THE INVESTIGATION OF PIGMENTS AND PAINT LAYER STRUCTURES OF MURAL PAINTINGS AT MAITEPNIMIT TEMPLE

การศึกษาผงสีและโครงสร้างชั้นสีของจิตรกรรมฝาผนัง ที่วัดใหม่เทพนิมิตร

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ABSTRACT

Twenty five samples covering all the colours were taken from mural paintings at Maitepnimit Temple for study. Methods of the investigation involved the microscopical examination of the pigments and of the cross-sections of the samples. The inorganic pigments were analysed by microscopical chemical tests or by electron probe microanalysis with energy-dispersive X-ray spectrometer and further identified by X-ray diffraction method with the help of Guinier-Hagg type focussing powder camera. The organic pigments were identified by thin-layer chromatography, high pressure liquid chromatography, and mass spectroscopy methods. The analyses revealed that the technique of the paintings was tempera. Before painting, the plaster of the wall was primed with a ground layer consisted of the white pigment of calcite. However, the white pigment used in the white patterns was hydrocerussite. In addition, gypsum and kaolinite were found as white pigments mixed as fillers in other paint layers of various colour samples. The red pigments found were cinnabar, minium, and hematite. The blue pigments were indigo and cumengeite. The green pigment found was malachite. Carbon was found as black pigment. Gamboge was found as yellow pigment under the gold layer in the gold sample and also found mixed in the paint layer of the leaf green sample.*

*This temple situates near Krungthon Bridge on Thonburi side.

บทคัดย่อ

การศึกษานี้ได้ทำการเก็บตัวอย่างจิตรกรรมฝาผนังที่วัดใหม่เทพนิมิตร* ทุกสีมาวิเคราะห์ โดยใช้วิธีการตรวจตัวอย่างและด้านตัดขวางของตัวอย่างด้วยกล้องจุลทรรศน์ วิเคราะห์ธาตุในผงสีอนินทรีย์ด้วยวิธีจุลทรรศน์เคมี หรือใช้กล้องจุลทรรศน์อิเลคตรอนร่วมกับเครื่องวัดพลังงานจากรังสีเอกซ์ และพิสูจน์เอกลักษณ์ด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์ โดยใช้ถ่ายภาพด้วยกล้องกีเนียร์เฮกชนิดปรับโฟกัส ส่วนผงสีอินทรีย์วิเคราะห์ด้วยวิธีทินเลเยอร์โครมาโตกราฟฟี (thin-layer chromatography) วิธีลิควิดโครมาโตกราฟฟีความดันสูง (high pressure liquid chromatography) และวิธีแมสสเปคโตรสโคปี (mass spectroscopy method) ผลการวิเคราะห์ปรากฏว่าเทคนิคของจิตรกรรมแห่งนี้ เป็นแบบเทมเพอรา (tempera) และพบว่าก่อนทาชั้นสีของทุกตัวอย่างจะมีการทาชั้นรองพื้นไปบนผิวผนังด้วยผงสีขาวของแคลไซท์ (calcite) ส่วนผงสีขาวที่ใช้ในลวดลายสีขาวคือ ไฮโดรเซอร์รัสไซท์ (hydrocerussite) ผงสีขาวที่ใช้ผสมเป็นเนื้อสีปนอยู่ในชั้นสีอื่น ๆ ได้แก่ยิปซัม (gypsum) และเคโอลิไนต์ (kaolinite) ผงสีแดงคือซินนาบาร์ (cinnabar) มีเนียม (minium) และฮีมาไทต์ (hematite) ผงสีน้ำเงิน คือครามและคูเมนไจท์ (cumengeite) ผงสีเขียวคือมาลาไคต์ (malachite) ผงสีดำคือคาร์บอน ในตัวอย่างที่ปิดลายด้วยทองพบว่า มีการใช้รงทาให้เป็นสีเหลืองก่อนที่จะปิดด้วยแผ่นทอง และรงนี้ก็ใช้ผสมในชั้นสีของตัวอย่างสีเขียวใบไม้ด้วย

INTRODUCTION

Traditional mural paintings of Thailand are beautiful works of art depicting lifestory of the Lord Buddha. They also illustrate here and there social and cultural activities of the past. Most of them were painted on the interior wall of ordination halls, pagodas, palaces and *prangs* (Cambodian-style towers). The scientific study of pigments and paint layer structures will bring light on the technological achievements of the time of mural execution and render important archaeological and art historical information about ancient pigments before they vanish. Moreover, the results can be of great help in proper conservation of the fast disappearing paintings which are invaluable cultural heritage.

In 1986, it was found[5] that the pigments of the mural paintings in the prang of Mahathat Temple at Ratchaburi are cinnabar, minium, gypsum, carbon, and gamboge**. The mural paintings were believed to be executed in early Ayutthaya period. It is interesting to

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** Gamboge[1, 8, 9] is a yellow gum resin from the tree *Garcinia hanburyi* Hook F.. It grows mostly in India, Sri Lanka, Thailand, Cambodia and South Vietnam. Gamboge has the principal acidic yellow component called gambogic acid ($C_{38}H_{44}O_8$).

continue investigation on the pigments used in the paintings of later period for comparison and find out some other Thai ancient pigments. Therefore the paint samples from the mural paintings in Maitepnimit Temple have been investigated in this study. The paintings in this temple have been believed to be of late Ayutthaya period or early Ratanakosin period[7]. The apparent colours of the paintings are white, black, red, orange-red, red-brown, purple, pink, green, gold and blue. Twenty five samples taken for analyses covered all the colours. In addition, the white pigment in the ground layers and the yellow pigments found in the gold gilded sample and in the paint layer of a leaf green sample were also analysed.

MATERIALS AND METHODS

Instruments

1. Stereo microscope, (Nikon)
2. Leitz Ortholux-Pol microscope
3. Elemental analyzer (Perkin Elmer 240C)
4. Scanning electron microscope with energy-dispersive X-ray spectrometer (JEOL JSM-35 CF, Link EDS 860)
5. Guinier-Hagg type focussing powder camera (Philips XDC 700)
6. Shimadzu Chromatopac C-RIA
7. Mass spectrometer (JEOL JMS-DX 300)

Methods

1. Explored and took photographs of the paintings.

2. Twenty-five samples were taken with a scalpel for analyses. The locations of the sample takings were recorded on the photographs. The samples included two white, one black, one light blue, two bluish green, five light green, one leaf green, four red, one orange-red, two flesh pinks, one orange-pink, one red-brown, one intense purple, one light purple, one blue and one gold gilded sample.

3. Examination of the sample cross-sections. A sample cross-section was prepared[6] by embedding a very tiny fragment of the sample in the epoxy resin (Araldite), and microscopically examined to study the paint layer structure and details in the paint layer.

4. Microscopical chemical tests[2, 3, 4]: Some elements and anions of components from ground layers and paint layers were analysed as follows:

4.1 Sulphide was detected by the reaction with sodium azide/iodine solution.

4.2 The test of Pb was carried out by the reaction with potassium iodide.

4.3 Gypsum was detected by the formation of white wheat-sheave like crystals, the characteristic of gypsum after adding diluted hydrochloric acid.

4.4 The detection of Fe was done by the reaction with potassium ferrocyanide.

4.5 The carbonate was detected by diluted hydrochloric acid.

4.6 The presence of Cu was proved by the test with potassium ferrocyanide solution.

5. Electron probe microanalysis of elements: Cl, Al, Si and Au in paint layers were analysed by scanning electron microscope with energy-dispersive X-ray spectrometer (SEM/EDX) at 20 kV. The analyses were done on the prepared sample cross-sections.

6. X-ray powder diffraction method: The components from the paint layers and from the ground layers were analysed by X-ray powder diffraction by use of Guinier-Hagg type focussing powder camera with $CuK_{\alpha 1}$ radiation (λ = 1.5405981 Å). The sample powder photographs were taken for 2 h at 40 kV, 30 mA. The pure silicon was added as internal calibration standard and the photographs were taken again under the same conditions. Peak intensity of diffraction lines were visually estimated. The d-spacing values were calculated by use of the Bragg's law. The identification was made by comparing the powder film data with those of the JCPDS diffraction files.

7. Identification of carbon. The black sample was washed[10] with toluene : methyl alcohol (3:1), benzene:ethyl alcohol (1:1), hydrochloric acid (3N), sodium hydroxide (3N), water and acetone, respectively. After drying at 105°C, it was analysed by the elemental analyser. Carbon was found.

8. Identification of gamboge: With acetone, the yellow pigment was extracted from the gold gilded sample and from the green sample painted as a leaf on dark tree. The extract was then analysed as follows:

8.1 Thin-layer chromatography method: The extract was applied on TLC plate of silica gel 60, with 0.25 mm thickness. The solvent system was chloroform: ethyl methyl ketone (5:1). By comparison with many standard yellow organic pigments, the sample and gamboge showed the separation of 3 yellow spots having the same shapes and same Rf at 0.08, 0.36 and 0.51 (main spot), and gambogic acid* showed a spot having Rf = 0.51.

8.2 High pressure liquid chromatography method : The main yellow spot of the sample was extracted from the TLC plate with ether, then dried and dissolved in methanol. The solution was then injected into the Zorbax-ODS column (25 cm × 4.6 mm I.D.) containing Zorbax-ODS particles (5 μm). The mobile phase consisted of methanol and 5% acetic acid in

*Gambogi acid used as standard was obtained by extraction from gamboge bought from a drug store in Bangkok. The extraction process followed Ahmad's method.[1]

water with the ratio 85:15. The flow rate was 1 ml/min and the column pressure was 60 kg/cm^2. The UV detector was set at 291 nm. By comparison with gamboge and gambogic acid under the same condition, the t_R values of the main yellow component of the sample, and the gambogic acid were 11.29 and 11.24 min, respectively. Also the gamboge showed the separation with major component at t_R 11.22 min (Figure 1).

8.3 Mass spectroscopy method: The mass spectrum of the dry extract from the sample yellow main spot on the TLC plate was then recorded by mass spectrometer at 250°C, 70 eV: m/e 628 ($M^{+\cdot}$, 12), 613 (5), 600 (16), 545 (100), 517 (31), 499 (12), 473 (16), 355 (13), 295 (15), 271 (10), 245 (19), 243 (3), 221 (21), 215 (25), 189 (13), and 147 (13).

The mass spectrum of the standard gambogic acid was also taken at the same condition: m/e 628 ($M^{+\cdot}$, 12), 613 (5), 600 (18), 545 (100), 517 (33), 499 (14), 473 (14), 355 (14), 295 (17), 271 (12), 245 (24), 243 (3), 221 (22), 215 (34), 189 (17) and 147 (15).

9. Identification of indigo : The tiny fragment of the blue sample was washed with diluted acetic acid, water and acetone, respectively. The mass spectrum of the blue pigment was taken at 200°C, 70 eV: m/e 262 ($M^{+\cdot}$, 100), 234 (24), 233 (7), 206 (7), 205 (17), 179 (3), 131 (13), 104 (25), 103 (20), 77 (9), and 76 (13).

For comparison, the mass spectrum of standard indigo was also taken at the same condition: m/e 262 ($M^{+\cdot}$, 100), 234 (26), 233 (7), 206 (8), 205 (19), 179 (3), 131 (13), 104 (27), 103 (20), 77 (9) and 76 (13).

RESULTS

The painting technique and ground layers

The microscopical examination of all the sample cross-sections showed that white ground layers were applied on the wall plaster before painting. The presence of carbonate and also further identification by X-ray diffraction showed that the ground layers were made of calcite ($CaCO_3$). The clear separation of the ground layers from the paint layers indicated that the paintings were executed by tempera technique, by which the pigments were mixed with binder and painted on the dry ground layers.

White samples

The detection of the Pb and carbonate together with the analysis by X-ray diffraction proved that the white pigment in the white paint layers of the white patterns was hydrocerussite or white lead (lead carbonate hydroxide, $Pb_3(CO_3)_2(OH)_2$). These white paint layers were painted upon the white ground layers.

Black sample

Black pigment of carbon was found in the black paint layers.

Gold gilded sample

A yellow layer of gamboge was found underneath the layer of gold leaf.

Light blue sample

Analysis of the contents in the light blue layer by SEM/EDX showed the presence of Pb, Cu, Cl, Al, Si, and Ca which supported the identification of cumengeite (lead copper chloride hydroxide hydrate, $Pb_4Cu_4Cl_8(OH)_8.H_2O$), gypsum ($CaSO_4.2H_2O$) and kaolinite ($Al_2Si_2O_5(OH)_4$ by X-ray diffraction.

Blue sample

Indigo was found as the blue pigment in the blue layer.

Green samples

From microscopical chemical test and X-ray diffraction, the green pigments in all the sample green layers were identified as malachite (copper carbonate hydroxide, $Cu_2CO_3Cu(OH)_2$). Besides the green pigment of malachite, the light green layers also contain the white pigment of gypsum. There is also white pigment of kaolinite as well as gypsum in the bluish green layers. In one light green layer, hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$ was found as white pigment, whereas in the other four samples, gypsum was found as the white pigments. In the leaf green layer, it was found that the yellow of gamboge was mixed with malachite and gypsum. This layer is painted as a leaf upon a dark layer consisted of malachite, black pigment and gamboge. This dark layer was painted as dark tree.

Red samples

In one sample red layer, only red pigment of cinnabar (mercury sulphide, HgS) was found. Besides cinnabar, white pigment of hydrocerussite was found mixed in other sample red layer. In another two sample red layers, cinnabar and orange-red pigment of minium or red lead (lead tetroxide, Pb_3O_4) were found. The mixture of cinnabar and minium was also found in the sample orange-red layer but the amount of minium was larger than that in the red sample.

Pink samples

In the two sample pink layers which were painted as flesh, the mixtures of cinnabar, gypsum, hydrocerussite and kaolinite were found. Whereas the mixture of minium, hydrocerussite and kaolinite was found in the paint layer of orange-pink sample.

Red-brown sample

Dark red pigment of hematite (ferric oxide, Fe_2O_3) was found mixed with red pigment of cinnabar and white pigment of hydrocerussite in the red-brown layer of the sample.

Purple samples

The analysis revealed that the purple layers were consisted of hematite and gypsum.

CONCLUSIONS

The wall plaster was primed with white ground layers before painting. The techniques of the paintings at Mahathat Temple and one of those at Maitepnimit Temple are the same, which are tempera. By this technique, the pigments were mixed with binder and painted on the dry ground layers. The same pigments found used in mural paintings of both temples are cinnabar, minium, gypsum, carbon and gamboge. It showed the continuity of using these pigments from early Ayutthaya to late Ayutthaya or early Ratanakosin periods. The other pigments found in the paintings at Maitepnimit Temple are malachite, indigo, hematite, cumengeite, hydrocerussite and kaolinite. In the paintings at Mahathat Temple, gypsum was used in the ground layer, in the white paint layer and also as filler whereas in the Maitepnimit Temple, more varieties of the white pigments were used. Calcite was used as white pigment in the ground layers, whereas hydrocerussite as white pigment in the paint layer of white patterns. Gypsum as well as hydrocerussite and kaolinite were used as fillers.

As a guideline for the consideration in conservation of the mural paintings at Maitepnimit Temple, caution should be taken for the application of chemicals to the painting areas which contain malachite and gamboge. Very often some alkaline solutions and organic solvents are used in the cleaning and coating steps in the painting conservation process. As malachite turns brown in strong alkaline solution and gamboge dissolves very well in many organic solvents, so the chemicals to be used in the conservation process should be tested with standard pigments before applying to the paintings. Therefore, the information about the materials to be conserved is necessary for the safety in the conservation of cultural heritage.

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REFERENCES

1. Ahmad, S.A., Rigby, W. and Taylor, R.B. Gamboge, Part II. *J. Chem. Soc.*, 1966, 772-779.
2. Chamot, E.M. and Mason, C.W. Handbook of Chemical Microscopy. John Wiley and Sons Ltd., New York, 1940, 106.
3. Feigl, F. Spot Test in Inorganic Analysis, 5th ed. Elsevier Publishing Company, Amsterdam, 1958, 438-439.
4. Plesters, J. Cross-section and Chemical Analysis of Paint Sample. *Study in Conservation*, 1956, 133-158.
5. Prasartset, C. The Study of Pigments and Layer Structures of the Murals in *Phra Prang* of Wat Mahathat at Rajburi. *Science* (The Science Society of Thailand), 1986, **40**(12), 649-663.
6. Mosk, J.A. Analytical Methods Applied in the Investigation of the Bardwell Samples. *Studies in Conservation*, 1975, **20**, 104.
7. Napaknarm, N. Maitepnimit Temple. Mural Paintings in Thailand. Muang Boran Publising House, Bangkok, 1983, 41-43.
8. Ollis, W.D., Ramsay, M.V.J. and Sutherland, I.O. The Constitution of Gambogic Acid. *Tetrahedron*, 1965, **21**, 1453-1470.
9. Tantiwat, P. Herbs. Herbs Association of Thailand, 1978, 56 (in Thai).
10. Winter, J. The Characterization of Pigments Based on Carbon. *Studies in Conservation*, 1983, **28**, 64.

Table 1. Conclusion of the Analyses

Pigments from	Microscopical chemical test, found	SEM/EDX found	X-ray diffraction found	Conclusion
ground layers of all samples	CO_3^{2-}	-	$CaCo_3$	calcite
2 white layers	Pb, CO_3^{2-}	-	$Pb_3(CO_3)_2(OH)_2$	hydrocerussite
1 black layer	-	-	-	carbon(analysed by elemental analyser)
1 light blue layer	-	Ca, Al Si, Pb, Cl, Cu	$Pb_4Cu_4Cl_8(OH)_8.H_2O$, $CaSO_4 2H_2O$, $Al_2Si_2O_5(OH)_4$	cumengeite, gypsum, kaolinite
2 bluish green layers	- -	Ca, Al Si, Cu	$CuCO_3$ Cu $(OH)_2$ $CaSO_4 2H_2O$ $Al_2Si_2O_5(OH)_4$	malachite, gypsum kaolinite
1 light green layer	CO_3^{2-}, Cu, Pb	-	$CuCO_3Cu(OH)_2$, $Pb_3(CO_3)_2(OH)_2$	malachite, hydrocerussite
4 light green layers	CO_3^{2-}, Cu, gypsum	-	$CuCO_3Cu(OH)_2$, $CaSO_4 2H_2O$	malachite, gypsum
1 leaf green layer	CO_3^{2-} Cu, yellow pigment	-	Cu $CO_3Cu(OH)_2$, $CaSO_4 2H_2O$	malachite, gypsum, gamboge (analysed by TLC, HPLC, mass spectroscopy)
1 red layer	S	-	HgS	cinnabar
1 red layer	Pb, S	-	HgS $Pb_3(CO_3)_2(OH)_2$	cinnabar, hydrocerussite

Table 1. (continued)

Pigments from	Microscopical chemical test, found	SEM/EDX* found	X-ray diffraction found	Conclusion
2 red layers	Pb, S	-	HgS, Pb_3O_4	cinnabar, minium(less)
1 orange red layer	Pb, S	-	HgS, Pb_3O_4	cinnabar, minium (more)
2 flesh pink	-	Hg, Ca, Pb,Al,Si	HgS, $CaSO_4.2H_2O$ $Pb_3(CO_3)_2(OH)_2$, $Al_2Si_2O_5(OH)_4$	cinnabar
1 orange pink layer	-	Pb, Al, Si	Pb_3O_4 $Pb_3(CO_3)_2(OH)_2$, $Al_2Si_2O_5(OH)_4$, SiO_2	minium, hydrocerussite, kaolinite, quartz
1 red-brown layer	Fe, Pb, S	-	Fe_2O_3, Hgs, $Pb_3(CO_3)_2(OH)_2$	hematite, cinnabar hydrocerussite
2 purple layers	Fe, gypsum	-	Fe_2O_3, $CaSO_4.2H_2O$	hematite, gypsum
1 gold gilded layer	-	Au	-	gold
1 blue layer	-	-	-	indigo (by mass spectroscopy)
yellow under gold leaf	-	-	-	gamboge (by TLC, HPLC, mass spectroscopy)

*SEM/EDX = Scanning electron microscope with energy dispersive X-rays analysis

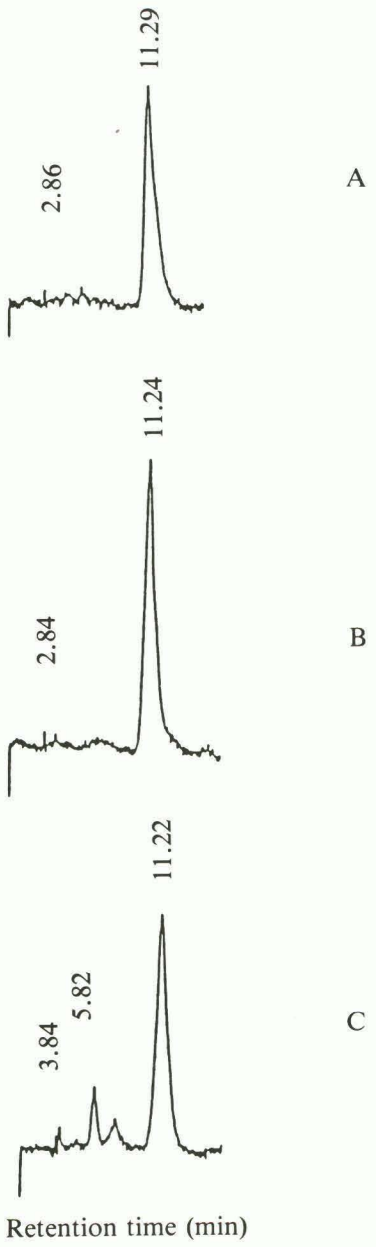

Fig.1 HPLC chromatogram of

A. Main yellow component of the sample
B. Gambogic acid
C. Gamboge

a. ground layer containing calcite

b. paint layer containing cinnabar and minium

c. paint layer containing malachite, gypsum, kaolinite and α -quartz

d. paint layer containing minium, hydrocerussite and kaolinite

e. paint layer containing cinnabar

Fig.2 X-ray powder diffraction pattern of some samples

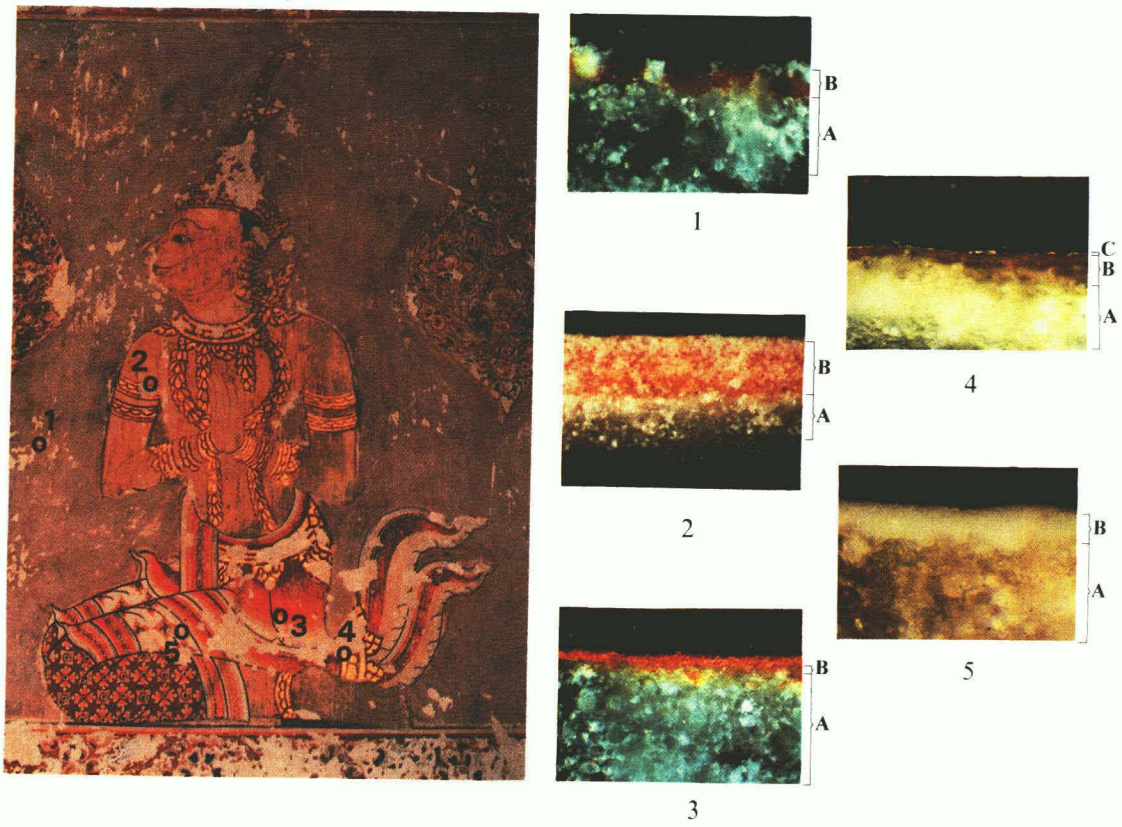

Fig.3 Microphotographs of cross-section of samples and position of the following:

1. Light purple
2. Flesh pink
3. Red
4. Gold
5. White

A. Ground layer
B. Paint layer
C. Layer of gold

Fig.4 Position of a bluish green sample of the rock and microphotograph of the cross-section

A. Ground layer

B. Bluish green paint layer of about 0.04-0.06 mm thickness