Abstract: The Afrasiab murals discovered in the northeast of Samarkand, Uzbekistan—the center of the ancient Silk Road—are presumed to date to the mid-seventh century during the Sogdian era. Although previous studies have examined the primary materials of the pigments used in these murals using chemical and microscopic analyses, in-depth investigations of the pigment raw material composition have not been conducted to verify the results of these studies. We applied X-ray diffractometry, Raman spectroscopy, and scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy for the first time to identify the raw materials of ancient pigments in fragments obtained from the Afrasiab murals. The results show that lazurite, cinnabar, and amorphous carbon were used as blue, red, and black pigments, respectively. Moreover, we identified that pigments were not directly painted on the wall surface; instead, they were painted on a white undercoat of gypsum plaster, similar to other ancient Silk Road wall paintings. The results of this study can benefit the provision of more accurate information with regard to the composition of raw materials and further support the selection of appropriate substances for the purposes of conservation and restoration of Afrasiab murals.

Keywords: Afrasiab murals; silk road; UNESCO world heritage; ancient pigment; raw materials; mineral composition; specimen analysis; XRD; Raman spectroscopy; SEM-EDS

1. Introduction

The Afrasiab murals [1] were discovered in 1965 in the vast palace site northeast of Samarkand, Uzbekistan, and they are currently curated and preserved in the Afrasiab Museum of Samarkand (Figure 1). The murals were located on the west, south, north, and east walls of the house and depict a wide range of content [2–8]. The southern wall mural is filled with a theme of the ancient Iranian world, Samarkand—a religious funerary procession in honor of the ancestors during the Nowruz festival. In addition, the northern wall mural represents ancient China—a Chinese festival, the Empress on a boat, and the Emperor hunting. Moreover, the much-destroyed eastern wall mural is interpreted as a depiction of ancient India—as the land of the astrologers and of the pygmies.

The topic on the main wall—the western wall facing the entrance—is debated among experts [2–10]. Köktürk soldiers are escorting ambassadors coming from various countries of the world—assumed to be ancient Korea, China, Iran, etc. According to the inscriptions on the west wall paintings—on which ambassadors from several countries appear—Afrasiab murals are assumed to date back to the mid-seventh century during the Sogdian era, showing that Samarkand was the thriving commercial center in the middle of the Silk Road [9,10].
restoration project—a collaborative effort between the Northeast Asian History Foundation of Korea and the Afrasiab Museum of Samarkand [13]. In addition, previous studies examined the primary materials of the pigments used in these murals through chemical and microscopic analyses [11,13]. However, a thorough investigation of the raw material composition of the pigments, complementing the results of existing studies, has not yet been conducted.

In general, studies that investigate the types of materials and technology used in creating the ancient murals employ techniques such as Raman spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy plus energy-dispersive X-ray spectroscopy (SEM-EDS), and X-ray diffractometry (XRD) to identify pigments and organic materials used in conservation treatments [14–19]. In particular, in recent years, nondestructive analytical methods based on portable X-ray fluorescence (P-XRF) spectrometry, particle-induced X-ray emission (PIXE), and false-color infrared imaging (FCIR), combining spectrophotometric colorimetry and spectral analysis, have been improved and applied to research on murals [13,20–30]. These techniques are noninvasive and, therefore, allow us to obtain the composition of the main elements on the sample surfaces at several points, as well as create maps. However, analyses using these types of nondestructive methods can sometimes be prone to errors due to the conservation of the painting, the presence of impurities, and incorrect identification of the mineral (in particular, polymorphs); therefore, careful interpretation of the results is required [13,31].
This study was aimed at accurately identifying the raw materials of each color pigment used in Afrasiab murals by applying XRD, Raman spectroscopy, and SEM-EDS; these techniques were applied in the investigations of this archaeological site for the first time. Furthermore, the results of this study can be used not only to provide accurate information on the mineral composition of raw materials but also for the selection of substances suitable for conservation treatments and restoration of Afrasiab murals; this will potentially facilitate a scholastic exchange between relevant fields.

2. Materials and Methods

2.1. Materials

As shown in Figure 2a, three fragments provided by the Ministry of Culture of Uzbekistan were used for the investigation; two were painted blue and red, whereas one had a black line. As can be observed from Figure 1, the blue specimen was presumably a fragment from a blue background. In contrast, the red specimen was potentially a fragment from a red area in any of the Afrasiab murals (such as the garment of a character in Figure 1, silk offered to the king, or the boat of a Chinese ambassador depicted on the north wall). The black line was painted thinly against a yellow background and was presumed to be part of the outline of a character or an object.

![Image](a) Sample fragments for blue, red, and black pigments; (b) residual soil under the red sample.

After surface inspection, a small amount of powder was collected from each specimen. Polished specimens were subsequently prepared for cross-section analysis. In addition, residual soil was observed underneath the red specimen, which presumably flaked off from a wall (Figure 2b); its powder was also collected for analysis.

2.2. Methods

The distribution pattern of the pigment particles on the surfaces of the fragments was observed using an optical microscope (AXIO Imager A2m, Zeiss, Oberkochen, Germany). XRD patterns were recorded using powdered samples, with a Cu-Kα diffractometer (Empyrean, Malvern Panalytical, Malvern, UK), which scanned in the 2θ range 5–60° at 45 kV/40 mA, with a scanning interval of 0.02° (2θ).

Raman spectroscopy was performed using a multifunctional Raman spectroscopy system (XperRam F2.8, NanoBase, Seoul, Korea) to examine the spectral properties of the pigment particles on the bulk fragments. For the analysis conditions, a 473 nm laser and a 633 nm laser were used in conjunction with a 40 × lens (OLYMPUS, Tokyo, Japan), and the measurement range was set to 100–2400 cm⁻¹. To prevent damage, laser wavelength, luminous intensity, and exposure time were adjusted for measurements according to the
type and condition of the samples. The measured Raman spectra were then compared to Raman data from the RRUFF project [32].

SEM-EDS was conducted on cross-section samples using a JSM-IT300 (JEOL, Tokyo, Japan). The SEM-EDS analysis of particulate distribution was completed after platinum-coating the samples, to identify the chemical composition.

3. Results and Discussion

3.1. Microscopic Observation

The distribution patterns of the pigment layers were examined microscopically. For the blue and red pigment layers, we observed that the pigments were painted on top of a white ground layer (Figure 3a,b). For the black pigment layer, the pigment was painted on yellow (yellow brown) particles distributed on a white primer (Figure 3c). In addition, the thickness of the colored layer observed in the cross-section was about 20 µm and 10 µm for the blue and red pigment layers, respectively. In the case of the black pigment, a very thin layer was observed on top of the yellow-brownish layer with a thickness of about 10 µm.

![Figure 3. Surface and cross-sectional optical micrographs of (a) blue, (b) red, and (c) black pigment layers.](image-url)
3.2. X-ray Diffractometry

The results of XRD for each specimen are illustrated in Figure 4. In all colored specimens, gypsum, which was considered to be a component of the white ground layer, was identified. In addition, lazurite and cinnabar peaks were observed in the blue and red specimens, respectively. Moreover, the blue-colored layer was confirmed as containing small amounts of quartz and mica as impurities in the lazurite ore. These results are consistent with those of previous studies that identified minerals by analyzing the chemical composition of pigments [11,13]. Gypsum, lazurite, and cinnabar, which were identified as base minerals for the white, blue, and red pigments, respectively, have been used as raw materials for pigments in various cultures and regions along the Silk Road [16,33–37].

Figure 4. X-ray diffraction patterns of (a) blue pigment, (b) red pigment, and (c) black pigment.

In the case of the black specimen, the diffraction pattern of mimetite, a mineral containing lead, was recorded, as shown in Figure 4c. This mineral has reportedly been used as a yellow and yellow-brown pigment in Central Asian and Egyptian cultures [38–40].
However, mimetite has not been previously reported in Afrasiab murals and was, therefore, analyzed for the first time in this study. The mimetite reported in present study is thought to be the mineral composition of the yellow or yellow-brown particles under the black painted layer observed in Figure 3c. In addition, previous studies on Afrasiab murals estimated that charcoal-based amorphous carbon was used as a raw material for black pigments [12,13]. However, since amorphous carbon is non-crystalline and, as such, cannot be identified by XRD analysis, an alternative approach is required for its investigation, such as Raman spectroscopic analysis.

In addition, minerals such as quartz, plagioclase, alkali feldspar, mica, and chlorite, as well as constituents of limestone, such as calcite and dolomite, were detected in the residue collected underneath the red specimen (Figure 5). On the basis of these findings, it can be confirmed that the Afrasiab mural was painted on top of a lime-plastered wall made of a mixture of soil and limestone. This lime-plastered wall was estimated to contain a higher proportion of soil than limestone, according to the relative area of the X-ray diffraction pattern. Furthermore, quartz was identified as the most abundant mineral in the soil, and the limestone was considered to be a calcite-rich type with a higher amount of calcite than dolomite.

![X-ray diffraction patterns of residual soil.](image)

**Figure 5.** X-ray diffraction patterns of residual soil.

### 3.3. Raman Spectroscopy

As shown in Figure 6a, the Raman spectra of the white specimen of the ground layer presented a strong peak at 1008 cm\(^{-1}\). This peak was almost identical to the symmetric stretching of SO\(_4\) tetrahedra, the strongest Raman spectral peak of gypsum; as such, the white ground layer was confirmed as gypsum. For the blue pigment particles, characteristic peaks were observed at 545, 586, and 1088 cm\(^{-1}\); these were almost identical to the Raman shifts of lazurite (Figure 6b). As for the red pigment particles, characteristic Raman peaks were identified at 253 and 344 cm\(^{-1}\), confirming that the red pigment was cinnabar (Figure 6c). As such, the results of Raman spectroscopy on the white, blue, and red pigments were consistent with the XRD results.
Figure 6. Raman spectra and target particles of (a) white background, (b) blue pigment, (c) red pigment, and (d) black pigment.

For the black particles, from the observation of a broad band comprising two peaks at 1320–1360 and 1500–1600 cm$^{-1}$ (Figure 6d), the particles were identified as carbon black—which was not detected via XRD [41–43]. This result confirms that charcoal-based amorphous carbon was used in the black pigment, consistent with the assumptions of previous studies [12,13].

3.4. SEM-EDS Mapping

The analysis of the elemental distribution through SEM-EDS mapping showed that the pigment layers were all painted on a gypsum (CaSO$_4$·2H$_2$O) surface. The mapping clearly revealed the distribution of calcium and sulfur on the gypsum surface (Figure 7).
Table 1. Results from SEM-EDS point analysis of the colored surface layer.

| Analyzing Point                  | EDS Spectrum | Elemental Composition (wt.%) ¹ |
|----------------------------------|--------------|-------------------------------|
| Blue layer                       |              | Na (25.25)                     |
|                                  |              | Al (24.37)                     |
|                                  |              | Si (27.67)                     |
|                                  |              | S (14.81)                      |
|                                  |              | Cl (0.63)                      |
|                                  |              | K (3.19)                       |
|                                  |              | Ca (4.08)                      |
| Red layer                        |              | Si (4.07)                      |
|                                  |              | S (15.81)                      |
|                                  |              | Hg (79.76)                     |
| Black-yellow-brown crossed layer |              | P (4.18)                       |
|                                  |              | Cl (3.32)                      |
|                                  |              | Ca (9.40)                      |
|                                  |              | As (11.22)                     |
|                                  |              | Pb (71.87)                     |

¹ Normalized data excluding oxygen content.
In the blue specimen, the lazurite \((\text{Na,Ca})_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{S,Cl,SO}_4,\text{OH}_2))\) layer was identified through the observed distribution of silicon, aluminum, and sodium (Figure 7 and Table 1). Likewise, in the red specimen, the cinnabar (\(\text{HgS}\)) layer was distinguished through the mapped distribution of mercury (Figure 7 and Table 1). Furthermore, for the surface carbon-painted layer in the black specimen, the raw material that was identified as amorphous carbon through Raman spectroscopy (Figure 6d) could not be distinguished through SEM-EDS owing to the penetration of the epoxy resin used in fabricating the cross-sectional specimen (Figure 7). However, the identification of the mimetite \((\text{Pb}_5(\text{AsO}_4)_3\text{Cl})\) layer was possible by analyzing the distribution of lead, arsenic, and chlorine (Figure 7 and Table 1).

From the above results, it can be concluded that lazurite, cinnabar, and amorphous carbon, which were raw materials for blue, red, and black pigments, respectively, were painted on top of the white ground layer plastered using gypsum. This painting technique has been commonly reported in murals in caves and buildings distributed across the regions crisscrossed by the ancient Silk Road [16,19,33–36], and the results of this study confirm that the same techniques were applied to the Afrasiab mural.

4. Conclusions

In this study, XRD, Raman spectroscopy, and SEM-EDS were applied for the first time on specimens—painted with blue, red, and black pigments—collected from an Afrasiab mural from Samarkand, the melting pot of world cultures on the ancient Silk Road. Consequently, we successfully identified the raw materials of each pigment. Previously, the characteristics of these raw materials were only hypothesized on the basis of analyses of the chemical composition and the observations of the particles. Additionally, the coloring techniques of the mural were examined using the results obtained.

We confirmed that, on Afrasiab murals, gypsum was used as a priming coat on lime-plastered wall; each pigment was then painted on top of the gypsum ground layer. For the blue and red specimens, the analysis results confirmed that the surfaces were colored using lazurite and cinnabar, respectively. For the black specimen, the black line was colored on top of a pale yellow (mimetite) surface using a black substance composed of amorphous carbon.

The raw materials of each pigment and the technique of painting on top of the white gypsum ground layer, which were identified in this study, indicate that the characteristics of murals distributed along the ancient Silk Road were also present on the Afrasiab murals. In the future, more precise analysis and interpretation will be possible if further research is performed on specimens with a greater variety of colors and on a larger scale.

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