Chapter 13
The Wall Painting Techniques and Materials of Kizil Grottoes

Zhibo Zhou, Ling Shen, and Hui Zhang

Abstract Ancient Kucha (Kuqa, Qiuci), situated at a midpoint on the Silk Road that traverses the Eurasian Continent, was one of the most important centers of trade and Buddhist culture in Central Asia. Kucha played a crucial role in the spread of Buddhism along the Silk Road. A large number of grottoes decorated with wall paintings remain in Kucha, showing us the prevalence of Buddhism in this area. The Kizil grotto site is the largest and most influential of the Kucha grottoes group. The paintings preserved here display an astonishing range of styles and techniques, testifying to the cultural and commercial importance of the site and its vital role in the dissemination of Buddhism along the Silk Road in ancient times. A number of previous studies have been undertaken into the materials and techniques of the Kizil wall paintings. On the basis of these, the authors have conducted further investigations, in the course of which some new discoveries were made. Both the inorganic and organic substances in fragment samples collected from several caves dating from the fifth to the seventh century were analyzed. Morphological studies were performed by optical microscope (OM), cross-section microscope and scanning electron microscope (SEM). Inorganic materials were analyzed by X-ray diffraction (XRD), Raman spectrometry, and elemental maps obtained by SEM with energy dispersive X-ray analyzer (EDX). Organic materials were studied by Fourier transform infrared spectroscopy (FTIR), liquid chromatography coupled to electrospray ionization quadrupole-time-of-flight mass spectrometry (LC–ESI-Q-TOF-MS) and by enzyme-linked immunosorbent assay (ELISA). We identified the white pigment as pyromorphite-mimetite ($Pb_5Cl[(P,As)O_4]_3$), and the yellow colorant as gamboge, which is applied over atacamite, turning it to a delicate shade of green. Stick lac was

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used in both the resinous mordant for gilding and for the red colorant in the wall paintings; and the resinous component (shellac) was also probably applied over tin foil to imitate gold. Plant gum was found to be the binder for a lump of blue pigment discovered in front of Cave 189. These studies throw light upon technical advances, trade intercourse and cultural exchanges along the ancient Silk Road.

Keywords Kizil grottoes · Wall painting · Analysis · Pigment · Binding medium

13.1 The Kucha Grottoes Group

The ancient settlement of Kucha (Kuqa, Qiuci) was located at the northern margins of the Taklamakan Desert, in the southern foothills of the Tianshan Mountains. Kucha was centered on the Kuqa oasis, which during its greatest period of prosperity encompassed the area occupied by the modern-day counties of Luntai, Kuqa, Shayar (Xayar), Baicheng (Bay), Aksu and Xinhe (Toksu) in the Xinjiang Uyghur Autonomous Region of China [1].

Since Zhang Qian's opening of the Silk Road (140 B.C.), Kucha has played a crucial role in the long-term cultural exchange and interaction between Eurasian civilizations. Kucha also played a significant role in the transmission of Buddhism along the Silk Road to China, the Korean Peninsula and Japan.

From the third to the eleventh centuries, officials, monks, and artists taking advantage of the unique natural and cultural environment of the Kucha area, constructed the grottoes of Kizil, Kumtura, Kizilkargha, Simsim, Mazarbaha, Wenbhash, Taitai'er, Tograk-eken and A'ai, which are collectively referred to as the Kucha Grottoes Group [2–6]. The art of the Kucha Buddhist grottoes, produced over a period of more than 800 years, is technically and iconographically rich, and the sheer quantity of surviving painting is staggering.

13.2 The Kizil Grottoes

The Kizil grottoes, the largest and most influential of the Kucha grottoes group, is situated in Kizil Town, Baicheng County, Xinjiang, China. The caves are excavated into the cliff face of Mingwutage Mountain in Weigan Valley (named the Muzart River Valley near the caves), and extend from east to west for 1.7 km, scattered on various levels of the cliff (Fig. 13.1). There exist 349 caves dating from the third century to the ninth century containing 5000 square meters of wall paintings, a small number of sculptures, and a number of architectural remains in front of the caves [7, 8].

There are a great many different types of cave at Kizil, including central pillar caves, Great Buddha caves, square caves, monks' quarter caves, niche caves, special-shaped caves, and combinations of these. The caves dating from the third to the fifth

Fig. 13.1 Aerial image of the Kizil grotto site and details of the wall paintings. (a) aerial image of the Kizil grottoes: the Sugete Valley divides the caves into four natural groups: the western ravine (marked with blue), the inner ravine (marked with yellow), the eastern ravine (marked with green), and the rear hill (marked with red); (b) Flying Apsaras from newly-found Cave 1; (c) Musical Apsaras from Cave 38; (d) Śākyamuni story paintings from Cave 114; (e) Śākyamuni story paintings from Cave 171; and (f) painting from Kizil detached by German exploration team

century are predominantly central pillar caves (Kucha style caves) and Great Buddha caves, and are decorated with wall paintings illustrating themes from traditional (*Hinayana*) Buddhism. These cave types originated at Kizil, and their distinctive western features testify to a fusion of the Indian cave style with Chinese traditions to form a unique Kucha style. These developments at Kizil exerted considerable influence on Buddhist cave art in the Hexi region (Dunhuang Mogao Grottoes), Longyou region, Central China (Longmen Grottoes and early Yungang caves), as well as Central Asia [9].

Abundant Buddhist narrative wall paintings are preserved in the Kizil caves, mainly illustrating Śākyamuni stories, including *Jataka* stories, *Karma* tales and Buddha's life stories. There are more than 100 *Jataka* stories and *Karma* tales, and over 60 Buddha's life stories, reflecting Buddhist worship in the Sarvastivadin school (说一切有部), a branch of Hinayana Buddhism, prevalent in Kucha region (Xuanzang 646). In addition to the religious content of the paintings, which was instrumental in disseminating and publicizing the Buddhist doctrine, the paintings of Kizil are a unique repository of illustrations of the different races living or trading in Kizil, the clothing people wore, the musical instruments played, as well as scenes of work, dancing and other aspects of daily life, providing a precious and vivid insight into otherwise lost aspects of Kucha civilization ([1], Xuanzang 646).

Kizil's claim to be one of the most important cultural sites along the Silk Road is demonstrated by the many artistic styles and painting techniques present in the grotto paintings. The Kucha style incorporated Greek influences via Gandhara in the earlier period, and also absorbed influences from Indian, Persia and the Central Plain [10]. Strong regional characteristics of the style include rhombic-shaped compositions (a significant feature of Kizil paintings), *Qutiepansi'* (a style endemic to the western regions, consisting of powerful outlines full of vitality, and unconstrainted and free script), composite line and halation methods (to enliven and invigorate painting, and to create plump, full images).

13.3 The Painting Techniques and Materials of Kizil

13.3.1 Previous Studies of Kizil Painting Techniques and Materials

The wall painting technology of Kizil is similar to that at other grottoes along the Silk Road, such as Bamiyan, Mogao, and Maijishan. The caves were excavated into a cliff face composed of conglomerate rock, and the walls were then plastered and smoothed over with layers of earthen plaster composed of earth, sand and natural plant fibers (wheat straw). In preparation for the paintings, a ground-layer (gypsum) was applied over the plaster. The plaster of Kizil is different from Mogao in that there is only one layer in the majority of paintings. There are even several caves where the paintings were executed onto a ground-layer applied directly onto the sandstone support without any plaster layers (newly-found Cave 1, Cave 69, Cave 171). The painting layers consist of pigments and colorants mixed with organic binding media.

Previous studies of the technology of the wall paintings of the Kizil Grottoes were carried out by Gettens in 1938 [11], and by Riederer in 1977 [12], who studied painting fragments detached by foreign exploration teams (Germany & Japan). Considerably later, Su Bomin investigated the pigments and binding media of the wall paintings [13, 14]. In 2015, the Tokyo University of the Arts and the Kucha Academy research team conducted further investigations of Kizil's wall painting materials and techniques [15]. The results of these previous studies results are summarized in Table 13.1.

Table 13.1 Previous studies of painting techniques and materials used at Kizil paintings

		Blue	Green	Red	White	Yellow	Black	Brown	Grey	Metal foil	Binder
Su Bo-min	Cave No.	1, 38, 114, 186, 180, 179, 171	1, 38, 114, 186, 180, 179, 171	1, 38, 77, 100, 186, 180, 171	1, 38, 77, 100, 186, 135		1, 38, 100, 186, 179	38, 77, 114	171		
	Methods	XRD PM	XRD PM	XRD PM	XRD PM	XRD PM	XRD PM	XRD PM	XRD PM	XRD PM	HPLC
	Results	Lapis Lazuli	Atacamite, Paratacamite	Red lead, Cinaber, Red Ochre	Gypsum, Anhydrite[a] Calcite		Lead dioxide	Lead dioxide			Animal glue
Kucha Academy & Tokyo University of the arts	Cave No.	69, 224	69, 224, 167	69, 167, 224	69	69	167, 69			69	
	Methods	XRF	XRF	XRF	XRF	XRF	XRF, OM				
	Results	Lapis lazuli	Atacamite	ed lead, ed ochre, Ac(T)	Gypsum	Lithargite	Carbon black			Gold, Tin	
Gettens, R. J(G) Riederer, J(R)	Methods	PM, Chemical analysis (G), PM, cross section, XRD (R)	PM, Chemical analysis (G), PM, cross section, FTIR, XRD (R)	PM, Chemical analysis(G), PM,cross section, XRD (R)	PM, Chemical analysis (G), PM, cross section, FTIR, XRD (R)	PM, Chemical analysis (G), PM, cross section, XRD (R)	PM,cross section, (R) FTIR, XRD (R)	PM, Chemical analysis (G),	PM, Chemical analysis (G),		Wetting PM (G)

(continued)

Table 13.1 (continued)

		Blue	Green	Red	White	Yellow	Black	Brown	Grey	Metal foil	Binder
	Results	Lapis Lazuli (G) (R) Indigo (R)	Chrysocolla (G), Atacamite (R)	Red lead(G) (R) Red ochre (G) (R)	Gypsum, Anhydrite (R)	Yellow Ochre(R) Orpiment (R) Lithargite (R)	Carbon black (R)	Lead dioride (G)	Uncertain, Pb, Ca(G)		Animal glue (G)

[a] Anhydrite: in Xinjiang Management Committee of Cultural Heritage 1997, the XRD spectrum of anhydrite is not given, but the identified results are summarized in a table. In the results summary, the anhydrite was found to be present both in the white paint layer and in combination with the blue pigment lazurite (lapis lazuli) in Caves 38, 171, 179 and 186. Elsewhere, anhydrite has also been detected in white paint layers in Maiji grottoes, and in Mati and Lingbing temples, in Gansu province [27], and in combination with lazurite in Dunhuang [28]. Anhydrite is insoluble in water, has no adhesive properties, and is not easy to use in wall paintings. Given that the anhydrite is detected with gypsum in all reported studies, it can be supposed that anhydrite is present in association with the raw mineral gypsum

13.3.2 Current Investigations of the Painting Techniques and Materials of the Kizil Grottoes

The previous studies discussed above imparted some basic information, but the latest investigations provide a much a deeper understanding of the wall painting techniques and materials employed at the Kizil grottoes. Pyromorphite-mimetite ($Pb_5Cl[(P,As)O_4]_3$) was found to have been used as a white pigment, while gamboge was used to give a yellow glaze over atacamite, to achieve a delicate shade of green. Stick lac, a complex red resinous substance yielding both lac dye and shellac, which is secreted by a number of species of the lac insect, was used both as a mordant for gilding and as a red colorant at Kizil, which is a new finding. Shellac was also probably used on tin foil to imitate gold. Plant gum was detected in the lump of blue pigment found in front of Cave 189.

13.3.2.1 Lead-Containing White Pigment and an Organic Yellow Colorant in Cave 69

Two samples were collected from painting on the vault of the back corridor in Cave 69. The first was a sample of white from the body of a flying apsara, and the second was a sample of green from the lower garment (Fig. 13.2).

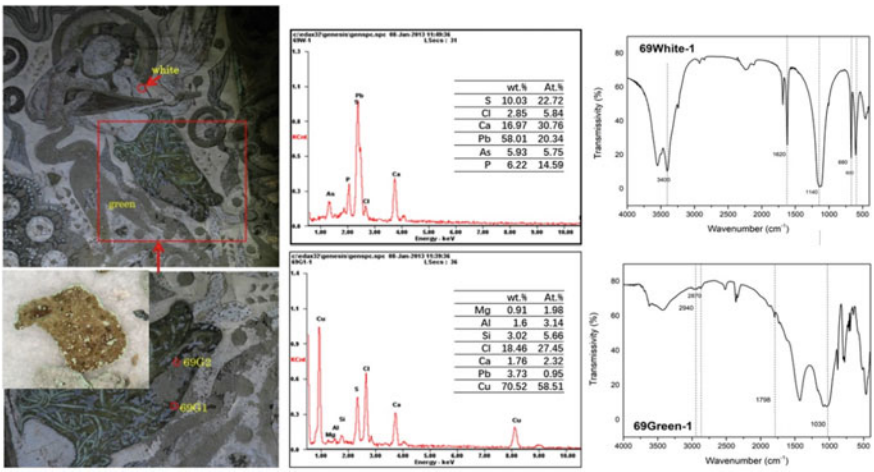


Fig. 13.2 Samples collected from Cave 6; locations shown on the left. 69 W-1 is the white from the flesh of the body of the Flying Apsaras. Samples 69 G1 and 69 G2 are green covered with a yellowish substance; there is a fine grey layer beneath green. There is no plaster layer and the painting has been applied directly onto the sandstone. In the middle and on the right, the EDX images and FTIR spectra of the samples

The white sample was taken because its whitish-yellow hue differed from the white of the ground, presenting the possibility that a different pigment was used in this case. Analysis by Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray analyzer (EDX) indicated that Pb, Ca, As, P, S, Cl were present in the white sample. Results showed that the element Pb predominated at 58.01wt%, indicating that a lead-based pigment was employed. Lead white ($Pb_3(CO_3)_2(OH)_2$) is the most common lead-based white pigment and has been used in numerous wall paintings. However, in the FTIR spectrum of the white paint layer from Cave 69, the C-O carbonate bonds usually occurring at 1420 cm^{-1} were not detected, suggesting that the pigment is not lead white. Considering the nature of the other elements in this pigment (As, P, Cl, S and Ca), it can be assumed that the white pigment is pyromorphite ($Pb_5Cl(PO_4)_3$) with gypsum. Pyromorphite usually contains a small amount of arsenic because phosphorus (P) and arsenic (As) often coexist in nature and replace each other in the molecular structure, forming pyromorphite-mimetite ($Pb_5Cl[(P,As)O_4]_3$) [16]. Fourier transform infrared spectroscopy (FTIR) spectra with absorption bands at 1200−1100 cm^{-1} can be attributed to $\left(SO_4^{2-}\right)$ antisymmetric stretching vibration; peaks at 1620 cm^{-1}−1680 cm^{-1} can be attributed to bands of OH−.

Pyromorphite-mimetite is not a familiar pigment, although it is quite widely found in a number of ancient murals. In its natural state, it is a secondary mineral of lead ore, having a white to yellow appearance. It is used as a white pigment in the Maijishan grottoes [17], for example, and as a yellow pigment in tomb murals in Gansu province [18]. However, its use as a pigment in the Kizil grottoes has rarely been reported.

The green sample was collected from the garments of the flying apsaras, which are yellowish in color. Observation under the microscope showed that there is a brown colorant layer above the bright green pigment. SEM-EDX analysis results indicate that Cu, Cl and Ca are present in both samples. Ca and S come from the ground ($CaSO_4 \cdot 2H_2O$). The presence of Cu and Cl indicates that atacamite ($Cu_2(OH)_3Cl$) is probably the green pigment. In its FTIR spectrum, the absorption bands at 2940 cm^{-1} and 2860 cm^{-1}(C-H asymmetric stretching vibration of CH_2 and C-H symmetric stretching vibration of CH_2) suggest the presence of organic materials. Based on its appearance, a yellow-brown colorant—most likely gamboge—was probably applied over the surface of the green to modify its colour. Among previous material studies in archaeological remains, the use of gamboge has been identified in the Astana tomb murals (680–880 A.D.), in Turfan, near ancient Chotscho, to the east of ancient Kucha [19].

13.3.2.2 The Blue Pigment

A lump of blue pigment was found in front of Cave 189 during remedial conservation in 2013. Its appearance is shown in Fig. 13.3a. Analysis was carried out to understand its properties. X-ray diffraction (XRD), Fourier Transform Infrared Spectrometry (FTIR) and enzyme-linked immunosorbent assay (ELISA) were used for studying inorganic and organic materials. The results show that the blue pigment is lapis lazuli

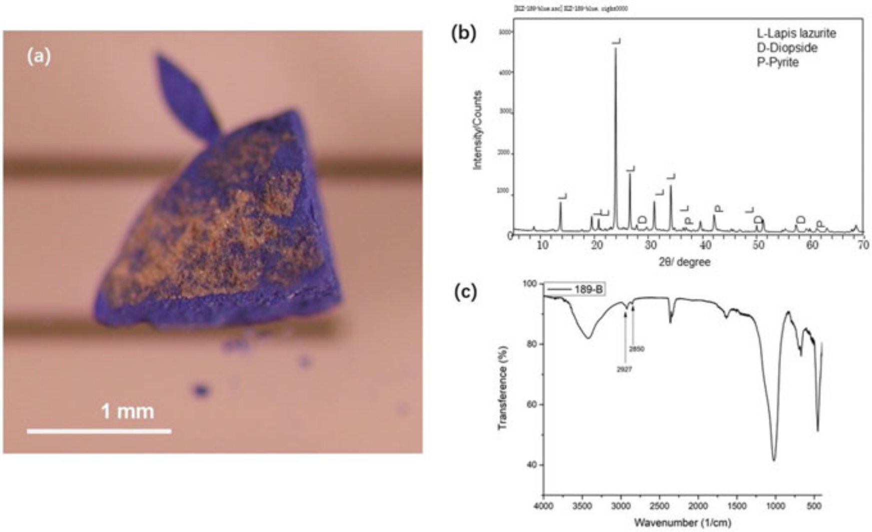


Fig. 13.3 The lump of blue pigment and analysis results: (a) image of the unearthed lump of blue pigment; (b) the indicative peaks on the XRD spectra are marked by L (Lapis Lazuli), D (Diopside) and P (Pyrite); (c) FTIR spectrum

and its binding medium is plant gum. This lump of pigment was presumably left by the ancient painters who created the wall paintings.

In the XRD spectrum, the characteristic peaks of lapis lazuli are very clear (Fig. 13.3b). In addition, the natural impurities diopside and pyrite can be seen, indicating that the blue pigment is made from natural lapis lazuli. The FTIR spectra (Fig. 13.3c) show bands at 1089 cm^{-1} (Si-O-Si Antisymmetric stretching vibration) and 694 cm^{-1} (S-O stretching vibration), which can be attributed to lapis lazuli. Other bands around 3421 cm^{-1} (O-H stretching vibration of carbohydrate) and 2927 cm^{-1} (C-H asymmetric stretching vibration of CH_2) indicate the presence of organic materials. Furthermore, the ELISA results shown in Table 13.2 indicate that the organic binder used with the blue pigment is a plant gum (sample 189B1). In order to confirm if plant gum is also used in the wall painting as a binder, an additional sample was collected and analyzed by ELISA (sample 189R). However, none of the OD absorbance values provide a clear result to identify the kind of binding media used.

While it can be supposed that the plant gum was probably used as a binding medium for the wall paintings, its presence in the lazurite block found in front of the cave may alternatively indicate that plant gum was used in the processing of the mineral for the separation out of fine particles.

Table 13.2 ELISA results [OD absorbance of samples (20 min)]

	bs0813R (casein)				JIM13 (plant gums)				MAC265 (tragacanth)			
	40μL	20μL	20μL	10μL	40μL	20μL	20μL	10μL	40μL	20μL	20μL	10μL
189R	0.091	0.093	0.095	0.096	0.099	0.107	0.118	0.116	0.104	0.058	0.102	0.111
189B1	0.103	0.105	**0.117**	0.099	**0.392**	**0.417**	**0.436**	**0.66**	0.117	0.121	0.084	0.122
ave + 3SD	**0.111**				**0.361**				**0.124**			
	ab19811 (collagenI, exclude goat)				ab34710 (collagenIIexclude rabbit)				ab1225 (ovalbumin)			
	40μL	20μL	20μL	10μL	40μL	20μL	20μL	10μL	40μL	20μL	20μL	10μL
189R	0.098	0.092	0.097	0.1	0.131	0.119	0.124	**0.171**	0.236	0.216	0.224	0.372
189B1	**0.105**	**0.107**	0.1	0.102	0.145	0.146	0.149	0.158	0.355	0.355	0.333	**0.419**
ave + 3SD	**0.103**				**0.163**				**0.392**			

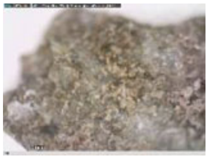
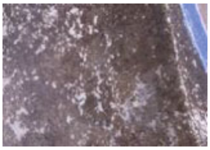
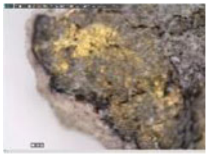
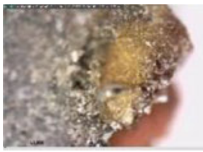
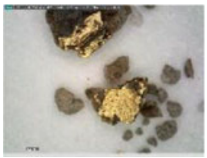
13.3.2.3 Gilding Techniques in the Kizil Grottoes

Six samples were taken from Caves 171 from areas where metal foil and/or resinous coatings had been observed: from inside the Buddha niche; from the sculpture above the niche; from the central pillar and from the main chamber (the sample locations are shown in Table 13.3, together with optical microscope [OM] images and detailed descriptions of the samples). Cross-sections were prepared and morphologically studied by OM and Scanning Electron Microscopy (SEM) observation. Elemental maps were obtained using SEM-EDS (Scanning Electron Microscope equipped with Energy Dispersive Spectrometer).

The cross-section images and elemental maps show that gold (Au) is present in two samples: KZ-C171-S8 and KZ-C171-S3. Tin (Sn) was detected in five samples: KZ-C171-S2, KZ-C171-S5, KZ-C171-S12, KZ-C171-S3 and KZ-C171-S7. Analytical results show that two samples, KZ-C171-S5 and KZ-C171-S3, have two layers of metal foils (Fig. 13.4b).

In BSE (Backscattered Electron) images, also shown in Fig. 13.4, a dark layer could be observed in all the samples just beneath the metallic leaf, suggesting the layer is composed of elements with smaller atomic numbers. Referring to the OM and cross-section images, this layer varies considerably in the samples, from a red-purple to brownish color. All these observations suggest it may be an organic mordant for the tin leaf. Lead (Pb) was detected in the orange-coloured lower layer of the sample, indicating use of minimum (red lead, Pb_3O_4). In all except sample KZ-C171-S8 Fig. 13.4, which was from the figure's dress, gold (Au) was detected above a red ground. Organic-looking mordant layers could be found in all the samples. In KZ-C171-S8, an extremely thin dark layer could be observed just beneath the gold leaf in the Backscattered Electron (BSE) images, meaning there are elements with smaller atomic numbers. Lead (Pb) was also detected in the orange layer beneath the gold leaf in KZ-C171-S12 and KZ-C171-S5, suggesting the use of minium. Moreover, in

Table 13.3 Detailed description of each sample with images of sampling locations and fragments

KZ-C171-S2		Niche wall		Grey-brown layer with red support and white plaster
KZ-C171-S12		Mount Summeru		Grey-brown layer applied over the dark-red layer
KZ-C171-S7		Decorative band on the wall of the main chamber		Grey-brown layer applied over the dark-red layer
KZ-C171-S8		Figure's dress on the wall of the main chamber		Gold-coloured layer with a metallic luster, dark-red layer beneath
KZ-C171-S5		Mount Sumeru		Brown resin and purple-red visible at the lower right edge of the sample
KZ-C171-S3		Budda mandorla, niche wall		Gold-coloured layer with brown material beneath

samples KZ-C171-S12, KZ-C171-S5 and KZ-C171-S7 where minium was present in the stratigraphy, a thin dark-red layer, probably made from a red colourant, was applied on top, presumably to adjust the color hue.

13.3.2.4 Organic Materials Used in the Application of Metal Foils

FTIR spectra of samples are shown in Fig. 13.5. The μ-FTIR spectra were obtained

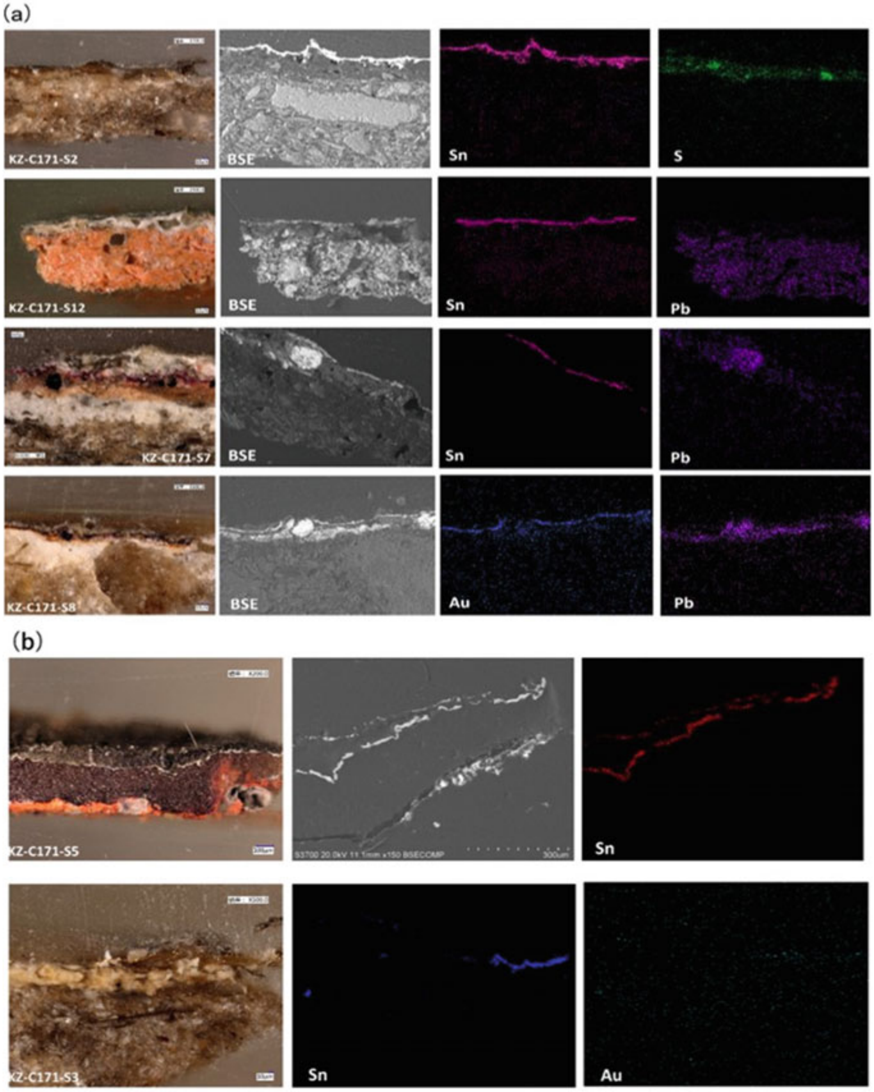


Fig. 13.4 (a) cross-section images, backscattered electron images and elemental mapping of samples with a single layer of metal foil; (b) cross-section images and elemental mapping of samples with a double layer of foil

from the yellow layer and the red layer beneath it in sample KZ-C171-S5 Fig. 13.4a and the yellow layer in KZ-C171-S2. Peaks occur at 1735 cm^{-1} [ν (C = O) ester] and 1710 cm^{-1} [ν (C = O) aldehyde, ketones, carboxylic]; shoulder peaks at 1775 cm-1 [ν (C = O) lactone, cyclic esters], 1465 cm^{-1} [δ (CH_2)], 1416 cm^{-1} [ω (CH_2)], 1377 cm^{-1} [δ (CH_3)], 1246/1165/1100 cm^{-1} [ν (C-O)] and 723 cm^{-1} [γ(CH_2)] are

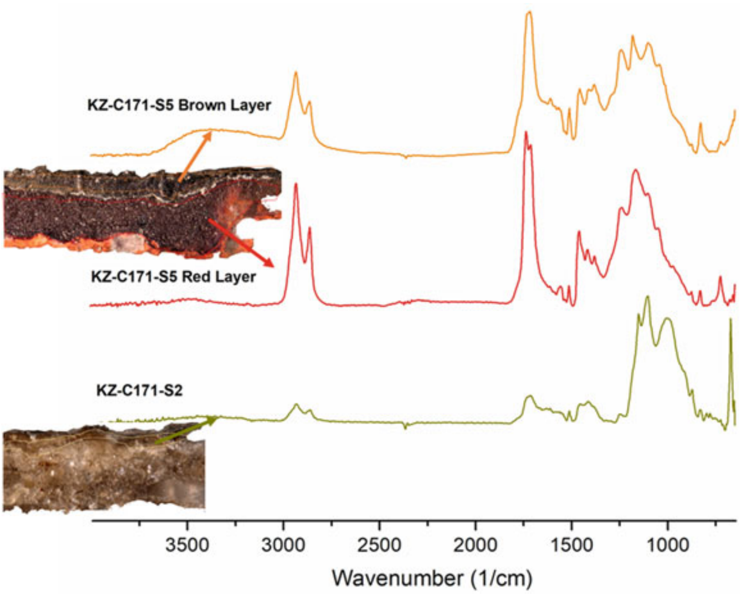


Fig. 13.5 FTIR spectra of organic materials: stick-lac (internet purchase from India); sample KZ-C171-S5 and KZ-C171-2 from wall painting (for the sample location and description, see, Table 13.3)

detected in both the yellow and red layers, suggesting the presence of carboxylic acids.

As shown in the FTIR spectra, the absorption bands at 2920 cm^{-1}, 2842 cm^{-1}, 1730 cm^{-1}, 1711 cm^{-1}, 1460 cm^{-1}, 1422 cm^{-1}, 1375 cm^{-1}, 1240 cm^{-1}, 1170 cm^{-1}, 870 cm^{-1} and 722 cm^{-1}were detected in the yellow-brown layer over the tin leaf, in the red-purple layer beneath the tin leaf of sample KZ-C171-S5, and in the yellow-brown layer of KZ-C171-S2, indicating all these organic compounds contain comparable functional groups, leading to similarities in their vibrational signatures. 1730 cm^{-1} can be attributed to C = O stretching vibration of esters, while 1710 cm^{-1} can be attributed to C = O stretching vibration of aldehyde, carboxylic acids and ketones. The IR bands of organic compounds at 1175 cm^{-1} (C-O stretching), 1240 cm^{-1} (the bending vibration of carboxyl), 1460 cm^{-1} (C-H_2 Bending vibration), 2845 cm^{-1} (C-H symmetric stretching vibration of CH_2), 2920 cm^{-1} (C-H asymmetric stretching vibration of CH_2) and antisymmetric vibration of CH_2 at 1422 cm^{-1} can be clearly seen. The characteristic peaks in the IR spectra coincide well with the typical peaks of carboxylic acids, indicating the possibility that oil was used in these layers.

In previous research, it has been speculated that lac was probably used in the wall painting of Cave 224 [15]. On this basis it was decided to try to establish whether it was also used as a colorant in Cave 171. The FTIR spectrum of the stick lac sample identified its main component as aleuritic acid, which, in common with other carboxylic acids, can indicate the presence of drying-oils. In order to get more information about the organic materials and confirm if the dark-red layer in samples KZ-C171-S5, KZ-C171-S12 and KZ-C171-S8 is red lac, analysis was performed using liquid chromatography coupled to electrospray ionization quadrupole-time-of-flight mass spectrometry (LC–ESI-Q-TOF-MS) in negative ion mode (results are shown in Table 13.4). The proposed compounds of shellac for target screening were obtained through the literature [20] and further identification of the molecule was achieved by comparison of its retention time with that of a prepared reference shellac sample (extracted in ethanol from raw stick lac). Comparative results of sample fragments from the wall paintings and of the raw stick lac are shown in Table 13.4. The results of target screening show the presence of typical natural shellac components including free hydroxy aliphatic acids and cyclic sesquiterpene acid in all the mural samples. Specifically, aleuritic acid ($[M\text{-}H]^-$, m/z 303, RT 13.56 min), a major ingredient in (30–40wt%) [21], is detected in all samples except KZ-C171-S2, in which the dark-red layer is absent, indicating that the red layer is composed of stick lac. Furthermore, the fact that typical components of stick lac were detected in the samples taken from the red background color supports the speculation that red lac was used both as a red colorant for painting by ancient painters and also as a mordant exclusively for gold foil.

13.4 Discussion

Our study of the materials and techniques of the Kizil wall paintings is only a beginning, but the results of analysis and examination have already provided ample evidence for the transmission of materials and techniques along the ancient Silk Road, which is enough to inspire us. As gamboge was not local to Kucha, it might have been transported from the Central Plains. Stick lac, which originated in Persia (Iran), Sindhu (India) and South Asia might have been introduced via trade to Kucha, thence to the Central plains. The technique of applying glazes to tin in imitation of gilding has not previously been found in Chinese wall painting. While the technique of applying safflower seed oil over silver foil and baking it to produce a gold appearance is recorded in the ancient book “Tian Gong Kai Wu” (天工开物), a technological encyclopedia written by Song Yingxing 宋应星 (1600–1660 A.D.) in 1637 ((Ming Dynasty) Song Ying-xing, “Tian Gong Kai Wu”), there is no record of using tin foil in the same manner. Tin foil has also been found in paintings in Afghanistan [22], and in Indian [23] and western paintings [24–26], but the tin foil used in Kizil seems to be the earliest recorded example (i.e., fifth–seventh century A.D.). It is therefore very likely that this unique imitation gilding technique originated in Central Asia, and then spread westward.

It is perhaps inevitable that the limited exploration undertaken so far of the painting materials and techniques used in Kizil has resulted in an incomplete and sometimes incorrect understanding of ancient painting procedures. However, we very much hope that these studies have thrown some new light upon the technical advances, trade

Table 13.4 Extracted ion chromatograms of aleuritic acid from mural samples and reference shellac. EICs obtained by LC–ESI-Q-TOF-MS analysis shows the nearly identical retention time of aleuritic acid with the reference, implying the presence of the compounds of stick lac

Chemical formula	Identified compounds of stick lac	Reference	KZ-C171-S5	KZ-C171-S8	KZ-C171-S7	KZ-C171-S12	KZ-C171-S2
$C_{14}H_{28}O_3$	Butolic acid	+	+	+	+		
$C_{16}H_{32}O_5$	Aleuritic acid	+	+	+	+	+	
$C_{16}H_{30}O_5$	Oxidised aleuritic acid	+		+		+	
$C_{14}H_{28}O_4$	9,10-dihydroxytetradecanoic acid	+	+	+		+	
$C_{14}H_{26}O_3$	6-oxotetradecanoic acid	+	+	+	+	+	
$C_{16}H_{32}O_4$	9,10-dihydroxyhexadecanoic acid	+	+	+	+	+	
$C_{16}H_{30}O_4$	9,10-dihydroxyhexadecenoic acid	+	+	+	+	+	+
$C_{15}H_{20}O_6$	Shellolic acid, Epishellolic acid	+		+	+		
$C_{15}H_{20}O_4$	Laccijalaric acid	+			+	+	
$C_{15}H_{18}O_5$	Oxidised jalaric acid	+		+	+		
$C_{31}H_{50}O_8$	Laccijalaric-aleuritic	+	+			+	
$C_{31}H_{48}O_8$	Laccijalaric- oxidised aleuritic	+	+	+			
$C_{31}H_{50}O_6$	Laccijalaric-(16-hydroxyhexadecanoic)	+	+	+	+		
$C_{30}H_{48}O_9$	Aleuritic-Llak	+	+	+		+	

intercourse and cultural exchanges along the ancient Silk Road. We are honored to have had the opportunity to study from the brief perspective of our own work the thousands of years of human achievement distilled into the art of Kizil.

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