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Cultural Arts Research and Development

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REVIEW

Historical Blue Pigments Used in India's Wall Paintings-A Review

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ABSTRACT

This review highlights the complexity of understanding historical blue pigments, focusing on their characterization, sources, and application in wall paintings. It discusses the Ajanta wall paintings, noting that past and current investigations have only scratched the surface. The dissemination of ideas along ancient trade routes influenced the sharing of painting materials and techniques, but each wall painting remains unique. A 13-year survey of Cappadocia's rock-cut churches illustrates continuity and diversity in Byzantine painting techniques. The use of mineral blue pigments in the Indian context is reviewed based on both analysis and literary sources. The article emphasizes the need for further research on pigment identification and durability in various types of paintings across regions and periods.

Keywords: Lapis Lazuli; Natural Ultramarine; Egyptian Blue; Chinese Blue; Azurite

1. Introduction

Wall paintings have served as expressions of power, wealth, and aspirations across different social strata. Religions and cults also used wall imagery to convey spiritual and temporal concerns in tombs, churches, and temples. Advances in non-invasive analytical techniques now allow for more detailed analysis of original painting materials, particularly organic compounds once difficult to detect. India's rich tradition of dyeing and painting on textiles is evident in its historical wall paintings, such as those at Ajanta and Ellora, with early literature referencing these arts[1] Natural dyes, derived from plants and insects, were historically used [2]. However, synthetic dyes, introduced with advances in chemistry, offer a wider color range and

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ARTICLE INFO
Received: 8 December 2024 | Revised: 18 December 2024 | Accepted: 24 December 2024 | Published Online: 27 December 2024
DOI: https://doi.org/10.55121/card.v4i2.228

CITATION
Sharma, A., Singh, M.R. 2024. Historical Blue Pigments Used in India's Wall Paintings-A Review. Journal Name. 4(2): 24–42.
DOI: https://doi.org/10.55121/card.v4i2.228

stability. Pigments, insoluble particles providing color, can be organic or inorganic, with synthetic variants playing a significant role in modern industries due to their vibrancy and cost-effectiveness [2,3]. This shift revolutionized mass production in the modern era.

India's rich natural mineral resources have historically provided pigments for various traditional art forms, including wall paintings, textiles, and manuscripts [4]. Notable natural pigments include:

Red Ochre: Derived from iron oxide, this reddish-brown pigment has been used for centuries in Indian art.

Yellow and Brown Ochre: Also from iron oxides, these pigments create yellow and brown hues, often seen in miniature paintings.

Green Earth: Based on celadonite, this green pigment was used in frescoes and murals.

Indian Yellow: Once believed to come from the urine of cattle fed mango leaves, it was used in textile dyes and traditional paintings, though its origin remains debated.

India's natural mineral resources offer potential for pigment production, but large-scale viability compared to synthetic pigments depends on factors like mineral quality, availability, and extraction costs. Research, investment, and technology are needed to explore their commercial potential. With growing demand for eco-friendly materials, natural pigments could serve as sustainable alternatives [4]. Blue pigments were commonly used for skies, garments, and water, with shades achieved by mixing with black or white pigments to create depth and highlights.

The choice of natural blue pigments in Indian wall paintings was historically limited, with blue pigments becoming common only around the 4th–5th century CE [5]. Before this, paintings primarily used red, yellow, green, black, and white. Though lapis lazuli and turquoise were mentioned in ancient texts, their practical use yielded poor pigments. The key blue pigments of historical significance include:

Ultramarine Blue: Derived from lapis lazuli, it was highly prized in Europe for its rich hue, used by Renaissance artists like Leonardo da Vinci [6].

Cerulean Blue: A cooler, lighter blue, often used for skies and water.

Prussian Blue: Discovered in the 18th century, it became popular for landscapes and blueprints.

Indigo: A natural dye used for centuries in textiles and art.

Egyptian Blue: One of the earliest synthetic pigments, used in ancient wall paintings.

Azurite: A natural mineral pigment used for skies and clothing.

Cobalt Blue: Developed in the 19th century, known for its bright, intense hue.

Modern Blue Pigments: Synthetic pigments like phthalo blue offer vibrant, versatile options for contemporary artists.

The use of blue pigments in art spans many cultures, with different pigments offering varied hues and lightfastness, allowing artists to create distinct moods [7]. In Indian wall paintings, blue pigments evolved over time, with notable examples including:

Indigo: A natural dye from the indigofera plant, used for centuries in Indian textiles and art.

Lapis Lazuli: Ground into ultramarine, this rare, costly stone produced a rich, vibrant blue.

Azurite: A more affordable mineral pigment providing a deep blue, commonly used in Indian art.

Prussian Blue: A synthetic pigment from Europe, known for its intense color and adopted into Indian art.

Copper-Based Blues: Derived from copper compounds, these pigments often had greenish or turquoise tints.

Ultramarine Substitute: Imitations of ultramarine were used due to the rarity of genuine lapis lazuli, offering a similar blue at a lower cost.

The availability and use of blue pigments in India varied by region and period, expanding as trade routes introduced new materials and techniques. Choices of pigment were influenced by factors like cost, availability, and desired effects. Different regions developed preferences based on local resources and artistic traditions [8]. Ultramarine, a valuable pigment, was made by grinding lapis lazuli. Its name, meaning "beyond the sea," reflects its importation from distant sources like Afghanistan [9].

Though India had no natural sources of lapis lazuli, the prized ultramarine pigment was imported from Afghanistan via trade routes like the Silk Road [10]. Indian artists used ultramarine in wall paintings, manuscripts, and textiles, especially in religious art. The vibrant blue symbolized divinity, often depicting gods like Krishna and Shiva [11]. Notable examples include the Ajanta and Ellora Caves, where ultramarine created striking blue tones in murals [12]. This trade highlights India's cultural exchanges with neighbouring regions, with ultramarine symbolizing purity and the infinite in Indian art [13]. **Figure 1** depicts some of the ancient artworks with blue coloration from India.

Ultramarine, an iconic pigment in art history, is exemplified by its use in Indian wall paintings, reflecting ancient cultural exchanges. Lapis lazuli, valued for its deep blue color, has a rich history dating back to around 7000 B.C. in regions like Western Pakistan, making it one of the earliest gemstones known to humanity. Early artisans employed simple techniques to extract the blue mineral from a calcareous matrix. In ancient Egypt, it was crafted into beads, amulets, and seals during the Naqada I period (4000-3500 B.C.). The stone held significant cultural value, symbolizing wealth and prestige in Mesopotamia and Egypt, where it featured prominently in mythology. Its association with Buddhism in Asia further highlighted its spiritual significance, as it was used in religious artefacts. The trade of lapis lazuli also facilitated cultural exchange, connecting ancient civilizations and promoting the flow of art, ideas, and technology across regions.

The historical use of lazurite, the blue component of lapis lazuli, is documented in numerous ancient artworks. Notably, lazurite was identified in murals in the Ajanta caves, dating back to the 4th and 5th centuries, showcasing exquisite blue pigments likely derived from lapis lazuli [14]. Similarly, murals in the Ellora caves, from the 6th to 10th centuries, demonstrate the significance of lapis lazuli-based pigments in ancient Indian art [15]. Along the Silk Road, lapis

Figure 1. Showing uses of blue pigment (**a-c**) Ajanta caves; (**d**) Ellora caves; (**e**) Tabo Monastery; (**f**) Goa Church.

lazuli was utilized in frescoes from the 6th to 9th centuries, depicting clear skies and clean water [16,17]. In Bamiyan, Afghanistan, murals from the 6th to 7th centuries provide early evidence of lapis lazuli's use [18]. Marco Polo's travels in the late 13th century introduced lapis lazuli to Europe, recognizing its trade potential [19]. However, extracting lazurite was labor-intensive and costly, enhancing its value [20]. **Figure 2** depicts the optical microscopic view of the crystal and powder of Indian wall ultramarine, which was used in the cave murals of Ajanta. This image showcases the fine details of the pigment and provides insights into the composition of the blue coloration that enriched the cave paintings.

The nomenclature and composition of ultramarine, primarily sourced from lapis lazuli, are complex and historically significant [21]. Lapis lazuli is a mineralized limestone containing lazurite, the key component of ultramarine pigment. It can also include other minerals such as hauynite and sodalite, both of which can appear in blue forms [22]. Additionally, lapis lazuli may contain silicate minerals like diopside and muscovite, along with calcite and pyrites. The quality of lapis lazuli varies, with the finest specimens exhibiting a uniform deep blue, while others may present paler shades or white crystalline inclusions [23].

1.1. Chemical Composition

Ultramarine is characterized by the chemical formula $Na_6Al_6Si_6O_{24}S_3$, where "n" can vary from 2 to 4 [24]. This formula indicates the presence of sodium (Na), aluminum (Al), silicon (Si), oxygen (O), and sulfur (S) ions within its structure.

1.2. Free Polysulfide Radicals

Modern spectroscopic techniques, including Electron Paramagnetic Resonance Spectroscopy, have identified free polysulfide radicals within the crystal structure of ultramarine. These typically unstable radicals are incorporated into the aluminosilicate lattice as negatively charged polysulfide ions (e.g., S_3^-), accompanied by sodium counter ions that help stabilize them [25].

1.3. Crystal Structure

The crystal structure of ultramarine is intricate. In its simplest form, it comprises equal numbers of silicon and aluminum ions. The fundamental lattice unit is represented as $Na_6Al_6Si_6O_{24}$ or $(Na^+)_6(Al^{3+})_6(Si^{4+})_6(O^{2-})_{24}$. The substitution of silicon ions with aluminum leads to the integration of aluminum into the structure [26]. Each Al^{3+} ion is paired with a Na^+ ion to maintain overall charge neutrality.

1.4. Sulfur Groups

Ultramarine contains two types of sulfur groups—S_3^- and S_2^-. Both species are free radicals that become stabilized within the crystal lattice. The presence and characteristics of these incorporated sulfur groups are crucial for the color of pigments derived from ultramarine. The complex chemistry and crystal structure of ultramarine contribute to its unique and highly valued properties as a blue pigment used in various artistic and decorative applications [27]. The crystal structure of ultramarine is shown in **Figure 3**.

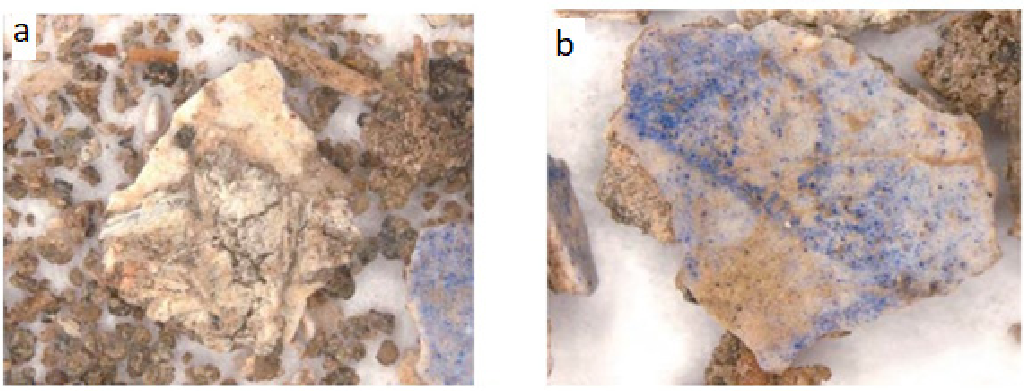

Figure 2. Optical images of blue pigment, cave no.17 showing (a) stratigraphy of layers; (b) crystals of ultramarine.

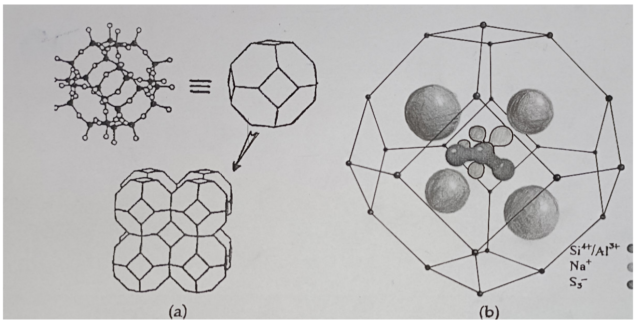

Figure 3. Images showing crystal structure of Ultramarine Blue.

Laurie (1914) noted that Byzantine manuscripts from the sixth to the twelfth centuries featured ultramarine pigments, often containing a high proportion of colorless material, prepared through relatively simple methods [28]. By the 13th century, improved extraction techniques were developed, as evidenced by references from that era [29]. Literary sources from the 14th century provide numerous instructions for extracting ultramarine.

Early Methods: The specific details of early Byzantine methods for preparing ultramarine are not well-documented, but they were relatively straightforward.

Improved Extraction Method (13th Century): An enhanced extraction technique emerged in the 13th century, leading to more refined ultramarine pigments [30].

Cennino Cennini's Method: Cennino Cennini, in the early 15th century, offered one of the most comprehensive accounts of the extraction process, with his methods compiled in tabular form [31].

Principle of Extraction: The process involved mixing ground lapis lazuli with melted wax, resins, and oils, kneaded under a dilute lye solution. This method washed out the blue lazurite particles, which settled at the bottom.

Multiple Extractions: Typically, at least three extractions were performed, yielding varying sizes and qualities of blue pigment. The final extraction, known as ultramarine ash, contained a high proportion of colorless material and was prized as a pale blue glazing pigment.

Continued Traditional Extraction: Traditional extraction methods persisted largely unchanged into the 19th century, despite the advent of synthetic ultramarine production [32]. Natural impurities, like calcite, often remained in the pigment, distinguishing it from synthetic alternatives.

Modern Synthetic Ultramarine: The 19th century saw the rise of synthetic ultramarine pigments, offering a cost-effective and consistent alternative to the labor-intensive natural extraction process. The extraction methods and their evolution reflect the importance and complexity of ultramarine as a valued artistic pigment, as illustrated in **Figure 3**.

The preferential wetting of the blue particles likely influences the effectiveness of the extraction method. The largest and most intensely colored blue particles are extracted first, typically requiring at least three separate extractions to yield several grades of pigment of decreasing quality. The final extraction, known as ultramarine ash, consists of a high proportion of colorless material and a few small blue particles, valued for its transparency as a pale blue glazing pigment. Traditional extraction methods have remained largely unchanged into the present century. Schmidt (1847) documented these methods in his pigment preparation handbook, noting that some natural impurities, particularly calcite, can still be present, distinguishing natural from synthetic ultramarine. **Figure 4 a & b** illustrates both natural and synthetic ultramarine blue pigments.

Figure 4. Visual comparison of natural and synthetic ultramarine blue pigments. (a) colour of natural ultramarine blue; (b) Synthetic ultramarine blue.

The history of ultramarine pigment, with its vibrant blue hue, reflects its rarity and immense value throughout the centuries. Derived from the scarce lapis lazuli stone, ultramarine was labor-intensive to refine, making it accessible to only a select few and as valuable as gold by the 18th century. The 19th century saw the beginning of synthetic ultramarine production, allowing for limitless quantities at a fraction of the cost, significantly increasing accessibility for artists and industries. Ultramarine & Pigments Ltd., established in 1960, is a prominent manufacturer and exporter of ultramarine blue in India, producing various grades and serving both domestic and international markets, with facilities in Ambattur, Chennai, and Ranipet in Tamil Nadu.

The shift from natural to synthetic ultramarine production significantly increased access to this exquisite blue pigment, enabling broader use among artists and industries. In lapis lazuli pigment, the blue particles are irregularly sized and angular, contrasting with the small, uniform, rounded grains of synthetic ultramarine [33]. Although lapis lazuli is a crystalline compound, its recognizable form is rare in pigment samples. Instead, particles often appear flattened, exhibiting conchoidal fracture patterns, which contribute to the unique properties and historical significance of lapis lazuli pigment in art [34].

The optical characteristics of ultramarine pigment can be summarized in tabular form as follows (**Table 1**):

Table 1. Optical properties of ultramarine pigment.

Property	Description
Crystal Structure	Cubic
Isotropy	Ultramarine is isotropic; blue particles do not exhibit birefringence.
Polarizing Microscope	Blue particles undergo complete extinction between crossed polaroid.
Calcite Crystals	Calcite crystals, if present, are strongly birefringent and appear as bright spots on a dark field when the analyzer of the polarizing microscope is rotated.
Appearance of Mineral	Ultramarine pigment may contain small, bright, metallic-appearing golden or silver-colored particles of pyrites, which can resemble stars in a blue sky and are sometimes mistaken for gold.

The optical properties of ultramarine pigment allow for its unique identification under a polarizing microscope [35]. Examining ultramarine from the Ajanta caves, including crystal shape and portable X-ray fluorescence analysis, enhances our understanding of these historic artworks [36,37]. Ultramarine's attributes, such as hiding power, tinting strength, and appearance in various media, are crucial for artists and conservators. Its pure bright blue remains vibrant in aqueous media but can appear dark blue in thick oil layers. It can be mixed with white for a brilliant opaque blue or used as a translucent glaze, demonstrating its versatility. Natural ultramarine shows remarkable stability to light and heat [38], maintaining its intense blue for centuries. Heating it to redness does not affect its color, but extreme temperatures can cause it to lose its hue, transforming into a yellowish-white glassy mass [39]. Ultramarine pigment's optical properties facilitate its identification under a polarizing microscope [35]. Analysis of ultramarine from the Ajanta caves improves our understanding of these historic artworks [36,37]. This pigment exhibits impressive stability to light and heat [38] and retains its vivid blue for centuries, although extreme temperatures can alter its hue [39].

To differentiate between ultramarine, azurite, and Prussian blue, heating a pigment sample to redness is effective. Ultramarine retains its blue color, while azurite turns to black copper oxide and Prussian blue becomes orange-brown ferric oxide. Unlike other blue pigments, such as indigo, which sublime, heat-resistant pigments like smalt and cobalt blues remain stable. Natural ultramarine can be identified microscopically [40] by its blue color under transmitted and reflected light, flattened and irregularly shaped particles, low refractive index, presence of colourless crystalline impurities, and the absence of birefringence. Bright blue particles often indicate overlap with birefringent calcite.

Singh M. examined the ultramarine from cave no. 2 Ajanta, through optical microscopy of the thin section**.** A table containing on site portable X-ray fluorescence analysis of various colours of Ajanta pigments including the blue has been provided [41]. The **Figure 5** shows the ultramarine blue pillow, wherein 5th CE beautiful artwork from Ajanta paintings has been examined in association with Italian experts.

Figure 5. Ultramarine blue pillow from cave no 17, Ajanta caves.

Ultramarine exhibits greater hiding power than its low refractive index would suggest, serving as a translucent glazing color in oil. Its tinting strength is notably better than early blue pigments like azurite and smalt due to its superfine structure, though it doesn't match modern phthalocyanine blues. The pigment retains its distinctive pure bright blue color when bound in aqueous media like gum acacia or egg tempera. However, in oil, it appears very dark blue in thick layers; for optimal results, it is either mixed with white pigment for an opaque effect or used as a thin translucent glaze over lighter under paint [42].

1.5. Raman Spectroscop

Raman spectroscopy has widely been used to investigate the origin of the various colours in natural and synthetic lazurites [43, 44,45,46]. In particular, the blue to green colouration has been attributed to S^{3-} and S^{2-} polysulfur radical anions. Because, the electronic transitions leading to the absorption in the blue to green visible region occur at a wavelength (400–600 nm) similar to that of the lasers used to perform Raman spectroscopy, the resulting spectra are resonant ones. Such spectra are characterized by the intensity enhancement of a symmetric fundamental of the scattering medium and by high-intensity overtones. This fact explains the reason for high signal-to-noise ratio obtained even in micro-Raman experiments. Raman spectra indicate the presence of both S^{3-} and S^{2-} as polysulfur radical anions in the lazurite of the pigment. In contrast to the Raman spectra of lazurite from Pamir and Siberia reported by Ostroumov et al. 2002, other researchers were not able to observe effects arising from the presence of SO_4 groups [46].

2. Discussion with Respect to Indian Paintings

Paramasivan (1937– 1938) reported finding natural ultramarine on Indian mural paintings of the 14–15th century AD Vijayalaya Choleeswaram temple in the Pudukkottai district of south India [47]. The use of ultramarine blue has also been reported in 16th century paintings of Brihadeswara temple, Thanjavur [48], and 580–630 AD Jain caves temples at Sittanavasal in south India. In the test for blue pigment, Parmasivan reported that the blue particles were not birefringent. They were decolorized by dilute HCl, but no green to brown residue was obtained as with the copper compounds. This experiment showed that the blue particles consist of ultramarine. A sample of the paint layer was also subjected to Lessaigne's test for nitrogen, but its failed to give the Prussian blue color. In Asia and central Asia *ultramarine 'blue'* was mainly used in connection with the spread of the Buddhist cult from India through central Asia. In most of the cases the Buddhist temples were excavated from cliffs. The early use of *lazurite* was identified in the 4th century murals of the Kizil Grotto caves 38 and 114, on the northern route of the Silk road around the northern edge of the Taklimakan desert (Central Asia) and also in Ajanta, early 4th CE paintings [49, 50].

The Ajanta Caves were excavated in two periods: the early caves between the second century B.C. and first century A.D.; and the late caves between the late fourth and fifth centuries A.D. The caves were decorated with polychrome sculpture and wall paintings, both on the interior and exterior. Although general technical investigations of the wall paintings were made as early as the 1930s, more in-depth studies have been produced in recent years. The analysis of the pigment sample from the blue pillow in the external porch of Cave No. 17 at Ajanta provides valuable insights into the complex layering and materials used in these ancient paintings [36,41]. The details of the layers observed in the sample are:

1) Preparatory Mud Layers: The first two layers are preparatory mud layers applied to the basaltic stone support. The first layer is a brown preparatory layer made from mud and ground rock. On top of this, there is a fine mud layer that serves as the base for applying color.

2) White Layer: Over the second mud plaster layer, there is a white layer, approximately 100 µm thick. This white layer is made from a thin coat of lime or kaolin.

3) Preparatory Drawing: Between the calcium carbonate (lime) and kaolin layers, a red ochre preparatory drawing is evident. This preparatory drawing likely served as a guide for the subsequent painting.

4) Blue Layer: The blue layer, approximately 20 µm thick, contains kaolin and lapis lazuli. Lapis lazuli is the precious blue pigment imported from Afghanistan and was used to create the blue color in the paintings.

5) Organic Layer: On the surface of the sample,

there is an organic layer that exhibits yellow fluorescence under UV light. This layer may be the result of a recent conservation intervention, possibly involving a synthetic polymer mixed with zinc white.

Painters of Ajanta used lime and white clay (kaolin) for white, carbon (soot) for black, yellow ochre for yellow, red ochre for red, gluconate or terraverte for green and lapis lazuli for blue. All the pigments viz. white, red, yellow and green are residual products of the volcanic rock [14]. They are locally available except blue. The analysis of the blue area in the porch of Cave No. 17 at Ajanta provides strong evidence for the use of lapis lazuli as the blue pigment. Here are the key pieces of evidence that support this conclusion:

1) Absence of Elements Indicating a Blue Mineral Pigment: The analysis did not detect elements that are indicative of a blue mineral pigment other than lapis lazuli. This absence suggests that lapis lazuli was indeed used for the blue color.

2) Reflectance Spectrum: The reflectance spectrum of the blue color shows a red tail component, which is characteristic of lapis lazuli. This spectral signature is consistent with the properties of lapis lazuli as a pigment.

3) Morphology of Blue Crystals: The morphology of the blue crystals observed in the sample further supports the presence of lapis lazuli. Lapis lazuli is known for its distinct crystal structure, and the morphology of the crystals aligns with this characteristic.

4) Micro Destructive Analyses: Micro-destructive analyses likely involved examining the composition and structure of the blue pigment at a microscopic level. These analyses likely provided additional evidence of lapis lazuli's presence.

5) Bibliographic Data: The findings are consistent with existing bibliographic data and historical records that mention the use of lapis lazuli as a blue pigment in ancient artworks.

These evidence strongly suggest that lapis lazuli was indeed employed as the blue pigment in the Ajanta Caves paintings, providing valuable insights into the historical materials and techniques, which seems to have been imported, because of its absence in the neighbourhood [51,52]. According to B.B. Lal [53], there is no evidence of any use of copper compounds (viz. malachite) for green and azurite for blue. All the pigments are of local origin except lapis lazuli which was probably imported from Persian countries through trade on silk route.

The earliest scientific study of painting materials on Ajanta was published in 1939 by Paramasivan. Since the original publication is not readily available outside India, its content is referenced from subsequent publications in which it is quoted [54]. Following Paramasivan, Lal [53] and Bharadwaj published the results of their technical studies [55]. Dabhade published a book in 1973 [56] on the techniques of wall paintings in India, which summarized previous studies, including that of Paramasivan's. Singh and Arbad published a detailed account on the various conservation measures undertaken for the Ajanta cave murals [57].

The number of naturally occurring blue pigments available for use when the Ajanta Caves were painted was limited. Technical studies on the Ajanta paintings are quite limited, and references to blue pigments tend to be confusing. In the Japanese translation of Lal's study [52], ultramarine blue is called 'gunjo' and 'lapis lazuli'. In Japan, 'gunjo' meant only azurite until the import of synthetic ultramarine blue, which the earliest known records indicate occurred in the middle of nineteenth century. After the Meiji period (which began in 1868), synthetic ultramarine blue was gradually introduced as a pigment, and was referred to as 'jinzo gunjo', which literally means artificial ultramarine blue (in colour); later this was abbreviated to 'gunjo'. In the twentieth century, production of azurite as a pigment declined, and it only continued to be made in small amounts for use by certain people such as artists. Therefore, it is quite possible that when this book was published in 1971, 'ultramarine blue' could have been translated into 'gunjo'.

The detailed analysis of the blue pigments used in the Ajanta Caves paintings provided valuable insights into the composition of these pigments as under:

1) Microscopic Images: Microscopic images revealed an uneven distribution of the blue paint, with concentrated spots of blue pigments scattered throughout the blue areas. This uneven distribution is indicative of the painting technique used.

2) Raman Spectroscopy: Raman spectroscopy of the blue pigment spots identified characteristic bands at low wavenumbers (239, 267 cm^{-1}) and a sharp intense band at

543 cm^{-1} with a shoulder band at 585 cm^{-1}. These bands are consistent with the resonance phenomenon observed in the Raman spectrum, which is a characteristic fingerprint of lazurite mineral, confirming the presence of lapis lazuli (**Figure 6a**).

3) FTIR Spectroscopy: FTIR spectroscopy of the blue pigments revealed the abundance of gypsum. Bands associated with hydroxyl stretching frequencies, H-O-H bending frequencies, and SO_4 tetrahedra stretching frequencies were present, all of which are characteristic of gypsum (**Figure 6b**) Additionally, diagnostic bands of carbonates indicated the presence of calcite in the mixture. Notably, no characteristic peaks of lapis lazuli were observed in the mid-IR region.

4) EDX Analysis: Energy-dispersive X-ray (EDX) analysis detected the major elements oxygen, calcium, lead, sulphur, carbon, titanium, and chromium, along with minor elements like arsenic, iron, cobalt, silicon, sodium, and aluminium. These findings are consistent with the probable composition of lapis lazuli, specifically $(Na,Ca)_8Al_6Si_6O_{24}(S,SO_4, Cl)_{1\text{-}2}$. The presence of calcium, silicon, and oxygen also indicated the presence of the mineral wollastonite ($CaSiO_3$), commonly associated with lapis lazuli.

The historical use of blue pigment at Ajanta can be summarised as:

1) Early Use of Blue: In the 2nd century B.C., during the initial period of the Ajanta Caves' construction and painting, there is no evidence of the use of blue pigments. Instead, paintings during this period predominantly featured other color like red, yellow, green, black, and white [6].

2) Introduction of Lapis Lazuli: The use of lapis lazuli as a blue color pigment appears to have started later, in the 4th to 5th centuries CE, during the subsequent phase of painting at the Ajanta Caves. Lapis lazuli, which was not naturally available in India, had to be imported from regions like Afghanistan or Persian countries through trade routes like the Silk Road.

3) Indigo in Manuscripts: In ancient Indian palm leaf manuscripts and archival materials from the 12th to the 18th centuries CE, indigo extracted from the leaves of the Indigofera tinctoria plant was commonly used as the main pigment for blue illustrations [58]. This indigenous source of blue pigment provided an alternative to imported lapis lazuli [59].

4) Unique Contribution: The novelty in Indian decorative art lies in the use of these blue and green pigments, which added vibrancy and diversity to the color palette. The incorporation of lapis lazuli as a blue pigment in later phases of painting at Ajanta demonstrates the influence of external trade connections on artistic materials.

3. Paintings in 16th Century Orchha Fort, India Use of Blue Colour

The microscopic images of the blue areas taken at 200X magnification by Dinolite digital microscope showed the inhomogeneous spread of the blue paint [60] with thick spots of the concentration of blue pigments scattered throughout the blue areas (**Figure 7a**). When the

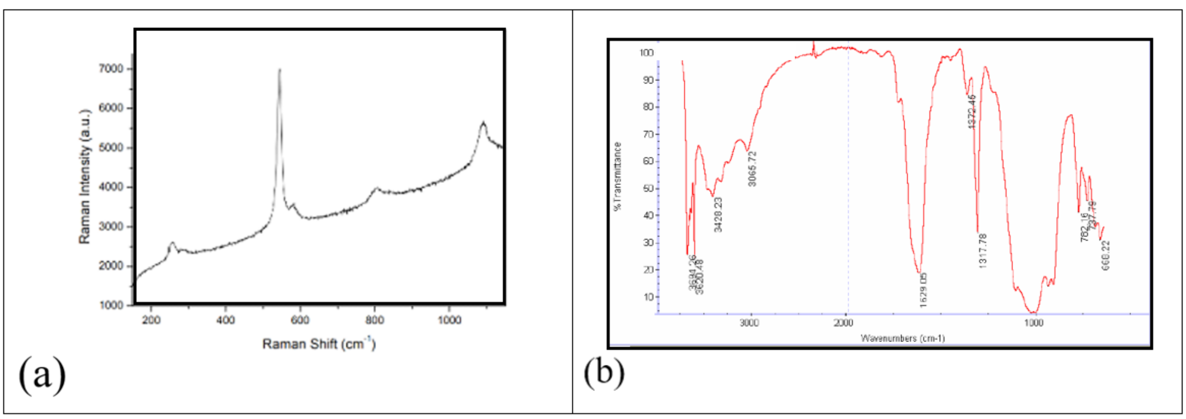

Figure 6: Spectroscopic characterization of lapis lazuli pigment from Cave No. 17, Ajanta Caves (a) Raman Spectra; (b) FTIR spectra of lapis lazuli from cave no.17, Ajanta cave.

785 nm Raman laser was targeted on the blue pigment spots in the blue area, the low wavenumber bands at 239, 267 cm^{-1} along with a sharp intense band at 543 cm^{-1} with a shoulder band at 585 cm^{-1} was recorded (**Figure 7b**). The Raman spectrum of the blue spots also showed the multiple bands (543 × 2 = 1086 cm^{-1}) and combination bands (267 + 543x2+ 810 cm^{-1}) which indicated the resonance phenomenon in the Raman spectrum, a characteristic fingerprint of lazurite mineral [61.62]. The FTIR spectrum of the blue pigments exhibited the abundance of gypsum (**Figure 7c**). The bands at 3526 and 3403cm^{-1} are due to the absorption vibration of hydroxyl stretching frequencies, bands at 1684 and 1618cm^{-1} are due to H-O-H bending frequencies, the bands at 1102 cm^{-1} with a shoulder peak at 1004 cm^{-1} are due to the absorption vibration of υ3 antisymmetric stretching of SO4 tetrahedra, the bands at 670 and 598 cm^{-1} are due to antisymmetric bending in the mid-IR spectra, all these are fundamental bands of calcium sulphate dihydrate (gypsum). The diagnostic bands of carbonates are also present at 1405 cm^{-1}, 871 and 712 cm^{-1} which indicated the presence of calcite in the mixture [63]. In the spectrum of the blue area, the presence of a mixture of calcium carbonate and calcium sulphate dihydrate dominated the IR spectrum and no characteristic peaks of lapis lazuli are noticed in the spectrum in the mid-IR region [64]. The EDX analysis detected the major element as oxygen,

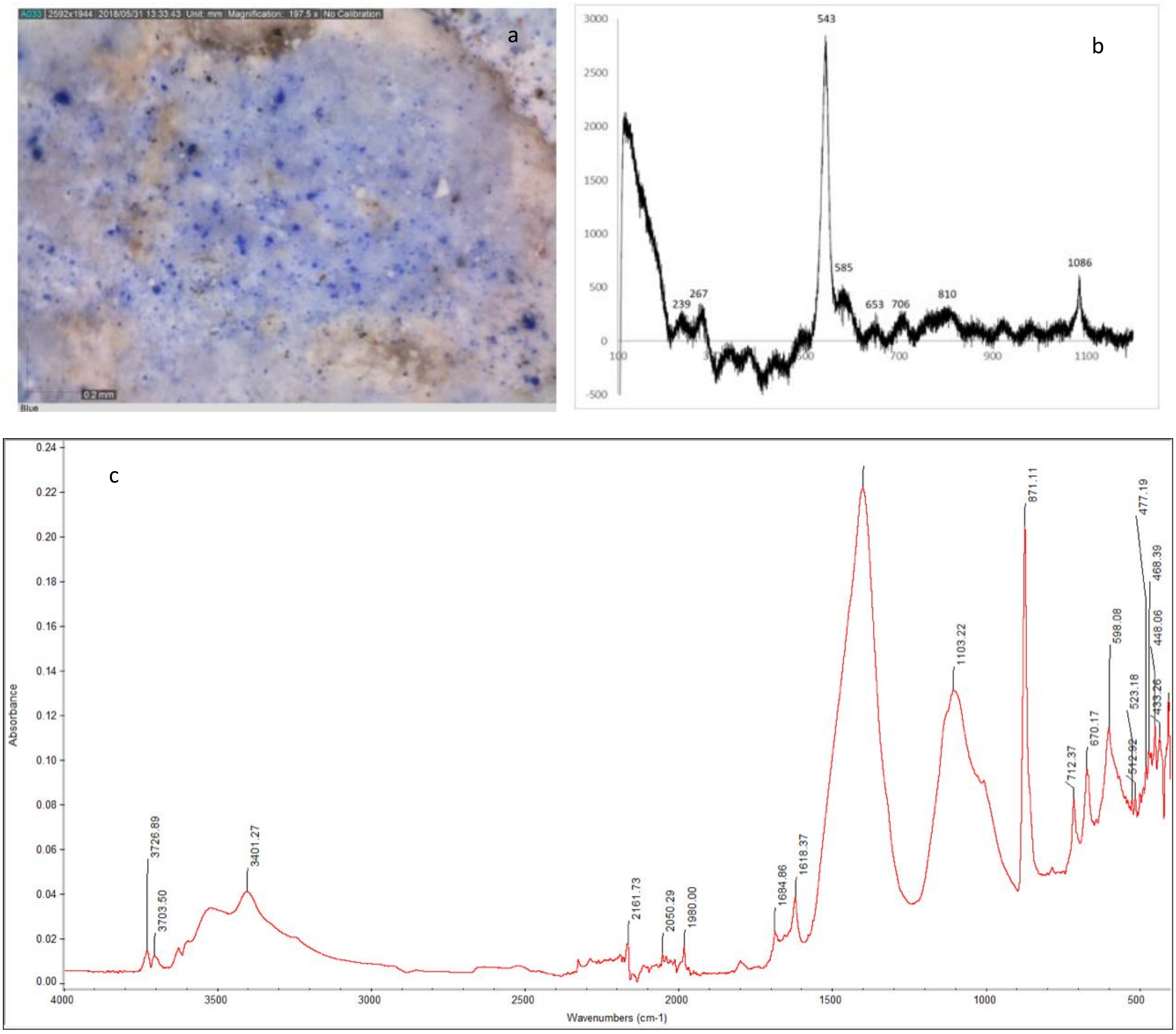

Figure 7. Microstructural and spectroscopic characterization of the blue pigment sample from Orchha Fort (a) optical microscopic image; (b) Raman spectra; (c) FTIR spectra of blue pigment, Orchha Fort.

calcium, lead, sulphur, carbon, titanium and chromium and the minor elements as arsenic, iron, cobalt, silicon, sodium and aluminium which indicates the probable composition of *lapis lazuli* $(Na,Ca)_8Al_6Si_6O_{24}(S,SO)_4$ and the weight percentages of calcium (12.95%), silicon (4.41%) and oxygen (39.88%) indicated the presence of the mineral wollastonite ($CaSiO_3$) which is commonly associated with lapis lazuli.

4. Natural Ultramarine in 18th Century Shiva Temple, New Delhi

The analysis of the blue pigment from the Shiva temple within the New Delhi airport campus provides valuable insights into its composition and origin [65]. The optical microscopic image of blue pigment is shown in **Figure 8a**.

1) Raman Spectroscopy:

A dominant spectral feature at 548 cm^{-1} is observed, which corresponds to the stretching mode of S^{3}- trisulfur radical anion chromophore, **Figure 8b**. This chromophore is responsible for the deep blue color of lapis lazuli. Another strong band at 1086 cm^{-1} indicates the presence of calcite, which is often found along with lazurite in lapis lazuli rocks.

2) FTIR-ATR Spectra:

The FTIR-ATR spectra support the probability of lazurite as the blue pigment. Characteristic peaks of lazurite are present, but they overlap with gypsum peaks in the same region, **Figure 8c.** The presence of kaolinite is indicated by doublet peaks at 1032 cm^{-1} and 1004 cm^{-1}. Peaks at 1118, 1004, 672, and 598 cm^{-1} are attributed to both gypsum and lapis lazuli. The characteristic peaks of calcium oxalate are observed at 1617, 1320, and 780 cm^{-1}.

3) SEM-EDX Spectra:

Major elements detected include oxygen (O), carbon (C), calcium (Ca), silicon (Si), aluminium (Al), sulfur (S), sodium (Na), and magnesium (Mg). These elements are consistent with the chemical composition of lazurite, further confirming the presence of lapis lazuli in the blue pigment.

Overall, the combined data from Raman spectroscopy, FTIR-ATR spectra, and SEM-EDX analysis strongly

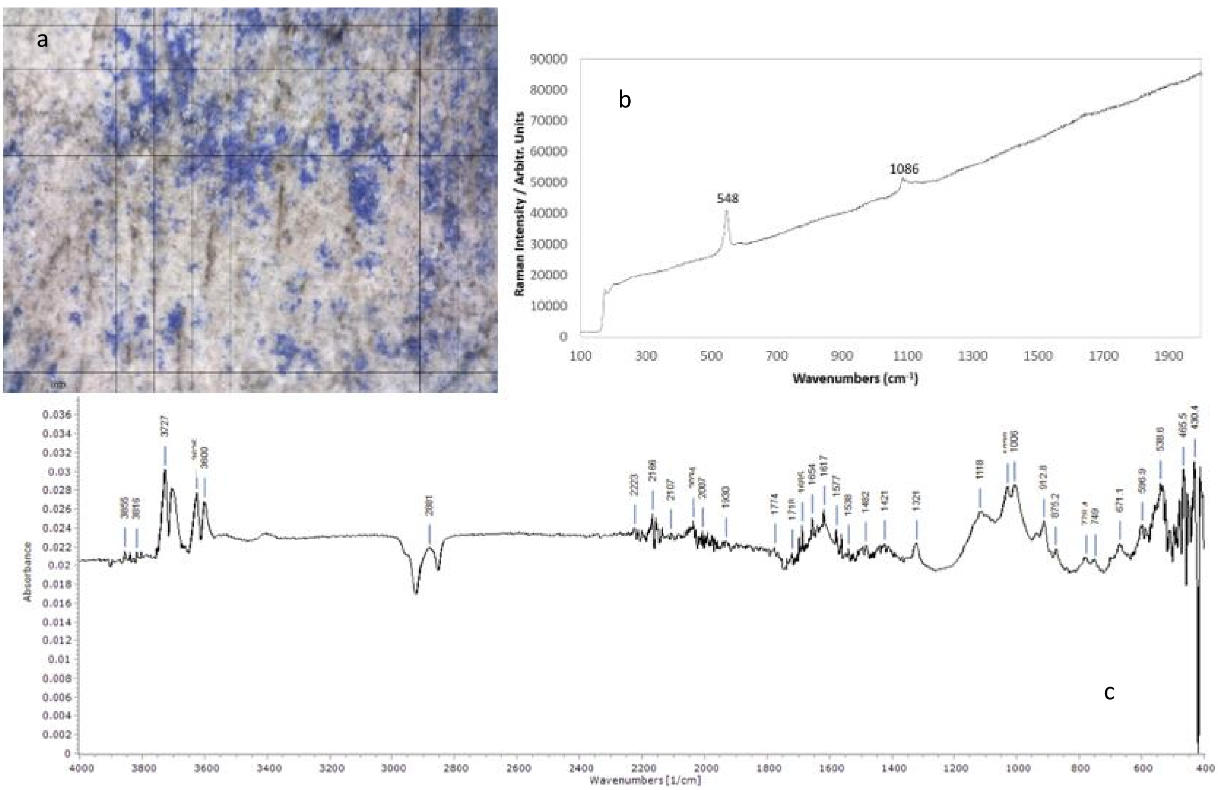

Figure 8. Microstructural and spectroscopic analysis of the blue pigment sample from the Shiva Temple, New Delhi. (a) Optical microscopic image; (b) Raman Spectra; (c) FTIR spectra of blue pigment, Shiva temple, New Delhi.

support the conclusion that the blue pigment used in the Shiva temple contains lapis lazuli, a material not naturally occurring in India and likely obtained through trade from Afghanistan, a well-known source of lapis lazuli.

Historically, several regions have been known for their lapis lazuli deposits, including:

1) Badakhshan, Afghanistan: Quarries in northeastern Afghanistan have been renowned sources of lapis lazuli for ancient times. This region is particularly famous for its high-quality lapis lazuli [66].

2) Pamir Mountains, Tajikistan: Evidence suggests that lapis lazuli quarries in the Pamir Mountains in Tajikistan were also exploited since ancient times. These deposits contributed to the availability of lapis lazuli [67].

3) Chagai Hills, Pakistan: Lapis lazuli deposits in the Chagai Hills in Pakistan have been another source of this valuable blue stone.

These multiple supply sources of lapis lazuli refute the notion that there was only a single origin for this precious material. Instead, various regions with the necessary geological conditions have yielded lapis lazuli, and it has been traded and used for artistic and decorative purposes throughout history.

The history of blue pigments in antiquity is indeed fascinating, and it involves both natural and synthetic developments.

5. Synthetic Blue Pigments

Egyptian Blue: Around 5,000 years ago, in ancient Egypt, the first synthetic blue pigment known as Egyptian blue was developed. It was created by heating a mixture of silica, lime, and a copper compound. This pigment played a significant role in ancient Egyptian art and was also used by other civilizations in the Mediterranean region.

Chinese Blue and Purple: In ancient China, around 800 BCE, a synthetic blue and purple pigment was developed. This pigment is found in the layers of the Terracotta Army, which dates to 221-207 BCE. Chinese blue and purple are chemically similar to Egyptian blue but are more complex to produce. This suggests a high level of technological sophistication in ancient China [68].

The development of Chinese blue and purple is particularly interesting. While it shares similarities with Egyptian blue, its complexity and the need for precise control of various factors during synthesis indicate an advanced level of technology. It's possible that knowledge of this pigment's production could have spread through trade along the Silk Road, which connected different civilizations.

Archaeometric analyses of blue pigments from various ancient sites can provide valuable insights into the spread of technology and trade networks in antiquity [69]. These studies can help confirm whether the development and dissemination of pigments like Chinese blue and purple were facilitated by interactions along ancient trade routes. Purple color was achieved by mixing blue pigment with red pigments like iron oxide and vermillion. While azurite, another blue pigment, is more abundant than lapis lazuli, it is less stable over time [70]. Due to the limited availability of natural blue pigments, many prehistoric paintings and artworks do not feature blue color. Lapis for the first time appeared as true blue pigment in the 6th century in Buddhist frescoes in Bamiyan, Afghanistan [66] and at Ajanta murals also. About 700 years later the blue pigment was introduced in Italy and thereafter became the most sought after colour in medieval Europe [71,72]

The scarcity of stable blue pigments likely encouraged the development of synthetic alternatives [73,74]. Egyptian blue and Chinese blue and purple were created through complex experimentation involving alkaline earth copper silicate chemistry. These synthetic pigments provided a more reliable source of blue and purple colours. The scarcity of stable blue pigments persisted into later civilizations, causing challenges in obtaining this color for art and decoration. The 19th century saw a significant change with the advent of industrialization. Mass production of dyes and pigments became possible, leading to greater availability of stable blue pigments.

Understanding the historical significance of pigments and the challenges faced by ancient civilizations in obtaining certain colours provides valuable insights into the evolution of art and technology over time. Indeed, azurite is an abundant source of natural blue pigment in the form of a copper carbonate mineral. However, azurite has limited solubility, and its color can fade or change over time [70]. To overcome these limitations, ancient cultures, including the Egyptians and Chinese, developed techniques to transform azurite and other copper minerals into stable blue or purple copper silicate pigments. These ancient pigment-making processes typically involved complex chemical reactions and experimentation. By carefully controlling factors such as temperature, the composition of materials, and firing conditions, they were able to produce pigments with more stable and vibrant colours. These synthetic pigments, like Egyptian blue and Chinese blue and purple, played a crucial role in art and cultural expression throughout history.

The production of Egyptian blue, one of the earliest synthetic pigments in history, involved a complex chemical process. It was typically prepared by heating a mixture of ground limestone (calcium carbonate), a copper mineral like malachite or azurite, and a flux (a substance that lowers the melting point of materials) at high temperatures, usually around 800-900°C. The exact stoichiometric ratio of these ingredients and the control of firing conditions were crucial for obtaining the desired blue color. The copper ions within the Egyptian blue, specifically the calcium copper tetra silicate complex ($CaCuSi_4O_{10}$), were responsible for its blue coloration [75]. Achieving the right conditions during production was essential for the quality and vibrancy of the pigment. Egyptian blue was not limited to Egypt; it spread to other ancient civilizations like Greece and Rome, and further east into regions like Mesopotamia, Persia, and potentially along trade routes like the Silk Road. The distribution and use of Egyptian blue across different cultures and geographic regions offer valuable insights into ancient trade, technology transfer, and artistic exchanges.

The Chinese blue and purple pigments indeed share similarities with Egyptian blue in terms of their chemical composition, as they are all alkaline earth copper silicates used for their blue and purple color in ancient art and artefacts [76]. However, there are notable differences between Chinese blue ($BaCuSi_4O_{10}$) and Egyptian blue ($CaCuSi_4O_{10}$):

1) Barium vs. Calcium: The most significant distinction is the replacement of calcium with barium in Chinese blue. This substitution of elements results in slightly different properties, including color and particle size.

2) Layered Structure: Chinese blue has a unique layered structure, which sets it apart from Egyptian blue. This structural difference can influence its physical and chemical characteristics.

3) Higher Synthesis Temperature: Chinese blue and purple were typically synthesized at much higher temperatures, around 900-1000°C, compared to Egyptian blue, which was produced at lower temperatures. This difference in production temperature likely contributes to variations in the pigments' properties.

4) Barium Source: To create Chinese blue and purple, a source of barium, such as barite ($BaSO_4$) or witherite ($BaCO_3$), was required. Barium minerals are less common than the limestone used in Egyptian blue production.

5) Lead Content: Chinese blue and purple often contain lead as a catalyst and flux during their preparation. Lead salts were added to break down barite and enhance pigment quality.

These differences, especially the use of barium and higher production temperatures, give Chinese blue and purple their distinct characteristics compared to Egyptian blue.

Historically, the range of tempera pigments used in India differed significantly from those in Europe, particularly Italy, due to local availability and cultural influences. While India had a rich artistic tradition, its pigments were derived from local sources. In contrast, Europe, especially during the Renaissance, saw a broader diversity of pigments thanks to advancements in production and trade, including cobalt blues and greens, chrome greens, and Prussian blue, introduced in the 18th century [77]. Although India later gained access to some of these new pigments, traditional tempera painting declined before this transition. Consequently, many Indian artworks continued to use older pigment palettes, highlighting regional variations in artistic traditions and techniques.

Ultramarine blue, made from pulverized lapis lazuli, was utilized in Indian wall paintings, notably in the Ajanta Caves. This natural pigment had distinct properties and challenges:

Vulnerability to Moisture: If the plaster ground wasn't adequately dried, ultramarine could become crumbly and unstable due to high humidity or poor ventilation.

Binder Choice: Egg emulsion, particularly egg white or albumin, provided better protection against moisture and alkali, preserving the pigment's color and stability.

Particle Separation: Artists often separated the more vibrant particles from less colorful grains to achieve a more intense blue.

Protection from Alkali: Mixing ultramarine with egg white or albumin helped shield it from alkali substances. Despite its extensive use in Indian art [78,79], ultramarine was notably absent in the Buddhist paintings of Sigiriya, Sri Lanka [80], highlighting regional artistic variations and pigment availability.

5.1. Azurite

Ultramarine blue, derived from lapis lazuli, was prominent in Indian wall paintings, especially in the Ajanta Caves. Its distinct properties included vulnerability to moisture, requiring adequate drying of the plaster. Egg emulsion, particularly egg white, was used as a binder to protect against alkali and moisture. Notably, ultramarine was absent in the Buddhist paintings of Sigiriya, Sri Lanka [78-80].

5.2. Indigo

Indigo, a natural pigment from the Indigofera plant, has a rich history in India for dyeing textiles but was rarely used in tempera painting [81].

5.3 Alizarin

The later invention of alizarin blues and greens in the 19th century, known for their lightfastness, saw limited use in tempera painting. Despite their resistance to fading, these pigments could turn very dark, almost black, when exposed to prolonged light [82]. Consequently, artists favoured traditional inorganic pigments for their stability. The Sheesh Mahal paintings in Ramnagar utilized various pigments, with purple created by mixing vermillion and indigo, and a darker shade achieved with lamp black and deep red ochre [83]. In Chamba's Rang Mahal paintings, blue pigments were made from indigo and ultramarine [83].

Analysis of 11th to 12th century Buddhist wall paintings at Nako monastery, Himachal Pradesh, indicates the use of azurite, with indigo present in some areas linked to modern restoration [84,85]. The paintings from the 12th to early 13th centuries at Sumdachun, Ladakh, also utilized azurite for blue [86]. Similarly, azurite was identified in the 14th century wall paintings at Tsuglag-khang Kangi, Ladakh [87]. In the 15th century Thubchen Lakhang temple, Nepal, blue was reported as either azurite or a mix of azurite and lazurite [88]. Conversely, the 16th to 19th century Sri Harminder Sahib in Amritsar features ultramarine for blue coloration [89].

In Rajasthan, known for its artistic heritage, scientific investigations have revealed a mix of ancient and modern blue pigments. Studies on 17th to 18th-century Mewar paintings documented ultramarine, azurite, and indigo [90]. The 16th-century Mughal gateway in Bairut featured Prussian blue, ultramarine, and azurite [91]. O.P. Agarwal reported indigo blue in the 18th to 19th-century Sheesh Mahal wall paintings [92]. In Goa's St. Monika Church, 17th-century wall paintings used Prussian blue [93], while ultramarine was found in 19th-century murals in Imphal [94]. In Kerala, detailed analyses of blue pigments were published [95].

Blue is a rare color in nature, often linked to precious materials like lapis lazuli, which is typically found with minerals such as diopside, quartz, calcite, and pyrite. Historically valued, lapis lazuli was used for jewellery and art in ancient civilizations like Egypt, Mesopotamia, and China, with primary sources in Afghanistan's Sare-Sang mines. It was a key pigment for frescoes along the Silk Road and in Sassanid and Buddhist artworks (6th to 9th centuries), as well as in Christian Georgian and Armenian churches in the 10th century. Its vibrant hue made it prized in illuminated texts across Europe and the Islamic world. Notably, in historical Indian and Central Asian wall paintings, Egyptian blue was absent, with natural ultramarine, azurite, and indigo identified instead, indicating their sufficient availability for artistic needs.

The use of blue pigments in historical paintings in India based on scientific analysis and literary survey is listed below (**Table 2**).

Table 2. Blue pigments and its use in historical decorative arts in India

Date	Location	Pigments	References
2nd B.C.E.–6th C.E.	Ajanta (Maharashtra)	Blue: Lapis lazuli	[14, 36, 54]
7th C.E.	Bagh Caves (Madhya Pradesh)	Blue: Lapis lazuli	[78]
Late 7th C.E.	Kanchipuram (Tamil Nadu)	Blue: ultramarine	[79]
9th C.E.	Sittannavasal (Tamil Nadu)	Blue: Ultramarine	[96]
11th C.E.	Thanjavur (Tamil Nadu)	Blue: Ultramarine	[48]
12th C.E.	Lakhang-Gongma Monastery, Nako (Himachal Pradesh)	Dark blue: Azurite + gypsum + quartz	[84,85]
13th C.E.	JunaMahal, Dungarpur (Rajasthan)	Violet blue: Ultramarine Pale blue: Ultramarine	[97]
16th C.E.	Moghul Gateway, Bairat, (Rajasthan)	Blue: Ultramarine	[91]
16th C.E.	Raja Mahal, Orchha (Madhya Pradesh)	Dark blue: Prussian blue Medium blue: Ultramarine	[60]
16th C.E.	Golden temple (Sri Harmandar SahebJi), Amritsar (Punjab)	Blue: Ultramarine blue	[89]
17th C.E.	Servent Chapel of St. Monica Church and Convent (Goa)	Blue: Prussian blue	[93]
18th C.E.	Indian Temple (New Delhi)	Blue: Lapis lazuli	[65]
18–19th C.E.	Sheesh Mahal, Nagaur (Rajasthan)	Blue pigment: Indigo	[92]
19–20th C.E.	Panchai Court, Imphal, (Manipur)	Blue: Ultramarine	[94]
14–15th C.E.	Vijayalaya Cholisvaram, Pudukkottai state (Tamil Nadu)	Blue: ultramarine	[47]
18th century	Rang mahal, chamba	Indigo, ultramarine	[83]
19th century	Shish mahal, ramnagar, j. k	Purple: vermilion+indigo	[83]
12-early 13th century	Sumda Chun monastery, Ladakh	Azurite	[86]
14th century	Tsuglag-Khang, Kanji,Ladakh	Azurite	[87]
15th century	Thubchen Lakhang, Nepal	Azurite and Lazurite	[88]
17-18th century	Mewar painting	Ultramarine, Azurite and Indigo	[90]
16th CE	Pundareekapuram Vishnu Temple Distt. Kottayam	indigo	[95]

6. Conclusions

This review traces the evolution of blue pigments in Indian art, revealing significant temporal and regional variations based on both literature and material analysis. In early Indian wall paintings, such as those from the 2nd century BC, the absence of blue pigments is notable, but by the 4th and 5th centuries, the use of lapis lazuli in Ajanta paintings points to well-established trade routes with Afghanistan as a likely source. The transition to the use of ultramarine blue, particularly in South Indian sites like Sittanavasal, Thanjavur, and Kanchipuram, suggests shifts in material sourcing, possibly from within the Indian subcontinent.

Regional diversity in blue pigment use is evident, with the Himalayan regions predominantly using azurite, while Rajasthan favored indigo, azurite, and ultramarine. In contrast, no blue pigments were detected in the Sigiriya paintings of Sri Lanka, highlighting geographical distinctions. The introduction of Prussian blue in Goa and the prevalence of indigo in Kerala further underscore the complexity of pigment use, influenced by both indigenous sources and trade. These findings underscore the intricate links between ancient Indian art, trade routes, and the availability of blue pigments across different regions and periods.

This review concludes that while significant progress has been made in understanding the materials used in Indian paintings, much remains to be explored, particularly regarding the identification, sourcing, and durability of pigments. Further interdisciplinary research will be essential to fully comprehend the evolution of painting techniques and material choices in Indian art history.

Author Contributions

For this research the individual authors have contributed equally as under: A. S. conceptualization, methodology, software, resources, writing original draft, visualization; M.R. S. conceptualization, validation, formal analysis, investigation, data curation, review and editing, project administration Certified that all authors have read and agreed to this published version of the manuscript.

Funding

The authors declare that no funding was received for this work.

Institutional Review Board Statement

Not Applicable.

Informed Consent Statement

Not Applicable.

Data Availability Statement

The data that support the findings of this study are available within the article.

Conflict of Interest:

The authors declare no conflict of interest.

References

[1] Punia, R., 2015. Dyeing in ancient Indian textile: An analytical study. Ascent International Journal for Research Analysis (AIJRA). 3(1), 1–6.

[2] Kumar, A., Dixit, U., Singh, K., et al., 2021. Structure and properties of dyes and pigments. In Dyes and pigments-novel applications and waste treatment. IntechOpen.

[3] Diacu E., 2016. Colours: Properties and Determination of Synthetic Pigments. Encyclopaedia of Food and Health, 284–290.

[4] Sharma, A., Singh, M.R., 2021. A Review on Historical Earth Pigments Used in India's Wall Paintings. Heritage. 4(3), 1970–1994.

[5] Singh, M., Arbad, B.R., 2012. Conservation and restoration research on 2nd BCE murals of Ajanta. International Journal of Scientific and Engineering Research. 3(10), 1–8.

[6] Ballinarno, P., Maras, A., 2006. Mineralogical characterization of the blue pigments of Michelangelo's fresco "The Last Judgement". American Mineralogist. 91, 997–1005.

[7] Gottesman, S., The 6,000-Year History of Blue Pigments in Art. *Artsy*. November 29, 2016 Accessed April 25, 2021 https://www.artsy.net/article/artsy-editorial-a-brief-history-of-blue

[8] Nardi, I., 2003. The theory of Indian painting: The citrasutras their uses and interpretations. University of London, School of Oriental and African Studies (United Kingdom) ProQuest Dissertations & Theses, 2003. 10673055.

[9] Plesters, J., 1993. Ultramarine blue, natural and Artificial In: Roy, A. (eds.). Artists' Pigments: A Handbook of their history and characteristics, volume 2. National Gallery of Arts, Washigton D.C., pp.37–65.

[10] Yusuf, M., Shabbir, M., Mohammad, F., 2017. Natural colorants: Historical, processing and sustainable prospects. Natural products and bioprospecting. 7, 123–145.

[11] Parikh, K., 2011. Colour symbolism: Emotional values of colour. Indian Journal of Applied Research. 3(1), 65–66.

[12] Singh, M., Arbad, B.R., 2013, August. Architectural history and painting art at Ajanta: Some salient features. Arts. 2(3), 134–150.

[13] Wyart, J., Bariand, P., Filippi, J., 1981. Lapis-lazuli from Sar-e-Sang, Badakhshan, Afghanistan. Gems & Gemology. 17, 184–190.

[14] Singh, M., 2011. Microclimatic condition in relation to conservation of cave no. 2 murals of Ajanta. Current Science. 101(1), 89–94.

[15] Sharma, A., Singh, M.R., 2020. Multi-analytical investigation of the composition and binders used in the earthen support layer of fifth–fourteenth century CE painted fragments from Bezeklik, China. Studies in Conservation. 65(4), 221–237.

[16] Ju, W., 2022. The Research on the Origin and Communication of Blue and Green Colors in Chinese Blue and Green Landscape Painting. Journal of Education, Humanities and Social Sciences. 5(2022), 119–125.

[17] Shui, B., Yu, Z., Cui, Q., et al., 2022. Blue pigments in Cave 256, Mogao Grottoes: a systematic analysis of murals and statues in Five dynasties, Song Dynasty and Qing Dynasty. Heritage Science. 10(1), 1–12.

[18] Aoki, S., Taniguchi, Y., Rickerby, S., et al., 2021. Conservation and Painting Techniques of Wall Paintings on the Ancient Silk Road. Springer: Singapore. Cultural Heritage Science, ISBN 978-981-33-4160-9 ISBN 978-981-33-4161-6 (eBook)

[19] Orna, M.V., Fontani, M., 2022. The modernity of ancient pigments: a historical approach. Colorants, 1(3), 307–346.

[20] Booth, D.G., 2002. The synthesis and structure of Ultramarine Pigments (Doctoral dissertation). University of Southampton Institutional Repository.

[21] Nečas, R., Všianský, D., 2016. Ultramarine–not just a pigment of traditional folk architecture plasters. Procedia Engineering. 151, 114–118.

[22] Chukanov, N.V., Sapozhnikov, A.N., Shendrik, R.Y., et al., 2020. Spectroscopic and crystal-chemical features of sodalite-group minerals from gem lazurite deposits. Minerals. 10(11), 1042.

[23] Schmidt, C.M., Walton, M.S., Trentelman, K., 2009. Characterization of lapis lazuli pigments using a multitechnique analytical approach: implications for identification and geological provenancing. Analytical chemistry. 81(20), 8513–8518.

[24] Favaro, M., Guastoni, A., Marini, F., et al., 2012. Characterization of lapis lazuli and corresponding purified pigments for a provenance study of ultramarine pigments used in works of art. Analytical and bioanalytical chemistry. 402, 2195–2208

[25] Eaton, G.R., Eaton, S.S., Stoner, J.W., et al., 2001. Multifrequency electron paramagnetic resonance of ultramarine blue. Applied Magnetic Resonance. 21, 563–570.

[26] Rejmak, P., 2018. Structural, optical, and magnetic properties of ultramarine pigments: A DFT insight. The Journal of Physical Chemistry C. 122(51), 29338–29349.

[27] Cato, E., Rossi, A., Scherrer, N.C., et al., 2018. An XPS study into sulphur speciation in blue and green ultramarine. Journal of Cultural Heritage. 29, 30–35.

[28] Laurie, A.P., 1926. The painter's methods and materials. J.B. Lippincott Company: Philadelphia, PA, USA pp. 249 pages, Courtesy of Science History Institute

[29] Plesters, J., 1966. 2. Ultramarine Blue, Natural and Artificial. Studies in conservation, 11(2), 62–91.

[30] Frison, G., Brun, G., 2016. Lapis lazuli, lazurite, ultramarine 'blue', and the colour term 'azure'up to the 13th century. Journal of the International Colour Association. 16, 41–55.

[31] Ganio, M., Pouyet, E.S., Webb, S.M., et al., 2018. From lapis lazuli to ultramarine blue: Investigating Cennino Cennini's recipe using sulfur K-edge XANES. Pure and Applied Chemistry. 90(3), 463–475.

[32] Arieli, D., Vaughan, D.E., Goldfarb, D., 2004. New synthesis and insight into the structure of blue ultramarine pigments. Journal of the American Chemical Society. 126(18), 5776–5788.

[33] Osticioli, I., Mendes, N.F.C., Nevin, A., et al., 2009. Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy. Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy. 73(3), 525–531.

[34] Verri, G., 2009. The spatially resolved characterisation of Egyptian blue, Han blue and Han purple by photo-induced luminescence digital imaging. Analytical and bioanalytical chemistry. 394(4), 1011–1021.

[35] Compendium, P., 2008. A Dictionary and Optical Microscopy of Historic Pigments Elsevier/Nicholas Eastaugh [et al.]. London and New York: Routledge Taylor&Francis Group, 950.

[36] Artioli, D., Capanna, F., Giovagnoli, A., et al., 2008. Mural paintings of Ajanta Caves, part II: Non-destructive investigations and microanalysis on execution technique and state of conservation. Proceedings of The 9th International Conference on NDT of Art; 25–30 May 2008; Jerusalem, Israel. pp. 25–30.

[37] Giovagnoli, A., Capanna, F., Ioele, M., et al., 2008. The mural paintings of the ajanta caves, part I: documentation on execution techniques and conservation condition. Art 2008-Non-destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage. Page 1–10

[38] Cacace, C., Giani, E., Giovognoli, A., et al., 2008. The mural paintings of cave 17 in Ajanta: the environmental study and the geographic information system (GIS) of the collected data. In ICOM Committee for conservation conference, 2, New Delhi, pp. 726 to 734.

[39] Brill, T.B., 1980. Light: its interaction with art and antiquities. Springer Science & Business Media: Publisher:Springer US. pp. 1–287.

[40] Coccato, A., Moens, L. and Vandenabeele, P., 2017. On the stability of mediaeval inorganic pigments: a literature review of the effect of climate, material selection, biological activity, analysis and conservation treatments. *Heritage Science*. *5,* 1–25.

[41] Cosentino, A., 2014. Identification of pigments by multispectral imaging; a flowchart method. Heritage Science. 2(1), 8.

[42] Bruce, H.D., 1928. Tinting strength of pigments. Bureau of Standards Journal of Research.Vol. 1, 125–150.

[43] Barsan, M.M., Butler, I.S., Gilson, D.F., 2012. High-pressure resonance Raman spectroscopic study of ultramarine blue pigment. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 98, 457–459.

[44] Clark, R.J., Cobbold, D.G., 1978. Characterization of sulfur radical anions in solutions of alkali polysulfides in dimethylformamide and hexamethylphosphoramide and in the solid state in ultramarine blue, green, and red. Inorganic Chemistry. 17(11), 3169–3174.

[45] Clark, R.J., Franks, M.L., 1975. The resonance Raman spectrum of ultramarine blue. Chemical Physics Letters. 34(1), 69–72.

[46] Ostroumov, M., Fritsch, E., Faulques, E., et al., 2002. Etude spectrometrique de la lazurite du Pamir, Tajikistan. The Canadian Mineralogist. 40(3), 885–893.

[47] Paramasivan, S., 1938. Technique of the painting process in the temple of Vijayalaya Cholisvaram in the Pudukkottai State. Proceedings of the Indian Academy of Sciences-Section A. 7(4), 282–292.

[48] Paramasivan, S., 1937. Technique of the Mural Paintings in the Brihadeswara Temple at Tanjore. Current Science, 6(6), 289–290.

[49] Gettens, R.J., 1938. The materials in the wall paintings from Kizil in Chi(nese Turkestan. Technical studies in the field of the fine arts. 6(4), 281–294.

[50] Brown, W.N. and Rowland, B., 1938. The Wall-Paintings of India, Central Asia, and Ceylon.Journal of the American Oriental Society, 58(3), 484–485.

[51] Rogala, D., 2014. Hans Hofmann's last lesson: a study of the artist's materials during the last decade of his career. In: van den Berg, K., et al. (eds.). Issues in Contemporary Oil Paint. Springer: Cham, Switzerland.

[52] Thompson, D.V., Berenson, B., 1936. The materials of medieval painting. CiNii Books, London, CRID: 1130000796799105280.

[53] Lal, B.; Ghosh, A., 1969, The Murals: Their Preservation; Gosh: New Delhi, India. pp. 56–59.

[54] Paramasivan, S., 1936. Technique of painting process in cave temples of Ajanta. Annual Report of the Archaeological, Highness the NizamVs Dominions.

[55] Bhardwaj, H.C. Some observations on the conservation of murals. In Proceedings of the Conservation of Cultural Property in India, New Delhi, India, 23–25 February 1966; pp. 37–46.

[56] Dabhade, S.B., 1973. The technique of wall painting in ancient India. the University of California, Page 1–48

[57] Singh, M., Arbad, B., 2013. Chemistry of preservation of the Ajanta murals. International Journal of Conservation Science. 4(2), 161–176.

[58] Sharma, D., Singh M., Krist, G., et al., 2020. Pigment analysis of palm leaf manuscripts of India. Current Science. 118(2), 285–292.

[59] Eastaugh, N. 2008, Pigment Compendium: A Dictionary and Optical Microscopy of Historic; Butterworth-Heinemann: Waltham, MA, USA.

[60] Kanth, A.P., Singh, M.R., 2019. Vibrational spectroscopy and SEM-EDX analysis of wall painted surfaces, Orchha Fort, India. Journal of Archaeological Science: Reports. 24, 434–444.

[61] Caggiani, M.C., Cosentino, A., Mangone, A., 2016. Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database. Microchemical Journal. 129, 123–132.

[62] Colomban, P., 2003. Lapis lazuli as unexpected blue pigment in Iranian Lâjvardina ceramics. Journal of Raman Spectroscopy. 34(6), 420–423.

[63] Al-Dabbas, M., Eisa, M.Y., Kadhim, W.H., 2014, Estimation of gypsum-calcite percentages using a Fourier transform infrared spectrophotometer (FTIR), in Alexandria Gypsiferous Soil-Iraq. Iraqi Journal of Science. *55*(4B), 1916–1926.

[64] Reig, F.B., Adelantado, J.G., Moreno, M.M., 2002. FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method. Application to geological samples. Talanta. 58(4), pp.811–821.

[65] Kanth, A.P., Singh, M.R., 2019. Spectroscopic and chromatographic investigation of the wall painted surfaces of an 18th century Indian temple, New Delhi. Vibrational spectroscopy. 104, 102947.

[66] Gettens, R.J., 1938. The materials in the wall paintings of Bamiyan, Afghanistan. Technical studies in the field of the fine arts. 6(3), 186–193.

[67] Delmas, A.B., Casanova, M., 1987. The lapis lazuli sources in the ancient east. South Asian Archaeology. 9, 393–426.

[68] Ji, J., Zhang, J.F., 2011. The Origin and History of Some Blue Pigments in Ancient China. Dunhuang Research. 2011(6), 09–14.

[69] Uda, M., Sassa, S., Yoshimura, S., et al., 2000. Yellow, red and blue pigments from ancient Egyptian palace painted walls. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 161–163, 758–761.

[70] Gettens, R.J. and Fitzhugh, E.W., 1974. Malachite and green verditer. Studies in Conservation, 19(1), pp.2-23.

[71] Szmelter-Fausek, B., Olszewska-Świetlik, J., 2016. Blue pigments in blue and purple painting layers of Gdańsks' paintings of the mid-16th to the end of the 18th century. Color Research & Application. 41(3), 270–275.

[72] Seldes, A.M., Burucúa, J.E., Maier, M.S., et al., 1999. Blue pigments in South American painting (1610–1780). Journal of the American Institute for Conservation. 38(2), 100–123.

[73] Sanz, E., Arteaga, A., García, M.A., Cámara, C., Dietz, C., 2012. Chromatographic analysis of indigo from Maya Blue by LC–DAD–QTOF. Journal of archaeological science. 39(12), 3516–3523.

[74] Tagle, A.A., Paschinger, H., Richard, H., Infante, G., 1990. Maya Blue: its presence in Cuban Colonial wall paintings. Studies in Conservation. 35(3), 156–159.

[75] Leona, M., Stenger, J., Ferloni, E., 2006. Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in

works of art. Journal of Raman Spectroscopy. 37(10), 981–992.

[76] Liu, L., He, J., Ye, M., et al., 2019. Spectral characterization of pigment from the No. 1 cave, Kizil cave-temple complex. Journal of Spectroscopy. 2019(1), 1–9.

[77] Abe, Y., Harimoto, R., Kikugawa, T., et al., 2012. Transition in the use of cobalt-blue colorant in the New Kingdom of Egypt. Journal of Archaeological Science. 39(6), 1793–1808.

[78] Paramasivan, S., 1939. August. The wall paintings in the Bagh caves—An investigation into their methods. Proceedings of the Indian Academy of Sciences-Section A. 10, 85.

[79] Paramasivan, S., 1938. Technique of the Painting Process in the Kailasanatha and Vaikunthaperumal Temples at Kanchipuram. Nature, 142, 757.

[80] Yoo, S.Y., Seneviratne, B.J.N., Kim, G.H., 2022. A Characteristic Analysis on Clay Pigments of Mural Paintings in Sri Lanka. Journal of Conservation Science. 38(4), 327–333.

[81] Asiatic, 1912. The rise and fall of indigo industries in India. The Economic Journal. 22(86), 237–247.

[82] Aceto, M., 2021. Pigments—the palette of organic colorants in wall paintings. Archaeological and Anthropological Sciences, 13(10), 159.

[83] Nagpal, J.C. Mural Paintings in India; Gyan Publishing House: New Delhi, India, 1988; ISBN 8121201497.

[84] Lal U. S., Nair M. V., 2009. Scientific study of Pigments and Plasters of 12th century wall paintings of Lakhang- Gongma Monastery at Nako (H. P.). Conservation of Cultural property in India. 38(2009), 21–25.

[85] Bayerová, T., 2018. Buddhist wall paintings at Nako monastery, North India: changing of the technology throughout centuries. Studies in Conservation, 63(3),171–188.

[86] Gill, M.S., Rendo, C.P., Menon, S., 2014. Materials and techniques: early Buddhist wall paintings and sculptures at Sumda Chun, Ladakh. Studies in Conservation. 59(5), 300–313.

[87] Skedzuhn, A., Oeter, M., Bläuer, C., et al., 2018. The secrets of 14th century wall painting in the Western Himalayas: Structural damage sheds light onto the painting technique in the Tsuglag-khang in Kanji in Ladakh.

[88] Mazzeo, R., Baraldi, P., Lujan, R. et al., 2004. Characterization of mural painting pigments from the Thubchen Lakhang temple in Lo Manthang, Nepal. Journal of Raman Spectroscopy. 35(8–9), 678–685.

[89] Jaspal, N., 2017, Conservation of Wall Paintings at the Golden Temple(Sri Harmandar Saheb Ji), Amritsar, India. Available online: https://heritagepreservationatelier.com/2020/06/13/conservation-of-wall-paintings-at-the-golden-templesri-harmandar-saheb-ji-amritsar-india/ (accessed on 10 June 2021).

[90] Babel, S., Rajvanshi, R., Sharma, S., 2014. Mewar Paintings: An Exploratory Study. Asian journal of Home Science (AJHS). 9(2), 636–640.

[91] Agarwal, O.P., Tiwari, R.,Yadav, A. K., 1988. Examination of the Technique of Paintings at the Moghul Gateway, Bairat, Rajasthan and its conservation problems. Conservation of Cultural Property in India. pp. 21, 73–79.

[92] Agrawal, O.P., 1989, Examination and Conservation of Wall Paintings of Sheesh Mahal, Nagaur: A programme under National Project on Wall Paintings; NRLC. INTACH Conservation Center: Lucknow, India.

[93] Yadav, A.K.; Savita, R.P.; Singh, K.; et al., 1995, Conservation of wall paintings in Servent Chapel of St. Monica Church and Convent, Goa; INTACH Trust: New Delhi, India.

[94] Lal, G.; Singh, K.; Yadav, A.K. Conservation of Mural Paintings at Panchai Court, Imphal; INTACH: New Delhi, India, 1995.

[95] Agrawal, O.P. and Pandey, A.K., 1990. Scientific study of Kerala wall paintings. Conservation of cultural property in India, 23, pp.1–6.

[96] Mariyapillai, M., Paranthaman, G., Napoleon, K., et al., 2021. A re-reading on vibrant mural paintings of Sittanavasal cave temples. International Journal of Mechanical Engineering. 6(special issue, Nov.–Dec. 2021), 1619–1623.

[97] Agrawal O.P., Ram S. P., Mamta M., 1994. Conservation of Wall Paintings in India-Achievements and Problems (Proceedings of the Seminar Held During October 22–24, 1994),. Indian National Trust for Art and Cultural Heritage: New Delhi, India. pp. [vi] + 178.