

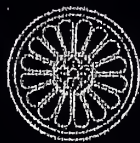
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STUDIES USING  
SCIENTIFIC METHODS

PIGMENTS IN  
LATER JAPANESE  
PAINTINGS

Elisabeth West FitzHugh,  
John Winter, and Marco Leona

FREER GALLERY OF ART  
OCCASIONAL PAPERS  
NEW SERIES VOL.1



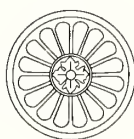
SMITHSONIAN INSTITUTION  
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FREER GALLERY OF ART  
OCCASIONAL PAPERS



NEW SERIES VOL. 1

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John Winter, and Marco Leona

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SMITHSONIAN INSTITUTION  
WASHINGTON, D.C.

NEW SERIES VOL. 1

FREER GALLERY OF ART

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## P R E F A C E

The Freer Gallery of Art Occasional Papers began publication in 1947 under the stewardship of Archibald G. Wenley, director of the museum, and produced a total of eleven titles between 1947 and 1971. Subject, format, and length ranged widely, from monographic treatments of a single object or group of objects to checklists, translations, and commentaries on a particular text — even to annotated bibliographies. The series was intended for a specialist readership, and it focused almost exclusively on material in the collections of the Freer Gallery of Art. A short-lived revival of the Occasional Papers produced three additional titles between 1998 and 2002. Unlike the original series, however, these papers consisted of brief treatments of individual works of art, were highly standardized in length and format, and were aimed at a broad readership.

As one of the world's premier research institutions for the study of Asian art, the Freer Gallery of Art demonstrates its commitment to this mission through the research activities it sponsors for its own staff and facilitates for other scholars. Disseminating the results of these research activities forms an equally important dimension of the museum's mission, and in this regard we have decided to relaunch the Occasional Papers series in its third incarnation.

The new series signals a return to the underlying principles of the series Wenley established in 1947. Likewise, it publishes for a specialist constituency research on Asian art from a variety of perspectives, although its purview is no longer confined to the museum's collections. As in the original series, future titles of the Freer Gallery of Art Occasional Papers will range widely in subject; they will include monographs, conference proceedings, multiauthor treatments of material or theme, and studies in conservation and scientific research. The first of the series is entitled *Studies Using Scientific Methods: Pigments in Later Japanese Paintings*.

This volume was funded by a publications endowment established with a grant from the Andrew W. Mellon Foundation and contributions from private donors, and by a grant from the Mellon Foundation that supports the scientific study of the materials and structures of East Asian paintings.

Julian Raby  
Director



# A Database of Pigments on Japanese Ukiyo-e Paintings in the Freer Gallery of Art

*Elisabeth West FitzHugh*

## ABSTRACT

The pigments were identified on five hundred Japanese ukiyo-e paintings on silk and paper supports in the Freer Gallery of Art. They date to the Momoyama period, the Edo period, and the early years of the Meiji period, from the late sixteenth to the late nineteenth century. Of the seventeen pigments identified, eleven were employed throughout the ukiyo-e period: shell white, vermilion, red lead, organic red, red and brown earths, organic yellow, yellow earth, malachite, azurite, indigo, and an organic brown. The other six pigments were not used before the late seventeenth century, and some were first used later: lead white, orpiment, various copper greens, smalt, Prussian blue, and artificial ultramarine. Further characterization is needed of the red and brown organic colorants and of some of the copper greens. Other pigments included mica and some metal pigments. Shell white is unique to Japan, as may be the organic brown. The other pigments were in use throughout East Asia. Identification methods were polarized-light microscopy, chemical microscopy, and x-ray diffraction, with limited use of scanning electron microscopy with energy-dispersive x-ray analysis.

## INTRODUCTION

The Freer Gallery of Art, Smithsonian Institution, owns over six hundred Japanese paintings, drawings, and sketches of the ukiyo-e school, dating from the late sixteenth to the late nineteenth century. The artists made use of color on some five hundred of these works, and the pigments used in this group were the subject of this investigation.

Paintings in the ukiyo-e style depicted the everyday life of the ordinary people of Japan, and their subject matter was known as “the floating world.” Ukiyo-e paintings first appeared in Japan in the late sixteenth century during the Momoyama period (1573–1615) and continued to be produced throughout the Edo period (1615–1868) and into the early years of the Meiji period (1868–1912). Some ukiyo-e artists produced both paintings and woodblock prints while others specialized in

either one or the other. Pigments on woodblock prints have been studied (Grove 1971; Feller, Curran, and Bailie 1984; Whitmore and Cass 1988); they generally require different analytical methods from those used here because the amount of pigment available from a print is substantially less than that available from a painting.

These paintings were executed on silk and paper supports and are in the form of hanging scrolls (*kakemono*), handscrolls (*makimono*), folding screens (*byōbu*), and drawings or sketches; some of the drawings and sketches were originally in albums or sketchbooks. In this report the term *painting* refers to all of these types of work.

This project was conceived by Rutherford J. Gettens, then head curator of the Technical Laboratory, the predecessor of the Department of Conservation and Scientific Research of the Freer and Sackler galleries, and Gettens himself carried out some of the earliest work. The study was begun in 1969 and completed by 1985. The present author published a progress report (FitzHugh 1979) and a shorter version of the final results (FitzHugh 2003).

This work forms a basic database (appendix) on pigment use on Japanese ukiyo-e paintings and has provided the groundwork for further work by others (Leona and Winter 2001; Winter, Giaccai, and Leona 2003). The intent was to characterize the pigments used and to determine if any chronological differences could be observed from the early to the late ukiyo-e period. Many pigments were used throughout the period; some were not used during the early years (table 1).

TABLE 1. SUMMARY OF PIGMENTS ON UKIYO-E PAINTINGS IN THE FREER GALLERY OF ART

Used late 16th to mid-19th century		Used after late 17th century	
Shell white	Organic yellow	17th century on	Smalt
Vermilion	Malachite		Copper greens
Red lead	Azurite	18th century on	Orpiment
Indigo	Red and brown earths	late 18th–19th century	Prussian blue
Yellow earths	Organic brown		Lead white
Organic red		19th century only	Ultramarine

The dating of these paintings is in some cases problematic. The first ukiyo-e painting in the collection of Charles Freer (1854–1919) was catalogued in 1896. By 1917 Freer had purchased three-quarters of the five hundred ukiyo-e paintings with color here under consideration. Of the paintings acquired before 1917 (no ukiyo-e paintings were acquired between 1917 and 1954), some are firmly dated, but the registrar's records for many of them supply only the information available when they were first accessioned. Attributions given here are based on the registrar's records, updated in some cases with more recent information from the catalogue published

at the time of the fiftieth anniversary of the Freer Gallery of Art (Stern 1973). In the appendix the column headed "Artist, Life/Activity Dates" indicates the attribution as far as is known. This attribution is superseded by any information in the column headed "Dated"; for example, if a painting is attributed to an eighteenth-century artist but "dated" to the nineteenth century, this indicates that the painting may only be in the style of that artist.

The information presented here should be of interest to a wide audience. In particular historians of Japanese art and culture may find some guideposts toward solving problems of the attribution and dating of ukiyo-e painting, a complex subject, indeed referred to as "the Augean stables" by one specialist in this field (Clark 1992). Other potential readers include scientists searching for facts in the history of East Asian technology and generalists with an interest in the art of the area who wish to learn more about the materials used to produce it.

#### DESIGN OF THE PROJECT

The range of colors on every painting was noted by visual inspection and at low magnification with a binocular microscope. Every color was sampled, within the limits of subjective judgments that had to be made. In some cases a color may have been missed; for example, two blues in different areas of the painting might appear superficially to be the same but are in fact two different pigments. It should be noted that on certain works, chiefly nineteenth-century drawings and sketches, some pigments were applied too thinly to permit analysis by the methods used, and thus not all the colors were sampled; these paintings are indicated in the appendix.

Pairs or sets of paintings were treated as one painting. Usually only one painting was sampled after it was ascertained that the same range of colors was found on other paintings in the pair or set. Variations in colors occasionally occurred from one painting to another in a pair or set, and in that case more than one painting was sampled in order to obtain a representative range. With an album or sketchbook, similar criteria were used. Samples were taken from areas showing no obvious evidence of retouch. Some retouched areas were sampled when questions arose, but generally the intent here was to obtain a record of the original pigments. The question of retouch is obviously an important one, but it was only peripheral to this investigation.

Only very small samples were required, so no damage was done to the painting. The identifications were carried out by traditional methods: polarized-light microscopy, chemical microscopy, and x-ray diffraction. Limited use was made of element determination by scanning electron microscopy with energy-dispersive

x-ray analysis. Also included here are the results of analysis by thin-layer chromatography carried out on three of these paintings in another investigation (Winter 1987). The analytical methods used here have inherent limitations, but they served to make possible firm identification of a large majority of the pigments. Some pigments could not be exactly characterized, and a few could only be described in a very general way. Nevertheless, the totality of the data gives a good idea of the colorant range.

No statistical deductions can be drawn from the results of these analyses. The absence of a pigment does not necessarily mean that it was never used by the painter. For example, if no yellow was used in a painting, it was not necessarily because no yellow was available, but only that the artist did not require that color to obtain a desired effect.

Carbon-based inks and pigments are obviously of tremendous importance in East Asian works of art, for their use in drawing outlines and for parts of the design. Important work has been done on carbon pigments (Winter 1983), but the investigation of their use on ukiyo-e paintings was beyond the scope of this project. The metal pigments were not searched for systematically. A few identifications of gold and silver, copper alloys, and silver sulfide are noted, but a comprehensive discussion of this subject merits a separate investigation.

Japanese pigment names have varied at different periods. Those most commonly in use in the Edo period are given here, and only an occasional attempt has been made to discuss other names when they relate to the pigment's history of use. The complex history of Japanese pigment terminology over the centuries is beyond the scope of this study.

When Buddhism reached Japan from China and Korea in the sixth century, new techniques and new coloring materials from China became available. The *Nihongi* (Chronicles of Japan), a famous seventh-century document, mentions the introduction from Korea of techniques of preparing painters' colors (Aston 1924, vol. 2, 140). Previously the range of pigments in Japan was limited chiefly to earth colors and clays (Yamasaki and Emoto 1979). Early writers on Japanese pigments often referred to China as the source of the best pigments, or sometimes as the best source of information about them. For this reason some information from Chinese documents and from reports of pigment use in China is included here, with a discussion of pigment history and use in the West, where appropriate.

## OVERVIEW OF RESULTS

Of the seventeen pigments identified on these paintings, eleven were employed



throughout the ukiyo-e period (see table 1). The common white was shell white. The reds used were vermilion, red lead, one or more organic reds, and red and brown earths, the iron oxide pigments. These two earths are classified together because their compositions are closely related. The yellow colorants used throughout the period were an organic yellow and yellow earth — the latter only rarely. Malachite was the common green, and there were two blues: azurite and indigo. The single brown colorant was an organic brown, discounting brown earth, which is not discussed separately.

The other six pigments were not used before the late seventeenth century, and some were first used even later (see table 1). Smalt has not been previously reported on Japanese paintings, yet it was used here on some sixty paintings, sometimes quite extensively, as seen in plate 1. The use of various copper green colorants on ukiyo-e paintings has also been unreported; further research is required to determine their identity and to account for the date of their first appearance on these paintings. The fact that orpiment was not used until the early eighteenth century also cannot at present be explained. Prussian blue was invented in the West at the beginning of the eighteenth century, and the chronology of its importation into Japan after the late eighteenth century is discussed below. Lead white was used after the late eighteenth century, by only two artists, evidently because ukiyo-e painters preferred shell white. Finally, the finding of few examples of artificial ultramarine is consistent with our knowledge that neither the natural nor artificial pigment is known on Japanese paintings on paper and silk.

Other pigments found rarely included mica, a selection of metal pigments, and two found only in repaint, kaolin and barite.

## THE PIGMENTS

### WHITE PIGMENTS

Shell white, *gofun*, is a form of calcite, calcium carbonate ( $\text{CaCO}_3$ ), made of crushed seashells, usually oyster shells. The shells are collected in piles and allowed to age outside for a protracted period to allow organic matter to deteriorate. They are then processed by crushing, grinding, and pulverizing, followed by levigation. In factory production observed by R. J. Gettens in Japan in 1970, the shells were left outside for fifteen years, followed by purely mechanical processing with no heating or calcining carried out (Gettens, FitzHugh, and Feller 1993). Shell white is the only pigment in this series that is unique to Japan, and the only white pigment used, except for lead white on nine late paintings.

There are early references to a shell white in China. “Clam shell white” was mentioned in seventh-century China as an ingredient of artificial jade (Needham 1976, 136). We know from documentary evidence from late-seventeenth-century China that pulverized oyster or clam shells were heated, ground, and mixed with water to make white paint (Sze 1956, 41). Heating, or calcining, the calcite of the shells would produce quicklime (calcium oxide,  $\text{CaO}$ ), and the subsequent addition of water would convert it to lime ( $\text{Ca(OH)}_2$ ). Exposure to air would then result in the reformation of calcium carbonate that would not retain the typical striated appearance so characteristic microscopically of the particles of ground shells. Early Western writers on Japanese pigments have said that shell white was calcined, but there may have been some confusion with the Chinese process (Anderson 1886; Conder 1911). Japanese shell white shows no evidence of calcination.

The term *gofun* literally refers to any white powder or pigment; therefore, in the older literature the name may refer to other pigments, such as lead white and white clay. Uyemura (1931) and Oguchi (1969) both point out that the term at early dates referred to lead white, and Anderson (1886) notes the application of the term to white clay as well as to lead white.

Shell white has been used in Japan since the time of the Kanō School in the fifteenth and sixteenth centuries, when it replaced clay as the common white pigment (Yamasaki and Emoto 1979). Artists used this pigment throughout the ukiyo-e period, as evidenced on these paintings, both as a white pigment and as an important constituent of pigment mixtures designed to obtain lighter color tones.

Calcium carbonate pigments other than shell white are known in both Japan and China. A calcite was used in Japan on masks in the Shōsōin, the eighth-century repository in Nara, but it is not known if it originated from shells or limestone (Naruse 1996). Calcite was used at various periods in the wall paintings in the Mogao caves at Dunhuang in western China (Hsü, Chou, and Li 1983). Yü Feian states that a “white chalk,”  $\text{CaCO}_3$ , was used as early as the Han dynasty (206 B.C.E.–220 C.E.) in China (Silbergeld and McNair 1988, 9). On a few of these paintings, a calcite pigment was identified that does not have the same microscopic appearance as typical shell white. It occurs mixed with shell white and also appears separately. It may be a variety of the typical shell white; further investigation may establish that calcite from a different source also was used.

Lead white, *empaku*, an artificially made basic lead carbonate,  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , was known in Japan by the seventh century; in 692 C.E. a monk was rewarded by the empress for preparing lead white (Aston 1924, vol. 2, 408). It was then used by Japanese artists through the seventeenth century, chiefly on small and valuable paintings (Yamasaki and Emoto 1979). Shell white then became the common white

pigment for reasons that have not been explored, perhaps because it was cheaper and easier to produce.

Lead white occurs on a number of pre-ukiyo-e Japanese paintings in the Freer Gallery, dating from the thirteenth through the fourteenth century (Winter 1981). It is found on only nine of the ukiyo-e paintings under investigation here, six by Hosoda Eishi (1756–1829) or in his style, and three by Katsushika Hokusai (1760–1849) (table 2).

TABLE 2. LEAD WHITE ON UKIYO-E PAINTINGS

F1898.93	Hosoda Eishi (1756–1829), style of
F1898.117	Hosoda Eishi, style of
F1906.11	Hosoda Eishi, style of
F1957.5	Hosoda Eishi
F1957.6	Hosoda Eishi
F1957.7	Hosoda Eishi
F1903.125	Katsushika Hokusai (1760–1849)
F1903.274	Katsushika Hokusai (or Sōri III)
F1906.233	Katsushika Hokusai

These occurrences indicate that lead white was still occasionally in use after shell white replaced it as the dominant white pigment in the seventeenth century. In the so-called Dutch process, the common preparation method used in the West, lead was exposed to acetic acid vapors from vinegar (Gettens, Kühn, and Chase 1993). This method was well established in Japan in the late nineteenth century (Takamatsu 1878).

The earliest literary reference to lead pigments in China, in a fourth-century B.C.E. text, appears to discuss the manufacture of lead white and red lead from the metal (Needham 1976, 103). The Dutch process was described in China as early as 300 B.C.E., but the early use there of lead white, as in Japan, was as a cosmetic (Needham 1976, 15, 16), and the first date of its use as a pigment is not known. It was used extensively on fifth-century wall paintings at the Tiantishan Grottoes (Zhou, Zhang, and Cheng 1997). Lead white appears to be one of the painters' pigments described in a fifth-century Chinese poem (Schafer 1956). The making of lead white from lead and vinegar in China was described in the late sixteenth century (Read and Pak 1928) and in the seventeenth century (Sung 1966, 256).

The few identifications of lead white on Chinese works include tenth- to eleventh-century Song-dynasty (960–1279) wall paintings in the Mogao caves at Dunhuang (Gettens, Kühn, and Chase 1993). It was also found on several tenth- to sixteenth-century Chinese paintings in the Freer Gallery and on Korean paintings of the fourteenth to the fifteenth century (Winter 1981).

Other kinds of "lead white" include a basic lead chloride that has been found on

some Japanese works of art, including objects from the eighth-century Shōsōin (Naruse 1996) and a number of twelfth- to fifteenth-century paintings in the Freer Gallery (Winter 1981). Of the nine lead white occurrences on these ukiyo-e paintings, five were confirmed as lead white by x-ray diffraction. The possibility that basic lead chloride might be present on the other four paintings has not been investigated.

#### RED PIGMENTS

Vermilion, *shu* or *shin-shu*, red mercuric sulfide,  $\alpha$ -HgS, appears on the paintings as a bright clear red. The former term generally refers to vermilion and the latter to mineral cinnabar, which is ground to produce the pigment. The synthetic form of vermilion can be prepared by two methods, the dry process and the wet process (Gettens, Feller, and Chase 1993). Dry-process vermilion is made by heating mercury and sulfur together to form black mercuric sulfide, which in turn is heated, causing the red mercuric sulfide to form by sublimation. This dry-process vermilion is ground to produce the pigment and is identical in microscopic appearance to ground mineral cinnabar. Either dry-process or natural vermilion was used on these paintings throughout the ukiyo-e period.

Wet-process vermilion is prepared by heating black mercuric sulfide in a solution of ammonium or potassium sulfide, yielding a product of fine and uniform size, typical of a chemically precipitated material. In the West this process was first used in Germany in 1687. We have no evidence that vermilion was ever made in this way in China or Japan. Wet-process vermilion is not found on these paintings.

In the West dry-process vermilion was known in the eighth century and was in common use by the fourteenth century; it has been suggested that knowledge of the process may have been transmitted to the West from China (Gettens, Feller, and Chase 1993). Interestingly, it has been referred to as the “Chinese method” in the West (Li 1948, 133). The first probable reference to vermilion in China was in the fifth century B.C.E., and distillation of mercury from cinnabar there was described as early as the third century B.C.E. (Needham 1976, 4). More than one author says that the process of heating mercury with sulfur was known to the Chinese in antiquity (Sung 1966, 280; Silbergeld and McNair 1988, 5). The manufacture of dry-process vermilion was described in late-sixteenth-century China (Read and Pak 1928). The process was well developed in China by the seventeenth century, and the pigment was imported into Japan during the Edo period (Oguchi 1969). Numerous authors say that the best vermilion was imported into Japan from China, and high-quality Chinese vermilion was exported to England in the second half of the eighteenth century (Harley 2001, 127).

In Japan production of dry-process vermilion is known to have begun under a monopoly in 1609 (Gettens, Feller, and Chase 1993). Tajima (1903) refers to the

preparation of artificial vermilion by roasting mercury and sulfur, and Anderson (1886) noted that vermilion could be prepared by “rubbing together yellow sulfur with mercury.” Takamatsu (1878) describes the preparation method used in China and later in Japan whereby native cinnabar is heated to obtain metallic mercury, which in turn is heated with sulfur to produce vermilion by sublimation. The mineral was sometimes pure enough to be ground and used as a pigment. The less pure mineral cinnabar was used as a source of mercury for dry-process preparation of the pigment (Sung 1966, 280).

Mineral cinnabar occurs in Japan in Yamato Province (Takamatsu 1878). There are deposits of cinnabar throughout China, with particularly rich deposits occurring in the south (Golas 1999, 139). Cinnabar was found as a pigment in graves at least as early as 4000 B.C.E. in China (Wang and Wang 1999).

Vermilion was used as a pigment in Japan from the eighth century on (Yamasaki and Emoto 1979). It was in common use on these paintings during the whole of the ukiyo-e period. The vermilion was sampled from the painting proper, not from the seals.

Red lead, *entan* or *tan*, artificial lead tetroxide,  $Pb_3O_4$ , appears on the paintings as a bright orange-red, or sometimes a dull orange. It is similar chemically and crystallographically to the mineral minium. There is no evidence that the mineral itself was ever used as a pigment in Japan or elsewhere. Red lead is made in two ways: by heating lead white, or by heating metallic lead in a two-step process, in which case the yellow compound litharge ( $PbO$ ) is an intermediate product (FitzHugh 1986). An eighth-century Japanese document describes the heating of “black lead” to produce “red lead,” evidently a reference to the second method; red lead powder from the eighth-century Shōsōin has a high litharge content, and it has been suggested that this indicates that it was prepared by the two-step process (Yamasaki 1959). The use of this method in the nineteenth century in Izumi Province in Japan was described by Takamatsu (1878).

The preparation of red lead from lead appears to have been known in the fourth century in China (Needham 1976, 103). A definite description of the process is known from the Han period (206 B.C.E. – 220 C.E.) (Schafer 1956). Several authorities, including Conder (1911), have suggested that the best red lead came from China. It was used on wall paintings as early as the fourth century at the Mogao caves at Dunhuang (Hsü, Chou, and Li 1983) but was less common on Chinese paintings on paper and silk (FitzHugh 1986).

The earliest known use of red lead pigment in Japan is on the late-seventh-century wall paintings of the Hōryūji temple in Nara (Yamasaki and Emoto 1979), and it has been in continuous use in Japan since that date. It was used throughout

the ukiyo-e period, as represented by the paintings in this series.

The darkening of red lead observed on some of these ukiyo-e paintings has two possible causes. Black lead oxide can form upon exposure to air, or black lead sulfide can form due to the presence of hydrogen sulfide or adjacent sulfur-containing pigments. The deliberate alteration of red lead to a silver gray in some Japanese prints has been described (Walsh, Berrie, and Palmer 1998), but no similar phenomenon is known in the paintings.

One or more organic red pigments supplied a pink or purplish-pink color on these paintings. *Enji* is the common term used during the Edo period for an organic red pigment, but it is also used as a general term referring to various colorants at different periods — any crimson or purplish-crimson dye used in painting (Oguchi 1969). Three types of red dye could have been available in Japan during this period.

The first of these red dyes is madder. Western madder, *Rubia tinctorum* L., contains alizarin and purpurin as coloring constituents, while Japanese madder, *Rubia akane* Nakai, contains purpurin alone (Schweppe and Winter 1997). Alizarin, the main constituent of Western madder, was first synthesized in the West in 1868. According to Needham (1986, 263) there is a fourth- to fifth-century Chinese reference to madder, which he suggests was *Rubia cordifolia*, Tibetan madder, which is known to have been available in western China in the twentieth century (Sewell et al. 1939).

The second group of organic red colorants that might have been used includes anthraquinone derivatives from scale insects. Two of these are carmine pigments, prepared from two different species of scale insects, kermes and cochineal. Kermesic acid is the principal component of kermes carmine; carminic acid is that of cochineal carmine. Kermes was the source of carmine in the Eastern Hemisphere and cochineal in the Western Hemisphere (Schweppe and Roosen-Runge 1986). Literary evidence indicates that cochineal was known in Japan by 1800 (FitzHugh 1979).

The other red anthraquinone derivative is lac dye from the Indian scale insect *Laccifer lacca*, the principal components of which are several laccaic acids. Stick lac, the material found on the tree, is a mixture of the dye with a hard resin produced by the scale insect (Schweppe and Roosen-Runge 1986). The presence of a specimen of stick lac, *shikō*, in the eighth-century Shōsōin (Asahina 1955) suggests the possibility of its use as a pigment in Japan beginning at that date. Documentary evidence indicates that lac was known in China in the early fourth century (Laufer 1919, 475) and was known to have been imported into China from Southeast Asia during the Tang period (618–907) (Schafer 1957).

The third red organic colorant that might have been available to ukiyo-e artists is safflower red, *beni*, which derives from the petals of the safflower, *Carthamus tinctorius* L., Japanese *benibana*. The chief red constituent is carthamic acid or

carthamin. It was known as a textile dye in Japan, where its preparation and use for this purpose were described in the late nineteenth century (Takamatsu 1878). It was mentioned in fourth-century China as a source of red for cosmetics (Laufer 1919, 327) and was illustrated in a Chinese treatise on pharmaceutical natural history dated to 1108 (Needham 1986, 285). It was described as a dye in seventeenth-century China (Sung 1966, 76), and in twentieth-century western China it was still used as a dye and for cosmetics (Sewell et al. 1939).

Few organic red pigments on Japanese paintings have been firmly characterized. Safflower red has been tentatively identified by spectral reflectance on a nineteenth-century Japanese print (Feller, Curran, and Bailie 1984). Its use as a painter's pigment has yet to be established. A reddish-purple colorant identified by name as *enji* on a late-seventeenth-century Japanese scroll has been shown by reflectance spectroscopy to be an anthraquinone, either laccaic or carminic acid — that is, lac dye or carmine (Taguchi and Taguchi 1977). On five Edo-period paintings in the Freer Gallery, fiber-optics reflectance spectroscopy showed the use of an anthraquinone colorant; three works contained carminic acid, identified by high-performance liquid chromatography, indicating the source to be cochineal carmine (Winter, Giaccai, and Leona 2003).

The red earth and brown earth pigments are here considered together, since they are related in composition. The coloring agents of both are various iron oxides in complex mixtures with quartz, calcite, clay minerals, and other materials (Helwig, forthcoming). The term *shido* refers to red iron oxide in general, *taisha* designates the natural mineral, and *bengara* refers to the natural material in ancient times and the artificial material more recently (Oguchi 1969). Yamasaki (1959) points out that *shido* literally means “purple earth.”

The colors supplied by the red earth pigments on these paintings can vary from dark brown or maroon to dark red, reddish-brown, or orange. The red mineral hematite, the anhydrous iron oxide,  $\alpha\text{-Fe}_2\text{O}_3$ , supplies their color. Hematite is also found in brown earth pigments that appear as brown or yellow-brown on the paintings. Other iron oxides, in addition to hematite, are undoubtedly present in the brown earths. The hydrated iron oxides, generally termed limonite, include goethite,  $\text{HFeO}_2$ , and lepidocrocite,  $\gamma\text{-FeO(OH)}$  (Roberts, Rapp, and Weber 1974). Goethite can be various shades of reddish or yellowish-brown and in the yellow form is the source of the color of yellow earth, while lepidocrocite is deep red to reddish-brown. The presence of these hydrated iron oxides can be assumed in the brown earths on these paintings, and they may also occur, with hematite, in the red earths. Other iron compounds can be present (Helwig, forthcoming) and might occur in these pigments.

Red and brown earth pigments were known early worldwide, even before their use

in Paleolithic cave paintings (Helwig, forthcoming). In China use of red earth pigments is also known as early as the Paleolithic (Needham 1976, 3). They have been used at all periods in China—for example, at the Mogao caves at Dunhuang (Hsü, Chou, and Li 1983). The red clay found there was natural hematite with quartz, talc, and clay minerals such as kaolin (Wang 1986). Red, brown, and yellow earths were used in fifth- to eighth-century Korea (Winter 1989). Hematite is the most abundant of Chinese iron ore minerals, and limonite was also an important ore (Golas 1999, 163), so the necessary materials were readily available for pigments. In Japan earth pigments were known before the third century B.C.E. and have been used at all periods since then (Yamasaki and Emoto 1979). Red earth is found at a number of locations in Japan (Geerts 1883, 390). Red and brown earths are common on these ukiyo-e paintings.

A number of artificial iron oxides, prepared by various methods, are known in the West. Heating one type of iron oxide to create another is common; yellow earth can thus be converted to a red or brown earth. Heating ferrous sulfate by different methods can produce the artificial red oxide, and it is also possible to produce iron oxide by oxidizing metallic iron in various ways (Helwig, forthcoming). Artificial iron oxides are known in East Asia. According to Oguchi (1969) they first were prepared in Japan in the early eighteenth century by heating iron sulfate. Kitano and Koezuka (1998) discuss the documentary evidence indicating that synthetic iron oxide was made in the Edo period by two methods, roasting iron sulfate and heating iron scraps. Chinese documents also refer to two sources: preparation from iron sulfate, and the fact that they were available from iron mines (Wang 1986). Synthetic iron oxides are generally more uniform than the natural earths, with no mineral impurities, but the two cannot be distinguished by polarized-light microscopy (Helwig, forthcoming). No obvious artificial iron oxides appear on these paintings, but no attempt was made to confirm this by noting the presence or absence of impurities.

Rarely, a purple color can be supplied by an iron oxide. Akiyama (1964) reports that a purple iron oxide pigment was known in Japan as early as the eighth to the tenth century. Geerts (1883, 392) notes that a purple clay used in painting occurs at several locations in Japan. A purple color was identified as a hematite-containing pigment on two of these ukiyo-e paintings: on F1898.104, mixed with shell white, and on F1903.132 (plate 2).

#### YELLOW PIGMENTS

Orpiment, *sekiō*, is the yellow arsenic sulfide,  $\text{As}_2\text{S}_3$ , a naturally occurring mineral that is ground to produce the pigment. Its micaceous character makes it difficult to grind finely and contributes to its glittery appearance on the painting.

The term *shiō* is a general word for a yellow color, and the material to which it



referred changed over the years. *Shiō* was an early designation for orpiment, but it came to be used for gamboge by the seventeenth century (Winter 1997). Orpiment has been said to be a standard painting material in Japan (Uyemura 1931; Oguchi 1969), although Anderson (1886) stated that it was “rarely used by painters.” Some writers seem to have been unaware of its use, because it is not mentioned in many lists of traditional Japanese pigments.

Realgar, *yūō*, a red to orange arsenic sulfide,  $As_4S_4$ , that occurs with orpiment, has had limited but persistent use as a pigment in the West and has been identified on wall paintings in western China and central Asia, but not on paintings on paper or silk in Japan or China. Other arsenic sulfides, ranging in color from yellow, to reddish-orange, to orange-brown, have been identified as pigments in the West (FitzHugh 1997), but they have yet to be found on paintings in East Asia.

Orpiment as a pigment was mentioned in Japanese sources as early as the tenth century (Schafer 1955). The mineral is known from a number of locations in Japan (Geerts 1878, 176; Morimoto 1954), occurring there most commonly at hot springs (Palache, Berman, and Frondel 1944; Noguchi and Nakagawa 1970).

Both orpiment and realgar are more widely available in China than in Japan (Geerts 1878, 175), and the world’s largest deposit of realgar is found in Hunan Province in China (Silbergeld and McNair 1988, 6). Orpiment and realgar were named early in Chinese sources, by the second century B.C.E. and possibly as early as the fourth century B.C.E., when they were important in Chinese medicine and were used to create gold-colored arsenical bronze (Needham 1974, 223). The first mention of the mining of realgar in China, and thus presumably also of orpiment, was in the fourth century (Golas 1999, 176). There was no direct mention of their use as pigments, although Schafer (1955) suggests that orpiment was in use as a pigment by the fifth to sixth century. In the nineteenth century it was used on Chinese paintings (Wise and Wise 1998) and exported to England, where it was sold as Chinese yellow (Harley 2001, 94).

Artificial orpiment is made by two processes. The terms *dry process* and *wet process* have been applied to its manufacture (Wallert 1984). Documentary evidence from 1837 appears to indicate that *sekiō* was made in Japan in the Edo period by grinding mineral orpiment, and that the artificial material was made by dry and wet methods learned from the Dutch (Kitano and Koezuka 2000). Wet-process orpiment produced by precipitation methods from solution does not appear to have been used as a pigment (FitzHugh 1997).

The dry-process material is prepared by heating sulfur with an arsenic compound, usually arsenic dioxide, to produce the pigment by sublimation. Takamatsu (1878) described the use of the dry process in Japan as the burning of “arsenical

stones” with sulfur to produce the yellow arsenic sulfide. In addition the natural mineral can be sublimed to get a more uniform product, a process described in Europe in the eighteenth century (FitzHugh 1997). Schafer (1955) suggests that Chinese alchemists may have known how to make realgar artificially, using native realgar as a starting material, evidently by sublimation. The preparation of realgar by sublimation of the mineral is described in a seventeenth-century Chinese painting manual (Sung 1966, 212).

It is not possible to differentiate objectively between mineral orpiment and the dry-process material. However, the natural mineral, as seen by polarized-light microscopy, includes both large and small particles, while the dry-process material tends to be more uniform in size. The orpiment from these ukiyo-e paintings shows great variety in particle size; therefore, it is almost certainly the natural mineral. Orpiment has not been identified on any non-ukiyo-e Japanese works in the Freer Gallery. On these paintings it was used most widely in nineteenth-century works, notably by Hokusai, and by some artists also active in the eighteenth century, the earliest (F1902.250) being Okumura Masanobu (table 3).

TABLE 3. ORPIMENT ON UKIYO-E PAINTINGS

F1902.250	Okumura Masanobu (1686–1764)
F1903.132	Katsukawa Shunchō (late 18th c.)
F1905.271	Katsukawa Shunshō (1726–1792)
F1905.309	Katsukawa Shunshō (1726–1792)
F1898.433	Tsukioka Settei (1710–1786), dated 1776
F1898.419	Hokuun, early 19th c.
F1899.18	Katsukawa Shun’ei (1762–1819)
F1898.423	Katsukawa Shunkō (1734–1827)
F1898.431	Sōri III (fl. late 18th–early 19th c.), style of
F1898.94	Utagawa Toyohiro (d. 1829), style of
F1903.245	Shumman (19th c.), style of
F1904.35	Shumman (19th c.), style of
24 paintings	Katsushika Hokusai (1760–1849)
F1898.108	Shigemasa II (Edo period, 1615–1868)

Yellow earth, *ōdo*, derives its color mainly from the mineral goethite, a hydrated iron oxide,  $\text{HFeO}_2$  (Helwig, forthcoming), the earthy varieties of which can be yellow to brownish-yellow (Roberts, Rapp, and Weber 1974). Brownish-yellow lepidocrocite may also be present. Yellow earths are found widely in Japan (Geerts 1883, 391) and were used there as pigments rarely but consistently from the sixth century

on (Yamasaki and Emoto 1979). They were found on only six of these paintings, which were of widely scattered dates. In China yellow earths were used on wall paintings as early as the fifth century (Piqué 1997).

The organic yellow on these paintings is probably gamboge, *tō-ō* or *gambōji*; it is sometimes called *shiō*, the general term for yellow. Gamboge is a gum resin, a yellow vegetable pigment, obtained from trees of the genus *Garcinia* throughout South and Southeast Asia; the resinous portion is the major component and is the source of the yellow color (Winter 1997). Schafer (1981, 213) states that it was imported into China from Southeast Asia during the Tang dynasty. Several authors report that it was imported into Japan from China (Conder 1911; Takamatsu 1878). An organic yellow, assumed to be gamboge, was widely used in Japan from the eighth century on (Yamasaki and Emoto 1979). Few firm identifications of gamboge have been made on Japanese paintings. It has been identified by reflectance spectroscopy on a late-seventeenth-century scroll (Taguchi and Taguchi 1977), and by thin-layer chromatography on four ukiyo-e paintings in this series: F1898.420, F1903.208, F1905.234, and F1957.2 (Winter 1987). On the remainder of these paintings it can only be characterized as an organic yellow colorant; it was used throughout the ukiyo-e period.

#### GREEN PIGMENTS

Malachite, *rokushō*, is the green basic copper carbonate mineral,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . It is the common green pigment of Japan and has been used there continuously from the seventh century to the present day (Yamasaki and Emoto 1979). It was used by ukiyo-e artists throughout the period. The mineral is crushed and ground, then washed, levigated, and sieved to produce the pigment. Grades of the pigment were produced by varying degrees of grinding, the more finely ground material being lighter in color.

Malachite is found widely in China in secondary copper ore deposits (Golas 1999, 62). Because of their colors, both malachite and azurite were easily recognizable, and they were the two most important early copper ores (Golas 1999, 225). A list in a Chinese alchemical text from the late fourth to early third century B.C.E. includes malachite (Needham 1976, 15). Several localities in Japan were known to supply good-quality malachite (Geerts 1883, 630).

Malachite is common on wall paintings from Central Asia (Gettens and FitzHugh 1993b), where the earliest use appears to have been in the third century C.E. at the Mogao caves at Dunhuang (Hsü, Chou, and Li 1983). It has yet to be identified on paintings on paper and silk from China proper.

There is no evidence that green verditer, the artificially made form of malachite, was ever used on Japanese paintings. In the paintings under investigation here,

there was one occurrence mixed with barite in a retouched area (F1902.229). An unusual artificial malachite, characterized by curious, rounded particles with a white center, has been identified on a twelfth-century Chinese wood sculpture (Larson 1988). This green has not been reported on paintings in East Asia. Elsewhere in the world it is only known on fifteenth-century Italian tempera paintings.

A green, copper-containing pigment from a few of these ukiyo-e paintings was identified by x-ray diffraction as malachite, but it did not have the appearance of typical malachite by polarized-light microscopy. The particles are more rounded than one would expect of mineral malachite that has been ground, but they are not the typical spherulitic particles of artificial malachite. Further investigation may show that this material is some other kind of artificial material.

Copper greens refer here to green, copper-containing colorants that are not malachite. Many of them appear on first examination of the painting to be a coarse granular malachite (plate 3). Sometimes they have a yellow tone. Detailed study has shown these pigments to be various materials other than malachite.

A number of these greens were atacamite or paratacamite, two dimorphic basic copper chlorides with the composition  $\text{Cu}_2\text{Cl}(\text{OH})_3$ . Recent research has shown that the mineral phase generally identified as paratacamite should more correctly be termed clinoatacamite (Scott 2000). These compounds occur in nature as minerals and are also found as corrosion products on bronze and copper. Most of these basic copper chloride greens are extremely finely divided material with every appearance of being artificially prepared (plate 4). In addition, quartz and calcite are often present. Anderson (1886) has described a “dull green powder” that was sold as a substitute for malachite in Japan, which he suggested was a copper oxychloride. Thus it appears that atacamite and paratacamite pigments might have been available there in the nineteenth century.

Atacamite and other basic copper chlorides are known to have been used as pigments in the West, although they may sometimes be alteration products of other copper-containing pigments (Scott 2000). Atacamite has been identified on early Chinese wall paintings (Duang et al. 1987; Hsü, Chou, and Li 1983), and a copper chloride, although not common, is reported on some nineteenth-century Chinese paintings (Wise and Wise 1998). In Japan atacamite has been found on eighth-century objects in the Shōsōin (Naruse 1996).

Other copper greens found on these paintings are complex mixtures that have yet to be classified. Quartz and sometimes calcite are often present, and occasionally glassy particles are seen. Green particles of atacamite or paratacamite (clinoatacamite), when present, are sometimes brownish in tone and do not have the finely divided appearance noted above. These types of green mixtures have been found as

retouch on two seventeenth-century paintings: on a hanging scroll (F1898.122) it is the only green and is found in several areas; on a screen (F1905.17, one of a pair) it is yellow-green in color and is used in widely scattered locations.

It is possible that a few of these copper greens are glass-matrix pigments. These pigments, called *shin iwaenogu*, were not made in Japan before the Meiji restoration in 1868 (Yamasaki and Emoto 1979). They are composed of a glassy frit, colored by the addition of suitable metal oxides (Oguchi 1969). A green pigment on one screen (F1966.35), which appears to be in a retouched area, may be one of these pigments.

These copper greens are found on forty-seven ukiyo-e paintings in the Freer collection, all dating after the late seventeenth century, twenty-three being by Hokusai or attributed to him (table 4).

TABLE 4. COPPER GREENS ON UKIYO-E PAINTINGS

17TH CENTURY		18TH–19TH CENTURY	
F1905.17	anon. (1624–44) (retouch)	F1898.94	Utagawa Toyohiro (d. 1829)
F1966.35	anon. (early 17th c.) (retouch)	F1898.419	Hokuun (early 19th c.)
		F1898.427	Utagawa Toyonobu (late 18th c.), style of
17TH–18TH CENTURY		F1902.101	Torii Kiyonaga (1752–1815)
F1898.14	Torii Kiyonobu I (1664–1729)	F1905.312	Toshinaga (early 19th c.)
F1898.122	Hishikawa Morofusa (fl. ca.1688–97) (retouch)	F1906.11	Hosoda Eishi (1756–1829), style of 23 paintings
F1903.68	anon. (Kambun era, 1661–73)		Katsushika Hokusai (1760–1849)
F1903.131	anon. (Kambun era, 1661–73)		
F1903.134	Miyagawa Chōshun (1682–1752), style of	19TH CENTURY	
			5 paintings
18TH CENTURY		EDO PERIOD (1615–1868)	
F1898.424	Tsunemasa (fl. 1730–80)		3 paintings
F1900.112	anon. (18th c.) (retouch)		
F1904.195	Ishikawa Toyonobu (1711–1785)		

Careful examination indicates that most of these copper greens are part of the original paint. Their use as repaint in the examples cited does not seem to be typical.

In addition to problems of identification, there is confusion in the naming of these copper greens. The term *verdigris* has been applied to malachite (Oguchi 1969) and also to emerald green (Geerts 1883, 632), so no exact designation can be assumed by the use of the term. Verdigris, an entirely different material, is an artificial copper acetate of varying composition and was known in the West from Roman times (Kühn 1993). The preparation of artificial verdigris in nineteenth- and early-twentieth-

century Japan, by application of vinegar to copper, has been described by several authors (Anderson 1886; Conder 1911; Tajima 1903). Takamatsu (1878) remarks that it is “not an important pigment, scarcely used in painting.” Yü Feian states that verdigris was one of China’s earliest invented pigments (Silbergeld and McNair 1988, 9), and Oguchi (1969) mentions its use in China in the Tang dynasty. Needham (1976, 244) refers to a Chinese text of uncertain date and provenance that describes the preparation of green and blue pigments from copper, but it is not clear what they might be. Verdigris has not been found on the ukiyo-e paintings here under discussion.

Emerald green, copper aceto-arsenite,  $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{CO}_2)_2$ , is a synthetic pigment first produced in Germany in the first decade of the nineteenth century (Fiedler and Bayard 1997). It appears on a single nineteenth-century painting by Hiroshige (F1898.123). Emerald green was probably introduced into Japan by the Dutch.

It is evident that a variety of artificial copper greens were available to artists in China and Japan, but because of confusion in naming and the need for further analytical confirmation, few definite conclusions can be drawn at this time.

#### BLUE PIGMENTS

Azurite, *gunjō*, is the blue basic copper carbonate mineral,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . As with malachite the pigment is prepared from the ground mineral. The grades of the pigment are determined by the amount of grinding, the lighter color being the more finely divided (Gettens and FitzHugh 1993a). The color of azurite on these paintings reflects these grades; it is usually a bright blue, occasionally a dark blue, and sometimes a pale blue. Azurite was used in Japan from the seventh century to the present day and is a common blue pigment in Japan (Yamasaki and Emoto 1979). It was used throughout the ukiyo-e period, but on these paintings the most widely used blue is indigo. Azurite occurs with malachite, but less abundantly. It is native to Japan, where a number of localities are known (Geerts 1883, 638). Anderson (1886) says it was discovered in Settsu Province in 104 C.E. A specimen of azurite from Kozuke Province was presented to the empress in 714 C.E. (Takamatsu 1878). In China azurite and malachite were important early copper ores (Golas 1999, 225). Azurite was listed in the Chinese alchemical literature in the late fourth to early third century B.C.E. (Needham 1976, 15). It was identified on Chinese wall paintings at the Mogao caves at Dunhuang as early as the fourth century (Hsü, Chou, and Li 1983).

Blue verditer, the artificial form of azurite, was not found on these paintings and to date has not been reported on works from East Asia.

Smalt, *hana-konjō*, is an artificially made pigment, a coarsely ground, potassium-rich glass, colored blue by the incorporation of cobalt oxide during manufacture. On these paintings it is usually a gray-blue, or occasionally a bright blue, often with

a granular, glittering appearance. The earliest example of the use of smalt on works on paper or silk in East Asia appears to be on a sixteenth- to early-seventeenth-century Japanese print in the Fogg Museum of Art (Magurn 1942). Smalt has not been found earlier than the late seventeenth century on these paintings, nor on any other East Asian paintings in the Freer Gallery, but ukiyo-e artists, as represented by the paintings here under discussion, used it widely in the late seventeenth to eighteenth century, and consistently but less often in the nineteenth century (table 5).

TABLE 5. SMALT ON UKIYO-E PAINTINGS

LATE 17TH–EARLY 18TH CENTURY	13 paintings	19TH CENTURY	4 paintings
18TH CENTURY	19 paintings	KATSUSHIKA HOKUSAI (1760–1849)	6 paintings
18TH–19TH CENTURY	11 paintings	EDO PERIOD (1615–1868)	7 paintings

Smalt was long thought to be a sixteenth-century European invention, but we now know of isolated, earlier occurrences on the Asian mainland, leading to the speculation that it might have an Asian origin. It has been identified on a seventh-century, Tang-dynasty, cast-iron head (Larson 1988), on eleventh-century wall paintings at Kara Khoto in Mongolia (Gettens and Stout 1966), and on fourteenth-century wall paintings in a Byzantine church in Istanbul (Mühlethaler and Thissen 1993).

Uyemura (1931) reports that a blue glass pigment made in China was used as a substitute for ultramarine in Japan, but writers on traditional Japanese pigments make no mention of smalt, with two exceptions. Takamatsu (1878) describes its preparation by “fusing crude oxide of cobalt with a mixture of clay and alkalies.” Oguchi (1969) says that an artificial, bluish glass pigment colored with cobalt oxide was introduced into Japan in the Kyoho era (1716–35), although this is later than the mid-seventeenth-century date, when smalt was first used on these ukiyo-e paintings.

The cobalt oxide used to make smalt was prepared by roasting cobalt minerals such as cobaltite or smaltite. Cobalt minerals are found in China and Japan, but according to Geerts (1883, 561) it was cheaper to import them from Europe. The fact that the acquisition of these cobalt minerals was mentioned supports the idea that smalt was made in Japan. Takamatsu (1878) notes that foreign smalt was largely used because it was cheaper, and Geerts (1883, 569) mentions that a blue glass pigment was imported by the Dutch.

Indigo, *ai*, an organic colorant, varies from bright to dull blue on the paintings; it can appear as greenish-blue when thinly applied. The blue constituent is indigotin ( $C_{16}H_{10}O_2N_2$ ), which is obtained from several species of plants, three of which are the most important. *Polygonum tinctorium*, dyer’s knotweed, is indigenous to Asia. It was the early source of blue dye in China (Needham 1986, 158). It is known

to grow in Japan and was reported there in the late nineteenth century (Takamatsu 1878). *Indigofera tinctoria* originates in India and elsewhere in South Asia and is the best-known source; it was known in China in the Tang period (Needham 1986, 158). *Isatis tinctoria*, dyer's woad, originated in Europe but was introduced elsewhere. It evidently did not reach China until the sixteenth century (Needham 1986, 158). Indigo is the common blue on these paintings; it is not known which plant or plants were the source of the pigment.

Indigo was used in Japan at least as early as the eighth century, as is known from objects in the Shōsōin (Yamasaki and Emoto 1979). It was characterized by spectral reflectance on nineteenth-century Japanese prints (Feller, Curran, and Bailie 1984) and on a late-seventeenth-century scroll by reflectance spectroscopy (Taguchi and Taguchi 1977). It has been identified by fiber-optics reflectance spectroscopy on over one hundred eighteenth- to nineteenth-century paintings in the Freer Gallery, in some cases confirming identifications reported here (Winter, Giacciai, and Leona 2003).

Indigo cultivation, preparation, and use as a dye has been described in fifth-century China, and it was known there at least as early as the third century B.C.E. (Sung 1966, 78). Its use as a cosmetic was reported in the Tang period (Laufer 1919, 370). Indigo was cultivated in southwest China, but competition from imported synthetic indigo caused a marked decrease in cultivation between 1875 and the 1930s (Sewell et al. 1939). In the nineteenth century the best kind of indigo for painting was said to be imported into Japan from China (Takamatsu 1878). Indigo was first synthesized in Germany in the late nineteenth century (Schweppe 1997), so the artificial material would not be expected here.

Prussian blue, *bero*, *bero-ai*, or *beroin*, is an artificial pigment, ferric ferrocyanide, with the basic formula  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3 \cdot x\text{H}_2\text{O}$ . It was first made in Germany in 1704 (Berrie 1997). Documentary evidence indicates that it was known in Japan, although not widely used, by the last half of the eighteenth century and that it was increasingly available after the 1820s (Smith, in press). Prussian blue was imported by Dutch and Chinese traders and appears never to have been manufactured in Japan. It is not mentioned in lists of traditional Japanese pigments.

The use of Prussian blue on Japanese prints is well known from documentary evidence (Feller, Curran, and Bailie 1984; Smith, in press). The only published identifications on Chinese paintings have been on four nineteenth-century paintings in the Freer (Giacciai and Winter, in press). Until the work herein presented, no occurrences had been reported on Japanese paintings. Recent studies at the Freer Gallery by UV-visible reflectance spectroscopy have expanded and confirmed our knowledge of the use of Prussian blue on many of these paintings (Leona and Winter 2001; Winter, Giacciai, and Leona 2003).



Prussian blue was used on ten nineteenth-century paintings, and on twenty paintings by Hokusai, and on one anonymous Edo painting. It also occurs on four earlier paintings. One work (F1898.429) by Miyagawa Chōshun (1682–1752) seems too early for the time frame suggested by Smith. The Prussian blue here does not appear to be retouch, and its presence suggests that they might be of a later date. Three paintings by Hosoda Eishi (1756–1829), or in his style, fit better into Smith's time limit. Three other paintings make use of a mixture of Prussian blue with kaolin, which is almost definitely retouch. On a pair of screens (F1907.126–.127), dated only to the Edo period, this mixture was applied over a mixture of artificial ultramarine and smalt. Since ultramarine is found only on later-nineteenth-century ukiyo-e paintings, its presence suggests a late ukiyo-e date, and that the mixture of kaolin and Prussian blue is retouch. On another much-damaged seventeenth-century painting (F1905.96), this same mixture is used in what is almost certainly a retouched area. Table 6 summarizes the occurrences of Prussian blue on these ukiyo-e works.

TABLE 6. PRUSSIAN BLUE ON UKIYO-E PAINTINGS

MID-18TH CENTURY?		F1903.145	Andō Hiroshige (1797–1858)
F1898.429	Miyagawa Chōshun (1682–1752)	F1903.146	Andō Hiroshige
		F1904.357	Andō Hiroshige
LATE 18TH–19TH CENTURY		F1906.46	Numata Gessai (fl. 19th–20th c.)
F1905.294	Hosoda Eishi (1756–1829), style of	F1976.41	Hokuga (early 19th c.)
F1906.11	Hosoda Eishi, style of	F1977.24	Hokutei Joren (ca. 1800–1868)
F1957.7	Hosoda Eishi		
20 paintings	Katsushika Hokusai (1760–1849)	EDO PERIOD	
		F1903.135	anon. (Edo period, 1615–1868)
19TH CENTURY			
F1898.8	Gakutei Harunobu, 19th c.		RETOUCH, MIXED WITH KAOLIN
F1898.124	Hiroshige II (1826–1869)	F1905.96	anon. (late 17th c.)
F1898.125	Hiroshige II	F1907.126–127	anon. (Edo period, 1615–1868)
F1903.106	Hiroshige II		

Ultramarine, *ruri*, in its natural form is the powdered blue mineral lazurite, a sulfur-containing sodium aluminum silicate that is the blue constituent of the rock lapis lazuli. Artificial ultramarine of the same composition was first made in France in 1828 (Plesters 1993). Artificial ultramarine is found on six nineteenth-century paintings in this series (table 7). On one of them (F1907.127), dated to the Edo period, it was mixed with smalt, as described above. No ultramarine, artificial or natural, has been found on any other Japanese works in the Freer Gallery. The source of artificial ultramarine in Japan is not known; it was probably imported by the Dutch. The Japanese name for azurite, *gunjō*, is sometimes used for ultramarine.

TABLE 7. ULTRAMARINE ON UKIYO-E PAINTINGS

F1899.17	Hiroshige II (1826–1869), style of
F1900.114	Hokuga (1st half 19th c.)
F1903.106	Hiroshige II
F1903.145	Andō Hiroshige (1797–1858)
F1903.146	Andō Hiroshige
F1907.127	anon. (Edo period, 1615–1868) mixed with smalt

Lapis lazuli is not found in China or Japan (Geerts 1883, 475). The Badakshan mines in Afghanistan were the only source of lapis lazuli for Western as well as Asian art until its discovery in the nineteenth century in Siberia near Lake Baikal (Plesters 1993). Its existence was known in China, as evidenced by the report of a thirteenth-century Chinese traveler of its occurrence in Afghanistan (Laufer 1919, 520). Anderson (1886), evidently referring to the natural material, says that lapis lazuli was used rarely by Chinese artists because of its costliness. Natural ultramarine was used early on wall paintings in north and west China, at Yungang in the fifth century, and widely at the Mogao caves at Dunhuang from the fourth century on (Hsü, Chou, and Li 1983; Wang, Guo, and Li 1995).

#### BROWN PIGMENTS

An organic brown colorant found on these paintings could not be characterized by the identification methods used here. Tests by chemical microscopy indicate that more than one pigment may have been in use. Work by Jennifer Giaccai, primarily by infrared spectroscopy, suggests a possible relationship to Vandyke brown but has not reached a definite conclusion (Winter, Giaccai, and Leona 2003).

#### MICA

The mineral mica, *ummo* or *kira*, has a glittery appearance on the painting, due to the platy quality of the particles of ground mineral. Mica is a general term that includes a number of silicate minerals with this property; they exhibit a range of colors or can be white or colorless (Roberts, Rapp, and Weber 1974). The four occurrences found, on eighteenth- to nineteenth-century ukiyo-e paintings, were all muscovite, a white mica. Mica is said to have come into use as a pigment after the Muromachi period (1333–1573) (Oguchi 1969), although a sample of mica powder was identified earlier in the collection of the eighth-century Shōsōin (Asahina 1955). Geerts (1878, 426) reports occurrences of mica in Japan.

## METAL PIGMENTS

As noted above, the metal pigments on these paintings were not researched systematically. Gold and silver in the form of metal leaf, or scattered grains or powder made into paint have been used on Japanese paintings since early times. Gold foil was found on the seventh- to eighth-century wall paintings in the Takamatsuzuka tomb, and gold and silver are known on paintings and objects in the eighth-century Shōsōin (Yamasaki and Emoto 1979). Loose gold and silver powder were also found in the Shōsōin (Naruse 1996). The precious-metal pigments found on these ukiyo-e paintings were gold powder, silver leaf, and silver powder. In addition, some gold-colored areas were revealed to be a copper alloy of unidentified composition, or in some cases a copper-zinc alloy. Copper-zinc alloys have been found on eighteenth-century Japanese paintings in the British Museum (Duncan, Daniels, and Fleming 1990). Also present occasionally on these paintings is black silver sulfide, which is probably tarnished silver.

## PIGMENTS USED AS REPAINT

Kaolin, a white clay, *hakudo*, was used in Japan as early as the seventh century, particularly on wall paintings (Yamasaki and Emoto 1979), and was found in China as a ground on a cast-iron sculpture of the Tang period (Larson 1988). It was generally replaced as the common white pigment by shell white in the fifteenth to sixteenth century (Yamasaki and Emoto 1979). It does not occur as a white pigment on any of these ukiyo-e paintings, but it was found mixed with Prussian blue, probably as retouch, as noted above.

Barite, a white pigment, barium sulfate,  $\text{BaSO}_4$ , came into use in the West in the early nineteenth century (Feller 1986). It occurs on two paintings. On one (F1902.229) by Nishikawa Sukenobu (1671–1751), it is mixed with green verditer on the retouched green floor. In a retouched area on an anonymous seventeenth-century painting (F1907.35), it is tinted with a yellow that may be yellow earth; this painting was retouched at an unrecorded location during conservation at the Freer Gallery in 1955.

## MIXTURES

A number of pigment mixtures were used on these paintings. The addition of various colorants to shell white to create a lighter tone is common. Other color combinations include blue with yellow to give green, red with blue to give purple, and mixtures of more than one red. In addition a few unusual pigment combinations were seen that have not been discussed elsewhere.

Some mixtures of blue and yellow to give green were used to produce a different shade of blue, rather than a green. Yamasaki has suggested that the combination of indigo and yellow earth found on the tenth-century Daigo-ji wall paintings was probably intended to be a substitute for azurite, evidently to give the indigo a greenish tone nearer to that of azurite (Yamasaki and Emoto 1979). This same combination, used in eighth-century Japan, was described as an “ultramarine blue,” implying a similar aim: to produce a different shade of blue (Mogi, Nakasato, and Emoto 1975). Yanagisawa (1985) reports that indigo was applied in several layers over yellow earth, as well as being mixed with it, on the Daigo-ji paintings. This observation points out the difficulty that can sometimes arise, even with careful examination, in determining whether two pigments are in two separate layers, rather than being mixed. This mixture of indigo and yellow earth was not observed on these ukiyo-e paintings.

The use of mixtures of blue and yellow to produce green on Japanese paintings has been noted by a number of authors. Takamatsu (1878) remarked that in “ordinary painting” a mixture of indigo and gamboge was used rather than mineral greens, implying perhaps that it was cheaper. Conder (1911), who lists a number of pigment mixtures with their names, noted that combining indigo and gamboge produced a “transparent green.” Taguchi and Taguchi (1977) have identified a mixture of indigo and gamboge on a seventeenth-century Japanese scroll by reflectance spectroscopy. The same mixture to create green was described at the same date in China (Sze 1956, 584). A mixture of indigo and orpiment was identified in a dark green on a sixteenth- to early-seventeenth-century Japanese print (Magurn 1942), and the use of orpiment with a blue colorant by Japanese artists to produce green has been reported by Geerts (1878, 176). On the Freer ukiyo-e paintings, mixtures of indigo with orpiment, as well as with an organic yellow, were used. In one case the organic yellow was found to be gamboge (Winter 1987); on another painting a green was made from orpiment and Prussian blue. Additional analysis of pigments on Japanese paintings in the Freer Gallery by fiber-optics reflectance spectroscopy has identified mixtures of indigo, and occasionally Prussian blue, with an organic yellow to produce green (Leona and Winter 2001).

On two of these paintings, malachite was mixed with azurite to give a green with a blue tone; on another one malachite and azurite were combined with smalt, resulting in a dark blue. A different combination of blue and green, described in China, consisted of verdigris tinted with indigo to give a bluer color similar to that of the more valuable pigment malachite (Needham 1976, 136).

Single, good purple colorants are rare. Iron oxide pigments can produce earths of a purple color, and organic red pigments sometimes have a purple tone. But artists worldwide have had to make use of mixtures of red and blue pigments to produce a purple

color. A number of these mixtures have been noted on East Asian paintings, and several that have not been previously reported have been found on these ukiyo-e paintings.

In Japan, on eighth-century wall paintings, red earth mixed with indigo has been noted (Mogi, Nakasato, and Emoto 1975), as has red earth with azurite (Yamasaki 1951). Vermilion has also been combined with indigo (Emoto 1962). These combinations have not been found here, but a number of other mixtures of red and blue were used by these ukiyo-e painters to produce varying shades of purple. Smalt was found combined with red earth, with organic red, and in one case with indigo and organic red. Indigo was mixed with organic red and in one case occurred over vermilion. Combinations of both vermilion and red earth with carbon black were also found.

Mixtures of different red colorants are known. Vermilion adulterated with red lead or with red earth was said to give an inferior color (Takamatsu 1878). The combination of vermilion with red lead was noted in a Chinese document of 1597 (Read and Pak 1928), and the same combination, sometimes with the addition of red earth, was found at several periods on the wall paintings in the Mogao caves at Dunhuang (Hsü, Chou, and Li 1983). On the wall paintings in the eighth-century Eizan-ji temple at Nara, vermilion was observed over red lead (Yamasaki 1951). A vermilion and red lead combination was found on eighteen of these ukiyo-e paintings. Other less common mixtures of reds were of red earth with either red lead, vermilion, or organic red, to produce varying shades of purplish, brownish, or dark red. A dark red was also created by mixing organic red with vermilion.

Shades of brown were produced on these paintings with mixtures — for example, red earth with red lead and orpiment, or in another case the same three pigments with the addition of vermilion; sometimes shell white was present. With these and other combinations, a variety of browns could be produced that were not attainable with brown earth or organic brown alone.

This survey of mixed pigments on these ukiyo-e paintings indicates that mixtures were more commonly used than was previously thought. The investigation of the use of indigo mixed with Prussian blue on Edo-period paintings in the Freer Gallery seems to support this observation (Leona and Winter, 2003). Further investigation of these mixtures would serve to expand knowledge of these painters' techniques.

## IDENTIFICATION METHODS

Identifications were carried out by traditional methods: polarized-light microscopy (PLM), chemical microscopy, and x-ray diffraction (XRD). Scanning electron

microscopy with energy-dispersive x-ray analysis (SEM-EDXA) was used in a few cases.

*PLM:* The sample was mounted in Canada balsam (refractive index 1.53) or Aroclor resin 5442 (refractive index 1.66) on a microscope slide under a cover slip. The mounted sample was examined by transmitted (plane-polarized) light, and between crossed polars, usually at magnifications up to  $\times 500$ , and sometimes with an oil immersion lens at  $\times 1250$ . PLM is an excellent and reliable way to determine how homogeneous or heterogeneous the sample is, to see if it is a single pigment or a mixture, to determine if it is organic or inorganic, and to detect traces of material which might be overlooked. Attributes such as color, particle characteristics, birefringence, and refractive index in relation to the mounting medium can be observed. The reported refractive indices are measured with sodium light, unless lithium light is indicated. It is an advantage to start off an examination of the sample dispersed on a microscope slide before proceeding to other methods.

The sampling and mounting techniques have been described (Gettens 1976) and the application of PLM to pigment identification has been summarized (Feller and Bayard 1986). Every pigment sampled in this series was examined by PLM, and the microscope slides have been retained permanently.

*Chemical microscopy:* Major elements present were determined by chemical tests carried out on an unmounted sample under the microscope. These methods were described in a seminal work by Chamot and Mason (1970), and their application to pigment identification was pioneered by Joyce Plesters (1956) and Walter McCrone (1982). The tests used are described briefly here; they are covered in detail in these references and in the chapters on the individual pigments in the volumes of *Artists' Pigments*, published by the National Gallery of Art. These methods are now rarely used, but at the time they served their purpose admirably. Chemical microscopy was used on selected samples of all pigments except smalt. The small amount of animal-glue medium present in these paintings did not interfere with chemical tests.

*XRD:* This technique was used on selected samples to confirm the identification of crystalline materials such as minerals and inorganic pigments by determining the crystallographic structure of the material. It is not applicable to amorphous materials such as organic colorants or dyes, nor to non-crystalline inorganic materials such as smalt.

*SEM-EDXA:* This method was used to determine elements in the copper greens and the copper alloy pigments.

The following summaries are intended to make clear the basis for the reported identifications. It will be seen that these methods have limitations, particularly with organic pigments such as indigo and the organic red, yellow, and brown pigments, but even in these cases some general observations could be made.

*Shell white, calcium carbonate or calcite, CaCO<sub>3</sub>.* As observed by PLM the parti-

cles of shell white vary in size and are elongated, flat, and lathlike with a striated appearance, sometimes described as fibrous. The particles reflect the way the calcium carbonate was deposited in layers at the edge of the growing mollusk shell. They are highly birefringent, with low refractive indices:  $\epsilon=1.486$ ,  $\omega=1.658$  (Gettens, FitzHugh, and Feller 1993). The characteristic microscopic appearance was generally accepted to be sufficient for identification. Chemical microscopy (effervescence with dilute HCl and a positive test for calcium with  $H_2SO_4$ ) was used in some cases to provide additional confirmation, and XRD was occasionally used. A few of the calcium carbonates on these paintings lack the striated appearance typical of shell white; these instances may be calcined shell white, or another material altogether.

*Lead white, basic lead carbonate,  $2PbCO_3 \cdot Pb(OH)_2$ .* By PLM lead white shows as finely divided rounded particles of uniform size. The particles are highly birefringent, with high refractive indices:  $\epsilon=1.94$ ,  $\omega=2.09$  (Larsen and Berman 1934, 92). Confirmation was supplied by chemical microscopy (effervescence with dilute  $HNO_3$  to form lead nitrate and a positive test for lead with potassium iodide) and by XRD.

*Vermilion, mercuric sulfide,  $\alpha$ -HgS.* By PLM ground cinnabar, the natural material, is identical to dry-process vermilion; both show variation in particle size, some particles being quite large, with a fractured look and sometimes a hexagonal shape. Large particles are often difficult to distinguish from hematite by PLM; by chemical microscopy its solubility in hydriodic acid serves to differentiate it from hematite (Gettens, Feller, and Chase 1993). Vermilion in transmitted light is a clear cherry red, less commonly with an orange tone. It is highly birefringent, yellow to orange between crossed polars, with high refractive indices:  $\epsilon=3.201$ ,  $\omega=2.854$  (Larsen and Berman 1934, 77). Vermilion was identified chiefly by PLM. Sometimes its presence was confirmed by chemical microscopy (insoluble in concentrated HCl or concentrated  $HNO_3$ , soluble in aqua regia and hydriodic acid, and a positive result from the double thiocyanate test for mercury). XRD was occasionally used.

*Red lead, lead oxide,  $Pb_3O_4$ .* By PLM red lead appears as tiny, irregularly rounded grains, red to orange-brown in transmitted light, weakly birefringent, with high refractive index:  $\eta=2.421_j$  (Palache, Berman, and Frondel 1944). The presence of highly characteristic blue-green interference colors visible between crossed polars (FitzHugh 1986) was usually considered sufficient for identification. Confirmation was supplied by chemical microscopy (see under lead white above). XRD was occasionally used.

*Organic red.* This shows by PLM as a red stain, with no particulate structure. By chemical microscopy the red color disappears with dilute nitric acid, as would be expected of an organic colorant. Plesters (1956) notes that madder turns purple with dilute NaOH and orange with dilute HCl, and similar color reactions are shown by

carmines (Schweppe and Roosen-Runge 1986). Some of the organic reds from these paintings show a violet color with the application of 5% NaOH by chemical microscopy, and the subsequent addition of dilute HCl occasionally causes an orange color to form, thus suggesting the presence of madder or carmine. Chemical microscopy suggests that more than one organic red pigment was used by ukiyo-e artists.

*Red and brown earths.* The chief colorant of red earths is hematite, the red iron oxide,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is also present in lesser quantities in most brown earths. Hematite is a clear transparent red by PLM; it is birefringent, when the particles are large enough, orange to dark red between crossed polars. The refractive indices are high:  $\epsilon=2.94$ ,  $\omega=3.22$  (Larsen and Berman 1934, 95). From optical appearance alone it is sometimes difficult to distinguish it from vermilion because of the similarity of the refractive indices. Red earth is sometimes so finely divided that it appears by PLM only as a rosy stain. Identification was by PLM supported by chemical microscopy (insoluble in concentrated and dilute HCl, soluble in aqua regia, insoluble in hydriodic acid, which differentiates it from vermilion, and a positive test for iron with potassium ferrocyanide). XRD was used rarely because the pigment is usually a complex mixture of minerals. Lepidocrocite  $\gamma$ -FeO(OH), with refractive indices  $\alpha=1.94$ ,  $\beta=2.20$ ,  $\gamma=2.51$  (Palache, Berman, and Frondel 1944), is brown to brownish red in color and is quite likely also to occur in brown earths and possibly in red earths, but it has never been identified. No attempt was made to determine if any of these iron oxides were synthetic materials. By PLM alone the synthetic materials are difficult to distinguish from the natural ochres, although they are usually more uniform and lack the presence of accessory minerals (Helwig, forthcoming).

*Orpiment, arsenic sulfide, As<sub>2</sub>S<sub>3</sub>.* By PLM orpiment particles are usually coarse, of limited transparency, with a foliated, micaceous structure. As already noted the natural material can include large and small particles, while the particles of dry-process material tend to be more uniform in size. Especially characteristic is the presence of distinctive anomalous green-to-blue polarization colors, which is generally considered sufficient for a firm identification. The material is highly birefringent, and the refractive indices are high:  $\alpha=2.4_{Li}$ ,  $\beta=2.8_{Li}$ ,  $\gamma=3.02_{Li}$  (FitzHugh 1986). Confirmation was occasionally supplied by chemical microscopy (a positive test for arsenic with ammonium molybdate) or by XRD.

*Yellow earths.* The principal source of the yellow color is the hydrated iron oxide, goethite, HFeO<sub>2</sub> (Helwig, forthcoming). Goethite is isotropic, with refractive indices  $\alpha=2.260$ ,  $\beta=2.393$ ,  $\gamma=2.398$  (Palache, Berman, and Frondel 1944). By PLM it is usually heterogeneous in composition, a mixture of silica with pale yellow particles and sometimes brown particles, mostly isotropic (Gettens and Stout 1966). By chemical microscopy it is insoluble in both concentrated and dilute HCl, is soluble in aqua



regia, and tests positive for iron with potassium ferrocyanide. XRD was not used.

*Organic yellow.* By PLM this shows as a yellow stain. The formation of a deep orange color results from the application of 5% NaOH by chemical microscopy. This phenomenon is characteristic of gamboge (Winter 1997) and strongly suggests the possibility of the presence of gamboge on these paintings.

*Malachite, basic copper carbonate,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ .* By PLM in transmitted light, particles of malachite are pale green, almost colorless when small or thin, sometimes fibrous, often with a squarish fracture. Large particles sometimes show banding, a vestige of the botryoidal structure of the mineral (plate 5). Malachite is pleochroic and highly birefringent, with high refractive indices:  $\alpha=1.655$ ,  $\beta=1.875$ ,  $\gamma=1.909$  (Larsen and Berman 1934, 204). The highly characteristic microscopic appearance of malachite was generally considered sufficient for identification. Some confirmation was carried out in a few cases by chemical microscopy (soluble in dilute acid usually with effervescence, with a positive test for copper with potassium ferrocyanide). XRD was also used in a few cases.

*Copper greens.* Criteria for the presence of a copper green was the appearance by PLM of a green material that is not malachite, coupled with a positive test for copper by chemical microscopy or SEM-EDXA. The only firm identifications in this general category of copper greens were of paratacamite or atacamite by XRD; these were confirmed by the presence of copper and chloride ions by SEM-EDXA. The single identification of emerald green, copper aceto-arsenite,  $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{CO}_2)_2$ , was made possible by its very characteristic appearance of rounded, doughnut-shaped particles by PLM (Fiedler and Bayard 1997).

*Azurite, basic copper carbonate,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ .* By PLM larger particles are deep blue with greenish undertone, and small or thin particles are pale blue. The particles are irregular and fractured in appearance, sometimes with conchoidal fracture. They are pleochroic and strongly birefringent, with high refractive indices:  $\alpha=1.730$ ,  $\beta=1.758$ ,  $\gamma=1.838$  (Larsen and Berman 1934, 135). The microscopic appearance is usually sufficient for identification. Chemical microscopy (soluble in dilute acid, usually with effervescence, and a positive test for copper with potassium ferrocyanide) was occasionally used. Confirmation by XRD was used to a limited extent.

*Smalt.* Particles of this ground blue glass are isotropic and transparent, and show square and angular corners, or thin flat edges sometimes with conchoidal fracture (plate 6). The refractive index is low and varies with composition, from  $\eta=1.49$  to 1.52 (Gettens and Stout 1966). Microscopically the particles vary from pale blue, often purplish in tone, to a bright blue similar in color to azurite. Tiny entrapped air bubbles are occasionally present. The microscopic appearance of smalt on these paintings was considered sufficient for identification (Mühlethaler and Thissen 1993).

Chemical microscopy of smalt is not possible because of its insolubility, nor can XRD be used because it is a glass and not a crystalline material.

*Indigo.* By PLM indigo appears as a blue stain, with tiny opaque particles sometimes visible. With chemical microscopy it is unaffected by 5% NaOH, whereas the blue color is destroyed by dilute HNO<sub>3</sub>, sometimes with the formation of yellow isatin. This characteristic behavior with alkali and acid was accepted as indication of the presence of indigo. Indigo is not distinguishable from Prussian blue by PLM, but the two can be distinguished by chemical microscopy because Prussian blue is insoluble in dilute HNO<sub>3</sub> but dissolves in 5% NaOH (Schweppe and Winter 1997).

*Prussian blue, Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub>·xH<sub>2</sub>O.* By PLM Prussian blue appears so finely dispersed that it often is seen by transmitted light only as a non-particulate greenish-blue stain, even at high magnifications. The refractive index is low:  $n=1.56$  (Berrie 1997). As noted above, by chemical microscopy Prussian blue is unaffected by dilute HNO<sub>3</sub>, but the color is destroyed by 5% NaOH, sometimes giving a reddish-brown color due to the formation of ferric hydroxide; if enough pigment is present, the application of dilute HCl will cause re-formation of the blue. In a single case enough material was available for identification by XRD. When an apparent mixture of Prussian blue and indigo was present, no firm identification of either pigment was possible by chemical microscopy.

*Ultramarine,* a complex sulfur-containing sodium aluminum silicate. By PLM ultramarine is isotropic with a low refractive index:  $n=1.50$  (Larsen and Berman 1934, 49), and is a deep blue in transmitted light. Particles of the natural material are irregular and angular in shape and are often found with calcite and silicate mineral impurities. Synthetic ultramarine, which was found here, shows uniform, finely divided particles, opaque and somewhat rounded (Plesters 1993). By chemical microscopy the blue color is destroyed by dilute HCl, and sometimes the odor of H<sub>2</sub>S can be detected. XRD can provide confirmation and was used in one case.

*Organic brown.* By PLM this shows as a non-particulate brown, sometimes reddish stain. Chemical microscopy indicates that more than one material was in use. Both 5% NaOH and concentrated H<sub>2</sub>SO<sub>4</sub> cause the brown color to form a brown stain. The behavior with NaOH was noted to be somewhat similar to that of Vandyke brown, which dissolves with the formation of an amber-colored solution (Feller and Johnston-Feller 1997).

*Metal pigments.* By chemical microscopy gold is insoluble in concentrated HNO<sub>3</sub>; silver is soluble in dilute HNO<sub>3</sub>, and with the addition of dilute HCl the formation of white AgCl indicates the presence of silver. Silver sulfide can be identified by XRD. Copper alloys give a positive test for copper with potassium ferrocyanide by chemical microscopy, and the presence of copper and zinc can be determined by SEM-EDXA.

*Other pigments.* Mica was identified as muscovite by XRD. Kaolin was identified by XRD as a kaolin-type mineral, chiefly nacrite, an aluminum silicate, and confirmed by the determination of Al and Si by SEM-EDXA. Barite was identified by PLM and confirmed by XRD.

## CONCLUSIONS

The majority of the pigments used by these artists have been characterized, within certain stated limitations. With two exceptions all of the pigments were in use throughout East Asia. Of these two, shell white is known to be a uniquely Japanese pigment, and it may be that the organic brown, which has yet to be fully described, is also a colorant specific to Japan. The wide variety of pigment combinations used by ukiyo-e artists merits further investigation. It has been established here that these painters included many pigment mixtures to obtain varying hues.

Most of these colorants were used throughout the ukiyo-e period, although orpiment, the copper greens, and smalt did not come into use until partway through the period. It is striking that so many pigments were used consistently over several centuries. Clark (1992) has said that “there is no clearly demonstrable technical ‘progress’ in Ukiyo-e painting.” He was referring to their style, but in a different sense his remark could equally apply to the pigments the artists used to create these paintings.

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F1975.14	Katsushika Hokusai (1760–1849)	dwg	paper	mcx	m	m	mcx											
GROUP 6: EDO PERIOD (1615–1868)																		
F1897.4	anon.	hng	paper	m	mc		mc	m									mc	
F1898.12	anon.	hng	silk	m	m	mc												mc
F1898.92	anon.	scr	silk	m	m			m										
F1898.425	anon.	hng	silk	mc	mc	m											mc	
F1901.12	anon.	hng	silk	mc	m												mc	
F1901.13	anon.	hng	paper	mc	m				mc								mc	
F1901.15	anon.	hng	paper	mc	m	m			mc								mc	
F1901.171	anon.	hnd	paper	m	m	mc												
F1902.90	anon.	hng	silk	mc	m												mc	
F1902.253	anon.	hng	silk	m	m													mc
F1903.66	anon.	hng	paper	mc	m				mc								mc	mc
F1903.76	anon.	hng	silk	mc	m					mcx								
F1903.100	anon.	scr	paper	m	mc													
F1903.135	anon.	hng	silk	mc	m	m												m
F1903.137	anon.	hng	paper	m	m	mc												mc
F1906.48	anon.	hng	paper	m	m													
F1907.126–127	anon.	scr	paper	m	mc	m			mc									
F1978.27	anon.	scr	paper	mc	m													
F1898.11	anon.	hng	paper	m	m	mc											mc	
F1898.108	Shigemasa II	hng	silk	m	m												mc	mc
F1975.25–26	Shuzen Eisai	hnd	paper	m	m	m				mcx								
				m	m													ultr mc; kaolin xs

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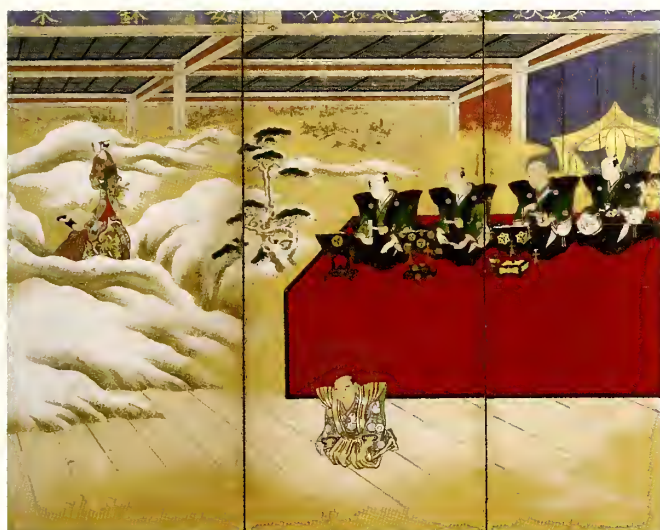


PLATE 1. Detail, *A Puppet-Show: The Story of "The Potted Trees,"* by Bunkaku (early 18th century). Japan, Edo period (1615–1868). Six-panel folding screen; color, ink, and gold on paper; 152.6 × 377 cm (F1898,505). Smalt is used on the blue area of the wall above the red dais in the right panel.



PLATE 2. *Interior: A Girl and a Kitten*, by Katsukawa Shunchō (late 18th century). Japan, Edo period (1615–1868). Hanging scroll; color and gold on silk; 91.5 × 30.8 cm (F1903.132). Purple iron oxide is used for the girl's robe.



PLATE 3. Detail of copper green pigment, paratacamite,  $\times 7$ , from *Dancer in a White Dress, Patterned with Colored Leaves and Flowers*, by an unknown artist. Japan, Edo period, Kambun era (1661–73). Hanging scroll mounted on a panel; color and gold on paper; 87.3  $\times$  29.0 cm (F1903.131).

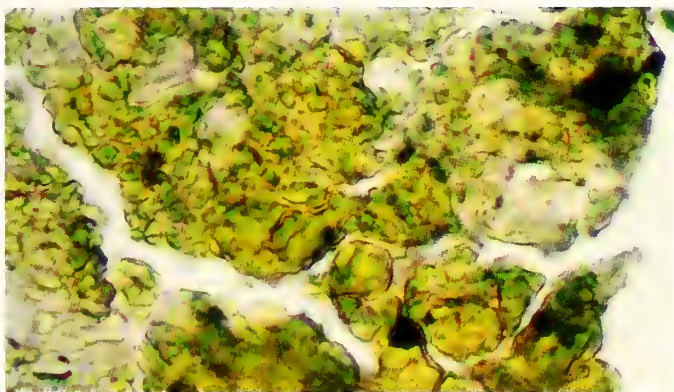


PLATE 4. Photomicrograph of copper green pigment, paratacamite and quartz,  $\times 1200$ , from *Yujo and Her Understudy (Kamuro), the Latter Reading*, by an unknown artist. Japan, Edo period (1615–1868). Hanging scroll; color and ink on paper; 87.9  $\times$  39.9 cm (F1901.13). In transmitted light, mounted in Canada balsam,  $n=1.53$ .

PLATE 5. Photomicrograph of malachite, showing banding,  $\times 180$ , from *River Landscape: Blossoming Cherry Trees*, by Andō Hiroshige (1797–1858). Japan, Edo period (1615–1868). Hanging scroll; ink and tint on silk; 43.6  $\times$  70.5 cm (F1903.105). In transmitted light, mounted in Canada balsam,  $n=1.53$ .

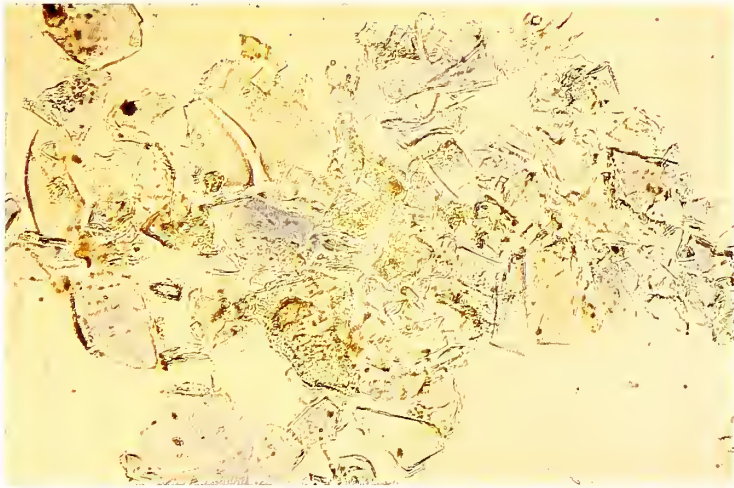
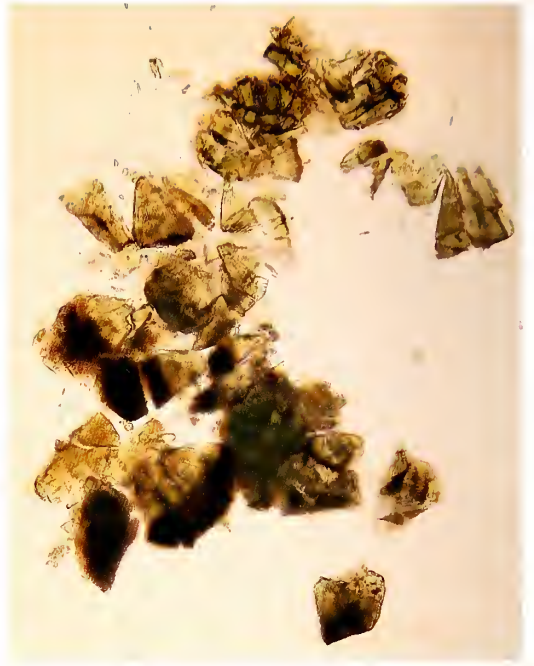


PLATE 6. Photomicrograph of smalt,  $\times 300$ , from *Yujo with a Pipe Standing in the Open Side of a Room and Looking Out*, in the style of Miyagawa Chōshun (1682–1752). Japan, Edo period (1615–1868). Hanging scroll; color and ink on paper; 98.6  $\times$  46.0 cm (F1903.134). In transmitted light, mounted in Canada balsam,  $n=1.53$ .





Prussian  
blue      Indigo  
-----  
1% in CaCO<sub>3</sub>

PLATE 7. Dispersions of  
indigo and Prussian blue,  
1% in calcium carbonate.



PLATE 8. *Landscape: "Red Cliff,"*  
by Ike Taiga (1723–1776). Japan,  
Edo period, 18th century. Hanging  
scroll; ink and color on paper;  
130.7 × 57.1 cm (F1964.11).



PLATE 9. Detail, *Dutch Couple Reading a Letter*, by Nanreisai (Nagasaki; 1771–1836). Japan, Edo period, dated 1817. Hanging scroll; ink and color on paper; measurements not available. Collection of Ambassador and Mrs. W. Leonhart, Washington, D.C.



PLATE 10. Album page, by Hokuga (act. early 19th century). Japan, Edo period, early 19th century. Ink and color on paper; 27.0 × 36.5 cm (F1976.41y).



*Clockwise from above:*

PLATE 11. Detail of plate 10

PLATE 12. Infrared image of detail in plate 11 (shows Prussian blue areas).

PLATE 13. Subtraction image of detail in plate 11 (shows indigo areas).



*Top and bottom left to right:*

PLATE 14. *The Lute and White Snake of Benten (Sarasvati)*, by Katsushika Hokusai (1760–1849). Japan, Edo period, date unknown. Hanging scroll; colors on silk; 35.3 × 44.6 cm (F1904.134).

PLATE 15. Detail of plate 14.

PLATE 16. Infrared image of detail in plate 15 (indigo areas suppressed).

# The Identification of Indigo and Prussian Blue on Japanese Edo-Period Paintings

*Marco Leona and John Winter*

## ABSTRACT

Indigo has long been used as a blue pigment on Japanese and other East Asian paintings. Prussian blue appears more recently, with occasional references in eighteenth-century historical sources, specific documentation of its importation into Japan in the late eighteenth and early nineteenth centuries, and identification on paintings in the nineteenth century. They are both dark blue, fine-particle pigments, and the tinting strength of indigo appears to be at least as high as that of Prussian blue. Methods for identification are reviewed briefly; the major technique used here was fiber-optic reflectance spectroscopy (FORS), supplemented by infrared absorption spectroscopy and x-ray fluorescence spectroscopy. Indigo and/or Prussian blue, alone, in mixtures with each other, or in mixtures with other pigments, were identified on 139 paintings. There was a total of forty-six occurrences of Prussian blue, the earliest that is reliably dated being from 1817, but only eight of these did not have a co-occurrence of indigo. Of a subset of thirty-four paintings dated fairly reliably to after 1830, eighteen had Prussian blue and thirty-one indigo, showing that the latter continued to be important as a pigment. There is no evidence that Prussian blue was more likely to be used on one support material rather than another, or on paintings of one particular format. There are numerous cases of both pigments being used on the same painting, either as a mixture or for separate design elements; some interesting examples of the latter are illustrated. There were sixty paintings with mixtures of these pigments with either yellow (to give a green color) or red (to give a purple color); indigo dominated these cases, Prussian blue occurring in only four, all in mixture with yellows.

## BACKGROUND

Indigo is a dark blue product obtained from a number of plant species. The actual plant metabolite is a glucoside, indican (fig. 1a); successive fermentation and oxidation of plant extracts converts this to the blue compound indigotin (fig. 1b). Most indigo in use in modern times is synthetic, but since this version has been available

only since the 1890s, our concern here is with the natural product. An overall review of indigo as a pigment is by Schweppe (1997).

Indigo has been in use throughout East Asia as both a dyestuff and a pigment for many centuries. Most of it is likely to have come from the indigenous plant *Polygonum tinctorium* (Polygonaceae), but the tropical species *Indigofera tinctoria* (Papilionaceae) is stated to have been introduced into China via Persia as early as the Tang period (7th–9th century), probably for use as a cosmetic (Needham 1986, 158; Schafer 1981, 212). Both the seventeenth-century *Mustard Seed Garden Manual* (Sze 1977, 584) and twentieth-century texts (March 1969; Silbergeld and McNair 1988) cite indigo as a pigment for Chinese painting.

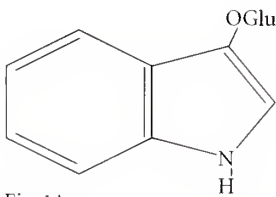


Fig. 1A

Fig. 1A: Structure of indican (indoxyl glucoside);  
Glu=glucosyl

Fig. 1B: Structure of indigotin

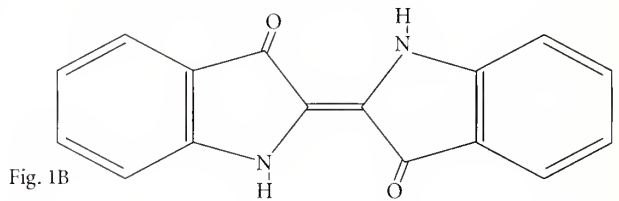


Fig. 1B

Prussian blue is an artificial pigment, made for the first time in Berlin around 1704; commercial manufacture started shortly thereafter (Berrie 1997). It is a hydrated iron hexacyanoferrate of somewhat variable composition; typical molecular formulas are  $KFe[Fe(CN)_6]$  and  $Fe_4[Fe(CN)_6]_3$ , both hydrated with a number of water molecules. Other cations, such as sodium and ammonium, can replace the potassium in the first formula. Along with variations in the color and handling properties, these differences are primarily a consequence of different methods of manufacture. This pigment has had (and continues to have) many different names, though *Prussian blue* appears to be the commonest in its application as an artists' pigment. *Iron blue* is considered to be a generic term for all varieties, and *Berlin blue* (see further below) is derived from its place of discovery.

The date of Prussian blue's first arrival in Japan is uncertain. According to Screech (2000, 203–4), Chinese intermediaries had imported some by 1782, and the Dutch began modest, formal imports from 1789. Screech considers that around 1790 the pigment was distributed more as a gift than as a regular trading good. Smith (1998) has examined the whole question of availability of Prussian blue in Japan in some detail. He found references to it in Japanese writings dated 1763 and 1778, with claims that it was used in certain eighteenth-century paintings of the Akita school. A study

of Nagasaki trading records led Smith to distinguish six phases of importation through that port.

1. 1782–97, sporadic imports by the Chinese at low prices
2. 1798–1809, more frequent but sporadic imports by the Dutch at higher prices
3. 1810–16, no imports
4. 1817–23, imports by the Dutch, prices initially high but declining
5. 1824–28, reentry of the trade by the Chinese, with steadily increasing quantities and declining prices
6. 1829 onward, trade entirely in Chinese hands until the mid-1840s and prices low

The overall picture is one of fluctuating but limited availability from some point in the eighteenth century until the 1820s, when increasing Chinese imports were associated with a decline in price.

From the late 1820s, the use of a dark blue in ukiyo-e woodcut prints increased to a striking degree, especially by Katsushika Hokusai (1760–1849) and his school. The pigment has been widely assumed to be Prussian blue, which became more prevalent as the price declined. However, pigment identifications in the published literature relevant to the question appear at present to be lacking.<sup>1</sup>

Prussian blue has also been reported on Edo-period silk textiles in Japan (Ito, Sinkai, and Sugisita 1999), presumably being a type of disperse dyestuff; it was held responsible for deterioration of the silk.

A Japanese name for the pigment in the eighteenth century was *beroin buraau*; shorter forms after about 1800 were *bero* and *berorin* (Smith 1998). The modern version is *bero-ai*. All of these are clear adaptations of Berlin blue and its close analogues in other Western languages. The name *Berlin blue* is often favored by scholars of Japanese history.

Indigo and Prussian blue are not identical in color or other properties, but they are quite similar. Both are fine-particle pigments that give a very dark blue in sufficiently heavy applications, and might well be considered by a painter for much the same design features. It is worth noting that blue pigments were not, before modern times, available in a great variety to the Japanese painter. Azurite was widely used but seems often to have been imported, and there is no evidence that natural ultramarine reached Japan (synthetic ultramarine appears there in the nineteenth century). In these circumstances, it is of interest to acquire information on the uses of indigo and Prussian blue in paintings from the late eighteenth to early nineteenth centuries.

1. Feller, Curran, and Bailie (1984) cite two or three identifications of indigo on ukiyo-e prints, but none of Prussian blue.

## PROPERTIES AND IDENTIFICATION METHODS

Both Prussian blue and indigo are a very dark blue, but in both cases the exact shade may vary — for example, with greenish or reddish undertones. Indigo, the natural product, can vary in purity; depending on the plant source, the isomeric compound indirubin, or “indigo red,” may be present in proportions of up to a few percent (Schweppe 1997). As described above, the chemical composition of Prussian blue, and perhaps also its purity, shows differences depending on the method of manufacture. Prussian blue is usually considered to be a “brighter” blue than indigo. This presumably means that the chroma, in the Munsell color system, is higher, but in light of the above comments it is clear that such statements need interpreting with caution. With both pigments the particle sizes are very small, making it fairly easy for the painter to apply the pigment thinly and control the intensity of color. Admixture with a white pigment may also have been used for lighter blues.

The tinting strength of a pigment is a measure of its ability to impart color to a white base pigment. Prussian blue is generally recognized to have a high tinting strength (Berrie 1997), a desirable property for making prints, though probably less important to the painter. It has sometimes been implied (Wehlte 1975) that indigo is much weaker in its tinting ability. However, we have been able to find no direct comparison of the two pigments. We describe below our own experiments comparing synthetic indigo with ferric ferrocyanide ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , see above), which showed that the indigo displayed a *higher* tinting strength in both calcium carbonate and barium sulfate than did this particular version of Prussian blue. We emphasize, however, that the possible variability of both pigments can affect such results appreciably; in particular, the natural product indigo may have been marketed in versions much less pure than the synthetic compound used here.

Under the optical microscope, particles of either pigment are often too small to be resolved, though larger clumps are commonly seen. It has long been recognized that the two pigments are extremely difficult to distinguish by microscopic examination. There are marked differences of chemical behavior. Strong oxidizing agents, such as nitric acid, convert indigo to isatin (yellow, and much less intense in color), and reducing agents reduce it to colorless leucoindigo, which may be reoxidized back to indigo. It is stable to dilute alkali and nonoxidizing acids. Prussian blue is also stable to cold dilute acids, but is readily decomposed by dilute alkali (which means that, as a pigment, it cannot be used in alkaline media).

These chemical properties have often been used for the identification on the microscope stage of microscopic samples (FitzHugh 1979). The main problem is that the amount of pigment in a permissible sample is generally very small. The intense



colors of indigo and Prussian blue (high absorption coefficients in the visible region) mean that the surface density of pigment is low, and especially so for light blue design features. A sample of blue, if it is visible at all, may be mixed with support fibers or other materials, and in some cases indigo and Prussian blue themselves may be present as a mixture. These problems have sometimes made unambiguous chemical identifications of indigo and Prussian blue impractical.

Prussian blue is a compound of iron, which affords another basis for chemical identification and may enable evidence for its presence to be obtained noninvasively by x-ray fluorescence spectrometry. This approach also is limited by low surface-density of the pigment, coupled with the near ubiquity of iron in various chemical forms; it is quite common to see a weak iron signal on many parts of a painting. In addition, x-ray fluorescence does not help with identifying indigo. Nevertheless, the ability to identify iron noninvasively can sometimes provide useful evidence.

The infrared absorption spectrum is characteristic for both compounds. The advent, some time ago, of the Fourier transform approach for capturing a spectrum meant that microscopic samples became adequate for study. The size of a permissible sample from the painting may still be a limitation, but within this limit, a Fourier transform infrared (FTIR) spectrum normally enables a definitive identification of both pigments, including mixtures of the two. Although infrared spectroscopy can also, in principle, be done in reflectance mode on the surface of a work, it suffers from serious difficulties when applied in this way. These are chiefly the low intensity of the diffusely reflected radiation and obscurement of the spectrum of interest by absorption by the support material, binder, sizes, and so forth. We are not aware of such a method having been investigated for application to East Asian paintings.

Reflectance spectroscopy has been used as a noninvasive technique in the ultraviolet and visible regions. As an identification method, this has not been as popular as some others and has the disadvantage of lower resolution of spectral features and poorer fingerprinting ability than, for example, FTIR. It does have at least one advantage for identification of colorants: by definition it is highly selective for materials that absorb in the visible region and discriminates against other components that are present in the painting. Compounds that absorb visible light usually have strong absorption in the ultraviolet also, and for identification purposes it is not necessary to be bound by the sensitivity limits of the human eye.

This identification method has proved to be well adapted to the indigo/Prussian blue problem. The main reason in the present case lies with the unusual absorption properties of indigo above about 700 nm, as the spectrum moves into the near-infrared region. The absorption of radiation in this region by indigo falls rapidly to a low value, a characteristically different behavior from that of Prussian blue or

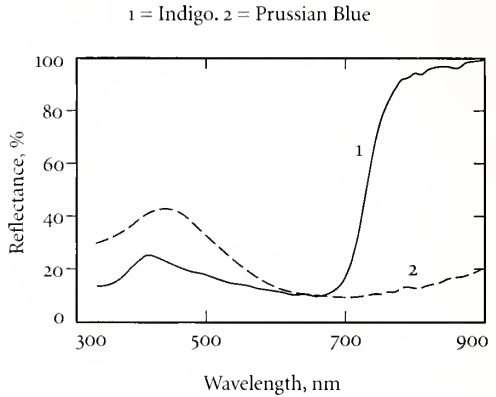
other possible blue pigments. It follows that the reflectance of indigo rises rapidly, as seen in the reflectance curves for indigo and Prussian blue dispersions shown in figure 2. A consequence of the same property is that images of indigo-painted areas in the near infrared appear very light in tone, to the extent that such areas can often be suppressed in such an image. This feature was exploited in the present work with certain paintings, as described below.

Visible reflectance spectroscopy has been used by others — for example, by Feller, Curran, and Bailie (1984) on Japanese ukiyo-e prints. Fiber-optic technology enabled an advance to be

made by solving the problem of coupling the spectrometer to any selected spot on the painting surface; pioneering work was done in the field of Italian paintings by Bacci and his coworkers (e.g., Bacci et al. 1996), who adopted the acronym FORS (fiber-optic reflectance spectroscopy) for this approach. In our hands, a flexible fiber-optic probe of special design has been coupled to a Cary 50 UV-visible spectrophotometer (Varian Associates, Inc.), an instrument with a spectral range of 190–1100 nm (other limitations tend to restrict reflectance spectra to a range above about 250 nm or so). This system enables a spectrum to be collected from a spot of about 0.7 mm diameter that can be accurately located on the painting surface. The particular spectrometer couples efficiently to fiber optics and may be used without special shielding from room lights; the specialized fiber-optic probe design gives an improved efficiency in collecting reflected radiation from the painting. The method is noninvasive: no sample is removed, and there is no contact between the probe and the work of art being examined. Furthermore, exposure to the wavelengths employed is safe even for extremely fugitive dyes for times much longer than those required for normal spectrum acquisition. The system has been described in detail in a separate publication (Leona and Winter 2001), which also describes the use of Kubelka-Munk transforms to identify mixtures of the two pigments.

The present work relied heavily on the FORS technique for an initial analysis of blue, green, or purple areas on the paintings. Where appropriate, this was supplemented with x-ray fluorescence spectroscopy (to confirm the presence of iron in suspected Prussian blue occurrences) and FTIR spectroscopy on a removed sample.

FIG 2. REFLECTANCE CURVES



The last approach complemented the FORS method, since FORS does not work as well with the heavy (and therefore dark and unreflective) applications that are more amenable to sampling.

#### TINTING STRENGTH

The tinting strength of a pigment is measured by dispersing a weighed proportion in a selected white pigment and assessing the resulting color either visually or instrumentally. It is a convenient method of quality control, and the importance of Prussian blue in commercial color technology has led to its tinting strength having often been measured. The same is not true of indigo, which is better known in the modern world as a dyestuff rather than a pigment.

We prepared mixtures of synthetic indigo (Fisher Scientific) and of ferric ferrocyanide (Fisher Scientific) with calcium carbonate (Aldrich Chemical Co., 99+%). In each case, the pigment (0.1 g) was mixed with calcium carbonate (10 g), the mixture made damp with ethanol and ground thoroughly with a pestle and mortar, and then dried to give a 1% (w/w) dispersion. The results are shown in plate 7. It is seen that the Prussian blue dispersion is lighter in color than indigo but also is a brighter blue color. Layers were prepared on microscope slides using methylcellulose in aqueous solution as a binder. Instrumental measurements of the colors (Minolta Chromameter Model 221) gave results in the  $L^*a^*b^*$  system shown in table 1.

Similar dispersions of 0.1%, 1%, and 10% (w/w) were made in barium sulfate (Sigma Chemical Co.). These were lighter in color overall, but they also showed higher tinting strength for indigo than for Prussian blue. A dispersion of 2% Prussian blue in barium sulfate was approximately the same tint as the 1% indigo preparation.

Prussian blue has been characterized in the literature as having a high tinting strength. This is undoubtedly true, but it seems clear from these results that indigo of a reasonable purity has a tinting strength at least comparable to, if not higher than, that of Prussian blue.

TABLE 1. COLOR MEASUREMENTS ON 1% DISPERSIONS IN CALCIUM CARBONATE

	L	a*	b*
Prussian blue	48.60±0.22	-7.21±0.02	-27.13±0.26
Indigo	38.23±0.46	-1.69±0.06	-14.59±0.18

## PREVIOUS IDENTIFICATIONS

The identification of these pigments in design features of paintings has been technically rather difficult for the reasons described above, particularly in cases where mixtures are likely. These points should be remembered when claims of identification are assessed. However, Prussian blue need not be considered before the eighteenth century, and is likely to be unusual before the nineteenth. Existing identifications of this pigment in East Asia appear to be confined to Japan.

Indigo as a pigment has been claimed on paintings and objects in the eighth-century Shōsōin repository as well as on temple wall paintings of the ninth to eleventh century (Yamasaki and Emoto 1979). In the latter usage it was suggested that indigo substituted for azurite when this was in short supply (Japan has often had to import azurite, and communications with the Asian continent were restricted during the time in question). Coming to Japan of later times, FitzHugh (2003), in an investigation of 284 ukiyo-e paintings or groups of paintings in the Freer Gallery collection, found indigo in 152 cases and Prussian blue in 36. The paintings ranged from the seventeenth through the nineteenth century, and, not surprisingly, Prussian blue occurrences were heavily weighted toward the later paintings. However, the identification method was chemical microscopy, and uncertainties attended some of the identifications because of small sample sizes and probable mixed occurrences.

## RESULTS

## PAINTING SELECTION

The great majority of paintings investigated were from the collection of the Freer Gallery of Art, and some were works also investigated, using different techniques, by FitzHugh (1979; 2003). Date attributions ranged from the eighteenth to the nineteenth century. A large proportion of the works are attributed to Hokusai or his pupils, a school that happens to be well represented in the Freer collection. Altogether 139 paintings were found to have indigo and/or Prussian blue, alone or in mixtures. Nine of these had one or the other only as a mixture with a pigment of another color (typically with a yellow to afford a green color), leaving 130 with indigo and/or Prussian blue in blue design features. The overall statistics are given in table 2. A complete list of paintings with their attributions and the results obtained is in the appendix.

## PRUSSIAN BLUE OCCURRENCES

Those paintings where Prussian blue was found and where indigo was not found as

a blue color are listed in table 3 (p. 66). In addition to twelve paintings in which Prussian blue appears as a blue, there is one where it is mixed with yellow to give a green color, also without the co-occurrence of indigo. However, of the twelve with Prussian blue as blue, three also had indigo in a yellow-blue mixture and one had indigo in a red-blue mixture. There were, therefore, only eight paintings that used Prussian blue without any use of indigo on the same painting.

#### INDIGO OCCURRENCES

Those paintings where indigo has been found without Prussian blue having also been found are listed in table 4 (p. 67). There are eighty-five paintings in which indigo occurs as blue (in eighteen of them, it is also present as a mixture with yellow, and in ten as a mixture with red), seven in which it occurs only mixed with yellow, and one in which it occurs only mixed with red. In none of these cases was any Prussian blue-based mixture found.

#### PRUSSIAN BLUE AND INDIGO CO-OCCURRENCES

Two situations are possible: the pigments may be applied separately (usually for different design elements), or they may be applied as a mixture. Both situations have been

TABLE 2. OVERALL STATISTICS

TOTAL NUMBER OF PAINTINGS	139
Having design elements in blue	130
Mixtures with other colors only	9
<hr/>	
ONLY ONE OF THE PIGMENTS AS BLUE	97
Indigo only as blue <sup>1</sup>	85
Prussian blue only as blue <sup>2</sup>	12
<hr/>	
BOTH PIGMENTS USED AS BLUE	33
Used in separate design elements	26
Used as mixtures	13
Both situations on same painting	6
<hr/>	
MIXTURES WITH OTHER COLORS	60
Indigo + yellow pigment	48
Prussian blue + yellow pigment	3
Indigo + Prussian blue + yellow pigment	2
Indigo + red pigment	13

1. Eighteen paintings had indigo also in a green mixture.

2. Three paintings had indigo in a green mixture.

TABLE 3. OCCURRENCES OF PRUSSIAN BLUE ONLY

PB = Prussian blue; I-gn = indigo green; PB-gn = Prussian blue green; IPB-gn = both in green; B+R = blue + red; Ind = indigo. Identifications: x = identification firm; (x) = identification probable. Accession numbers refer to the collection of the Freer Gallery of Art.

Accession #	Artist	Title	Support	PB	I-gn	PB-gn	IPB-gn	B+R
F1898.107	Katsushika Hokusai	A girl holding a pipe	paper	x				
F1898.123	Utagawa Hiroshige II	Landscape of the season: Spring	silk	x				
F1898.126	Utagawa Hiroshige II	Landscape of the season: Summer	silk	x	x			
F1903.216	Katsushika Hokusai	A seated man looking at potted peonies	paper	x	x		x	
F1904.132	Katsushika Hokusai	Rats and rice bales	silk	x				
F1904.180	Katsushika Hokusai	Flowers, birds, animals of twelve seasons	paper	x	x			
F1904.185	Katsushika Hokusai	A girl holding a letter behind her back	silk	x				
F1904.218	Katsushika Hokusai	A man carrying backpack and lantern	paper	x				Ind
F1905.228	Katsushika Hokusai	Landscape: Mountain, stream, and boat	silk	x				
F1954.119	Katsushika Hokusai	Portrait of a courtesan walking	silk	x				
F1986.66	Tani Bunchō	Peach blossom spring	silk	x				
F1997.23.3	Kawahara Keiga	Ningyo	paper	(x)				
Following painting had Prussian blue in a green mixture only								
F1904.73	Katsushika Hokusai	Walking figure of a courtesan	paper			x		

found, sometimes on the same painting; table 2 gives the overall numbers. In addition, as before, there may be mixtures with other colors. Table 5 (p. 69) lists the thirty-three paintings in which these various co-occurrences have been found. This increases the number of paintings on which any Prussian blue has been found at all to forty-six, and the number of paintings on which any indigo has been found at all to 127.

#### MIXTURES WITH YELLOW OR RED PIGMENTS

The sixty paintings where mixtures of either pigment with a yellow or red, to give respectively a green or purple color, are listed in table 6 (p. 70). As seen from table 2, these are additional to the use of indigo or Prussian blue in blue design elements in all but nine cases.

#### RELATIONSHIP TO SUPPORT OR FORMAT

In table 7 (p. 72), the numbers of occurrences of Prussian blue as a function of support material (silk or paper) and of painting format (hanging scroll, screen, etc.) are listed.

TABLE 4. OCCURRENCES OF INDIGO ONLY

Ind = indigo; I-gn = indigo green; B+R = blue + red.  
IDENTIFICATIONS: x = identification firm.  
Accession numbers refer to the collection of the Freer Gallery of Art.

Accession #	Artist	Title	Ind	I-gn	B+R
F1894.30	Kishi Ganku	Bamboo stems with branches and foliage	x	x	
F1898.6	Mori Sosen	A peacock	x		
F1898.74	Sōri III	Women at their toilet	x	x	Ind
F1898.96	Shiba Kōkan	A young woman with a cage of fireflies	x		
F1898.97	Katsushika Hokusai	River landscape	x		
F1898.101	Miyagawa Chōshun	A yūjo and her understudy	x		
F1898.103	Sōri III	A lady and a faggot-gatherer under a cherry tree	x		
F1898.105	Sōri III	A girl playing battledore and shuttlecock	x		
F1898.111	Katsushika Hokusai	Flowering squash-vine and a bee	x		
F1898.114	Hishikawa Moroyasu	A yūjo doing her hair	x		
F1898.121	Utagawa Toyokuni	Seashore: Three girls under a flowering cherry tree	x		Ind
F1898.135b	Katsushika Hokusai	Blossoming plum branches	x		
F1898.135e	Katsushika Hokusai	A man with a fan, butterflies, and a bowl of water	x	x	
F1898.135h	Katsushika Hokusai	A tree and four red Torii	x	x	
F1898.135i	Katsushika Hokusai	A young crow and maple leaves	x		
F1898.423	Katsukawa Shunkō	An actor in character	x		
F1898.429	Miyagawa Chōshun	A yūjo sitting on a bench	x		
F1898.508	Shibata Zeshin	Ashinaga and Tenaga worshipping the rising sun	x		
F1899.16	Kitagawa Utamaro	A courtesan playing a samisen	x		Ind
F1899.17	Utagawa Hiroshige II	River Landscape	x	x	
F1899.19	Nishikawa Sukenobu	A girl sitting on her bed	x		
F1900.58	Katsushika Hokusai	An old fisherman standing on the shore	x		
F1901.13	Anonymous	A yūjo and her understudy	x		
F1901.166	Suzuki Harunobu	Murasaki Shikibu	x		
F1902.3	Katsushika Hokusai	Miscellaneous subjects	x		
F1902.27	Katsushika Hokusai	The Chinese hermit Sun Teng	x	x	
F1902.41	Katsushika Hokusai	Standing figure of a girl	x		
F1902.42	Katsushika Hokusai	Miscellaneous subjects	x	x	
F1902.48	Katsushika Hokusai	Country scenes	x	x	Ind
F1902.49	Katsushika Hokusai	Country scenes	x		
F1902.100	Katsushika Hokusai	A courtesan under a cherry tree	x		
F1902.178	Katsushika Hokusai	New Year's day: Two strolling mountebanks	x	x	
F1902.222	Katsushika Hokusai	A boy fishing from the limb of a tree	x		
F1903.2	Katsushika Hokusai	Clam-gatherers on the shore	x	x	
F1903.52	Katsushika Hokusai	New Year rituals	x		
F1903.53	Katsushika Hokusai	New Year rituals	x		
F1903.97	Utagawa Hiroshige II	Landscape: Flowering cherry trees along the banks of a stream	x		
F1903.109	Katsushika Hokusai	River landscape, ferry-boat, and Mt. Fuji	x	x	
F1903.125	Katsushika Hokusai	Landscape: Parties of men and women looking at cherry blossoms	x		Ind
F1903.126	Katsushika Hokusai	A courtesan standing	x		
F1903.127	Katsushika Hokusai	A dancer, Kiyohime, a cherry tree, and the bells of dōjō-ji	x		
F1903.128	Katsushika Hokusai	Interior: A courtesan writing, another looking on	x		Ind
F1903.129	Katsushika Hokusai	A courtesan	x		
F1903.134	Anonymous	A yūjo with a pipe	x		
F1903.135	Anonymous	A yūjo reclining	x		
F1903.143	Katsushika Hokusai	Viewing cherry blossoms	x		
F1903.144	Katsushika Hokusai	Viewing cherry blossoms	x		

TABLE 4. (CONTINUED)

Accession #	Artist	Title	Ind	I-gn	B+R
F1903.291	Andō Hiroshige	Landscape	x		
F1904.142	Katsushika Hokusai	Suikoden	x		
F1904.173	Katsushika Hokusai	Standing figure of a tall girl	x	x	
F1904.174	Katsushika Hokusai	Landscape: Bridge, houses, and distant hills	x		
F1904.177	Katsushika Hokusai	A shinto priest, three women, and a child under a pine tree	x		
F1904.186	Katsushika Hokusai	A traveling mountebank under a tree	x	x	
F1904.188	Katsushika Hokusai	The six poets	x		
F1904.190	Katsushika Hokusai	Descending dragon	x		
F1904.206	Katsushika Hokusai	Landscape: Boatman poling his raft	x	x	
F1904.357	Andō Hiroshige	Miscellaneous sketches	x	x	
F1904.383	After Tsunenobu	Birds and flowers	x		
F1904.400	Shibata Zeshin	A faggot-gatherer looking at a waterfall	x		
F1905.270	Katsushika Hokusai	An amusement resort at the seashore	x		Ind
F1905.294	Hosoda Eishi	Lady viewing cherries at Goten Yama	x	x	
F1906.11	Hosoda Eishi	Yang Kuei-Fei	x		
F1906.51	Katsushika Hokusai	Filial piety	x	x	
F1906.52	Katsushika Hokusai	Two drunken men returning from a cherry blossom party	x		
F1906.233	Katsushika Hokusai	Landscape: Two of the four seasons, spring and summer	x		
F1906.234	Katsushika Hokusai	Landscape: Two of the four seasons	x		
F1907.368	Katsushika Hokusai	One of the six poets	x		
F1907.369	Katsushika Hokusai	One of the six poets	x		Ind
F1955.2	Tani Buncho	A peacock and peonies	x		
F1957.7	Hosoda Eishi	Beauties of the season: Spring	x		
F1959.12	Miyagawa Chōshun	Festivals of the twelve months	x		
F1960.31	Sakai Hōitsu	The master poets	x		Ind
F1963.3	Mori Sosen	Monkeys and waterfall	x		
F1964.12	Ike Taiga	Tower	x		
F1967.18	Yosa Buson	Mynah birds on a plum tree	x		
F1967.19	Yosa Buson	Mynah birds on a plum tree	x		
F1974.16	Jogan	Barbarians	x		
F1977.22	Anon.	Ryūkyū man	x		
F1978.6	Yamawaki Toki	One hundred boys playing	x		
F1978.14	Kawanabe Gyōsai	Activities of the twelve months	x		
F1986.60	Kusumoto Rin	Parrot on a branch	x		
F1992.24	Katsushika Hokusai	Pounding rice for rice cakes	x	x	
F1995.15	Kishi Ganku	Eagle	x		
F1995.17	Utagawa Kunisada	Courtesan beneath a mosquito net	x		Ind
F1998.297	Shūki Okamoto	Auspicious symbols	x		
Following eight paintings have indigo mixed with other color only					
F1894.29	Kishi Ganku	A female immortal riding a deer		x	
F1898.421	Shunman	Two <i>oiran</i>		x	
F1904.131	Yōsai Kikuchi	Three gardeners of the emperor Takakura		x	
F1904.428	Katsushika Hokusai	Woman facing the right beckoning		x	
F1969.29	Kawanabe Gyōsai	Fan with scenes of the tale of Shuten Dōji		x	
F1969.30	Kawanabe Gyōsai	Fan with scenes of the tale of Shuten Dōji		x	
F1997.31.1	Izuhara Makoku	Flowers of the four seasons		x	
F1999.5.3	Ikeda Koson	Gosekku			Ind



THE IDENTIFICATION OF INDIGO AND PRUSSIAN BLUE

TABLE 5. OCCURRENCES OF PRUSSIAN BLUE AND INDIGO ON SAME PAINTING

Ind = indigo; PB = Prussian blue; Mix = mixture of both; I-gn = indigo green;  
 PB-gn = Prussian blue green; IPB-gn = both in green; B+R = blue + red.  
 IDENTIFICATIONS: x = identification firm; (x) = identification probable.  
 Accession numbers beginning with "F" designate paintings in the collection of the Freer Gallery of Art.

Accession #	Artist	Title	Ind	PB	Mix	I-gn	PB-gn	IPB-gn	B+R
F1898.8	Gakutei Harunobu	Two geisha reading from a book		x	(x)	x			
F1898.110	Katsushika Hokusai	Boy and Mt. Fuji	x	x	x	x			
F1898.124	Utawaga Hiroshige II	Landscape of the season: Winter	x	(x)					
F1898.135a	Katsushika Hokusai	A fat old man sitting beside an old bell	x	x					
F1901.165	Katsushika Hokusai	River landscape: Village and tall trees	x	x		x			
F1902.2	Katsushika Hokusai	Cherry blossom viewing	x		x		x		
F1902.40	Katsushika Hokusai	A herd boy seated on a tree trunk	x	x	x	x			
F1902.221	Katsushika Hokusai	Chung Kuei (Shoki) killing a demon	x	x	x	x			
F1902.254	Katsushika Hokusai	Crustaceans of various kinds	x	x		x			
F1902.258	Katsushika Hokusai	Hawk and fish	x	x		x	x	x	
F1903.106	Utawaga Hiroshige II	River landscape and temple in the rain	x	x					
F1903.145	Andō Hiroshige	Famous sites of Edo	x	x	x	x			
F1903.146	Andō Hiroshige	Famous sites of Edo	x	x					
F1903.274	Katsushika Hokusai (Sōri II) or Sōri III	A courtesan standing near a clothes rack			x				
F1904.134	Katsushika Hokusai	The lute and white snake of Bente	x	x					
F1904.175	Katsushika Hokusai	Mt. Fuji and Enoshima		x	(x)	x			
F1904.176	Katsushika Hokusai	Mt. Fuji and Enoshima			x				
F1904.178	Katsushika Hokusai	Four fan papers	x	x		x			
F1904.179	Katsushika Hokusai	Flowers, birds, and animals of the twelve seasons	x	x					
F1904.181	Katsushika Hokusai	A fisherman seated at the shore	x		x	x			
F1904.182	Katsushika Hokusai	A faggot-gatherer	x		x	x			
F1904.184	Katsushika Hokusai	Interior: Two ladies seated on a veranda	x	x	(x)	x			
F1904.189	Katsushika Hokusai	Ascending dragon	x	x	x				
F1904.204	Katsushika Hokusai	The six Tama rivers	x	x		x			
F1904.205	Katsushika Hokusai	The six Tama rivers	x	x		x			
F1905.276	Katsushika Hokusai	Breaking waves	x	x		x			
F1905.282	Katsushika Hokusai	A priest (Kobō Daishi) practicing the tantra	x	x					
F1964.11	Ike Taiga	Red Cliff	x	x	x	x			
F1975.14	Katsushika Hokusai	Album of forty-two sketches	x	x		x			
F1976.41	Hokuga	Album	x	x		x			Ind
F1977.24	Hokutei Joren	Choi and Kanyu	x	x					
F1996.32	Totoya Hokkei	The first <i>katsuo</i> of the season	x	x		x			
LT'S1987.1.72	Nanreisai (Nagasaki)	Dutch couple reading a letter	x	x					

TABLE 6. OCCURRENCES OF BLUE/YELLOW AND BLUE/RED MIXTURES

Accession #	Artist	Title	Ind	PB	Mix	I-gn	PB-gn	IPB-gn	B+R
F1894.29	Kishi Ganku	A female immortal riding a deer				x			
F1894.30	Kishi Ganku	Bamboo stems with branches and foliage	x			x			
F1898.8	Gakutei Harunobu	Two geisha reading from a book		x	(x)	x			
F1898.74	Sōri III	Women at their toilet	x			x			Ind
F1898.110	Katsushika Hokusai	Boy and Mt. Fuji	x	x	x	x			
F1898.121	Utagawa Toyokuni	Seashore: Three girls under a flowering cherry tree	x						Ind
F1898.126	Utagawa Hiroshige II	Landscape of the season: Summer		x		x			
F1898.135e	Katsushika Hokusai	A man with a fan, butterflies, and a bowl of water	x			x			
F1898.135h	Katsushika Hokusai	A tree and four red Torii	x			x			
F1898.421	Shunman	Two <i>oiran</i>				x			
F1899.16	Kitagawa Utamaro	A courtesan playing a samisen	x						Ind
F1899.17	Utagawa Hiroshige II	River landscape	x			x			
F1901.165	Katsushika Hokusai	River landscape: Village and tall trees	x	x		x			
F1902.2	Katsushika Hokusai	Cherry blossom viewing	x		x		x		
F1902.27	Katsushika Hokusai	The Chinese hermit Sun Teng	x			x			
F1902.40	Katsushika Hokusai	A herd boy seated on a tree trunk	x	x	x	x			
F1902.42	Katsushika Hokusai	Miscellaneous subjects	x			x			
F1902.48	Katsushika Hokusai	Country scenes	x			x			Ind
F1902.178	Katsushika Hokusai	New Year's day: Two strolling mountebanks	x			x			
F1902.221	Katsushika Hokusai	Chung Kuei (Shoki) killing a demon	x	x		x			
F1902.254	Katsushika Hokusai	Crustaceans of various kinds	x	x		x			
F1902.258	Katsushika Hokusai	Hawk and fish	x	x		x	x	x	
F1903.2	Katsushika Hokusai	Clam-gatherers on the shore	x			x			
F1903.109	Katsushika Hokusai	River landscape, ferry-boat, and Mt. Fuji	x			x			
F1903.125	Katsushika Hokusai	Landscape: Parties of men and women looking at cherry blossoms	x						Ind
F1903.128	Katsushika Hokusai	Interior: A courtesan writing, another looking on	x						Ind
F1903.145	Andō Hiroshige	Famous sites of Edo	x	x	x	x			
F1903.216	Katsushika Hokusai	A seated man looking at potted peonies		x		x		x	
F1904.73	Katsushika Hokusai	Walking figure of a courtesan					x		
F1904.131	Yōsai Kikuchi	Three gardeners of the emperor Takakura				x			
F1904.173	Katsushika Hokusai	Standing figure of a tall girl	x			x			
F1904.175	Katsushika Hokusai	Mt. Fuji and Enoshima		x	(x)	x			
F1904.178	Katsushika Hokusai	Four fan papers	x	x	x	x			
F1904.180	Katsushika Hokusai	Flowers, birds, and animals of the twelve seasons		x		x			
F1904.181	Katsushika Hokusai	A fisherman seated at the shore	x		x	x			
F1904.182	Katsushika Hokusai	A faggot-gatherer	x		x	x			

TABLE 6 (CONTINUED)

Accession #	Artist	Title	Ind	PB	Mix	I-gn	PB-gn	IPB-gn	B+R
F1904.184	Katsushika Hokusai	Interior: Two ladies seated on a veranda	x	x	(x)	x			
F1904.186	Katsushika Hokusai	A traveling mountebank under a tree	x			x			
F1904.204	Katsushika Hokusai	The six Tama rivers	x	x		x			
F1904.205	Katsushika Hokusai	The six Tama rivers	x	x		x			
F1904.206	Katsushika Hokusai	Landscape: Boatman poling his raft	x			x			
F1904.218	Katsushika Hokusai	A man carrying backpack and lantern		x					Ind
F1904.357	Andō Hiroshige	Miscellaneous sketches	x			x			
F1904.428	Katsushika Hokusai	Woman facing the right beckoning				x			
F1905.270	Katsushika Hokusai	An amusement resort at the seashore	x						Ind
F1905.276	Katsushika Hokusai	Breaking waves	x	x		x			
F1905.294	Hosoda Eishi	Lady viewing cherries at Goten Yama	x			x			
F1906.51	Katsushika Hokusai	Filial piety	x			x			
F1907.369	Katsushika Hokusai	One of the six poets	x						Ind
F1960.31	Sakai Hōitsu	The master poets	x						Ind
F1964.11	Ike Taiga	Red Cliff	x	x	x	x			
F1969.29	Kawanabe Gyōsai	Fan with scenes of the tale of Shuten Dōji				x			
F1969.30	Kawanabe Gyōsai	Fan with scenes of the tale of Shuten Dōji				x			
F1975.14	Katsushika Hokusai	Album of forty-two sketches	x	x		x			
F1976.41	Hokuga	Album	x	x		x			Ind
F1992.24	Katsushika Hokusai	Pounding rice for rice cakes	x			x			
F1995.17	Utawaga Kunisada	Courtesan beneath a mosquito net	x						Ind
F1996.32	Totoya Hokkei	The first <i>katsuo</i> of the season	x	x		x			
F1997.31.1	Izuhara Makoku	Flowers of the four seasons				x			
F1999.5.3	Ikeda Koson	Gosekku							Ind

## DISCUSSION

An elementary point to deal with first is whether Prussian blue was more likely to have been used on one support material rather than another, or for paintings of one format rather than another. The relevant numbers are in table 7; the statistical  $\chi^2$  test was used to test the null hypothesis that there were equal probabilities for Prussian blue being chosen for silk or for paper, and also for each of the formats listed. This was done for both total Prussian blue usage and its employment without indigo also being present. In no case was the null hypothesis rejected: there is no reason based on these results to suspect a bias toward use on one or the other support material or in one or another format. It is true that, in the case of format, the great majority of works were hanging scrolls (these include paintings that were clearly intended for hanging scrolls, though at the time either unmounted or mounted as panels), which limits the extent to which the results can surmount random variations.

TABLE 7. PRUSSIAN BLUE OCCURRENCES BY SUPPORT AND FORMAT

	Total	Support		Format				
		Silk	Paper	Hng	Scr	Hnd	Alb	Fan
All paintings	139	69	70	102	17	5	8	7
Prussian blue, total	46	25	21	36	4	0	5	1
Prussian blue, not indigo	12	7	5	8	1	0	3	0

As noted already in the background section, historical evidence argues for the ready availability of Prussian blue for pigment use after the 1820s. Of the paintings investigated here, although it is clear that a majority are from the nineteenth century, many of them have serious uncertainties associated with the dating. However, thirty-four of them could be dated to later than 1830 with reasonable confidence. Of these, eighteen had Prussian blue identified on the painting, and three of them had Prussian blue without indigo. Thirty-one of the same group had indigo identified, and of these sixteen had indigo without Prussian blue. Thus, as far as these paintings are concerned, indigo was used more frequently than Prussian blue, whether the criterion is sole use of the pigment or includes cases where both are used. The latter includes the use of mixtures of the two, which are considered further below. However, it seems clear from these results that indigo continued to be used extensively by painters as a dark blue pigment even when Prussian blue was available to them.

From table 2, we see that there were thirteen paintings (of the whole suite examined) where mixtures of indigo and Prussian blue were identified (table 5 specifies the paintings). It may be that, in some or all of these cases, the painter was making a fine adjustment to the shade of blue desired. The fact that, as described below, cases are found where both indigo and Prussian blue are used separately for different design elements on the same painting may support the hypothesis that such color discrimination could occur. An alternative hypothesis is that, in some or all cases, Prussian blue was either adulterated by a pigment supplier with indigo (which, as a domestic product, was presumably cheaper) or was being “eked out” by the painter.

It is also clear from the background section that examples of Prussian blue use from the eighteenth or early nineteenth century would be of some interest, though obviously one does not expect many. It was possible to attribute seventeen paintings with some confidence to before 1820. Of these, Prussian blue was found on two. The earliest was a landscape by the *bunjinga* artist Ike Taiga (1723–1776), believed to have been painted in the 1760s (plate 8).

Both indigo and Prussian blue are present, sometimes separately, sometimes as

either mixtures or overpainted areas. The Prussian blue is present in the rocks by the river near the bottom of the painting, and in the blue areas of the trees approximately halfway up. However, the painting, though believed to be firmly attributed, is extensively restored in the upper part, with significant areas of paper support having been replaced. Although the Prussian blue is present in unrestored areas, clearly its later addition cannot be ruled out. It is interesting that Screech (2000, 204) refers to a different Taiga work as the earliest known Japanese painting in which the sky is represented in a blue color.

The second painting (plate 9) is a portrait of a Dutch couple by the Nagasaki painter Nanreisai (1771–1836), dated from an inscription to 1817.<sup>2</sup> This also had light applications both of indigo (decorations on the figures' scarves) and of Prussian blue (flowers on the woman's dress). This firmly dated painting is at the early edge of "serious" importation of Prussian blue as a pigment, on the basis of historical evidence. The pigment was of, course, entering Japan through Nagasaki.

There were some individual cases of interest because of the use of indigo and Prussian blue for separate design features of the same painting. An example is the album leaf by the early-nineteenth-century painter Hokuga, seen in plate 10. To the lower right of this painting is a representation of a piece of blue and white porcelain (plate 11); some of the blue details of this feature were shown by the FORS technique to be indigo and others to be Prussian blue. It was possible to separate these details by an imaging method. As described previously (Properties and identification methods), indigo has a relatively high reflectance in the near infrared, and features in this pigment are suppressed in an infrared image. Such an image of the same area is shown in plate 12, which shows (in black and white) the Prussian blue features only. An exactly corresponding image of the same area taken with visible light will, of course, register both pigments, and subtraction of the plate 12 image from it removes the Prussian blue features to leave those in indigo, as seen in plate 13. We have to assume that the rather small differences in blue tint between the indigo and the Prussian blue areas were what was desired by the painter in this case.

Plate 14 shows a painting by Hokusai entitled *The Lute and White Snake of Benten*. The decorated lute bag features two shades of blue, as seen in plate 15, showing a darker blue apparently overpainting a medium and rather duller blue. Reflectance spectroscopy showed the darker blue to contain Prussian blue and the less dark to be indigo. Once again the latter could be suppressed in an infrared image, shown in plate 16.

Table 2 summarizes identifications of indigo or Prussian blue (or, in one case, both) with a yellow pigment to give a green color, and of indigo with a red pigment to give purple. Table 6 lists the paintings where these situations were found. The first

2. Collection of Ambassador and Mrs. W. Leonhart, on loan to the Sackler Gallery, loan number LTS1987.1.72.

point is that mixed colors seem to be relatively common, especially where indigo is concerned, perhaps more than had hitherto been suspected. Out of the 139 paintings examined, no fewer than fifty-two had a mixed green of some kind. Only four of these used Prussian blue (including two where indigo and Prussian blue were both found), showing that indigo was strongly favored for this purpose. When it comes to producing a purple color from a blue/red mixture, indigo is also strongly favored, since all thirteen cases found used this pigment. Reasons for the disparity in choice of blue can only be surmised; possibly it was made on economic grounds, with the cheaper blue usually being chosen. It is of interest that at one time a mixture of Prussian blue and gamboge was marketed in the West for watercolor use under the name "Hooker's green" (Gettens and Stout 1966, 119).

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APPENDIX. COMPLETE RESULTS

FORMAT: hng = hanging scroll; hnd = handscroll; scr = screen; alb = album or album leaf; fan = fan painting. Early/Late: early = before ca. 1820; late = after ca. 1830.

Ind = indigo; PB = Prussian blue; Mix = mixture of both; I-gn = indigo green; PB-gn = Prussian blue green; IPB-gn = both in green; B+R = blue+red.

IDENTIFICATIONS: X = identification firm; (X) = identification probable. Accession numbers beginning "F" designate paintings in the collection of the Freer Gallery of Art.

Accession #	Artist	Artist Dates	Titles	Attributions	Format	Support	Early/Late	Ind	PB	Mix	I-gn	PB-gn	IPB-gn	B+R
F1894.29	Kishi Ganku	1749–1838	A female immortal riding a deer	early 19th c.	hng	silk					X			
F1894.30	Kishi Ganku	1749–1838	Bamboo stems with branches and foliage	19th c.	hng	silk		X			X			
F1898.6	Sosen Mori	1747–1821	A peacock	late 18th–early 19th c.	hng	silk	early	X						
F1898.8	Gakutei Harunobu	1786?–1868	Two geisha reading from a book	19th c.	hng	silk			X	(X)	X			
F1898.74	Sōri III	late 18th–early 19th c.	Women at their toilet		hng	silk		X			X			Ind
F1898.96	Shiba Kōkan	1747–1818	A young woman with a cage of fireflies		hng	silk	early	X						
F1898.97	Katsushika Hokusai	1760–1849	River landscape		hng	paper		X						
F1898.101	Miyagawa Choshun	1682–1752	A yujo and her understudy	18th c.	hng	paper	early	X						
F1898.103	Sōri III	late 18th–early 19th c.	A lady and a faggot-gatherer under a cherry tree		hng	silk		X						
F1898.105	Sōri III	late 18th–early 19th c.	A girl playing battledore and shuttlecock		hng	silk		X						
F1898.107	Katsushika Hokusai	1760–1849	A girl holding a pipe		hng	paper			X					
F1898.110	Katsushika Hokusai	1760–1849	Boy and Mt. Fuji	ca. 1839	hng	silk	Late	X	X	X	X			
F1898.111	Katsushika Hokusai	1760–1849	Flowering squash-vine and a bee		hng	silk		X						
F1898.114	Hishikawa Moroyasu	fl. 18th c.	A yujo doing her hair	18th c.?	hng	paper	early	X						
F1898.121	Utagawa Toyokuni	1769–1825	Seashore: Three girls under a flowering cherry tree		hng	silk		X						Ind
F1898.123	Utagawa Hiroshige II	1826–1869	Landscape of the season: Spring		hng	silk	late		X					
F1898.124	Utagawa Hiroshige II	1826–1869	Landscape of the season: Winter		hng	silk	late	X	(X)					
F1898.126	Utagawa Hiroshige II	1826–1869	Landscape of the season: Summer		hng	silk	late		X		X			
F1898.135a	Katsushika Hokusai	1760–1849	A fat old man sitting beside an old bell		fan	paper		X	X					
F1898.135b	Katsushika Hokusai	1760–1849	Blossoming plum branches		fan	paper		X						
F1898.135c	Katsushika Hokusai	1760–1849	A man with a fan, butterflies, and a bowl of water		fan	paper		X						
F1898.135h	Katsushika Hokusai	1760–1849	A tree and four red Torii		fan	paper		X			X			
F1898.135i	Katsushika Hokusai	1760–1849	A young crow and maple leaves		fan	paper		X						

## APPENDIX (CONTINUED)

Accession #	Artist	Artist Dates	Titles	Attributions	Formal	Support	Early/Late	Ind	PB	Mix	I-gn	PB-gn	IPB-gn	B+R
F1898.421	Shumman	1757-1820	Two oiran	19th c.	hng	silk					x			
F1898.423	Katsukawa Shunko	1734-1827	An actor in character	18th c.	hng	silk	early	x						
F1898.429	Miyagawa Choshun	1682-1752	A yūjo sitting on a bench	18th c.	hng	silk	early	x						
F1898.508	Shibata Zeshin	1807-1891	Ashimaga and Tenaga worshipping the rising sun	19th c.	hng	paper	late	x						
F1899.16	Kitagawa Utamaro	1753-1806	A courtesan playing a samisen	19th c.	hng	silk	early	x			x			Ind
F1899.47	Utagawa Hiroshige II	1826-1869	River landscape	19th c.	hng	silk	late	x						
F1899.49	Nishikawa Sukenobu	1671-1731	A girl sitting on her bed	17th-18th c.	hng	silk	early	x						
F1900.58	Katsushika Hokusai	1760-1849	An old fisherman standing on the shore		hng	paper		x						
F1901.13	Anonymous		A yūjo and her understudy		hng	paper		x						
F1901.165	Katsushika Hokusai	1760-1849	River landscape: Village and tall trees	dated 1843	hng	silk	late	x	x					
F1901.166	Suzuki Harunobu	1724-1770	Murasaki Shikibu	18th-19th c.	hng	paper		x						
F1902.2	Katsushika Hokusai	1760-1849	Cherry blossom viewing	1820s?	hng	silk		x	x					
F1902.3	Katsushika Hokusai	1760-1849	Miscellaneous subjects		scr	paper		x						
F1902.27	Katsushika Hokusai	1760-1849	The Chinese hermit Sun Teng		hng	paper		x			x			
F1902.40	Katsushika Hokusai	1760-1849	A herd boy seated on a tree trunk		hng	paper		x	x					
F1902.41	Katsushika Hokusai	1760-1849	Standing figure of a girl		hng	paper		x						
F1902.42	Katsushika Hokusai	1760-1849	Miscellaneous subjects		hnd	paper		x						Ind
F1902.48	Katsushika Hokusai	1760-1849	Country scenes	1806	scr	paper	early	x			x			
F1902.49	Katsushika Hokusai	1760-1849	Country scenes	1806	scr	paper	early	x						
F1902.100	Katsushika Hokusai	1760-1849	A courtesan under a cherry tree		hng	silk		x						
F1902.178	Katsushika Hokusai	1760-1849	New Year's day: Two strolling mountebanks		hng	paper		x			x			
F1902.221	Katsushika Hokusai	1760-1849	Chung Kuei (Shoki) killing a demon		hng	silk	late	x	x					
F1902.222	Katsushika Hokusai	1760-1849	A boy fishing from the limb of a tree	ca.1840	hng	silk	late	x						
F1902.254	Katsushika Hokusai	1760-1849	Crustaceans of various kinds		hng	silk		x	x					
F1902.258	Katsushika Hokusai	1760-1849	Hawk and fish		hng	paper		x	x					
F1903.2	Katsushika Hokusai	1760-1849	Glam-gatherers on the shore		hng	paper		x	x					
F1903.52	Katsushika Hokusai	1760-1849	New Year rituals		hng	silk		x			x			
F1903.53	Katsushika Hokusai	1760-1849	New Year rituals		hng	silk		x						
F1903.97	Utagawa Hiroshige II	1826-1869	Landscape: Flowering cherry trees along the banks of a stream		hng	silk	late	x						
F1903.106	Utagawa Hiroshige II	1826-1869	River landscape and temple in the rain		hng	silk	late	x	x					
F1903.109	Katsushika Hokusai	1760-1849	River landscape, ferry-boat, and Mt. Fuji		hng	silk		x			x			
F1903.125	Katsushika Hokusai	1760-1849	Landscape: Parties of men and women looking at cherry blossoms		hng	paper		x						Ind
F1903.126	Katsushika Hokusai	1760-1849	A courtesan standing		hng	paper		x						



F1903.127	Katsushika Hokusai	1760-1849	A dancer, Kiyohime, a cherry tree, and the bells of <i>adôjo-ji</i>	hng	paper	x			
F1903.128	Katsushika Hokusai	1760-1849	Interior: A courtesan writing, another looking on	hng	silk	x			Ind
F1903.129	Katsushika Hokusai	1760-1849	A courtesan	hng	paper	x			
F1903.134	Anonymous	1760-1849	A yûjo with a pipe	hng	paper	early	x		
F1903.135	Anonymous	1760-1849	A yûjo reclining	hng	silk	x			
F1903.143	Katsushika Hokusai	1760-1849	Viewing cherry blossoms	scr	paper	x			
F1903.144	Katsushika Hokusai	1760-1849	Viewing cherry blossoms	scr	paper	x			
F1903.145	Andô Hiroshige	1797-1858	Famous sites of Edo	scr	silk	late	x	x	x
F1903.146	Andô Hiroshige	1797-1858	Famous sites of Edo	scr	silk	late	x	x	
F1903.216	Katsushika Hokusai	1760-1849	A seated man looking at potted peonies	hng	paper	x		x	x
F1903.274	Katsushika Hokusai (Sori II) or Sori III	late 18th- early 19th c.	A courtesan standing near a clothes rack	hng	silk	x			
F1903.291	Andô Hiroshige	1797-1858	Landscape	hng	silk	x			
F1904.73	Katsushika Hokusai	1760-1849	Walking figure of a courtesan	alb	paper				x
F1904.131	Yosai Kikuchi	1788-1878	Three gardeners of the emperor Takakura	hng	silk				x
F1904.132	Katsushika Hokusai	1760-1849	Rats and rice bales	hng	silk	late	x		
F1904.134	Katsushika Hokusai	1760-1849	The lute and white snake of Benten	hng	silk	late	x	x	
F1904.142	Katsushika Hokusai	1760-1849	Suikoden	hnd	silk	late	x		
F1904.173	Katsushika Hokusai	1760-1849	Standing figure of a tall girl	hng	paper	x			x
F1904.174	Katsushika Hokusai	1760-1849	Landscape: Bridge, houses, and distant hills	hng	paper	x			
F1904.175	Katsushika Hokusai	1760-1849	Mt. Fuji and Enoshima	scr	paper	x	(x)	x	
F1904.176	Katsushika Hokusai	1760-1849	Mt. Fuji and Enoshima	scr	paper	x			
F1904.177	Katsushika Hokusai	1760-1849	A shinto priest, three women, and a child under a pine tree	scr	paper	x			
F1904.178	Katsushika Hokusai	1760-1849	Four fan papers	scr	paper	late	x	x	
F1904.179	Katsushika Hokusai	1760-1849	Flowers, birds, and animals of the twelve seasons	scr	paper	late	x		
F1904.180	Katsushika Hokusai	1760-1849	Flowers, birds, and animals of the twelve seasons	scr	paper	x	x		
F1904.181	Katsushika Hokusai	1760-1849	A fisherman seated at the shore	scr	paper		x		
F1904.182	Katsushika Hokusai	1760-1849	A faggot-gatherer	hng	silk	late	x	x	
F1904.184	Katsushika Hokusai	1760-1849	Interior: Two ladies seated on a veranda	hng	silk	late	x	(x)	x
F1904.185	Katsushika Hokusai	1760-1849	A girl holding a letter behind her back	hng	silk		x		x
F1904.186	Katsushika Hokusai	1760-1849	A traveling mountebank under a tree	hng	silk	late	x		
F1904.188	Katsushika Hokusai	1760-1849	The six poets	hng	paper	late	x		
F1904.189	Katsushika Hokusai	1760-1849	Ascending dragon	hng	paper	x			
F1904.190	Katsushika Hokusai	1760-1849	Descending dragon	hng	silk	late	x	x	
F1904.191	Katsushika Hokusai	1760-1849	aged 86 = 1846	hng	silk	late	x		

## APPENDIX (CONTINUED)

Accession #	Artist	Artist Dates	Titles	Attributions		Formal	Support	Early/ Late	Ind	PB	Mix	I-gn	PB-gn	PB-gn	B+R
				Titles	Attributions										
F1904.204	Katsushika Hokusai	1760-1849	The six Tama rivers			scr	paper		x	x					
F1904.205	Katsushika Hokusai	1760-1849	The six Tama rivers			scr	paper		x	x					
F1904.206	Katsushika Hokusai	1760-1849	Landscape: Boatman poling his raft			alb	paper		x						
F1904.218	Katsushika Hokusai	1760-1849	A man carrying backpack and lantern			alb	paper		x						Ind
F1904.357	Andō Hiroshige	1797-1858	Miscellaneous sketches			alb	paper		x						
F1904.383	After Tsunenobu		Birds and flowers		19th c.	hng	paper		x						
F1904.400	Shibata Zeshin	1807-1891	A faggot-gatherer looking at a waterfall		19th c.	hng	paper	late	x						
F1904.428	Katsushika Hokusai	1760-1849	Woman facing the right beckoning			alb	paper								
F1905.228	Katsushika Hokusai	1760-1849	Landscape: Mountain, stream, and boat			hng	silk		x						
F1905.270	Katsushika Hokusai	1760-1849	An amusement resort at the seashore			hng	silk		x						Ind
F1905.276	Katsushika Hokusai	1760-1849	Breaking waves		aged 88 = 1848	hng	silk	late	x	x					
F1905.282	Katsushika Hokusai	1760-1849	A priest (Kobō Daishi) practicing the tantra...			hng	paper		x	x					
F1905.294	Hosoda Eishi	1756-1829	Lady viewing cherries at Goten Yama		late 19th c.?	hng	silk		x						
F1906.11	Hosoda Eishi	1756-1829	Yang Kuei-Fei		late 19th c.?	hng	silk		x						
F1906.51	Katsushika Hokusai	1760-1849	Filial piety		dated 1844	hng	silk	late	x						x
F1906.52	Katsushika Hokusai	1760-1849	Two drunken men returning from a cherry blossom party			hng	paper		x						
F1906.233	Katsushika Hokusai	1760-1849	Landscape: Two of the four seasons, spring and summer			scr	paper		x						
F1906.234	Katsushika Hokusai	1760-1849	Landscape: Two of the four seasons			scr	paper		x						
F1907.368	Katsushika Hokusai	1760-1849	One of the six poets			hng	paper		x						
F1907.369	Katsushika Hokusai	1760-1849	One of the six poets			hng	paper		x						Ind
F1954.119	Katsushika Hokusai	1760-1849	Portrait of a courtesan walking			hng	silk		x						
F1955.2	Tani Bunchō	1763-1840	A peacock and peonies		1840	hng	paper	late	x						
F1957.7	Hosoda Eishi	1756-1829	Beauties of the season: Spring		late 18th-early 19th c.	hng	silk		x						
F1959.12	Miyagawa Chōshun	1682-1752	Festivals of the twelve months			hnd	paper		x						
F1960.31	Sakai Hoitsu	1761-1828	The master poets		after 1797	hng	silk		x						Ind
F1963.3	Mori Sosen	1747-1821	Monkeys and waterfall			hng	paper		x						
F1964.11	Ike Taiga	1723-1776	Red Cliff		1760s	hng	paper	early	x	x					
F1964.12	Ike Taiga	1723-1776	Tower		1760s	hng	paper	early	x						
F1967.18	Yōsa Buson	1716-1783	Mynah birds on a plum tree		1776	hng	silk	early	x						
F1967.19	Yōsa Buson	1716-1783	Mynah birds on a plum tree		1776	hng	silk	early	x						
F1969.29	Kawanabe Gyōsai	1831-1889	Fan with scenes of the tale of Shuten Doji		19th c.	fan	paper	late							x
F1969.30	Kawanabe Gyōsai	1831-1889	Fan with scenes of the tale of Shuten Doji		19th c.	fan	paper	late							x



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