JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2008; **39**: 1057–1065
DOI: 10.1002/jrs.1985

JRS

Examination of pigments on Thai manuscripts: the first identification of copper citrate

Katherine Eremin,[1]* Jens Stenger,[1] Jo-Fan Huang,[3] Alan Aspuru-Guzik,[2] Theodore Betley,[2] Leslie Vogt,[2] Ivan Kassal,[2] Scott Speakman[4] and Narayan Khandekar[1]

[1] Harvard University Art Museums, 32 Quincy Street, Cambridge, MA 02138, USA
[2] Department of Chemistry and Chemical Biology, 12 Oxford Street, Harvard University, Cambridge, MA 02138, USA
[3] Philadelphia Museum of Art, Benjamin Franklin Parkway, Philadelphia, PA 19130, USA
[4] Center for Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

Received 13 December 2007; Accepted 5 March 2008

Samples from Thai manuscripts dated to the 18th to 20th century were analyzed by Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR) to determine the pigments used. This suggested a change in palette from the 18th to 20th century, with use of imported pigments in the later manuscripts. In the 18th century, the main green used was an organic copper salt, which was replaced by emerald green and mixtures of Prussian blue with gamboge, chrome yellow and zinc yellow (zinc potassium chromate). Chrome yellow was used in addition to gamboge in one later 19th century manuscript. Similarly, indigo in the 18th century manuscripts was replaced by Prussian blue and then synthetic ultramarine in the 19th century manuscripts.

Lead white was the main white pigment in all but one manuscript, which contained huntite, a magnesium calcium carbonate. Huntite also occurred in mixtures with other pigments in two other manuscripts. In all the works studied, red lead, vermilion and red earth were used for red, orange and pink shades and red earth in brown areas.

The organic copper salt used in the 18th century gave good FTIR spectra but could not initially be matched with any published compound. X-ray diffraction (XRD) suggested this was a copper citrate phase, and examination of the literature showed that the FTIR spectra matched those published for a hydrated copper citrate. Raman spectra were obtained from this organic copper salt, which showed close agreement with those obtained from synthetic copper citrate. Copper citrate has not been identified previously as an artist's material, although its use has been postulated on the basis of historical texts. Minor copper formate and/or copper chloride were also identified by XRD and scanning electron microscopy (SEM) in some green samples containing copper citrate. Copyright © 2008 John Wiley & Sons, Ltd.

KEYWORDS: Thai manuscripts; pigments; copper citrate; art works

INTRODUCTION

The Harvard University Art Museums has one of the most important collections of Southeast Asian manuscripts in the United States. This includes a large number of Thai manuscripts dating from the 18th to 20th centuries. These were part of a bequest to the Harvard University Art Museums in 1984 from Philip Hofer, Curator of Printing and Graphic Arts at Harvard's Houghton Library and a collector of Chinese and Japanese painting and calligraphy, of Japanese printed and graphic arts, and of Thai and other Southeast Asian manuscripts. The present study focused on 12 horizontal accordion-fold manuscripts with ink, color, and gold on khoi paper, made from the inner bark of the khoi tree (*streblus aspera*). All but one of the manuscripts studied (1984.506) were two-sided. The manuscripts examined vary in subject, text and proposed date, as shown in Table 1. A leaf from the earliest manuscript, 1984.511, dated to the late 17th to early 18th century is shown in Fig. 1.

EXPERIMENTAL

Following a nondestructive X-ray fluorescence study to determine the elemental composition of all colors in the manuscripts, micro-samples were removed from

---

*Correspondence to: Katherine Eremin, Harvard University Art Museums, 32 Quincy Street, Cambridge, MA 02138, USA.
E-mail: Katherine_eremin@harvard.edu

Table 1. Summary of examined Thai manuscripts in the collection of the Harvard University Art Museums

Object #	Title	Text details	Given dates
1984.511	Illustrated Jataka Tales	Pali language, written in Cambodian script	Late 17th to early 18th
1984.512	Illustrated	Pali text, written in Cambodian script	18th century
1984.501	Illustrated Dharma Quotes/10 Jataka Tales	Pali language, written in Cambodian script	Late 18th to early 19th century
1984.517	Illustrated text on Cosmology, Traiphum Phra Ruang	Pali captions, written in Thai script	Late 19th century
1984.524	Illustrated Phrai Malai	Pali language, written in Cambodian script	19th century
1984.506	Illustrated Phrai Malai	Cambodian script	Mid- to late 19th century
1984.507	Illustrated Vessantara Jataka	Pali language, written in Mon script	Late 19th century
1984.508	Illustrated 10 Jataka Tales	Pali language, written in Cambodian script	c.1800
1984.521	Illustrated Phrai Malai	Pali language, written in Cambodian script	19th century
1984.510	Illustrated Phrai Malai	Pali and Thai languages, Cambodian script	Early 20th century
1984.433	Illustrated manual of divination	Thai script	c. 1900
1984.516	Illustrated Phrai Malai	Thai language, Cambodian script	Late 19th to early 20th century

selected areas for analysis by Raman spectroscopy and Fourier-transform infrared (FTIR) spectrometry. Some samples were also examined by scanning electron microscopy (SEM) and/or by X-ray diffraction (XRD) to obtain additional information.

The Raman spectrometer used was a Bruker Optics 'Senterra' dispersive Raman microscope with an Olympus BX51M microscope. The Raman spectrometer is equipped with 532, 633 and 785 nm excitation laser sources. There are three gratings for the 785 nm laser, covering the 70–3283 cm^{-1} range, four gratings for the 633 nm laser covering 60–3532 cm^{-1} and three gratings for the 532 nm laser covering 65–3700 cm^{-1}. The spectrometer resolution is ~3–5 cm^{-1} (depending on the wavenumber). The system uses an Andor 'iDus' CCD detector, operated at −55 °C. There are five software-controlled settings for the power of each laser: 100, 50, 25, 10 and 1%. The estimated actual power on the sample at the 100% setting is 8.5 mW for the 532 nm laser, 10.9 mW for the 633 nm laser and 37.5 mW for the 785 nm laser. The microscope has 20×, 50× and 100× objectives, with laser spot sizes of approximately 5, 2 and 1 μm, respectively. The microscope contains a joystick-controlled motorized stage and setting of the analysis area is accomplished with the aid of an attached video camera. The instrument is controlled via the OPUS software version 5.5. Most samples were analyzed using the 785 nm laser at 2–5 mW setting. Samples of green, and in some instances blue, pigments were analyzed using the 532 nm laser at 0.2–2 mW setting to prevent the samples from burning and to obtain better spectra. All spectra were baseline-corrected to subtract florescence.

Following Raman analysis, FTIR spectrometric analyses were carried out using a Nicolet 510 instrument coupled to a Spectra-tech IR-plan infrared microscope with a 32× objective. The sample was compressed onto a diamond cell (2 mm × 2 mm) with a stainless steel roller, and the sample area was defined by double apertures contained in the microscope. An absorbance spectrum (4000–500 cm^{-1}) was measured (resolution setting 8 cm^{-1}) and subtracted against a blank background. The spectrum was compared with a database of artists' materials at the Straus Center for Conservation.

A Jeol JSM-6460 LV scanning electron microscope with an Inca X-sight Oxford Instruments energy dispersive detector was used to examine a few samples to confirm the elemental composition and help with identification of the Raman spectrum. The samples were analyzed in low vacuum (35 Pa) without carbon coating at a voltage of 20 kV.

XRD of selected samples was undertaken on a Bruker D8 Multipurpose Diffractometer. Samples were collected over a 2θ range of 30–90° using Cu Kα radiation at 40 kV, 40 mA. The primary X-ray beam was collimated to approximately 0.5 mm with a monocapillary, and the diffracted X-rays were detected with a General Area Detector Diffraction System (GADDS) 2-D detector.

DOI: 10.1002/jrs

Figure 1. Detail from the late 17th to early 18th century Thai manuscript 1984.511. Photo: Imaging Department © President and Fellows of Harvard College.

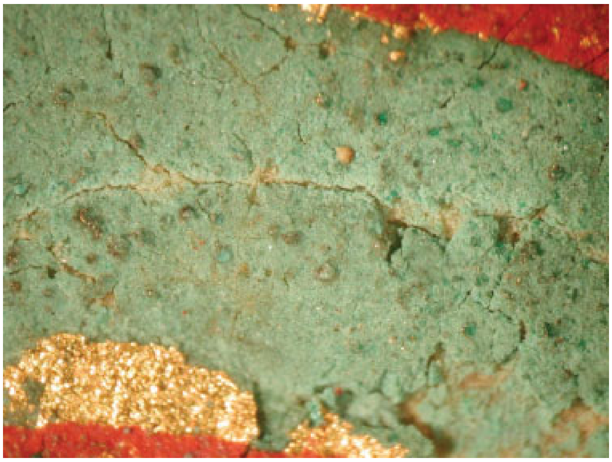

Figure 2. Photomicrograph of a green area on manuscript 1984.506. The large green crystals and the powder yielded the same vibrational spectra and could be identified as mainly copper citrate.

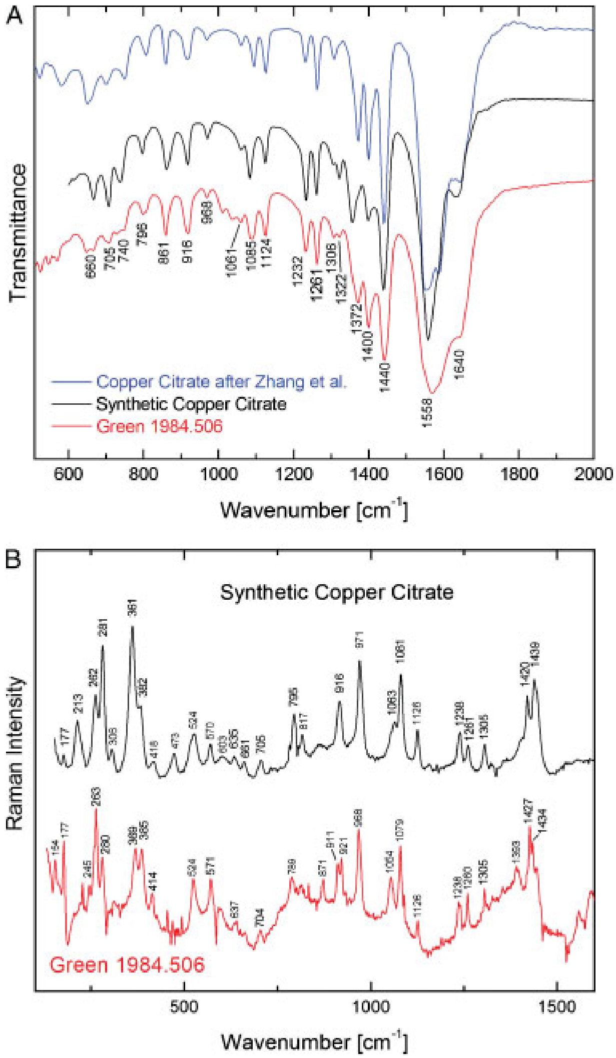

Figure 3. (a) FTIR spectra of copper citrate synthesized and measured by Zhang *et al.*[1] (blue), of copper citrate synthesized using the historical recipe with verdigris and lemon juice (black), and of the green sample from Harvard manuscript 1984.506. (b) Raman spectra of synthetic copper citrate produced from verdigris and lemon juice (532 nm excitation, 2 mW) and of the green sample from Harvard manuscript 1984.506 (532 nm excitation, 0.2 mW).

RESULTS

Green pigments

The green pigments proved the most varied in these manuscripts. Most manuscripts contained more than one green shade, and in many of the 19th century manuscripts a light green was used for the under-drawing. A number of different green pigments and mixtures were identified in the project, which are discussed below. Identification of additional shades in some manuscripts is ongoing.

Samples of the bright green pigments used in the three oldest manuscripts, shown in Fig. 2, 1984.501, 1984.511 and 1984.512, and also in 1984.506 and 1984.507 gave good Fourier-transform infrared spectroscopy FTIR spectra, but initially failed to give Raman spectra. A Raman spectrum was eventually generated using the 532 nm laser at 0.2 mW and with a collection time of 100 min. The use of higher power resulted in the burning of the sample. The FTIR and Raman spectra are shown in Fig. 3(a) and (b), respectively, over the ranges 500 to 2000 cm^{-1} for the FTIR and 0 to 1600 cm^{-1} for the Raman spectra. No peaks were observed at higher wavenumbers in either spectrum apart from those due

DOI: 10.1002/jrs

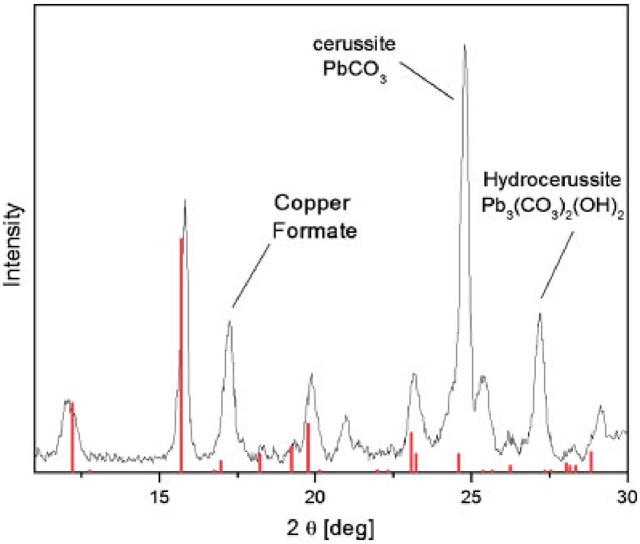

Figure 4. X-ray diffraction pattern of the unknown green (black line) and the copper citrate reference. Other compounds present are copper formate, cerussite and hydrocerussite.

to the CH stretch around 3000 cm^{-1} and the OH stretch at around 3400 cm^{-1}. Initially it proved impossible to match either spectrum to any available reference or published spectra. SEM analysis showed that the only inorganic element detected was copper, suggesting an organic copper salt. XRD of these samples yielded spectra that matched those of hydrated copper citrate, as shown in Fig. 4. Examination of the recent literature showed that the FTIR spectra were similar to those published[1] for a hydrated copper(II) citrate $Cu_2C_6H_4O_7(H_2O)_2$, illustrated in Fig. 3(a). The structure of copper(II) citrate is unusual because the Cu(II) has 5-fold coordination and occurs in a 3D open framework structure that has large void channels.[1] Minor copper formate and/or copper chloride was also identified by XRD and SEM in some of the green copper citrate samples, possibly as alteration products. Although copper citrate salts have been discussed in the conservation literature, it was noted that it had not yet been found on any art works.[2] The presence of copper citrate on these manuscripts therefore represents the first known use of copper citrate as a pigment. The lack of significant associated phases and the prevalence of this phase in the 18th to 19th century manuscripts indicate that copper citrate was the original pigment used, rather than an alteration product of another copper green pigment.

Replication of a mid- to late-17th century Venetian recipe for reacting verdigris with lemon juice to give a 'most beautiful green color. . .like an emerald' produced copper citrate pentahydrate,[2] $Cu_4(C_6H_5O_7)_2(H_2O)_5$. Color measurements showed that the color spectrum for the copper citrate was shifted into the blue compared to verdigris itself.[2] The Venetian recipe states that care should be taken not to let the brush touch water, and it was noted that the copper citrate salts 'have dubious stability'.[2] Water was easily lost from the copper citrate complex even at ambient temperatures, the gray green crystals becoming opaque and then light blue as water loss progressed.[1] The dehydrated copper citrate then slowly absorbed water from the air over time.[1] This behavior was attributed both to the large bond lengths of the two $Cu-O_{(H2O)}$ bonds, which allow the weakly bonded water molecules to be removed readily and to the fact these loosely bond water molecules occur on the edge of the large unoccupied void channels and therefore are able to move through them once released.[1]

No published Raman reference spectra for the copper citrates have been identified. Synthesis of hydrated copper citrate was undertaken following the Venetian recipe by reacting commercial verdigris, copper acetate, with lemon juice. The resulting dark green precipitate was confirmed by XRD and FTIR (Fig. 3(a)) to correspond to copper citrate. The Raman spectrum from the synthetic copper citrate and the copper citrate pigment on the manuscripts are shown in Fig. 3(b) and, as far as the authors are aware, represent the first published Raman spectra for this phase. The Raman spectrum from the manuscript and synthetic copper citrate samples showed close agreement, although some peak-shifts are apparent and the manuscript sample contains some additional peaks, as seen in Fig. 3(b). It is not clear why the FTIR spectrum matches more closely than the Raman spectrum for the two phases, but it may be related to the precise hydration phase of the samples and/or presence of trace elements in the manuscript samples (although none was detected by SEM or XRF). The precise color of the crystals reported by previous authors[1,2] and of those synthesized in this study differ from each other and also differ from those found in the Thai manuscript samples, possibly due to differences in hydration. The potential instability of the copper citrate raises the question of whether any alteration has occurred to the manuscript samples and hence whether the hydration state and color of the original phase differed significantly from the present one. Visual examination indicates that the bright green areas on the manuscripts contain scattered translucent bright green crystals in a more powdery and slightly lighter matrix. A number of copper citrate species are recorded in the literature with different degrees of hydration, e.g. copper citrate pentahydrate, copper citrate sesquihydrate, copper citrate hemiquihydrate and copper citrate dihydrate, but thermal analysis is required to determine the degree of hydration and thereby to differentiate these. There was no obvious difference between the FTIR or Raman spectra from the larger translucent crystals and those of the more powdery matrix on the manuscripts. Thermal analysis is currently being carried out to determine the hydration state of the synthesized and manuscript phases.

A number of these manuscripts contained areas of darker green and yellow-green in addition to the bright blue-green areas containing the copper citrate green. Samples from 1984.507 indicated that gamboge was the main component of the yellow-green, while visual inspection showed that the dark green contained abundant blue particles.

In contrast to the earlier works, samples from bright green areas of manuscripts 1984.508, 1984.510, 1984.516 and 1984.517 contained emerald green. Samples from dark green areas of these manuscripts contained a mixture of Prussian blue and gamboge. The same mixture, Prussian blue and gamboges, was identified in samples from the under-drawing of manuscripts 1984.506, 1984.516 and 1984.517.

Optical examination of samples from the bright green areas of 1984.521 showed that these consisted of red, white and yellow-green particles. Raman and FTIR spectroscopy indicated that these were a hitherto unidentified red, barite and a mixture of zinc yellow and Prussian blue, respectively. SEM analysis indicated that the green particles contained zinc, potassium and chromium, indicating that the form of zinc yellow used was zinc potassium chromate rather than pure zinc chromate. SEM analysis of reference pigments of zinc yellow, Forbes 327 MFA and Forbes 59 SCCC, confirmed the presence of potassium in these, showing that these are also the zinc potassium chromate form. This has the approximate composition $K_2O \cdot 4ZnCrO_4 \cdot 3H_2O$, although this can vary considerably owing to variations in $ZnO{:}Cr_2O_3$ ratio.[3] The Raman spectra of the samples from the manuscript and from these reference pigments are shown in Fig. 5. These are very similar to a spectrum published for zinc chromate, suggesting that the published data may also have come from zinc potassium chromate rather than zinc chromate.[4] Yellow-green areas of 1984.521 and the green under-drawing from 1984.521 contained a mixture of Prussian blue and gamboge.

Three different greens can be distinguished visually in 1984.524, which appear to consist of a mixture lead chromate and Prussian blue, with ultramarine (the blue pigment used in this manuscript) mixed in order to control the shade. The bright green contained significant barite, while the yellow-green and dark green contained significant gypsum.

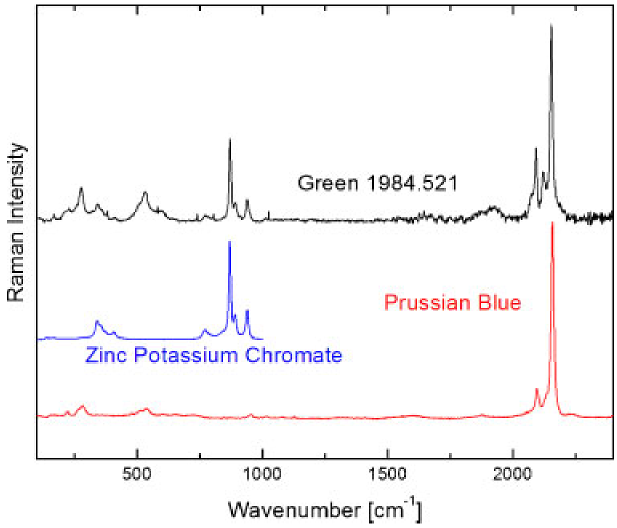

Figure 5. The green color in manuscript 1984.521 achieved by mixing zinc potassium chromate with Prussian blue. The Raman spectrum of the sample is compared with reference spectra for these two pigments. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

Only one green pigment has been identified to date in 1984.433. Emerald green appears to have been used in all areas of 1984.433, often over black to give a darker shade.

White pigments

Lead white, basic lead carbonate $2PbCO_3 \bullet Pb(OH)_2$, was the most common white used in the manuscripts either alone or mixed with other colors. However, in 1984.512 the only white present in any area was huntite, $Mg_3Ca(CO_3)_4$, while in 1984.506 both huntite and lead white were present in white and colored samples, and in 1984.501 huntite was present in the blue samples. The use of huntite in some manuscripts is interesting and requires further investigation. Cerussite, lead carbonate $PbCO_3$, was associated with the lead white in some samples from 1984.506 and 1984.508. Calcite and kaolin were both present in many samples, both white and colored, while barite and gypsum occurred in samples from 1984.521 and 1984.524.

Yellow pigments

The main yellow identified was gamboge mixed with a white or clear material: huntite in 1984.512; kaolin in 1984.501 and 1984.511; lead white in 1984.507, 1984.508 and 1984.510; and huntite and lead white in 1984.506. The main yellow in 1984.521 also appears to be gamboge, again with lead white, but zinc yellow (zinc potassium chromate) was found in one sample; XRF analysis revealed low levels of zinc in some yellow areas. Visual examination indicates two different shades of yellow in some of these areas, suggesting that gamboge was the main yellow, with zinc yellow possibly used to highlight details. Manuscript 1984.524 was the only one to contain significant amounts of two different yellows, with gamboge and lead chromate, $PbCrO_4$, occurring in separate samples.

Blue pigments

Three distinct blue pigments were identified by Raman spectroscopy. Indigo was used in manuscripts 1984.511, 1984.501 and 1984.512. Prussian blue was used in manuscripts 1984.506, 1984.507, 1984.510, 1984.516 and 1984.521. Ultramarine was used in manuscripts 1984.433, 1984.508, 1984.517 and 1984.524. The fine particle size and rounded shape indicate the use of synthetic rather than natural ultramarine.

Red, orange and other pigments

Vermilion, sometimes combined with red lead, was the main pigment detected in all red areas, while all orange areas had red lead, sometimes combined with vermilion. Pink areas contained red ochre, red lead or vermilion mixed with lead white and/or calcite, while red-brown areas contained mainly red ochre.

DOI: 10.1002/jrs

DISCUSSION

Previous analytical studies of the materials used in Thai manuscripts are somewhat lacking. Most notably, *in situ* Raman microscopy was used to study four Thai manuscripts from the British Library Oriental Department.[5] The authors found that indigo was used in the manuscript dating from 1800, with ultramarine in those from 1880 and 1900. Orpiment was used for yellow in the manuscript from 1800, with lead chromate plus barite and orpiment used in the manuscript from 1900. Chalk and lead white in manuscripts from 1800 and 1880 were replaced by anhydrite, gypsum, barite and lead white in the manuscript from 1900. Red lead was used in all four manuscripts, vermilion in the manuscripts from 1780, 1800 and 1880 and red ochre only in the manuscript from 1780. The green pigment used on three of the Thai manuscripts and the yellow on the three oldest manuscripts did not give a Raman spectrum. The authors suggest that this rules out the common copper-based green pigments, inorganic yellow pigments, Indian yellow or berberine, as these have well-known spectra.[5]

In addition, three analytical studies of Thai murals have been published and were thought relevant to this study, particularly as art historians have noted parallel relationships between Thai murals, manuscripts, banners and sculptures. Two studies noted a change in pigments with time, from azurite in the 17th century to indigo and cumengeite (a lead copper chloride hydroxide hydrate) in the 18th century to Prussian blue in the early 19th century to ultramarine in the late 19th century.[6,7] The green and yellow pigments also changed from malachite in the 17th to early 19th century to emerald green in the late 19th century and from gamboge in the 14th to early 19th century to an unspecified lead pigment mixture in the late 19th century.[6,7] Clay, gypsum and calcite dominated in the 14th to mid-17th century, lead white in the 18th and early 19th century and lead white with barite in the late 19th century.[6,7] The change from traditional to imported pigments (Prussian blue, emerald green and synthetic ultramarine) in the 19th century was compared to the decline in style of traditional Thai painting due to the influence and introduction of Western ideas after the third quarter of the 19th century.[7] Another study of mural paintings found lead white, calcium carbonate, silica, vermilion, and green verditer.[8] All three studies suggested that the paints applied were usually not homogeneous in composition and various transparent whites such as gypsum, kaolin, or calcite were mixed into all the colors.[6–8]

The findings of these previous studies suggest a transition from local to imported pigments during the 19th century. The current study of manuscripts from the Harvard University Art Museums also indicates a transition from local to imported pigments over this period. These imported pigments could have come via a number of routes, as Thailand traded actively with other countries in the area, China, Japan, India and Persia, and with the Western nations trading in the South China Seas – the Portuguese, Dutch and British. The most important sea routes were to China, Japan and India, and the Europeans often traded between the key ports of the intra-Asian routes rather than direct to Europe. Trade with China was the most important, as shown by the detailed list of imports and exports to Thailand compiled by D. E. Malloch, an employee of the British East India Company in 1852.[9] Malloch categorized his lists into four parts: *Production of Siam Annually, British imports, Imports of India Goods to Siam, and China goods imported into Siam,* and mentions artists' pigments specifically (Table 2). Arthur Neale, a local resident in Siam, also stated that merchants imported boxes of watercolors, cakes of finest indian ink, gum, and glue from Canton and Macao to Bangkok.[10]

Artists could hence choose between foreign and local materials, with the greatest volumes of imported paints apparently coming from China. It is therefore pertinent to consider the palette used in China and in Thailand's other main trading partners, particularly India, and when imported chemicals first appeared in these areas. For example, although some manufactured watercolors were probably available in Calcutta, India, in the early 19th century, these became much more accessible in 1842 when N.C. Dutt and Aukhoy Coomar Laha opened the first specialist paint shop and eventually became the fist importers of Winsor and Newton brands, selling prepared paints and dry pigments.[11]

Emerald green was discovered at the beginning of the 19th century and was first commercially manufactured in Schweinfurt, Germany, in 1814.[12] The pigment was adopted in China in the late 1840s to early 1850s and widely used by third quarter of the 19th century, although it was often mixed with malachite rather than used alone.[13] It has been suggested that Foreign Blue and Foreign Green were successful from around 1851 onwards, as they were cheap, convenient to use and gave good results.[14] This suggests that emerald green could have been imported into Thailand from China from the 1850s onwards. Although studies of Indian paintings are less extensive, emerald green was found in one 19th century and one late 19th to early 20th century painting.[15,16] Prussian

Table 2. Selected items from D.E. Malloch's record on Siam[9]

Siam local resources	Dragon's blood, gamboge, gold dust (for local temple), indigo (local use only), lead white and black, lac
Siam's import from India	Arsenic (white and yellow), red and yellow ochre, turpentine, gum tragacanth or gum dragon, from Turkey, gum Arabic, verdigris, safflower
Siam's import from China	Gold leaf, mock gold leaf, glue, varnish, paint (red, blue, black, white, and green), vermilion, coarse and fine, saffron
British Imports	Paints (green, blue, black, and red)

DOI: 10.1002/jrs

blue also occurred on late 18th to early 19th century and on 19th century Japanese Ukiyo-e paintings.[17]

Prussian blue was developed in Berlin in 1704 by Diesbach.[18] Although it is unclear when Prussian blue was first imported into China, small amounts were imported into China and Bengal, India, by the Swedish East India Company in 1759,[19] and larger amounts were imported into Canton, China, by the East India Company by 1775–1776.[20] The amount imported by the East India Company ten years later was more than four times that in 1775–1776, suggesting an expanding and profitable trade.[20] Prussian blue has been found in 19th century Chinese paintings in place of the azurite and indigo found in 18th century paintings.[21] Prussian blue was imported sporadically from China to Japan as early as 1782.[22] Import from China ceased around 1810 and was resumed by the Dutch from 1817 and then by the Chinese, who rapidly dominated import, in 1824.[22] However, references to Prussian blue in Japanese writings dated 1763 and 1778 and the claims that it was used in some 18th century paintings suggest some earlier import.[22] Prussian blue has been found on two Japanese Edo-Period paintings dated before 1820, one from the 1760s and the other from 1817.[23] The presence of both indigo and Prussian blue on Edo-Period paintings dated after 1830 shows that Prussian blue did not completely replace indigo.[23] Prussian blue also occurred on late 18th to early 19th century and on 19th century Japanese Ukiyo-e paintings.[17] Prussian blue was found with ultramarine on 19th century Kalighat pats from Bengal, India.[11] Hence, Prussian blue could have been imported into Thailand from China, Japan or India during the late 18th to early 19th century.

Lead chromate is the main constituent of chrome yellow, and mixed with Prussian blue in chrome green. Lead chromate came on the market sometime in the 1800s and was widely used by the second quarter of the 19th century.[3] Zinc potassium chromate occurs in zinc yellow and with Prussian blue in zinc chrome green. Vauquelin discovered zinc yellow in 1809, but it was not developed as an artist colorant until 1847 by Murdock.[3] Zinc yellow and zinc chrome green both occur in Western art works painted after 1855.[3] Again, some delay in the transfer of these pigments to Thailand from the Western art market might be expected. Chrome and zinc yellow have not been noted in Chinese painting but chrome yellow was used in the 19th century Kalighat pats from Bengal.[11] However, these authors also found lead chromate in one sample of an earth pigment from the area and suggested that the natural mineral crocoite may have been used in some instances rather than the synthetic pigment.[11] It seems likely that chrome yellow (lead chromate) could have been imported into Thailand during the 19th century, with zinc yellow or zinc green imported sometime after the mid-19th century but probably not until the late 19th century.

Another pigment likely to have been imported from Europe was synthetic ultramarine, which was discovered in 1826 and sold commercially from 1828.[24] This was rapidly adopted by Western artists and their suppliers.[24] Synthetic ultramarine replaced Prussian blue in Thai murals in the late 19th century[7] and occurs with indigo in 19th century murals from Mysore, India.[25]

The results of our current study of Thai manuscripts from the Harvard University Art Museums indicate a chronological variation in the green, blue and to a lesser extent yellow pigments. However, if the materials used by mural artists and manuscript artists are directly comparable and if the assumed dates of introduction for materials are correct, revision of the dates proposed for some manuscripts may be necessary. For example, copper citrate appears to have been used in the earliest manuscripts, late 17th to early 19th century, and then replaced by emerald green sometime after 1855 in the later 19th century manuscripts. This would suggest either that 1984.506 and 1984.507, attributed to the mid- to late 19th century and the late 19th century, respectively, are either early 19th century or perhaps of more provincial manufacture and hence lack the more modern imported pigments used in the other manuscripts. An early 19th century date is also suggested by the presence of the imported Prussian blue rather than indigo (18th century) or synthetic ultramarine (late 19th century) in these manuscripts. The presence of Prussian blue and Emerald green in 1984.516 and 1984.510 suggests a mid-19th century date, while the presence of chromates in 1984.521 and 1984.524 suggests a late 19th century date. The results are summarized in Table 3. The current data suggest that the green, blue and yellow pigments present allow these art works to be divided into those produced during or prior to the early 19th century, those dating from the mid- to late 19th century and those dating from the late 19th to early 20th century. It is hoped that this may help future chronological attribution of Thai art based on the pigments present.

CONCLUSIONS

A new pigment, copper citrate, was identified for the first time on works of art. The FTIR and Raman spectra of this pigment were compared with those from synthesized copper citrate. The Raman spectrum presented here is believed to represent the first published Raman spectrum for this phase. Further work is required to understand the properties and stability of this phase and possible changes in the phase(s) used on the manuscripts. A transition was observed in the green and blue pigments from the 18th to 20th century: copper citrate to emerald green and indigo to Prussian blue to synthetic ultramarine. Gamboge, which was abundant in Thailand and a major export product, was never replaced by a new western pigment, but chrome yellow was also used in the late 19th century. The chronological relationships observed might help future chronological attribution of Thai art works based on the pigments present. The results indicate some relationship between the materials used in murals and manuscripts: the notable exception being the use of copper

DOI: 10.1002/jrs

Table 3. Green, blue and yellow pigments identified in the manuscripts and comparison of dates inferred from the pigments with those given in the museum records

Manuscript accession number	Green pigment	Blue pigment	Yellow pigment	Given date ('analytical date' where different)
1984.511	Copper citrate	Indigo	Gamboge	Late 17th to early 18th century
1984.512	Copper citrate	Indigo	Gamboge	18th century
1984.501	Copper citrate	Indigo	Gamboge	Late 18th to early 19th century
1984.506	Copper citrate	Prussian blue	Gamboge	Mid- to late 19th century (early 19th?)
1984.507	Copper citrate	Prussian blue	Gamboge	Late 19th century (early 19th?)
1984.516	Emerald green; Prussian blue and gamboge	Prussian blue	Gamboge	Late 19th to early 20th century (mid-19th?)
1984.510	Prussian blue, gamboge; Emerald green	Prussian blue	Gamboge	Early 20th century (mid-19th?)
1984.521	Prussian blue, zinc potassium chromate	Prussian blue	Zinc potassium chromate	19th century (late 19th century?)
1984.508	Emerald green; Prussian blue, gamboge	Synthetic ultramarine	Gamboge	Early 19th century (c.1800) (late 19th?)
1984.517	Emerald green; Prussian blue, gamboge	Synthetic ultramarine	Gamboge	Late 19th century
1984.524	Prussian blue, lead chromate, synthetic ultramarine,	Synthetic ultramarine	Gamboge, lead chromate	19th century (Late 19th to 20th century)
1984.433	Emerald green	Synthetic ultramarine	Gamboge	Early 20th century (c. 1900)

citrate in the 18th century for manuscripts but malachite for murals. The reason for this difference is unknown but it is tempting to attribute it to the instability of copper citrate and the probable greater susceptibility of murals to changes in humidity. Further work on the properties of copper citrate pigments is required to understand their use and preservation.

Acknowledgements

The authors would like to thank Robert Mowry, Anne Rose Kitigawa and Melissa Moy in the Asian department of the Harvard University Art Museums; Craigen Bowen and Anne Driesse in Straus Center for Conservation, Harvard University Art Museums; Richard Newman, Michelle Derrick, Tanya Uyeda and Joan Wright in the Museum of Fine Arts, Boston; and Guoqiang Yang for providing the FTIR data. J. S. thanks the Andrew W. Mellon Foundation for a generous fellowship.

REFERENCES

1. Zhang G, Yang G, Shi MA. *J. Cryst. Growth Des.* 2006; **6**(2): 375.
2. Scott DA. *Copper and Bronze in Art: Corrosion, Colorants, Conservation*. Getty Publications: Los Angeles, 2002; 287.
3. Kuhn H, Curran M. In *Artists Pigments: A Handbook of their History and Characteristics*, vol. 1, Feller RL (ed). National Gallery of Art: Washington, DC, 1986; 187.
4. Burgio L, Clark RJH. *Spectrochim. Acta* 2001; **A 57**: 1491.
5. Burgio L, Clark RJH, Gibbs PJ. *J. Raman Spectrosc.* 1999; **30**: 181.
6. Prasartset C. *J. Natl. Res. Counc. Thai.* 1990; **22**(1): 73.
7. Prasartset C. *ICOM Committee for Conservation Preprints*, vol. 1, Edinburgh, Scotland, 1996; 430.
8. Suigisita R. *Scientific Papers on Japanese Antiques and Art Craft*, vol. 28, 1983; 20.
9. Malloch DE. *Siam: Some General Remarks on its Productions, and Particularly on its Imports and Exports and the Mode of Transecting Business with the People*. J. Thomas at the Baptist Mission Press: Calcutta, 1852; 34.
10. Neale FA. *Residence in Siam*. Office of the National Illustrated Library: London, 1850.
11. Mackay C, Sarkar AN. In *Scientific Research on the Pictorial Arts of Asia, Proceedings of the Second Forbes Symposium at the Freer Gallery of Art*, Jett P, Winter J, McCarthy B (eds). Archetype Publications: London, 2005; 135.
12. Fiedler I, Bayard M. In *Artists Pigments: A Handbook of their History and Characteristics*, vol. 3, Fitzhugh EW (ed). Oxford University Press: Oxford, 1997; 219.
13. Wise D, Wise A. *Proceedings of the Fourth International Conference of the Institute of Paper Conservation 6–9 April 1997*. The Institute of Paper Conservation: London, 1998; 125.

14. Feian Yu. In *Chinese Painting Colors: Studies of their Preparation and Application in Traditional and Modern Times*, Silbergeld J, McNair A (eds). University of Washington Press: Washington, DC, 1988.
15. Bowen CW, Snodgrass A. In *Gods, Kings and Tigers: The Art of Kotah*, Welch SC (ed). Asia Society Galleries and Harvard University Art Museums: New York, 1997; 83.
16. Fitzhugh EW. In *An Annotated and Illustrated Checklist of the Vever Collection*, Lowry GD, Beach MC, Marefat R, Thackston WM, Arthur M (eds). Sackler Gallery and University of Washington Press: Washington, DC, 1988; 425.
17. Fitzhugh EW. *Pigments in Later Japanese Paintings; Freer Gallery of Art Occasional Papers*. Smithsonian: Washington, DC, 2003; 1.
18. Berrie BH. In *Artists Pigments: A Handbook of their History and Characteristics*, vol. 3, Fitzhugh EW (ed). Oxford University Press: Oxford, 1997; 91.
19. Koninckx C. *The First and Second Charters of the Swedish East India Company (1731–1766)*. Van Ghemmert Publishing Company: Kortrijk, 1980.
20. Pritchard EH. *J. Econ. Soc. Hist. Orient* 1957; **1**(1): 108.
21. Giaccai J, Winter J. In *Scientific Research on the Pictorial Arts of Asia, Proceedings of the Second Forbes Symposium at the Freer Gallery of Art*, Jett P, Winter J, McCarthy B (eds). Archetype Publications: London, 2005; 99.
22. Smith H. *Ukiyoe Geijutsu*, vol. 128, 1998; 3.
23. Leona M, Winter J. *Pigments in Later Japanese Paintings; Freer Gallery of Art Occasional Papers*. Smithsonian: Washington, DC, 2003; 57.
24. Plesters J. In *Artists Pigments: A Handbook of their History and Characteristics*, vol. 2, Roy A (ed). Oxford University Press: Oxford, 1993; 37.
25. Vasnatha R. In *Scientific Research on the Pictorial Arts of Asia, Proceedings of the Second Forbes Symposium at the Freer Gallery of Art*, Jett P, Winter JB, McCarthy B (eds). Archetype Publications: London, 2005; 143.

DOI: 10.1002/jrs