

Technical note

Technical analysis of a Central Asian wall painting detached from a Buddhist cave temple on the northern Silk Road

Birgit Angelika Schmidt¹, Martin Andreas Ziemann², Simone Pentzien¹, Toralf Gabsch³, Werner Koch⁴, Jörg Krüger¹

¹BAM Bundesanstalt für Materialforschung und –prüfung, Berlin, Germany, ²Institut für Erd- und Umweltwissenschaften, Universität Potsdam, Potsdam, Germany, ³Staatliche Museen zu Berlin, Museum für Asiatische Kunst, Berlin, Germany, ⁴Fachhochschule Potsdam (FHP), Potsdam, Germany

A great number of Central Asian wall paintings, archeological materials, architectural fragments, and textiles, as well as painting fragments on silk and paper, make up the so called *Turfan Collection* at the Asian Art Museum in Berlin. The largest part of the collection comes from the Kucha region, a very important cultural center in the third to ninth centuries. Between 1902 and 1914, four German expeditions traveled along the northern Silk Road. During these expeditions, wall paintings were detached from their original settings in Buddhist cave complexes. This paper reports a technical study of a wall painting, existing in eight fragments, from the Buddhist cave no. 40 (*Ritterhöhle*). Its original painted surface is soot blackened and largely illegible. Grünwedel, leader of the first and third expeditions, described the almost complete destruction of the rediscovered temple complex and evidence of fire damage. The aim of this case study is to identify the materials used for the wall paintings. Furthermore, soot deposits as well as materials from conservation interventions were of interest. Non-invasive analyses were preferred but a limited number of samples were taken to provide more precise information on the painting technique. By employing optical and scanning electron microscopy, energy dispersive X-ray spectroscopy, micro X-ray fluorescence spectroscopy, X-ray diffraction analysis, and Raman spectroscopy, a layer sequence of earthen render, a ground layer made of gypsum, and a paint layer containing a variety of inorganic pigments were identified.

Keywords: Wall paintings, Central Asia, Silk Road, Pigments, Microscopy, EDX, XRF, Raman spectroscopy

Introduction

Historic context

The region associated with East Turkestan was an important site of Buddhism between the second and tenth centuries (Fischer *et al.*, 1994). From the tenth century, Buddhism as the major religion lost its importance and was replaced by Islam. As a consequence, Buddhist buildings and monuments gradually disappeared due to desert sandstorms, excavations, and pillaging, all resulting in the destruction of monastic and temple complexes. Today, the mentioned territory is located in the province of Xinjiang Uyghur Autonomous Region, in the far west of the People's Republic of China.

By the early twentieth century expeditions hailing from countries like Japan, the United Kingdom,

Russia, and Germany, then deemed to be the 'Great Powers' (Taniguchi, 2010), led to a series of research journeys following the northern Silk Road. During these expeditions, wall paintings were detached from their original settings, i.e. the interior walls and ceilings of Buddhist cave complexes (Russell-Smith, 2012). Geological and archeological reports of four Prussian expeditions formed the basis of the following research (Yaldiz & Zieme, 1987). Moreover, expedition diaries document the wall paintings in a very detailed manner in the form of descriptions, photographs, sketches, and tracings, and map the context and work *in situ*. They represent the primary sources of information on the expeditions today.

In 1906, during the third Prussian *Turfan* expedition, Buddhist cave sanctuaries were rediscovered in the valley of Sim-sim close to Kiriš in the district of Kucha (Fig. 1). Cave temples hewn into rock cliffs were found, for example cave no. 40, the so

Correspondence to: Birgit Angelika Schmidt, BAM Bundesanstalt für Materialforschung und –prüfung, Unter den Eichen 87, Berlin D-12205, Germany. Email: Birgit-Angelika.Schmidt@bam.de

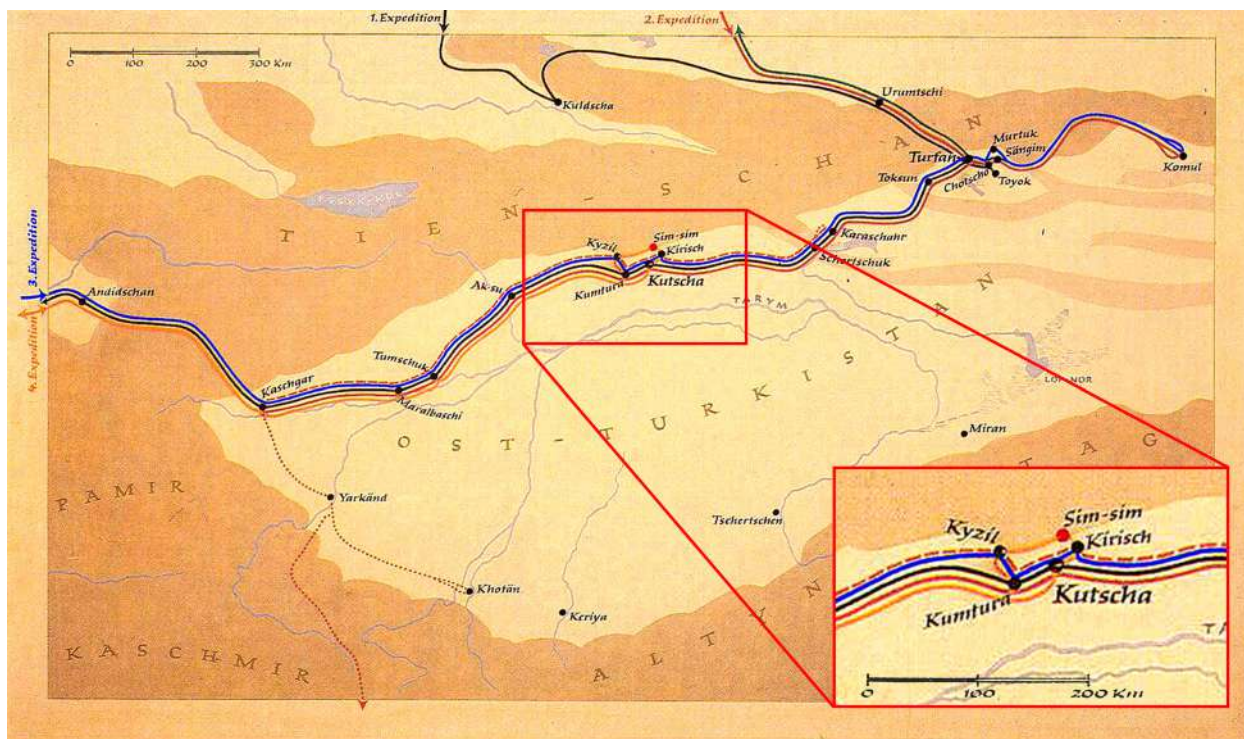


Figure 1 Map of the northern Silk Road region in East Turkestan. The lines represent the four Prussian expedition routes (1902–1914). The blue line marks the third expedition (1905–1907). The inset in the lower right corner shows a detailed magnification of the region around Kucha, including the Buddhist cave sanctuary area in Sim-sim. Figure based on original maps owned by the Asian Art Museum.

called *Ritterhöhle* (see Fig. 2A, exterior view and floor plan). The cave's name arises from the representation of a knight figure in a suit of armor located on the central wall paintings (Grünwedel, 1912). The interior walls, arches, and vaults of those Buddhist places of worship were entirely decorated with religiously influenced paintings (Fischer *et al.*, 1994). Due to the style

of their letter band, Pinault (1993–94) assigned the wall paintings to the first half of the seventh century.

The objects examined in this work are wall painting fragments that were detached in eight pieces (Fig. 3). Despite their heavily sooted surfaces, Grünwedel (1912) justified their removal by their high artistic quality. The paintings show three prophecy scenes.



Figure 2 (A) North entrance of cave no. 40 (photograph by T. Gabsch). The inset lower left shows the floor plan made by Grünwedel (in the collection of the Asian Art Museum); the annotations describe the dimensions (2M35c = 2.35 m). The red line on the left wall of the inset indicates the location where the wall painting fragments of this study were detached. (B) South side of the interior space (cella) of cave no. 40 (photograph by T. Gabsch).

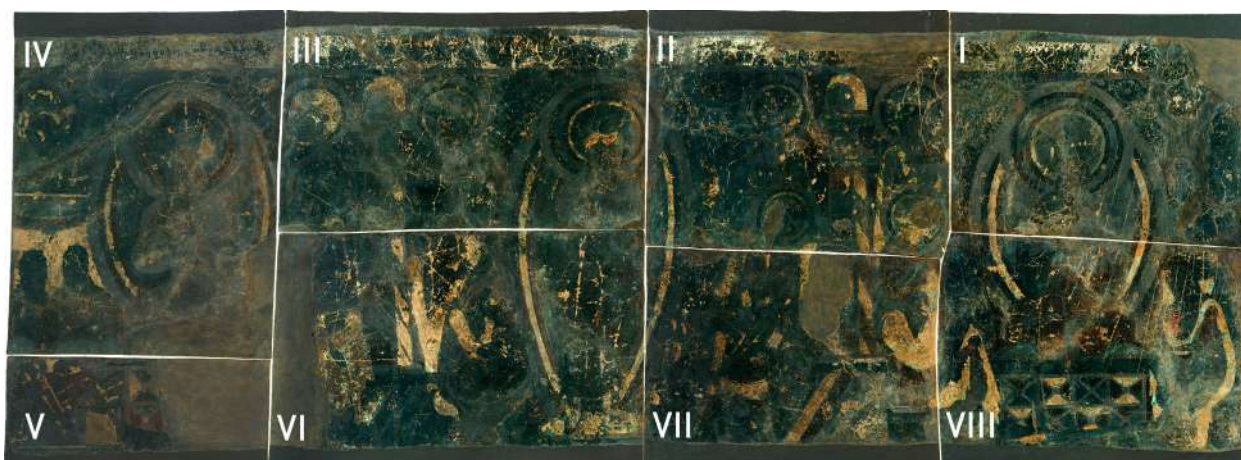


Figure 3 Photograph of the eight wall painting fragments; total dimensions 2.45 × 0.90 m.

In his expedition diary, Grünwedel (1912) assigned these paintings to the side walls of the cella (Fig. 2B) of cave no. 40, marked red in the left part of the floor plan shown in Fig. 2A.

Bartus participated in all four Prussian expeditions and developed a unique method for detaching the paintings. A detailed description of the method is given by von Le Coq (1926). First, the surfaces of the paintings were cut with a sharp knife into appropriate shape to have them fit into the packaging in transport crates. The cut was made through the whole painting and render. Later, a cut was made into the side of the wall with a hoe, allowing the use of a padesaw to detach the painting. The fragile fragments were transported overland to Europe, and in 1907 they were brought to the Indian Department of the Museum of Ethnology in Berlin. Because of the start of the First World War, a continuous scientific investigation became impossible.

Fig. 2B shows the condition of the interior space of cave no. 40 in 2011. It can be recognized that in large areas the wall paintings are widely removed and that heavy soot deposits are present in the dome (note that in this and other figures, the dimension refers to the full scale bar and not the individual sections).

Due to loss or damage incurred during transport and/or handling, many of these fragile objects were in a poor condition and not easy to handle after their arrival in Berlin. To preserve and prepare them for exhibition, each fragment was stabilized and placed in a bed of gypsum during a restoration campaign in the 1920s. The gypsum was reinforced with anchoring elements. During this treatment, parts of the wall painting were positioned erroneously, both regarding their surface level and their horizontal position in the pictorial composition.

Fig. 3 shows an overall photograph and Fig. 4 shows a stratigraphic schematic of the eight wall painting fragments at the Asian Art Museum. Each fragment is embedded in the 1920s gypsum support

backing (labeled '0' in Fig. 4). On earthen render (1), which consists of layers of rough and fine render, a thin white ground layer (2) can be seen. On that, a single or multilayered painting (3) is applied (now partially covered with soot).

More than one third of the wall paintings of the *Turfan Collection* are considered lost as a result of the First and Second World Wars. Other wall painting fragments and artefacts (especially manuscripts) were taken from Berlin to the Soviet Union in 1945; today fragments of the *Ritterhöhle* are also in the collection of the Hermitage in St Petersburg.

No written documents provide evidence for further interventions and treatments until 1973, when the paint layer surfaces were cleaned with ethanol and consolidated using a polyvinyl acetate dispersion with the trade name *Caparol*[®].

Studies on Central Asian wall paintings – a review

The following is a brief review of research into Central Asian painting technology, including a summary of analytical techniques used in the most relevant studies. Although not all objects investigated are from the same century and area as those investigated in this study, they still give useful comparative and contextual information on the polychromy of Central Asian wall paintings.

Painting materials

Painting materials of Central Asian wall paintings corresponding to the Late Antique and early middle Medieval periods were first investigated in a scientific manner at the beginning of the twentieth century (Gettens, 1938b).

In the 1970s, Riederer (1977) undertook scientific research on paintings from the Berlin collection. By employing analytical methods such as X-ray diffraction (XRD), infrared (IR) spectroscopy, emission spectroscopy, microscopy, and microchemical

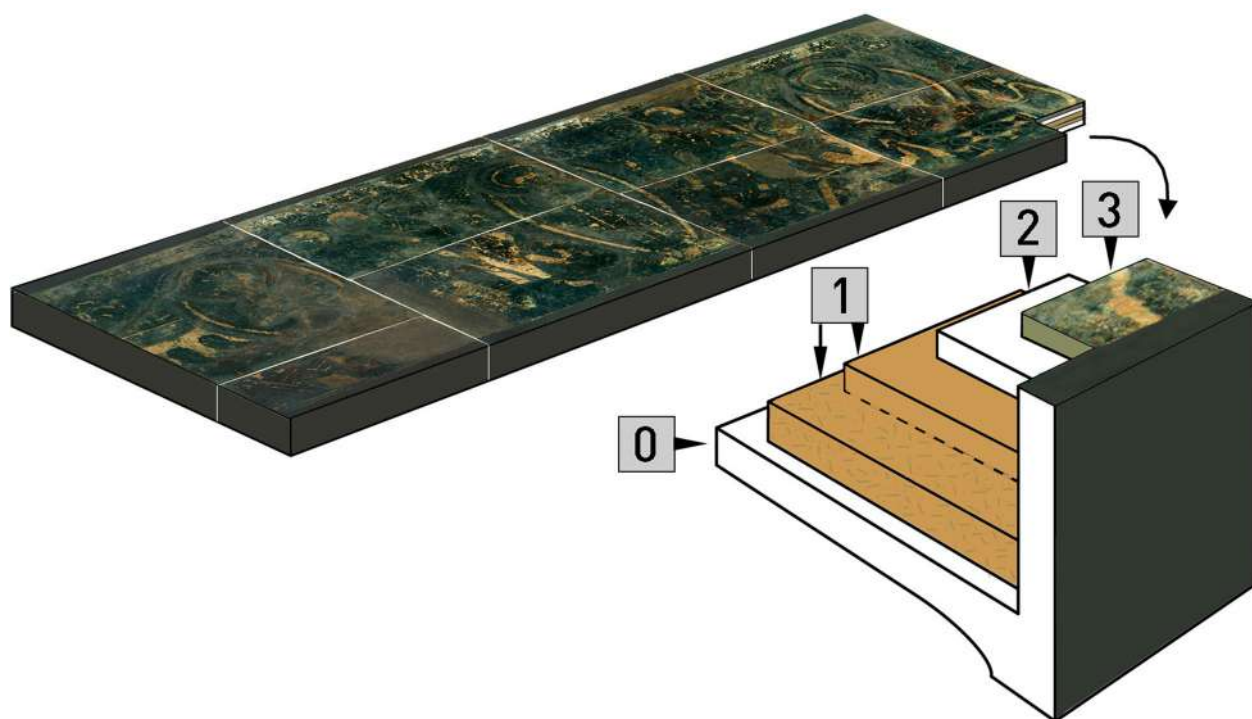


Figure 4 Schematic representation of the detached fragments. The numbered stratigraphy is explained in the text; total thickness of the fragments is approximately 6 cm.

methods, he derived general conclusions concerning the use of pigments and colorants of the wall paintings from East Turkestan. The identified white pigments included gypsum, anhydrite, and, rarely, lead white. The blues were lapis lazuli and indigo. The green pigment was identified as atacamite. Concerning red pigments, Riederer mentioned mercuric sulfide in its mineral (cinnabar) or synthetic form (vermilion). He did not detect this pigment in wall paintings from the Kucha region, however, where mainly red iron oxide was detected. The presence of the pigments lead oxide and massicot is also mentioned by Riederer, who associated the brown-violet painting areas in fragments from Kizil with discoloration of a red lead oxide. Regarding organic colorants, in addition to indigo, Riederer (1977) suggested the possible use of gamboge, kermes, and red lake (rose madder).

Results obtained for binding media are consistent with scripts dating from the seventh century CE which report that animal skin glue was used in paintings (Riederer, 1977). Early studies of the wall paintings in Bamiyan (Gettens, 1938a) and Kizil (Gettens, 1938b) as well as Nagpall and Agrawal have indicated that glue was the binding medium in these cases, based on microchemical tests. Birstein (1975) also found evidence for animal glue (gelatin) as the organic component of paint and plaster layers in Central Asian paintings, as well as plant gums such as apricot or cherry, using chromatographic analysis of hydrolyzed samples.

Recent studies at the Hermitage on paintings from Kucha (it is not mentioned from which cave) used microchemical and spectroscopic methods to identify lapis lazuli, cinnabar, lead oxide, red arsenic sulfides, copper green, bone black, white lead, gypsum, and calcite (Kossolapov & Kalinina, 2007). A similar range of pigments was reported by Zuixiong (2010) for the Kizil Grottoes, located close to the Kucha region. XRD analysis confirmed the presence of vermilion, lead oxides, red ocher, lapis lazuli, copper hydroxychloride minerals such as atacamite, and gypsum. High-performance liquid chromatography indicated an animal glue binder, thought to be made from ox hide.

Between 2004 and 2009, studies of fragments of the giant Buddha statues in Bamiyan were performed with polarized light microscopy, XRD, XRF, and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and element mapping, allowing the detection of gypsum, red iron oxide, white lead, minium, ultramarine, and charcoal black (Blänsdorf *et al.*, 2009).

Another recent study applied synchrotron-based micro-analytical techniques to the characterization of pigments and binders in Bamiyan Buddhist wall paintings. Combined XRF, X-ray absorption spectroscopy, XRD, and Fourier-transform IR spectroscopy carried out on cross section samples indicated the presence of protein and polysaccharide binders, as well as atacamite, minium, and goethite pigments (Cotte *et al.*, 2008).

More detailed reviews of scientific research on Central Asian wall painting techniques can be found elsewhere (Yamauchi *et al.*, 2007; Agnew, 2010).

Preparation techniques

For providing a better adhesion for the earthen render (made of local clay), rock faces were first roughened using a chisel. Multi-layer preparations were typically used. The first rough layer of render was prepared with chopped straw or animal hair for reinforcement. A second, thinner earthen layer generally contained less fibrous material, although sand was sometimes added. The materials used for the subsequent ground layer varied widely, depending on the region: gypsum, anhydrite, calcite, and lead-containing pigments have been detected. It can be assumed that organic binders (plant gums and/or animal glues) were added to extend the processing duration. Typically, the ground layer is thin (10–20 µm), although this may also vary depending on the region (Riederer, 1977).

Additional techniques for preparing the paintings include preliminary sketches, tracings, and the use of a compass. In this context, Riederer refers to von Le Coq who provided evidence for the use of pouncing (Riederer, 1977); this preparation technique was found in paintings from cave no. 123, which were restored and reconstructed in 2002 and are now part of the permanent exhibition at the Asian Art Museum in Berlin.

Methodology of technical analyses

Pigment analysis was the focus of the current study; binding agents have not yet been investigated. The methods used were optical microscopy (OM), polarized light microscopy (PLM), SEM with EDX, XRF, X-ray diffraction (XRD) analysis, and Raman spectroscopy. Table 1 summarizes the techniques used, the objectives of the analyses, and the areas/samples analyzed.

Optical (digital) microscopy was used first to study the appearance and condition of the surface of the eight wall painting fragments and to select appropriate sites for analysis and sampling. XRF was performed preferentially as a non-invasive method, since only very limited sampling of the original paint layers was possible.

In cases where sampling was feasible, original material was removed with a scalpel in the form of microscopic, multilayered flakes and prepared as cross sections for microscopic analyses. Additional samples were taken in the form of surface scrapings to investigate the constituents of individual layers.

In addition to the paint layers, the materials used for the ground and the earthen render layers, as well as the soot and synthetic binder that had been applied on the surface, were investigated. Altogether nine samples were taken, as listed in Table 1.

Table 1 Analytical methods used for investigation with sample numbers and locations

Method	Sample material, location, and number
OM	Cross sections from fragment IV, samples 1 and 2 (blue and red paint areas, Fig. 6), and from fragment I, samples 3 (red paint area, Fig. 7) and 4 (green paint area, Fig. 10)
Polarized light microscopy (PLM)	Pigment identification of particles from red paint layer, fragment V, sample 5
Digital microscopy*	Imaging of surface of fragment no. V (red paint area, Fig. 5)
SEM/EDX	Cross section from fragment I, sample 3 (red paint area, Fig. 7) and layered paint sample from fragment V, sample 6 (Fig. 11)
XRF*	Qualitative determination of elemental composition of painted surfaces in fragment V (red paint area, Fig. 9)
XRD	Analysis of crystalline components of samples from fragment I, sample 7 (ground layer, Fig. 8) and fragment V, sample 8 (white paint, data not shown)
Raman spectroscopy	Pigment identification of particles from green paint, fragment V, sample 9

*These methods were non-invasive, i.e. not requiring samples.

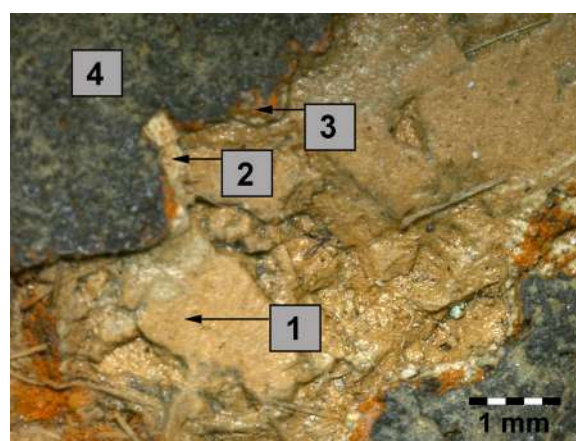


Figure 5 Optical micrograph detail of fragment V, with arrows and numbers marking the different layers: earthen render (1), white ground (2), red paint layer (3), and soot layer (4).

Experimental methods

OM

Detailed images of painting fragments were acquired with a digital microscope (Keyence Deutschland GmbH, Neu-Isenburg, Germany), while images of cross sections were taken using a conventional optical microscope (Olympus Deutschland GmbH, Hamburg, Germany) in darkfield mode and under ultraviolet illumination, employing magnifications of 5–50×. The samples were embedded in Technovit® 2000LC (Heraeus Kulzer GmbH, Wehrheim/Ts,

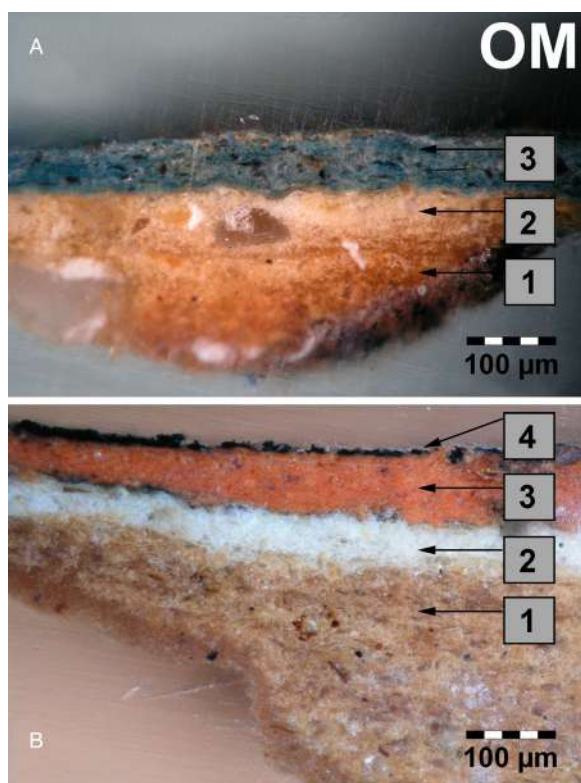


Figure 6 Cross sectional image (darkfield) of samples from a blue paint area (A) and a red paint area (B) of fragment IV.

Germany), a single component light curing embedding resin, and polished.

PLM

An Olympus BX 51 microscope was employed in polarization mode to investigate pigment samples embedded in Meltmount[®] (Cargille-Sacher Laboratories Inc, Cedar Grove, USA) with a refractive index of $n_D = 1.66$.

SEM and EDX

A Zeiss Gemini SUPRA 40 SEM (Carl Zeiss Microscopy GmbH, Oberkochen, Germany) was used at 20 kV accelerating voltage, with a Bruker X-Flash 3404 EDX spectrometer (Bruker Nano GmbH, Berlin). The samples were gold coated prior to imaging in secondary electron mode.

Energy dispersive XRF

A Fischer Scope XDAL XRF (Helmut Fischer GmbH + Co KG, Sindelfingen, Germany) was used, equipped with a tungsten anode, operated at 50 kV with a nickel filter (probed area 0.1×0.1 mm, data acquisition time 60 seconds).

X-ray diffraction

A Seifert XRD 3000 TT (GE Inspection Technologies GmbH, Ahrensburg, Germany) with Bragg–Brentano geometry was used (probed area 1×12 mm, data

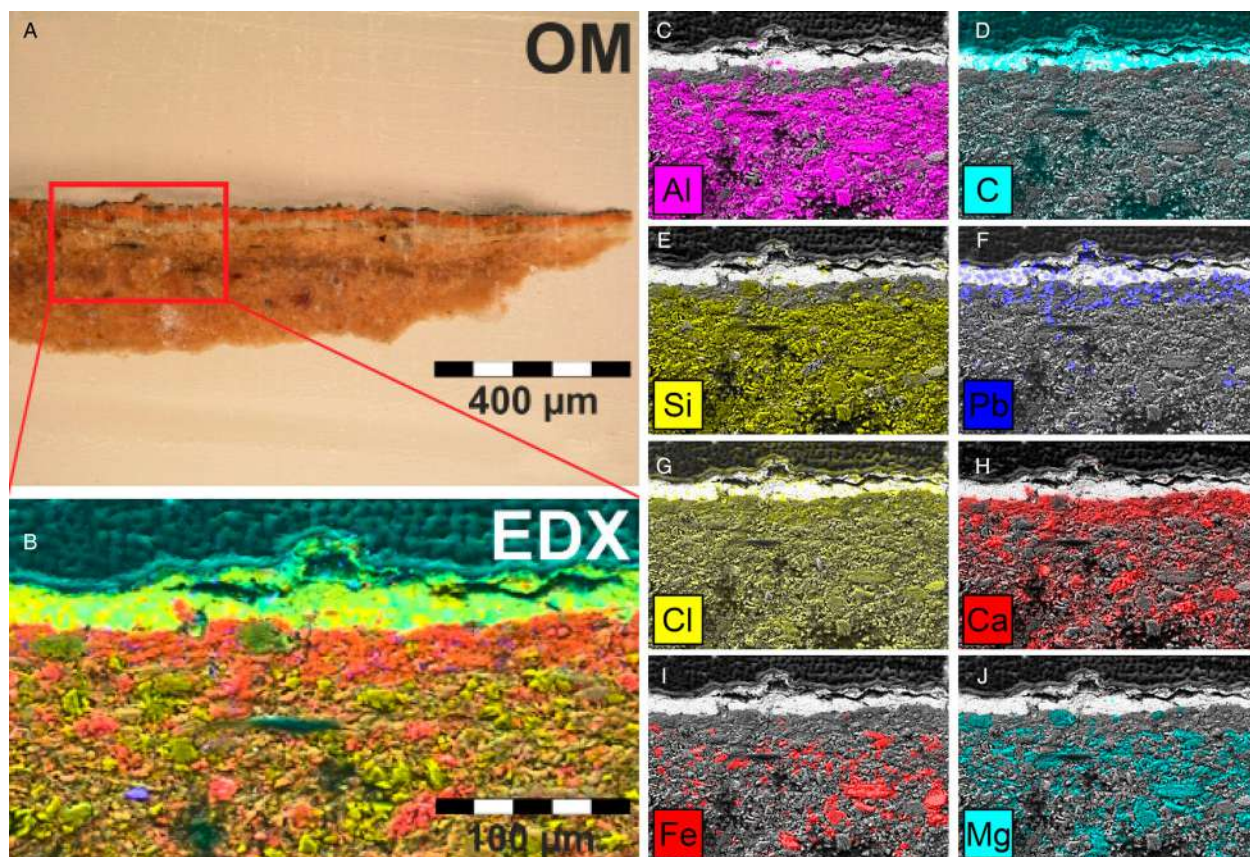


Figure 7 Cross sectional image (darkfield) of sample from a red paint area of fragment I (A) with SEM detail of the rectangular area indicated (B), shown overlaid with EDX elemental maps; the individual element maps are shown in (C–J).

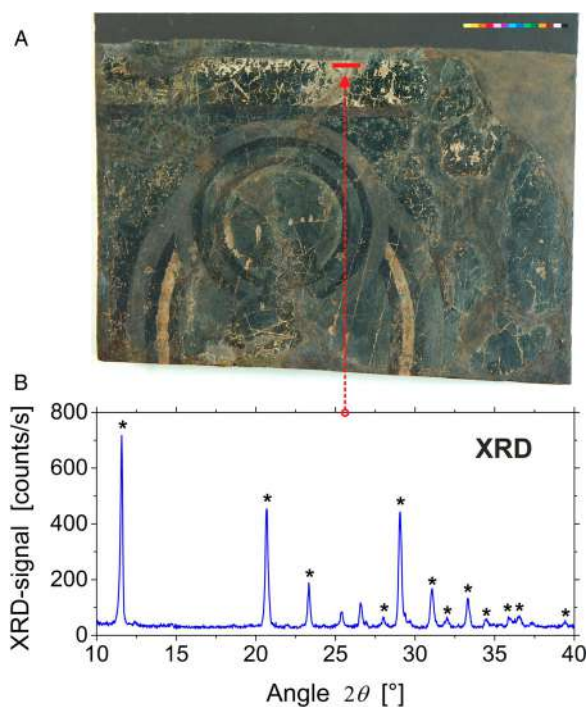


Figure 8 Detail of fragment I (A) with XRD spectrum (B) of a sample taken from the region indicated by a red rectangle. The asterisks indicate peaks for gypsum.

acquisition time 70 minutes), with K_{α} -radiation at 1.542 Å of a copper anode operated at 40 kV with a nickel filter.

Raman spectroscopy

A LabRam HR800 (Horiba Scientific, HORIBA Jobin Yvon GmbH, D-64625 Bensheim, Germany) confocal micro-Raman system was used, equipped with a Nd:YAG laser (532 nm wavelength), BX-41 microscope (Olympus), and cooled CCD-detector (Andor). The spatial resolution of the analyses is c. 2 µm using a 100× long working distance objective (Leica Microsystems, D-64625 Bensheim, Germany). The laser power was reduced by a neutral density filter (D1) to about 3 mW at the sample surface to avoid local heating and effects of laser-induced degradation of the analyzed pigments. The measurement time was set to 100 seconds.

Results and discussion

Fig. 5 shows a micrograph detail of a red-painted area in fragment V. The arrows and numbers mark the different layers indicated in Fig. 4; the contaminating soot layer is also marked in this image (labeled 4). The highly reflective appearance of some parts of the surface is caused by the presence of the *Caparol*[®] (Farben u. Lacke Bautenschutz GmbH, Ober-Ramstadt, Germany) consolidating layer. Fig. 6A shows a cross section taken from a blue paint area of fragment IV. The micrograph confirms the layer sequence shown in Fig. 5: the earthen render (1), ground layer (2), and paint layer (3) are indicated.

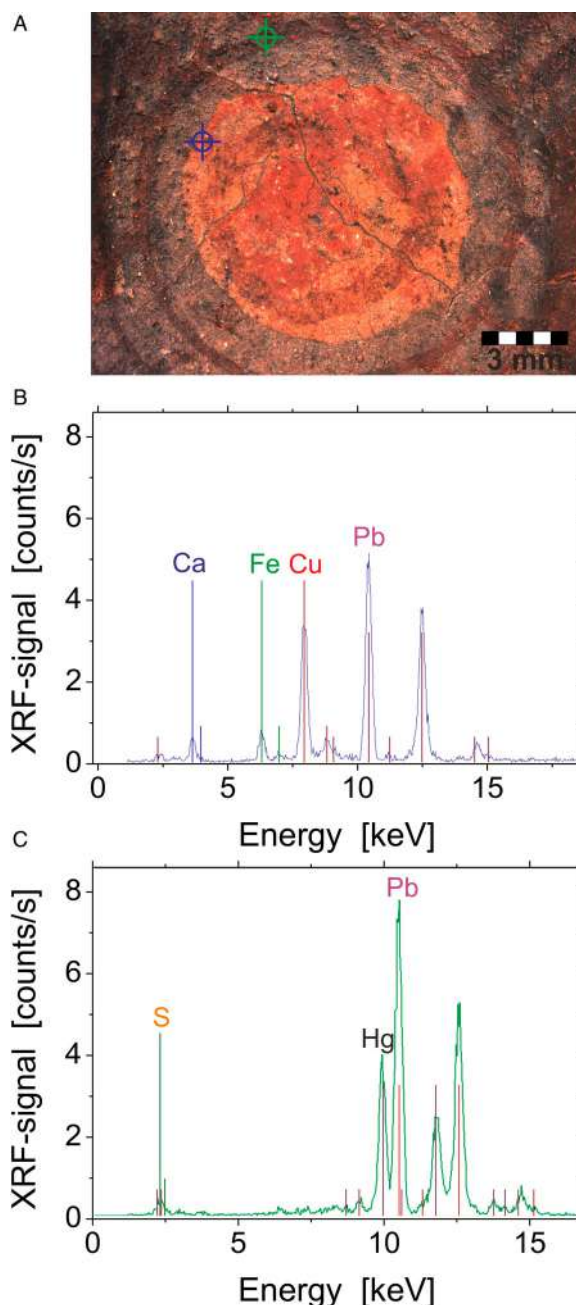


Figure 9 Detail of a decorative area of fragment V showing multilayered application of red paint (A). The blue and green marked areas indicate locations of XRF analyses (data shown in (B) and (C), respectively).

The blue paint layer (3) has a thickness of c. 70 µm on top of a ground with a thickness of c. 50 µm. Fig. 6B shows a cross section taken from a red paint area of fragment IV. Here, a c. 60 µm thick ground (2) covered by a c. 65 µm paint layer (3) and a contaminating soot layer a few µm thick (4) are visible. Both samples exhibit a single paint layer with comparable thicknesses. The composition of the individual layers is discussed in detail in the following sections.

Support layer: fine earthen render

For additional information about the support layer, EDX elemental mapping was performed on a cross section sample taken from a red paint area in fragment



Figure 10 Detail of fragment I (A) along with a more highly magnified detail (B) and a cross sectional image of a sample from the green paint area (C).

I. The red rectangle in Fig. 7A shows the area subjected to elemental mapping in order to visualize the distribution of typical constituents of the clay-based earthen render. Individual element maps are shown in Figs. 7C–J and a combined element map in Fig. 7B.

In the upper part of the sample mainly carbon is detected (Fig. 7D), corresponding to the embedding resin. The sample shows a paint layer rich in lead (Fig. 7F) and a calcium-based ground layer (Fig. 7H); these are discussed in the following sections. In the underlying support layer made of fine earthen render, the dominant elements are silicon, aluminum, potassium, calcium, iron, and magnesium. They are

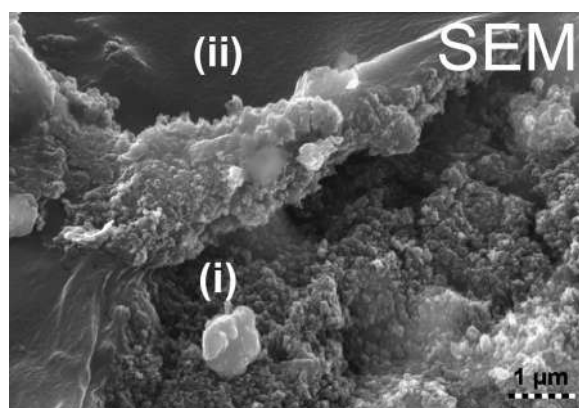


Figure 11 Secondary electron (SEM) image of a sample from fragment V (20° angle) showing (i) soot and (ii) synthetic binder.

all indicative of clay consisting, for example, of calcium carbonate, kaolinite, and iron- and magnesium-rich silicate minerals (Minke, 2004). It can be assumed that local materials were used for preparing the earthen render. The results of this and other analyses are summarized in Table 2.

Ground layer

In Fig. 7, the ground is clearly visible from its increased calcium signal (Fig. 7H). To obtain more precise information on the composition, a powdered sample was investigated by XRD. Fig. 8A shows a detail of fragment I, with the red rectangle representing the area sampled for XRD analysis. The spectrum is shown in Fig. 8B and exhibits the strongest peaks at 11.5°, 21°, 29°, 31°, and 33.5°, characteristic of gypsum (calcium sulfate dihydrate) as the main component (ICDD reference spectrum #33–311 from the PDF-2 database was used for comparison).

Gypsum is a soft mineral (Klein & Hurlbut, 1985) and it is found naturally in large deposits. During the calcination of gypsum, crystal water is lost and anhydrite (CaSO_4) is formed. This process was already known during the creation of the Sim-sim wall paintings, and Riederer mentioned in 1977 that gypsum and anhydrite were used as ground for preparing wall paintings in East Turkestan (Riederer, 1977). Since gypsum can be formed from anhydrite by incorporation of water, it cannot be determined conclusively whether gypsum was originally used in the preparation of the ground or whether we identify gypsum today as an alteration product of anhydrite. If gypsum was used for the preparation, it is not known whether it was obtained from a natural deposit or was artificially prepared.

The paint layers

White pigments

XRD analysis of a white paint sample from fragment V indicated the use of gypsum as a pigment (data not

Table 2 Summary of the results of pigment analysis and the methods employed

Layer	Results	Methods
Earthen render	Signals for Si, Al, K, Ca, Fe, Mg	SEM-EDX
Ground	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	XRD, SEM-EDX
Paint (pigments)	White: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	XRD
	Green: copper green pigments [atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$)]	Raman
	Red: mercuric sulfide (HgS) in the form of natural cinnabar; lead- and iron-containing red pigments	PLM, XRF
Soot deposits	Predominantly carbon detected	SEM-EDX

shown). As in the case of the ground layer, gypsum was likely used as an inexpensive material occurring in the area local to the cave and applied alone or in mixture with other pigments to change the appearance/brightness of a paint layer. The use of gypsum as an extender in other paint areas was shown by Riederer (1977), and in the current study, Raman spectra revealed its presence in a sample of green paint (data not shown).

Red pigments

Fig. 9A shows a detail of a red-painted area of fragment V. Different red pigments appear to have been used in a multilayered arrangement. In the two areas marked by blue and green circles, XRF analyses were performed; results are shown in Figs. 9B and C, respectively. In Fig. 9B, the peaks are indicative of the elements lead, iron, copper, and calcium. Lead was also detected by EDX analysis of the red paint layer in the cross section shown in Fig. 7, and these results suggest the use of a lead oxide pigment such as red lead. Raman spectroscopy has not yet been carried out to confirm the oxide form, and XRD analysis was not possible because of sampling restrictions. Analogous observations on the use of lead-based pigments were made by Riederer (1977) who associated the brown-violet painting areas with such pigments in wall painting fragments from Kizil. The peak in Fig. 9B corresponding to iron may indicate the use of an iron oxide-based pigment such as red ochre. However, since XRF will also generate a signal from lower layers in the painting, it is possible that the iron is present in a separate layer such as the earthen render. For the same reason, the calcium signal likely comes from the underlying ground layer. The reason for the presence of copper in the spectrum is not clear but it may also indicate an underlying paint layer.

In the spectrum corresponding to the dark red paint area, Fig. 9C, in addition to lead, mercury, and sulfur are detected, indicating a mercuric sulfide pigment. Because of the chemical similarity between synthetic vermilion and natural cinnabar, PLM was necessary to confirm the presence of cinnabar (based on

optical properties such as pleochroism and interference colors).

Green pigments

The surfaces of the green-painted areas exhibit poor condition particularly due to the delamination of large parts of the paint layers. This is exemplified in the detail of fragment I shown in Figs. 10A and B. The central damaged region in Fig. 10B indicates the location where a sample was extracted to prepare a cross section, shown in Fig. 10C.

Raman spectra were obtained from a separate sample to determine the green pigments. Bands were observed in the spectra indicating the presence of malachite (151, 179, 218, 269, 432, 509, 534, 1070–1097 broad band, 1366, 1493, 3315, 3380 cm^{-1}) and atacamite (119, 137, 148, 511, 818, 910, 974, 3351, 3435 cm^{-1}).

The soot layer

As visible in Fig. 3, the wall paintings are covered by a black soot layer of varying thickness that obscures their legibility. Already during the rediscovery of the Buddhist temple complex in Sim-sim in the year 1906, Grünwedel (1912) stated that in all ruins, free standing, and caves, strong scorch marks were evident. Hence, it is reasonable that a fire created the soot layer. The paintings underneath appear to retain luminous colors, however, as shown in the cross sections in Figs. 6 and 10. This indicates that they were not exposed directly to high temperatures and no direct fire damage seems to have occurred.

The cross section in Fig. 6B shows a polymer-covered soot layer of thickness up to 10 μm in the left part of the image. A detailed SEM magnification (Fig. 11) of a sample from fragment I indicates that the soot grain size is typically in the order of a few tens of nanometers. EDX confirms that the main soot constituent is carbon, although it must be noted that the polymeric *Caparol*[®] layer also generates a carbon signal. In the SEM image, it appears that the polymeric material did not completely embed the soot and instead forms a layer on the surface.

Conclusions

Central Asian wall painting fragments detached from the Buddhist cave no. 40 (*Ritterhöhle*) on the northern Silk Road were studied using microscopic and spectroscopic techniques. From close examination of the paint surfaces and the analysis of cross sections and pigment samples, it was shown that the artist(s) applied a single layer or several layers of paint on a white ground which had been applied to an earthen render. The earthen render was clay based and composed of rough and fine layers, and the white ground was composed primarily of gypsum. In the paint layers, gypsum, atacamite, malachite, and cinnabar were detected. Based on the elemental data and in comparison to the published literature, red lead and red ochre may also have been used, but their presence is still not experimentally confirmed. Additional deposits, namely a soot layer and a synthetic polymer consolidant, were also investigated. The soot covers the surface of the paintings and may be the result of an *in-situ* fire. Material transformations which can occur over time in complex materials such as those of wall paintings were not within the scope of this case study. The wall paintings at the Asian Art Museum are well documented both in the original expedition records and in earlier technical investigations by Riederer and others. Although the fragments are in poor condition, the combination of analytical techniques allowed the characterization of the paint stratigraphy and the pigments used. The results are consistent with earlier studies of wall paintings from this region.

Acknowledgements

The authors would like to thank Mario Sahre (BAM 6.7) for the XRF and XRD measurements, Sigrid Benemann (BAM 6.8) for the SEM-EDX analyses, the Rathgen Research Laboratory, Berlin, for loaning the Keyence digital optical microscope to the Asian Art Museum, and Christine Fuchs and Prof. Dr Steffen Laue (both FH Potsdam) for the support with the PLM and valuable discussions. They also thank Dr Jörn Bonse (BAM 6.4), Dr Ines Konczak and Dr Lilla Russell-Smith (Asian Art Museum), Kamilla Usabaev, Manuel Wiese, and Patrick Wolter for helping in the preparation of the manuscript.

List of suppliers

http://www.caparol.de/uploads/pics/caparol_import/caparol_de/ti/2570/TI_001.pdf

References

Agnew, N. ed. 2010. *Conservation of Ancient Sites on the Silk Road: Proceedings of the Second International Conference on the Conservation of Grotto Sites, Mogao Grottoes, Dunhuang, People's Republic of China, June 28-July 3, 2004*. Los Angeles, CA: Getty Conservation Institute.

- Birstein, V.J. 1975. On the Technology of Central Asian Wall Paintings: The Problem of Binding Media. *Studies in Conservation*, 20: 8–19.
- Blänsdorf, C., Pfeffer, S. & Melzl, E. 2009. The Polychromy of the Giant Buddha Statues in Bamiyan. In: M. Petzet, M. Jansen & E. Emmerling, eds. *The Giant Buddhas of Bamiyan: Safeguarding the Remains*. Berlin: International Council on Monuments and Sites (ICOMOS), pp. 237–64.
- Cotte, M., Susini, J., Solé, V.A., Taniguchi, Y., Chillida, J., Checroum, E. & Walter, P. 2008. Applications of Synchrotron-based Micro-imaging Techniques to the Chemical Analysis of Ancient Paintings. *Journal of Analytical Atomic Spectrometry*, 23: 820–8.
- Fischer, C.-O., Yaldiz, M., Leuther, W. & Slusallek, K. 1994. Neutron Autoradiography of Central Asian Wall Paintings. In: E. Mundry, ed. *Fourth International Conference: Non-destructive Testing of Works of Art, Berlin, 3–8 October 1994*. Berlin: Deutsche Gesellschaft für zerstörungsfreie Prüfung e.V., pp. 753–65 [in German].
- Gettens, R.J. 1938a. The Materials in the Wall Paintings of Bamiyan, Afghanistan. *Technical Studies in the Field of the Fine Arts*, 6: 186–93.
- Gettens, R.J. 1938b. The Materials in the Wall Paintings from Kizil, Chinese Turkestan. *Technical Studies in the Field of the Fine Arts*, 6: 132–8.
- Grünwedel, A. 1912. *Altbuddhistische Kultstätten in Chinesisch-Turkistan: Bericht über archäologische Arbeiten von 1906 bis 1907 bei Kuča, Qarašar und in der Oase Turfan*. Berlin: Reimer [in German].
- Klein, C. & Hurlbut, C.S., Jr. 1985. *Manual of Mineralogy*, 20th ed. New York: John Wiley, pp. 352–3.
- Kossolapov, A. & Kalinina, K. 2007. The Scientific Study of Binding Media and Pigments of Mural Paintings from Central Asia. In: K. Yamauchi, Y. Taniguchi & T. Uno, eds. *Mural Paintings of the Silk Road – Cultural Exchanges between East and West. Proceedings of the 29th Annual International Symposium on the Conservation and Restoration of Cultural Property, National Research Institute for Cultural Properties, Tokyo*. London: Archetype, pp. 89–92.
- Minke, G. 2004. *Das neue Lehm-Bau-Handbuch: Baustoffkunde, Konstruktionen, Lehmarchitektur*. Staufen bei Freiburg: Ökobuch-Verlag [in German].
- Pinault, G.-J. 1993–94. Une nouvelle inscription koutchéenne de Qumtura – Légende de scènes bouddhiques de Pranjidhi. *Bulletin d'études indiennes*, 11–12: 171–220 [in French].
- Riederer, J. 1977. Technik und Farbstoffe der frühmittelalterlichen Wandmalereien Ostturkistans. In: H. Härtel, ed. *Beiträge zur Indienforschung: Ernst Waldschmidt zum 80. Geburtstag gewidmet*. Berlin: Museum für Indische Kunst, pp. 353–423 [in German].
- Russell-Smith, L. 2012. In the Footsteps of Grünwedel: Conservation and Research on Central Asian Wall Paintings. *IDP News*, 40: 4–5.
- Taniguchi, Y. 2010. Conserving Mural Paintings as Intermediate Layers between Immovable and Movable Heritage: Case studies from Central and East Asia. In: *Japanese-German Colloquium Proceedings*, pp. 1–8 [accessed 07 January 2014]. Available at: <<http://www.tu-cottbus.de/fakultaet2/de/denkmalpflege/forschung/studentenworkshops/world-heritage-for-tomorow-what-how-and-for-whom/colloquium-proceedings.html>>
- Von Le Coq, A. 1926. Die buddhistische Spätantike in Mittelasien – Ergebnisse der Kgl. Preußischen Turfan-Expeditionen. Band I–VII, Berlin 1922–1926, pp. 116–7 [in German].
- Yaldiz, M. & Zieme, P. 1987. Archäologie und Kunstgeschichte Chinesisch-Zentralasiens (Xinjiang). Dritter Band Innerasien. Zweiter Abschnitt. In: J. Stargardt ed. *Handbuch der Orientalistik. Siebente Abteilung. Kunst und Archäologie*. Köln: Brill Academic Publishers, pp. 1–232 [in German].
- Yamauchi, K., Taniguchi, Y. & Uno, T. 2007. *Mural Paintings of the Silk Road – Cultural Exchanges between East and West. Proceedings of the 29th Annual International Symposium on the Conservation and Restoration of Cultural Property, National Research Institute for Cultural Properties, Tokyo*. London: Archetype.
- Zuixiong, L. 2010. Deterioration and Treatment of Wall Paintings in Grottoes along the Silk Roads. In: N. Agnew, ed. *Conservation of Ancient Sites on the Silk Road: Proceedings of the Second International Conference on the Conservation of Grotto Sites, Mogao Grottoes, Dunhuang, People's Republic of China, June 28–July 3, 2004*. Los Angeles, CA: Getty Conservation Institute, pp. 46–55.