in the analyzed samples.¹

In the Tomb of Murongzhi, azurite was identified as a primary blue pigment used in mural fragments from the Tang dynasty. Micro-Raman spectroscopy confirmed the presence of $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ with strong peaks near 400, 765, and 1090 cm^{-1} , consistent with crystalline azurite. Scanning electron microscopy (SEM)-energy-dispersive X-ray spectroscopy analysis showed copper-rich layers interbedded with mineral accretions, suggesting environmental influence on pigment stratigraphy. Fourier transform infrared spectroscopy (FTIR) also supported azurite's presence, with characteristic carbonate absorption (Figure 9). This case highlights the pigment's application in elite funerary art and its relatively intact preservation after more than a millennium.¹

IR spectroscopy analysis of azurite provides insight into its molecular structure, particularly focusing on the carbonate groups and hydroxyl vibrations within the

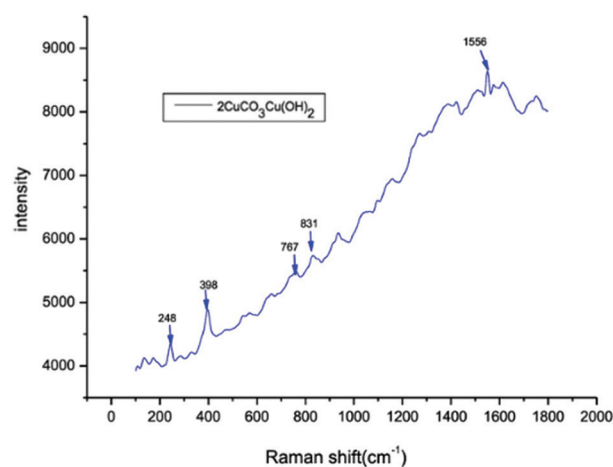


Figure 8. Raman spectra of azurite pigments from the Tomb of Murongzhi showing characteristic vibrational bands. Reprinted with permission from Wei *et al.*¹ Copyright © 2023, American Chemical Society.

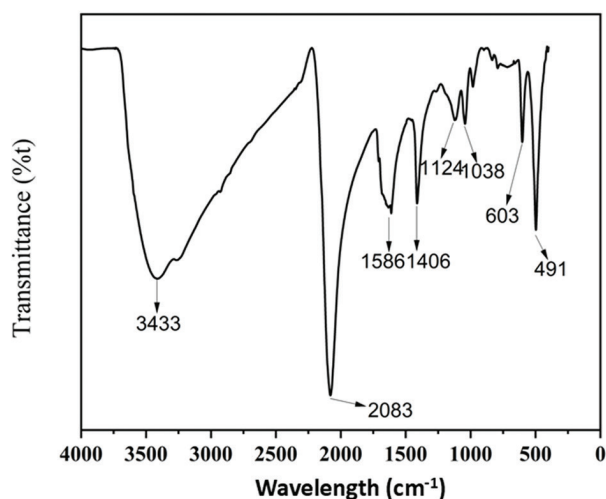


Figure 9. Fourier transform infrared spectroscopy spectrum of azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), showing characteristic absorption bands near $1,406\text{ cm}^{-1}$ (CO_3^{2-} stretching), $1,038\text{ cm}^{-1}$ (bending), and $3,433\text{ cm}^{-1}$ (OH^-). Image created by the authors.

mineral. Key absorption bands appear in the range of $1,350\text{--}1,650\text{ cm}^{-1}$ for the carbonate stretching modes, while OH bending modes are generally observed around $3,400\text{--}3,500\text{ cm}^{-1}$. These IR spectra help distinguish azurite from other copper carbonates, such as malachite, due to their unique band patterns, which are valuable for verifying the mineral's presence in artworks, geological samples, or conservation projects.³⁵

In recent years, hyperspectral imaging techniques, especially in the short-wave IR (up to $2,500\text{ nm}$), have been used to map azurite and its alteration products non-invasively. For instance, reflectance features at approximately $2,285$ and $2,350\text{ nm}$ help in identifying azurite across paintings and heritage objects.³⁶ Electrochemical methods such as cyclic voltammetry and impedance spectroscopy have also demonstrated potential for *in situ* monitoring of copper carbonate pigments, offering new insight into redox behavior and degradation pathways.

10. Provenance studies and mineral impurity profiling

Recent advancements in mineral impurity profiling have enhanced the ability to trace the geological origins of azurite pigments. By combining Raman spectroscopy, XRD, and elemental mapping, researchers have begun to differentiate azurite samples from key historical mining sites based on unique combinations of mineral inclusions such as hematite, goethite, malachite, and quartz. For example, Aru *et al.*³⁴ successfully classified azurite specimens from regions such as Chessy (France), Harz (Germany), and Cornwall (United Kingdom) by analyzing

impurity patterns and crystal morphology. These findings offer potential for provenance determination in artworks and painted surfaces, allowing scholars to reconstruct pigment trade routes and workshop practices. Although still an emerging field, such studies demonstrate how analytical mineralogy can contribute meaningfully to cultural heritage investigations.

11. Discussion

The findings synthesized in this review illustrate how azurite, while visually compelling and historically widespread, presents unique challenges for conservation due to its chemical instability and complex provenance. Integrating art historical contexts with multi-analytical studies reveals broader patterns in pigment sourcing, workshop practices, and long-term material behavior. These insights bridge heritage science, analytical chemistry, and cultural history, reaffirming azurite's value as both a scientific subject and cultural marker.

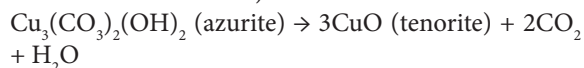
The literature on azurite as a historical pigment reveals the evolution of its use, significance, and scientific investigation. Across cultures and time periods, azurite was selected not only for its vibrant hue but also for its accessibility and ease of preparation, particularly in contrast to the rarer and more expensive ultramarine. However, differences in pigment processing methods—ranging from simple hand grinding to complex levigation—have resulted in varying particle morphologies and optical properties, affecting both visual aesthetics and analytical interpretations. A critical comparison of spectroscopic studies demonstrates that while azurite can be reliably identified through Raman and FTIR spectroscopy, overlapping signals with associated minerals like malachite or cerussite often complicate interpretation. This highlights the need for multi-analytical protocols to distinguish natural alteration products from intentional pigment mixtures, especially in complex polychrome surfaces.

The reviewed studies further show that azurite is particularly sensitive to environmental conditions such as humidity, temperature, and pH fluctuations. Its known conversion to malachite or basic copper oxides under such stressors raises important concerns for the long-term stability of azurite-containing artworks, especially those on exposed architectural surfaces or in poorly controlled museum environments. The degradation of azurite under acidic, humid, or thermal stress typically follows these reactions:

- (i) Formation of malachite (under moist carbon dioxide [CO_2]-rich conditions):

$$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2 \text{ (azurite)} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 3\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \text{ (malachite)}$$
- (ii) Formation of copper oxide (under high temperature)

or oxidative conditions):



These reactions are central to the pigment's long-term instability and guide the development of conservation strategies for azurite-containing artifacts. Yet, the specific mechanisms and thresholds of these transformations remain incompletely understood, suggesting a promising avenue for future experimental work. Furthermore, the geographical sourcing of azurite based on trace impurities or mineral inclusions has opened new pathways for provenance studies, although this remains an underexplored field requiring a more robust mineralogical database. Finally, the role of azurite in non-Western traditions, especially in East Asia, merits greater scholarly attention to enrich the global narrative of pigment use and evolution.

Despite the substantial research on azurite's mineralogy and degradation, key gaps remain. There is a need for integrated long-term monitoring of azurite-containing artworks under real environmental conditions, as well as broader use of high-resolution imaging and isotope analysis in provenance studies. Future investigations should also explore historical pigment recipes and workshop techniques that may influence azurite's performance. Such interdisciplinary approaches will not only refine conservation strategies but also deepen understanding of artistic materials and trade networks in historical contexts.

12. Conclusion

This review consolidates current knowledge on azurite, a historically significant blue pigment widely used across cultures and time periods in mural paintings, manuscripts, and polychrome sculptures. Drawing from a wide range of analytical studies, this work underscores azurite's distinct mineralogical identity, variable particle morphology, and unique optical behavior, which are closely tied to its preparation techniques and intended artistic effects. Through methods such as XRD, Raman spectroscopy, FTIR, and SEM, past studies have illuminated the pigment's structural integrity, chemical composition, and sensitivity to environmental stressors. The degradation of azurite into malachite or other copper-based products, especially under humid, alkaline, or thermally unstable conditions, emerges as a critical concern for conservators. These transformations not only alter the visual character of artworks but also compromise the pigment's stability and authenticity. Furthermore, the presence of mineralogical impurities and associated phases offers valuable clues to geological sourcing and historical trade routes, enriching our understanding of pigment provenance and workshop

practices. The review emphasizes the importance of non-destructive, multi-analytical approaches in the study of azurite to support both scholarly research and conservation planning. As cultural heritage professionals strive to balance preservation with public display and environmental exposure, the insights gained from these characterizations become indispensable. Future research should focus on the long-term monitoring of azurite-based artifacts, the development of conservation strategies tailored to its vulnerabilities, and the exploration of historical recipes that may influence its behavior.

Acknowledgments

The authors would like to acknowledge the support provided by Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, and Tezpur University, Assam.

Funding

None.

Conflict of interest

The authors declare that they have no competing interests.

Author contributions

Conceptualization: All authors

Visualization: All authors

Writing—original draft: All authors

Writing—review & editing: All authors

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data

Not applicable.

References

1. Wei Y, Gu W, Zhong L, *et al.* Investigation of Asian dyes and pigments from the artifact of “Murongzhi” and the Silk Road in China. *ACS Omega*. 2023;8(2):2508-2519.
doi: 10.1021/acsomega.2c06572
2. Abel A. *The History of Dyes and Pigments: From Natural Dyes to High Performance Pigments*. *Colour Design*. Netherlands: Elsevier; 2012. p. 557-587.
doi: 10.1016/B978-0-08-101270-3.00024-2
3. Chen G, Yu Z, Chai B, *et al.* On the application of nondestructive in situ analysis on wall paintings of the Lu

- Tusi Yamen building in Yongdeng County. *Dunhuang Res.* 2018;169(3):28-37.
4. Dana JD, Dana ES, Frondel C, Berman H, Palache C. *Dana's Manual of Mineralogy-Volume 2: Halides, Nitrates, Borates, Carbonates, Sulfates, Phosphates, Arsenates, Tungstates, Molybdates. Entirely Rewritten and Greatly Enlarged.* New York, NY: John Wiley and Sons, Incorporated; 1951.
 5. Gettens RJ, Fitzhugh EW. Azurite and blue verditer. *Stud Conserv.* 1966;11(2):54-61.
doi: 10.1179/sic.1966.008
 6. Lucas A, Harris J. *Ancient Egyptian Materials and Industries.* United States: Courier Corporation; 2012.
 7. Agostino A, Pellizzi E, Aceto M, Castronovo S, Saroni G, Gulmini M. On the hierarchical use of colourants in a 15th century book of hours. *Heritage.* 2021;4(3):1786-1806.
doi: 10.3390/heritage4030100
 8. Laurie AP. VII.—Ancient pigments and their identification in works of art. *Archaeologia.* 1913;64:315-336.
doi: 10.1017/S0261340900010754
 9. Gettens RJ, Stout GL. A monument of byzantine wall painting: The method of construction. *Stud Conserv.* 1958;3(3):107-119.
doi: 10.1179/sic.1958.016
 10. Zsivny V. Ein neues azuritvorkommen aus Ungarn. In: *Annales Historico-Naturales Musei Nationalis Hungarici.* Vol. 41. Oxford: Oxford Academic; 1948. p. 25-31.
 11. Pérez-Arantegui J, Rupérez D, Almázan D, Díez-De-Pinos N. Colours and pigments in late ukiyo-e art works: A preliminary non-invasive study of Japanese woodblock prints to interpret hyperspectral images using in-situ point-by-point diffuse reflectance spectroscopy. *Microchem J.* 2018;139:94-109.
doi: 10.1016/j.microc.2018.02.015
 12. Smith W, Ewing LH. *Kiva Mural Decorations at Awatovi and Kawaika-a: With a Survey of other Wall Paintings in the Pueblo Southwest.* Vol. 37. United States: Harvard University Press; 2006.
 13. Kühn H. Verdigris and copper resinate. *Stud Conserv.* 1970;15(1):12-36.
doi: 10.1179/sic.1970.15.1.002
 14. Dana JD. *Manual of Mineralogy, Including Observations on Mines, Rocks, Reduction of Ores, and the Applications of the Science to the Arts.* United States: White and Peck; 1864.
 15. Thompson DV, York LE. *The Practice of Tempera Painting.* United States: Dover Publications; 1962.
 16. De Boer JVA. An examination of particle size distributions of azurite and natural ultramarine in some early netherlandish paintings. *Stud Conserv.* 1974;19:233-243.
doi: 10.2307/1505730
 17. Simpson DR, Fisher R, Libsch K. Thermal stability of azurite and malachite. *Am Mineral J Earth Planet Mater.* 1964;49(7-8):1111-1114.
 18. Frondel C. Memorial of charles palache. *Am Mineral J Earth Planet Mater.* 1956;41(3-4):306-314.
 19. Klein C, Dutrow B. *Manual of Mineral Science.* United States: John Wiley and Sons; 2007.
 20. Orna MV. Historic mineral pigments: Colorful benchmarks of ancient civilizations. In: *Chemical Technology in Antiquity.* Washington, D.C: ACS Publications; 2015. p. 17-69.
doi: 10.1021/bk-2015-1211.ch002
 21. Augusti S. *Alterazioni Dei Dipinti Murali: Loro Natura e Cause;* 1948. Available from: <https://www.com/openlibrary/org> [Last accessed on 2025 Jul 27].
 22. Dei L, Ahle A, Baglioni P, Dini D, Ferroni E. Green degradation products of azurite in wall paintings: Identification and conservation treatment. *Stud Conserv.* 1998;43(2):80-88.
doi: 10.1179/sic.1998.43.2.80
 23. Barbu OH. *pXRF and FTIR Spectrometry Applied to the Study of Azurite and Smalt in Romanian Medieval Wall Painting. Conservation and Painting Techniques of Wall Paintings on the Ancient Silk Road.* Berlin: Springer; 2021. p. 105-117.
doi: 10.1007/978-981-33-4161-6_6
 24. Wyld M, Roy A, Smith A. *Gerard Davids' The Virgin and Child with Saints and a Donor.* *National Gallery Technical Bulletin.* Vol. 3. 1979. P. 51-65. Available from: <https://www.nationalgallery.org.uk/paintings/gerard-david-the-virgin-and-child-with-saints-and-donor>
 25. Gutscher D, Miethaler B, Portmann A, Reller A. Conversion of azurite into tenorite. *Stud Conserv.* 1989;34(3):117-122.
doi: 10.1179/sic.1989.34.3.117
 26. Singh K, Kumar P, Singh N. Natural dyes: An emerging ecofriendly solution for textile industries. *Poll Res.* 2020;39(2):S87-S94.
 27. Silvie Š, Hradil D, Janka H, Zdeňka Č. Pigments—copper-based greens and blues. *Archaeol Anthropol Sci.* 2021;13(11):190.
doi: 10.1007/s12520-021-01406-0
 28. Larsen ES. *The Microscopic Determination of the Nonopaque Minerals.* United States: Government Printing Office; 1921.
 29. Available from: <https://geology.com/minerals/azurite.shtml> [Last accessed on 2025 Jun 20].
 30. Brown IW, Mackenzie KJ, Gainsford GJ. Thermal decomposition of the basic copper carbonates malachite and azurite. *Thermochimica acta.* 1984;75(1-2):23-32.

- doi: 10.1016/0040-6031(84)85003-0
31. Hiley CI, Hansford G, Eastaugh N. High-resolution non-invasive X-ray diffraction analysis of artists' paints. *J Cul Herit*. 2022;53:1-13.
doi: 10.1016/j.culher.2021.10.008
32. Frost RL, Ding Z, Kloprogge JT, Martens WN. Thermal stability of azurite and malachite in relation to the formation of mediaeval glass and glazes. *Thermochimica Acta*. 2002;390(1-2):133-144.
doi: 10.1016/S0040-6031(02)00127-2
33. Frost RL, Martens WN, Rintoul L, Mahmutagic E, Kloprogge JT. Raman spectroscopic study of azurite and malachite at 298 and 77 K. *J Raman Spectrosc*. 2002;33(4):252-259.
doi: 10.1002/jrs.848
34. Aru M, Burgio L, Rumsey MS. Mineral impurities in azurite pigments: Artistic or natural selection? *J Raman Spectrosc*. 2014;45(11-12):1013-1018.
doi: 10.1002/jrs.4469
35. Vahur S, Teearu A, Peets P, Joosu L, Leito I. ATR-FT-IR spectral collection of conservation materials in the extended region of 4000-80cm⁻¹. *Anal Bioanal Chem*. 2016;408:3373-3379.
doi: 10.1007/s00216-016-9411-5
36. Liggins F, Vichi A, Liu W, *et al*. Hyperspectral imaging solutions for the non-invasive detection and automated mapping of copper trihydroxylchlorides in ancient bronze. *Herit Sci*. 2022;10(1):142.
doi: 10.1186/s40494-022-00765-8