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RESEARCH ARTICLE

Color Properties of Natural Ultramarine Pigments with the Effect of Preparation Processes and Raw Rock Quality

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ABSTRACT

Natural ultramarine is a traditional and expensive blue pigment widely used around the world. It has been found recently in the decorative paintings (*caihua 彩畫*) of historical Chinese buildings. Interestingly, the preparation and application methods for this pigment have not been documented in Chinese painting reviews and artisans' manuscripts before the 20th century. The sedimentation method (also named "*Shuifei 水飛*") was likely the approach used by Chinese artists and craftsmen to produce this blue pigment. The extraction method (recorded by Cennino Cennini) was another representative method. Both methods have been used to prepare this blue pigment. Through the experiments of pigment and color sample, 21 natural ultramarine pigments produced by these two methods were collected. By means of color measurement and polarized light microscopy, this study aimed not only to summarize the color properties of this pigment mixed with gelatin but also to try to reveal how preparation process and raw rock quality influence its color effect. The colorimetry study of natural ultramarine pigments will provide data and visual references for heritage conservation and restoration, as well as traditional color design. Analyzing the pigment's color properties from the perspective of materials and techniques will help uncover the intentions behind its history.

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lapis lazuli; natural ultramarine; raw rock quality; traditional preparation process; ultramarine blue

1. Introduction

"Natural Ultramarine" is made from ground lapis lazuli rock and lazurite gives it the blue color, which is also the key coloring composition in the "Synthetic Ultramarine" (Frison and Brun 2016). The vivid blue with a purple tone is considered to be the remarkable color effect of this pigment.

The term "*ultramarine*" first appeared in European artist's handbooks in the 14th century. The prefixes '*ultra-*' or '*oltra-*' referred to its status as an imported commodity (Plesters 1966). While ancient Greek and Roman scholars mentioned lapis lazuli rock in their writings, but its use as a powdered pigment during that period remains unclear. In Europe, it started being used as a powdered pigment in the early medieval period, with the earliest illustrations of blue dating back to around the 6th to 7th century in Byzantine Gospel manuscripts (Aceto et al. 2012; Laurie 1914, 62–70). By the 14th to 15th centuries, it was widely applied in murals and easel paintings (LeCroy 2022; Plesters 1966). The 6th–7th century cave temples of Bamiyan and Turkestan in Afghanistan were the earliest examples of its application as a mural pigment in Central Asia (Gettens 1938; Taniguchi and Cotte 2022).

In China, this pigment has been used for centuries, but the terms "*ultramarine (Qunqing群青)* " or "*natural ultramarine (天然群青)*" did not appear in historical records until the 20th century. "*ultramarine*" was introduced from Japan along with "*synthetic ultramarine (人造群青)* ". Lapis lazuli powder, used as a pigment, was referred to as "*Jinqing (金青)*," "*Huiqing (回青)*," "*Huihuiqing (回回青)*," "*Shaqing (沙青)*," "*Ziyanqing (紫艶青)*," or "*Ziyuantian Daqing (紫原天大青)*" in literature from Tang dynasty. This pigment was used as early as the 3rd century for decorating cave murals and Buddha sculptures (Wang 1996a). Recently, it was also found in the remains of decorative paintings from Yuan, Ming and Qing buildings[1] (Li and Liu 2018; Liu 2019, 362–372), In the cave murals, such as in the Kizil and Dunhuang Grottoes, this powder could be used alone, with deep, vivid colors and larger particles but more severe flaking. Often, it was mixed with gypsum,

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[1]There are only two decorative remains of Chinese buildings that can be identified with the traces of the use of natural ultramarine. The first is the painted ceilings of the Linxi Pavilion in the Forbidden City, Beijing (Qing Dynasty), and the second is the interior decoration of the Sanqing Hall in the Yongle Taoist Temple, Shanxi (Yuan Dynasty). Although lazurite has been found in the decorative wooden elements of the Main Hall of Qutan Temple (Ming Dynasty), it is not clear whether it is natural or synthetic, and its age is also disputed.

lead white, and other white powders to create shades of blue (Su et al. 2000; Wang 1996a, 1996b; Zhou 2022). In the buildings, it tended to be mixed with other blue particles, such as azurite and smalt (Li and Liu 2018; Zheng et al. 2023).

Western craftsmen recognized early on that this mineral contained various associated minerals and had continually worked to refining the processes to enhance its color effect. From the medieval period to the late 19th century, craftsman's handbooks documented various processes for preparing this blue pigment. These processes were collated, translated and annotated by Merrifield (1849), Thompson (1933) and Frison and Brun (2016). Most of the processes and their products were then compared experimentally by Denninge (1964), Kurella and Straus (1983) and Wallert (1991), with Kurella's research proving that extraction through a doughy mixture termed "*pastello*" (a paste with resin, wax, and mastic) was the most efficient method to obtain a purer powder. With advanced science techniques, such as ERS (Electron Paramagnetic Resonance), Raman (including Raman spectroscopy and micro-Raman spectroscopy), XANES (X-ray Absorption Near-Edge spectroscopy), etc., the physical and chemical principles behind the extraction method have been further elucidated (Favaro et al. 2012; Fuchs and Oltrogge 1990; Gambardella et al. 2020; Gobeltz et al. 1998; Tauson et al. 2012). At the same time, the principles around "*ultramarine degradation*" (a color change phenomenon of ultramarine containing layers in paintings, usually called "*ultramarine disease*") continues to be studied in depth (De la Rie et al. 2017; Del Federico et al. 2006). Current researchers have focused on the quantitative analysis of the composition, content and chemical structure of chromophores and impurities contained in pigments before and after extraction, but they have not paid more attention to quantifying its color change and cannot describe the achievable color gamut of this pigment yet.

Unlike in the West, Chinese painting reviews and artisans' manuscripts before the 20th century lacked specific descriptions of natural ultramarine preparation. Since the latter half of the 20th century, some researchers have used various scientific methods to analyze trace elements or associated minerals in pigments from painted relics to infer their ore sources (Fu, Yu, and Ma 2006; Wang 1997; Zheng et al. 2023). However, these studies cannot determine whether the pigment was transported and traded as powder or reprocessed from raw rock. Due to the lack of documentation and the difficulty of empirical verification, the ways in which historical Chinese painters or artisans obtained this blue pigment remain uncertain (Zhou, Yang, and Gao 2019). Exploring how Chinese craftsmen prepared this special blue pigment and the color effects they achieved is urgently needed.

This study follows the methods proposed by Li (2019, 2021) for researching traditional Chinese pigments. Twenty-one natural ultramarine pigments will be studied, of which 17 samples are taken from previous research (Liu, Li, and Yang 2022) and 4 are newly added for this study. The added pigments have different production backgrounds, including the brand, quality and preparation process. The colors of all pigments are available to be quantified using the spectrophotometer. The color properties will be discussed and summarized in the CIE-LCH color space. Furthermore, the effect of the quality of the raw ore and the preparation process on color properties will be investigated using the polarized light microscopy.

2. Preparation process and source information for pigments

Search results from Western and Chinese historical literature on the preparation processes of natural ultramarine pigment indicate that two traditional methods are most representative and have been continuously used to this day. One is the Cennini's extraction method, and the other is the Chinese sedimentation method (also known as "*Shuifei (水飛)* "). The first method results in the purified pigment, while the second produces the unpurified pigment, due to the mineral characteristics of lapis lazuli. This pigment sold in market today still adheres to these two methods, but modern production often uses automated machinery like ball mills and high-speed pulverizers instead of manual labor to increase efficiency and shorten production cycles.

This study obtained 21 typical natural ultramarine pigments (Table 1), of which 13 were bought from the market and 8 from laboratory production. Market-sourced pigments included 3 made by extraction and 10 by sedimentation, while all laboratory-produced pigments used the sedimentation method. Based on their preparation methods, these pigments were categorized into purified and unpurified groups for next study and discussion.

2.1. Two traditional preparation processes and their characteristics

2.1.1. Cennini's extraction method

Recent findings demonstrate that lapis-lazuli pigments could have been of high quality in medieval times (Vieira et al. 2024; Nabais et al. 2016). The earliest Western references to the extraction method are found in three alchemists' manuscripts of the 8th–13th centuries: *Liber claritatis* (in Arabic), *Ms. Sloane*. 342 (in

Table 1. Classification and statistics of the preparation processes and source information for all pigments.

Preparation process	Pigment group	Pigment source	Pigment brand and number		
Cennini's extraction method	Purified	Market	Zecchi	Florence, Italy	2*
			Dominique 多米尼格	Chongqing, China	1
Chinese sedimentation method	Unpurified	Market	Dominique多米尼格	Chongqing, China	1
			Jiang Si Xu Tang 姜思序堂	Suzhou, China	1
			Tian Ya 天雅	Beijing, China	3*
			Qing Jin Fang 青金坊	Beijing, China	5*
		Laboratory production	\	\	8*

More details on laboratory-produced pigments can be found in section 3.1 and Table 2.
The numbers marketed "*" indicates that these pigments are graded according to their quality or particle size.

Table 2. List of eight natural ultramarine pigments produced in the laboratory.

Rock grade	Typic color category of rock	Pigment type	Pigment number	Range of particle sizes
Gem-quality	Medium color and light (B2/B3)	A	A1	Φ > 75 μm
			A2	38 μm < Φ ≤ 75 μm
			A3	Φ ≤ 38 μm
	Purplish (C2)	B	B1	Φ > 75 μm
			B2	38 μm < Φ ≤ 75 μm
			B3	Φ ≤ 38 μm
Fragmented	Purplish (C2)	C	C	Φ ≤ 38 μm
	Grayish (C1)	D	D	Φ ≤ 38 μm

English), and *Caius College Ms. 181* (in English) (Jörg 2011, 30–34). By the 14th-15th centuries, this process for preparing purified pigment was very common in a variety of Italian artisans' manuscripts. Although there are some differences in the recorded details, the main steps are basically consistent. The most comprehensive and complete documentation is found in "*Il Libro dell' Arte*", written by the master artist Cennino Cennini in 1390.[2] Thus, this study refers to this traditional process as "*Cennini's extraction method* ".

This process usually consists of six steps: 1) crushing and washing rocks; 2) sieving the finer and grinding into powder; 3) melting pine resin, mastic, and wax; 4) mixing with powder and kneading to a paste; 5) scrubbing the paste with lukewarm lye to separate several pigment grades; 6) settling and drying the extracted particles (Broecke 2015, 89–94; Frezzato 2003, 64–69; Thompson 1933, 145–146). Steps 3) to 5) are key for extracting blue pigment particles. While this method leaves most impurities in the paste, but some, like calcite still remain (Denninge 1964). About 20 g of high-quality powder can be obtained from every 500 g of high-quality lapis lazuli rock (Coles 2022, 182). Despite its extraction yield being just about 4%, people were still willing to spend a lot of money and time for its unique blue color.

It is important to note that both Cennini's method and the next method separate the pigment grades based on their settling order, but their grades represent different meanings. For the extraction method, the grade indicates quality, with the pigment from the first extraction being of the highest quality and containing the fewest impurities. For the sedimentation method, the grade reflects particle size, with the pigment from the first sedimentation having the largest particles.

2.1.2. Chinese sedimentation method

The book "*Mineralfarbe Stoffe (礦物顏料)*", edited by Wan (1935), 34–52) in the 20th century, is the earliest Chinese literature that clearly records the preparation processes of natural ultramarine pigment. Prior to this, there were no other documentations of this pigment's process in painting reviews and artisans' manuscripts. However, the method of preparing other natural mineral pigment, generally known as "*Shuifei (水飛)*", has been established for a long time and can be found in the 12th-century official book "*Yingzaofashi (營造法式)*". Repeated sedimentation is the key to separate several particle sizes and colors, so this study refers to this traditional process as "*Chinese sedimentation method* ".

This process usually consists of five steps: 1) crushing and selecting the good quality raw rocks; 2) washing and grinding into fine powder with water; 3) settling the ground slurry and grading; 4) collecting and washing the graded slurry; 5) drying and storage the pigment powders. The grading principle in step 3) is based on the specific gravity differences caused by different particle sizes. The larger the particle size, the greater the gravity, and the faster it settles.

As a multi-mineral aggregate, the densities of the associated minerals are similar to lazurite, except for pyrite and diopside, which have higher densities

[2]Kurella and Straus (1983) have classified and compared the various types of natural ultramarine production processes contained in the literature of the 13th-19th century period in a more systematic way, which will not be repeated in this paper.

Figure 1. Main steps for Dominique's customized pigment preparation process. (These images were taken from the officially released video of the process. 1) Smashing and washing; 2) Ball mill grinding; 3) Standing and collecting sedimentation; 4) Melting pine resin, mastic and wax; 5) Kneading the paste; 6) Lukewarm lye scrubbing).

(Jörg 2011, 16) Before the introduction of Cennini's method to China, the sedimentation method would have been the most likely approach craftsmen or artists adopted to produce this pigment, similar to other natural rocks.

We cannot determine if they noticed that the associated mineral particles of this pigment could not be removed solely through sedimentation, or if they added some extraction steps. Currently, leading traditional pigment manufacturers in China, such as *Jiang Si Xu Tang (姜思序堂)* and *Tian Ya (天雅)*, continue to use this traditional method to produce this pigment. However, this study found that the pigments from these brands fail to achieve the remarkable colors. Therefore, we purchased lapis lazuli rocks of different qualities and produced eight pigments in the laboratory, using the same sedimentation method for their preparation.

2.2. Two pigment groups

2.2.1. Purified pigment: prepared by extraction method

Three pigments were available for purchase: two qualities of Afghan lapis lazuli blue pigments from *Zecchi*[3] in Florence, and one customized lapis lazuli powder from *Dominique's Oil Painting Materials Studio*[4] in Chongqing (Figure 1).

2.2.2. Unpurified pigments: prepared by sedimentation method

Except for the eight unpurified pigments produced in the laboratory, the remaining 10 unpurified pigments were purchased from 5 different pigment brands: *Jiang Si Xu Tang (姜思序堂)*, *Tian Ya (天雅)*, *Qing Jin Fang (青金坊)*, and *Dominique (多米尼格)*. All brands except Jiang and Dominique grade and number their pigments.

Due to the small amount of pigments produced in the laboratory, it was difficult to separate pigment grades by settling speed. Instead, they were divided into three grades using 400-mesh and 200-mesh sieves. Tianya's pigments were screened and graded using computer-controlled equipment (Wang and Yu 2008, 30), and 3 pigments from this brand were selected in this study, graded as No.9, 11, and 13.

The grades of Qing's pigments do not solely indicate particle size but also reflect the quality of the raw rocks used.

3. Methodology

This study focuses on investigating the color properties of this natural pigment through pigment experiment, color sample experiment, color measurement, and microscopic observation.

The pigment experiment supplemented eight natural ultramarine pigments, with six made from gem-quality raw rocks being particularly significant. Based on the visual observation, the classification of raw rocks was refined by color measurement and colorimetric calculation for greater precision. These laboratory-produced pigments not only addressed the issue of poor raw rock quality in market-sourced pigments but also provided samples for further analysis of how raw rock quality affects color effect of this pigment.

[3]Official website: https://zecchi.it/. The official trade names of the two pigments are "*(AZZURRO OLTREMARINO) — BLU DI LAPISLAZZULI AFGANO -extra- prima scelta" and "(AZZURRO OLTREMARINO) — BLU DI LAPISLAZZULI AFGANO- seconda scelta*".
[4]Official website: https://dominiquepigments.taobao.com/.

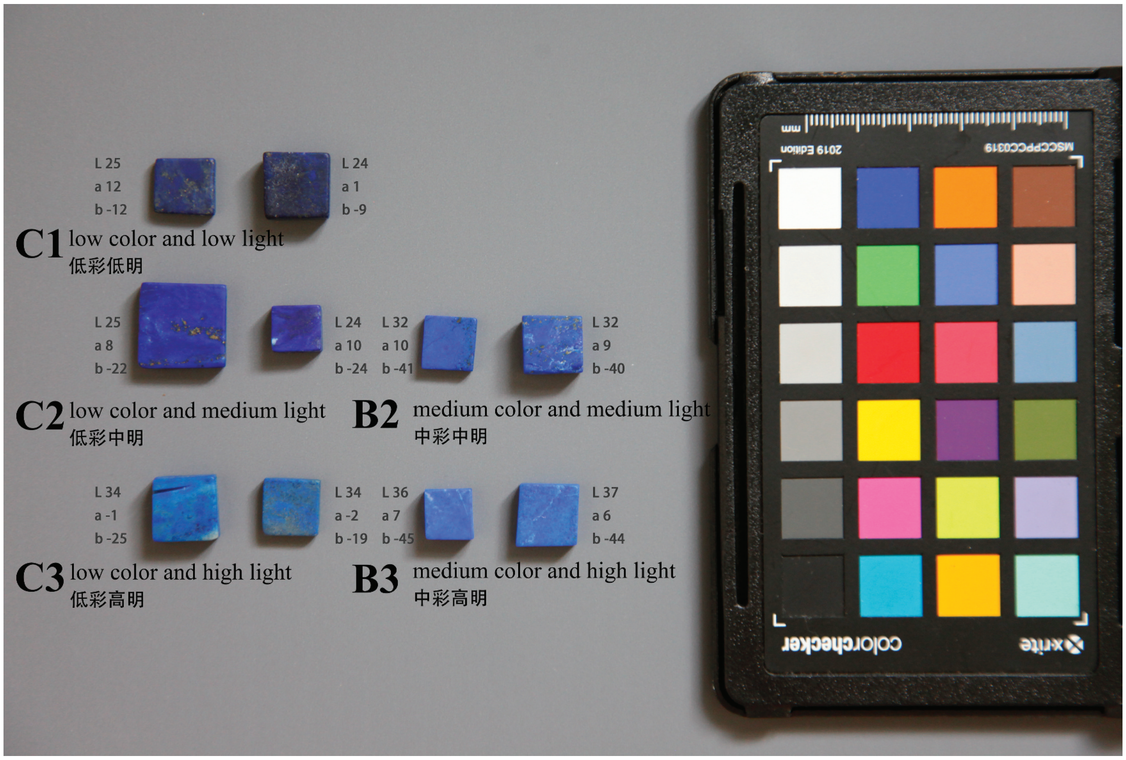

Figure 2. 5 typical colors of gem-quality rocks in natural light.

Color sample experiment and color measurement was foundational methods in traditional color research of painting pigments. This study used these two methods to collect CIE colorimetric values for 21 natural ultramarine pigments, using gelatin as a binder. All colorimetric data, measured by a CR-730 spectrophotometer, was analyzed and calculated according to the standard "*Uniform color space and color difference formula (GB/T 7921-2008)* " (AQSIQ, 2008) to evaluate the color effects and summarize the pigments' color properties.

Polarized light microscopy, a basic technique for identifying painting materials and widely used in cultural heritage preservation, was used to explore the microscopic causes of the pigments' color characteristics, focusing on particle morphology, purity, and uniformity. The observation equipment was a Nikon LV100ND microscope equipped with polarizing accessories and a DS-Ri2 micro camera.

3.1. Pigments experiment

3.1.1. Sources and categories of raw rocks

The raw rocks was purchased from the *Qing Jin Fang (青金坊)* in Beijing, available in two grades: gem-quality rock and fragmented rock. Both were natural lapis lazuli mined in Afghanistan, with a notable price disparity.[5]

In natural light, the color of rocks showed significant variations. Gem-quality rocks could be classified into five categories of typical colors based on visual observation, and they were numbered and named according to their lightness and chroma as "*C1 low color and low light*", "*C2 low color and medium light*", "*C3 low color and high light*", "*B2 medium color and medium light*", and "*B3 medium color and high light*"(Figure 2). After using a spectrophotometer to measure the colorimetric values of five types of rocks, we could found that C3 had the smallest hue angle and was greenish; C2 had the largest hue angle and was purplish; C1, B2 and B3 had the middle hue angle. The chromatic aberration between B2 and B3 was small, and the visible impurities on their surface were also less. As a result, B2 and B3 could be merged into the type of "*medium color and medium light*". C1 had a large number of dark-blue or black-gray impurities on the surface and was the most grayish.

The optimized classification of typical colors for gem-quality rocks was displayed in Figure 3,

[5]The price of gem-quality rock is RMB 20 per gram and it can be purchased at https://item.taobao.com/item.htm?spm=a1z09.2.0.0.116d2e8deylv3L&id=625256225804&_u=vc438e8c24. The trade name of the fragmented rock is "*New Treasure Blue S004*" and its price is 0.06 RMB per gram. It can be purchased at https://item.taobao.com/item.htm?spm=a1z10.3-c.w4002-22697063005.20.f4a74bf5C9PTyK&id=616815085309.

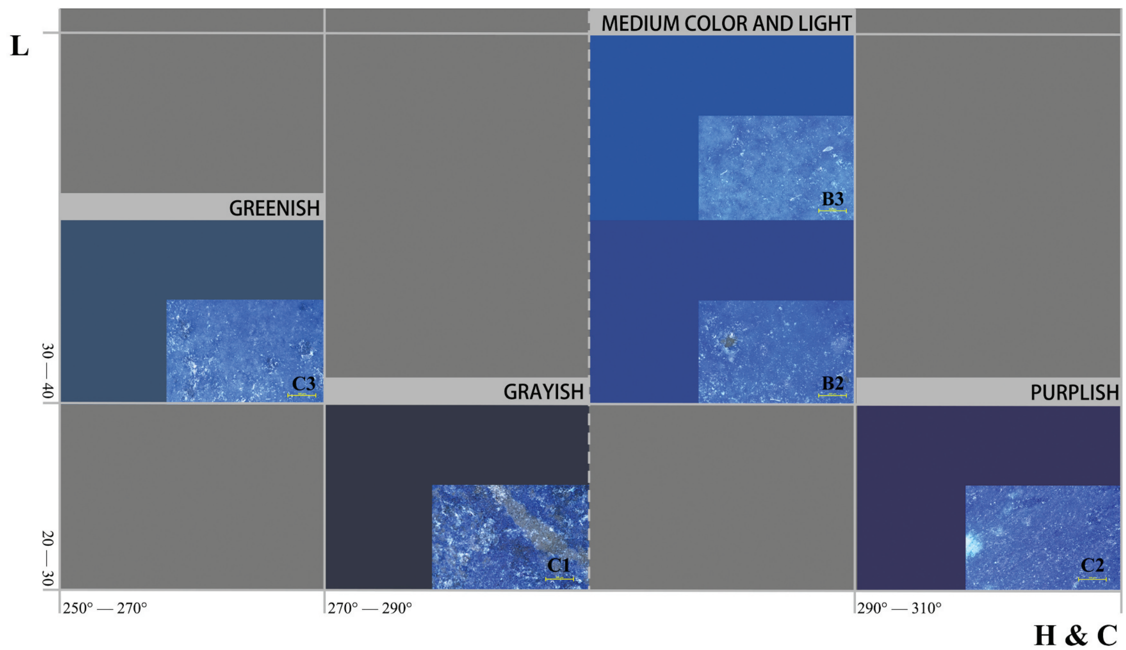

Figure 3. Surface micromorphology, optimized classifying of typical colors and distribution of gem-quality rocks. (The vertical axis represents lightness (L), and the horizontal axis represents both hue angle (H) and chroma (C). Within the same hue interval, chroma is smaller on the left and large on the right.)

segmented into four categories: "*Greenish (C3)*", "*Purplish (C2)*", "*Medium color and light (B2&B3)*" and "*Grayish (C1)*".

3.1.2. Preparation process

The pigment preparation process was primarily based on the Chinese sedimentation method, and used modern instruments and tools. The process included the following eight steps (Figure 4):

(1) Good-quality rocks were selected and classified according to their color in natural light.
(2) The rocks were washed in hot water and dried with a paper towel.
(3) Warping in gauze, the rocks were smashed by a Deli claw-hammer (made of carbon steel) until particle sizes were less than 8 mm for easier grinding.
(4) The crumbs were ground 5–6 times in a high-speed pulveriser (made of alloy steel and bought from Hebi Chengxin Instrument Company) for about 10 s each, and then sieved through a 400-mesh sieve.
(5) The finer powders were mixed in a glass dish with hot water and stirred. The suspension was left to stand for 5 min to allow the pigment particles to settle before pouring off the upper part of the water. This step was repeated three times until the water was completely clear.
(6) Water was added again. A round magnet (48 mm diameter and 11 mm thickness) was used to remove ferrous impurities from the suspension, and must be cleaned in time to ensure adsorption. This step continued until the magnet showed no significant impurities followed by another 5-min settling and pouring off the upper part of the water.
(7) The pigments were quickly dried with a temperature-controlled plate (MG-846 electronic hot plate) until completely dry to produce the final No. 3 pigment ($\Phi \leq 38$ μm).
(8) The larger powders from step 4) were processed similarly through steps 5), 6) and 7), and then sieved through a 200-mesh sieve to separate into No. 2 pigment (38 μm $< \Phi \leq 75$ μm) and No. 1 pigment ($\Phi > 75$ μm).

3.1.3. Laboratory-produced pigments

The experiment supplemented with eight natural ultramarine pigments, with six made from gem-quality rocks and two from fragmented rocks, as detailed in Table 2.

The six gem-quality pigments were categorized into Types A and B. Type A, exhibiting the highest chroma in Figure 3, was crafted from "*medium color and light*" rocks, while Type B, with the highest hue angle, was

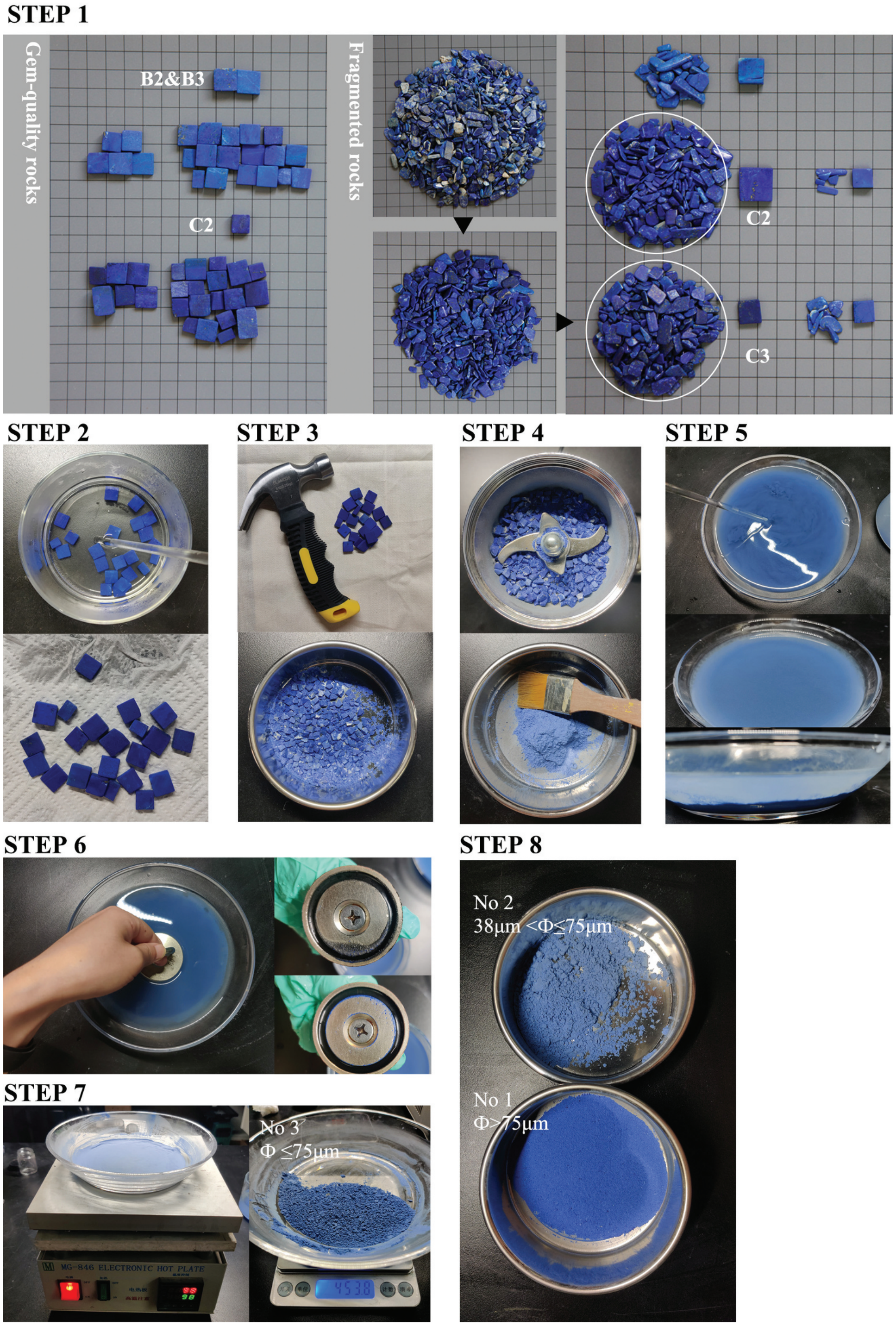

Figure 4. Main steps of pigment preparation experiment.

made from "*purplish*" rocks. Each type was numbered from 1 to 3 based on particle size, with larger numbers representing smaller particles.[6]

Fragmented rocks, in contrast to gem-quality ones, required initial sorting to remove less pure rocks. These were then classified under natural light according to the

[6]According to Feller and Bayard's classification standard for pigment particle size, mineral pigment particles larger than 40 μm are "very coarse" and 10-40 μm are "coarse", Mrock details can be found in Eastaugh et.al's book (2008,516-517). So, the particle size of pigment No. 3 is 400 mesh (about 38μm), which is a coarse particle, while pigment No. 1 and No. 2 are very coarse particles. After the following color sample painting experiments, it is found that the particle size of No.1 pigment is too large, which is not convenient for glue mixing, and its adhesion and covering are poor, so it is not recommended to be used as a color pigment.

Figure 5. The photograph of 21 natural ultramarine color samples.

color standard of gem-quality rocks (Figure 4 Step 1). Ultimately, the two most common groups, "*greenish*" and "*purplish*" were selected to produce two pigment types, C and D, with only one particle size.

3.2. Color samples experiment

Based on the expertise of Wang Guangbin, an artisan of intangible cultural heritage, and the studies of earlier scholars on historical documents (Bian 2007, 70–72; Jiang 2005, 220–231; Wang and Yu 2021, 52–55), we drew a total of 21 color samples (Figure 5), simulating the traditional process of decorative painting used in official buildings during the Ming and Qing dynasties. The process involved five steps (Figure 6):

(1) **Sanding and wiping the surface layer of the wood block**. The wood block was made of pine, with dimensions of 14.5 × 6.5 × 1.5 cm.
(2) **Rubbing the draft**. Firstly, the draft was drawn on the kraft paper, and then the kraft paper was pricked with a silver needle according to the pattern on the paper. Secondly, white talcum powder was wrapped in gauze to form a powder packet. Finally, the kraft paper was placed on a wooden block and tapped repeatedly with the powder packet to imprint the pattern onto the surface of the wooden block.
(3) **Preparing the glue**. Gelatin granules (bought from *Jiang Si Xu Tang*) and hot water at 90°C were put in a small beaker with a weight ratio of 1:6. Then, stirring the gelatin granules in the small beaker until they were completely melted.
(4) **Mixing the paints**. A small amount of pigment powder was placed on a white porcelain plate, and then glue was added gradually in small amounts (the weight ratio of the two was based on the painter's experience, not quantified). They were mixed with the forefinger.
(5) **Drawing the sample**. Each color block was first outlined and then filled in one direction. After the first layer dried, 2–5 more layers were applied in the same manner until the wood block was fully covered.

Further details on the materials, tools, and techniques used can be found in the reference (Liu, Li, and Yang 2022).

3.3. Color measurement method

The color data, including colorimetric value and spectral reflectance, were measured by a CR-730

Figure 6. Main drawing steps for color samples.

spectrophotometer from Beijing Coloreader Company (北京科美潤達). The measurement geometry was d/8°, with a D65 light source, a measurement area diameter of 6 mm (SAV), and a measurement mode of Specular Component Include (SCI). The wavelength range of the spectrum was 400–700 nm with intervals of 10 nm. The results were obtained from repeated measures (average of three different acquisitions).

The colorimetric values were the coordinates of all samples in CIE-LAB space,[7] including L*, a*, b*. The coordinates a* and b* were converted to the coordinates C* and H*, which could more intuitively reflect the color changes in visual perception. The next analysis was calculated all colorimetric elements that exhibit color differences, including ΔL*, ΔC*, ΔH*and CIE-DE2000(ΔE_{00}). All data were calculated according to the requirements of the Chinese standard (AQSIQ, 2008) by the Color Management Network at https://www.colortell.com/.

When color samples from varying raw rock qualities and preparation processes had similar colorimetric values, they could be represented by a "typical color". Each typical color was calculated as the arithmetic mean of the group's colorimetric values, ensuring that the color difference between any sample and its typical color was less than or equal to 3 ($\Delta E_{00} \leq 3$).

This study used the "typical color" method to summarize the colors of 21 natural ultramarine pigments. Building on the seven colors published in the "*The standard chromatogram for the decorative painting in Ming and Qing official architectures*", this study adds three new colors, resulting in 10 typical colors of natural ultramarine pigments arranged in a specific order.[8]

3.4. Microscopic observation method

The main method used in this study was polarized light microscopy. Each sample was observed and

[7]In the CIE-LAB color system, the coordinates are L*, lightness; a*, the red-green coordinate; and b*, the yellow-blue coordinate. In addition, colors can also be described using the cylindrical coordinates L*, C* (Chroma), and H* (Hue angle). Lightness measures the ability of the sample to transmit diffusely the incident light, so that L* = 100 for a white sample and L* = 0 in a black sample. The chroma, C*, coordinate is perpendicular to L* and is calculated as C* = [(a*)2 + (b*)2]1/2, and it represents the amount of chromatic component in the pigment (as opposed to achromatic or gray). The hue is an angle, also calculated from a* and b* and given by the expression h* = arctan(b*/a*).

[8]The abbreviated numbering of the three added typical colors is "pB-4-5," "pB-6-5," and "B-2-9." For the specific calculation steps and arrangement logic of the ten "typical colors," please refer to the reference (Liu, Li, and Yang 2022).

Table 3. The CIE colorimetric values of the 21 color samples.

Preparation process	Pigment group	Pigment brand or source	Pigment grade & number	Pigment abbreviation	CIE colorimetric value					Standard deviation of the values		
					L	a	b	C	H	L	a	b
Cennini's extraction method	purified	Dominique	customized	D-1	32	9	−43	44	281	0.1	0.1	0.2
		Zecchi	extra-prima	Z-1	31	21	−58	61	290	0.3	0.4	0.3
		Zecchi	second	Z-2	36	8	−42	43	281	0.4	0.1	0.2
Chinese sedimentation method	unpurified	Dominique	normal	D-2	53	−6	−25	26	256	0.1	0.3	0.8
		Jiang Si Xu Tang		J-1	49	−5	−20	21	255	0.1	0	0.2
		Qing Jin Fang	1#	Q-1	46	−2	−29	29	266	0.8	0.2	0.8
		Qing Jin Fang	2#	Q-2	43	−5	−28	28	259	0.2	0.1	0.5
		Qing Jin Fang	3#	Q-3	45	−5	−19	20	254	0.4	0.2	0.8
		Qing Jin Fang	4#	Q-4	48	−4	−22	22	258	0.7	0.3	0.2
		Qing Jin Fang	9#	Q-9	52	−7	−17	19	249	0.6	0.1	0.2
		Laboratory	C	L-C	44	−6	−21	22	254	0.3	0.1	0.1
		Laboratory	D	L-D	41	−5	−19	19	254	0.7	0.1	0.4
		* Tianya	9#A30	T-9	49	−6	−24	24	256	0.8	0.1	0.7
		* Tianya	11#A30	T-11	39	−3	−24	25	263	0.7	0.1	0.6
		* Tianya	13#A30	T-13	50	−7	−17	18	248	0.2	0.1	0.7
		* Laboratory	A1	L-A1	33	0	−28	28	270	0.9	0.7	0.9
		* Laboratory	A2	L-A2	36	−5	−25	25	259	0.9	0.5	0.8
		* Laboratory	A3	L-A3	49	−8	−23	24	251	0.3	0.1	0.2
		* Laboratory	B1	L-B1	35	2	−22	22	275	0.8	0.4	0.9
		* Laboratory	B2	L-B2	35	−1	−28	28	268	0.6	0.2	0.4
		* Laboratory	B3	L-B3	43	−4	−29	30	262	0.2	0.3	0.5

"*" indicates that the pigment's grades only represent particle sizes, with higher numbers indicating smaller particles.

photographed in plane polarized light and crossed polarized light. The color, size, shape and impurity content of the pigment particles were observed at three different magnifications: 100×, 200× and 500 × .

All pigment powders were used to make microscopic observation samples using the mounting media Meltmount™ 1.662, with a refractive index (nD @ 25°C) of 1.662 and an Abbe V dispersion of 26. The observation equipment was a Nikon LV100ND microscope equipped with polarizing accessories and a DS-Ri2 micro camera. The preparation steps of microscopic sample were as follows:

(a) both sides of a microscope slide were cleaned with acetone using a cotton swab, and then the sample area was marked on the back with an oil-based pen;
(b) a small amount of pigment was placed on the slide and evenly dispersed with a probe;
(c) the slide was heated on a temperature-controlled plate (MG-846 electronic hot plate) and covered with a cover slip;
(d) the mounting media was melted into a viscous liquid at 80°C;
(e) drops of the mounting media were placed on the edge of the cover slip and heated continuously to allow the droplets to slowly penetrate between the cover slip and the slide. After sufficient penetration into the slide-covered area, the slides were removed from the heating plate and allowed to cool and solidify naturally.

The microscopic morphology of natural mineral pigment particles not only reflected the differences in preparation materials and processes but also contributed to the color differences of the samples. Thus, these microscopic features could bridge the preparation materials, processes, and visual properties of the pigments, enabling comprehensive research.

In order to reveal the causes of the unique color properties of natural ultramarine pigments from both material and process perspectives, this study compared the microscopic morphology of particles within the same typical color group based on colorimetric measurements. Additionally, it cross-compared the morphology of pigments made from the same raw rock quality or preparation process.

4. Result and analysis

4.1. Colorimetric value results

The CIE colorimetric values of the 21 color samples are shown in Table 3. Their spectral reflectance curves (SRF%) generally show the highest peak at 460 nm and the lowest peak at 600 nm.

Table 4. Comparison of colorimetry fluctuation ranges and average values in color samples grouped by preparation processes.

	All samples	Purified vs unpurified	Purified samples		Unpurified samples	
			All	Graded	All	Graded
Sample amount	21	3/18	3	2	18	9
ΔE_{00max}	27.8	27.8	8	8	19.2	10.7
ΔL^*_{max}	22	22	5	5	22	12
ΔC^*_{max}	43	43	18	18	43	10
ΔH^*_{max}	42°	42°	10°	10°	42°	17°
L^*_{ave}	42.3	\	33	33.5	43.9	46.8
C^*_{ave}	27.5	\	49.3	52	23.7	22.8
H^*_{ave}	262.3°	\	284°	285.5°	259.6°	257.3°
a^*_{ave}	−1.9	\	12.7	14.5	−4.3	−5
b^*_{ave}	−26.8	\	−47.7	−50	−23.3	−22.2

L^*_{ave}, a^*_{ave}, b^*_{ave}, C^*_{ave} and H^*_{ave} are arithmetic averages. L^*_{ave}, a^*_{ave} and b^*_{ave} were calculated from the L*, a*, b* data of the pigments made by the same process in Table 3, and were then converted to C^*_{ave} and H^*_{ave}.

4.2. Color property analysis based on colorimetric values

4.2.1. Range and fluctuation of colorimetric values

From the measurement data of the color samples (Table 3), it can be seen that natural ultramarine pigments fluctuate widely in terms of lightness (L*), chroma (C*) and hue angle (H*). The fluctuation range of lightness is 31–53, the fluctuation range of chroma is 18–61, and the fluctuation range of hue angle is 248°–290°.

Due to different pigment preparation processes, the color effects of samples vary significantly, which can be reflected in the fluctuation range and average of the colorimetric values (Table 4). The maximum chromatic aberration ($\Delta E_{00\ max}$) for the "*All samples*" group is 27.8, matching that of the "*Purified vs Unpurified Samples*" group. The maximum differences in other colorimetric elements (ΔL^*_{max}, ΔC^*_{max}, and ΔH^*_{max}) are identical for both groups (as shown in red in Table 4). These results confirm the efficacy of the extraction method in enhancing pigment color effects.

4.2.2. Color property shown by color space distribution

Under natural light, most unpurified natural ultramarine samples show a light gray-blue color, while some, like sample T-13, exhibit a blue-green hue. After purification, the pigment turns deep purplish-blue, closely matching the visual effect of both raw lapis lazuli rock and synthetic ultramarine.

Figure 7 illustrates the distribution of the colorimetric coordinates in the CIE-LCH color space for all samples. The three purified samples differ markedly from the 18 unpurified ones, with higher chroma and hue values and lower lightness values. The maximum chromatic aberration ($\Delta E_{00\ max}$ = 27.8) and hue aberration (ΔH^*_{max} = 42°) are both between sample Q-9 and sample Z-1. Samples D-1 and D-2, drawn by two pigments sold in Dominique, show a lightness difference (ΔL^*) of about 21, very close to the maximum aberration (ΔL^*_{max} = 22) between purified and unpurified samples. The chroma aberration (ΔC^*) between these two samples reaches 28, the hue angle aberration (ΔH^*) is 25°, and the chromatic aberration (ΔE_{00}) is as high as 22.2.

In the purified ones, sample Z-1 has the maximum colorimetric coordinates. It has a better visual effect than sample D-1 and the chromatic aberration (ΔE_{00}) between the two is about 6.4. Sample D-1 has similar chroma and hue values to sample Z-2, and their chromatic aberration (ΔE_{00}) is about 3.3.

In the unpurified ones, sample L-B3 has the maximum chroma, while sample L-B2 has the maximum hue, both made from the gem-quality rocks. samples L-A3 and L-B3, using the same particle sizes as samples L-C and L-D, have greater chroma and hue than the latter. Unpurified pigments were divided into two categories based on whether they were graded. The differences in their distribution areas and colorimetric coordinates in color space are shown in Figure 7 and Table 4, the graded samples have a larger color gamut. Therefore, the achievable color gamut and visual effect of natural ultramarine pigments, like other natural mineral pigments, can be improved by upgrading the raw rock quality and finely controlling of particle size, regardless of extraction.

Type A and Type B pigments produced in the laboratory are identical in their propagating processes. As mentioned above, the raw rocks used for Type A pigments have more beautiful color and fewer visible impurities on surface. Thus, the quality of raw rocks for Type A pigments is slightly better. A comparison of these two types of samples reveals two specific details: first, Type A samples are not the unpurified samples with the maximum

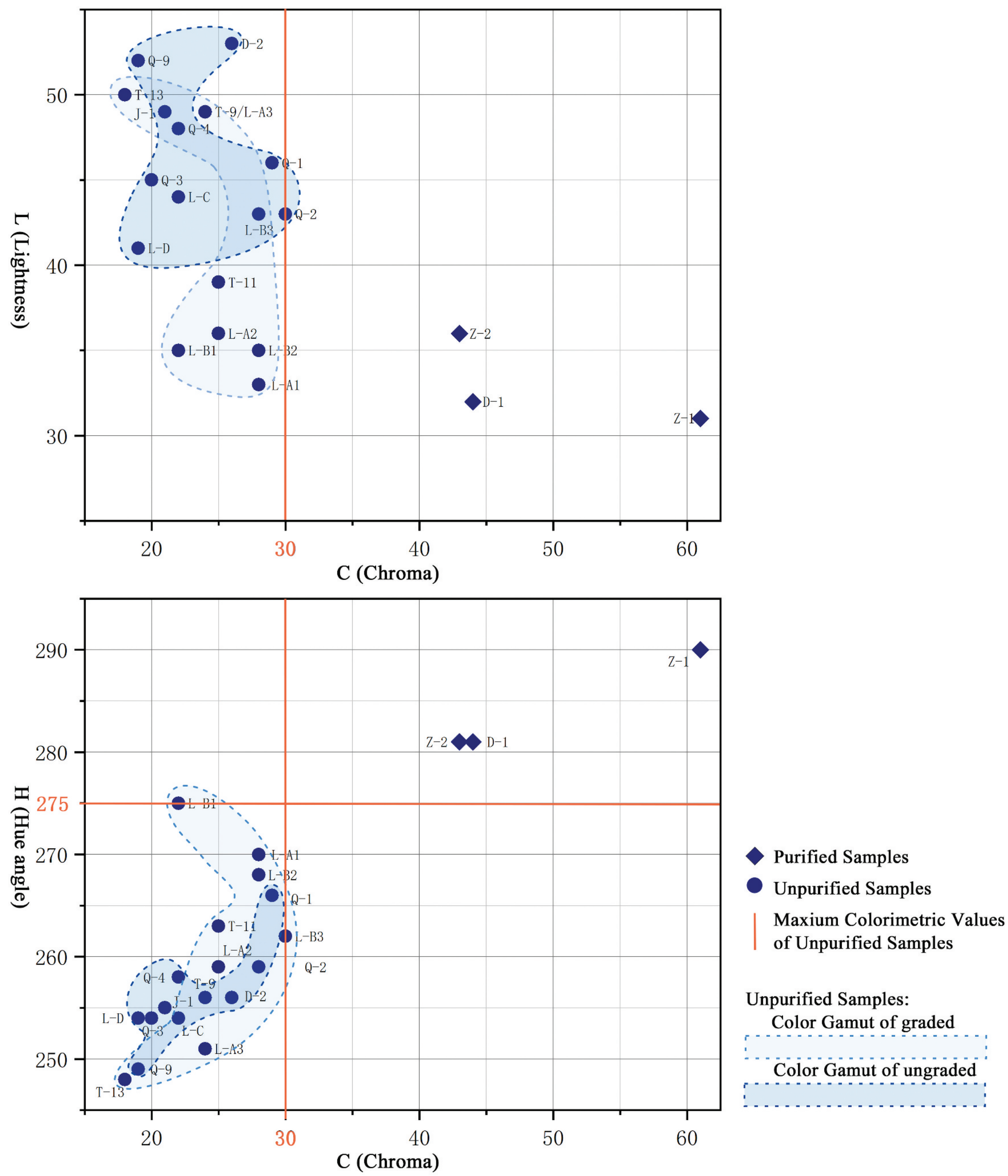

Figure 7. The distribution of the colorimetric coordinates in the CIE-LCH color space for all samples.

chroma and hue in this study; second, there is no consistent correlation between the particle size variation and the colorimetric coordinate changes for these samples.

We will discuss two specific samples, L-A3 and L-B3, and compare them with market-sourced pigments of similar particle sizes, which are made from ordinary-quality rocks. The colorimetric coordinates of sample L-A3 are close to several market-sourced samples, with the smallest chromatic aberration with sample T-9 ($\Delta E_{00} = 1.7$). However, sample L-B3's colorimetric coordinates are similar to those of sample Q-1, resulting in a color difference (ΔE_{00}) of about 3.1. Although sample Q-1 is the most colorful among the market-sourced samples, it does not appear as bright and vivid as sample L-B3. Apparently, in the absence of extraction, merely enhancing the quality of the raw rock has an unstable effect on improving the color performance of this blue pigment.

4.2.3. Relationship between particle size and color change of unpurified pigments

In the unpurified pigments, we have found no consistent correlation between the particle size variations of Type A and B pigments and changes in their color coordinates. Pigments purchased from Tianya will be added to further analyze the relationship between particle size and color changes in these unpurified blue pigments.

Type A and Type B pigments are graded by sample screening, while Tianya pigments are graded by computer-controlled equipment. In all cases, a higher-grade number corresponds to a smaller particle size. Figure 8 shows how the colorimetric values of Type A, Type B, and Tianya pigments vary across different grades.

In terms of lightness, only three Type A pigments display a regular pattern where smaller particles correspond to higher lightness. Although the three Type B pigments generally follow this trend, No. 1 (L-B1) and No. 2 (L-B2) pigments exhibit similar lightness levels with negligible variation due to particle size. In contrast, the three Tianya pigments show no regular pattern: No. 9 (T-9) and No.13 (T-13) have nearly identical lightness ($\Delta L = 1$), while No. 11 (T-11), which is between them, appears the lightest.

In terms of chroma, Type A and Type B pigments show contrasting relationships with particle size: Type A pigments have higher chroma with larger particles, whereas Type B pigments have higher chroma with smaller particles. Tianya pigments also show no regularity, chroma increasing firstly with the grade number, but decreasing eventually. The middle grade (T-11) has the largest chroma.

In terms of hue angle, both Type A and Type B pigments present a regular pattern: smaller particles correspond to smaller hue angles. Conversely, Tianya pigments display irregular changes in hue angle, similar to their chroma behavior.

Among these three groups of unpurified pigments graded by particle size, Type A pigments show the best regular relationship between particle size and color variation, followed by Type B, with Tianya showing the least regular. Overall, it is difficult to stably control the color change of these blue pigments across different grades solely based on particle size without purification.

4.2.4. Spectral reflectance curve analysis of multiple color grades juxtaposed

In the decorative paintings of historical Chinese buildings and murals, various shades of blue were often juxtaposed in a technique known as “*demitin*” or “*Dieyun (叠晕)* “. This technique not only enriched the decorative details but also aimed to create a 3D visual impression. The shades of these color grades can be separated by particle size or by mixing white pigments.

This study combines Type A, Type B, and Tianya pigments, graded by particle size, in forms commonly seen in decorative painting of Chinese building, and compares them with combinations mixed with white pigments. Figure 9 presents the distribution differences in their spectral reflectance curves and also shows the differences in visual effects between these combinations.

The spectral reflectance curve distribution of Type A pigments has two characteristics: firstly, the curves of different shades are independent and spaced apart;

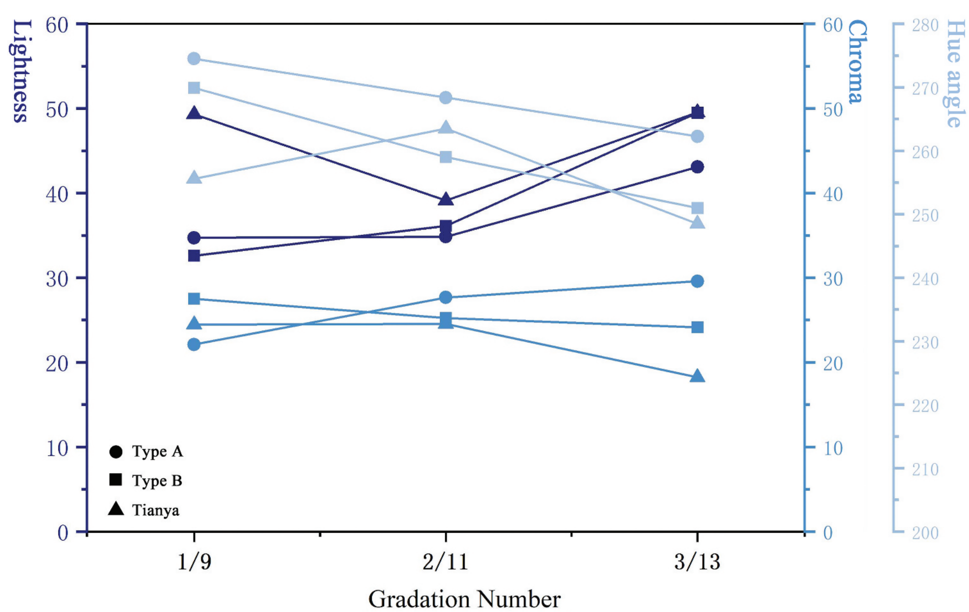

Figure 8. Variation in colorimetric values across different grades of type A, type B, and Tianya pigments: lightness, chroma and hue angle.

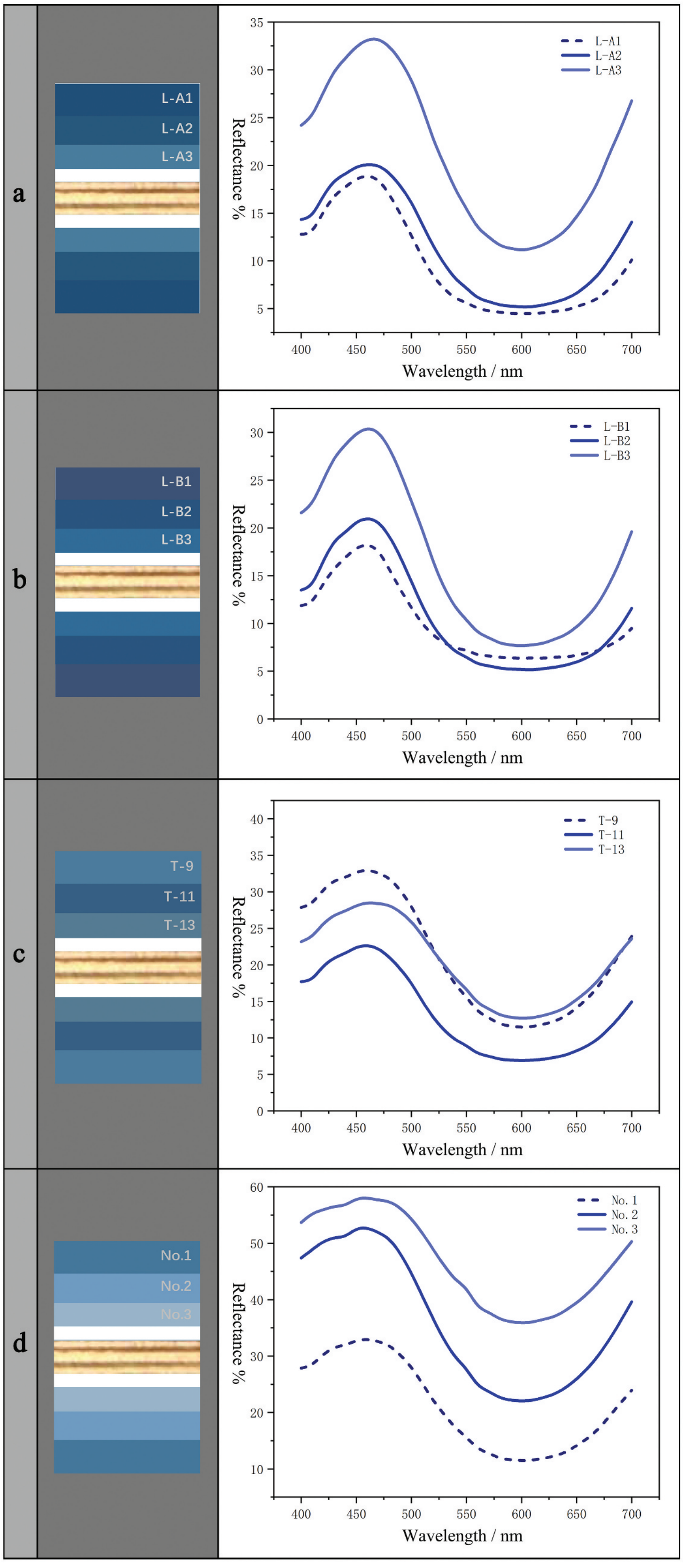

Figure 9. Comparison of 4 color combinations and their spectral reflectance curve distributions ((a) color combination plotted by Type Apigments. (b) color combination plotted by Type Bpigments. (c) color combination plotted by Tianya pigments (d) color combination plotted by T-9 pigment mixed lead white).[9]

secondly, the smaller the pigment particle size, the higher the position of the curve distribution. These features are also present in combinations mixed with white pigment, which exhibit more evenly spaced curves. Conversely, Type B pigments show curve overlaps in specific spectral bands, indicating distinct reflectance levels compared to other bands. Tianya's curves are disorganized with overlaps in shades No. 9 and 13.

The images of these pigment combinations reveal that Tianya pigments do not produce smooth, continuous visual transitions, making it hard to create a concave-convex perception. In contrast, white-mixed combinations exhibit the most uniform visual transitions.

4.2.5. Comparison of the achievable color gamut between natural ultramarine with azurite and synthetic ultramarine

Azurite, natural ultramarine and synthetic ultramarine are blue pigments commonly used in different periods in China. Azurite, which was cheaper than natural ultramarine, has a much longer history of application, particularly in the painted decorations of official buildings. In the Dunhuang Mogao Caves, early murals used primarily imported natural ultramarine. By the Sui and Tang dynasties, due to the excavation of azurite in the Hexi region and the influx of azurite pigment produced in the Central Plains region, the use of natural ultramarine was reduced and gradually replaced by azurite (Li 2005, 41). Synthetic ultramarine, invented in Europe in the early 19th century, was imported to China by the mid-19th century, eventually replacing azurite as the main blue pigment by the late Qing dynasty.

According to current research (Liu, Li, and Yang 2022), the gamut of each blue pigment as shown in Figure 10 highlights the following similarities and differences:

(1) Unlike synthetic ultramarine, natural ultramarine can achieve a wide color gamut from dark to light and from greenish-blue to purplish-blue, covering the gamut of the other two pigments.
(2) High-chroma of natural and synthetic ultramarine are both deep blue, while high-chroma of azurite is a medium-light blue, and the former two can achieve higher chroma than the latter.
(3) The color of purified natural ultramarine can achieve the chroma of synthetic ultramarine.
(4) Unpurified natural ultramarine and azurite differ more distinctly in chroma and hue; the former has a lower chroma and a greenish-blue hue.

4.3. Particle observation results

This study reconfirms that all natural ultramarine pigments, even the extracted ones, contain a variety of accompanying impurities such as tremolite, mica, calcite and other white particles, along with traces of black, yellow, orange-red, reddish-brown, and yellow-green particles. The amount and type of impurities in the purified pigments are obviously reduced.

Furthermore, this study finds that lazurite particles in any pigment are all extinguished in crossed polarized light, but in plane polarized light, there are distinct differences between purified and unpurified pigments in terms of particle size, shape, and uniformity. The shapes of these blue particles have irregular shapes in unpurified pigments, while they feature rounder edges and a more uniform size in the purified ones.

4.4. Color property analysis based on particle microscopy

4.4.1. Grouping of particle micrographs of pigments with similar color

The vertical coordinates represent the lightness and the horizontal coordinates represent the hue angle and chroma, and the hue angles of all the samples can be divided into three main categories: purplish-blue, blue, and greenish-blue. More details of typical color arrangement method can be found in the reference (Liu, Li, and Yang 2022).

Figure 7 shows that the chromatic coordinates of some natural ultramarine samples in this study are very close, and their visual color perceptions are quite similar. So, this study takes the method to identify 10 typical colors representing for all pigments, arranged as shown in Figure 11. Additionally, microscopic photographs of all pigments' particles are grouped and arranged according to these typical colors.

As noted above, there is no consistent correlation between the particle size variations of unrefined pigments and changes in their chromaticity coordinates. For all the natural ultramarine pigments studied in this research, Figure 11 clearly shows that the relationship between their particle size and color is more contradictory, especially in terms of lightness. For instance, samples like D-2, L-A3, and L-B3 have similar brightness levels despite significantly differing particle sizes.

[9]The color samples No. 2 and No. 3 in color combination d were both mixtures of T-9 ultramarine and lead white (purchased from Jiang Si Xu Tang). The ratio of ultramarine to lead white in sample No. 2 was 4:1, while in sample No. 3, it was 11:13. These two samples are cited in the reference (Liu, Li and Yang 2022).

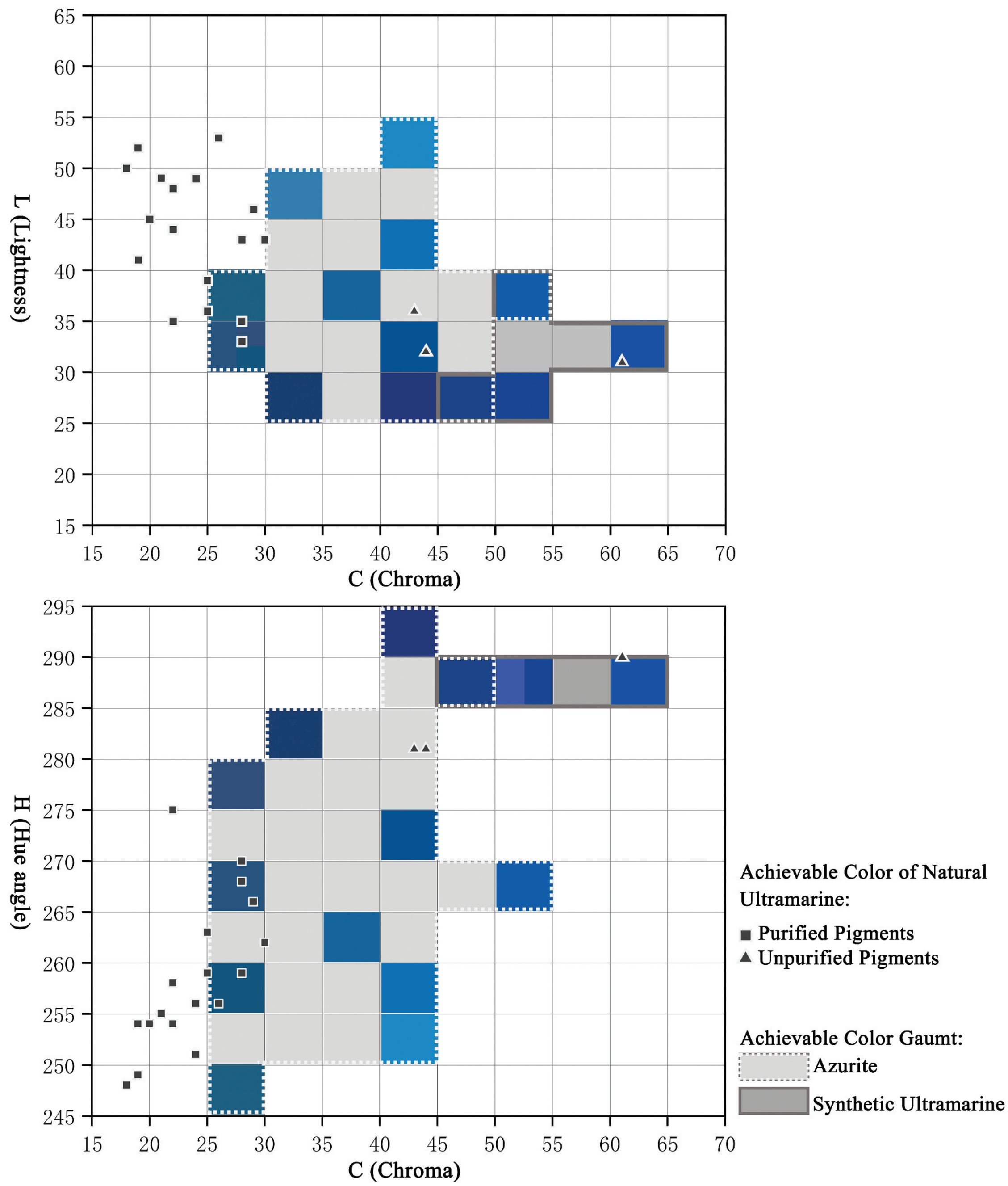

Figure 10. Comparison of achievable color gamuts for three blue pigments: natural ultramarine, azurite and synthetic ultramarine.

The special color effects of natural ultramarine pigments, produced from various raw rock qualities and preparing processes, will be meticulously analyzed in the next section, incorporating microscopic observations of some pigment particles.

4.4.2. Interpretation of special phenomena by microscopic observation of particles

Based on the grouping in Figure 11, this study conducts microscopic comparisons between purified and unpurified pigments with similar colors (Figures 12 and 13), reaffirming that the purity is the most important factor influencing the visual effects of this blue pigment. Further analysis with microscopic comparisons of different grades of unpurified pigment particles (Figure 14) shows that visual effects of these blue pigments are influenced not only by particle size but also by uniformity and color of the particles, leading to no consistent relationship between particle size and color. Moreover, the complexity of the impurities further contributes to this irregularity.

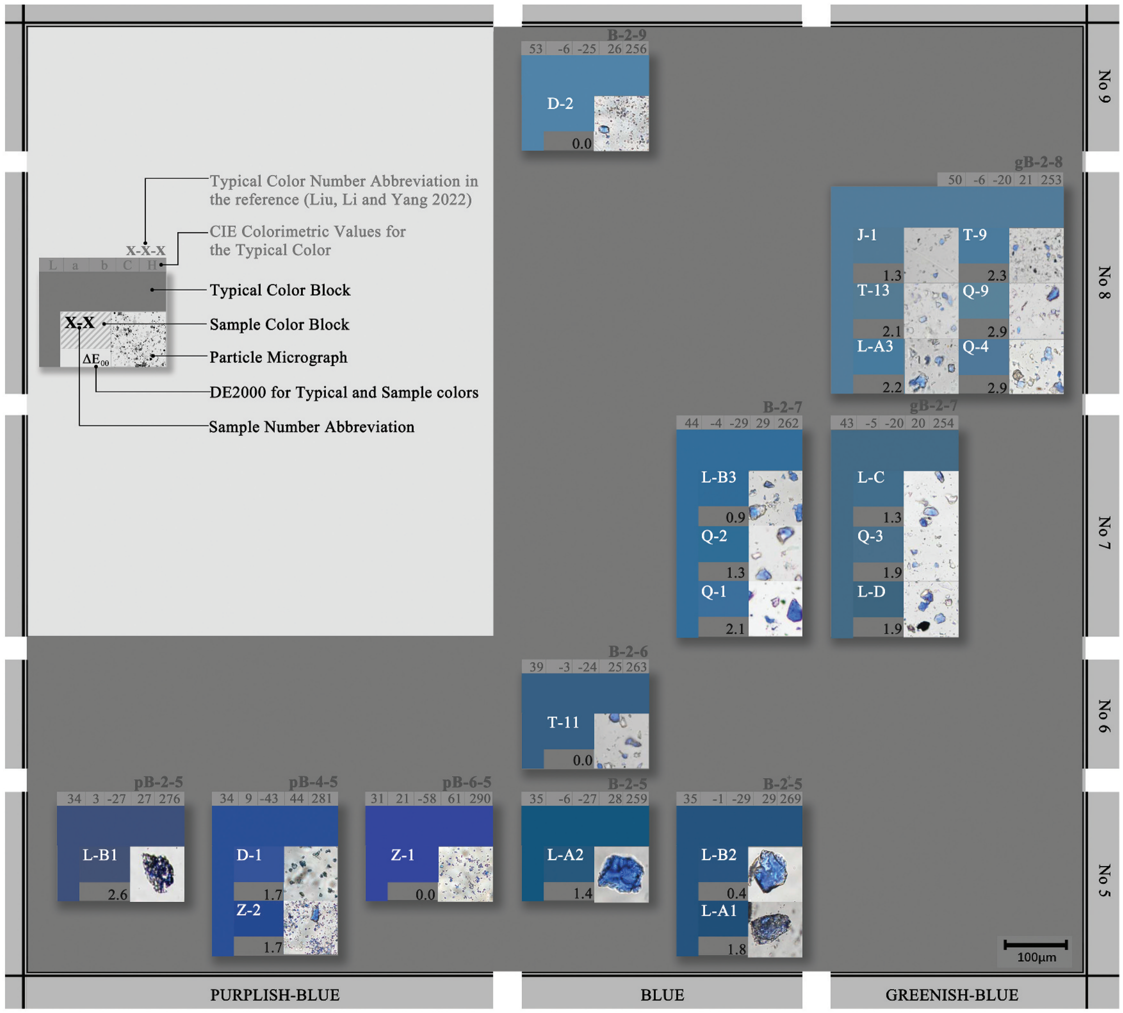

Figure 11. Micrographs of particles arranged in the typical colors order of pigments.

The microscopic observations of particles from samples Z-1, Z-2 and D-1 in Figure 12 show that the particle colors of Zecchi's pigments are vivid-blue, while that of Dominique's pigment is greenish-blue. Despite similar particle sizes in samples Z-1 and D-1, differences in lazurite particle color affect their chroma and hue in a way. Furthermore, sample Z-2 shows less particle uniformity and higher impurity levels compared to Z-1, both of which contributed to their differences in visual color.

In Figure 13, the microscopic characteristics of samples D-1 and D-2 illustrate the differences between purified and unpurified pigments. Sample D-1, representing the purified pigment, has better visual effects in lightness, chroma, and hue. This improvement is likely due to its smaller particle size, better uniformity, more rounded edges, and fewer impurities, especially white transparent ones. Despite this, the lightness of D-1 is similar to that of samples L-A2 and L-B2, which are unpurified, yet have significantly larger particles. However, the lightness of sample D-1 is very close to that of samples L-A2 and L-B2, both of which represent for the unpurified pigments, while their particle sizes are significant different from that of D-1. This similarity is probably due to the process of removing the large amount of white transparent impurities by the paste, allowing pigments with smaller particles to achieve a deeper color.

Figure 14 presents microscopic photos of Type A, B, and Tianya pigments, each magnified 500 times. Each type of pigments is divided into three grades, with their color characteristics previously discussed. This section further analyzes the causes behind their color features, incorporating factors such as particle size uniformity and impurity content based on microscopic observations.

Overall, Type A and B pigments, crafted from gem-grade rocks, have slightly higher purity and deeper, bluer particle colors. These advantages visually enhance their chroma and hue, making them superior to Tianya pigments.

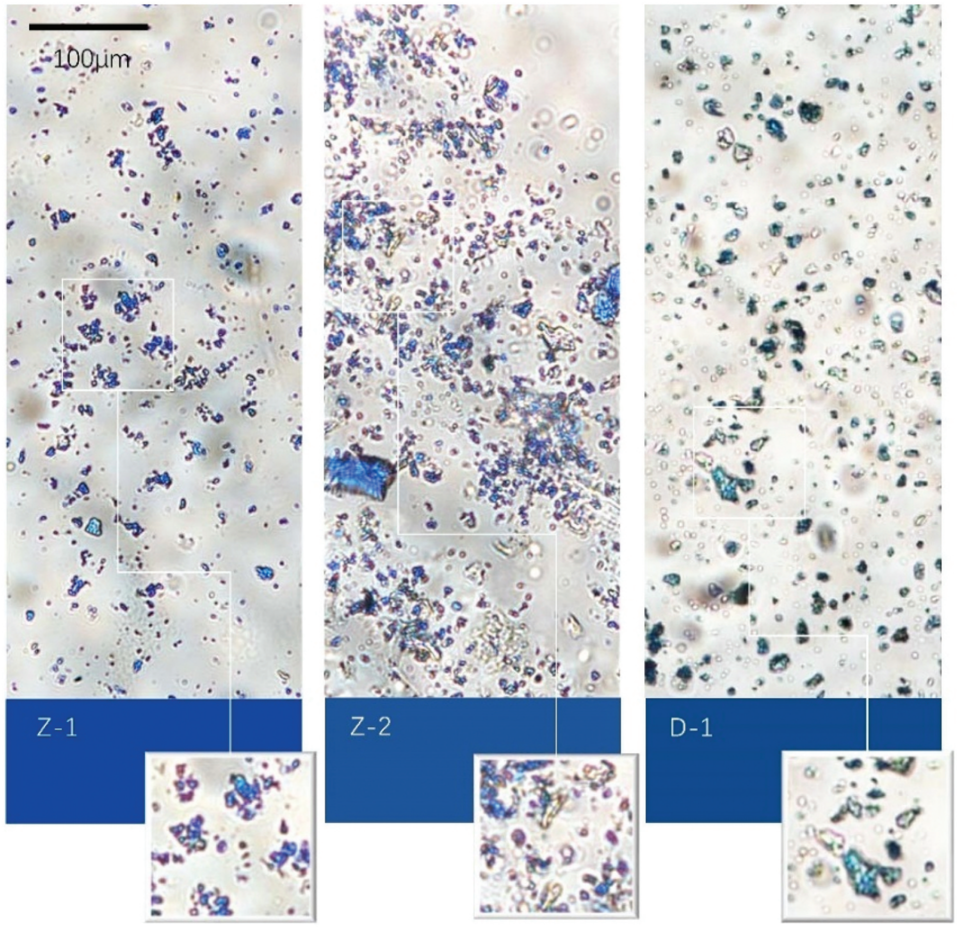

Figure 12. Particle micrographs of three purified pigments (PPL 500×).

In three Tianya pigments, sample T-11 has the darkest and largest particles (about 15–20 μm) with the fewest impurities. Samples T-9 and *T*-13 have similar sizes (about 10–15 μm) but contain a lot of black and white impurities. The particle color of T-9 is darker and bluer than T-13. Clearly, contrary to the typical trend where a higher pigment number indicates smaller particles, these three samples do not follow this rule. Other micro-variations like particle color and impurity type may result from batch-to-batch differences in rock quality. Present study on azurite has found that even the pigments from the same band with the same grade number and production process can vary in color between batches. Their color difference (ΔE^*_{ab}) can reach up to 18.6 (Li, Shi, and Song 2021). The research on lapis lazuli has found that the quality of this rock is influenced by several factors, including the location of the rock layer and the content and distribution sequence of its core chemical structure (S_3^-) (Gobeltz et al. 1998, 2002; Peng et al. 1983).

As described, the raw rocks used for Type A and Type B pigments have different visual colors in natural light. However, under various magnifications, the color, morphology and size of these pigment particles show no notable differences within the same numbering. Very coarse particles are formed by the translucent blue and transparent white crystals attached to each other with a fibrous surface. Coarse particles are mostly composed of separated blue crystals, with the geometric shape clearly broken. Combined with the microscopic observations of these pigments, the following two reasons could explain the variability and irregularity in their colors. First, these pigments have poor uniformity in particle size, especially the pigments numbered 1 (L-A1 and L-B1). Second, unpurified pigments always contain a variety of impurities. Their crystalline states of them change complexly with deeper grinding, which to some extent exacerbates the disorder in the color grade variations. It has been found that there is a tendency of all particles to convert from crystalline to amorphous, and the crystallinity of the lapis lazuli decreases with increasing grinding time, while the structure of other fragile crystals is similarly destroyed and altered (Liu et al. 2022).

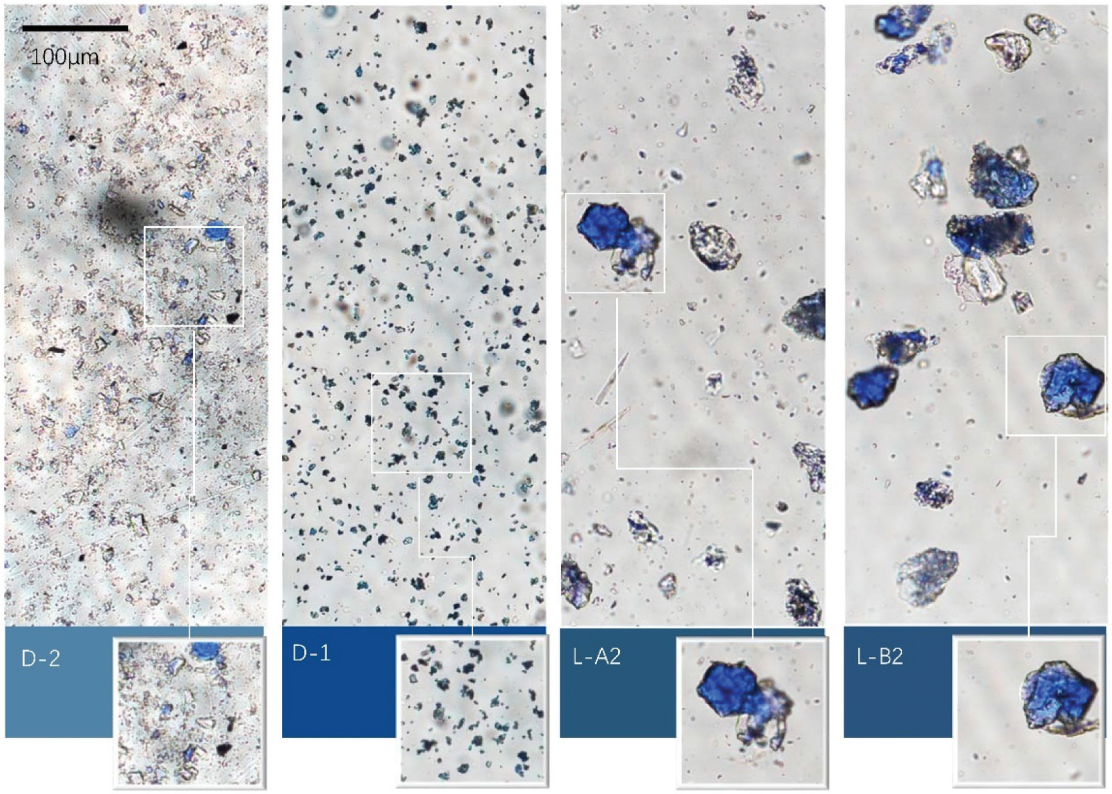

Figure 13. Particle micrographs of sample D-1 and three unpurified pigments (PPL 500×).

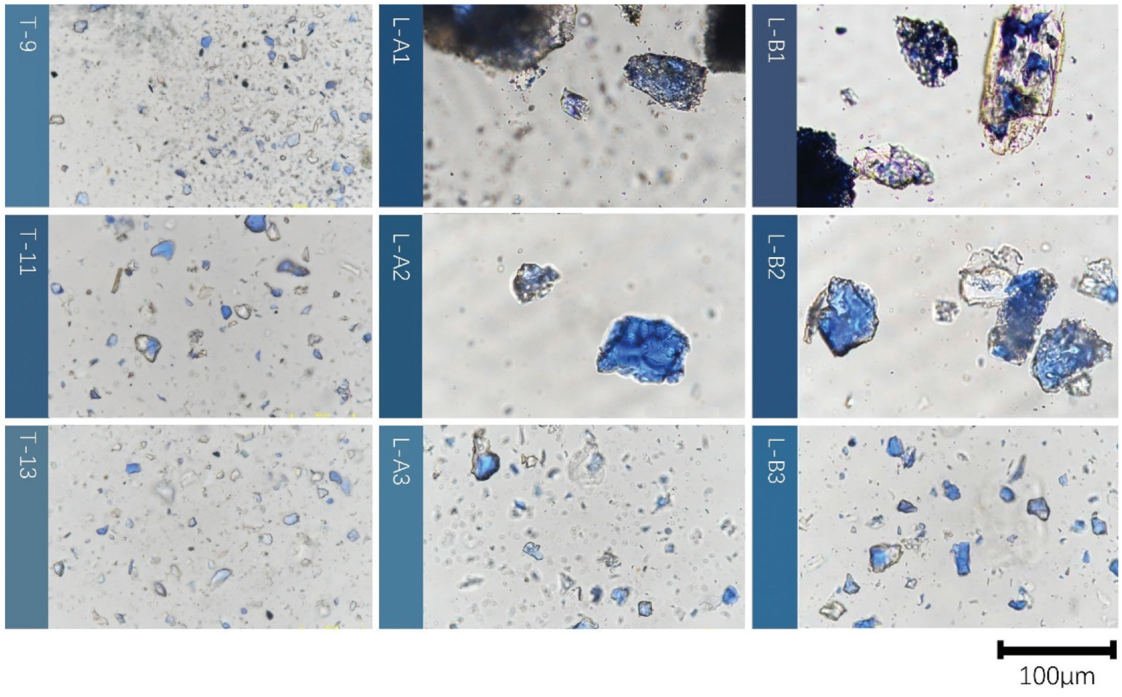

Figure 14. Micrographs of graded pigments with different particle sizes (PPL 5000×)

5. Conclusion

5.1. Color data of 21 natural ultramarine pigments and their application value

This study examined 21 natural ultramarine pigments prepared by two different methods: the classical extraction method described by Cennino Cennini and the traditional sedimentation method inherited from Chinese historical handbooks. All pigment samples were measured for CIE colorimetric values by a spectrophotometer. From their color data, we found the achievable gamut of natural ultramarine pigments modulated with glue in traditional decorative paintings, with a lightness fluctuation of 31 to 53, a chroma fluctuation of 18 to 61, and a hue angle fluctuation of 248° to 290°.

The colorimetric values and information for these 21 pigments will provide valuable physical and visual references for the conservation and restoration of heritages, and the application design of traditional colors.

5.2. Color properties

By comparing their colorimetric values and analyzing their distributions in the CIE-LCH color space, we found that the color change of the pigment extracted using the Cennini's recipe could reach 22.2 (DE2000). We also found that the chroma and hue angle of the purified pigment sample increased very significantly, and its color would visually shift from light greyish-blue to dark purplish-blue.

Furthermore, we could see that the achievable lightness and hue angle ranges of natural ultramarine roughly overlapped those of the known azurite and synthetic ultramarine. Purified natural ultramarines could exhibit colors similar to synthetic ultramarines, while unpurified natural ultramarines tended more towards greenish-blue than azurite.

5.3. Factors affecting color property

Microscopic analysis of pigment particles at different magnifications reaffirmed that the purity of the blue particles was crucial for the visual effect of natural ultramarine pigment. For low-purity pigments, especially unpurified ones, improving raw rock quality and refining particle size grading could expand the color gamut to some extent. However, factors such as particle size uniformity, particle color, and crystal crystallinity created an unstable relationship between color change and particle size. The irregularity relationship could be further aggravated by the complexity of the impurities contained.

This study reaffirmed that this natural blue pigment could not be made absolutely pure, regardless of the process used. When unpurified pigments, graded by particle size, were used for color combinations, their spectral reflectance curves became disordered and overlapped in the local wavelength band, making it difficult to form a smooth and continuous visual variation.

The discovery of the color properties of natural ultramarine pigments in this study may explain the historical application of decorative paintings in traditional Chinese architecture as follows. To achieve a more saturated visual effect or control costs, other blue mineral pigments were mixed with natural ultramarine and gradually replaced it. For a more systematic variation in color combinations, creating effects with multiple shades juxtaposed, it was preferable to use pigments mixed with white rather than those graded by particle size.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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