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STUDY ON THE PIGMENTS IN THE CRUCIFORM GALLERY OF ANGKOR WAT, CAMBODIA*

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In the cruciform gallery of Angkor Wat in Cambodia, red, orange, white and black pigments were widely painted on the surfaces of pillars, walls and friezes. The application sequence of the pigments is different from area to area. The following substances were confirmed from the pigments: hematite (laterite), minium, calcium oxalate hydrates (whewellite and weddellite), Pb–Cl compounds (cotunnite, laurionite and blixite), calcium phosphates (whitlockite), gypsum, hydrocerussite, calcite, anglesite, lead dioxide, azurite and carbon black. The orange pigment (minium) underlies the red pigment (hematite). The former may have been applied at the time of the foundation (the Angkor Wat style period), and the latter in the Bayon style period or later, but mainly before the early 17th century of the current era.

KEYWORDS: PIGMENT, CRUCIFORM GALLERY, ANGKOR WAT, CAMBODIA

INTRODUCTION

The Angkor monuments in Cambodia were mainly built of sandstone and laterite (Delvert 1963; Uchida *et al*. 1998, 1999a). Brick is also used in the buildings constructed in the early period from the 9th to the 10th centuries CE (AD). The buildings where pigments were applied to the surface are rare in the Angkor monuments. Even when pigments were applied, in most cases it is a red pigment containing hematite. The red pigment is frequently observed in the Terrace of Elephants. Apart from this, it survives locally in Preah Khan, Banteay Kdei, Ta Nei, the Terrace of the Leper King and other monuments. On the other hand, various pigments were widely applied in the cruciform gallery of Angkor Wat, which was built by Suryavarman II (1113–1150 CE) and is the best representation from the Angkorian age (Fig. 1). The cruciform gallery is situated between the western gopuras of the outer and middle galleries (Fig. 2). There exist 130 pillars supporting vaults and half-vaults, and four rectangular basins. The bottoms of the pillars show severe deterioration due to bat guano (Uchida *et al*. 1999b). This area was known as ‘The Hall of the Thousand Buddhas’, and has been used as a pilgrimage site by Theravada Buddhists since the 16th century CE (e.g., Freeman and Jacques 1999). Most of the Buddhas were removed for safety in the early 1970s (Freeman and Jacques 1999). At present, a few statues remain along the south wall.

Preliminary research has been conducted by Kiesewetter *et al*. (2001) on the pigments in Angkor Wat, including the cruciform gallery. In the work reported here, the distribution and application sequence of the pigments in the cruciform gallery were clarified on site by qualitative analysis, using a portable X-ray fluorescence analyser. In addition, under a microscope, the sequence of the overpainting of pigments was examined in the cross-section of delaminated

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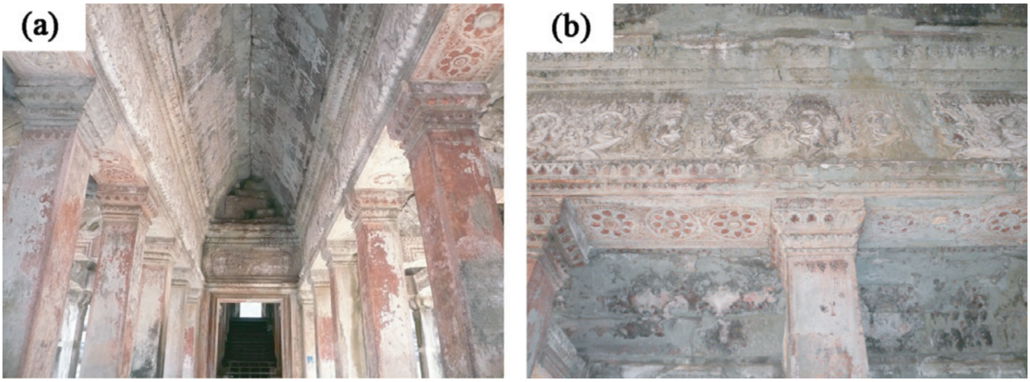

Figure 1 *(a) The cruciform gallery of Angkor Wat, painted extensively with pigments. (b) The frieze with Apsara reliefs and the cornices of the cruciform gallery. (See online for a colour version of this figure.)*

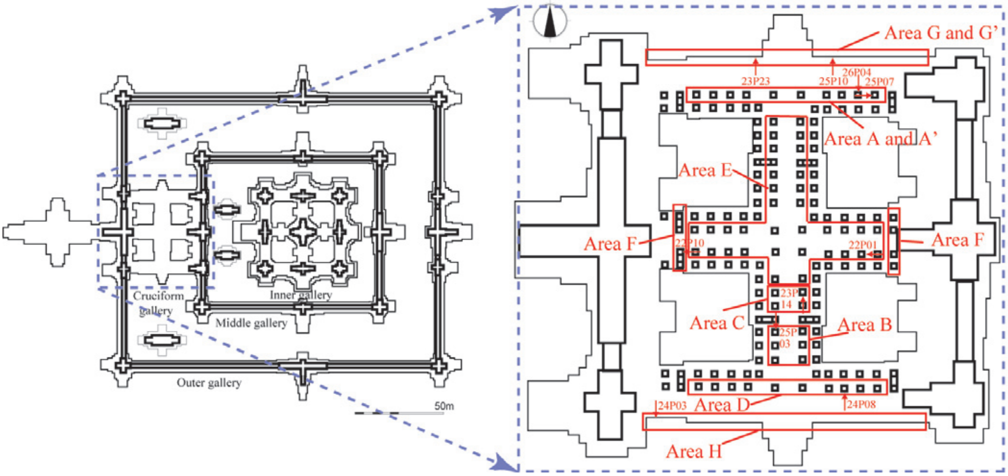

Figure 2 *The location of the cruciform gallery (surrounded by a rectangle) in Angkor Wat (left), and the division of the cruciform gallery based on the applied pigments (right). Area I corresponds to the undersides of the beams and the capitals of the pillars, and Area J to the friezes. The sampling points of the pigments in Figure 4 are also shown.*

fragments. Moreover, identification of the constituent substances of the pigments was carried out using an electron probe X-ray microanalyser and an X-ray microdiffractometer.

APPLICATION STATUS OF THE PIGMENTS

Pigments seem to have been applied in the wide area of the cruciform gallery, but they have become detached over time in many places, especially on the lower part of the pillars. Thus urgent conservation work is necessary. The pigments were applied to the inner pillars (no pigments on the outer pillars), to the northern and southern walls, to the undersides of beams and to friezes. The application sequence of the pigments is different from area to area. The pigments were generally painted in many times. Based on observations by the naked eye and by a digital microscope (Scalar SG-3), and a qualitative analysis using a portable X-ray fluorescence analyser (Innov-X Systems α-4000), it was clarified that the application sequence of the pigments is different between the north and south walls, and that the pillars can be classified into five areas based on the application sequence of the pigments. In this study, a detailed investigation of the pigments was conducted for the 10 areas shown in Figure 2: the north wall (Areas G and G′), the south wall (Area H), the eastern and western doorframes (Area F), the pillars (subdivided into the five areas: Areas A–E), the undersides of beams and the insides of eaves (Area I), and the friezes (Area J). The application sequence of the pigments is different between the upper (Area G) and lower (Area G′) parts of the north wall, and between the north face (Area A′) and the other faces (Area A) of the northernmost pillars.

METHODS OF THE INVESTIGATION AND ANALYSIS

Detailed investigation of the pigments was conducted in the 10 areas mentioned above (Fig. 2). Photographs of the pigments in each area are shown in Figure 3. Because repeated painting was conducted in many areas, the application sequence of the pigments was elucidated both by the naked eye and by the digital microscope. Qualitative analysis was carried out to identify the pigments using the portable X-ray fluorescence analyser. In addition, several tiny fragments of the pigments were collected from the delaminated part in each area. After being embedded with an epoxy resin (EpoFix), the fragments of the pigments were ground with waterproof sandpaper and then were polished with diamond paste. The polished fragments of the pigments were observed under the optical stereo microscope (Nikon SMZ-U) (Fig. 4). The identification of the pigments was carried out using an X-ray microdiffractometer (Rigaku RINT-RAPID) and an energy-dispersive type electron probe X-ray microanalyser (the JEOL JSM-6360 scanning electron microscope, equipped with an Oxford Instruments INCA Energy energy-dispersive spectrometer). The analysis by the X-ray microdiffractometer was conducted using Cu–K_α Ni-filtered radiation generated under the condition of 40 kV and 30 mA. The X-ray beam was collimated down to 100 μm in diameter. In the analysis by the X-ray microanalyser, the surfaces of the pigment samples were coated with carbon in order to avoid charging effects.

RESULTS OF THE INVESTIGATION AND ANALYSIS

The results of the investigation and the analysis are described below for each area.

Areas A and A′

Areas A and A′ correspond to the northernmost pillars. Area A′ is the northern surface of the pillars. The other surfaces belong to Area A. The remaining state of the pigments is not good in these areas. Almost all of the pigments are detached in the lower part. The pigments show a dark red colour in Area A (Fig. 3 (a)). Black pigment is found under the red pigment layer in Area A′ (Fig. 3 (b)).

In Area A, two painting layers are observed (Fig. 4 (a)). The red pigment of the first layer from the surface consists mainly of hematite (Fe_2O_3) and calcium oxalate hydrates (whewellite, $CaC_2O_4{\bullet}H_2O$; weddellite, $CaC_2O_4{\bullet}2H_2O$), accompanied by small amounts of Pb–Cl compounds (cotunnite, $PbCl_2$; laurionite, PbClOH; blixite, $Pb_2Cl(O,OH)_{2-x}$), calcium phosphates (whitlockite, $Ca_9(Mg,Fe^{2+})(PO_3OH)(PO_4)_6$, and others) and gypsum ($CaSO_4{\bullet}2H_2O$). The red pigment

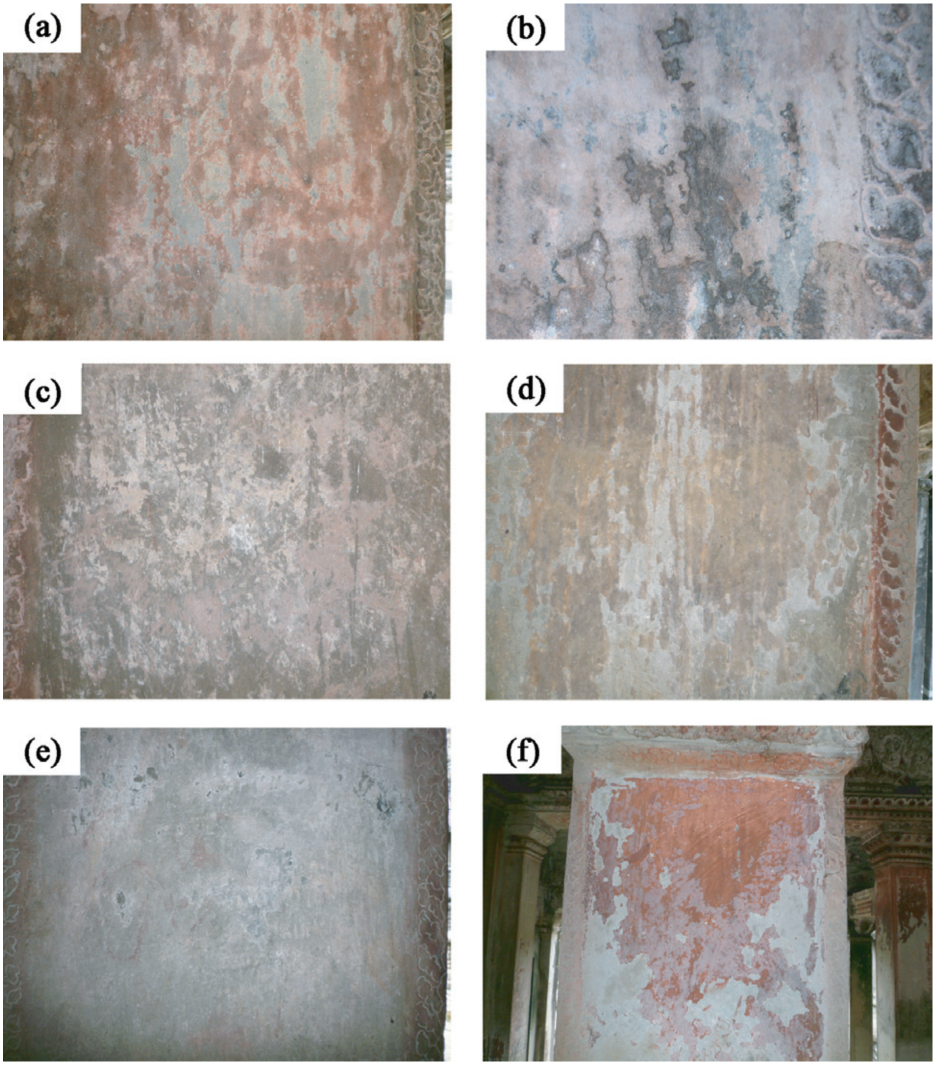

Figure 3 *Pigments on the pillars in (a) Area A, (b) Area A′, (c) Area B, (d) Area C, (e) Area D, (f) Area E and (g) Area F. (h) Pigments in the north wall (Areas G and G′). (i) Pigments in the petal decorations (G′-3) in Area G′ of the north wall (indicated with a rectangle in (h)). (j) Black pigment in the south wall (Area H). (k) Red (hematite), black (carbon black) and blue–green pigments (Cl-bearing sodium copper phosphate) found locally in the cornice in the northern part of the cruciform gallery. (l) Graffiti painted with a blue pigment (azurite). (See online for a colour version of this figure.)*

contains abundant impurities such as SiO_2 and Al_2O_3. The second layer is white and consists mainly of calcium phosphates and gypsum, accompanied by Pb–Cl compounds, white lead (hydrocerussite, $2PbCO_3{\bullet}Pb(OH)_2$), calcium oxalate hydrates and calcite ($CaCO_3$).

In Area A′, three painting layers are observed (Fig. 4 (b)). The first layer is red, with a flesh tint. It is composed of hematite, calcium phosphates and calcium oxalate hydrates. The second layer is black and consists mainly of calcium phosphates, accompanied by small amounts of gypsum and calcium oxalate hydrates. The black discolouration may be attributable to the

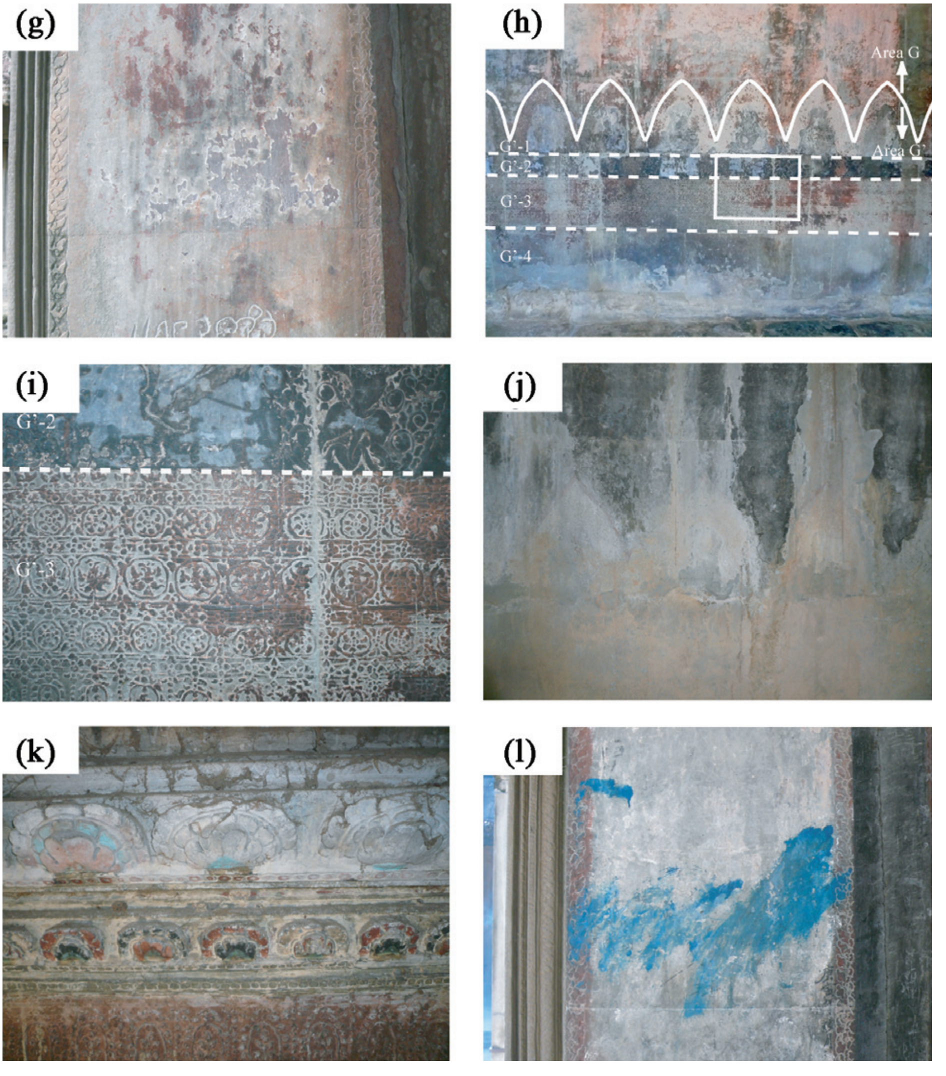

Figure 3—*continued.*

absorption of soot and dust by gypsum. The third layer is white and is composed mainly of Pb–Cl compounds, accompanied by calcium phosphates, calcium oxalate hydrates, calcite and white lead.

Area B

The pigments in Area B show a reddish grey colour (Fig. 3 (c)). The pigments consist of two layers (Fig. 4 (c)). The first layer is white and consists mainly of Pb–Cl compounds, accompanied by small amounts of calcium oxalate hydrates, calcite, calcium phosphates and white lead. Many small grains showing a claret red colour are found in the first layer. They are composed of red lead

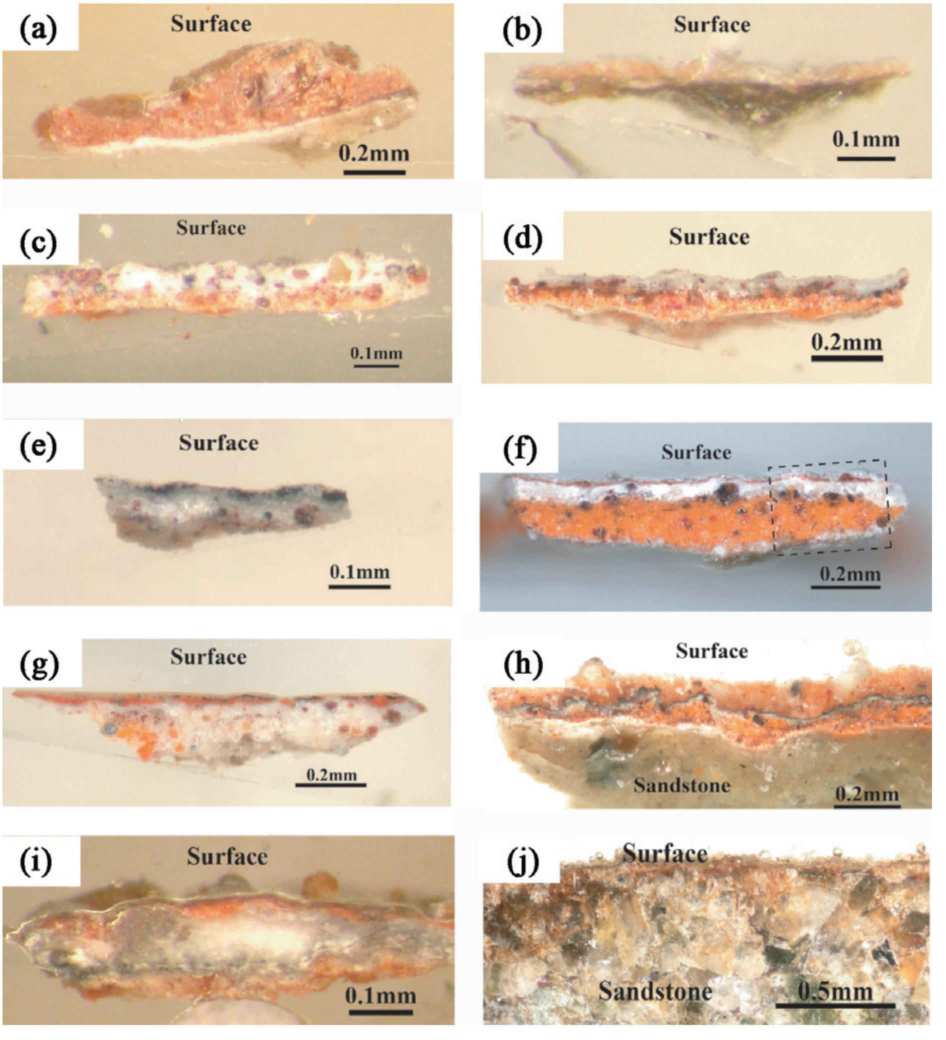

Figure 4 *Cross-sections of (a) sample 25P07 from Area A, (b) sample 26P04 (the third layer is missing) from Area A′, (c) sample 25P03 from Area B, (d) sample 23P14 from Area C, (e) sample 24P08 from Area D, (f) sample 22P01 from Area E, (g) sample 22P10 (the fourth layer is missing) from Area F, (h) sample 23P23 from Area G, (i) sample 25P10 from Area G′ and (j) sample 24P03 from Area H. The sampling points of these pigments are shown in Figure 2. (See online for a colour version of this figure.)*

(minium, Pb_3O_4) and lead dioxide (PbO_2). Minium was partly changed into lead dioxide with a black colour. The second layer is orange and consists mainly of minium, Pb–Cl compounds and white lead.

Area C

Almost all of the pigments were detached, but grey pigments remain on the upper parts of the pillars (Fig. 3 (d)). There are three layers of pigments (Fig. 4 (d)). The first layer shows a grey colour, the second layer shows an orange colour and the third layer a white colour. The first layer consists mainly of Pb–Cl compounds, white lead and anglesite ($PbSO_4$). This layer also contains calcium phosphates, calcium oxalate hydrates and calcite. Near the boundary with the second layer, abundant particles of lead dioxide with a black colour are observed. The second layer consists mainly of minium and is accompanied by Pb–Cl compounds, white lead, calcium phosphates, calcium oxalate hydrates and calcite. The third layer consists mainly of Pb–Cl compounds and calcium oxalate hydrates. It is accompanied by small amounts of calcium phosphates, gypsum and calcite.

Area D

The southernmost pillars belong to Area D. The pigments show a grey colour (Fig. 3 (e)). The pigments consist of three layers (Fig. 4 (e)). The first layer is grey, and consists mainly of lead dioxide and Pb–Cl compounds, accompanied by calcium phosphates. Lead dioxide may be an alteration product from minium. The second layer is white, and consists mainly of Pb–Cl compounds, accompanied by calcium phosphate and calcite. The third layer shows an orange colour, and is composed mainly of minium and Pb–Cl compounds. Minium is partly altered into lead dioxide with a black colour.

Area E

Many pillars in the cruciform gallery belong to Area E. The pigments show a colour variation from pink to red on the surface (Fig. 3 (f)). The pigments consist of five layers (Fig. 4 (f)). The scanning electron microscope image, backscattered electron image and element mapping images for sample 22P01 (Fig. 4 (f)) are shown in Figure 5. The X-ray diffraction patterns obtained by the microdiffractometer for each layer of the same sample are shown in Figure 6. The first layer is white, but shows a pinkish colour due to the presence of the red pigment in the second layer. It consists mainly of calcium oxalate hydrates, accompanied by calcium (or magnesium) phosphates (whitlockite; newberyite, $MgHPO_4 \cdot 3H_2O$), anglesite, gypsum, Pb–Cl compounds and white lead (Fig. 6 (a)). The second layer shows a red colour and is composed mainly of hematite and calcium oxalate hydrates, accompanied by white lead, calcite, gypsum, Pb–Cl compounds, calcium phosphates and anglesite. The third layer is a white layer and consists mainly of Pb–Cl compounds and white lead (Fig. 6 (c)). These are accompanied by calcium oxalate hydrates, calcium phosphates, calcite and anglesite. The fourth layer is orange and is composed mainly of minium, accompanied by Pb–Cl compounds, calcium oxalate hydrates and anglesite. However, part of the minium is oxidized into lead dioxide, showing a black colour near the boundary with the third layer. The fifth layer is white and consists mainly of white lead, Pb–Cl compounds, and small amounts of calcium oxalate hydrates, anglesite and calcite.

In the inner wall of the corner pavilions of the middle gallery, pigments with the same painting sequence without a white surface layer are observed.

Area F

The pigments in Area F (Fig. 3 (g)) consist of four layers (Fig. 4 (g)). The first surface layer is blackish with a lustre. It consists mainly of calcium phosphates and lead dioxide, and is accompanied by calcium oxalate hydrates and white lead. Lead dioxide is distributed along the boundary with the second layer. The second layer shows a red colour. It is composed mainly of hematite, and is accompanied by calcium oxalate hydrates, Pb–Cl compounds, calcium phos-

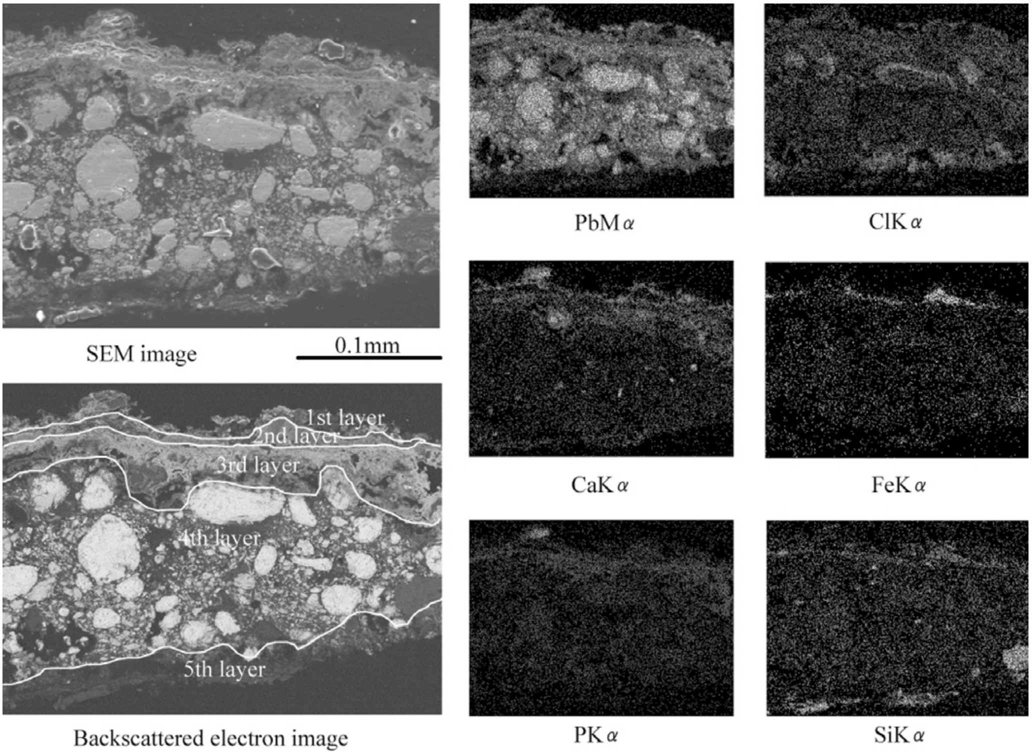

Figure 5 *The scanning electron microscope image, backscattered electron image and element mapping images for sample 22P01 from Area E, in the area indicated with a rectangle in Figure 4 (f).*

phates and anglesite. The third layer is a white layer, and consists mainly of Pb–Cl compounds and white lead, accompanied by calcium oxalate hydrates and calcium phosphates. Many particles found in the third layer have an orange colour, composed mainly of minium. The fourth layer is an orange layer and consists mainly of minium and small amounts of Pb–Cl compounds.

Areas G and G′

Areas G and G′ correspond to the north wall of the cruciform gallery (Fig. 3 (h)). Area G is the upper wall above the Apsara relief, and Area G′ is the lower wall.

In Area G, the pigments consist of five layers (Fig. 4 (h)). A flesh-coloured pigment is almost wholly painted on the surface with a wide brush. The first layer consists mainly of hematite and calcium oxalate hydrates, and is accompanied by calcium phosphates, gypsum and calcite. The second layer is black. It is composed mainly of lead dioxide and is accompanied by calcium phosphates, gypsum, calcium oxalate hydrates, white lead and Pb–Cl compounds. The black colour is due to the presence of lead dioxide. The third layer is white, and is composed of Pb–Cl compounds and white lead, accompanied by small amounts of calcium phosphates, calcium oxalate hydrates and gypsum. The fourth layer is orange, and is composed mainly of minium, accompanied by Pb–Cl compounds, anglesite, calcium phosphates, gypsum and calcium oxalate hydrates. The fifth layer is a white layer, consists mainly of calcium oxalate hydrates, calcite, calcium phosphates and gypsum, and is accompanied by a small amount of white lead.

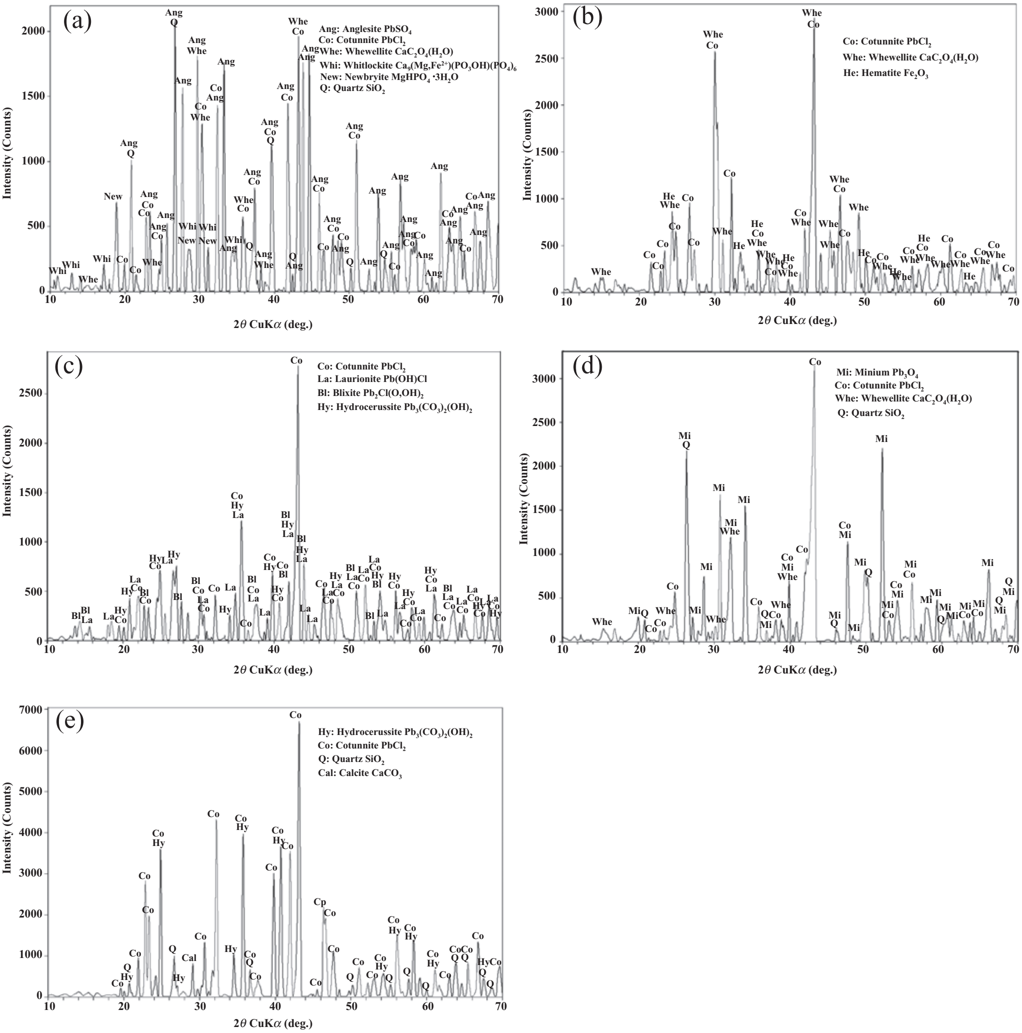

Figure 6 *X-ray diffraction patterns obtained by the microdiffractometer for each layer of sample 22P01 from Area E: (a) the white pigment of the first layer; (b) the red pigment of the second layer; (c) the white pigment of the third layer; (d) the orange pigment of the fourth layer; (e) the white layer of the fifth layer.*

The pigments used in Area G′ differ from place to place (Figs 3 (h) and 3 (i)). The Apsara relief (G′-1) shows a black or flesh colour. The surface of the Apsara relief is coated with a lacquer-like substance. No pigment sample was collected from the Apsara relief. However, one sample was collected from the surrounding floral decoration. Hematite, gypsum, calcium phosphates and calcite were confirmed.

The zone with a 20 cm width directly below the Apsara relief (G′-2), and also the lowest zone (G′-4), show a black colour. Gypsum, calcium phosphates and a small amount of calcium oxalate hydrates were confirmed from these zones. The black colour seems to be ascribed to the discolouration of gypsum due to the absorption of soot and dust.

The zone with the petal decoration (G′-3), which is situated between the above-mentioned black zones, G′-2 and G′-4, shows a red or black colour. The pigments are composed of three layers (Fig. 4 (i)). The first layer shows a red colour and consists of hematite with small amounts of calcium phosphate and calcium oxalate hydrates. The second layer shows a grey to white colour, and consists mainly of calcium oxalate hydrates and calcium phosphates, accompanied by a small amount of gypsum. Black discolouration seems to be caused by the absorption of soot and dust by gypsum. The third layer is orange and is composed mainly of minium, accompanied by calcium phosphates. In the zone beneath the Apsara relief, a red pigment was partially applied on the surface. This pigment consists mainly of hematite and is accompanied by calcium oxalate hydrates, calcite, calcium phosphates and gypsum.

Area H

Area H corresponds to the south wall of the cruciform gallery. The pigments show grey to black colours (Fig. 3 (j)) and consist of two layers (Fig. 4 (j)). The first layer shows a black colour and is composed mainly of gypsum and calcium phosphates, accompanied by small amounts of calcium oxalate hydrates and calcite. Due to a lack of black pigment, the cause of a black discolouration seems to be due to the absorption of soot and dust by gypsum. The second layer is white, and consists mainly of Pb–Cl compounds and calcium phosphates, accompanied by gypsum.

Area I

Area I corresponds to the underside of the beam, the capital of the pillar and the inner surface of the eave. A red pigment is painted in this area (Fig. 1 (b)). The pigment consists of a single layer. It is composed mainly of hematite and is accompanied by calcium oxalate hydrates, calcium phosphates, calcite and gypsum.

Area J

Area J corresponds to the frieze, which is sandwiched between the cornices in the top and bottom (Figs 1 (b) and 7). Many fine Apsara reliefs were carved on the frieze, with floral decorations. A white pigment is almost wholly painted, but a red pigment is also observed in the concavity of the relief.

The Apsara reliefs show a white colour and the pigment is composed of calcium phosphates, calcium oxalate hydrates and gypsum. A white pigment consisting mainly of Pb–Cl compounds and gypsum, with small amounts of calcium phosphates, calcium oxalate hydrates and white lead, was painted in the concavity around the Apsara reliefs. In some places, a red pigment consisting mainly of hematite was applied on the surface. The Naga niches around the Apsara reliefs show a white colour. The white pigment consists mainly of calcium oxalate hydrates, calcium phosphates and gypsum. Up to 11 petal decorations on the surface of each Naga niche were painted with an orange pigment (circled areas in Fig. 7). A pigment sample could not be collected from the petal decorations, but lead was detected by the portable X-ray fluorescence spectrometer. This suggests that minium was used as an orange pigment. The floral decorations around the Naga niches were painted with a white pigment, which consists mainly of gypsum and calcium phosphates, with a small amount of calcium oxalate hydrates. An orange pigment was painted in the centre of the floral decorations in the uppermost part of the frieze (Fig. 7, squares).

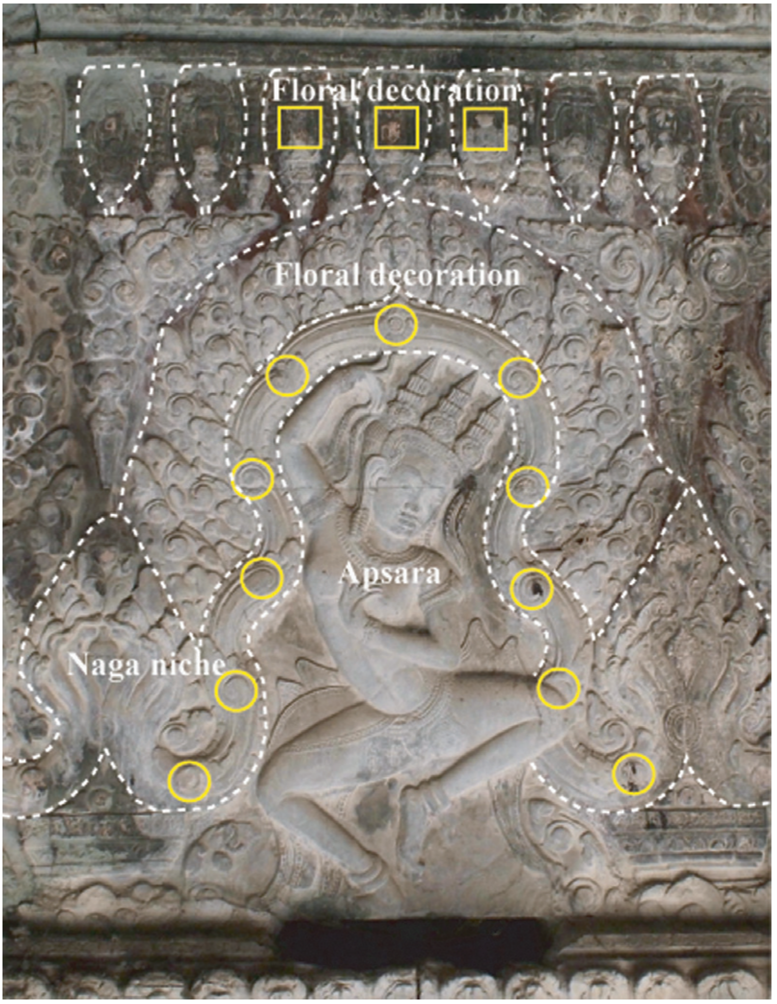

Figure 7 *Apsara reliefs in the frieze (Area J). Minium was confirmed from the parts indicated by circles and squares.*

The orange pigment is composed mainly of minium and calcium phosphates, and is accompanied by gypsum and calcium oxalate hydrates. In the concavity outside of the floral decorations, a red pigment is observed in some places. The red pigment consists mainly of hematite and gypsum and is accompanied by calcium oxalate hydrates.

The others

On the cornices at the top and bottom of the frieze, red, blue–green and black pigments are painted locally in the northern part of the cruciform gallery (Fig. 3 (k)). Using the portable X-ray fluorescence spectrometer, Fe was detected from the red pigment, but neither Pb nor Hg. Therefore, the red pigment is assumed to contain hematite. Copper and phosphorus were detected as major elements from the blue–green pigment. Based on analysis using the electron probe

X-ray microanalyser, the presence of potassium calcium sulphate, magnesium phosphate, aluminium phosphate, potassium aluminium phosphate and Cl-bearing sodium copper phosphate were confirmed. The blue–green colour of the pigment is attributable to the presence of Cl-bearing sodium copper phosphate. Because no heavy element was detected from the black pigment, it may be identified as carbon black.

Recent graffiti with a blue pigment are found on the surface of several pillars (Fig. 3 (l)). Analysis using the X-ray microdiffractometer revealed that the blue pigment consists of azurite ($Cu_3(CO_3)_2(OH)_2$).

Remnants of gold leaf are observed on some of the lintels in the cruciform gallery.

DISCUSSION

Summary of the pigments

Based on the analyses by the electron probe X-ray microanalyser and the X-ray microdiffractometer for several samples of pigments collected from each area, the substances constituting the pigments in the cruciform gallery of Angkor Wat are summarized in Table 1.

Red, orange, white and black pigments were mainly used in the cruciform gallery. The red pigment consists mainly of hematite and quartz, and contains abundant impurities such as SiO_2 (10–40 wt%) and Al_2O_3 (10–20 wt%). Because laterite consists mainly of hematite, goethite, quartz and kaolinite, and the major components are Fe_2O_3, SiO_2, Al_2O_3 and H_2O (Uchida *et al.* 1999a), it is supposed that laterite was used as a raw material for the red pigment. Abundant iron hydroxide (goethite) with a yellowish brown colour is contained in laterite. Therefore, it is possible that laterite was burned to obtain a vivid red colour. The orange pigment consists mainly of minium and contains Pb–Cl compounds, calcium phosphates, calcium oxalate hydrates, calcite, anglesite and gypsum. The white pigment is composed of Pb–Cl compounds, white lead, calcium oxalate hydrates, calcium phosphates, calcite, anglesite and gypsum. Three kinds of black pigments were found: lead dioxide derived from minium by oxidation, carbon black and gypsum discoloured into a black colour due to the absorption of soot and dust. Calcium phosphates are frequently found in the pigments. Some calcium phosphates may be derived from bat guano (Fusey 1991; Uchida *et al.* 1999b).

In all cases, the orange pigment (minium) underlies the red pigment (hematite). This means that the orange pigment was painted in an earlier period before the red pigment was applied. White pigment is usually observed under the orange and red pigments, respectively. The white pigment is considered to have been painted as a ground coat for the red and orange pigments. Red pigments have also been frequently observed on the inner walls of the sanctuaries in the other monuments in the Angkor area. Red and orange colours may have been painted to protect temples from evil and to indicate the sacred area.

The pigments used in the cruciform gallery are mixtures of several substances, not single substances. Therefore, it seems that almost all of the pigments, except for hematite (laterite), are synthetic substances and not natural ones. Synthetic methods of manufacturing minium and lead white have been known from the Roman era (Gettens and Stout 1966).

Around nine thousand treasures dating from the 8th to the 16th centuries CE are stored in the Shosoin, Nara, Japan, which belongs to Todai-ji, built in 756 CE. Many of them are of domestic production, from the 8th century, but treasures originating from China, India, Iran, Greece, Rome and other countries are also stored. The pigments applied to around 150 treasures from the Shosoin have been investigated by Naruse (2004). He found more than 20 species of pigments in

Table 1 *The substances constituting the pigments painted in the cruciform gallery of Angkor Wat*

Area A	*Area A′*	*Area B*	*Area C*	*Area D*	*Area E*
First layer: red	*First layer: red with a flesh tint*	*First layer: white*	*First layer: grey*	*First layer: grey*	*First layer: white*
Hematite, calcium oxalate hydrates, Pb–Cl compounds, calcium phosphates, gypsum	Hematite, calcium phosphates, calcium oxalate hydrates	Pb–Cl compounds, calcium oxalate hydrates, calcite, calcium phosphates, white lead, minium, lead dioxide	Pb–Cl compounds, white lead, anglesite, calcium phosphates, calcium oxalate hydrates, calcite, lead dioxide	Lead dioxide, Pb–Cl compounds, calcium phosphates	Calcium oxalate hydrates, calcium phosphates, anglesite, gypsum, Pb–Cl compounds, white lead
Second layer: white	*Second layer: black*	*Second layer: orange*	*Second layer: orange*	*Second layer: white*	*Second layer: red*
Calcium phosphates, gypsum, Pb–Cl compounds, white lead, calcium oxalate hydrates, calcite	Calcium phosphates, gypsum, calcium oxalate hydrates	Minium, Pb–Cl compounds, white lead	Minium, Pb–Cl compounds, white lead, calcium phosphates, calcium oxalate hydrates, calcite	Pb–Cl compounds, calcium phosphate, calcite	Hematite, calcium oxalate hydrates, white lead, calcite, gypsum, Pb–Cl compounds, calcium phosphates, anglesite
	Third layer: white		*Third layer: white*	*Third layer: orange*	*Third layer: white*
	Pb–Cl compounds, calcium phosphates, calcium oxalate hydrates, calcite, white lead		Pb–Cl compounds, calcium oxalate hydrates, calcium phosphates, gypsum, calcite	Minium, Pb–Cl compounds	Pb–Cl compounds, white lead, calcium oxalate hydrates, calcium phosphates, calcite, anglesite
					Fourth layer: orange
					Minium, Pb–Cl compounds, calcium oxalate hydrates, anglesite, lead dioxide
					Fifth layer: white
					White lead, Pb–Cl compounds, calcium oxalate hydrates, anglesite, calcite

Table 1 *(Continued)*

Area F	*Area G*	*Area G′*	*Area H*	*Area I*	*Area J*
First layer: black with lustre	*First layer: flesh*	*G′-1: black or flesh*	*First layer: black*	*First layer: red*	*Apsara relief: white*
Calcium phosphates, lead dioxide, calcium oxalate hydrates, white lead	Hematite, calcium oxalate hydrates, calcium phosphates, gypsum, calcite	Hematite, gypsum, calcium phosphates, calcite	Gypsum, calcium phosphates, calcium oxalate hydrates, calcite	Hematite, calcium oxalate hydrates, calcium phosphates, calcite, gypsum.	Calcium oxalate hydrates, calcium phosphates, gypsum
Second layer: red	*Second layer: black*	*G′-2 and G′-4: black*	*Second layer: white*		*Naga niche: white*
Hematite, calcium phosphates, calcium oxalate hydrates, Pb–Cl compounds, anglesite	Lead dioxide, calcium phosphates, gypsum, calcium oxalate hydrates, white lead, Pb–Cl compounds	Gypsum, calcium phosphates, calcium oxalate hydrates	Pb–Cl compounds, calcium phosphates, gypsum		Calcium oxalate hydrates, calcium phosphates, gypsum
Third layer: white	*Third layer: white*	*G′-3: red or black* *First layer: red*			*Petal decoration on naga niche: orange*
Pb–Cl compounds, white lead, calcium oxalate hydrates, calcium phosphates	Pb–Cl compounds, white lead, calcium phosphates, calcium oxalate hydrates, gypsum	Hematite, calcium phosphates, calcium oxalate hydrates			Minium + a
Fourth layer: orange	*Fourth layer: orange*	*Second layer: white to grey*			*Floral decoration around naga niche: white*
Minium, Pb–Cl compounds	Minium, Pb–Cl compounds, anglesite, calcium phosphates, gypsum, calcium oxalate hydrates	Calcium oxalate hydrates, calcium phosphates, gypsum.			Gypsum, calcium phosphates, calcium oxalate hydrates
	Fifth layer: white	*Third layer: orange*			*Concavity* *First layer: red*
	Calcium oxalate hydrates, calcite, calcium phosphates, gypsum, white lead	Minium, calcium phosphates			Hematite, gypsum, calcium oxalate hydrates
					Second layer: white
					Pb–Cl compounds, gypsum, calcium phosphates, calcium oxalate hydrates, white lead

these treasures. These pigments are considered to be standards from the 8th to the 16th centuries. Eleven of these pigments have been found in the cruciform gallery at Angkor Wat.

The time of application of the pigments

There is little direct evidence to ascertain the date when these pigments were applied. Therefore, it is difficult to obtain definitive conclusions. However, it is evident that the orange pigment (minium) was painted earlier than the red pigment (hematite). The Apsara reliefs surrounded by floral decorations, in the friezes of the cruciform gallery, were highly finished and the orange pigment was applied in the petal decorations of the Naga niche and in the centre of the floral decorations in the uppermost sections of the frieze. It is, therefore, highly possible that the orange pigment was applied at the time of the foundation (the Angkor Wat style period, from the end of the 11th century CE to the middle of the 12th century). On the other hand, it is considered that the red pigment was painted in the Bayon style period (the end of the 12th century CE to the early 13th century), because the red pigment has frequently been found in temples constructed in the Bayon style period. Alternatively, it may have been applied in the reign of Ang Chan I (1526–66 CE), because a large-scale restoration was conducted in Angkor Wat at that time (1546 CE) (Coedès 1962). Many inscriptions, with Chinese ink, made by the Japanese in the early 17th century remain on the pillars in Area E of the cruciform gallery (Sugiyama 2009). Because the inscriptions were written on the surface of the red pigment and were covered by the white pigment (a pinkish colour), it is evident that the red pigment was applied before the early 17th century CE. The red pigment was also painted on the surface of delaminated sandstones. There is a possibility that the red pigment was painted again after the 17th century CE, as a small-scale repair.

Blue–green, black and red pigments were found locally in the cornices at the top and bottom of the frieze. Because hematite (laterite) was used as the red pigment, these pigments are considered to have been painted in the Bayon style period or later.

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REFERENCES

Coedès, G., 1962, La date d'execution des deux bas-relief tardifs d'Angkor Vat, *Journal Asiatique*, **250**(2), 235–48.

Delvert, J., 1963, Recherches sur l'èrosion des grès des monuments d'Angkor, *Bulletin, de l'École Française d'Extrême-Orient*, **LI-2**, 453–534.

Freeman, M., and Jacques, C., 1999, *Ancient Angkor*, Weatherhill, New York.

Fusey, P., 1991, *Altération biologiques des grès Cambodgiens et recherché de moyens de protection*, École Française d'Extrême-Orient, Paris.

Gettens, R. J., and Stout, G. L., 1966, *Painting materials: a short encyclopedia*, Dover Publications, New York.
Kiesewetter, A., Leisen, H., and v. Leisen, E. P., 2001, On the polychromy of Angkor Vat: results of initial paint color investigations, *UDAYA*, **2**, 57–66.
Naruse, M., 2004, Inorganic pigments found on objects in the Shosoin, *Bulletin of the Office of the Shosoin Treasure House*, **26**, 13–60 (in Japanese).
Sugiyama, H., 2009, *The studies of medieval site and Japanese settlement in Cambodia*, Report of Grant-in-Aid for Specially Promoted Research, no. 19900125, 65 pp. (in Japanese).
Uchida, E., Maeda, N., and Nakagawa, T., 1999a, The laterites of the Angkor monuments, Cambodia: the grouping of the monuments on the basis of the laterites, *Journal of Mineralogy, Petrology and Economic Geology*, **94**, 162–75.
Uchida, E., Ogawa, Y., and Nakagawa, T., 1998, The stone materials of the Angkor monuments, Cambodia: the magnetic susceptibility and the orientation of the bedding plane of the sandstone, *Journal of Mineralogy, Petrology and Economic Geology*, **93**, 411–26.
Uchida, E., Ogawa, Y., Maeda, N., and Nakagawa, T., 1999b, Deterioration of stone materials in the Angkor monuments, Cambodia, *Engineering Geology*, **55**, 101–12.