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Characterization of mural painting pigments from the Thubchen Lakhang temple in Lo Manthang, Nepal

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Very few publications are available on materials and techniques used by ancient Nepalese artists to paint mural decorations. This paper presents the first results of scientific examination aimed at characterizing the composition of the pigments present in paint samples collected from the south and east wall decorations of the 15th century Thubchen Lakhang monastery located in Lo Manthang, upper Mustang, Nepal. The temple was built in rammed mud and wood by order of King bKra.shis.mgon in 1470 and completed by 1472. Cross-sections of the 14 collected samples were prepared and the pigment composition was analysed stratigraphically. The same samples were also investigated, without preparation, for surface pigment characterization. The first results of the micro-Raman analyses showed that different blue pigments were used, sometimes alone, as in the case of azurite, and sometimes in combination with lazurite. The red and orange paint layers are constituted of orpiment and vermilion, both alone and in combination. A very interesting gilding technique that makes use as mordant of pararealgar with traces of orpiment and vermilion has been identified. Red ochre is present in the brown colour decorations. Malachite was used to paint the green decorations. Some samples also showed the presence of the copper sulfate hydrate brochantite, which may represent an alteration product of malachite. Further research will be needed in order to characterize the organic binding media composition that, in conjunction with these results, will guide restorers in the identification of the most appropriate restoration procedures to be adopted.

KEYWORDS: Nepal; mural painting; pigments; micro-Raman; painting technology

INTRODUCTION

Very few publications[1] are available on materials and techniques used by ancient Nepalese artists to paint mural decorations. This paper presents the first results of scientific examination aimed at characterizing the composition of the pigments present in paint samples collected from the south and east wall decorations of the 15th century Thubchen Lakhang monastery located in Lo Manthang, upper Mustang, Nepal.

The monastery[2] was built in rammed mud and wood by order of King bKra.shis.mgon in 1470 and completed by 1472. King Aham bSam.grub.dpal.'bar was responsible for some restoration work after a probable earthquake in the 1660s. A large portion of the north wall collapsed in 1815 and was rebuilt one entire bay inwards linked to the extant portion by a short wall in rammed mud. This intervention is attributed to Queen Padma.bhu.ti and King 'Jam.dpal dgra.'dul. The new north wall was again rebuilt in mud-brick after the 1898 earthquake. The north wall was prolonged towards the east, forming a northeastern chamber. Some repairs were carried out during the late 1950s.

Description of the building and the wall paintings

The Lakhang at present is a single-storey building consisting of a porch that opens at the east and covers six steps leading down to the vestibule's floor level that accesses a vast assembly hall. The vestibule contains sculptures of the guardians of the four directions and remains of wall paintings are depicted on the west and south walls. A doorway on the middle of the west wall access the assembly hall [Plate 1(a)] that originally formed a rough square in plan and contained 40 pillars with their capitals supporting their respective brackets and composite beams that gradually

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protrude towards the top and support the ceiling's joists. All these elements were polychromed with different colours according to precise rules and geometry. These composite beams were built on a north–south axis. Therefore, seven bays wide by eight bays long formed the interior of the Lakhang.

Apart from some paintings and restoration dating from later times, the majority of the mural decoration belongs to the period of construction of the Lakhang. Original wall paintings are found on the extant north (very fragmentary), east, south and the southwestern portion of the west wall. The decorative programme is basically very simple; at the centre of each bay there is a gigantic image sitting on a throne and flanked by two standing jewelled attendants disguised as Bodhisattwas. These scenes are divided by rows of smaller encircled Buddha images or other divinities that correspond to the axis given by the pillars of the hall. Unfortunately, very few portions of the lower mural décor remain as found below the two Bodhisattwa flanking the doorway.

Above the doorway on the east wall, the Buddha Vairochana is depicted with two attendants. On the remaining bays of the east wall and on the adjacent north and south bays, there are represented eight Bodhisattwa, one per each bay. Opposite the latter, on the south wall (on the second bay from the east) there is another image of Amoghashiddhi. The eighth bay reproposes Akshobhya in the *Bhumisparsa Mudra* that refers to the Buddha Sakyamuni [Plate 1(b)].

Local carpenters, wall painting conservators from Italy, coordinated by one of the authors, with local trainers and a support team by John Sunday Consultants[3] are carrying out conservation of the wall paintings depicted in the Buddhist monastery. The project includes building repairs and the consolidating and cleaning [Plate 1(c)] of the wall paintings that suffer from the wash down of clayish materials from the temple roof [Plate 1(d)].

Here we present the results of the Raman spectroscopic analysis of 14 paint samples collected from the east and south walls of the Lakhang monastery (Table 1). The primary purpose of this research was to determine the original scheme of polychromy by means of optical microscopy observation of cross-sectioned samples and pigment characterization with a micro-Raman spectrometer equipped with an optical microscope. In this regard, Raman spectroscopy provides an ideal technique for the layer-by-layer characterization of pigments and other inorganic materials used to prepare the walls for decorations.

EXPERIMENTAL

Samples were embedded in a resin support, then cross-sectioned and polished according to conventional methods. Dark field observation of cross-sectioned samples was performed using a Leitz Laborlux S microscope equipped with fixed oculars of 10× and objective of 10× magnification. Microphotographs were taken using a Photoautomat Leica Wild MPS46 system equipped with an exposimeter spot Leica Wild MPS 52.

The micro-Raman analyses of the paint samples were performed by placing fragments of the paint samples and the cross-sectioned samples on the microscope stage and directing the laser light through a 50× objective of an Olympus microscope on to the required spot of the surface and the different paint layers visible under cross-section. The Raman analyses were carried out with a micro-Raman Labram and a laser at 632.8 nm, at a power ranging from 0.5 to 5 mW (slit 5 cm^{-1}), according with to sensitivity of the compounds to be investigated.

A charge-coupled device (CCD) (330 × 1100 pixels) detector cooled by the Peltier effect at 200 K was used. All

Table 1. Position and description of the samples analysed

Sample	Colour	Location
1	Blue	East wall, 6th bay, lower northern side. Right arm of the Boshisattwa
2	Blue	East wall, north side. Skirting board buttress
4	Light blue	South wall, 5th bay, upper eastern side. Halo of a small Buddha
5	Blue	South wall, 4th bay, eastern side of the Buddha's halo
6	Blue	South wall, 5th bay, central eastern side. Buddha's robe
7	Gilding	South wall, 5th bay, central eastern side. Buddha's face
8	Green	South wall, 5th bay, upper eastern side. Buddha's halo
9	Gilt 'pastiglia'	South wall, 5th bay, lower western side. Decoration of cloud from Buddha's robe
10	Blue	South wall, 5th bay, lower western side. Figure on the throne back
11	Blue	South wall, 6th bay, upper eastern side. Sky
12	Brown–red	South wall, 5th bay, central western side. Shoulder of the throne
13	Red	South wall, 5th bay, lower western side. Buddha's robe
14	Brown	South wall, 5th bay, upper western side. Makhara's tail
15	Red	South wall, 5th bay, upper western side. Makhara's tail

Table 2. Pigments and grounds identified in the Lakhang wall paintings

Sample	Colour	Surface	Layers[a]	Mineral name
1	Blue	Lapis lazuli, azurite, calcite	Ground layer	Haematite, goethite
			White preparation (1 μm)	Calcite
			Grey	Quartz
			Blue (5 μ)	Azurite, lapis lazuli
2	Blue	Lapis lazuli, vermilion	Ground layer	Quartz, albite, gypsum
			Blue	Lapis lazuli, vermilion
4	Light blue	Azurite, lapis lazuli, calcite, vermilion, quartz, haematite	Ground layer	Orthoclase, calcite, microcrystalline calcite, quartz
			White preparation (4 μm)	Calcite
			Light blue (4 μm)	Azurite, lapis lazuli, small amounts of vermilion, malachite
5	Blue	Azurite, calcite	Ground layer	Clasts of calcite
			White preparation (6 μm)	Calcite
			Blue (10 μm)	Azurite, small amount of haematite
6	Blue	Azurite, charcoal black, graphite, calcite	Ground layer	Clasts of calcite
			White preparation	Calcite
			Thin black	Carbon
			Blue (5 μm)	Azurite
			Coarse render with small amounts of green and blue pigments on top	Microcrystalline calcite, haematite
7	Gilding	Pararealgar	Ground layer	Calcite, quartz, orthoclase, haematite
			White preparation (3 μm)	Calcite
			Yellow	Pararealgar, small amounts of orpiment, vermilion, carbon and gypsum
			Gold leaf	
8	Green	Brochantite, azurite, small amount of calcite	Ground layer	Quartz, calcite
			White preparation	Calcite, small amounts of vermilion
			Green	Malachite, small amounts of azurite, vermilion and calcite
9	Gilt 'Pastiglia'[b]	Vermilion, quartz, calcite	Ground layer	Calcite, quartz
			White preparation (4 μm)	Calcite
			Orange	Fluorescent
			Gold leaf	—
			Brown preparation	Vermilion, charcoal black, calcite
10	Blue	Azurite, vermilion	Ground layer	Clasts of calcite
			White preparation (3 μm)	Microcrystalline calcite
			Red	Vermilion
			Blue	Azurite

(*continued overleaf*)

Table 2. (*Continued*)

Sample	Colour	Surface	Layers[a]	Mineral name
11	Blue	Azurite, haematite, graphite, calcite, quartz, albite, gypsum	Ground layer	Calcite, small amounts of gypsum and quartz
			White preparation (3 μm)	Calcite
			Thin black	Carbon
			Blue (5 μm)	Azurite
			Clay deposit	Haematite, graphite, calcite, quartz, albite, gypsum
12	Brown–red	Haematite, small amounts of vermilion, carbon and quartz	Ground layer + red	Haematite, carbon
			Blackish	Carbon
			Red	Haematite, calcite
13	Red	Haematite, vermilion	Ground layer	Calcite, quartz
			White preparation (2 μm)	Calcite
			Red	Vermilion
			Orange red	Haematite, vermilion
			Reddish lake	
14	Brown	Fluorescent with malachite, brochantite, azurite and small amount of vermilion	Ground layer	Calcite, small amounts of carbon, haematite and goethite
			White preparation (3 μm)	Calcite, quartz
			Brown (6 μm)	Fluorescent with haematite and quartz
15	Red	Fluorescent with vermilion	Ground layer	Clasts of calcite and quartz
			White preparation (5 μm)	Calcite, quartz
			Thin black	Graphite
			Red	Vermilion
			Reddish lake	Fluorescent

[a] As observed in cross-section under the optical microscope.

[b] The gilded decoration is prepared separately as small tablets and then glued to the paint surface.

the reported Raman spectra were baseline corrected using Grams 32 AI (Galactic Industries).

The spectral interval was changed according to the type of compounds, but was generally between 1100 and 100 cm^{-1}. The organic compounds were studied at high wavenumber intervals, whereas the inorganic compounds, and in particular oxides and sulfides, at lower wavenumber intervals. The spectra collection time was also variable according to the magnitude of the scattering signal. Each paint sample was investigated by analysing an average of 30 particles of different shape and colour, even though not all the resulting spectra were recorded. As this technique is characterized by a minimum sample quantity requirement, a selective investigation of heterogeneous materials is made possible.

In this study, scanning electron-microscope–energy-dispersive x-ray (SEM-EDX) analyses were carried out on the same cross-sectioned samples already prepared for the optical microscopy observations and micro-Raman analyses. They were mounted on stubs and then sputter-coated with a thin layer of graphite. A Philips XL 20 scanning electron microscope was used. The elemental composition of the samples was determined by using a computerized spectrometer connected to an XL20 solid-state detector for EDX analysis at an acceleration voltage of 25–30 keV, lifetime >50 s, CPS $\approx$ 2000 and working distance 34 mm. EDX-4 software equipped with a ZAF correction procedure for bulk specimens was used for semi-quantitative analyses of the collected x-ray intensities.

RESULTS AND DISCUSSION

Ground and preparation layers

The techniques and materials that conservators now employ are virtually identical with those used over 500 years ago.[4] Historical information and the interviewed local carpenters both mention the fact that before painting the walls are made of rammed mud mortar (*gyang*), first flattened with a blend of chopped straw, *shi sa* clay and a slurry of cow dung as binder. Two or three additional thinner layers are then applied. A first layer of river sand and small pebbles mixed with a yellowish clay (*pimbo*), a second of very fine sand (*chema*) mixed with *pimbo* and a greenish-brown clay known as *shi pi pema* and a third layer composed of *shi pi* *pema* and *ghi sa*, a light beige clay. The final preparation layer consists of *khsa*, an extremely fine white clay. No mineralogical investigations aimed at characterizing the composition of the above-mentioned materials have been carried out so far.

In spite of this, the results of the analyses (Table 2) seem to be in agreement with the above-mentioned historical and technical information. Cross-sectioned samples showed an original scheme of polychromy characterized by the presence of a ground layer composed of a yellowish clay (probably *pimbo*) (sample 4), sometimes mixed with a greenish-brown clay (probably *shi pi pema*) (sample 15), whose green pigments showed fluorescence under Raman investigation [Plate 2(a)]. Only calcite has been identified within the preparation layer whereas orthoclase, microcrystalline calcite and quartz were present in the ground (Fig. 1). Therefore, in order to confirm the use of both *pimbo* and *khsa*, cross-sections were further examined by x-ray microanalysis, using a scanning electron microscope equipped with secondary and backscattered electron detectors and an x-ray spectrometer. The preparation layer was found to be composed mainly of aluminium and silicon, with the presence of potassium and calcium and traces of sodium, magnesium, chlorine, titanium and iron [Fig. 2(a) and (b)]. The presence within the ground layer of quartz and microcrystalline calcite embedded in a clayish matrix was also confirmed. These compositions are consistent with the use of fine clay for the preparation layer (*khsa*) and a yellowish one for the ground (*pimbo*). The smoothness of the preparation layer provides a compact surface for the paint layers.

Furthermore, in two cases (samples 2 and 12), no preparation layer was observed in cross-section and the paint layer applied directly on to the ground layer [Plate 2(b)]. This may represent an example of over-paintings done later, on the occasion of the first restoration interventions carried out in the 17th century.

Blue paint layers

The blue palette was found to be constituted of azurite (samples 5, 6,10 and 11) of high quality and large particle size, sometimes mixed with haematite (sample 5) or lazurite, the main component of the semi-precious stone lazurite (samples 1 and 4), a sodium aluminosilicate mineral with sulfur radical anions residing in the aluminosilicate crystal lattice (Fig. 3), together with traces of vermilion and malachite. Lazurite has been ascribed to various sources in Persia, China and Tibet. The best quality lazurite comes from Badakhshan in northeastern Afghanistan and was first identified on 5th century wall paintings from Kizil in Chinese Turkestan.[5]

The blue pigment present on sample 2, taken from the skirting board buttress, is mainly composed of lazurite with traces of red vermilion.

Apart from sample 2, which is probably a later over-painting, the other blues (samples 1, 6 and 11) were applied over a very thin black layer composed of carbon [Plate 2(c)]. It is our opinion that this black layer was added intentionally

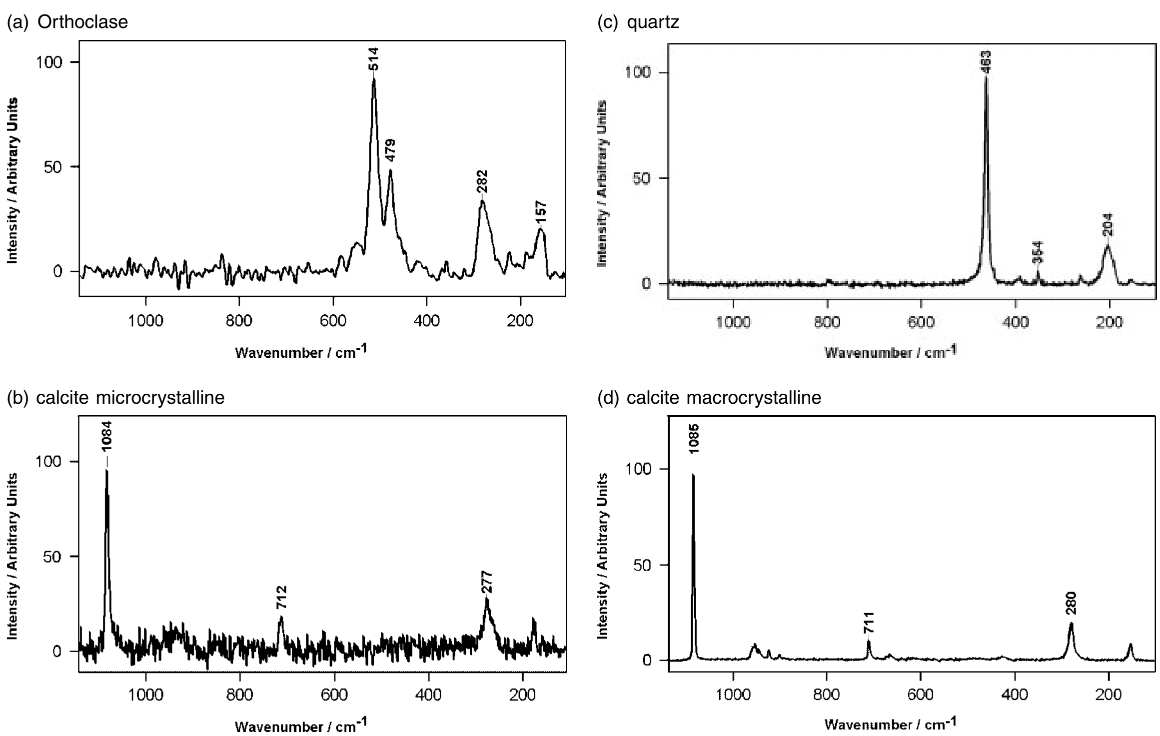

Figure 1. Raman spectra obtained from the ground and whitish preparation layer of sample 4, indicative of the presence of (a) orthoclase, (b) microcrystalline calcite, (c) quartz and (d) calcite.

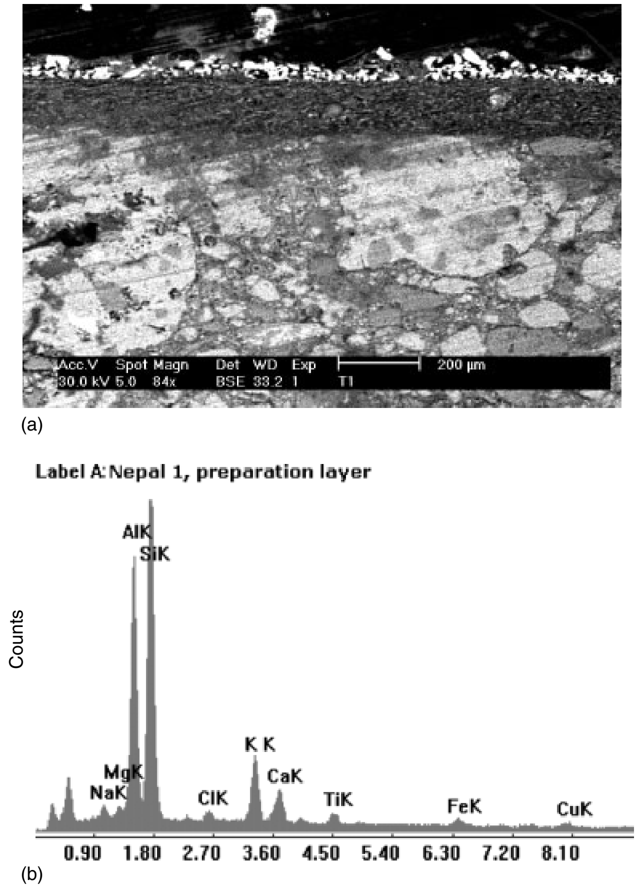

Figure 2. (a) Backscattered electron microscope image of sample 1 showing the coarse ground layer, the preparation layer and the paint layer. (b) Elemental composition of the preparation layer.

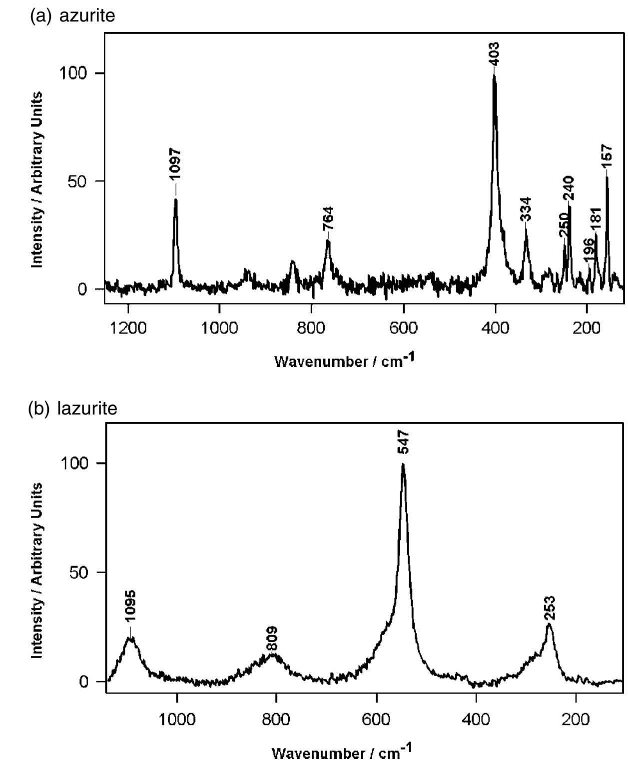

Figure 3. Raman spectra obtained from the blue paint layer of samples 6 and 1: (a) azurite and (b) lazurite.

because of both the high transparency of the pigments and the very low thickness of the blue paint layers (about 5 μm). The carbon black layer is not present in sample 10 probably because the figure was first painted with a flesh colour (vermilion) and then covered with blue at the time of painting. This may, therefore, represents a '*pentimento*' of the painter.

Red paint layers

The red (samples 12 and 15) and orange–red paint layers are constituted of haematite, a natural variety of anhydrous ferric oxide (Fe_2O_3) and vermilion (HgS), a pigment that has been known in China since prehistoric times (Fig. 4). Sometimes they were mixed in order to obtain an orange tonality (sample 13) and a very thin application of reddish lake, observed in cross-sections of samples 13 and 15 under fluorescence optical microscopy, was applied on top for aesthetic purposes [Plate 2(d)]. The absence of the whitish preparation layer in sample 12 (Table 2) may be indicative of an overpainting. Furthermore, the presumed presence of a silver leaf decoration still has to be confirmed by using other analytical techniques. The micro-Raman analysis in fact just identified the presence of a black thin layer made of carbon.

Gilding

To gild the Buddha's face (sample 7) [Plate 1(e)], gold leaf was affixed to a mixture of orange–red particles of pararealgar [an arsenic(II) sulfide polymorph of realgar (AsS)] (Fig. 5), some orpiment [a yellow arsenic(III) sulfide (As_2S_3)] and vermilion and probably glue as binding medium. This is certainly an unusual type of gilding technique [Plate 3(a)], as generally for wall paintings an oil mordant was much more common and also the use of a bole which is similar to ochre and has served since ancient times as a ground for gilding.[6] Another gilding technique identified on Asian wall paintings involves the use as mordant of gamboge, a yellow gum resin.[7] As pararealgar has not, to our knowledge, been reported as occurring in Far Eastern mural paintings but only identified on two Chinese realgar figurines first as arsenic(III) oxide and orpiment[8] and subsequently as pararealgar (V. Daniels, personal communication, 1994), it is necessary to carry out further research on its occurrence in Tibetan paintings as it may either have been used as an original yellow pigment[9] or represent a light-induced alteration product of realgar.[10]

Orpiment, which often contains orange–red particles of realgar, to which it is closely associated in nature, may have come largely from hot springs in eastern Tibet.

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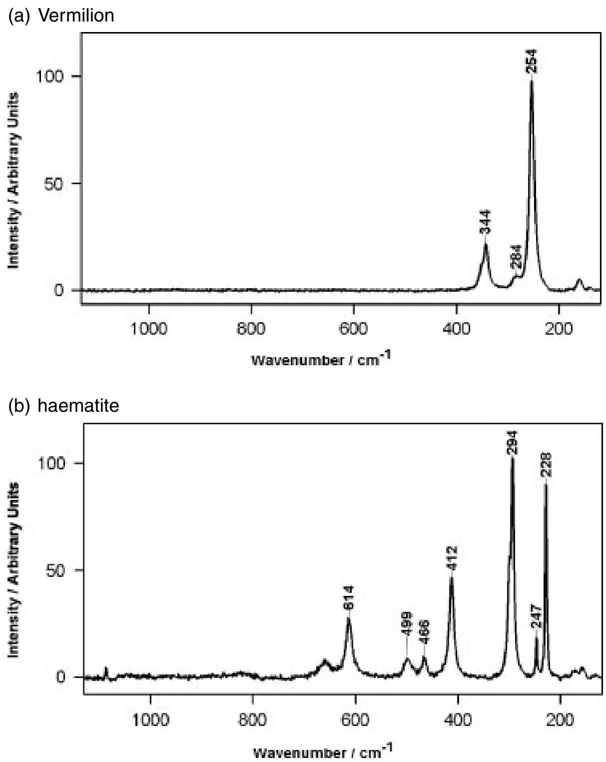

Figure 4. Raman spectra obtained from the orange and red paint layers of sample 13: (a) vermilion and (b) haematite.

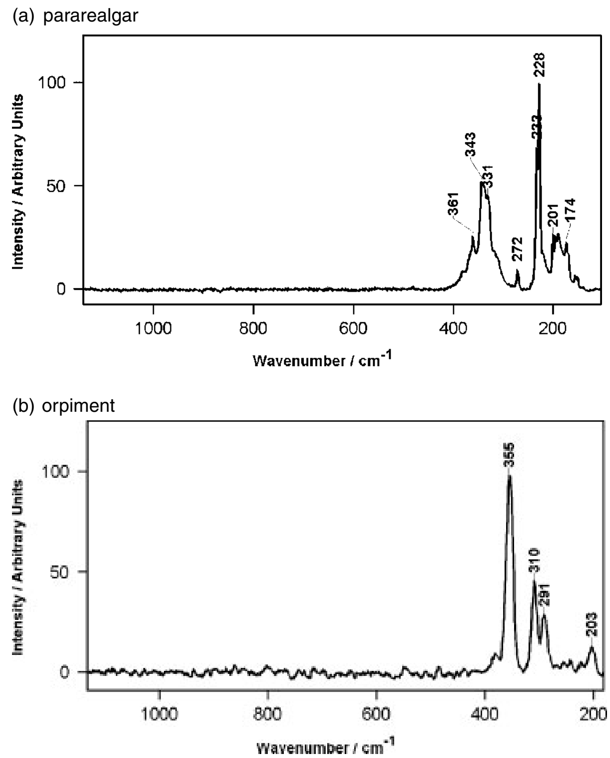

Figure 5. Raman spectra obtained from the yellow layer underneath the gold leaf of sample 7: (a) pararealgar and (b) orpiment.

In spite of the results of the analysis of sample 7, sample 9 presents, as mordant for the gold leaf, a yellow pigment that showed fluorescence under Raman analysis. The optical microscopy observations suggest the presence of a yellow ochre but further investigations by x-ray microanalysis using a scanning electron microscope will be undertaken.

Brown paint layer

A cross-section of sample 14, collected from the Makhara's tail in an area forming a scroll decoration [Plate 1(f)], shows the presence of a brownish layer that appears translucent under reflected light microscopy [Plate 3(b)] and fluorescent under Raman examination. Therefore it, was not possible to identify its nature even though the above-mentioned observations suggest the possible use of an organic yellow–brown pigment. An additional very thin brown layer is visible in the outermost part of the sample over which malachite, brochantite [$Cu_4(OH)_6SO_4$], azurite and few particles of vermilion have been identified.

Green paint layers

The green paint layer was found to be composed of malachite [$CuCO_3{\cdot}Cu(OH)_2$] and brochantite (Fig. 6), in the outermost area, with traces of azurite [$2CuCO_3{\cdot}Cu(OH)_2$] and vermilion dispersed in the paint layer [Plate 3(c)].

Even though it is well known that artificial basic copper sulfates have been used as pigments,[11] the brochantite particles, which are located in the outermost part of the green layer of sample 8, are likely to be an alteration product of original malachite pigments, that are still present within the layer. Hence the green pigments of Lakhang require consideration for their conservation needs, because of the possible role that might be played by the sulfur in their deterioration. It is our opinion that the traces of vermilion and azurite may be ascribed to the use of a not well-cleaned brush and the calcite to deposition materials.

CONCLUSIONS

The coupling of reflected light microscopy and Raman microscopy applied to cross-sectioned paint samples taken from the mural paintings of the Thubchen Lakhang monastery provides a useful tool for the contemporary characterization of the original scheme of polychromy and the identification of the nature of the pigments used.

In this study, the analyses not only are meant to assist in the assessment of the authenticity of the materials used but are also aimed at guiding conservators in planning and implementing conservation interventions, hence the need to involve other analytical techniques is of the utmost importance. Therefore, these first research results will be further integrated with gas chromatography–mass

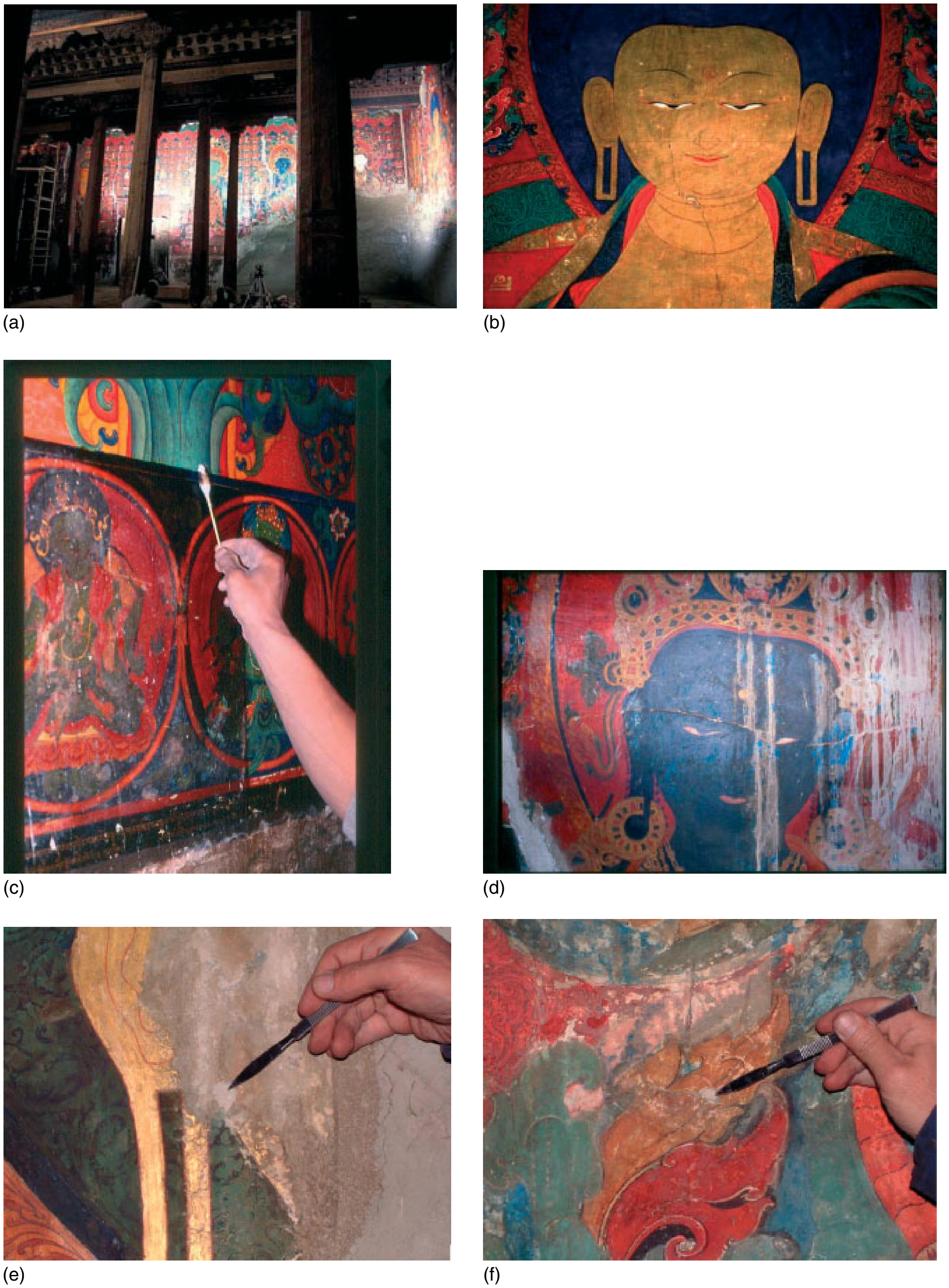

Plate 1. (a) Thubchen Lakhang monastery, Assembly Hall. (b) Sakyamuni Buddha depicted on the south wall. After restoration. (c) Cleaning operation carried out on the surface of the mural paintings depicted on the east wall. (d) Mural paintings covered with clayish material washed down from the temple roof. (e) South wall, 5th bay, central eastern side. Buddha's face. Collection area of sample 7. (f) South wall, 5th bay, upper western side. Makhara's tail. Collection area of sample 14.

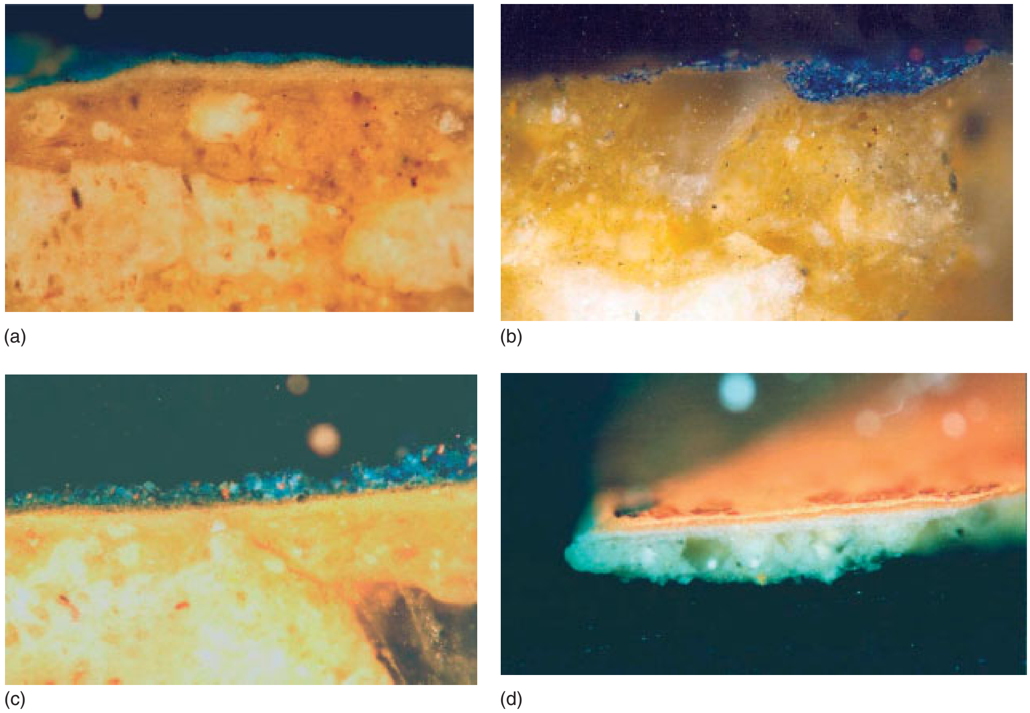

Plate 2. Paint cross-sections (×100 original magnification). (a) Sample 4: starting from the upper part, a blue paint layer over a whitish preparation layer and a yellowish clay ground layer (probably *pimbo*) is visible. (b) Sample 2: a blue layer of lazurite applied directly on to the ground layer. (c) Sample 1: starting from the upper part the cross-section shows a blue paint layer composed of azurite and lazurite, a very thin black layer of carbon, a whitish preparation and a yellowish clay ground layer (probably *pimbo*). (d) Sample 13: traces of reddish lake can be observed on the top of the orange and red paint layers.

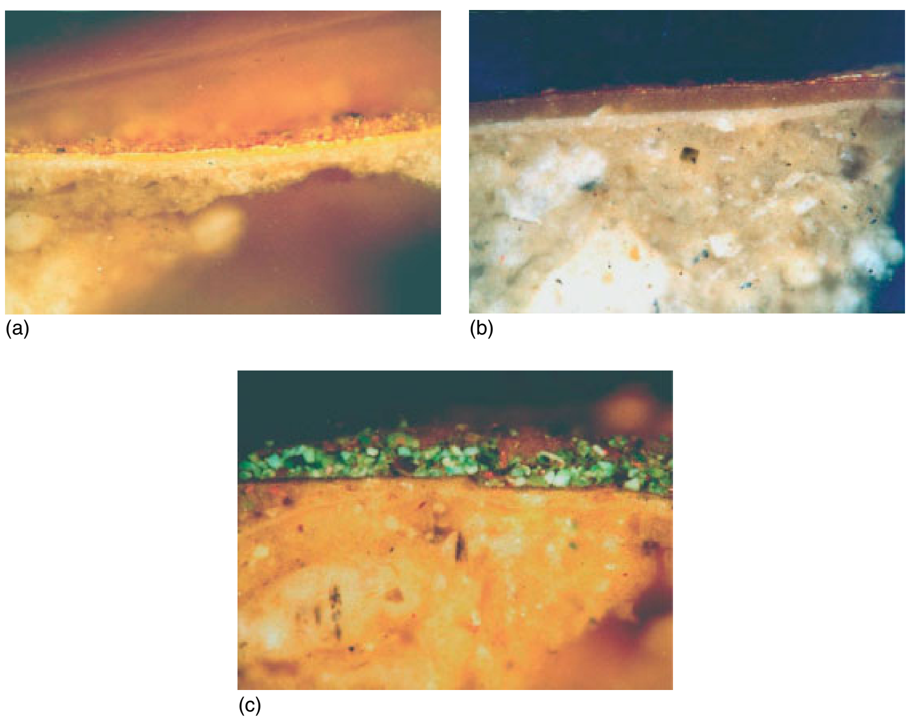

Plate 3. Paint cross-sections (×100 original magnification). (a) Sample 7: a yellow paint layer composed of pararealgar, traces of orpiment and vermilion, is visible under the external gold leaf. (b) Sample 14: a translucent brownish paint layer with an additional very thin brown layer is visible above the whitish preparation. (c) Sample 8: particles with different shape and green tonality, mixed with blue and red ones, can be observed within the paint layer.

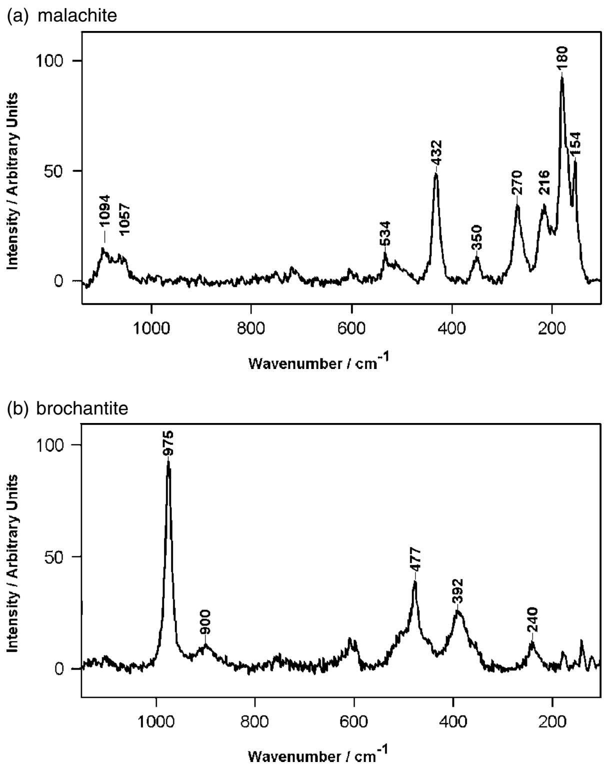

Figure 6. Raman spectra obtained from the green paint layer of sample 8: (a) malachite and (b) brochantite.

spectrometry and FTIR microscopy investigations in order to characterize the nature of the organic components of paint layers, which are not suitable for detection using Raman spectroscopy owing to their fluorescence effect. Furthermore, the atmospheric environment of the Lakhang monastery needs to be determined in order to assess the presence of polluting gases, such as sulfur, which may have a role in the deterioration of some pigments and particularly of the green paint layers composed of malachite.

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REFERENCES

1. Jian Z, Wang C-S, Xu G-J, Zhao HB. *Chin. Spectrosc. Lett.* 1999; **32**: 841.
2. Harrison J, Vitali R. *Two Temples in Lo Monthang*. German Research Council, Nepal–German Project on High Mountain Archaeology, 1997.
3. Sanday J. *Orientations* 1999; **30**: 84.
4. http://www.pbs.org/wgbh/nova/tibet/painting.html. Date of access: 6 September 2003.
5. Gettens RJ. *Tech. Stud. Field Fine Arts* 1938; **6**: 281.
6. Sankrityayana R. *Asia* 1937; **37**: 776.
7. Prasartset C. *J. Nat. Res. Counc. Thailand* 1990; **22**: 73.
8. Daniels V. *MASCA J.* 1983; **6**: 170.
9. Corbeil M-C, Helwing K. *Stud. Conserv.* 1995; **40**: 133.
10. Douglass DL, Shing C, Wang G. *Am. Mineral.* 1992; **77**: 1266.
11. Puriton N, Watters M. *J. Am. Inst. Conserv.* 1991; **30**: 125.