In situ Raman microscopy applied to large Central Asian paintings

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Procedures and versatile Raman instruments are described for the non-destructive *in situ* analysis of pigments in large paintings. A commercial Raman microscope is mounted on a gantry for scanning paintings with dimensions exceeding 1 m². Design principles and the physical implementation of the set-up are outlined. Advantages/disadvantages and performance of the gantry-based instrument are compared with those of a mobile Raman probe, attached to the same Raman microscope. The two set-ups are applied to Central Asian thangka paintings. The utility of the gantry-mounted Raman microscope is demonstrated on a 19th century Buddhist painting from Buriatia, South Siberia. Surprisingly, three arsenic-based pigments, i.e. orpiment, realgar, and pararealgar, are found all in the same painting. Pararealgar is used for painting the numerous yellow areas. Realgar is admixed with red lead for adjusting its orange tint. Finally, orpiment is blended with Prussian blue for producing green. Traditional malachite is used in addition as a non-adulterated green pigment. The mobile Raman probe was employed for examining a Tibetan painting of the 18th century from Derge monastery in the Kham area of Sichuan. The highly unique painting could be dated well and its origin accurately located. In fact, the painter's workshop, where the thangka has been executed, is shown in great detail on the painting itself. The painter's palette of this thangka matches the canonical set of pigments used in Tibet for more than 10 centuries. Copyright © 2009 John Wiley & Sons, Ltd.

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Introduction

Pigments in ancient paintings provide a rich source of information on provenance, the date of production, and the development of painting traditions. Some pigments were locally available; others have travelled over long distances and served, sometimes, as convenient means of 'international currency,' being lightweight and of high monetary value. Knowledge of the pigments applied by the painter is also of great importance in the context of the conservation and restoration of ancient paintings. The scroll paintings to be studied in this project are rather fragile and often seriously damaged, requiring special care in conservation.

Non-destructive examination methods of objects are indispensable when investigating historical artworks. Picking pigment samples by mechanical means from precious paintings is highly undesirable. It is understandable that taking samples from paintings in public collections is discouraged by curators and conservators who care for the immaculate preservation of the irreplaceable heritage.

On the other hand, methods for the non-destructive analysis of pigments are rather scarce. X-ray fluorescence (XRF) spectroscopy is a powerful non-destructive method for determining the local atomic composition in paintings.[1–6] Sometimes, pigments can be identified uniquely by XRF. However, often ambiguities remain when several pigments possess similar atomic composition; and mixtures of pigments are notoriously difficult to disentangle.

Fibre-optic reflectance spectroscopy (FORS) in the visible and infrared is another method suited for the non-destructive identification of pigments.[7–10] However, the spectral resolution is often limited; and modern Raman spectroscopy is outperforming FORS in many applications.

Today, Raman spectroscopy is often the method of choice for non-destructive pigment analysis.[11–13] It provides information on molecular vibrations similar to infrared spectroscopy, but exhibits better resolved and unique spectra with characteristic bands. Excitation and detection procedures are normally part of a confocal Raman microscope. Raman microscopy has become a revealing tool for studies in the arts and in archaeology.[14–18]

The efforts described in this paper are parts of an exploratory project devoted to the identification of pigments in historic paintings on canvas. The studies concentrate on treasures from Central Asia. The painted area of these artworks can easily exceed 1 m². Two approaches are explored for investigating non-destructively large paintings by Raman microscopy: (1) A special design of *a gantry-mounted versatile Raman microscope* has been implemented. It allows free movements in two dimensions across a large painting surface under investigation; (2) *A mobile Raman probe*, attached via fibre optics to the Raman spectrometer, permits the exploration of painted surfaces tens of metres away from the usually rather bulky stationary Raman set-up. Both approaches are discussed in the following.

The current interests of the author focus on ancient Central Asian painting traditions and on the historical and local variability of pigments. Much of Central Asian art is connected to Buddhist traditions, all of which are related to Tibetan Buddhism. Buddhist paintings on canvas may originate from a wide geographic range covering Northern India, Nepal, Bhutan, Tibet, Central China, Mongolia, and even Buriatia in Siberia. A great number of Buddhist scroll paintings can be found in public and private collections and cover at least the past 1000 years. Buddhist wall paintings have

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an even longer tradition and are found, for example, in the world-famous Mogao Caves of Dunhuang in Gansu Province, China, and in the monumental Ajanta Caves in Maharashtra, India. Most of the scroll paintings are on cotton, rarely on silk, and sometimes on paper. The pigments are usually of mineral origin; and they are fixed to the canvas by hide glue.

Recently, we started an extensive series of experimental investigations of pigments on ancient scroll paintings from the above-mentioned countries and periods. The unlimited direct access to the author's personal collection of several hundred Central Asian paintings from the 12th to the 19th century proved essential for this study, which otherwise would have been very difficult to accomplish.

So far, few Raman studies of Asian paintings on fabric or paper support have been reported[19–24] in spite of the enormous wealth of such artworks in public and private collections. Raman investigations of pigments in frescos are somewhat more abundant.[25–30] This may be explained by the ease of sampling wall paintings by means of a tungsten needle or a scalpel without causing noticeable damage of the rather coarse fresco structures. Usually, one finds plenty of ancient defects, which permit virtually 'non-destructive' sampling. An Indian polychrome figure was also studied by Raman microscopy.[31]

Often, Central Asian paintings on fabric and paper are enormously detailed with essential sub-millimetre features. These details can be appreciated only by means of a good magnification glass or even a microscope. Obviously, sampling by mechanical means would cause irreparable damage of the details. Moreover, Buddhist paintings on canvas are frequently quite large, easily exceeding 1 m^2. In graphical terms, such paintings can possess more than 100 MB of visual information, rendering the spectroscopic investigation (as well as photography) quite demanding. A comprehensive Raman study of such elaborate paintings by mechanical sampling is clearly out of question.

This first publication by the author on pigment analysis by Raman spectroscopy describes procedures for *in situ* non-destructive Raman microscopy. The utility of the procedures is demonstrated on two thangka paintings, one from Buriatia, South Siberia, and one from the region of Kham in East Tibet. More extensive accounts of the exploratory endeavour on Central Asian thangka paintings will be published on other occasions.

Design of a Gantry-Mounted Raman Microscope

In collaboration with Bruker-Optics, Ettlingen and Fällanden, the author designed a versatile mount of a modified SENTERRA Raman Microscope Spectrometer (Bruker Optik GmbH) on a mobile gantry. The latter accepts large paintings with a width of 1200 mm and a length limited only by the accessible laboratory space. The dispersive Raman spectrometer SENTERRA that was used is equipped with two diode lasers operating at 532 nm with nominally 20 mW and at 785 nm with nominally 100 mW. The Raman module forms part of a split reflected-light brightfield/darkfield Olympus microscope BX51M.

The design of the gantry mount for the Raman microscope is illustrated in Figs 1 and 2. All the basic features of the high-quality Raman Microscope SENTERRA are retained by mounting the upper part of the Raman microscope, including all the optical components and the charge-coupled device (CCD) detector, on a gantry that can be moved in two dimensions across large paintings. The following features are incorporated in the design:

1. The microscopy table on which the investigated painting resides has an area (X/Y) of 1200/1000 mm. The gantry can be moved manually on steel rollers and steel shafts by 850 mm in the Y direction. The microscope itself is mounted on a carriage that can be moved across the gantry by 1100 mm in the X direction, again on steel rollers moving on steel shafts. (Due to limitations of the accessible laboratory space, the ranges of mobility in X and Y had to be slightly reduced for the first implementation of this design.)

2. The microscope is attached to the mobile carriage via a vertical linear translation stage (supplied by Bruker Optik GmbH). The z-axis position can be adjusted under computer-control to an accuracy of better than 1 µm for focusing the microscope. Autofocusing by means of a computer routine, forming part of the OPUS operating system, is also implemented.

3. The coarse positioning of the gantry can be done manually. For achieving a positioning accuracy of 1 µm, the painting to be examined is placed on an extended motorized and computer-controlled stage for movements in the incremental range of 150×150 mm.

The ease of operation of the gantry-mounted Raman microscope is virtually identical to that of a standard SENTERRA Raman Microscope. All the essential features of a standard Olympus BX51M reflected brightfield/darkfield microscope with objectives from $5\times$ to $100\times$ and with polarized optical observation are retained.

The instrument design is reminiscent of a SENTERRA Raman Microscope in operation at the Metropolitan Museum in New York. The latter incorporates also a modified mounting of the microscope part and an enlarged stage, accepting somewhat larger paintings than a standard Raman microscope (private communication by Marco Leona, The Metropolitan Museum of Art, NY 10028-0198; cf. Internet Address: http://www.cogito.org/Interviews/InterviewsDetail.aspx?ContentID=17267.).

Some Essential Construction Details

1. The design of Figs 1 and 2 allows most of the required mechanical elements to be procured commercially. The gantry is assembled from Kanya extrusion aluminium profile (Base 50 mm) with its proprietary PVS extrusion connecting system (Kanya AG, CH-8630 Rüti, Switzerland, http://www.kanya.ch/global/PVS-pdf/2003_PVS_engl.pdf). Also the steel rollers with ball bearings, running on 12-mm steel shafts, are chosen from the Kanya set of building blocks. Except for the plates that carry the steel rollers, little mechanical work arises where a professional workshop would be needed. The standard elements can be ordered from Kanya AG, pre-cut to the proper dimensions. Only the z-axis motional assembly with the screw-thread mount of the spectrometer, under computer-control, was specially manufactured and supplied by Bruker-Optics. The base rails, inserted into the 1080×1280 mm microscopy table, are using Base 40-mm Kanya extrusion profile.

2. The motions of the gantry in the Y direction and of the carriage in the X direction are guided by polycarbonate sliding extrusion profiles, inserted into the grooves of the aluminium
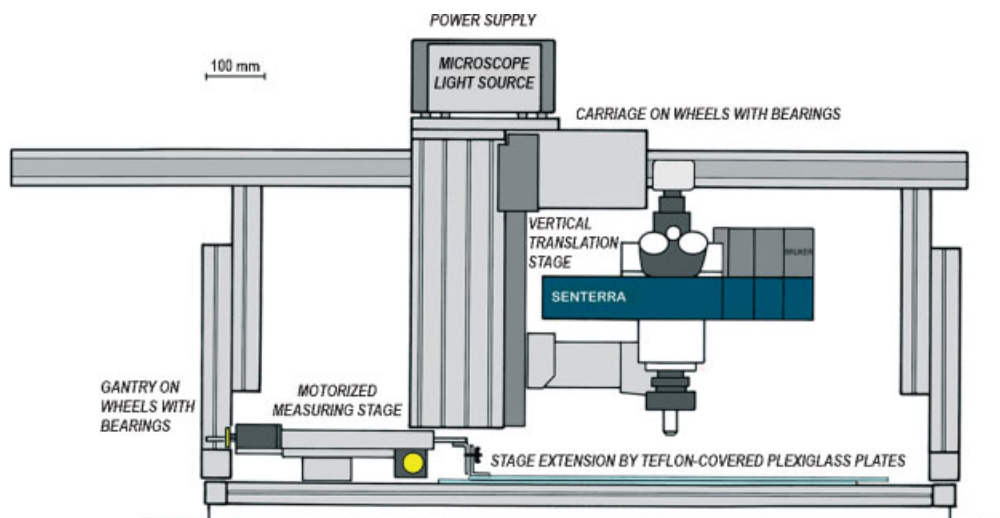
Figure 1. Front view of the gantry with the mounted SENTERRA Raman microscope. The mount consists of a ground plate of X/Y = 1200/1000 mm; a gantry on wheels with a free height of 500 mm; a carriage on wheels carrying the SENTERRA Raman microscope mounted on a motorized vertical translation stage; and a motorized measuring stage to which optionally a stage extension by Teflon-covered Plexiglas plates can be attached. The measuring stage can easily be removed for accommodating larger paintings.
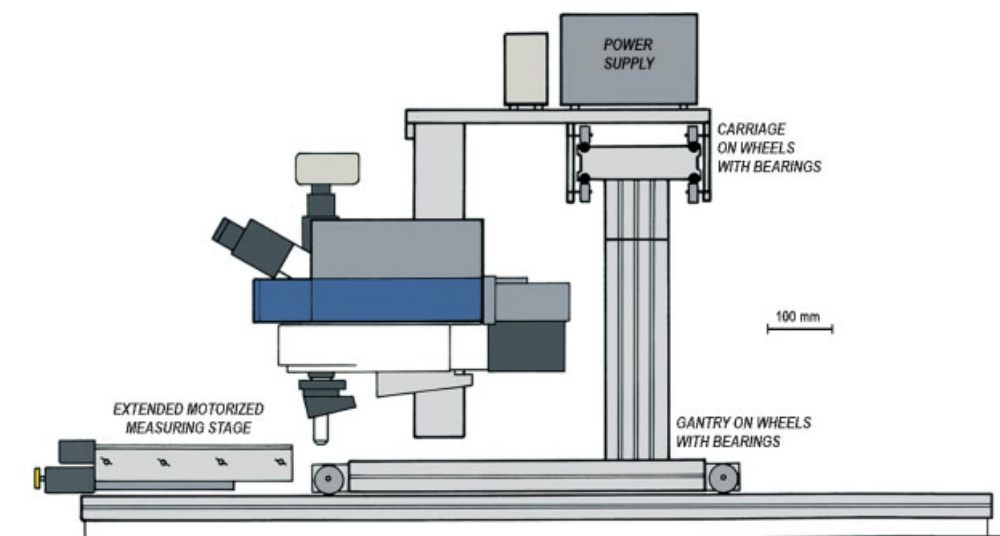

Figure 2. Side view of the gantry with the mounted SENTERRA Raman microscope. The stage extension by two Teflon-covered Plexiglas plates and the breaks, acting on the front wheels, mentioned in the text, are not shown.

profile, while the full load of carriage and gantry is borne by the steel rollers. For controlling the Y motion, two adjustable friction breaks (not shown in the drawings) have been installed. They act directly onto the wheels on the left and right leg of the gantry for adjusting the ease of motion and can arrest the gantry for particularly critical measurements.

3. The stage for moving large paintings is built around a commercial 150 × 150 mm microscope stage (supplied by Bruker-Optics). The object table of 300 × 211 mm can be moved under computer control by 150 mm in both X and Y by the OPUS operating system. Its repeatability of positioning is better than 1 μm. For accepting medium-size objects, such as small thangka paintings and tsakalis, the object table is extended to 450 × 320 mm by covering it with a 5-mm aluminium plate without measurably affecting the repeatability of positioning.

4. For the movement and for positioning of larger paintings under computer control, the stage is extended by attaching a 900 × 700 × 6 mm Plexiglas plate. It is gliding on another equally sized Plexiglas plate, residing on the microscopy table. Both are covered with self-adhesive 0.25-mm PTFE fibreglass cloth (Techflon, Technische Gewebe, D-78467 Konstanz, Germany) for reducing the motional friction. The upper Plexiglas plate is attached to the microscope stage (it can easily be detached by loosening five wing-nuts, as shown in Fig. 2) and tightly follows its motion. In this way, it is possible to move conveniently large (up to 1000 × 700 mm) and reasonably heavy paintings (up to 10 kg). Not unexpectedly, the repeatability of motion and positioning of this extension is reduced, especially at the end of the Plexiglas plate most remote from the point of fixation to the stage.

When working on even larger paintings, up to a maximum width of $X_{max} = 1200$ mm, it becomes necessary to move manually the Raman microscope on its gantry across the painting. Long paintings exceeding $Y_{max} = 850$ mm, can be brought by hand into a range that can be covered by the gantry motion. Here, obviously, some convenience and reproducible positioning must be sacrificed. Finally, the ultimate step towards investigations of objects without upper size limit is to take advantage of a fibre-optic Raman probe, as described below.

Stability Limitations of the Gantry-Mounted Raman Microscope

The larger the dimensions of the gantry, the longer the 'mechanical pathway' from the painting detail under investigation to the microscope objective and the more critical the stability issues. In the present design, the 'mechanical pathway' from the painting through the gantry, through the carriage, and through the screw-thread mount, to the microscope and to its objective can measure up to 3 m. It requires a stability of 1 part in 3×10^6 of the entire gantry assembly for maintaining an accuracy of positioning the objective to 1 µm. It is indeed amazing that under 'regular' conditions the necessary stability is met without difficulty. But 'irregular' events may occur that may affect adversely stability. For example, it is not permitted to touch during a measurement the microscopy table on which the gantry is residing or to stamp on the floor of the spectroscopy room. External vibrations, arising, for example, from construction work using heavy machinery, may also seriously affect stability and performance. The construction of a new motor road 100–300 m away caused serious perturbations. On 'bad days,' the measurement had to be postponed until evening after the workers' closing time! Sometimes, minor motions are tolerable, leading to spatially averaged chemical compositions, which are not undesirable. Installing the gantry on a vibration-isolated optical table would certainly ease the operation of the Raman microscope. Fortunately, Raman spectroscopy is less sensitive to motional artefacts than visual imaging; and excellent results could be obtained in the past without an optical table.

It was found that the halogen illumination lamp of the Olympus microscope can cause temperature effects on the focus and induce slow positional shifts of up to 20 µm in X and 40 µm in Y. Obviously, these drifts can be prevented by applying constant illuminating power during the entire experiment, reducing the drifts to less than 3 µm per hour in both directions.

In this paper, all indications of the laser power refer to power levels measured in front of $10\times$ objectives by a *LaserCheck* power meter from Coherent Inc. The ratios R of the measured laser power to the 'nominal' laser power indicated by the OPUS operating system of the SENTERRA Raman microscope are as follows: red laser at 785 nm for the SENTERRA microscope: $R_{S785} = 0.44$ and for the UNILAB Raman probe: $R_{U785} = 0.22$; green laser at 532 nm for the SENTERRA microscope: $R_{S532} = 0.67$.

Application to Pigment Analysis of a Thangka Painting from Buriatia That Includes Three Arsenic Sulfides

The utility of the gantry-mounted SENTERRA Raman microscope is demonstrated by a pigment study of an ancient painting

Figure 3. Thangka painting (ET98) from 19th century Buriatia depicting the 'Western Paradise', Sukhavati, with Buddha Amitabha in his palace surrounded by monks and reborn souls. In the lower half, two 'soul boats' are paddled by ferrymen across a lake into the Western Paradise. Below are shown two processions of monks and musicians, surrounding two appearances of the living Buddha Sakyamuni. The areas selected for Raman measurements, mentioned in the text, are marked by numbered rectangles.

from Buriatia, Southern Siberia. An accidental finding was the motivation for putting a special focus on arsenic-based pigments. More comprehensive studies of pigments in historical Central Asian paintings will be described in further publications.

Thangka paintings represent a most remarkable expression of Mahayana Buddhist tradition.[32–36] Thangkas are painted on a canvas, usually consisting of cotton, sometimes also of linen or silk. At first, the canvas is primed by applying a 'gesso' consisting of chalk, gypsum, or clay components. The binding medium for painting in distemper is hide glue, i.e. gelatine, prepared from the skins or bones of local animals, such as yaks.[37] The pigments consist primarily of finely powdered inorganic minerals, supplemented by a few organic dyes from plants. Some synthetic pigments, such as red lead, have been prepared already since ancient times by chemical procedures. The scroll paintings with their fragile surfaces, sensitive to humidity, are frequently rolled for storage and transports. Correspondingly, they often show serious damage by abrasion and require special care in conservation.

The thangka painting from Buriatia (designation: ET98) to be analysed is shown in Fig. 3. It depicts Buddha Amitabha in his

palace in the centre of the Western Paradise, called Sukhavati, a desirable place into which deceased Buddhist believers hope to be reborn. The painting was published in Ref. [38]. The philosophical and psychological significance of its contents are analysed in Ref. [39]. The painting, dealing with the process of rebirth, is quite remarkable by the unique appearance of two 'soul-boats,' each with a ferryman who paddles the souls of diseased Buddhists across a sacred lake, a reminder of Lake Baikal, into the Western Paradise. Some souls are being reborn into the Western Paradise, emerging from lotus flowers, the symbol of the origin of life, as is visible in the lower centre of Fig. 3. In the bottom part, two processions with monks and musicians, each with Buddha Sakyamuni in their midst, are shown. The strict symmetrical and geometrical arrangement of many details is a characteristic for the Buriatian painting style and differentiates itself from those of other areas of Central Asia, which prefer a more freely conceived design.

Buriatia is a rather latecomer in the Buddhist painting tradition with the earliest preserved paintings stemming from the 17th century. Most of the paintings that have survived originate from the 18th or 19th century. For the dating of the present painting, Raman spectroscopy will be of further help.

The Raman measurements on this thangka were made without removing the covering mineral glass of the painting, using a long-distance MPlan N 10×/0.25 Olympus objective with a working distance of 10.6 mm. Thus, the preparations for the measurements were minimal. The painting with its frame measures 750×560 mm. Much larger paintings have been explored recently with the same set-up.

Blue pigment

The blue pigment, dominating the sky and background, was found to be Prussian blue, $Fe_4[Fe_3(CN)_6]_3 \cdot 14-16H_2O$. Prussian blue exhibits in the Raman spectrum of Fig. 4(A) a solitary characteristic peak at 2154 cm^{-1}. Prussian blue is known to be a poor Raman scatterer, and the peak is invariably very weak and often not discernable within the rather strong fluorescence background. However, when visible, the peak can hardly be misinterpreted and clearly indicates the presence of this pigment in the painting. It is well known that Prussian blue was synthesized for the first time in 1704 by the colourist H. Diesbach in Berlin. It is also documented that Prussian blue was manufactured, among many other places, in Gorodets, Western Siberia, even before 1778.[40] It is therefore possible that this pigment has found its way from Gorodets to Buriatia and into the present painting. A dating of the thangka to the 19th century, probably to its first half, appears to be reasonable, also based on its characteristic painting style.

Red pigment

The red pigment, applied abundantly to this painting, is cinnabar, HgS, a very common pigment that occurs virtually in any coloured painting across entire Central Asia.

White pigment

The white pigment in this painting is lead white, $(PbCO_3)_2 \cdot Pb(OH)_2$.[41] It was applied, for example, for colouring the two soul boats as is verified by Fig. 4(B). In addition, it was also mixed with other pigments. For example, the blue areas (Fig. 4(A)) invariably contain some lead white for adjusting the tint of the rather dark Prussian blue.

In the course of this study, it was found that lead white is quite susceptible to damage by laser power, more than other pigments. Especially, the mixture of lead white and Prussian blue in the areas of sky and background could easily be impaired by the laser beam, as is demonstrated by Fig. 4(A). With laser power of 1.3 mW at 532 nm, no damage could be observed. However, irradiation by 3.4 mW at 532 nm for 20 s leads already to a significant attenuation of the lead white band at 1050 cm^{-1} and of the Prussian-blue band at 2154 cm^{-1}, as well. At the same time, two new Raman signals emerge at 143 and 289 cm^{-1}. These Raman bands closely correspond to massicot, which is orthorhombic PbO, possibly with a contribution from litharge, which is tetragonal PbO. The laser-induced decomposition reaction appears to be $(PbCO_3)_2 \cdot Pb(OH)_2 \rightarrow 3PbO + 2CO_2 + H_2O$. Visually, the paint layer is not damaged; and no 'hole burning' occurs. The characteristic lead white peak at 1050 cm^{-1} is often very weak (Fig. 4) and difficult to discern. On the other hand, the photodegradation products are exhibiting Raman bands of much higher intensity and may indicate the presence of lead white, even when the lead white band itself remains obscure.

It is revealing to compare the behaviour of lead white in the presence of Prussian blue with 'pure' lead white, as applied, for example, for the colouring of the soul boats. Figure 4(B) (blue line) shows clearly a lead white band at 1050 cm^{-1}. It was found that a 30-s irradiation of 3.4 mW at 532 nm reduces the background fluorescence level by 50%; further irradiation of 6.7 mW at 532 nm during 30 s cuts fluorescence by another 10%. But the Raman bands remain, so far, unaffected. Only when the laser power is increased to 13.4 mW for 20 s, the decomposition of lead white sets in with new resonance bands appearing at 143, 289, and 385 cm^{-1}. The variable relative band intensities in Fig. 4(A) and (B) suggest that the laser-induced decomposition of lead white leads to a mixture of lead oxides, predominantly containing massicot and litharge.

Lead white purum, as purchased from Fluka Company, product no. 15323, could not be damaged at all by the available laser power. However, heating to 270 °C on a heat stage leads to a similar decomposition, producing Raman bands at 143 (vs), 289 (s), 336 (m), and 385 cm^{-1} (w). This suggests again the presence of massicot and litharge. A careful study of the photodegradation of lead white and of lead oxides has been published by Burgio et al.[42] Similar observations have also been made by De Santis et al.[43] in a study of laser-induced degradation of pigments. These authors also stress the importance of Prussian blue in promoting the photodegradation of lead white, in agreement with the present accidental findings.

From surface-analytical measurements, it has been concluded by other authors that 'laser-induced discolouration' of lead white leads to the appearance of an altered surface layer containing elemental lead.[44,45] This process cannot be excluded by the present Raman measurements. However, the appearance of lead oxides by the degradation of lead white seems to be more relevant in the context of Raman studies.

Green pigments

The green aura of Amitabha is painted with malachite, $Cu_2CO_3(OH)_2$, a very traditional green pigment, used widely in Tibet and China. Often, green is obtained by mixing blue and yellow pigments. In South Asia, normally a mixture of indigo and orpiment, As_4S_6, is used for producing a warm green tone. This green is very abundant in paintings from India and Nepal,
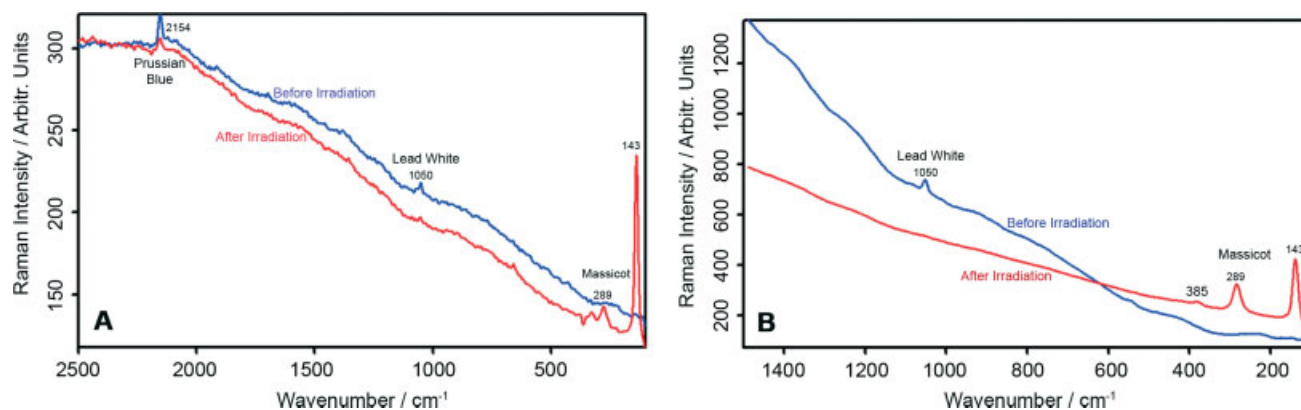
Figure 4. Decomposition of lead white by laser irradiation. (A) Area of blue background in thangka of Fig. 3 (marked □1). The spectrum recorded with 10×2 s scans of 1.3 mW at 532 nm (blue line) shows a Prussian blue peak at 2154 cm^{-1} and a lead white peak at 1050 cm^{-1}. Both peaks are notoriously weak and often not discernible. After continuous irradiation for 20 s with 3.4 mW at 532 nm, a second spectrum, recorded under the same conditions, (red line) reveals additional strong peaks at 143 and 289 cm^{-1}, indicating the partial conversion of lead white into massicot. (B) Area of white soul boat in thangka of Fig. 3 (marked □2). Spectrum recorded with 10×2 s scans of 1.3 mW at 532 nm (blue line) reveals a lead white peak at 1050 cm^{-1}. After irradiation with 13.4 mW at 532 nm for 20 s, a spectrum recorded under the same conditions (red line) shows strong peaks at 143, 289, and 385 cm^{-1} that correspond to massicot. The Prussian blue and lead white peaks are attenuated. Pure lead white shows no decomposition under the same conditions.
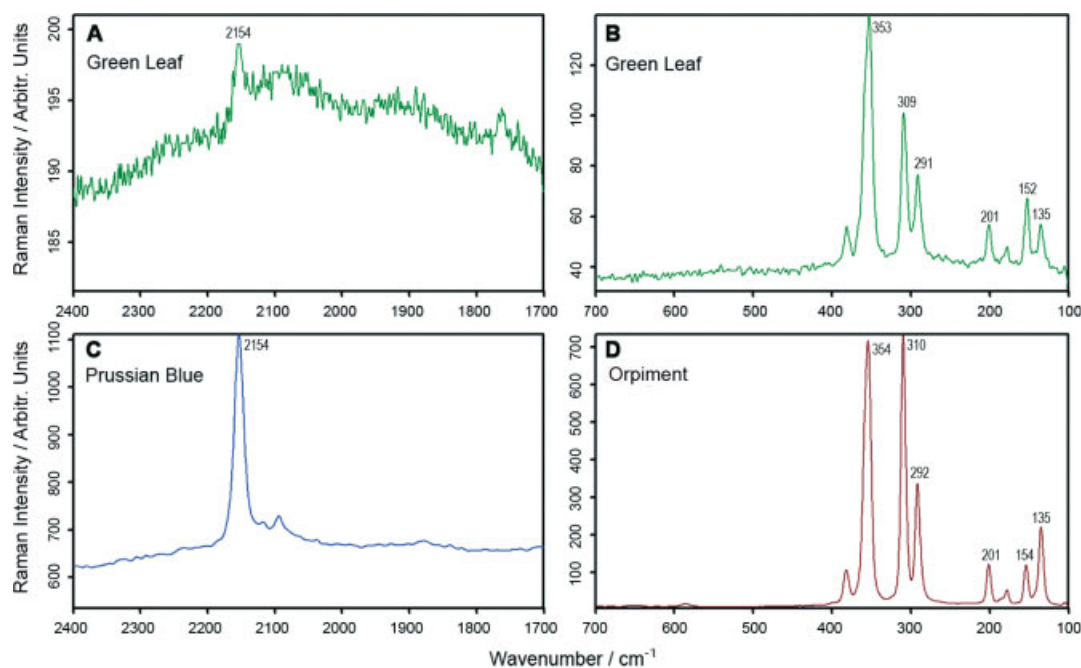

Figure 5. (A, B) Raman spectrum of a dark green leaf in thangka of Fig. 3 (marked □3), revealing the presence of Prussian blue and orpiment. The characteristic Prussian blue peak at 2154 cm^{-1} is rather weak. Spectrum A was recorded with 80×5 s scans with 1.3 mW at 532 nm, spectrum B with 10×10 s scans with 4.4 mW at 785 nm. (C) Reference spectrum of commercial Prussian blue (Redeker & Hennis, Nürnberg, ~1920) recorded with 10×4 s scans with 1.3 mW at 532 nm. (D) Reference spectrum of orpiment recorded with 10×4 s scans with 4.4 mW at 785 nm on a conglomerate mineral sample specimen from Realgar Mine, Shimen (Chujiang), Changde Prefecture, Hunan Province.

but occurs also in Tibet. In Northern regions, where indigo is less common, the latter is sometimes substituted by lazurite, $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$, or, as in the present painting, by Prussian blue, $Fe_4[Fe_3(CN)_6]_3 \cdot 14-16H_2O$. Indeed, one finds for the dark green borders of the meadow and for the green plant leaves in the lower half a mixture of orpiment and Prussian blue. The corresponding spectrum is shown in Fig. 5. While the orpiment bands are very strong, the Prussian blue peak at 2154 cm^{-1} is again difficult to discern; it just barely points out of the strong fluorescent background. But several repeated measurements confirmed its presence. Already the pure Prussian blue of sky and lake gave a

rather weak Raman peak; and an even weaker peak for the mixed green is no surprise.

The large variety of green pigments in Central Asian paintings is quite fascinating and revealing as will be discussed at another place.

Yellow pigments

Any bright yellow colouring in Central and East Asian paintings is normally associated with orpiment, As_4S_6. Indeed, orpiment was used quite abundantly up to the 19th century despite its poisonousness. The present painting contains several yellow areas,
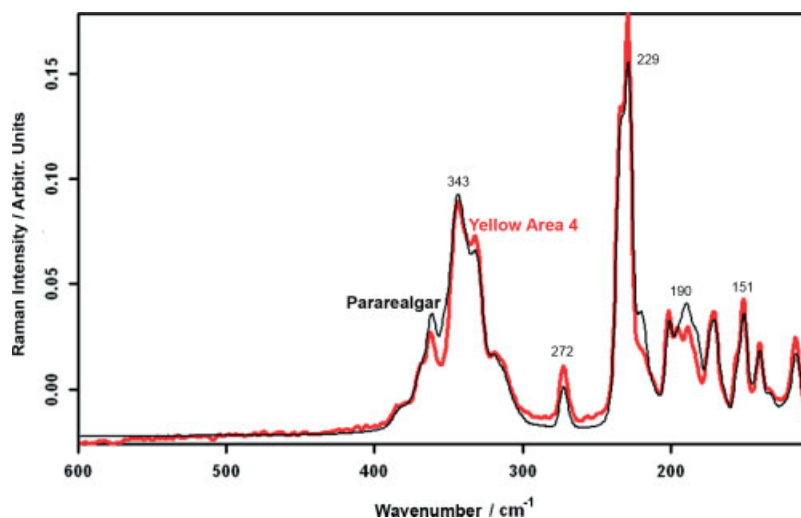
Figure 6. Raman spectrum of yellow area, marked ☐4 in Fig. 3, fitting perfectly to a spectrum of pararealgar. Instead, orpiment would have been expected! The spectrum was recorded with 10 × 2 s scans and 4.4 mW at 785 nm. The reference spectrum of pararealgar was obtained with 10 × 4 s scans and 4.4 mW at 785 nm on a mineral sample specimen from Realgar Mine, Shimen (Chujiang), Changde Prefecture, Hunan Province.
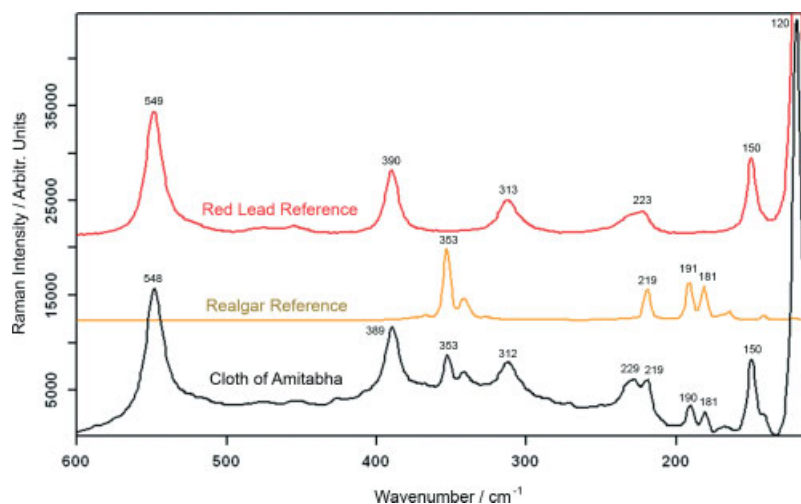

Figure 7. Raman spectrum of the orange cloth of Amitabha (black line), marked ☐5 in Fig. 3, showing the presence of red lead and, surprisingly, of realgar for adjusting the tint. The spectrum was recorded with 50 × 2 s scans with 4.4 mW at 785 nm. The reference spectrum of red lead (Kremer no.4250) (red line) was recorded with 10 × 4 s scans with 4.4 mW at 785 nm. The reference spectrum of realgar (orange line) was recorded with 10 × 4 s scans with 4.4 mW at 785 nm on a mineral sample specimen from Realgar Mine, Shimen (Chujiang), Changde Prefecture, Hunan Province.

such as the framework of the five temples, the two yellow monks in the lower procession, and the yellow part of the two-coloured scarp left and right of the vase in the bottom centre. They all exhibit the same Raman spectrum, shown by the red line in Fig. 6. Surprisingly, this spectrum does not fit the expected spectrum of orpiment, As_4S_6. However, it closely matches the spectrum of pararealgar with the formula As_4S_4, represented in Fig. 6 by the black line. Pararealgar is a light yellow to orange-brown mineral found at numerous places, for example in British Columbia, Canada, but also in China and in Central Asia.

It has often been emphasized that pararealgar results from a sun-light-induced conversion of the better known but less stable realgar, As_4S_4, an orange-red mineral. Because the application of pararealgar as a pigment in Central Asian scroll paintings was so far virtually unknown, it would be tempting to attribute its presence to this light-induced degradation of realgar. To check for a possible sun-light effect, a Raman depth profile was recorded. It did not show the slightest variation throughout the entire paint layer in all three dimensions. It is thus likely that, indeed, pararealgar was used as a veritable yellow pigment in this painting, replacing the more common orpiment. The reason for the painter's preference is unknown.

So far, only rare occasions around the globe have been reported in literature where pararealgar was applied as a pigment. In Western paintings, the most remarkable findings, to the author's knowledge, refer to a painting in the Winnipeg Art Gallery (Canada), which has been tentatively attributed to the School of Titian[46], and to a painting by Tintoretto (1518–1594) 'The Dreams of Men.'[47] In a 13th century Byzantine illuminated manuscript, all three pigments: i.e. orpiment, realgar, and pararealgar, were discovered; and is argued by the authors that the painter purposely took advantage of the colour shades of the three arsenic sulfides.[48,49] Further observations of pararealgar have been made on an Egyptian papyrus,[50] in Iraqi stuccoes from Samarra,[51] and within

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illuminations of 16th to 18th century Islamic manuscripts.[52] The author is aware of only a single report on the usage of pararealgar as a pigment in Central Asian painting art.[28] It refers to mural paintings within a 15th century Buddhist temple in Nepal where gilding was applied to a priming layer consisting of pararealgar and small amounts of orpiment. In all these cases, the question was raised whether pararealgar might arise as a photodegradation product of realgar or as an autonomous pigment.

The painting from Buriatia exhibits yet another yellowish pigment in the rows of tiles of the five temples, the frame of the painting, the two ladders, and the lower part of the dress of Amitabha (Fig. 3). Orpiment was expected again, although the tint is a little bit too brownish. Raman scattering revealed, however, a spectrum with only two rather weak bands at 143 and 1052 cm^{-1}. The latter peak corresponds undoubtedly to lead white. The peak at 143 cm^{-1}, on the other hand, must be responsible for the yellowish tint. Tentatively, we assign it to a low concentration of massicot, orthorhombic PbO. It is rather unlikely that the yellow colour is the result of degrading of lead white, as discussed above; the mentioned areas need to be yellowish for functional reasons and cannot have been painted in white originally.

The painting of Fig. 3 is indeed remarkable by the extensive usage of pararealgar. Not many other paintings are known with such a large-scale application of this rather unusual pigment.

Just before completion of this study, the author discovered accidentally pararealgar in yet another thangka painting (painting designation: ET830), showing as the central figure the deity of death, Yama on a bull, accompanied, as usual, by his sister Yami. It was acquired from Ulaanbaatar, Mongolia. A possible origin of the painting, or of the applied yellow pigment, from neighbouring Buriatia cannot be excluded nor confirmed. The painting is remarkable by the fact that the two yellow pigments pararealgar and orpiment are used side by side, orpiment with a little bit more brownish shade. Again, a Raman depth profile was taken without any significant depth variation. Although by Raman microscopy a few grains of realgar were accidentally found in the pararealgar layer, it is likely again that pararealgar was the originally applied pigment. This opinion is supported by the fact that orange tints in other parts of the painting are achieved by a variable mixture of orpiment and cinnabar, for example in the yellow-orange flames of the fierce deities. Thus there was no obvious need for another orange pigment, such as realgar. Based on further pigments found in this painting and on stylistic considerations, ET830 is likely to originate from the late 18th century.

Orange pigments

Orange-red shades in thangka paintings are usually produced by the ancient synthetic pigment red lead,[53] Pb_3O_4, which is occasionally mixed with red cinnabar, HgS, to adjust its tint. Surprisingly, however, for this painting, red lead was blended with realgar. For example, the orange-red cloth of Buddha Amitabha is painted with this mixture. The addition of realgar leads to a rather subtle change in tint that was obviously essential to the painter. The corresponding Raman spectrum is shown in Fig. 7 and compared with the reference spectra of its two components.

It appears that the skilled Buriatian painter had a large variety of pigments at hand, including the three arsenic sulfides mentioned. *A priori*, it is not possible to exclude the possibility of their synthetic origin. Several recipes are known for the synthesis of orpiment and realgar.[54] They start all with arsenic trioxide (As_2O_3) and sulfur.

Normally, the synthetic product contains a significant remainder of white arsenic trioxide. The latter possesses a characteristic Raman spectrum with a very strong peak at 372 cm^{-1} and two peaks at 271 and 563 cm^{-1}. None of these was found in the present spectra. It is thus likely that the pigments have a mineral origin. Well-known mineral deposits in Russia, which could have supplied orpiment, realgar, and pararealgar, are the Elbrusskiy mine in the Northern Caucasus and mines of Yakutia in Siberia.

As a side line, it may be mentioned that orpiment is also an unstable pigment. It can decompose, in time, into arsenic trioxide and sulfur. Both decay products form pronounced (cubic and orthorhombic, respectively) crystals that are, sometimes, well visible in ancient paintings. They may give the yellow areas a glittering appearance as if mica had been incorporated into the paint. This explanation of a widely observed phenomenon was published first by Leona and Jain.[21] The remarkable glittering effect is thus due to aging of the pigment and was not caused by purpose. It can also be seen in several ancient paintings within the author's personal collection.

An Alternative Solution: the Fibre-Optic Raman Probe

A newly developed Raman Video Probe, the 'UNILAB Probe', was purchased recently from Bruker Optics for remote Raman studies of pigments in paintings that cannot easily be transported to the stationary Raman microscope. A fibre-optic light guide of 50 µm diameter feeds the laser beam of the SENTERRA Raman microscope to the UNILAB Probe, while a light guide of 300 µm diameter carries the Raman signal back to the Raman microscope. Two light guides with a length of 30 m were acquired in order to allow for convenient measurements also in other exhibition rooms, even on other floors of the building without having to move the Raman microscope. The purchased Raman probe can be used, however, only for the red 785-nm laser.

The UNILAB Probe is equipped with a digital camera that generates a 720 × 576 pixel colour image of the sampled area. For operational convenience, it is necessary to place a second computer in direct vicinity of the UNILAB Probe for localizing a suitable measurement spot on the painting and for checking the focusing. A DELL X1 laptop was installed on the mount of the UNILAB Probe. In this way, a photographic image of the sampled area can be recorded. It is possible, in principle, to operate the SENTERRA Microscope computer remotely from the front-end computer; but such a feature has not yet been implemented, without causing too much operational inconvenience.

The UNILAB Probe incorporates standard infinity-corrected optics with an RMS 25-mm thread. The measurements described below utilize a 10×/0.20 Zeiss Epiplan objective No. 442930 with a convenient working distance of 18.5 mm. Other objectives can be used as well. In particular, the lens supplied by Bruker-Optics for the UNILAB Probe gives Raman signals stronger by a factor 2 but has rather poor video imaging properties.

The Raman probe was mounted on a heavy Manfrotto tripod, equipped with wheels. To allow for reaching heights of up to 2.5 m, a quadratic 40-mm Kanya rail profile of 1100 mm length was mounted vertically on the tripod. To this rail, a horizontal side arm of 700 mm length was attached, borrowed from a Sinar large-format camera system (Sinar AG, CH-8245 Feuerthalen, Switzerland). (The side arm could easily be extended by further

Figure 8. Photograph of the mount of the Raman UNILAB Probe (Bruker Optics) in front of the thangka ET10 of Fig. 9. A Manfrotto tripod on wheels (not visible) was vertically extended by a 40 × 40 mm Kanya rail. It holds a horizontal arm, taken from the Sinar large-format camera module system, that carries a Sinar P Front Standard allowing the UNILAB Probe to be moved in a controlled manner in all directions. The video image of the area sampled by a 10× objective is displayed on a Dell X1 computer screen.

Sinar system elements.) The Raman probe is attached to a Sinar P Front Standard, which allows controlled movements and tilts in virtually all directions. The Raman probe can easily be mounted and detached by a single winged screw. The upper half of the mount is shown in Fig. 8.

The stability of the mount was of some concern. However, it was found that the major source of instability is actually not the tripod itself but minute movements of the floor on which tripod is positioned; and there is little universal remedy to improve this situation. But with some care, excellent measurements are nevertheless feasible.

Not surprisingly, the optical performance of the UNILAB Probe is somewhat reduced in comparison to direct measurements with the stationary SENTERRA Microscope. Using the 785-nm laser with a nominal output of 100 mW, 44 mW is available at the focus of the 10×/0.25 Olympus objective being part of the SENTERRA Microscope, while 22 mW is measured at the focus of the 10×/0.20 Zeiss objective of the UNILAB Probe (measured with a *LaserCheck* power meter of Coherent Inc.). Thus only a factor 2 in laser power is lost through the 30 m of fibre-optic cable from the microscope to the UNILAB Probe. The loss in Raman signal returning to the microscope is larger. Measurements with the UNILAB Probe produce a signal weaker by a factor 8 than when the same sample is measured with the Raman microscope using the same objective. In spite of this marked loss, in many situations the sensitivity of the UNILAB Probe is more than adequate for obtaining excellent Raman spectra.

The application of the UNILAB Probe, described in the following, is certainly not the first reported usage of portable Raman equipment for pigment analysis. In Ref. [55], for example, the usage of a Renishaw RP10 compact spectrometer and the application of a portable micro-Raman apparatus of Horiba Jobin-Yvon, Model HE, are described for characterizing pigments in medieval illuminated manuscripts. Another group has used a Renishaw fibre-optic Raman micro-probe for exploring hand-crafted wallpaper.[56] Further applications of a modified Spectracode portable Raman imaging microscope are mentioned in Ref. [57]. Indeed, mobile Raman probes have become quite popular during the past years for application in the context of cultural heritage.

Figure 9. Detail of thangka ET10, painted in Derge monastery, East Tibet, in the workshop of the great Master Zhu-chen about 1760–1770. The entire thangka[35,58] depicts scenes from the monasterial life in Derge monastery and from the life of the Ngor-pa scholar Rin-chen-mi-'gyur-rgyal-mtshan (b.1717). The detail displayed[59] shows the painter's workshop with the Master Zhu chen in the room on the right, outlining the drawing for a thangka in black ink, and in the room on the left, monk and lay disciples are filling in the colours according to the Master's prescriptions. The areas studied by the UNILAB Probe, mentioned in the text, are numbered 1–4.

Performance of the Unilab Probe Demonstrated on an 18th Century Thangka from Derge Monastery

The thangka (designation: ET10) chosen for demonstrating the UNILAB Probe is highly unique for historic and artistic reasons. The full painting (measuring with its frame is 800 × 1400 mm) has been published in Ref. [58], pl. 63, and Ref. [35], pl. 114. Based on the Tibetan inscriptions and the narrative representations, the origin of the thangka can be associated with the Sa-skya-pa Monastery of Derge in the Kham area of East Tibet, presently administered by the Kandze Autonomous Prefecture of Sichuan Province. According to the inscriptions, it was executed within the workshop of the great master Zhu-chen Tshul-khrims-rin-chen (1697–1774).[58] Zhu-chen was a gifted master painter and an influential editor as well. He is known for having edited the Derge print version of the Tengyur, a monumental 213-volume collection of Tibetan wisdom. The thangka was painted on the occasion of a visit of the Ngor-pa scholar Rin-chen-mi-'gyur-rgyal-mtshan (b.1717), who acted from 1746 to 1751 as Abbot of the famous Ngor Monastery in Central Tibet, which also belongs to the Sa-skya tradition, and was home of a stupendous mandala painting school. The Monastery of Derge had particularly close relations to the Ngor-pa school. It is likely that this visit took place around 1760–1770. Rin-chen-mi-'gyur-rgyal-mtshan is known to have founded in 1767 the Lhagyel monastery (lha rgyal dgon) in Gonjo County not too far from Derge. (The Tibetan Buddhist Resource Center, Rubin Museum of Art, New York; c.f. the Internet address: http://www.tbrc.org/kb/tbrc-detail.xq;jsessionid=7561E93F8C6513238DCF1FE553B666F2?RID=P5947). The thangka shows scenes from Derge monastery itself and from the life of its important visitor.

Surprisingly, the painting permits a very rare glimpse into the 18th century painters' workshop of Zhu-chen on the middle right of the painting. The relevant detail with the workshop is shown in Fig. 9. The workshop consists of two rooms. On the right, the master is outlining the painting in black ink on the canvas, adopting instructions from a wide script resting on his lap. He is assisted by a monk who re-mounts the canvas, by a monk preparing the black ink on a mixing palette, and by a small monk holding the ink pot. In the second room, monk and lay painters apply the coloured pigments, following the coded instructions that the master has inscribed onto the canvas.

Single-letter-coded instructions in black ink are frequently used to identify the pigments to be applied.[37] The codes become invisible in the finished painting as they are covered by the paint layer. However, with an infrared camera that penetrates many of the pigments, they can easily be brought to reappear. Several areas in this painting have been marked in this way. One can find the Tibetan letter 'la' for minium orange (*li khri*) and the Tibetan letter 'ma' for cinnabar red (*dmar*). A convenient tool for finding these codes, hidden underneath the pigment layer, is an infrared scope, such as the *Find-R-Scope 84499A* by FJW Optical Systems, Inc., equipped with an *80389 close-up lens*. As an alternative, it is also possible to record directly an infrared photographic image. It is easy to convert commercial digital cameras into infrared cameras by attaching a front-end infrared filter, for example the filter *Infrared RM90* by Hoya Corporation. Many pigments, but not all, are infrared-translucent. It is, for example, difficult to penetrate malachite and azurite, as well as black pigments.

The Raman measurements with the UNILAB Probe have been made on the painting hanging at its regular exhibition place,

remote by two doors from where the SENTERRA Raman microscope is installed. The connection was established by the 30-m fibre-optic cables mentioned above. The mineral glass covering the painting was not removed for the Raman studies. As was expected, measuring with a single UNILAB Raman probe, in this case tuned to 785 nm, limits the identification of all pigments in the painting. Ideally, two UNILAB Probes tuned to 532 and 785 nm, respectively, would be necessary for a comprehensive investigation.

Red pigment

It was no surprise that the abundant dark-red pigment in the painting consists again of cinnabar, HgS. For example, the darker parts of the dress of the master painter at work in the painter's workshop (marked by '1' in Fig. 9) are coloured with cinnabar, mixed with the white pigment gypsum, $CaSO_4 \cdot 2H_2O$, with a peak at 1007 cm^{-1}, as is documented in Fig. 10. Cinnabar occurs at numerous other places in this painting.

Orange pigment

The brighter orange-red parts of the master painter's cloth (marked by '2' in Fig. 9) are coloured with red lead or minium, Pb_3O_4, as verified by a characteristic Raman spectrum shown in Fig. 10. There is again a weak peak at 1007 cm^{-1}, indicating the presence of gypsum, possibly for adjusting the tint or as a gesso component. The interplay of the two reds is a traditional means of Tibetan painting art for enlivening scroll paintings and tsakalis. Advantage has been taken of this combination since very early times, in the author's collection documented by paintings from the 12th to the 13th century. The red parts of the tricoloured monastery walls are also coloured by red lead. Tricoloured monastery walls (blue, red, white) are characteristics of Sa-skya-pa monasteries still today.

White pigment

According to our Raman measurements, two different white pigments were utilized in this painting. As mentioned above, gypsum was mixed with coloured pigments, such as cinnabar, red lead, and azurite. Gypsum was also used as part of the gesso for priming the cotton canvas on which the coloured pigments were then applied. Wherever the surface paint layer is locally damaged, one finds underneath a gesso layer that contains gypsum with a peak at 1007 cm^{-1}. For example, in the white areas of the tricoloured walls, one may peek through such cracks to verify underneath the presence of gypsum.

On the other hand, it was found that the polished white surface paint layers are free of gypsum and produce a rather dull Raman spectrum without any sharp lines. Sometimes, a broad band appears near 915 cm^{-1}. This excludes not only gypsum but also the other common white pigments, such as chalk and lead white. The most likely white pigments forming the white areas in this painting and exhibiting bands near 915 cm^{-1} are clay materials, i.e. calcium, magnesium, and aluminium silicates. For example, the Al–OH libration bands of kaolinite [triclinic $Al_2Si_2O_5(OH)_4$] and dickite [monoclinic $Al_2Si_2O_5(OH)_4$] lie at 916 and 915 cm^{-1}, respectively.[60] To identify positively these pigments in a complex environment is rather difficult with the available Raman techniques. Often, they produce strong fluorescence and interfere with the detection of other pigments. Gesso pigments were needed in large quantities for covering the canvas, usually on front and back sides. For this reason, they had normally a local
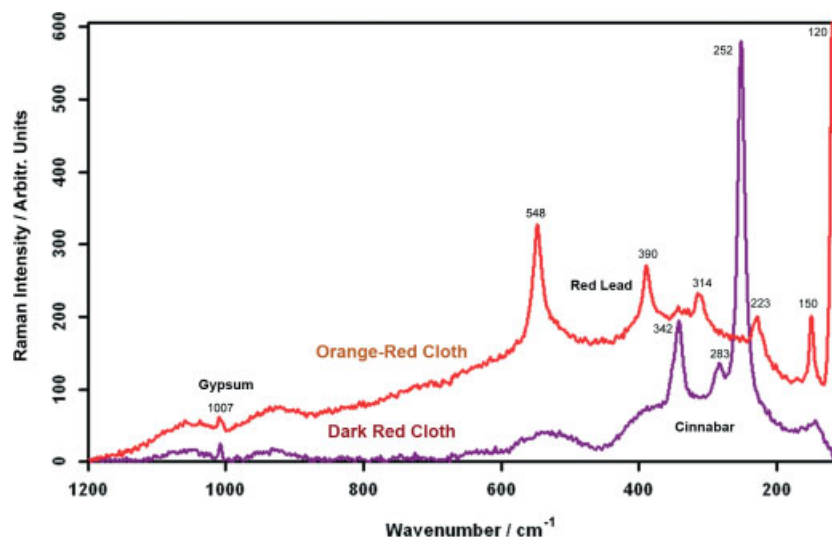
Figure 10. Two Raman spectra of the dress of the master painter in the painter's workshop of Fig. 9. The dark-red cloth (marked by '1' in Fig. 9) reveals the presence of cinnabar, blended with gypsum. The spectrum of the orange-red cloth (marked by '2' in Fig. 9) shows the presence of red lead, also blended with gypsum. Both spectra were recorded with the UNILAB Probe, 10 × 4 s scans, and 22 mW at 785 nm. No damage by the relatively high laser power was noticed.
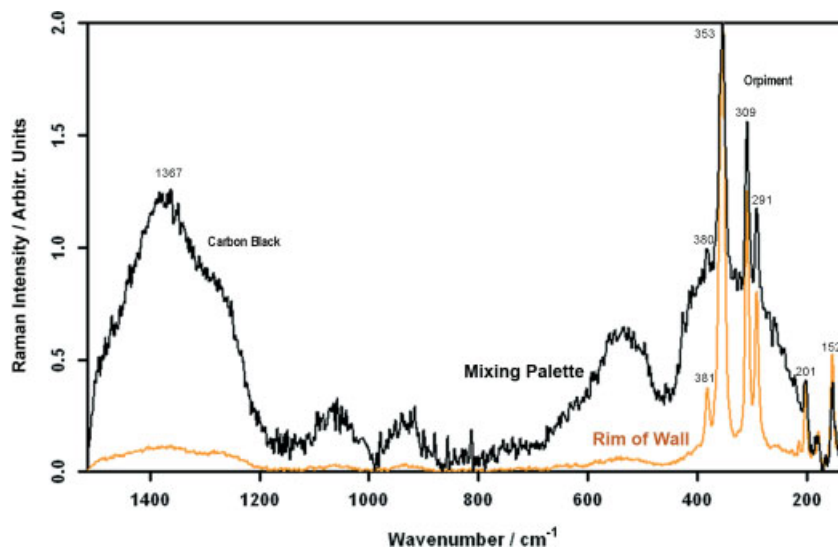

Figure 11. Black line: Raman spectrum of the mixing palette (marked by '3' in Fig. 9) in use by a monk in the Master painter's room. The spectrum shows that the palette was painted in orpiment and carbon black (band near 1400 cm^{-1}), representing the ink in preparation. Orange line: The Raman spectrum of the brown-yellow rim of the monastery's wall (marked by '4' in Fig. 9) revealing unambiguously orpiment. Both spectra were recorded with the UNILAB Probe with 10 × 4 s scans and 22 mW at 785 nm. No damage by the relatively high laser power was noticed.

origin; and whatever white material was available has been used as a gesso. Commonly utilized gesso pigments were chalk, gypsum, and clays. For shining a clearer light on the question of these gesso pigments, XRF and X-ray crystallography would be helpful.

Yellow pigment

The mixing palette of the monk helper in the Master's workshop (marked by '3' in Fig. 9) is painted in orpiment (Fig. 11). It is covered in the centre with carbon black with a broad band near 1400 cm^{-1}, representing the ink that is just in preparation for the Master to be applied. For comparison, the orpiment spectrum of the yellow rim of the monastery wall (marked by '4' in Fig. 9) is shown in Fig. 11. The only yellow pigment found in this painting is orpiment; realgar and pararealgar have not been detected.

Blue pigments

Blue pigments are difficult to discern with the 785-nm laser alone. Nevertheless, from measured blue areas, weak signals for azurite, $2CuCO_3 \cdot Cu(OH)_2$, were localized at 403 cm^{-1}. Azurite is indeed the most common traditional blue pigment in Tibet. It dominates Tibetan paintings, except where indigo was in use that had been brought into Tibet first by migrant painters from Nepal.

Green pigments

Green pigments are notoriously the most difficult ones to be measured with a 785-nm laser. Indeed, no decent signals of green pigments could be found. However, from its appearance and

from comparisons with other paintings, it is likely that the green pigment in this painting is malachite, $CuCO_3 \cdot Cu(OH)_2$.

In conclusion, this fascinating painting from Derge exhibits a typical classic Tibetan palette of pigments that has been in use for more than 10 centuries.

Concluding Remarks

The Raman spectroscopic tools presented in this paper proved to be useful for *in situ* pigment studies. They eliminate all needs of picking pigment samples from large paintings for microscopic Raman examinations. It is possible to perform all required measurements directly on the paintings in an entirely non-destructive manner. The described instrumentation may widen the range and power of Raman spectroscopic studies, especially for precious cultural heritage objects. For example, it is conceivable to map the pigment distribution by computer-controlled scanning of larger areas, a task that is virtually impossible to perform by picking samples. *In situ* Raman measurements, undoubtedly, are a first choice for studying pigments for the almost inexhaustible wealth of incredibly detailed and finely painted Central Asian thangkas. Non-destructive testing is indeed essential in this context and well justifies the efforts described in this paper.

A handicap of *in situ* Raman measurements is the omnipresence of the supporting medium with fabric and gesso used for priming. These materials often cause strong fluorescence signals that might compete with the weak Raman signals of a thin pigment layer. Sometimes, it is rather difficult to localize even the strongest peak of a particular pigment, not to mention the possibility of multiple-peak fingerprinting of pigments. In unfavourable situations, their identification may remain uncertain. Clever procedures for automatic fluorescence rejection (AFR) that are based on measurements at two shifted laser frequencies[61] can improve the situation in marginal cases only where the peaks are already barely discernable. In the presence of an unstructured fluorescence background that fully covers the relevant signals, these remedies are of little practical usage.

A remote, mobile Raman probe is an indispensable tool in situations where the object to be explored cannot be fitted into a stationary Raman set-up. However, Raman probes possess also their inherent disadvantages. Sensitivity is lower than for a stationary Raman microscope. Stability issues become of concern; and the flexibility of the probe may be limited. With the Raman probe used in the present work, only one laser frequency was available; and having to use separate probes, one for each laser frequency, would render virtually impossible multiple-frequency investigations at the same sample spot. The change of objectives on a Raman probe in the midst of a measurement series is also inconvenient, as usually no objective turret is installed.

For extended studies, it is advisable to employ, whenever possible, a versatile gantry-mounted Raman set-up as described above. It usually pays out to move paintings to the Raman installation where all features of the Raman microscope can be used and where an undisturbed working atmosphere is warranted.

Note Added in Proof

One of the referees added the following illuminating comment regarding the question of a realgar–pararealgar conversion taking place within the paint layer: 'It may be of use to the author that I did find pararealgar seemingly used on purpose on a Khotanese scroll, although the results were not published as they were only part of an extensive survey. It was used to decorate the tip of some big flowers, which were otherwise painted red with vermilion. If the pararealgar had been a degradation product of realgar, the original flower would have had two very similar red pigments used to decorate different areas, which stylistically did not make much sense.'

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