



# Scientific Studies of Pigments in Chinese Paintings

Editors Blythe McCarthy and Jennifer Giaccai



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John Winter in the laboratory.



Photo Credit: Owen MacDonald



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# Foreword

Long before the Freer Gallery of Art opened in 1923, museum founder Charles Lang Freer regularly brought specialists from Japan to care for the Asian artworks on view in his Detroit mansion. Today, as a leading center in the United States for the care and scientific study of the arts of Asia, the Department of Conservation and Scientific Research continues the work begun in the East Asian Painting Conservation Studio, established when the museum opened, and the Technical Laboratory, founded in 1951. Our specialist colleagues use a combination of traditional and contemporary methods for conservation and a range of scientific techniques for their research. Our scientists and conservators strive to improve methods of preservation, advance education in conservation practices, and conduct research into artists' materials. This volume shares years of research on pigments used in Chinese paintings.

The authors completed their work during 2020–21, the time of COVID, when conditions required new modes of working and communicating, both internally and externally. Of the many ways that we have adapted our practices is how we publish. *Scientific Studies of Pigments in Chinese Paintings* will be the first publication from our Department of Conservation and Scientific Research to be made available both in print and online (as a pdf). This is the path we plan to follow with succeeding volumes from the department to ensure that research has the widest possible dissemination.

Research into the history, provenance, and significance of the more than two hundred Chinese paintings examined in this study was carried out by our curatorial staff, who attributed the paintings to artists and schools, assigned dates, and told their stories through publications and exhibitions. Focusing the lens of twenty-first-century science on the materials of Chinese paintings, colleagues in Conservation and Scientific Research have been able to build on that curatorial work, identifying the colorants the artists used in specific paintings, research that would not have been possible one hundred years ago when Charles Lang Freer formed his collection. As science pushes forward the frontier of the possible, staff at the National Museum of Asian Art will continue to examine and evaluate the paintings in the collections as part of an interdisciplinary community of scholars. Such collaborative interdisciplinary research is critical to form a comprehensive understanding of the complex processes of creation, use, and creative reuse of works of Asian art. I hope that this glimpse into the materials and working methods of Chinese painters will provide a resource for scholars as they continue to explore the richness of the cultures of Asia.

Chase F. Robinson  
Dame Jillian Sackler Director  
Arthur M. Sackler Gallery and the Freer Gallery of Art  
Smithsonian Institution



# Preface

The Freer Gallery of Art has carried out efforts in the scientific analysis of Asian art since the 1950s, when Rutherford J. Gettens arrived to establish the Technical Laboratory. His studies on Chinese bronzes, still considered the standard authority, integrated science and art, utilizing the Freer's collections to promote a greater understanding of materials and production methods. Gettens studied the colors and formation of bronze patinas, natural and man-made, of which malachite, the common Chinese pigment, was often a component. This investigation was only one of the projects Gettens pursued at the Freer Gallery. Together with Elisabeth West FitzHugh, he carried out investigations of pigments in paintings as well as other types of objects, and his findings on Chinese paintings are referenced in this volume. His projects had relevance beyond the arts of Asia, for it was during his tenure at the Freer that, together with George Stout, he reissued *Painting Materials: A Short Encyclopaedia*, and he began to pursue the idea of in-depth essays on pigments. Following discussion with J. Carter Brown, the director of the National Gallery of Art, this idea was realized in the launch of the series *Artists' Pigments: A Handbook of Their History and Characteristics*. In his preface to volume 1, Brown recounted his discussion with Gettens about this "project of international importance."

John Winter, who joined the Technical Laboratory in 1971, continued Gettens's research tradition, pursuing investigations into the materials and structure of East Asian paintings. With the addition of the Arthur M. Sackler Gallery in 1987, the Technical Laboratory became the Department of Conservation and

Scientific Research. Winter's research on paintings in the museums' collections included investigations into the use of painting materials, especially differences over time and between regions. These projects produced a body of knowledge that can aid the attribution of paintings to specific artists or schools. His efforts also included the study of deterioration mechanisms, an understanding of which is important both to conservation efforts and to the interpretation of aged and deteriorated paintings.

A generous grant from the Andrew W. Mellon Foundation, starting in 1997, supported an expanded research effort into focused questions within the framework of scientific research on East Asian paintings. Researchers Christina Bisulca, Christina Cole, Jennifer Giaccai, Jeffrey Joseph, Marco Leona, Joseph Swider, and Yae Ichimiya (née Takahashi) investigated the introduction of Prussian blue in Japanese painting, studied the surface characteristics of Chinese ink, and analyzed the weaves of painting silks. They also researched Chinese colorants, explored organic brown pigments on Japanese paintings, and developed analytical methods using new nondestructive and microsampling techniques. Their work produced several publications (listed at the end of the introduction), but much of the research on Chinese paintings remained unpublished. More recently, a Samuel H. Kress Conservation Publication Fellowship, awarded by the Foundation for Advancement in Conservation allowed several members of the research team to reunite and complete the Chinese colorant research, resulting in this publication. During this time, Yue Shu joined the team for the production of an

appendix on pigment terminology as found in Chinese manuscripts. The volume benefited from the expertise of several scholars who reviewed the manuscript and those who helped with project details. We are indebted to Stephen Allee, Barbara Berrie, Xiangmei Gu, Grace Jan, Paul Jett, Marco Leona, Donna Strahan, and Jan Stuart for their comments and suggestions. Alice Tracy, Christine Lee, and Gail Yano provided help with proposals, Chinese language issues, and tables and figures, respectively. Chika Mouri and Diego Tamburini carried out limited dye analysis. Our Smithsonian colleagues at the Hirshhorn Museum and Sculpture Garden and Jeffrey Post and Timothy Rose of the Mineral Sciences Department of the National Museum of Natural History provided access to needed scientific equipment for confirmation of some of the analyses. The careful editing of Ann Hofstra Grogg ensured accuracy and readability.

This book is the first in-depth study of colorants in Chinese paintings on silk or paper and the first time the results have been compiled in a single volume. Initially developed as a companion to *Studies Using Scientific Methods: Pigments in Later Japanese Paintings*, this publication has been expanded to include the earlier Song and Yuan dynasty paintings that used a traditional palette. In addition, the onset of digital publishing made it possible to include more images, resulting in a well-illustrated volume.

Heretofore studies of Chinese pigments have concentrated on cave and wall paintings, such as those at Dunhuang, while the few analyses of colorants used in paintings on silk or paper have been scattered and incomplete. The information compiled in this volume now provides scholars with an overview of pigments used in Chinese paintings from the traditional palette through the importation of new pigments in the modern era. The history of European painting has greatly benefited from studies of the pigments and colorants used over time, and the chronology of pigment use has been especially helpful in determining a painting's authenticity or degree of restoration. We anticipate that our volume will begin to do the same for the study of Chinese paintings.

With pigment identifications of more than two hundred paintings in the Freer Gallery of Art and Arthur M. Sackler Gallery collections, this volume provides scholars with a large database of primary source material that can be used in further technical studies and comparative investigations. Adding to previous studies, it pushes forward efforts to develop a chronology for pigment use in East Asian painting. The availability of this information will be increasingly important as Asian art continues to be collected and exhibited worldwide.

Blythe McCarthy

# Introduction: Pigments in Chinese Paintings

Blythe McCarthy

## Chinese Paintings in the Collections

The Freer Gallery of Art's collections of Chinese paintings were established with an initial gift from Charles Lang Freer of works he had purchased between 1893 and 1919 from dealers, many in Japan and China or with sources there. His purchases include paintings from the Song and Yuan dynasties (tenth–fourteenth centuries) that are considered among the best outside of China. Freer wanted to build a collection of early works, as evidenced by his directive to Wang Jiantang (K. T. Wang) in a handwritten postscript to his letter of February 28, 1919: “Do not send me any Ming or later pictures. I buy only Sung [Song] and earlier paintings” (quoted in Larsen 2001, 8). However, some of the works he acquired, thought at that time to be from these earlier periods, were actually from the later Ming (1368–1644) and Qing (1644–1912) dynasties. Thus the works collected by Freer span from the Song to the Qing dynasty in date.

The paintings in the collection, some by well-known artists or schools and others anonymous, cover a range of subjects, styles, and genres. The works are in a variety of formats—handscrolls, hanging scrolls, fans, and those mounted on panels or in albums. Albums may contain paintings from multiple

artists that were assembled by a collector or may be a collection of the works of a single artist. Since Freer's death in 1919, paintings have been added to the museum collection from multiple sources, by purchase or gift. Notable are two groups of paintings, one a transfer of eighty-eight paintings from the United States Customs Service, Department of the Treasury, in 1979 per the settlement agreement arising from their seizure in 1960 from the dealers Chen Rentao (also known as J. D. Chen), Hong Kong, and Frank Caro of C. T. Loo & Co., New York. The second, a collection of the paintings and calligraphy of the Qing dynasty artist Bada Shanren (1626–1705), came to the Freer Gallery of Art in 1998 through a bequest and purchase from the estate of Fred Fangyu Wang (Wang Fangyu, 1913–1997) and his wife, Sum Wai (1918–1996). The Freer Gallery of Art's holdings are complemented by those of the Arthur M. Sackler Gallery, which include paintings dated from the Ming dynasty through the twenty-first century, encompassing a number of styles and genres, but notably portrait paintings.

A highlight is the collection of Chinese portraits and figure paintings that came to the Arthur M. Sackler Gallery in the early 1990s from Richard G. Pritzlaff (1902–1997), who acquired them in the

late 1930s to 1940s from Wu Laixi, a Chinese collector and dealer. The portraits collected by Pritzlaff include ancestor portraits and commemorative portraits of some members of the imperial family, as well as of courtiers and the social elite of the Qing dynasty. There are also one Ming dynasty portrait and a few post-Qing portraits.

More than two hundred paintings from the collections of the Freer Gallery of Art and the Arthur M. Sackler Gallery were selected for this project examining the pigments in Chinese portable paintings from the Song dynasty (960–1279) to the early twentieth century. They represent multiple painting types, including hanging scrolls and handscrolls as well as entire albums or selected paintings from them. They include works by artists who studied and practiced in the cultural centers of the Yangtze delta with at least one from Beijing, places where new artists' materials were likely to have been available early. While the paintings selected represent works from most major artists and schools, there are areas that are not represented. Therefore, the results presented in this volume are not encyclopedic in nature and may be augmented by future research on other collections.

## Terminology

Several terms are used at the Smithsonian's National Museum of Asian Art (the Freer Gallery of Art and Arthur M. Sackler Gallery) to link artists to the paintings, based on the history of attribution and the current attribution: use of the artist's name by itself or the term "by" indicates a firm authorship; "attributed to" indicates an attribution by Freer and Sackler curators; "formerly attributed to" signifies that the painting was attributed to an artist, likely by dealers, but is not currently believed to be associated with the artist; and "traditionally attributed to" indicates that the subject matter has a long history of being associated with the artist or there are many known versions of the painting. These designations are used in this volume.

Historic place names were used in discussions that tracked the import of pigments into China and their use across four centuries, with modern place names identified in parentheses. Asian personal names in the text and in citations use the order of the names as found in the sources. For clarity, in References all surnames are shown in full capital letters.

Ancestor portraits were created for private family veneration. In many cases, determining the

original purpose of a painting can be difficult, so in this volume we refer to them as "portraits," reserving the term "ancestor portrait" for when it seems abundantly clear that a painting was originally made for family ritual use.

The names used for colors observed in the paintings were also standardized throughout the volume, and the use of "violet" or "purple" received particular attention. After several discussions, where there was little agreement on the color represented by the two words, a decision was made to use the term "purple" for all examples in which both blue and red colorants were present. We then extended the usage and also designated colors that visually appear violet or purple as "purple." Another matter of terminology arose around the red organic colorants—lac and cochineal—which appear to be used as dyes. For this reason, we have used the term "colorant" as opposed to "pigment" for the organic reds. See the introduction to appendix 5 for further discussion of pigment terminology.

## Considerations in Examining the Introduction of New Pigments

Through analysis of pigments, we have followed the use of painting materials over time from the Northern Song period (960–1127) through the Qing dynasty. The earlier paintings in the study include those from scholar-painters and academic artists. The later Ming and Qing dynasty paintings are from the area of Beijing and from places outside the capital. While the research presented in this volume documents pigments used in the Freer Gallery of Art and Arthur M. Sackler Gallery paintings, it also allows for a broader understanding of the materials and methods used in Chinese paintings. Scientific analysis has provided the physical proof of imported pigments, and analysis of when and how they were used can enhance future studies on the interactions between China and the rest of the world.

Beginning in the seventeenth century, increased trade with Europe and the Americas introduced non-indigenous materials to China, such as cochineal, a red dye from the Americas. European synthetic pigments followed, with the first being Prussian blue, a pigment invented in Germany in 1704. By the early nineteenth century, trade was well established, and Chinese artisans in Canton used European synthetic pigments and produced works for export to European and American markets (fig. I.1).



**Figure I.1.** *Shop of Tingqua, The Painter*, studio of Tingqua (1840–1870), ca. 1830. Gouache on paper; 18 × 26 cm (7<sup>1</sup>/<sub>16</sub> × 10<sup>1</sup>/<sub>4</sub> in.). Peabody Essex Museum, Gift of Leo A. and Doris C. Hodroff, 1998, AE85592. This image depicts the Canton studio of Guan Lianchang, also known as Tingqua, a painter of Chinese paintings for export at a time of active trade between China and the West.

Determination of the earliest date for the use of cochineal and Prussian blue in these paintings is complicated by uncertainties in painting dates and attribution. A case in point is the fan *Small Birds and Morning Glories* (fig. I.2), attributed to the artist Jiang Tingxi (1669–1732), which contains Prussian blue and cochineal. Jiang Tingxi's active dates place the fan in the early eighteenth century, a time frame that seems too early for Prussian blue. In this research, *Small Birds and Morning Glories* was the only painting attributed to the eighteenth century in which Prussian blue was found, as well as the earliest instance of cochineal; a few paintings containing cochineal date to the late eighteenth century. It is unfortunately not possible to use the poem on the reverse to confirm the painting's date. As the calligraphy is attributed to the Qianlong emperor whose reign started in late 1735 and postdates the active dates of Jiang Tingxi, the painting and the calligraphy must be examined separately.



**Figure I.2.** *Small Birds and Morning Glories*, attributed to Jiang Tingxi (1669–1732), early 18th century. Fan; paper; 32.2 × 48.5 cm (12<sup>1</sup>/<sub>16</sub> × 19<sup>1</sup>/<sub>8</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Transfer from the United States Customs Service, Department of the Treasury, F1980.152.



*Small Birds and Morning Glories* is in excellent condition; no restoration is visible, so the pigments are assumed to be original. Prussian blue is thickly painted throughout the painting. As an explanation for the early use of this pigment, Jiang Tingxi worked near the imperial court and may have had access to imported European pigments. Moreover, this early date is not without precedent in Asia. Marco Leona and John Winter (2003) identified Prussian blue in an early eighteenth-century Japanese painting from Nagasaki as well as in two paintings in the Freer Gallery of Art collection, although these were thought to be retouching (see chap. 3). Another Japanese painting dated 1765–66, the final in a series called *Colorful Realm* by Itō Jakuchū, contains Prussian blue in a single fish, a soapfish (Hayakawa 2012), a probable testament to the rarity of the pigment at this early date. In this study, every effort was made to avoid areas of retouching, including by analyzing multiple locations in the paintings. Given the complexity of trying to confirm the date of *Small Birds and Morning Glories* as well as other paintings, interdisciplinary discussions regarding the implications of the scientific results on painting history, authorship, and date are ongoing.

## Preview of Contents

Chapter 1 discusses the results from the analysis of Song and Yuan dynasty paintings (960–1368) in the Freer Gallery of Art. These paintings and their analysis provide information on the traditional palette utilized by several artists and for varied painting subjects and formats.

The next three chapters address the colorants used in Ming through post-Qing dynasty paintings. They document the introduction of nontraditional pigments and present information on the ways in which they were used. Chapter 2 discusses red colorants, including the use of organic reds in Chinese painting, the advent of the use of cochineal, and the methods in which lac dye and cochineal—the primary two organic reds found in this study—were used. In chapter 3, the blues and their uses in Chinese paintings are examined, with a focus on azurite and indigo, followed by a discussion of Prussian blue in China and in Japan.

Chapter 4 synthesizes information from chapters 2 and 3 that specifically relates to portraits, a painting genre on which little analytical work has been done. This chapter surveys colorants beyond the reds

and blues addressed in previous chapters, examining the palette more broadly in terms of its use in the corpus of painted works being produced during the Qing dynasty in China, including those produced by workshops or professional painters. Consideration is given to emerald green and synthetic ultramarine as among the synthetic pigments introduced to China during the nineteenth century. This chapter expands on a previous publication that reported results from five paintings (Giaccari and Winter 2005). As many of the Sackler Gallery examples represent members of the imperial family, their date can be narrowed by the identity of the sitter. Moreover, they are primarily from workshops that had access to, and used, many of the new imported colorants, as evidenced by the analysis results. Therefore, this study provides valuable information on the introduction of imported materials.

Chapter 5 summarizes the pigments identified in this study and their use. The trade environment surrounding the import of colorants to China during the Qing dynasty is also discussed, as well as the availability of these new pigments in greater Asia at the time.

Pigments were identified using the same instruments and methods throughout the volume, and these are described in appendix 1. Appendix 2 gives details on distinguishing lac dye from cochineal on Chinese paintings using fiber optic reflectance spectroscopy (FORS). It discusses the variation in absorption peaks seen in the pigments on the paintings and tentatively links them to colorant preparation. In appendix 3 the interpretation of FORS spectra, especially in the case of blue colorant mixtures, is discussed.

A fourth appendix compiles the colorants identified in this volume, their chemistry, and their Chinese and English names. While the Chinese romanizations in the text use pinyin, Wade-Giles is also included in this appendix, as it was used in many of the references. Taiwanese and some traditional artists' names also use the Wade-Giles system of romanization.

The results of all the analyses are presented in comprehensive tables at the end of the book, in appendix 5, that list painting, date range, pigment identification, and analytical method used for identification. Questionable results were not included in the appendix, only positive identifications. The studies presented in chapters 2 and 3 were performed independent of each other, utilizing some but not all of the same paintings. For this reason, the lack of an identified blue or red in appendix 5 can indicate that the color was not used on the painting, that it was not analyzed, or that nothing was positively identified. Similarly, due to the focus on reds and blues, not all

colors were analyzed on every painting for the Ming through Qing dynasty paintings. The information for the Song and Yuan paintings is more inclusive.

The information in appendix 5 was acquired primarily in the studies discussed in this volume. It also benefited, however, from the research carried out by previous staff during the course of the research program in the materials and structures of East Asian paintings led by John Winter and funded by the Andrew W. Mellon Foundation. The methods developed in the earlier research, whose publications are given below, were applied here to Chinese paintings. The many years of research combined in this publication are presented to spur new scholarship in the study of Chinese paintings.

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## Additional Publications and Presentations from the Research Project



# 1

## Pigments in Song and Yuan Paintings from the Freer Gallery of Art

Jennifer Giaccai, Jeffrey Joseph, and John Winter

### Introduction

Chinese painting has a long history. Portable paintings have been found from the Warring States period (475–221 B.C.E) onward but seem to have become a more common artistic format with the rise of Buddhism in the early part of the first millennium. Painting manuals from the Tang dynasty (618–907) demonstrate the significant role painting had begun to play in Chinese culture as it developed from a craft producing Buddhist paintings into an artistic pursuit (Acker 1954). By the time of the Song dynasties, painting had significant support from the emperors, who themselves often actively painted. Northern Song (960–1127) emperors founded an academy for painting, and when the Northern Song capital was demolished, the painting academy moved along with the remaining rulers and continued as an active part of the culture during the Southern Song dynasty (1127–1279). During the Song dynasties landscape painting became very popular, alongside the rise of scholar-painters. The scholar-painters generally preferred ink-based paintings over the more

colorful, pigment-filled paintings produced historically and at the painting academy. However, both academic and scholar-painters used color to achieve the desired artistic effect. Divisions between scholar and academic painters continued during the course of the Yuan dynasty (1279–1368), although interactions between the two groups were frequent. The Freer Gallery of Art's Song and Yuan dynasties online catalog (Allee et al. 2010) and past research into the use of pigments in Chinese paintings, including a Yuan dynasty painting (Giaccai and Winter 2005), prompted this survey of the painting pigments used in the Song and Yuan dynasties. Although both academic and scholar paintings are represented in this study, no attempt was made to differentiate in pigment use between the two styles of paintings.

### Literature Sources

While a number of historic Chinese texts discuss paintings and painting methods, few describe the pigments used or explain how they might be used.

Special attention is paid in this chapter to those pigments mentioned by Chinese painters in Song and Yuan painting treatises as well as in earlier painting treatises available to Song and Yuan painters. Detailed descriptions of many of the pigments mentioned in this chapter can be found in the National Gallery of Art's series titled *Artists' Pigments* (Feller 1986; FitzHugh 1997a; Roy 1993; Berrie 2007) and, with more specific information about their use in Chinese painting, in John Winter's *East Asian Paintings: Materials, Structures and Deterioration Mechanisms* (Winter 2008). Chinese terms, primary sources, and identifications can be found in appendix 4.

That pigments are rarely mentioned in painting manuals and commentaries might be a consequence of the scholar-painters' focus on the skill of the painter and the assumption that a skillful painter need not depend on the use of colors. Writing in 847, the Tang dynasty painter Zhang Yanyuan (ca. 815–after 875) exemplifies many of the early thoughts of Chinese painters on color:

Grasses and trees spread forth their glory without depending upon cinnabar and azurite; clouds and snow whirl and float aloft, and are white with no need for ceruse. Mountains are green without needing malachite, and the phoenix is iridescent without the aid of the five colors. For this reason one may be said to have fulfilled one's aim when the five colors are all present in the management of ink. If one's mind dwells on the five colors, then the images of things will go wrong. In painting things one should especially avoid a meticulous completeness in formal appearance and coloring, and extreme carefulness and detail that display skill and finish (Bush and Shih 2012, 62–63).

Here Zhang Yanyuan is referring to the five primary colors—red, black, blue-green, white, and yellow—and to their symbolic associations with the five elements of fire, water, wood, metal, and earth, respectively. Although focusing on the skill of the artist as the most important quality in painting, Zhang Yanyuan also discusses the pigments used in paintings and their origins. Whereas above he is referring to the colors of the five elements, he also lists the specific pigments used in painting. Zhang's is the first list of pigments used in early Chinese painting, although the common names often lead to further questions: “pewter extract” (lead white), cinnabar/vermilion, “ant-ore” (lac dye), “lead flower” (red lead),

“female yellow” (orpiment), “flat green” (malachite), azurite, and “sky blue” (quoted in Acker 1954, 187–89). The “female yellow” is thought by William Acker to be the arsenic-based yellow pigment orpiment, particularly as it is described in Zhang's text as discoloring lead white when the two are used in combination (Acker 1954, 189). “Sky blue” is described as coming from Yuesui (Xichang, Sichuan) and is thought by Acker to be natural ultramarine rather than another name for azurite, although ultramarine does not come from this region and azurite is found in the area (Acker 1954, 187).

Several sources from the Yuan dynasty mention pigments, either explicitly or in passing. In writing about the painting of various landscape features, Huang Gongwang (1269–1354) describes the use of small amounts of “rattan yellow” and “shell blue” (Bush and Shih 2012, 263). Rattan yellow, or gamboge, was therefore known in the Yuan dynasty, although it has been difficult to identify in paintings in the Freer collection, perhaps because it has faded or was used only to tint other colors. “Shell blue” is also cited in Rao Ziran's (mid-fourteenth century) *Twelve Points to Be Avoided* (ca. 1340), where, together with “composite green,” it is described as a wash applied to complement the textured, or heavily painted, mineral blues and greens used in colored paintings (Bush and Shih 2012, 269). Indigo, both alone and mixed with a yellow colorant, is often used to shade blues and greens in Asian painting, so it is likely that both “shell blue” and “composite green” refer to indigo and indigo mixtures.

The *Bamboo Manual* (ca. 1318) by the Yuan artist Li Kan (1245–1320) describes a method of sorting different malachite green colors as well as the use of indigo, sophora yellow, and gamboge. This Yuan dynasty description is cited extensively in a study by Yu Feian (1988), although Yu is focused primarily on pigments used by Ming dynasty (1368–1644) and Qing dynasty (1644–1912) artists.

A more explicit list of pigments and colors is found in Wang Yi's (1333–ca. 1368) *Technique of Painting in Colors*, as quoted in Tao Zongyi's (ca. 1316–1402) *Retirement to the Countryside* (1366), which focuses on painters and paintings of the Yuan dynasty (Franke 1950). This treatise and Wang Yi's treatise on portraiture describe how to make certain shades of color and list the following pigments: lead white, cinnabar/vermilion, *yan zhi* (this could be one of several red organic pigments, see app. 4), “rattan yellow” (gamboge), “yellow vermilion” (Herbert Franke [1950] thought this was minium,

but it may refer to orpiment, which is otherwise not listed), earth yellow, sophora yellow (槐花 *huai hua*), malachite and azurite in different shades, “shell blue,” and umber or ocher. In addition, several unidentified greens are described in the pigment section of Wang Yi’s treatise, and it is unclear if they are further types of malachite, mixtures of blue and yellow, or references to atacamite, a copper trihydroxychloride pigment described further below. Other references to what is believed to be atacamite use the terms “green salt” or “copper green” (*tong lü*) (Lei 2012). Although *yan zhi* is used now to mean lac dye or cochineal, during the Song and Yuan dynasties *yan zhi* is thought to have been safflower red (see app. 4) and in Dunhuang it was also used to designate what must have been safflower red (Trombert 2004). Similarly, “shell blue”—listed in all the Yuan sources—likely refers to indigo, which is otherwise unmentioned but is described by Li Kan as Fujian snail shell blue (cited in Yu 1988, 63).

### Scientific Studies of Song and Yuan Dynasty Paintings

There have been only a few scientific studies of Song and Yuan pigments in portable paintings; most studies have concentrated on pigments in wall paintings or painted statues from sites outside the capital region. Unless specifically listed below, all black pigments, if investigated, were identified as Chinese ink or soot.

A tenth-century Five Dynasties (907–979) or Northern Song painting on silk from the Guimet Museum of Asian Art, Paris, originally from Dunhuang, was investigated using x-ray fluorescence (XRF). The pigments identified were lead white, vermilion, red lead, atacamite and paratacamite, azurite, iron oxide brown, and gold leaf (Delbourgo 1980). A study on manuscripts and portable paintings from Dunhuang in the Stein Collection at the British Library using XRF and reflectance spectroscopy found cinnabar/vermilion, red lead, an arsenic-based yellow pigment thought to be orpiment, a copper- and chlorine-containing pigment thought to be atacamite, indigo, and iron-based red and brown pigments (Van Schaik et al. 2015).

Three portable paintings from cave 17 of the early eleventh-century Mogao Caves in Dunhuang, now in the collections of the Harvard University Art Museums and Museum of Fine Arts, Boston, underwent a technical examination. Pigments identified

were lead white, talc, vermilion, iron oxide red (used in purples), red lead, orpiment, atacamite, indigo, ultramarine, and lampblack (Mysak et al. 2011).

A study of a Yuan dynasty painting at the Museum of Fine Arts, Boston, *Mongol Hunters*, attributed to Zhao Mengfu (1254–1322), identified an unusual use of pigments. Using XRF, lead white, mercury sulfide, malachite, and azurite were identified. Moreover, XRF and further analysis with scanning electron microscopy–energy dispersive x-ray spectroscopy (SEM-EDS) also identified the use of galena, a black lead sulfide, in black and dark brown regions of the painting (Landwehr 2006). Galena has rarely been identified in Chinese paintings but was previously detected in a Han dynasty (206 B.C.E.–220 C.E.) painted textile (Wang 1975).

More frequent have been scientific studies of wall paintings. Studies of wall paintings—both paintings remaining in caves and paintings that have been removed and are currently in museums—have found gypsum, kaolin, and lead white, along with occasional identifications of calcium carbonate, magnesium carbonate, talc, cinnabar/vermilion, red iron oxides, red lead, yellow iron oxides, copper trihydroxychlorides (mainly atacamite), and azurite (Cauzzi et al. 2013; Chen et al. 1997; Egel and Simon 2013; Liu et al. 2016; Malenka and Price 1997; Mazzeo et al. 2010; McLean et al. 2008; Twilley and Garland 2005; Webb et al. 2007; Xu et al. 1983). Studies of the atacamite in Shanxi province wall paintings from the Yuan dynasty, now located at the Nelson-Atkins Museum of Art, Kansas City, strongly suggest the use of a man-made copper trihydroxychloride (Twilley and Garland 2005).

X-ray diffraction (XRD) studies of pigments from the wall paintings and painted statues of the Mogao Caves in Dunhuang identified an increase in the use of gypsum in the Song and Yuan dynasties (Xu et al. 1983). The studies also identified the use of copper chloride as a green pigment and malachite present only as mixed with azurite in a blue shade, not as green, in three Song dynasty grottoes. The Yuan dynasty grotto painting that was investigated had a unique identification of a white magnesium carbonate pigment.

Two studies of statues in the Song dynasty Zhongshan Grottoes in northern Shaanxi province identified gypsum, kaolin, lead white, vermilion, iron oxide red, red lead, atacamite as well as botallackite (a structural isomer of atacamite), malachite, and iron oxide brown (Cauzzi et al. 2013; Egel and Simon 2013). The Royal Ontario Museum, Toronto,



**Figure 1.1.** *Portrait of Wang Huan*, ca. 1056. Album leaf; silk; 41.7 × 31.7 cm (16<sup>7</sup>/<sub>16</sub> × 12<sup>1</sup>/<sub>2</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1948.10. The white has been identified as a lead-based white, cerussite.

undertook a study of fourteen Jin dynasty (1115–1234) and Yuan dynasty polychrome sculptures from Shanxi province, analyzing various stratigraphies and pigments. Atacamite and botallackite were identified as the primary green pigments, with one identification of a copper phosphate. Other pigments found in the original paint layers were kaolin, lead white, vermilion, iron oxide red, red lead, iron oxide yellow, orpiment, azurite, smalt, carbon black, and charcoal (Webb et al. 2007). Paratacamite was also identified in an eleventh–thirteenth-century polychrome Guanyin sculpture at the Art Institute of Chicago (Lei 2012).

The pigments identified scientifically in the studies above are dominated by identifications of gypsum or calcium sulfate, kaolin, lead white, cinnabar/vermilion, iron oxide red, red lead, atacamite or other copper trihydroxychlorides, and azurite. In light of the pigments suggested for use by painters in the historic texts, the few scientific identifications of malachite and orpiment are notable. The infrequency of malachite despite the common use of azurite is worth special attention. If malachite might be chemically unstable in certain applications, and therefore not used, one would expect azurite to be similarly unstable. Azurite and malachite are generally found together as ores, with malachite being the more commonly found mineral, and both are processed into pigments using the same levigation techniques. Some of the differences between the use of pigments mentioned in the historic texts and those that have been identified in paintings may be explained by considering that the majority of scientific examinations of Song and Yuan dynasty paintings have been in wall paintings and paintings from Dunhuang, rather than of the paintings on silk or paper produced in painting academies or by scholar-painters.

The frequent identification of atacamite in the wall paintings described above indicates that atacamite seems to have been the most commonly used copper green pigment, at least in wall paintings, during this time. Studies by Lei Yong (2012) have shown that, as suggested by John Twilley and Kathleen M. Garland (2005), this pigment appears to be both man-made and available naturally in its mineral form. Lei (2012) also suggests that copper trihydroxychloride pigments may have been cheaper than malachite. However, atacamite does not appear to be mentioned in the historic texts described above. One of the difficulties in translation of the historic texts is that the literal translation is often not a specific scientific identification, and, in addition, meanings may



**Figure 1.2.** *Ksitigarbha Bodhisattva*, Dunhuang, China, late 10th–early 11th centuries. Hanging scroll; silk; 106.6 × 58.1 cm (41 $\frac{5}{16}$  × 22 $\frac{7}{8}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1935.11. This painting contains ultramarine, orpiment, and atacamite, pigments characteristic of the Dunhuang palette.

have changed over time. Is it possible some of the various green shades mentioned by Wang Yi refer to atacamite? Or does the dominance of scientific investigation of wall paintings rather than the hanging scrolls and handscrolls focused on by Wang Yi and Li Kan explain the more frequent identification of atacamite rather than malachite?

The lack of mention of non-lead-white pigments in historic texts may be explained by the fact that these





**Figure 1.3.** *Guanyin of the Water Moon*, Dunhuang, China, 968. Hanging scroll; silk; 106.8 × 58.9 cm (42 $\frac{1}{16}$  × 23 $\frac{3}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1930.36.

texts describe only portable paintings on silk or paper, not wall paintings or statues. Different white pigments may have been preferred in the latter situations.

### Pigments Identified in Paintings in the Freer Gallery of Art

Thirty-seven paintings from the collection of the Freer Gallery of Art were examined, thirteen of them

from the Song dynasty and twenty-four from the Yuan dynasty (see app. 5). Paintings with distinctly colored areas were selected. Nine of those chosen were on paper; the rest were on silk. No differences were observed in pigments used in paintings on paper versus paintings on silk.

#### *Northern Song (960–1127) and Southern Song (1127–1279)*

A small group of pigments was observed in Song dynasty paintings. They were mainly lead white or cerussite (an example is *Portrait of Wang Huan*, ca. 1056, fig. 1.1), but anglesite (lead sulfate), was also identified in a few paintings, as well as cinnabar/vermillion, red lead, gamboge, atacamite, malachite, azurite, and red, yellow, and brown iron oxides. In addition to the mineral pigments, indigo was detected. Lac dye, ultramarine, and orpiment were not found in Song paintings other than those from Dunhuang.

Two of the paintings examined—*Ksitigarbha Bodhisattva* (late tenth–early eleventh centuries) (fig. 1.2) and *Guanyin of the Water Moon* (968) (fig. 1.3)—both from Dunhuang, used atacamite as the green pigment and were the only two paintings in which the artists employed ultramarine as the blue pigment. They were also the only two paintings where orpiment was used as a yellow pigment and the only paintings examined from the Song dynasty in which lac dye was identified. The Dunhuang paintings otherwise used the same lead white, cinnabar/vermillion, and red lead found in other paintings from the Song dynasty. An iron-based brown was also identified in *Ksitigarbha Bodhisattva*; no brown pigment was detected in *Guanyin of the Water Moon*.

The ultramarine pigment would most likely have come from mines in Afghanistan and have been traded along the Silk Road to Dunhuang (Plesters 1993). Obtaining ultramarine in Dunhuang does not seem to have been difficult; it has been identified in many other paintings from Dunhuang as well as cataloged in inventories of Dunhuang (Rong 2004; Zhang et al. 2015). While certainly other materials traded along the Silk Road made their way to the more central locations in Song and Yuan times, in this study ultramarine was identified only in the two paintings known to have come from Dunhuang.

Although orpiment was known in Song and Yuan China, it seems to have been used primarily for cosmetic, medicinal, or purposes other than as a pigment



**Figure 1.4.** *Palace Ladies and Attendants*, traditionally attributed to Zhou Wenju, 12th–13th centuries. Fan mounted as an album leaf; silk; 23.2 × 25.1 cm (9 $\frac{1}{8}$  × 9 $\frac{7}{8}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1935.9. The yellow pigment used in the gift box has been identified as iron oxide earth.



**Figure 1.5.** *Consort Yang Mounting a Horse*, traditionally attributed to Qian Xuan, 14th century. Handscroll; paper; 29.5 × 117 cm (11 $\frac{5}{8}$  × 46 $\frac{1}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1957.14. The yellow pigment used for the robe of the figure on horseback has been identified as gamboge.

in paintings (Schafer 1955), although it was found as a pigment to color lacquer (Chase 1988; FitzHugh 1997b; Li et al. 2009). In this study, orpiment has been found only in Chinese paintings from Dunhuang.

#### *Yuan (1271–1368)*

All of the pigments used in Song paintings were also identified in Yuan dynasty paintings, as well as the rare use of some calcite and muscovite. In addition,



**Figure 1.6.** *Bird on an Apricot Branch*, formerly attributed to Li Zhi, 13th–14th centuries. Album leaf; silk; 27.7 × 22.7 cm (10 $\frac{7}{8}$  × 8 $\frac{5}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1954.126. The green pigment in this painting is atacamite—the only atacamite identified in a non-religious painting.



**Figure 1.7.** *Bodhisattva and Attendants*, Yuan dynasty, 14th century. Hanging scroll; silk; 121.8 × 53.6 cm (47<sup>15</sup>/<sub>16</sub> × 21<sup>1</sup>/<sub>8</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1913.65.

lac dye was more commonly identified in Yuan paintings, while in the Song dynasty paintings examined lac dye was found only in the two paintings from Dunhuang. Gamboge was detected more frequently in

the Yuan dynasty paintings than in the Song dynasty paintings, for which iron oxide yellow was most commonly identified. For example, iron oxide yellow was found in the Song dynasty fan mounted as an album leaf, *Palace Ladies and Attendants* (twelfth–thirteenth centuries) (fig. 1.4), and gamboge in the Yuan dynasty handscroll *Consort Yang Mounting a Horse* (fourteenth century) (fig. 1.5).

Although gamboge has been known to have been imported into China both for medicinal use and as a painting pigment since the Tang dynasty (Schafer 1963), it was securely identified in only three of the paintings examined, all from the Yuan dynasty. Six additional paintings (two from the Song dynasty and four from the Yuan dynasty) produced tentative identifications of an organic yellow pigment. The thin layers in which yellow was applied and the infrequency of yellow colors in the paintings themselves may have contributed to the infrequent identifications in the Freer study. However, iron oxide-based yellows remain more frequently identified in the Yuan paintings, twice as often as any other yellow pigment. The infrequent use of gamboge and orpiment suggests the prominence of iron-based yellows during this time period.

In addition to the Dunhuang paintings discussed above, three other paintings used atacamite or paratacamite as a green pigment: *Bird on an Apricot Branch* (thirteenth–fourteenth centuries) (fig. 1.6), *Bodhisattva and Attendants* (fourteenth century) (fig. 1.7), and *Luohan, Holding a Fly Whisk, with Attendant* (fourteenth century), formerly attributed to Wu Daozi (F1916.521). The second two are religious paintings, although not from Dunhuang or related regions. Religious communities may have had freer access to some foreign pigments through informal trade among monasteries. A number of recent studies have attributed copper trihydroxychlorides to a man-made pigment (Twilley and Garland 2005; Twilley and Garland 2011; Lei 2012). Polarized light microscopy (PLM) of the atacamite identified in the two paintings from Dunhuang, *Ksitigarbha Bodhisattva* and *Guanyin of the Water Moon*, as well as in *Luohan, Holding a Fly Whisk, with Attendant*, showed the rounded green particles that suggest the atacamite in these paintings is man-made. The identification of the copper trihydroxychloride atacamite in the non-religious painting, *Bird on an Apricot Branch*, is an anomaly in this study, and although atacamite has been detected in many wall paintings, as referenced above, it has been less commonly identified in portable paintings outside of Dunhuang.

## Summary of Results

Pigments from thirty-seven paintings on silk and paper from the Song and Yuan dynasties were examined. Although two paintings were from Dunhuang, the majority came from more central regions of China. The two paintings from Dunhuang used some pigments not identified in other Song dynasty paintings in this study: natural ultramarine and atacamite were both identified in these paintings and are well documented as being part of the traditional palette of Dunhuang paintings. The two paintings from Dunhuang were also the only Song dynasty paintings in which lac dye was identified. The pigments identified in the Freer paintings from more central regions of China are generally consistent with the pigments listed for use in paintings by Li Kan and Wang Yi, given earlier in this chapter. The primary differences observed between the Song and Yuan periods were that lac dye, gamboge, and indigo were more frequently identified in Yuan paintings than in Song paintings, although lac dye and indigo did occur in paintings from both periods.

### White Colorants

The white pigments identified were mainly lead white (hydrocerussite) or cerussite, but lead sulfate was also confirmed in a few paintings. Anglesite was identified as the white pigment in *The Buddha Addressing Yamaraja at Kusinagara* (twelfth–thirteenth centuries) (F1926.1) and in combination with hydrocerussite in *Palace Ladies Playing Double Sixes*, traditionally attributed to Zhou Fang (late twelfth–mid-thirteenth centuries) (F1939.37/F1960.4). Anglesite was also found in the green atacamite pigment in *Luohan, Holding a Fly Whisk, with Attendant* but was not identified in white regions of the painting. Five paintings showed traces of clays or calcite in the lead white pigment, but neither clay nor calcite appears to be the primary white pigment used in any paintings studied.

### Red and Orange Colorants

Cinnabar/vermillion was identified as the red pigment in all but one painting that had bold red pigment areas; in *Bird on an Apricot Branch* the only red colorant present was lac dye. Insect dye was identified in all the organic red colorants found in the paintings examined and was presumed to be lac dye. Red lead was detected in both Song and Yuan paintings, but only in a handful of them. Iron-based

red pigments were identified in eight paintings, in all but one case in paintings that also used cinnabar/vermillion in other areas of the painting.

### Yellow Colorants

Iron-based yellow pigments were identified in approximately half the paintings studied. They were the most frequently used yellow pigment in both Song and Yuan paintings that were not from Dunhuang. Orpiment was found only in the two paintings from Dunhuang despite being listed as a painting pigment in most literature sources on Chinese painting. In addition, although gamboge was also frequently mentioned in texts on painting pigments, it was firmly identified only in three paintings, all from the Yuan dynasty.

### Green Colorants

Malachite appears to be the primary green pigment used in Song and Yuan paintings. As mentioned previously, five paintings, including the two paintings from Dunhuang, used copper trihydroxychlorides as the green pigment instead of malachite. Copper trihydroxychlorides have been observed more frequently in religious paintings associated with various grotto locations, and this study is the first, to our knowledge, to observe them in a nonreligious Song or Yuan dynasty painting. Paintings that contained indigo used it as a blue colorant as well as in mixtures with a yellow pigment to create green tones. In paintings with no blue areas, indigo was found only in green mixtures. In two paintings—*Seated Luohan* (1345) (F1919.107) and *Panthaka, the Tenth Venerable Luohan* (1345) (F1919.163)—azurite mixed with an unidentified yellow colorant was used in the green areas rather than malachite or copper trihydroxychlorides. This mixture appeared infrequently, however, in the paintings examined.

### Blue Colorants

Indigo and azurite were frequently identified in Song and Yuan paintings. In the five paintings in which azurite and indigo were both identified, they were used in separate areas as well as, in some paintings, with indigo as a wash over azurite to add shading. In general, azurite and malachite were used in the same paintings for bright blue and green areas, respectively. There were a few exceptions where green areas were painted with azurite and an unidentified yellow. Ultramarine was found only in the two paintings from Dunhuang.

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# 2

## Red Insect Dyes in Paintings from the Ming and Qing Dynasties

Christina Bisulca and John Winter

### Introduction

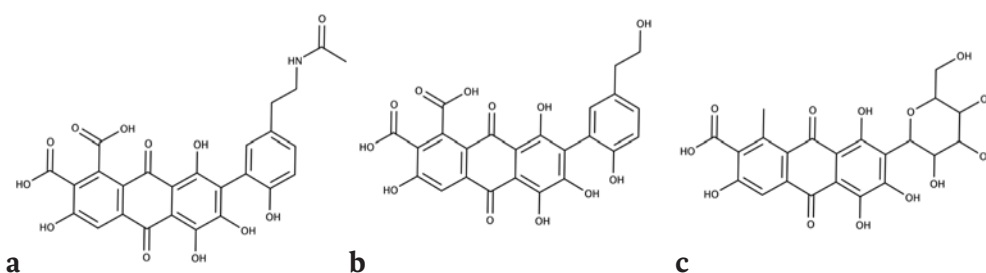
Red colorants are traditionally prepared from either inorganic mineral pigments or organic dyes derived from plants or animals. There is already an extensive literature on the mineral colorants cinnabar/vermilion, red lead, and iron-based pigments concerning their source, preparation, and use in Chinese paintings (Winter 2008), but little research has been carried out on organic-based reds. For organic colorants, definitive identification requires specific analytical techniques, most of which also necessitate the removal of a small sample from the painting. Due to their high tinting strengths, dyes can be present in very limited quantities, requiring an analytical method with a low limit of detection, given the small sample size. Moreover, organic dyes are prone to deteriorate, further complicating identification.

Analysis to date has pointed to lac dye and cochineal as the most likely organic red colorants in Chinese paintings (Giaccari and Winter 2005; Winter 2008). Lac dye is derived from insects endemic to

Southeast Asia and was available in China as early as the third century (Laufer 1919; Tsai 1982). Cochineal derived from insects native to the Americas could have been available in China, through trade, as early as the sixteenth century: the Manila Galleon carried cochineal as early as the 1580s (Phipps 2010, 40). Although there are other sources for cochineal, such as Polish cochineal derived from insects in Europe and Armenian cochineal obtained from insects in West Asia, no historical records indicate trade of these materials or suggest that they would have been available in East Asia.

Historical sources suggest other possible sources for organic reds used in Chinese paintings. Most notable are madder reds and safflower (Yu 1988), both of which are known in China as textile dyes (Han and Quye 2018). Other possible sources mentioned include the tree resin dragon's blood (Schafer 1957) as well as extracts from various plants, such as sappanwood (*Saesalpinia* spp.), flowers and berries from *Sophora japonica* (*keng hua*), flowers and leaves from *Mirabilis jalapa*, and pomegranate, among others (Winter 2008; Tamburini and Dyer 2019).





**Figure 2.1.** Molecular structure of the main components of lac dye and cochineal: (a) laccaic acid A; (b) laccaic acid B; (c) carminic acid.

## The Scale Insect Dyes

The colorants in both lac dye and cochineal are substituted hydroxyanthraquinones derived from scale insects (fig. 2.1). Scale insects (Coccoidea superfamily) are insects that feed from the phloem of plants. During reproduction, the female insect attaches to the plant and secretes a waxy or hard, resinous substance around its body for protection. The anthraquinones are produced in the bodies of the insect and are typically yellow to red in color (Shamim et al. 2014).

Lac dye is obtained from “lac insects,” scale insects of the *Kerria* genus (Kerriidae family) that are distributed throughout Southeast Asia, India, and West Asia. These insects secrete a hard polyester exudate that has been used since antiquity for the production of shellac (Winter 2008; Sharma et al. 2006). The literature on historic dyes cites *Kerria lacca* and *Kerria chinensis* as the species used in dye and shellac production. *Kerria lacca* is distributed primarily in India and Southeast Asia and is the source of commercial lac dye today. *Kerria chinensis* is also native to Southeast Asia, particularly Thailand and Cambodia (Garcia Morales et al. 2016). The dye derived from these insects is most likely to have been available historically to China via trade with Southeast Asia. A sample imported from Siam (Thailand) in the Imperial Warehouse Collections, Nara, Japan, dated to the eighth century, has been identified as the *Kerria chinensis* species (Mahdihassan 1952).

It is possible that other species could also have been used as a dye source. There are more than twenty other species of the *Kerria* genus in Asia, many of which are known to produce significant amounts of shellac (Ben-Dov 2009; Garcia Morales et al. 2016). Other lac species are cultivated in China in addition to *K. lacca* and *K. chinensis*, including *K. greeni*, *K. sindica*, *K. ruralis*, and *K. fici* (Chen 2005; Zhang et al. 2008). The shellac exudate from *Kerria yunnanensis*

is strongly red and is used unbleached as a varnish for furniture in China (Saint-Pierre and Ou 1994).

In analysis of the extracts of *Kerria lacca*, the water-soluble dye portion was found to vary from 4% to 8% by weight of exudate (Wadia et al. 1969). The dye itself is composed of various related hydroxyanthraquinones, designated laccaic acid A–F, with laccaic acid A (fig. 2.1) in the highest proportion. The amount of recoverable dye and relative quantity of the laccaic acids are known to vary with locality, host tree, and season (Oka et al. 1998; Sharma et al. 2006; Wouters and Verhecken 1989). However, there has been little research into the components of the dye in other species of lac insects, and the identity and proportion of components likely vary among species. For instance, another form, laccaic acid F, has been found only in Thai stick lac (Hu et al. 1997).

Historic extraction procedures for lac dye are generally based on the evaporation of the wash water used in the initial processing of shellac. The raw stick lac, which contains both the female insect and eggs, is simply submerged in a trough of water, broken up, and washed repeatedly until clear. This wash water is evaporated, and the dye residue that is left is pressed into cakes (Watt 1908, 1061). The dye can also be isolated by precipitation (O’Conor 1876, 59), which is carried out by the formation of a salt (Srivastava et al. 2013).

Cochineal is derived from *Dactylopius coccus* scale insects that are distributed in regions of the Americas (Schweppe and Roosen-Runge 1986). Chemically, the colorant in cochineal is carminic acid, a hydroxyanthraquinone with carboxylic acid and glucose substituents (fig. 2.1c). The amount of coloring matter in each insect depends on various conditions, including the subspecies and how and when it is harvested; for the domesticated species, it can be up to 22% of the dry weight of the insect (Lloyd 1980). A complete description of these insects and cochineal dye is given by Helmut Schweppe and Heinz Roosen-Runge (1986).

The coloring properties of these dyes are highly dependent on their preparation (mordant, lake, pH, substrate, etc.). As a painting pigment in Europe and America, these dyes are typically “laked,” a process whereby the dye is precipitated onto an insoluble substrate. However, that no similar laking process is described in historic Chinese painting treatises suggests that Chinese artists used the organic colorants directly in mixtures with hide glue (Giaccai and Winter 2005; Yu 1988). Some treatises recommend boiling the dye cake before use to intensify the color (Sze 1956; Yu 1988), a process also suggested for textile dyes (Song 1966, 73). Others recommend that the dye be applied with alum (Yu 1988)—in effect creating a laked pigment—most likely to improve color and lightfastness properties (Schweppe and Roosen-Runge 1986; Saunders and Kirby 1994).

### Historical Accounts of Lac Dye in China

Accounts as early as the third century describe the cultivation of the lac insect for the production of both shellac and dye (Tsai 1982). The earliest centers of production were in India and Southeast Asia (Donkin 1977a). Lac dye was known in China in the Han dynasty (206 B.C.E.–220 C.E.) as a silk dye (Donkin 1977a). Records as early as the fifth century document the importation of lac dye into China from Southeast Asia, where the largest centers of production were Myanmar (Burma), Vietnam (Indochina), and Thailand (Winter 2008; Yu 1988; Laufer 1919, 475–78; Donkin 1977a; Donkin 1977b; Hirth and Rockhill 1911).

The term “lac” is Indian in origin, probably derived from *lak*, meaning “a hundred thousand,” likely in reference to the numerous insects embedded in the shellac (also *lak-ka* in Cambodia) (Donkin 1977b; Laufer 1919). In China lac dye is referred to as “red gum” (*chi jiao*—see app. 4 for information on historic pigment terminology). It is called “ant lac” or “ant ore” from Vietnam (Indochina) in the third-century C.E. *Records of the Wu Kingdom* (Wu Lu) (Laufer 1919; Schafer 1957). Lac dye is also believed to be the “ant-ore of Nan-hai” in the artist Zhang Yanyuan’s 847 treatise on Chinese painters (Acker 1954, 189). The term “ant ore” is interesting, as it may be a reference to the mutualistic relationship between ants and lac insects: many ant species “tend” to lac insects, providing protection from predators and parasites, and in return they feed on a sugar secretion (“honeydew”) that the lac insects produce (Bhattacharya et al. 2016; Gullan and Kosztarab 1997).

The designation “ant ore” could be due to the fact that during their growing seasons shellac would be associated with these tending ants. Some accounts suggest it was believed that the ants themselves produced shellac (Laufer 1919). The designation may also be a reference to the appearance of the female lac insects that are embedded in the unprocessed lac exudate.

A red dye referred to as “purple mineral” (see app. 4) is typically interpreted as lac dye (Schafer 1957). *Tzu-k’uang* is cited in the seventeenth century as preferred by “the Ancients” over safflower or pomegranate (Song 1966). In the thirteenth century a special type of “lacquer”—likely the same material—is cited as one of the chief products of the area that is approximately present-day northern Vietnam (Tongking) and Cambodia (Donkin 1977b; Hirth and Rockhill 1911). In the present study it is believed to be a reference to lac.

The change in description of lac dye from “ant ore” to “purple mineral” in later accounts is noteworthy and may indicate a change in the commercial product from unprocessed shellac or stick lac to the processed dye. In other accounts red dyes are referred to non-specifically as “rouge” (*yan zhi*, see app. 4 for further information), which were sold as cakes or as “cottonball rouge”—a wadded cotton substrate onto which the dye was poured (Sze 1956; Yu 1988). In these cases, however, “rouge” could refer to any red dye.

The inherent caveat with historical references is that they are often nonspecific and descriptive, so interpretation is difficult and at best speculative. Because lac dye is derived from an insect secretion on trees, it can be confused with colorants derived from tree resins like dragon’s blood (Schafer 1957). For example, E-tu Zen Sun and Shiou-chuan Sun in their 1966 translation, *T’ien-kung k’ai-wu: Chinese Technology in the Seventeenth Century*, interpret “purple mineral” to be a dye obtained from lichen, although in the present study it is believed to refer to lac dye (Song 1966).

### Cochineal and the China Trade

In the sixteenth century, shortly after Spanish colonization of Mexico, cochineal became one of Spain’s largest exports because it was considered a stronger red dye than others available at the time in Europe (Lee 1951). Spain oversaw native production of cochineal, particularly in Oaxaca, monopolizing its production and exportation through Cádiz and Seville. Although at certain times Spain limited

**Table 2.1.** The cochineal trade with specific reference to China.

1526	First recorded shipment of cochineal reaches Spain.
1564	Annual shipment from the Viceroyalty of New Spain to Spain (Seville and Cadiz) begins (Lee 1951).
1570s	Regular trade between Mexico and the Philippines begins (Lee 1951). The Manila Galleon's annual trip from Acapulco to Manila carries cochineal for Asian markets, where it was highly desired (Salinas 2018, 270).
<b>17th C</b>	Cochineal trade expands, reexported from Spain throughout Europe and to Asia, primarily to Persia and India. Trade with China comes by the Manila Galleon, and in China cochineal becomes known as "foreign red" (Donkin 1977a, 867).
1650s	Cornelis Drebbel, a Dutch chemist, produces a brilliant scarlet, called "Holland red," by mordanting cochineal with tin. In Europe, Holland red replaces kermes-based Venetian scarlet (Donkin 1977b; Lee 1951).
<b>18th C</b>	British trade with Latin America increases dramatically and includes the import of cochineal (Naylor 1960).
1757	Canton (today Guangzhou) is decreed by the Chinese emperor to be the only port open to foreign trade, and all trade must be conducted via licensed Chinese merchants (Ebrey 1996).
1765	Cochineal is a trade item in China, Cambodia, Siam, and Cochin China. The English, French, Dutch, Swedish, and Danish all report taking on cochineal at Canton (Lee 1951, 212), evidence that it was reexported.
1784	Chinese trade with the new United States begins after the first U.S. ship, <i>Empress of China</i> , sails to Canton.
<b>19th C</b>	Early in the century cochineal is primarily traded by Spain, routed through the Philippines and on to the rest of Asia. Spain maintains a monopoly on cochineal, the price of which peaks around 1810 (Salinas 2018).
1821	Cochineal becomes more widely available as Mexico achieves independence from Spain, ending Spain's monopoly, and cochineal begins to be produced for commercial trade outside of Mexico. In the decades before and after Mexican independence, Guatemala surpasses Oaxaca in cochineal production (Donkin 1977b, 30).
1830s	Britain monopolizes trade from Central America to Europe through Belize. Guatemalan cochineal becomes a major export, "essential" for British textile factories (Naylor 1960). U.S. cargo bound for China also includes cochineal (Wildman 1900).
1842	Treaty of Nanking (today Nanjing) following the First Opium War opens four ports in addition to Canton to foreign trade, including Shanghai.
1840s–50s	Cochineal production is introduced to the Canary Islands, where it becomes a major product, the sale of which peaks in the 1870s. It is also cultivated on Java and nearby islands by the Dutch, and most of it exported to China or Holland (Donkin 1977b).
1856	With the discovery of mauve and commercialization of aniline dyes, trade in cochineal becomes less profitable.
1858	Treaty of Tientsin (today Tianjin) during the Second Opium War and other treaties open eleven more ports to England, France, the United States, and Russia and open Peking (today Beijing) to foreigners.
1860s–80s	Many new red dyes are synthesized, including synthetic alizarin, Congo red, magenta (fuchsin), and, most important, azo reds, all of which greatly depress the market for cochineal (Lee 1948).

the use of cochineal for dyeing to Spanish artisans (Donkin 1977b, 28), by the middle of the sixteenth century cochineal was being traded throughout Europe, in particular to the important cloth centers in England, Italy, and Antwerp in the Spanish Netherlands (Lee 1951). By the close of the eighteenth century, cochineal was widely available (table 2.1).

Early accounts suggest that cochineal was soon available in China. In 1577, the Franciscan missionary Bernardino de Sahagún wrote that cochineal was known around the world, as far as China and Turkey (Donkin 1977b). Yu Feian (1988, 30) writes that Zeng Qing (1568–1650), a painter of portraits in Nanking (today Nanjing), was an early adopter in China of cochineal as an artists' material as he used "Western red" in portraiture. Zeng Qing is known for the Western-inspired realism in his paintings (Osswald 2020), which is possibly due to the influence of Matteo Ricci (1552–1610), a missionary and

painter also in Nanking. Such a connection may have spurred his use of the imported cochineal. Largely due to these specific references, it has been assumed that cochineal then became a common source for red dye, particularly in flower and plant painting, because of its superior color. Yu Feian (1988, 30) states that "carmine was used from 1582 on . . . in traditional flower-and-plant painting; because Western red was so highly refined it has been very widely used down to the present time."

Although numerous accounts describe the presence of cochineal in the port city of Canton (today Guangzhou) in the early seventeenth century, its availability throughout China at this time and its use as a painting material are not known. Robin Arthur Donkin (1977b, 48) has observed that by the end of the seventeenth century, as the China trade developed, cochineal "was at all times costly and found a ready market only where luxury materials

were manufactured” (see also Lee 1951). Records seem to indicate that, in the eighteenth century, with increased foreign trade through Canton, cochineal became a more important article of commerce because it was the preferred red dye for silks (Donkin 1977b).

British East India Company trade records suggest it was the major supplier of cochineal into China. In the seventeenth and eighteenth centuries, unprocessed cochineal (“ungarbled”) from Spain was traded through Manila, while the refined (“sifted”) English product (“garbled”) sold at a higher price (Bridgman and Williams 1834, 457–58; Fairlie 1965; Ljungstedt 1836). Based on the examination of British East India Company records dating from 1727 to 1776, Leanna Lee-Whitman (1982) suggests that cochineal was exported to China specifically so it could be used to dye textiles that were then exported to Europe. From the late eighteenth to the early nineteenth century, records indicate that large quantities of cochineal were traded through Canton (Pritchard 1957), the only port open to foreign trade 1757–1842 and were sometimes reexported when the supply exceeded the demand (Donkin 1977b; Oliphant 1859). In the early nineteenth century the cochineal trade was at its height worldwide. With Mexican independence from Spain in 1821, competing production centers and trade houses were established throughout Mexico and Central America. With these changes, prices dropped significantly, by more than 75% from 1815 to 1850 (Naylor 1960; Salinas 2018).

## Scientific Research Results and Discussion

Paintings from the Freer Gallery of Art and Arthur M. Sackler Gallery collections were chosen for analysis if visual examination suggested areas of organic red. Relatively few paintings from the Ming dynasty (1368–1644) were selected for analysis, primarily because visual examination did not identify many with areas that appeared to have an organic red colorant. While it is known that earlier paintings had a more limited palette, with many using only ink, this lack of color could also be a result of fading, which is more likely with older paintings that have been exhibited. The results presented here therefore most likely represent a subset of the situation in Chinese paintings.

Organic red areas were first noninvasively examined with fiber optics reflectance spectroscopy

(FORS) and x-ray fluorescence (XRF). Insect dyes are characteristic in FORS analysis and can be distinguished from plant-based anthraquinones (madder) (Giaccai and Winter 2005). In this study, the vast majority of the organic reds examined were identified by FORS as insect dyes, and only in one case was a plant-based anthraquinone detected. In total, 104 paintings from the Ming dynasty forward were found to have insect dyes present.

Paintings in which an organic red dye was indicated were then sampled for high-performance liquid chromatography (HPLC) analysis for confirmation (see app. 1 for experimental details). The seventy-seven paintings analyzed by HPLC were from the Ming and Qing (1644–1912) dynasties except for four, dating from later in the twentieth century. Thirty-four were from the Arthur M. Sackler Gallery portraits. Formerly in the collection of Richard G. Pritzlaff, the paintings came as a group to the Gallery. Where carminic acid was identified in samples, it was assumed that the organic colorant was cochineal and, given the historical context, most likely obtained from the Americas, through trade. While there are other scale insect dyes from Europe and West Asia that also contain carminic acid as the primary dye component and that can be distinguished by the relative ratio of minor dye components (Wouters and Verhecken 1989), these secondary compounds were not observed due to the small size of the samples removed from paintings.

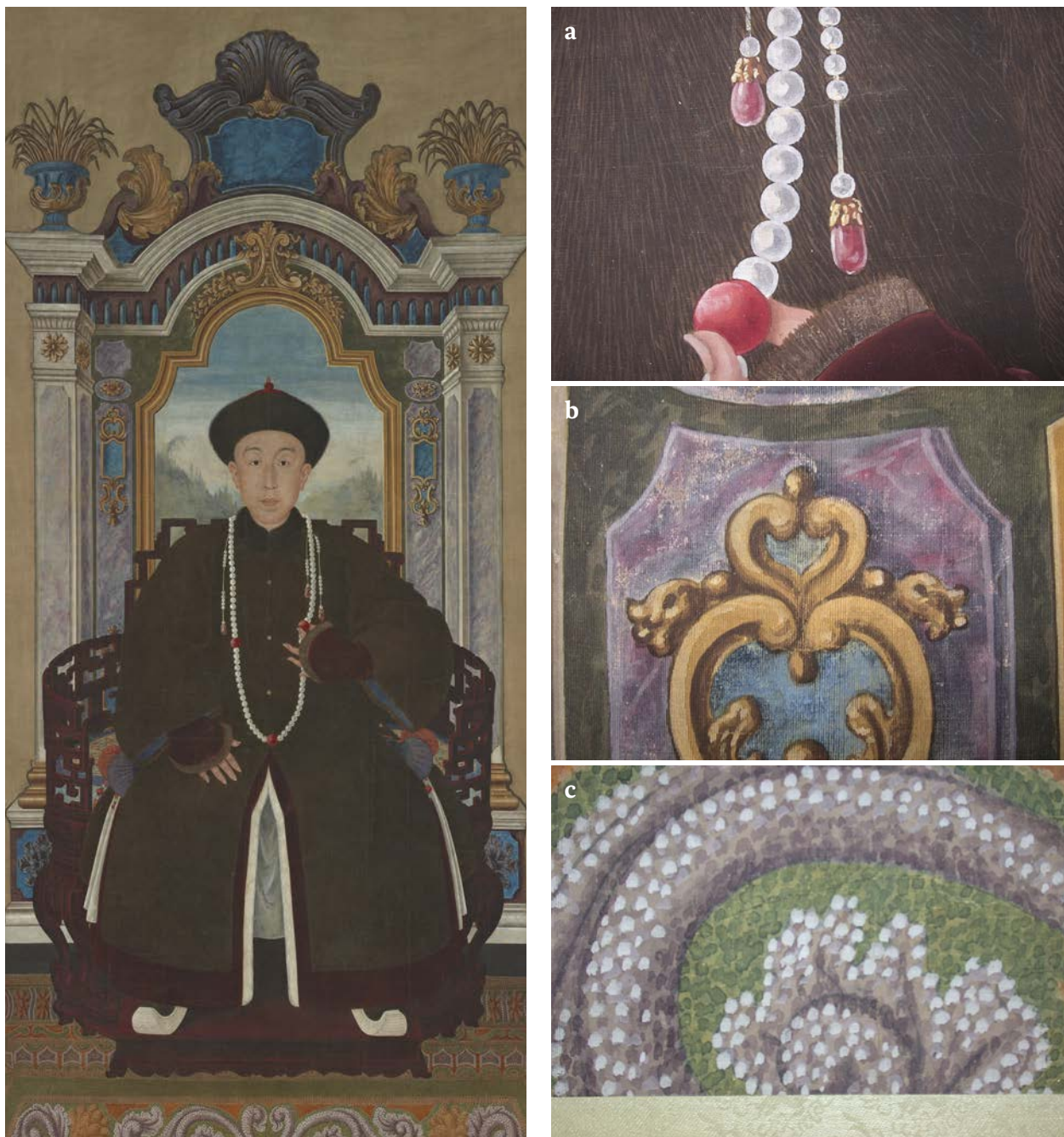
During this study it was noted that there are differences in FORS spectra between lac dye and cochineal (see app. 2). Where both lac dye and cochineal were indicated by FORS in the same painting, multiple areas were sampled for HPLC. In total, 179 samples were analyzed with HPLC. This chapter includes results only where the dye was confirmed with HPLC. Additional paintings in which insect dyes are indicated by FORS but not analyzed with HPLC are listed in appendix 5.

### *Insect Dyes in Chinese Paintings and the Introduction of Cochineal*

Table 2.2 lists the red dyes identified in paintings by period. Lac dye was the only organic red dye identified during the Ming dynasty and was still by far the most common dye throughout the Qing dynasty. Cochineal was found as the only organic red in just eight paintings, all of which were from the Qing dynasty or later. Although historical accounts report that cochineal was in China as early as the sixteenth century (Schweppe and Roosen-Runge 1986), it does

**Table 2.2.** Number of Chinese paintings in which lac and cochineal were identified by HPLC ( $n = 76$ ).

Red Dye	Ming (1368–1644)	Qing (1644–1912)	Post-Qing (1912–1949)	Total
Lac only	10	49	1	60
Cochineal only	0	6	2	8
Both	0	8	0	8
Total	10	63	3	76



**Figure 2.2.** *Portrait of Hongyan, Prince Guo (1733–1765)*, mid-late 18th century. Hanging scroll; silk; 222.1 × 103.7 cm (877/16 × 4013/16 in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.47. Details show pigments. Cochineal was found in the elongated red beads (a), the first use of cochineal in a portrait in this study. In the purples of the marble (b) and carpet (c), lac dye was used to generate the color.

not appear to have been used in paintings until much later. In this study the earliest use of cochineal is in the eighteenth century. In the nineteenth century, it was found in a third of the paintings examined. By the early twentieth century, cochineal was the most common organic red dye identified, and the majority of the paintings analyzed contained cochineal, although this finding may reflect the small number of paintings analyzed from the twentieth century, the majority of which were portraits. Similar results have been found for the use of cochineal as a textile dye, as there is little evidence of its use prior to the mid-nineteenth century (Phipps 2010). Moreover, the use of the traditional lac dye continued into the twentieth century even as the use of cochineal increased.

The earliest occurrence of cochineal identified is in Jiang Tingxi's (1669–1732) early eighteenth-century *Small Birds and Morning Glories* (F1980.152) (see fig. I.2), but the date of this painting is contested. This painting also contains the first occurrence of Prussian blue, also an unusually early date for this synthetic colorant. However, Jiang was a court painter at a time when there was greater influence of European art in the Chinese court than previously, and Jesuit artists were working for the imperial court, including the enameler Jean Baptist Gravereau (1733–1771) in the Kangxi reign (Shih 2005) and the painter Giuseppe Castiglione (1688–1766) during the subsequent Yongzheng and Qianlong reigns. The influence of the Catholic missionaries during this time on the materials and techniques of painted enamels has been established (Shih 2005). Thus, it is possible that European painting materials were available to artists associated with the court.

Cochineal was found in only two other paintings dated to the eighteenth century: Yuan Tong's *On a Branch of Willow* (probably 1770) (F1980.142h) and *Portrait of Hongyan, Prince Guo* (1733–1765) (mid-late eighteenth century) (fig. 2.2). In this portrait, however, cochineal was found in only one area (fig. 2.2a), so it is possible that it was introduced in a later retouching.

This increased use of cochineal in paintings from the nineteenth century aligns with historical accounts from the British East India Company that document the peak of the cochineal trade in the late eighteenth century (Morse 1936; Lee-Whitman 1982; Van Dyke 2005; Koninckx 1980; Donkin 1977b). Cochineal was still expensive, however (Donkin 1977b; Yu 1988; Salinas 2018), and its use further expanded after its price dramatically decreased following Mexican independence in 1821 (Salinas 2018).

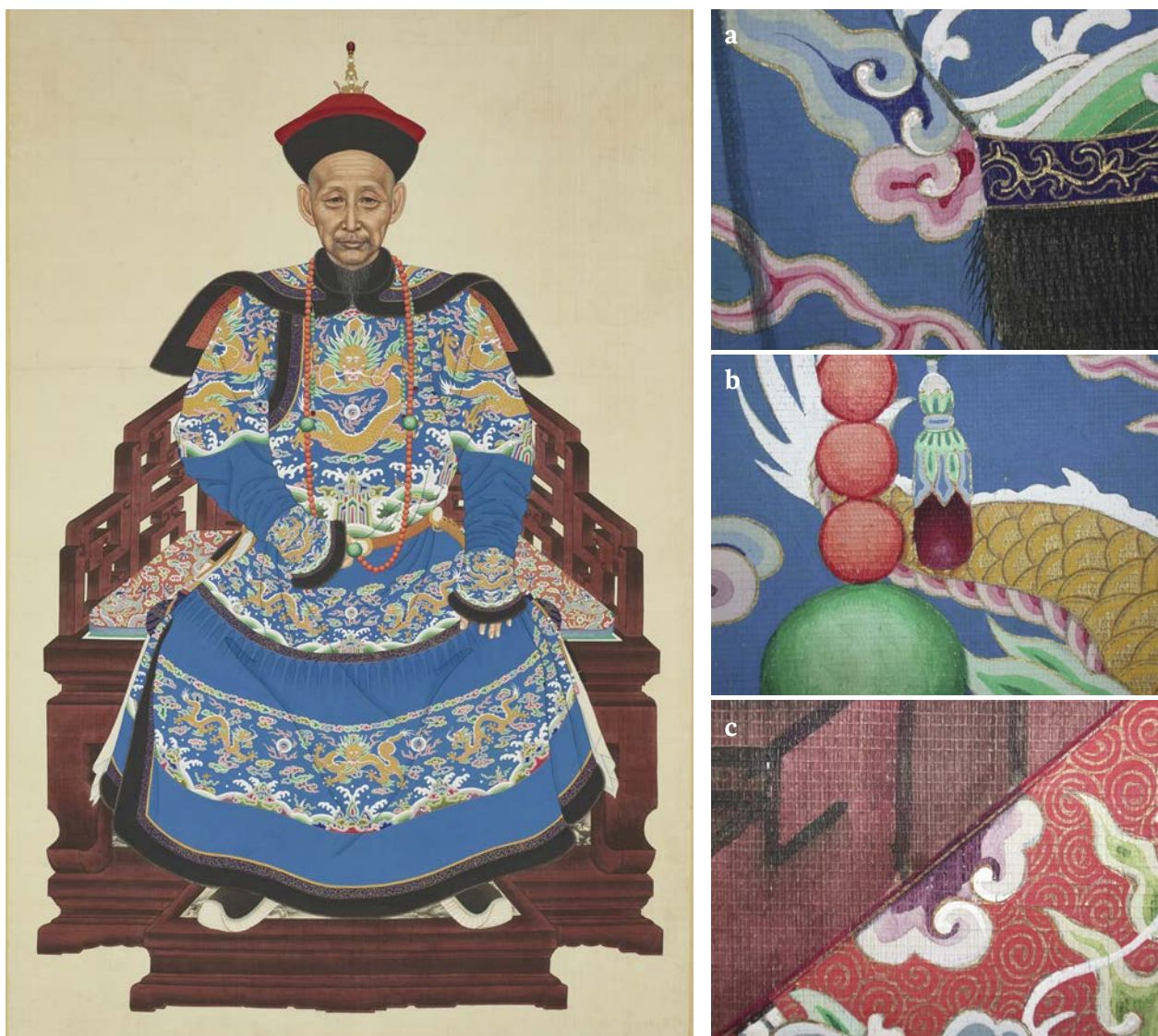
Cochineal was found in portraits of Qing courtiers and members of the imperial household. These were in theory mostly painted in Peking (today Beijing), where cochineal would have been available at the imperial court. Cochineal was also found in paintings on paper that are part of an acquisition from the United States Customs Service, Department of Treasury. Some of these paintings are by known artists from the Yangtze delta, suggesting cochineal would have been available, through the southern port of Canton, which was the only port open to foreign trade from 1757 until 1842. The lack of cochineal in landscape and genre paintings suggests that their painters may not have had cochineal available to them.

#### *Lac and Cochineal in Combination*

Eight paintings, primarily portraits, were found to contain both cochineal and lac dye, most judged to be from the nineteenth or the twentieth century (see table 2.2). Lac and cochineal dyes were found both as a direct mixture and as separate applications for different elements within one painting. The use of both dyes in a single painting was common: of the sixteen paintings in which cochineal was identified, half also contained lac dye.

In seven of the paintings each dye was used singly or combined for specific areas. In *Portrait of a Qing Courtier* (mid-late nineteenth century) (S1991.105), cochineal without lac was found in all areas of pinks and purples tested, with the exception of the wash applied over the sitter's robe, where a mixture of lac dye and cochineal was used. In *Portrait of the Sixth Prince Yi* (1905) (fig. 2.3), cochineal without lac was used to create bright pinks and orange-red beads, but a lac dye-cochineal mixture was employed in purple areas, as a wash over cinnabar/vermilion to create the deep red in the sitter's court necklace and mixed with iron-based pigments to obtain the red-brown coloration of the luxury wooden chair. Further details on the use of cochineal are listed in tables 2.3 and 2.4.

The separate uses of these two dyes indicate that Chinese painters distinguished between them, most likely on account of their different coloring properties. In general, cochineal was found in bright pink and red areas, while pink-to-purple areas were achieved with the addition of lac. The brighter red nature of cochineal was recognized by Yu (1988, 75): "In the modulated washes of cinnabar, the early Chinese painters all relied on rouge. Washed on in much quantity, rouge becomes dark and is not as bright and pleasing to the eye as a wash of carmine [cochineal]."



**Figure 2.3.** *Portrait of the Sixth Prince Yi*, 1905. Hanging scroll; silk; 185.3 × 119.7 cm (72<sup>15</sup>/<sub>16</sub> × 47<sup>7</sup>/<sub>8</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, \$1991.86. Details show the selective use of cochineal and lac dye. The bright pinks in the robe (a) and orange-red beads (b) were created with cochineal alone. In the deep red bead (b) and purple clouds in the seat cushion (c), a mixture of lac dye and cochineal was used, while in the red-brown wood of the chair iron-based pigments were added to the lac dye–cochineal mixture.

**Table 2.3.** Number of occurrences of red and blue mixed to create purple.

Colorant(s)	Indigo	Prussian Blue	Smalt	Azurite	Ultramarine
Lac dye	28	2	1	3	0
Cochineal	1	6	0	0	1
Lac dye and cochineal mixture	1	1	0	1	0
Cinnabar/vermilion	1	0	0	0	0

The different use of these dyes could also be related to their cost. In earlier centuries, expensive cochineal may have been reserved for the most important elements of a painting, or it may have been extended

with lac dye, particularly for decorative elements that did not need to be as brightly colored. Different uses may also reflect workshop practices in which different artists painted certain areas of the painting (e.g.,

**Table 2.4.** Occurrence and use of cochineal.

Artworks	Title	Date	Artist	# HPLC Samples	Colors	Notes
<b>Paintings</b>						
F1980.139	<i>Zhong Kui and His Assistants under Willows</i>	1832	Fei Danxu	1	pink	cochineal applied as a layer over lead white for <b>pink</b> flowers
F1980.142e	<i>Lady and Maid in a Garden in Moonlight</i>	1822	Gai Qi	1	pink	cochineal with lac dye applied directly on paper in <b>pink</b> robes; although both dyes were found in a single sample, it is possible that they were applied separately based on layering observed in visual examination
F1980.142h	<i>On a Branch of Willow</i>	probably 1770	Yuan Tong	1	pink	cochineal applied directly on paper in <b>pink</b> flower petals
F1980.152	<i>Small Birds and Morning Glories</i>	possibly early 18th century	Jiang Tingxi	1	purple	cochineal used in a mixture with Prussian blue for <b>purple</b> bird
F1980.168	<i>Bamboo, Orchid and Rock in a Tub</i>	mid-late 19th century	Luo Qing	1	red	cochineal applied as a thin wash directly on paper in <b>red</b> leaf details ( <b>red-violet</b> in color without the addition of blue)
S1987.220	<i>Morning Glories and Grasshopper</i>	1941	Qi Baishi	1	pink, red	cochineal alone used as a wash on paper for all <b>pinks</b> and <b>reds</b>
S1991.46	<i>Beautiful Ladies Riding</i>	mid-late 19th century	formerly attributed to Giuseppe Castiglione	4	pink, purple	cochineal used in a mixture and a wash over lead white in <b>pink</b> flowers; cochineal and vermilion in <b>red</b> leaves; cochineal in a mixture with indigo and lead white in dark <b>purple</b> flowers
<b>Portraits</b>						
S1991.47	<i>Portrait of Hongyan, Prince Guo (1733–1765)</i>	mid-late 18th century		4	red	cochineal applied with lac dye over vermilion in bright <b>red</b> elongated beads; all other <b>pink</b> and <b>purple</b> areas sampled in marble and carpet contained lac dye alone
S1991.65	<i>Portrait of Lady Hejia, Secondary Wife of Prince Zaizhi</i>	late 19th century		5	pink, red, purple	cochineal applied over lead white in bright <b>pink</b> flowers in the carpet; cochineal used in a mixture with lac dye for deep <b>red</b> beads; cochineal in <b>red-orange</b> carpet details over lead white (may contain yellow dye); two <b>purple</b> mixtures found: cochineal mixed with lac dye and indigo; cochineal alone with Prussian blue in the medallions in the robe
S1991.84	<i>Portrait of Yinxiang, the First Prince Yi (1686–1730)</i>	1905		8	pink, purple, brown	cochineal used in all <b>pinks</b> (cloud designs, flesh tones, and pink lips); cochineal mixed with Prussian blue in <b>purple</b> stripes in the robe; cochineal used in a mixture with lac dye, iron oxides, and Prussian blue for the <b>red-brown</b> of the wooden chair
S1991.86	<i>Portrait of the Sixth Prince Yi</i>	1905		7	pink, red, purple, brown	cochineal applied as a wash over lead-based white for <b>pinks</b> ; cochineal mixed with lac as a wash over vermilion in deep <b>red</b> beads; cochineal mixed with Prussian blue (FORS) in <b>purple</b> in the cloud decoration in the seat cushion; cochineal used in mixture with lac dye and iron-based pigments in the <b>red-brown</b> wooden chair
S1991.98	<i>Spurious Portrait of the Jiaqing Empress</i>	ca. 1920–48		3	pink, purple	cochineal used as a wash and mixed with lead-based white in <b>pink</b> flower and beads; cochineal used in a mixture with ultramarine in <b>purple</b> cloud in the robe
S1991.102	<i>Portrait of the Seventh Prince Yi</i>	1911		8	pink, red, purple	cochineal used with lac dye in the <b>pink</b> and <b>red</b> cloud and dragon scales on the robe, and deep <b>red-pink</b> areas contain more cochineal; cochineal used in a mixture with lac dye, and Prussian blue and azurite in <b>purple</b> cloud designs; lac dye and Prussian blue possibly used as <b>purple</b> over an azurite robe
S1991.105	<i>Portrait of a Qing Courtier</i>	mid-late 19th century		6	pink, purple	cochineal applied over lead-based white for the bright <b>pink</b> crane in the carpet and <b>pink</b> beads; cochineal mixed with lac dye as a wash over azurite for <b>purple</b> shading on the robe; cochineal mixed with Prussian blue alone for the <b>purple</b> cloud detail in robe; cochineal mixed with Prussian blue and lac dye as a <b>purple</b> wash over lead-based white in dragon claw
S1991.117	<i>Portrait of a Qing Court Lady</i>	mid-late 19th century		2	pink, purple	cochineal found in <b>pink</b> spots in the carpet; cochineal mixed with Prussian blue for the <b>purple</b> flower in the carpet
S1991.135	<i>Portrait of a Qing Courtier, Possibly Jing Shou (d. 1889)</i>	late 19th century		5	pink	cochineal found only in bright <b>pink</b> beads as a wash over lead white; all other <b>pinks</b> and <b>purples</b> in the carpet and seat cushion created with lac dye.





**Figure 2.4.** Scene from *Landscape with Gibbons and Cranes*, formerly attributed to Qiu Ying, 18th century. Handscroll; silk; 27.7 × 271.1 cm (10 $\frac{7}{8}$  × 106 $\frac{3}{4}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1904.396. Detail of flowers in the tree (a), showing lac dye wash over white. The paper arrow indicates the location of the HPLC sample.



**Figure 2.5.** Scene from *Beautiful Ladies Riding*, formerly attributed to Giuseppe Castiglione (Lang Shining), mid-late 19th century. Handscroll; silk; 81.3 × 2669.5 cm (32 × 1051 in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.46. Detail of flowers (a), showing cochineal and lead-based white. The paper arrow indicates the location of the HPLC sample.

the setting, the robe, and the face and hands) or in which they used premixed colors.

The greater co-occurrence of the insect dyes found in portraits may also be due to the need for more variations in color to depict different motifs. In smaller paintings of landscape and genre scenes, by contrast, there may be only one element in which an insect dye was identified. While much of this discussion is based on portraits, it is possible that greater variation in the use of cochineal and lac dye will be found with further analysis of other painting types.

### Insect Dyes and Chinese Painting Techniques

The insect dyes lac and cochineal were used for a variety of shades including pink, red, purple, and brown, with the dye as a component in a mixture or used as a wash over another pigment. Washes are

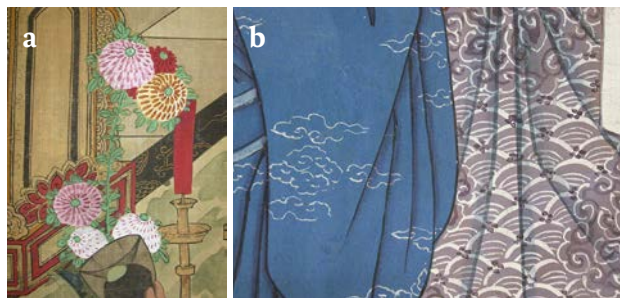
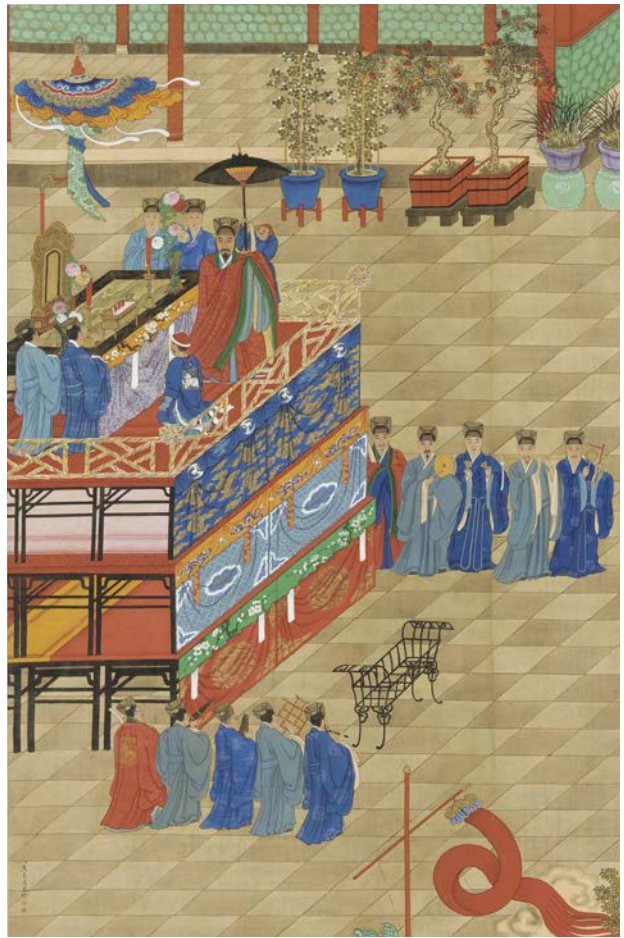
thin, translucent layers, often employed in Chinese paintings with dye-based colorants. They may be used similarly to the glazes found in oil paintings, but the colorant is not thickly bound as in oil paintings. Yu Feian (1988, 32, 62), quoting the *Technique of Painting in Colors* (Cai hui fa) (1621–44) by Wang Yi and the *Bamboo Manual* (Zhu pu xiang lu) (ca. 1318) by Li Kan, calls this technique “overlaid wash,” and so the term “wash” is used in this essay. Washes were used to create color, to modulate color intensity, or to create shadow, as described in historical painting manuals. The following discussion highlights these painting techniques, noting any differences between lac and cochineal.

#### *Pinks and Reds*

Pinks were generally used in the depiction of flowers as well as decorative elements of dragon robes, typically created with a combination of insect dye and



**Figure 2.6.** *Magpies in a Pine Tree, Ducks and Hollyhocks; with Spurious Signature*, 17th–19th centuries. Hanging scroll; silk; 185.7 × 108.5 cm (73 $\frac{1}{8}$  × 42 $\frac{11}{16}$  in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.138. Detail of pink peonies (a), showing lac dye and lead-based white.



**Figure 2.7.** *The Yongzheng Emperor's Nephew at a Daoist Ceremony for the Recovery of His Father*, attributed to Jiao Bingzhen (active 1689–1726), 1723–26. Hanging scroll; silk; 185.7 × 108.5 cm (73 $\frac{1}{8}$  × 42 $\frac{11}{16}$  in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.99. Detail of pink flowers (a), showing washes of lac dye over lead-based white. The red flower at the rear has washes of insect dye over cinnabar/vermillion. Detail of the purple textile (b), showing lac dye and indigo, which were mixed.



**Figure 2.8.** *Blending Soup in a Metal Tripod*, Gai Qi (1774–1829), 1816. Hanging scroll; silk; 115.4 × 54.6 cm (45 $\frac{7}{16}$  × 21 $\frac{1}{2}$  in). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Transfer from the United States Customs Service, Department of the Treasury, F1980.138. The paper arrow indicates the locations of the HPLC samples. Detail of the pink robe (a), showing lac dye. Detail of the red robe (b), showing lac dye details over cinnabar/vermilion.

lead white. For examples, see *Landscape with Gibbons and Cranes* (eighteenth century) (fig. 2.4), *Beautiful Ladies Riding* (nineteenth century) (fig. 2.5), *Magpies in a Pine Tree, Ducks and Hollyhocks; with Spurious Signature* (seventeenth–nineteenth centuries) (fig. 2.6), *The Yongzheng Emperor's Nephew at a Daoist Ceremony for the Recovery of His Father* (1723–26) (fig. 2.7), and *Blending Soup in a Metal Tripod* (1816) (fig. 2.8). In a few cases, XRF also identified cinnabar/vermilion, and it was most commonly found when the insect dye was present as lac dye. Presumably, the trace of cinnabar/vermilion was added to shift the color to red, as lac dye tends to be purplish in tone. Cochineal is typically a brighter pink, based on visual comparison, and no instances of cinnabar/vermilion were found in mixtures of cochineal and lead white.

For the rendering of flowers, historical painting treatises recommend the application of rouge (organic reds) as an “overlaid wash” over white. This method of applying washes is specifically mentioned

in the treatise *Painting Trivia* (Hui shi suo yan) (1797) by Ze Lang, which also states that additional applications of alum should be added over the rouge (cited in Yu 1988, 66). The presence of alum or gelatin in certain concentrations affects the color of lac and cochineal. In the paintings studied, there was wide variation in the pinks and reds achieved with insect dyes even when one or the other was used alone, but whether alum was intentionally utilized to modulate color in this fashion is not certain.

### Purples

Purples are most frequently seen in flowers, as in *Quail and Flowers* (eighteenth century) (fig. 2.9). They are also observed in robes, especially in decorative elements of dragon robes, and were typically created by insect dyes mixed with blues and modulated by lead white.

Most of the purple areas examined were in portraits dated to the Qing dynasty, where purples were



**Figure 2.9.** *Quail and Flowers*, formerly attributed to Zhao Boju 18th century. Album leaf; silk; 23.5 × 21.8 cm (9¼ × 8⅝ in). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1909.249c. Lac dye was used to create pinks and purples in this bird-and-flower painting. The purples were created with lac dye, indigo, and lead-based white. The pinks were created with lac dye and lead-based white.

most commonly found. In the majority of instances, the purple color was created with a mixture of lac dye and indigo (see table 2.3); in one example cinnabar/vermillion was mixed with indigo. Three paintings had two different purple mixtures in the same painting. For example, the portrait *Hongyan, Prince Guo (1733–1765), Reading in a Spring Garden (1750s)* (fig. 2.10) contains two different purples created with lac dye: one with indigo and cinnabar/vermillion, and the other an atypical mixture of lac dye with azurite.

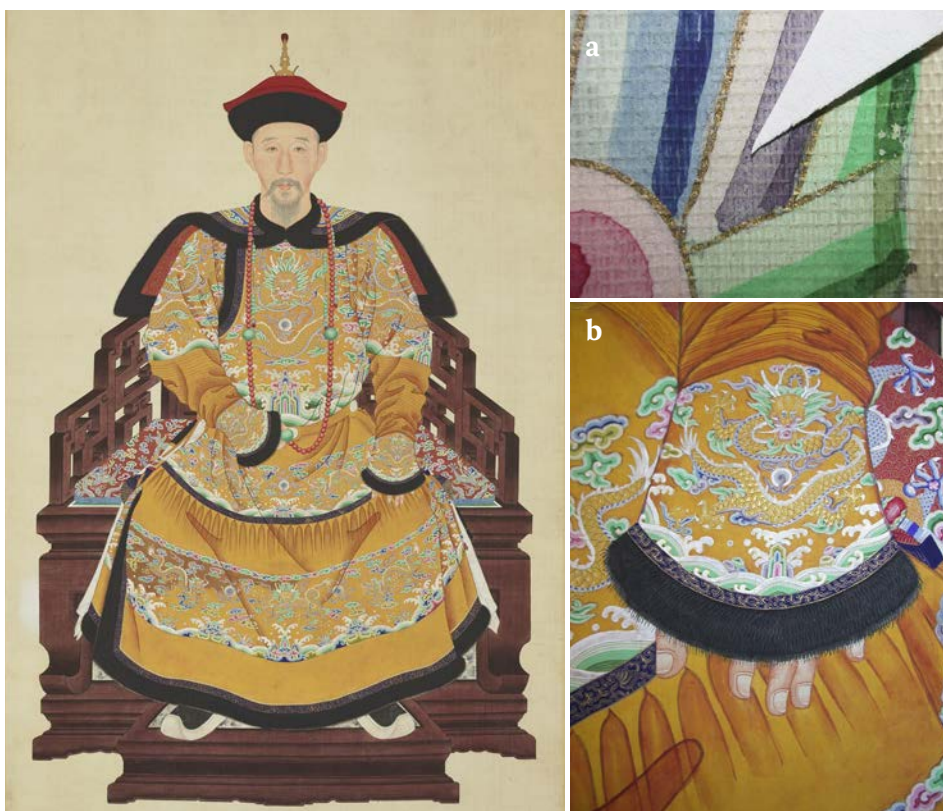
Purples made with cochineal were found in paintings dating to the nineteenth and twentieth centuries, most commonly created as a mixture using Prussian blue rather than indigo, as in *Portrait of Yinxiang, the First Prince Yi (1686–1730) (1905)* (fig. 2.11). An earlier example of the mixture of cochineal and Prussian blue was observed in *Small Birds and Morning Glories (F1980.152)*, but, as already noted, the date of this fan is contested. Only one cochineal and indigo mixture was identified even though Yu Feian (1988, 75–76)



**Figure 2.10.** *Hongyan, Prince Guo (1733–1765), Reading in a Spring Garden*, 1750s. Hanging scroll; silk; 162.7 × 107.7 cm (64⅞ × 42⅜ in). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, \$1991.48. This painting shows atypical purple mixtures. The purple of the robe of the central figure was created with lac dye, indigo, and cinnabar/vermillion. The purple of the robe on the figure on the left was created with lac dye and azurite.

specifically describes this mixture to render purple: “If flower petals are to be a velvety purple . . . it is necessary to first lay down a good ground of light indigo and then add several layers of wash in carmine, which will make a purple that issues from the red or a red that emerges from the purple, uncommonly beautiful and radiant.” In later painting manuals a combination of cochineal and ultramarine is recommended (Yu 1988), but this combination was identified in only one painting.

Yu Feian (1988, 75–76) cites separate applications of “red” and “blue” to generate purple areas, but purple areas created by red washes applied over a base of



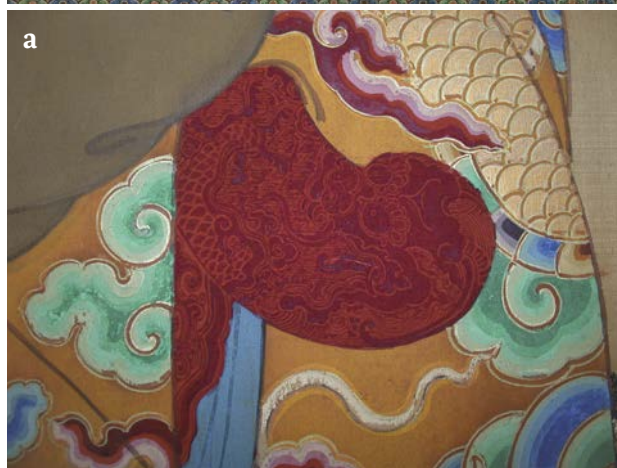
**Figure 2.11.** *Portrait of Yinxiang, the First Prince Yi (1686–1730), 1905.* Hanging scroll; silk; 186.7 × 121.9 cm (73½ × 48 in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, \$1991.84. Detail of the dragon robe (a), showing purple details created with cochineal and Prussian blue. The paper arrow indicates the location of the HPLC sample. Bright pink created with cochineal and lead white can also be seen to the left. Detail of gold in the dragon robe (b), showing a translucent cochineal wash over arsenic sulfide yellow to create the folds and shadows.



**Figure 2.12.** *Autumn Landscape with Birds and Berries and Rabbits*, traditionally attributed to Yi Yuanji (active mid–late 11th century), late 17th–18th centuries. Handscroll; silk; 41.8 × 288 cm (16⅞ × 113⅜ in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1909.201. Detail of berries (a), showing where lac dye was washed over cinnabar/vermillion to modulate color and create shadows. The wooden pointer indicates the location of the HPLC sample.

indigo were not found in this study. In the vast majority of paintings examined there were no observable red or blue brushstrokes; more commonly the purples appear premixed. A detail from Jiao Bingzhen's (active 1689–1726) (attributed) *Yongzheng Emperor's Nephew at a Daoist Ceremony for the Recovery of His*

*Father* (see fig. 2.7b) shows a purple robe in which the two colorants—lac dye and indigo—were clearly premixed before application to the silk. Premixed colorants can also be seen in the purple designs in the seat cushion in *Portrait of the Sixth Prince Yi* (see fig. 2.3c).



**Figure 2.13.** *Portrait of Daisan*, 18th–19th centuries. Hanging scroll; silk; 258.7 × 162.1 cm (101<sup>7</sup>/<sub>16</sub> × 63<sup>13</sup>/<sub>16</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, \$1991.74. Detail of the arm of the chair (a), showing lac dye wash over cinnabar/vermillion to create the deep red designs.

### Other Pigments

The insect dyes were often used as washes over other pigments to modulate color. In all painting types, this technique was most commonly found with cinnabar/

vermillion. This technique is specifically mentioned in two Qing dynasty texts, *Painting Trivia* and *The Mustard Seed Garden Manual of Painting*. In *Painting Trivia*, Ze Lang writes, “For washes of crimson, take second red [cinnabar/vermillion] as the ground layer, use a wash of light rouge six or seven times, then use thick rouge for a fine outline and it will be naturally bright and beautiful” (quoted in Yu 1988, 65). *The Mustard Seed Garden Manual of Painting* states “rouge red and vermillion produce the highest degree of red” (Sze 1956, 585–86).

*Autumn Landscape with Birds and Berries and Rabbits* (late seventeenth–eighteenth centuries) (fig. 2.12), traditionally attributed to Yi Yuanji (active mid–late eleventh century) but dated based on its Qing dynasty style shows an area (a) in which insect dye was applied over a base of cinnabar/vermillion to create the shadows in the berries. In *Portrait of Daisan* (eighteenth–nineteenth centuries) (fig. 2.13) lac dye was applied over cinnabar/vermillion to create the deep red designs of the arm of the chair. This technique can also be seen in the red flower in figure 2.7a and the robe details in figure 2.8b.

Insect dye washes were also used over other pigments to modulate color, although less frequently. In *Portrait of Yinxiang, the First Prince Yi* (1686–1730) (see fig. 2.11b), a cochineal wash over arsenic sulfide yellow was used to create the folds and shadows in the gold dragon robe. These and many other examples demonstrate that cochineal and lac dye were used in the same manner. Another common combination was the use of an insect dye wash over azurite to indicate shadow. This technique can be seen in *Hongyan, Prince Guo* (1733–1765), *Reading in a Spring Garden* (see fig. 2.10), where a thin wash of lac dye was applied over azurite to create the purple robe of the figure on the left. This technique was often encountered in the dragon robes of portraits (see chap. 4).

Insect dyes were also commonly found with iron-based pigments to create a ruddy brown. This color was most frequently encountered in the wooden chairs used in the portraits, as in figure 2.3, *Portrait of the Sixth Prince Yi*, in which lac dye was used in combination with iron-based pigments to render the red-brown wood of the chair. In *Portrait of Yinxiang, the First Prince Yi* (1686–1730) (see fig. 2.11), lac dye and cochineal were found in the colorant for the chair. Insect dyes were also often found in pink flesh tones and lips in combination with lead white, frequently with the addition of cinnabar/vermillion and iron-based pigments.



**Figure 2.14.** *Enjoying a Meal on Board a Boat*, 16th–17th centuries. Fan mounted as an album leaf; silk; 23.2 × 21.1 cm (9 $\frac{1}{8}$  × 8 $\frac{5}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1911.490. The pinks in the robes were created with cinnabar/vermilion and lead-based white; no organic red dyes were detected.

## Other Reds

In six paintings analyzed by HPLC, no dyes were identified in pink or purple areas, and analysis with FORS did not indicate the presence of insect dye. These areas were sampled to investigate the possible presence of other organic reds. In each case, the color is believed to be due to an inorganic pigment only, usually cinnabar/vermilion or iron-based pigments, based on FORS and XRF results. Most typically, the paint appears to be a very thin wash of finely ground cinnabar/vermilion, sometimes mixed with lead white, as in *Enjoying a Meal on Board a Boat* (sixteenth–seventeenth centuries) (fig 2.14).

Pink areas are much more common in Qing dynasty paintings than those produced during the Ming dynasty: Ming paintings have a much more restricted palette, although pink, when it appears, seems to have been more often created by the use of inorganic pigments. While the number of Ming dynasty paintings analyzed in this study is limited, the results do point to the wider availability of organic reds during the Qing dynasty than during the Ming

dynasty. The expanded palette and use of organic reds could also simply reflect changes in painting styles.

Cinnabar/vermilion and lead white mixtures are described in several historical painting formulations for pink (Yu 1988) but were rarely encountered in this study. Most of the paintings with these mixtures date to the Ming dynasty, and in all cases the inorganic red was determined to be finely ground cinnabar/vermilion, red lead (in one instance), or iron-based pigments. The use of inorganic pigments may be less common for the creation of pink because cinnabar/vermilion can be orange in tone and much less dye than pigment is necessary to obtain light pinks and purples.

Other dyes were found in only three instances: madder, indicated by the identification of purpurin, one of its major coloring materials; an unidentified yellow dye; and an unidentified red dye that is likely a synthetic azo dye. The sample containing purpurin is likely from a later restoration. It is possible that other dyes were present but not located. Other organic reds including safflower (carthamin), sappanwood, and brazilwood (haematoxylin) do not have obvious or characteristic absorption bands in FORS and may have remained undetected. Additionally, many of these dyes are fugitive, and their primary dye component may have deteriorated, or they may not be as efficiently extracted by the procedures used for this study (Koren 2001; Laursen and Mouri 2013). If madders and other dyes were present in these samples but deteriorated, they may not have been detected by the exceedingly small samples taken for HPLC analysis, especially as in landscape and genre paintings the paint layer can be extremely thin or applied directly to the substrate, making sampling very difficult.

## Conclusions

All the organic red dyes identified in Chinese paintings in this study were scale insect dyes—lac dye or cochineal. Lac dye was the only organic red colorant found in Ming and in early Qing paintings, and other dyes such as safflower or madder, whose use is suggested historically, were not found. Although cochineal may have been available in China as early as the sixteenth century given its source in the Americas, its earliest use as a painting material in the Freer and Sackler collections examined was in a painting dating to the early eighteenth century. Moreover, based on this survey, cochineal does not appear to be a common painting material until the nineteenth century. Lac and cochineal were used in similar

fashion, although the separate uses of the two dyes within a single painting suggest that Chinese artists distinguished between the two. This chapter presents results for paintings in the Freer Gallery of Art and Arthur M. Sackler collections. Future analysis of paintings with a wider geographic distribution than represented here will help form a clearer picture of the painting materials available and techniques used during the Ming and Qing dynasties in China.

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# 3

## Blue Pigments in Paintings from the Ming and Qing Dynasties

Yae Ichimiya and John Winter

### Introduction

Blue pigments are traditionally prepared from either inorganic mineral pigments or organic dyes derived from plants. During the Qing dynasty (1644–1912), synthetic colorants, first produced in Europe, began to be available to artists in China. The earliest of these was Prussian blue, first synthesized in Berlin in 1704. This chapter looks at blue pigments identified in paintings from the collections of the Freer Gallery of Art and the Arthur M. Sackler Gallery, with a particular focus on the introduction of Prussian blue to China. Its usage is compared to that of other blue colorants and to its introduction and usage in Japan.

### European Influences in the Qing Court

Under the patronage of the Qing court, many types of painting flourished in China, from the decoration of rooms with paintings to the production of hanging scrolls and handscrolls. Regional schools of art were fostered by the emperors, who also employed court

painters (Nie 1997). Painting styles incorporated traditional approaches as well as foreign techniques and creative blends of Chinese and European influences.

European painting techniques such as realism, illusionism, and three-dimensionality began to be introduced into China in the fifteenth and sixteenth centuries by Jesuit missionaries and merchants from Europe (Chou and Brown 1985; Cahill 1982; Miyagawa 1983; Osswald 2020). Jesuit missionaries such as the Italian Giuseppe Castiglione (Lang Shining, 1688–1766) and the Frenchman Jean-Denis Attiret (Wang Zhicheng, 1702–1768) served as court painters during the Qing dynasty (Wang 1995) and were supported by emperors in the Kangxi (1654–1722) through the Qianlong (1735–1796) periods (Chou and Brown 1985). European painting styles contributed to a new “court” style in Qing paintings (Wang 2007) that developed from a mixture of elements from both European and Chinese painting styles (*zhong xi he bi*). These were also supported by the Kangxi and Qianlong emperors (Chou and Brown 1985; Nie 1997). Court painters such as Yuan Jiang (ca. 1671–ca. 1746), who was from

Yangzhou and active in the Kangxi era, combined styles descended from Northern Song (960–1127) landscape painting with a European style of realism (Miyagawa 1983). The synthesis of European and Chinese styles is evident in *The Qianlong Emperor as Manjushri, the Bodhisattva of Wisdom* (mid-eighteenth century) (F2000.4) (see fig. 4.1), in which the face of the emperor is painted by Castiglione while the rest of the painting is associated with the imperial workshop. Because of the limited freedom afforded court painters, the imperial court's control of many aspects of international trade, and the limited number of people who saw the Jesuit paintings (Chou and Brown 1985), European influence would be expected to be strongest in paintings produced in the imperial court or near the official trading port of Canton (today Guangzhou). It is also through this port that European pigments were introduced to China.

## Blue Colorants Found in Chinese Paintings

Several traditional blue colorants have been identified in Chinese paintings. Most common are azurite and indigo, which have a long history of use (see chap. 1). Ultramarine and smalt were also occasionally found. Summaries of available information on pigments and dyes found in East Asian paintings are given in publications by Elisabeth West FitzHugh (2003) and John Winter (2008), and reviews of indigo are found in publications by Helmut Schweppe (1997) and FitzHugh (2003).

### *Traditional Blue Colorants*

Azurite, the copper carbonate mineral ( $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), is one of the most important mineral colors in Chinese paintings. Different shades of blue, ranging from bright to dark, can be produced by differences in the heating and grinding of this mineral. Multiple groups are characterized by particle size, or grades, with larger particles producing darker blues and fine powders the lighter blues. The particle sizes are separated by washing and levigation in water, creating darker to lighter blue pigments (Winter 2008).

Indigo was used as a vat dye and an organic pigment in China as early as the third century B.C.E. (Song 1966). An object of early date in which indigo was identified is a painted clay statue of the Tang dynasty (618–907) from Dunhuang, where it was found also as a blue layer under azurite in a wall

painting (Gettens and Stout 1942, 121). According to E-tu Zen Sun and Shiou-chuan Sun in the notes in *T'ien-kung k'ai-wu: Chinese Technology in the Seventeenth Century* (Song 1966, 78), the methods for preparing indigo were described in the fifth century in *Essential Arts of the Common People* (Qimin yaoshu). Several names exist in Chinese for this organic colorant, such as *dian hua* and *hua qing*. The indigo-producing plant *Polygonum tinctorium* (dyer's knotweed) is indigenous to China, although several indigo species were imported from elsewhere. The tropical species *Indigofera tinctoria* was imported via Persia to China as early as the seventh to the ninth century (the Tang dynasty) and used as a cosmetic. *Isatis tinctoria* (European woad) is also found in China, although it is believed to have a late introduction, possibly in the sixteenth century. *Isatis indigotica* (Chinese woad), traces of which remain in eastern China (around Jiangsu), is termed *tianqing* or *songlan* in Chinese. A mid-nineteenth-century French delegation described it as one of the most common sources of indigo in China (Cardon 2007, 379). Plants that produce indigo contain the molecular precursors of indigotin ( $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2$ ), a blue colorant that forms after a long process of fermentation of the leaves (Winter 2008; Cardon 2007).

Ultramarine ( $(\text{Na,Ca})_8(\text{AlSiO}_4)_6(\text{SO}_4,\text{S,Cl})_2$ ) is extracted from lapis lazuli, of which the mineral lazurite is the essential blue constituent (Winter 2008). Natural ultramarine was found in China in painted sculpture dated to the fifth century in the Yungang and Mogao Caves (Wang 1995; Winter 2008). The pigment was also identified in Chinese beads from the eighth to the fourth century B.C.E., where it was used with Han blue (barium copper silicate,  $\text{BaCuSi}_4\text{O}_{10}$ ) and Han purple (barium copper silicate,  $\text{BaCuSi}_2\text{O}_6$ ) (Ma et al. 2006).

Smalt, blue in color, is an artificial pigment composed of potassium-rich glass. Cobalt oxide, made by roasting minerals containing cobalt sulfides or arsenides, is incorporated into the glass, turning it blue, and this deep blue glass is pulverized to produce a blue pigment. Impurities such as copper, magnesium, manganese, nickel, bismuth, barium, calcium, sodium, arsenic, iron, copper, and aluminum may be found in smalt (Ajò et al. 2004; Magurn 1942; Mühlethaler and Thissen 1993). Smalt has been found in paintings from several parts of Asia, including in two wall paintings in the Harvard Art Museums, in a wall painting from Kara Khoto in Central Asia, dated perhaps as early as between the eleventh and the thirteenth century, and in a wall painting of a seated

Buddha of the Ming dynasty (1368–1644) (Magurn 1942). Smalt was not found in Japanese paintings in the collection of the Freer Gallery of Art earlier than the late seventeenth century (FitzHugh 2003). The earliest example of the use of smalt on paper or silk in East Asia is in a sixteenth–early seventeenth-century Japanese print in the Fogg Museum, Harvard Art Museums (Magurn 1942). Artists in Europe began to use smalt about 1517–40 (Berrie 2015). The earlier occurrence of smalt in mainland Asia than in Europe may indicate that smalt was Asian in origin (Magurn 1942; FitzHugh 2003). It was beyond the scope of this project to determine if smalt was imported or made in China during this period, although recent research suggests that it has been imported since the Ming dynasty (Xia et al. 2019).

### *European Synthetic Blue Colorants*

Artificial azurite (blue bice, blue verditer) was available in Europe as early as the seventeenth century, and recipes for copper blue pigments are known from the twelfth century (MacTaggart and MacTaggart 1980). Blue synthetic copper carbonates were also available in Europe during the nineteenth century but have not been found in Asian paintings (Winter 2008), perhaps because of the ready availability of natural azurite from Chinese ores.

Methods of manufacturing synthetic ultramarine were discovered in 1828. Ji Juan and Zhang Jiafeng (2011) write that it was used in mural painting in the Qing dynasty. It is not certain, however, that the pigment was being produced in China at the time. The production of synthetic ultramarine in China by a Chinese chemist first occurred in 1927 (Winter 2008; Ji and Zhang 2011). Synthetic ultramarine has been found elsewhere in Asia prior to its manufacture in China, for example in a votive tablet in Japan dated 1864 (Kuchitsu and Shimomura 2002). Synthetic ultramarine is chemically identical to natural ultramarine but may be differentiated from the natural pigment by the small, uniform particle size and the lack of grains from accessory minerals.

The synthetic blue pigment Prussian blue became available in China in the eighteenth century. First made in Berlin in 1704, Prussian blue was precipitated by adding a solution of ferric salt to a solution of sodium ferrocyanide (Winter 2008). Prussian blue is ferric ferrocyanide ( $M^I\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ ), where  $M^I$  is potassium, ammonium, or sodium. The typical compositions are  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$  and  $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ . One current commercial production method is oxidation of a mixture of ferrous

sulfate, sodium ferrocyanide, and ammonium sulfate in an acidic bichromate solution. The particle size of Prussian blue is in the colloidal range and appears similar to indigo under observation with the microscope. Both indigo and Prussian blue have a similar dark blue color and fine particles, although Prussian blue can create a brighter blue compared to indigo. The reflectance of indigo and ultramarine in the red range above 650 nm is high, while Prussian blue does not show a high reflectance in this range. The characteristic infrared (IR) absorption band of Prussian blue is approximately  $2083 \text{ cm}^{-1}$  (Leona and Winter 2001).

Commercial manufacture of Prussian blue and its use as an artists' pigment seem to have started shortly after its first production (Berrie 1997). The earliest use in European paintings has been dated to 1709 (Bartoll 2008), and it was widely used in easel painting in the eighteenth century (Berrie 1997). In the United States, Prussian blue was used as early as 1723 as an interior wall paint (Berrie 1997). These facts suggest the rapid and widespread adoption of Prussian blue, but when it was first imported into China is less certain. Trade records show that a significant quantity of Prussian blue was exported to China for the purpose of coloring old green tea to look fresh (Morton 1980; Russell 2000). But private trade, carried out by ships' commanders and officers, was not necessarily recorded at the official trading port of Canton and may have provided an early route for the introduction of Prussian blue to China. The earliest record of Prussian blue in China is in a private trade dated to 1764 (Tuck 1999). Documentation of known Prussian blue trade and use is listed in table 3.1.

Several sources report how the production of Prussian blue began in China (Bowra 1874; Warington 1845; M'Culloch 1845; Bailey 2012). It is said that after a common Chinese sailor learned the manufacturing method in England, he introduced it to the Chinese so they could also prepare "native Prussian blue." This story is related in John Ramsey M'Culloch's commercial dictionary:

Blue is a favourite colour with the Chinese: and in 1810–11 the imports of Prussian blue into Canton from England amounted to 253,200 pounds. But for some years past the Chinese have not imported a single pound weight. The cause of the cessation of the trade deserves to be mentioned. A common Chinese sailor, who came to England in an East Indiaman, having

**Table 3.1.** The Prussian blue trade with specific reference to China.

1704	Prussian blue is first synthesized in Berlin.
No later than 1709	The Royal Academy of Arts in Berlin begins to send samples of Prussian blue to painters across Europe (Bartoll 2008). Prussian blue begins to be sold in Europe.
1709	Prussian blue is seen in paintings by the French painter Antoine Watteau (Bartoll 2008).
1710	A recipe for Prussian blue is published, and it is mentioned in scientific literature (Bartoll 2008; Kraft 2008).
Before 1722	Prussian blue is used by the Dutch painter Adriaen van der Werff (B., R. D. 1964).
1723	A receipt for wall paint for Trinity Church, Boston, lists Prussian blue (Berrie 1997).
1724	The preparation for Prussian blue is published by John Woodward of the Royal Society in London, in <i>Philosophical Transactions</i> (B., R. D. 1964; Sasaki 1985; Bailey 2012).
1757	Canton (today Guangzhou) is decreed by the Chinese emperor to be the only port open to foreign trade, where it must be conducted via licensed Chinese merchants (Ebrey 1996).
1764–1800	Private trade is conducted in Canton. Many materials including Prussian blue are traded privately between England and China at Canton, and they are not recorded in Chinese customs house books (Tuck 1999).
About 1770	A London manufacturer, Wilkinson, begins production of Prussian blue (Bailey 2012).
1775–76	4000 Tls (taels, £1 = 3 taels, currency unit) of Prussian blue are imported in private trade at Canton between England and China (Pritchard 1957).
1778	“Bleu de Prusse de diverse nuances” is offered for sale in Jean Félix Watin, <i>L’Art du peintre, doreur et vernisseur</i> (Liege, 1778) (B., R. D. 1964).
1782–97	Prussian blue is sporadically imported to Japan from China, and there is no evidence for imports from other countries during this period (Leona and Winter 2003; Smith 1998).
1785–86	24200 Tls of Prussian blue are imported into Canton from England through private trade, doubling 10 years later in 1795–96. Imports continue to increase, with 67020 Tls in 1805–06 (Pritchard 1957).
1809	3387 piculs of blue (1 picul = about 60 kg) are imported into China (blue may include Prussian blue as well as other blue colorants) (Pritchard 1957).
1810	Price of Prussian blue is mentioned in the Hamilton family’s private trading record: 100 dols. per picul (dols is a Spanish unit of currency) of Prussian blue (Sasaki 1985).
1810–11	1899 piculs or 253,200 pounds of Prussian blue are imported into Canton from England (M’Culloch 1847, 366).
1811–19	41,971 £ (currency unit) of blue are imported into China from England (blue may include Prussian blue as well as other blue colorants) (Pritchard 1957).
1815–24	The Canton diary mentions eleven ships from the British East India Company arriving in 1815 in Canton carrying Prussian blue, and a steady trade in each of the following years (Bailey 2012). At the same time, private trade continued and 13563 £ of Prussian blue was imported into Canton from England in 1815–16 through private trade (Pritchard 1957).
1824 onward	Prussian blue is imported from China to Japan in large amounts at lower cost than previous years (Leona and Winter 2003; Miyashita 1995; Smith 1998).
1825–26, 1833–34	No mention of Prussian blue is made in private trade records at Canton (Sasaki 1985).
1827	Prussian blue is listed as “no demand” in the trading at Canton (Sasaki 1985).
1828 or earlier	<i>Canton Register</i> reports Prussian blue is no longer imported into Canton because the Chinese supply is currently manufactured in China. Precise date of the opening of the Chinese factory is unknown, although it may be as early as the 1820s ( <i>Canton Register</i> 1828; Warington 1845, 80; Bowra 1874; Sasaki 1985; Bailey 2012).
1828–30	A drawing showing a shop in Canton with an advertisement for Prussian blue was created for John Reeves (Sasaki 1985).
1842	Treaty of Nanking (today Nanjing) following the First Opium War opens four ports, in addition to Canton, to foreign trade, including Shanghai.
1875	Archdeacon of Hong Kong describes walking to the Prussian blue factory in Canton (Bailey 2012).

frequented a manufactory where the drug was prepared, learned the art of making it, and on his return to China he established a similar work there with such success that the whole empire is now supplied with native Prussian blue (M’Culloch 1847, 366).

M’Culloch’s assertion about the production of Prussian blue in China is supported by trade records showing that China discontinued importing Prussian blue by 1825–26 (Pritchard 1957; Bailey 2012) and that in 1827 there was “no demand” at Canton (Sasaki 1985). A report from the *Canton Register* (1828) states

**Table 3.2.** Number of Chinese paintings in which blue pigments were identified (*n* = 222).

Blue Pigments	All Paintings except Portraits ( <i>n</i> = 185)	Portraits ( <i>n</i> = 37)	Total
Azurite	108	33	141
Indigo	152	27	179
Ultramarine	3	8	11
Smalt	3	3	6
Prussian blue	4	10	14
Cobalt blue	1		1

Note: some paintings contain more than one blue pigment.

**Table 3.3.** Number of Chinese paintings in which blue pigments were identified before and after the beginning of the 18th century (Prussian blue invented 1704).

Blue Pigments	10th–17th centuries ( <i>n</i> = 63)			18th century and later ( <i>n</i> = 159)		
	All Paintings except Portraits ( <i>n</i> = 62)	Portraits ( <i>n</i> = 1)	Total	All Paintings except Portraits ( <i>n</i> = 123)	Portraits ( <i>n</i> = 36)	Total
Azurite	36	1	37	72	32	104
Indigo	42	1	43	110	26	136
Ultramarine	2	0	2	1	8	9
Smalt	0	0	0	3	3	6
Prussian blue	0	0	0	4	10	14

Note: some paintings contain more than one blue pigment. Two of the paintings with smalt (*Travelers Crossing a Mountain Stream* [F1909.247a], and *Two Figures amidst Clouds* [F1909.398a]) are dated to the Qing dynasty, which began in 1644.

that the Chinese were manufacturing their own supply of Prussian blue by 1828.

The application of Prussian blue as a pigment in paintings is mentioned in several sources, but these are without analytical confirmation. A drawing of a Chinese pigment shop at Canton in the John Reeves Collection at the British Museum, dated ca. 1828–30, displays an advertisement for Prussian blue (Sasaki 1985). The British East India Company’s chief inspector of tea at Canton, John Reeves (resident in Canton 1812–31), had local Chinese draw fish and other subjects that have been visually examined and said to contain Prussian blue (Sasaki 1985), but no scientific methods are stated to have been used in its identification. More recently Kate Bailey (2012) studied botanical paintings sent by Reeves to London between 1817 and 1830. After carrying out polarized light microscopy (PLM) and microchemical testing on loose pigments from the bindings, she suggested Prussian blue was present. However, studies by Sotiria Kogou and colleagues (2015) of thirty-two of the paintings were not able confirm the finding.

Yu Feian (1988, 30) claims that the impact of European pigments in China began after the First Opium War (1839–42), when

foreign chemical pigments were imported in increasingly large amounts. By the first year

of the Xianfeng reign (from 1851 on), foreign blue (made in Germany), foreign green (Grumbacher brand, made in Germany) and carmine (this carmine was made in Japan, England, and Germany in many types) were used everywhere in dyeing textiles, in the colored paintings done on architecture, and in folk artisans’ paintings. The reason for this is that they were inexpensive, gave good results, and were convenient to use. Thus, first the indigo-growing and indigo dye-manufacturing industries broke down, followed by safflower and madder cultivation. “Foreign blue” and “Grumbacher green” replaced azurite and malachite in painting architecture in color.

This assertion that the foreign green in the Xianfeng reign was made by Grumbacher may reflect the fact that Yu Feian was writing in the twentieth century, not describing the situation from the perspective of the nineteenth century. The American color supplier, Grumbacher, was founded in 1905; we did not find other pigment suppliers of that name.

Yu (1988, 14) also states that by the end of the Guangxu era (1875–1908), foreign indigo was used everywhere to dye cloth, and Chinese painters had changed their practice to use Prussian blue instead of indigo.

**Table 3.4.** Number of Chinese paintings with azurite and/or indigo, 18th century and later ( $n = 152$ ).

Blue Pigments	All Paintings except Portraits	Portraits	Total	Notes [n = total painting number (n = portraits)]
Azurite only	7	1	8	
Indigo only	47	0	47	
Azurite + indigo	60	19	79	
Azurite + indigo + other blues	3	6	9	with: ultramarine 1(1), Prussian blue 2(2), smalt 4(2), Prussian blue + ultramarine 1(1), cobalt blue (may be retouch)1(0)
Azurite + other blues	2	6	8	with: ultramarine 3(2), Prussian blue 3(2), ultramarine + Prussian blue 2(2)
Indigo + other blues	0	1	1	with: smalt 1(1)

**Table 3.5.** Number of Chinese paintings with Prussian blue, 18th century and later ( $n = 14$ ).

Blue Pigments	All Paintings except Portraits	Portraits	Total
Prussian blue only	3	1	4
Prussian blue + azurite	1	2	3
Prussian blue + azurite + indigo	0	2	2
Prussian blue + azurite + indigo + ultramarine	0	1	1
Prussian blue + azurite + ultramarine	0	2	2
Prussian blue + ultramarine	0	2	2

**Table 3.6.** Occurrence and use of Prussian blue.

Accession Number	Title	Date	Artist	Other Blue Pigments	Colors Where Prussian Blue Is Found	Notes
<b>Paintings</b>						
F1911.167i	<i>A Toy-Peddler and Children</i>	19th century	traditionally attributed to Li Gonglin	none	blue	Prussian blue as a <b>blue</b> wash on lead-based white on a boy's head
F1980.152	<i>Small Birds and Morning Glories</i>	possibly early 18th century	Jiang Tingxi	azurite	blue, purple, green	Prussian blue as <b>blue</b> over azurite in flowers Prussian blue as <b>purple</b> with cochineal in birds Prussian blue as <b>purple</b> in flower buds Prussian blue as <b>green</b> in veins on leaves
F1980.163	<i>Bean Vines and Insects</i>	mid-20th century	forgery of Qi Baishi	none	green	Prussian blue as <b>light green</b> in a bean
F1980.168	<i>Bamboo, Orchid and Rock in a Tub</i>	mid-late 19th century	Luo Qing	none	blue, green	Prussian blue as <b>blue</b> in the tub Prussian blue as <b>green</b> in a leaf with organic yellow
<b>Portraits</b>						
S1991.65	<i>Portrait of Lady Hejia, Secondary Wife of Prince Zaizhi</i>	late 19th century		azurite, indigo, ultramarine	blue, purple, green	Prussian blue as a <b>dark blue</b> wash over ultramarine and cinnabar/vermillion mixture in robe Prussian blue as <b>dark purple</b> with cochineal as spots in the carpet and in medallions in robe Prussian blue as <b>dark green</b> mixture with gamboge as dots over emerald green in carpet and robe medallions Prussian blue as <b>yellow-green</b> with gamboge and emerald green in petals and leaves in carpet
S1991.84	<i>Portrait of Yinxiang, the First Prince Yi (1686–1730)</i>	1905		ultramarine	purple, green, red-brown	Prussian blue as <b>purple</b> with cochineal in lower part of robe Prussian blue as <b>green</b> with gamboge in triangular detail on robe Prussian blue as <b>green</b> (possibly layered) over emerald green and barium sulfate as cloud design on robe Prussian blue as <b>red-brown</b> with lac and cochineal in chair
S1991.86	<i>Portrait of the Sixth Prince Yi</i>	1905		ultramarine	purple	Prussian blue as <b>purple</b> with cochineal in cloud decoration in robe; greens were not analyzed

Accession Number	Title	Date	Artist	Other Blue Pigments	Colors Where Prussian Blue Is Found	Notes
S1991.102	<i>Portrait of the Seventh Prince Yi</i>	1911		azurite, indigo	purple, green	Prussian blue as <b>purple</b> with azurite, lac dye, and cochineal as a minor component in cloud in seat cushion Prussian blue as <b>green</b> with emerald green in cloud in seat cushion
S1991.105	<i>Portrait of a Qing Courtier</i>	mid-late 19th century		ultramarine, azurite	purple	Prussian blue as <b>purple</b> with cochineal in cloud design on robe Prussian blue as <b>purple</b> in pattern in carpet (red not analyzed)
S1991.117	<i>Portrait of a Qing Court Lady</i>	mid-late 19th century		azurite, ultramarine	blue, purple, green	Prussian blue as <b>blue</b> in shading on dragon's snout on robe Prussian blue as <b>blue</b> in area of blue bead Prussian blue as <b>blue</b> with azurite and unidentified organic red in the robe Prussian blue as <b>purple</b> with cochineal and lead white in a flower in carpet and in multiple shades Prussian blue as <b>dark green</b> in spots on stripe pattern in carpet
S1991.119	<i>Portrait of Chinese Woman in a Kingfisher Headdress</i>	19th–early 20th centuries		azurite	purple	Prussian blue as <b>purple</b> with unidentified red insect dye in spot decoration on carpet Prussian blue as dark <b>purple</b> with possible ink layer in diamond pattern of robe
S1991.122	<i>Portrait of Princess Shouzang (1829–1856), Fifth Daughter of Emperor Daoguang</i>	mid-19th century or later		azurite	blue, purple, green	Prussian blue as <b>dark blue</b> over azurite in robe Prussian blue as <b>dark blue</b> as dot on carpet Prussian blue as <b>light blue</b> with lead white in carpet stripe under red dots Prussian blue as <b>dark green</b> with gamboge over atacamite in carpet and robe details Prussian blue as <b>light and medium purple</b> with lead white and lac dye in robe details Prussian blue as <b>olive green</b> with lead white and an unidentified component in carpet field and stripe on robe Prussian blue as <b>olive green</b> in dark spot on carpet
S1991.135	<i>Portrait of a Qing Courtier, Possibly Jing Shou (d.1889)</i>	late 19th century		azurite, indigo	blue, purple, green	Prussian blue as <b>deep blue with azurite</b> in robe Prussian blue <b>possibly as grayish blue</b> with indigo in carpet Prussian blue as <b>light purple</b> with lac dye, lead white, and azurite in carpet spots and robe stripes Prussian blue as <b>yellow-green</b> with gamboge in stripe at side of robe Prussian blue as <b>dark green</b> with gamboge as dots over medium green in carpet
S1991.137	<i>Portrait of Mother Mujia</i>	ca. 1890		none	blue	Prussian blue as <b>dark blue</b> in hair accessory, carpet flower detail, and blue line on chair Prussian blue as <b>light blue</b> with lead white in the background

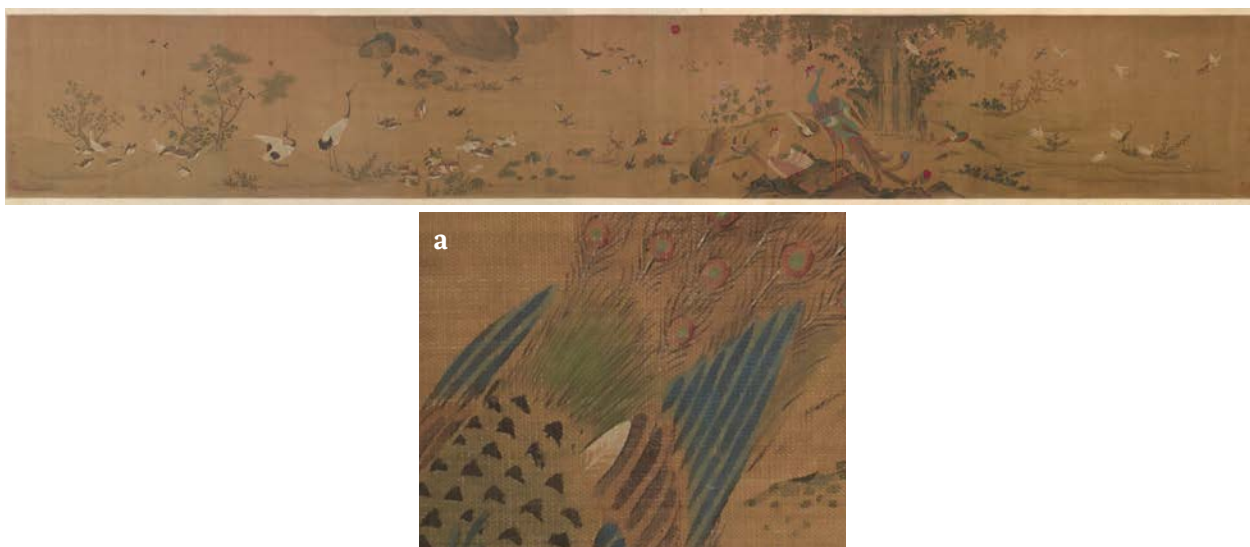
\* = the term cochineal is used when carminic acid was found with HPLC

## Blue Pigment Identification

For the analysis of blue pigments, Chinese paintings from the Freer Gallery of Art and the Arthur M. Sackler Gallery were examined under the microscope and using PLM, x-ray fluorescence (XRF), x-ray diffraction (XRD), fiber optics reflectance spectroscopy (FORS), and Fourier transform infrared spectroscopy (FTIR) (see app. 1).

Azurite, indigo, ultramarine, smalt, cobalt, and Prussian blue were all identified in the paintings studied. Azurite and indigo were found in a majority of the paintings from the Song (960–1279) and Yuan (1279–1368) dynasties. Ultramarine was identified in two Song paintings from Dunhuang (for more details, see chap. 1). Detailed results for each painting are given in appendix 5. Tables 3.2 and 3.3 show the frequency of each pigment in portraits and other types





**Figure 3.1.** *A Hundred Birds Worship the Phoenixes*, formerly attributed to Xu Xi, 18th century. Handscroll; silk; 34.3 × 236.9 cm (13½ × 93¼ in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1909.218. Although azurite blue was often applied in a thick layer, here (a) a thin layer of azurite was used effectively over lines drawn by ink.



**Figure 3.2.** *Two Crested Birds on a Branch; Autumn Leaves*, formerly attributed to Zhao Boju, 18th century. Album leaf; silk; 23.4 × 21.8 cm (9¼ × 8⅞ in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1909.249h. Detail of the features (a), showing varieties of blue tones from dark blue to light blue, achieved either by varying the azurite grain size or by utilizing a heating process during pigment preparation.

of paintings, before (including paintings from the Song, Yuan, and Ming dynasties) and after the synthesis of Prussian blue in 1704. Table 3.4 lists the number of paintings in which azurite and indigo were used alone, together, and with other blues. Table 3.5 provides similar information for Prussian blue. Table 3.6 gives details on the use of Prussian blue in fourteen paintings dated to the eighteenth century and later.

#### *Azurite and Indigo in Paintings Dated to the Eighteenth Century or Later*

Azurite was found in 104 paintings dated to the eighteenth century or later, either as blue or as a blue component in mixtures. Azurite blue was often applied in a thick layer. However, for background color it was sometimes applied as a thin layer, or, as seen in *A Hundred Birds Worship the Phoenixes* (eighteenth



**Figure 3.3.** *Palace Ladies and Children*, Ding Guanpeng, mid-18th century. Handscroll; paper; 17.4 × 93.5 cm (6<sup>7</sup>/<sub>8</sub> × 36<sup>13</sup>/<sub>16</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Transfer from the United States Customs Service, Department of the Treasury, F1980.126. Detail of a child's blue robe (a), showing azurite used as dark blue and light blue. Also partially visible is a woman whose clothing includes purple and green in which indigo was used as the blue component.

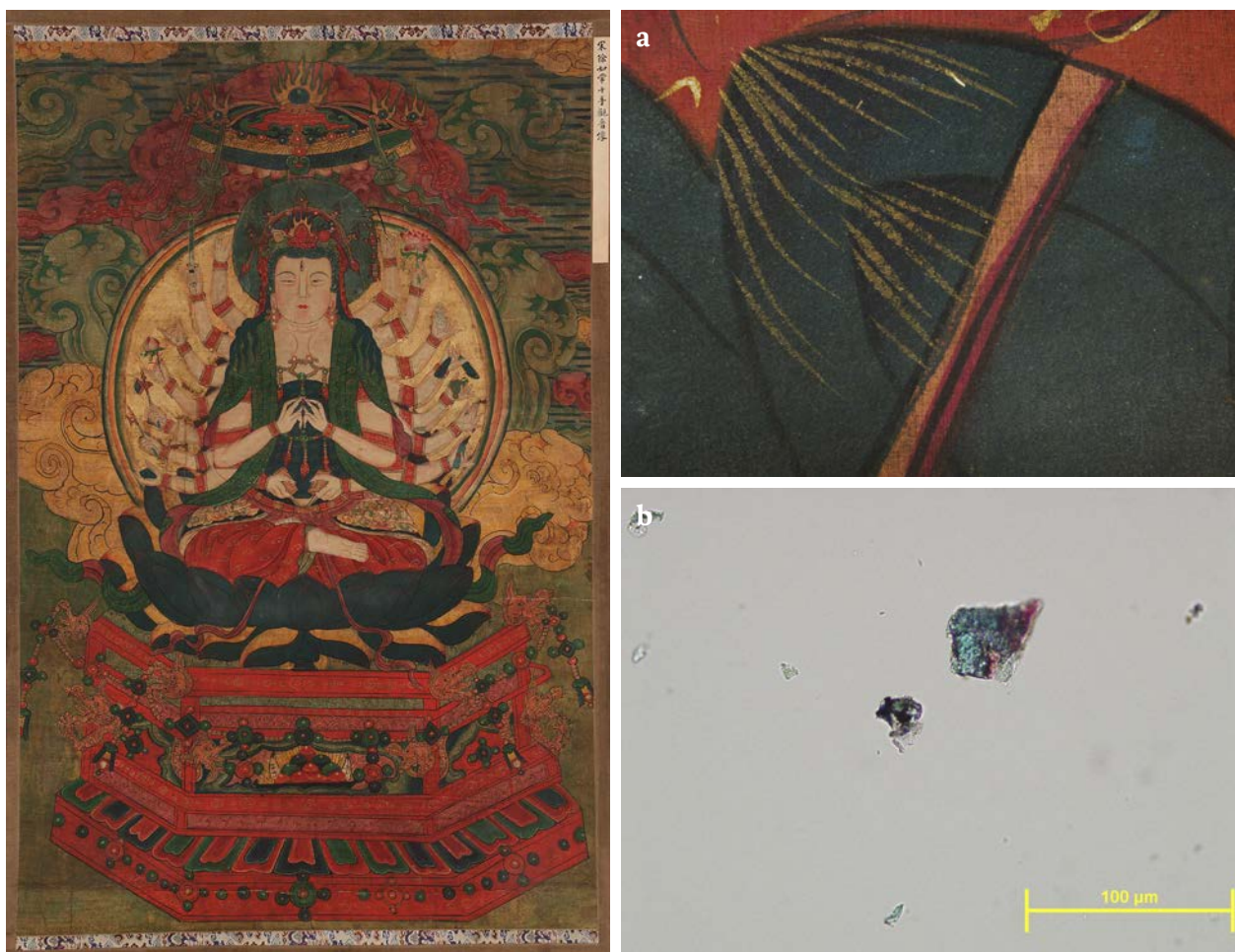


**Figure 3.4.** *Portrait of Oboi*, mid-18th–early 20th centuries. Hanging scroll; silk; 193.7 × 125 cm (76<sup>1</sup>/<sub>4</sub> × 49<sup>3</sup>/<sub>16</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, \$1991.93. Detail of the upholstery (a), showing indigo details over azurite blue and azurite blue under a red pigment layer that has worn away.

century), as lines drawn over carbon black ink outlines (fig. 3.1). It was also used in verso painting, a technique in which pigment was applied to the reverse of a painting to deepen the color. Azurite was a popular pigment that was utilized not only for details but also for covering large areas, especially in portraits. Its wide-ranging

use in Chinese paintings was made possible by abundant azurite in China (Winter 2008).

Areas painted using several azurite layers of different tones of blue are seen in *Two Crested Birds on a Branch*; *Autumn Leaves* (eighteenth century) (fig. 3.2) and *Palace Ladies and Children*



**Figure 3.5.** *Thousand-Armed Guanyin*, formerly attributed to Xu Zhichang, Qing dynasty, 1644–1912. Hanging scroll; silk; 115.2 × 74.6 cm (45% × 29% in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1919.167. Detail of the lotus pedestal under the statue (a), showing purple or deep blue obtained through an unidentified red wash on azurite blue on the petal tips. In (b), the red wash is visible on one side of a particle of azurite in plane polarized light under the microscope.

(mid-eighteenth century) (fig. 3.3). There are also several layers in *Portrait of Chinese Woman in a Kingfisher Headdress* (nineteenth–early twentieth centuries) (S1991.119), where the lower layer can be seen under a microscope because the top layer of azurite had been damaged.

Indigo was found in 136 paintings dated to the eighteenth century or later, alone as blue or as a layer over other colorants, applied as a thin wash. It was also often identified in a variety of shades of purple (most often with lac dye and/or cochineal) and green (more frequently with gamboge). Indigo was used for both large areas and for details. Indigo as the sole blue pigment was found in 47 paintings, all of them landscape, flower, animal, and genre paintings. Indigo was not found as the sole blue pigment in portraits.

Both azurite and indigo blues, individually or as a mixture, were often observed in the same painting. Thin layers of indigo blue seemed to be used to indicate that an object was at a distance, while azurite blue (or sometimes copper-based green) in a thick layer indicates that an object was in the foreground. This observation accords with the study by Fritz van Briessen (1962). A mixture of azurite and indigo to form blue was only rarely observed, but it does occur in *Morning Bell at Mount Jing* (late eighteenth–early nineteenth centuries) (F1911.166d) and in *Birds and Flowers* (1747) (F1960.25d). The presence of copper in the XRF spectra of *Lions and Cubs* (Qing dynasty, 1644–1912) (F1916.593) suggests that azurite as an underlayer (or verso painting) under indigo is present.



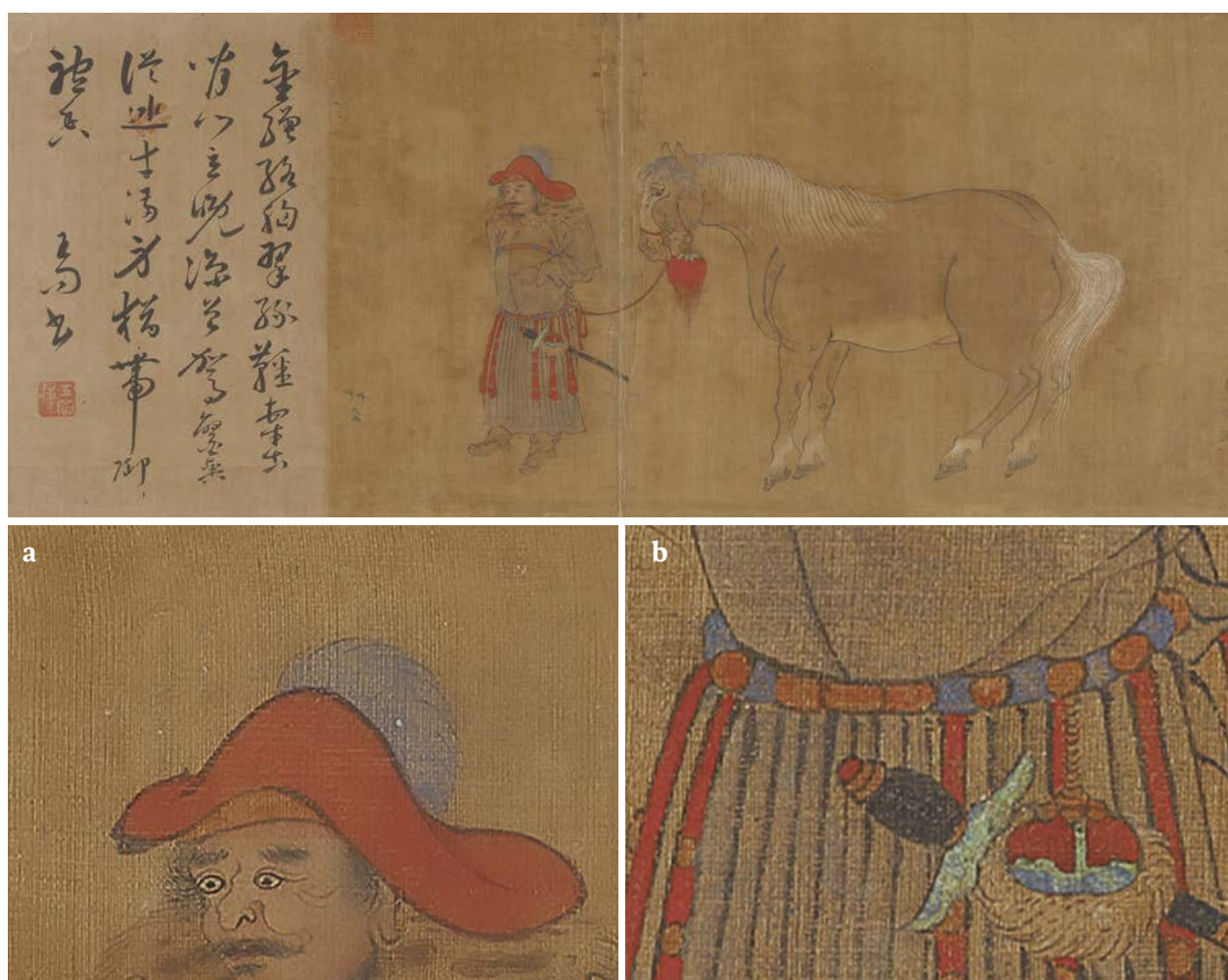
**Figure 3.6.** Detail of *Blending Soup in a Metal Tripod*, Gai Qi (1774–1829), 1816. Hanging scroll; silk; 115.4 × 54.6 cm (45<sup>7</sup>/<sub>16</sub> × 21<sup>1</sup>/<sub>2</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Transfer from the United States Customs Service, Department of the Treasury, F1980.138. The bright blue on the shawl is azurite. A red wash, likely lac dye, was applied to create the folds. Indigo was used to create the pattern on the cloth and as a wash for the folds. See figure 2.8 for the entire painting.

The combination of a blue formed by azurite and a green obtained from indigo was often observed. Azurite was used as blue (both dark and light) when indigo was employed in either purple or in green in paintings in the album *Birds and Flowers* (1747) (F1960.25a–j), and it was used as blue when indigo constituted the blue component in both purple and green in *Palace Ladies and Children* (see fig. 3.3). The bright blue color of azurite was used to express leaves, as for example in *A House and Garden: A Man Receiving Guests* (Qing dynasty, 1644–1912) (F1909.247g), where, in addition, there are also indigo-based green leaves. Other techniques found together with azurite as blue include the use of a second blue formed of indigo, as seen in *Portrait of Oboi* (mid-eighteenth–early twentieth centuries) (fig. 3.4). In this painting indigo washes were used,



**Figure 3.7.** Scene from *Spring Festival on the River*, traditionally attributed to Qiu Ying, 18th century. Handscroll; silk; 33.8 × 794.8 cm (13<sup>3</sup>/<sub>16</sub> × 312<sup>15</sup>/<sub>16</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1915.2. Blue colorants used in this painting were azurite, indigo, smalt, and possibly carbon ink. Detail of valance (a), where the arrow points to an area in which smalt and azurite were identified and appear to have been applied as a mixture. Detail of clothing (b), showing blue colorants including azurite, indigo, smalt, and possibly carbon ink.

for example, to create details over an azurite background in the carpet. In another location, a purple consisting of indigo, lac dye, and a red wash was used over azurite to darken the pigment. It is of interest that a similar use of indigo to darken azurite



**Figure 3.8.** *An Armed Man Leading a Horse*, formerly attributed to Chen Juzhong, Qing dynasty, 1644–1912. Album leaf; silk; 30.6 × 50.8 cm (12 $\frac{1}{16}$  × 20 in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1911.167c. Details of the hat (a) and belt (b). Ultramarine alone was used in some locations, and in others it was found together with azurite.

was found in a Japanese painting by Ogata Kōrin (1658–1716) and in a fifteenth-century thangka from Nepal (Leona and Jain 2005; Leona and Perry 2016).

In portraits and other types of paintings, purples or deep blue were often seen under the microscope to have been obtained from a red wash over azurite blue. Motifs that had purple formed by azurite include the tip of a flower petal on the *renza* (the pedestal under the figure) in *Thousand-Armed Guanyin* (Qing dynasty, 1644–1912) (fig. 3.5), where it was used with an unidentified red wash, and the shawl in *Blending Soup in a Metal Tripod* (1816) (fig. 3.6), in which vermilion was used for the red. In this study, no azurite mixed with other colorants to form green was found. Colors obtained with azurite were created by layers, not by mixing colorants.

Another dark blue color formed by azurite likely was made by a mixture with carbon black ink or a wash of ink over azurite, as seen in *Spring Festival on the River* (eighteenth century) (fig. 3.7), where black particles were observed by PLM. A similar area was observed in *Two Peasants Crossing a Rocky Ford* (early eighteenth century) (F1911.166c), and, although PLM was not performed, the area revealed low iron in XRF and had a flat reflectance in FORS, suggesting the use of carbon black ink. *The Mustard Seed Garden Manual of Painting*, compiled early in the Qing dynasty, recommends blending colors with ink to form gradations of tone and to create distinction in depth and dimension (Sze 1956). In addition to mixtures with ink, azurite is used also as an accent on black, as in *Cat, Rock, and Peonies* (early twentieth century) (F1909.245r).



**Figure 3.9.** *Travelers Crossing a Mountain Stream*, formerly attributed to Fan Kuan, Qing dynasty, 1644–1912. Album leaf; silk; 34.6 × 28.4 cm (13 $\frac{5}{8}$  × 11 $\frac{3}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1909.247a. Detail of the clothing (a), showing smalt used sparingly.



**Figure 3.10.** *Two Figures amidst Clouds*, Chen Xiang, Qing dynasty, 1644–1912. Album leaf; silk; 34.8 × 32.3 cm (13<sup>11</sup>/<sub>16</sub> × 12<sup>11</sup>/<sub>16</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1909.398a. Detail of the right figure (a), showing blue painted using smalt in the collar and cuffs.

### *Ultramarine in Paintings Dated to the Tenth Century or Later*

Eleven paintings contained ultramarine, including two paintings from Dunhuang dated to the Song dynasty and nine (eight portraits and one genre painting) from the eighteenth century or later. The Song dynasty paintings used natural ultramarine by itself both as a dark blue and, when mixed with lead white, as a light blue. While the Song dynasty paintings pre-date the discovery of synthetic ultramarine,

the later paintings do not, and most of the ultramarine seen is synthetic, although this assumption was not confirmed for all the paintings with PLM. In the eighteenth century or later, all nine paintings (eight of them portraits) used ultramarine where azurite, indigo, and/or Prussian blue were also found. Ultramarine, mostly synthetic (see chap. 4), was often used with azurite (six portraits). One genre painting, *An Armed Man Leading a Horse* (Qing dynasty, 1644–1912) (fig. 3.8), has ultramarine and azurite, applied as a mixture, in both the hat and the belt. Unlike most of the later paintings, this painting is associated with western China and contains natural ultramarine, as it is nearer the source of natural ultramarine. Ultramarine was sometimes found over a layer of azurite, mainly in blue areas. This application was also observed in fifteenth- and sixteenth-century European easel paintings, in which azurite was used as underpaint for natural ultramarine (Gettens and FitzHugh 1993). The use of ultramarine and Prussian blue together in the same painting was observed only in five of the portraits studied (for further details, see chap. 4).

### *Smalt Dated to the Qing Dynasty or Later*

Smalt was found as blue in six paintings, all painted in the Qing dynasty or later. Although smalt was used both in portraits and paintings of other types, it was employed differently: in portraits it was used for large areas, while in other types of paintings, such as *Spring Festival on the River* (see fig. 3.7), it was used in small areas. A similar usage is found in *Travelers Crossing a Mountain Stream* (Qing dynasty, 1644–1912) (fig. 3.9), where a layer of dull blue such as indigo was observed in the large areas and to depict a distant mountain, while smalt was used in a small area to depict clothing. XRF analysis for this painting found copper, cobalt, bismuth, arsenic, lead, nickel, potassium, iron, and calcium—elements similar to those found in smalt by Bruno Mühlethaler and Jean Thissen (1993). Smalt was also used for thin layers. In *Two Figures amidst Clouds* (Qing dynasty, 1644–1912) (fig. 3.10), which contains only a few colors, all applied in thin layers, visual examination revealed blue painted with smalt in the robe's collar and cuffs. Under the microscope, both deep blue and slightly purple particles were visible.

Many colorants were found in various motifs on the long handscroll *Spring Festival on the River* (see fig. 3.7). Blue colorants include azurite, indigo, smalt, and possibly carbon ink. Smalt was used as a mixture with azurite and also by itself (possibly a mixture with



**Figure 3.11.** *Li Yinzu* (1629–1664), 18th–19th centuries. Hanging scroll; silk; 222.7 × 100.1 cm (87<sup>11</sup>/<sub>16</sub> × 39<sup>7</sup>/<sub>16</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.104. Detail of the robe (a), showing where smalt was used extensively.

lead white) in motifs of clothing, rocks with copper-based green (mountains), and the light blue valance.

Like other blues in portraits, smalt was used to cover large areas such as striped patterns in robes (see chap. 4). Although it was not observed in many portraits, smalt did appear as a light blue wash over azurite in *Li Yinzu* (1629–1664) (eighteenth–nineteenth centuries) (fig. 3.11), where it was used heavily in the robe. Azurite and indigo were also employed as blue in several areas in the robe and its folds.

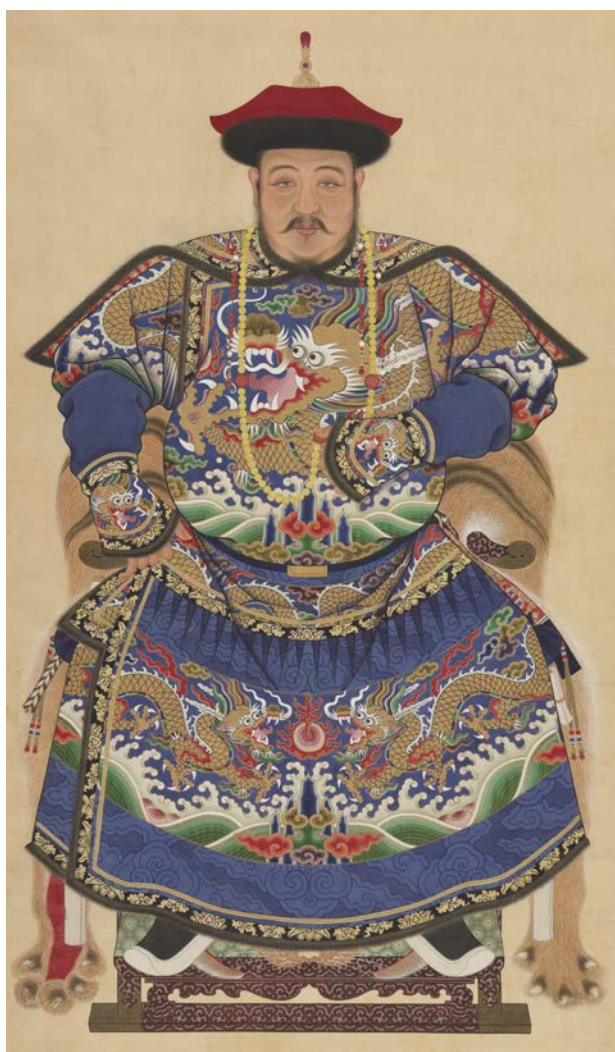
In *Qing Courtier in a Winter Costume* (nineteenth–early twentieth centuries) (fig. 3.12), smalt was widely used in the robe for dark and light blues, together with a lead-based white. An unidentified blue layer,

possibly indigo, was found together with smalt in the blue diamond pattern and in the dark blue in the belt. Indigo was present, together with lac, in a purple dragon at the bottom of the robe and in purple shading on the left arm.

#### *Prussian Blue in Paintings Dated to the Eighteenth Century or Later*

Prussian blue was found in the blues, purples, or greens of fourteen paintings (see tables 3.5, 3.6), where it was used for various objects such as leaves, flowers, birds, robes, and carpet patterns as well as other motifs. Prussian blue was often used with other blue colorants. Sometimes lead-based whites were found together with Prussian blue to lighten the color.





**Figure 3.12.** *Qing Courtier in a Winter Costume*, 19th–early 20th centuries. Hanging scroll; silk; 188.7 × 98.5 cm (74 $\frac{1}{16}$  × 38 $\frac{3}{4}$  in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.125. Detail of the cloud patterns in the robe (a), where smalt was found in the dark and light blues.

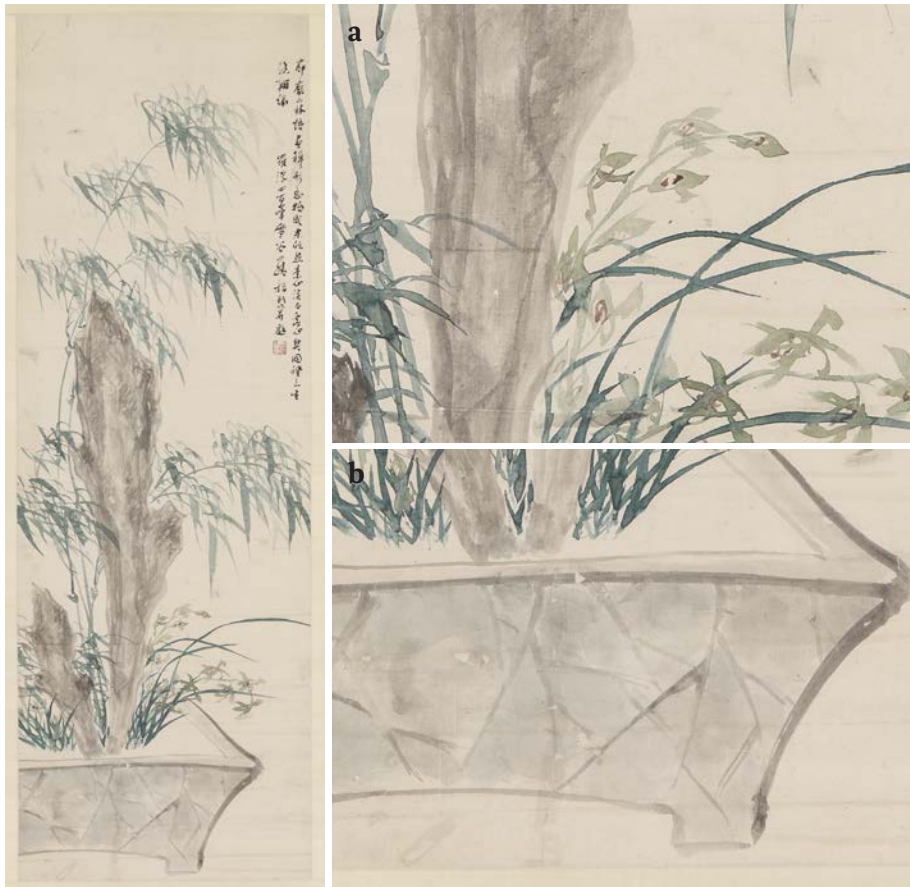
In at least one case, barium sulfate was identified in a green area containing Prussian blue and emerald green. However, it was determined to be associated with emerald green and not Prussian blue as it was detected with emerald green in areas where Prussian blue was absent. It likely was used to lighten the color or as an extender. In some cases, the thin layers of pigment in the paintings did not allow sampling for FTIR to confirm Prussian blue. A few of the paintings with Prussian blue are discussed in detail below.

The painted fan *Small Birds and Morning Glories*, from the early eighteenth century but with contested date (F1980.152) (see fig. I.2) by Jiang Tingxi (1669–1732) has Prussian blue in blue, purple, and green. The dark green in the veins of the leaves is a mixture of Prussian blue and an unidentified yellow colorant over a copper-based green. Purple in the flower buds and birds is a mixture of Prussian blue and cochineal. Prussian blue was used as a wash over azurite to deepen the blue color in the flowers. No indigo was found in this fan.

Prussian blue is present in the green bamboo leaves and in the pale blue area of the tub in *Bamboo, Orchid and Rock in a Tub* (mid–late nineteenth century) (fig. 3.13). The green color of the leaves is strong and opaque, while the light blue color of the wall of the tub is thinly painted using sparse pigment. Small Prussian blue particles can be used in both light and dark colors by controlling the amount of the pigment to achieve color variation. No indigo was identified in this painting.

Prussian blue was observed in various colors in portraits. *Portrait of Yinxiang, the First Prince Yi* (1686–1730) (fig. 3.14) has Prussian blue in a purple that was mixed with cochineal, in a green, and in the red-brown of a wooden chair. Ultramarine was used as blue. *Portrait of a Qing Courtier, Possibly Jing Shou* (d. 1889) (late nineteenth century) (S1991.135) utilized Prussian blue as blue, purple, and green. Also found in the painting were azurite as blue and indigo as purple. Both Prussian blue and azurite were identified together as blue in a robe, and Prussian blue is also present in yellow-green in a mixture with gamboge.

In the one painting studied that used oil paints—a European technique—Prussian blue was the only blue used. This is the hanging scroll *Portrait of Mother Mujia* (ca. 1890) (fig. 3.15) in which Prussian blue was found in a flower pattern in the carpet and in hair ornaments. Both light and dark blues were painted with Prussian blue. The light blue was a mixture with lead white. Prussian blue was also used for the shadows to emphasize details of the subject's face (Stuart



**Figure 3.13.** *Bamboo, Orchid and Rock in a Tub*, Luo Qing (mid-late 19th century), mid-late 19th century. Hanging scroll; paper; 140.7 × 47.5 cm (55 $\frac{3}{8}$  × 18 $\frac{11}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Transfer from the United States Customs Service, Department of the Treasury, F1980.168. Details showing thin layers of Prussian blue in the green leaves (a) and in the blue on the wall of the tub (b).



**Figure 3.14.** Details of *Portrait of Yinxiang, the First Prince Yi (1686–1730)*, 1905. Hanging scroll; silk; 186.7 × 121.9 cm (73 $\frac{1}{2}$  × 48 in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.84. Detail showing the purples of the wave pattern in the robe (a), where Prussian blue is used with cochineal. Detail of a small round bag (b), in which ultramarine was used as blue. The wooden pointer indicates the sample location. Prussian blue is also found in the dark greens with emerald green and in the yellow greens with gamboge. See figure 2.11 for the entire painting.



**Figure 3.15.** *Portrait of Mother Mujia*, ca. 1890. Hanging scroll; silk; 123.4 × 67.9 cm (48 $\frac{1}{16}$  × 26 $\frac{3}{4}$  in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.137. Detail showing the pattern of the robe (a), where Prussian blue is found in the light and dark blue in the location where the FORS probe points. In this ancestor portrait, unusual for being painted in oils, Prussian blue was applied as blue and was the only blue used.

and Rawski 2001), although shadows were rare in portraits before photography became widespread.

The most common blue colorant used together with Prussian blue was azurite (eight paintings) (see table 3.5). Often Prussian blue was also used with ultramarine, but the combination was observed only in half of the portraits in which Prussian blue was found.

#### *Paintings with Multiple Blue Pigments*

In some of the paintings, more than one blue pigment was observed in the same location, most often when one pigment was layered over the other to adjust tone or create shadows. One portrait, *Portrait of Ser Er Chen* (mid-late nineteenth century) (S1991.57), used ultramarine as a wash over azurite in small portions of the robe and its folds, while azurite alone was employed extensively in other areas. *Spurious Portrait of the Jiaqing Empress* (ca. 1920–48) (S1991.98) used ultramarine as a wash over azurite, as observed in PLM. The purple in this painting was made by mixing cochineal with ultramarine. *Portrait of the Sixth Prince Yi* (1905) (S1991.86) (see fig. 4.3) also used ultramarine for blue decorations on the robe and mixed with emerald green in the blue of the robe itself. Prussian blue was used for purple. *Portrait of a Qing Court Lady* (mid-late nineteenth century) (S1991.117) employed synthetic ultramarine as bright blue in a small area that was part of a bead's motif. The painting contains other blue colorants—azurite as blue and Prussian blue as blue, purple, and green. Ultramarine was the only blue used for blue in *Portrait of Yinxiang, the First Prince Yi (1686–1730)* (see fig. 3.14). Blue tones varied from dark to light; the light blue was made with ultramarine and a lead white. Prussian blue, rather than ultramarine, is present in purple, green, and red-brown mixtures. *Portrait of Lady Hejia, Secondary Wife of Prince Zaizhi* (late nineteenth century) (S1991.65) has ultramarine in blues and greens. In addition to ultramarine alone as blue, dark green was obtained by a mixture of ultramarine with emerald green. Dark blue appears to have been produced by Prussian blue applied over a mixture of ultramarine and cinnabar/vermilion. *Portrait of an Elderly Couple* (nineteenth–early twentieth centuries) (S1991.128) contains the blue colorants smalt, indigo, and azurite (see chap. 4). Smalt and azurite were used as shades of blue, while indigo was utilized for purple. This is one of several paintings in which azurite was observed in the same painting with smalt.

## Discussion

This study of blue pigments in Chinese paintings produced insights on their timelines, uses, and associations with other colorants. The following discussion focuses primarily on Prussian blue.

#### *Occurrence of Prussian Blue in Chinese Paintings*

Prussian blue was found in portraits and in flower and other types of paintings. It was used not only as blue but also with other colors, such as gamboge, lac dye, cochineal, azurite, and indigo, to create purples or greens. A Prussian blue wash over another color was also found in both portraits and other types of paintings.

Prussian blue was identified throughout the fan painting *Small Birds and Morning Glories* (F1980.152). The life dates of the court painter Jiang Tingxi (1669–1732) suggest that this fan is from the early eighteenth century, yet the date seems too early for the occurrence of Prussian blue, according to the time frame for the introduction of this pigment to China (Sasaki 1985; see table 3.1). Moreover, Prussian blue was not otherwise found in eighteenth-century paintings examined in this study. In addition, unlike other types of paintings in which Prussian blue was found, the pigment was used here in large areas of the painting. Nevertheless, it is possible Jiang Tingxi was exposed to European paintings and pigments in the early Qing dynasty court, and records document the import of Prussian blue to China in the eighteenth century and its later manufacture there.

Prussian blue appears more frequently in the nineteenth century, especially after mid-century, and all the portraits that contain Prussian blue were painted after 1800. Some of these are portraits that were executed by unidentified professionally trained studio painters (Giaccari and Winter 2005) in a multistep process that involved collaboration among two or more artists (Stuart and Rawski 2001). The body part might be painted first and then the head by another artist who specialized in faces. In workshops where designs were used repeatedly—in robes and carpets, for example, that were not specific to any one person—Prussian blue was widely used as the color blue, in mixtures for purples and greens, and as a secondary or top pigment layer. Three paintings contained Prussian blue, the only blue in the painting, as blue without mixing with other colorants (see table 3.6). Several paintings used a Prussian blue layer over another color.

There is no indication that the use of Prussian blue differs from the way traditional colorants were

employed in Chinese paintings. The time frame for the use of Prussian blue found in the results of this study agrees with the time frame outlined by Yu Feian (1988). During the years of the Qing dynasty, Prussian blue did not completely replace azurite or indigo.

#### *Introduction of Prussian Blue Relative to the Use of Azurite and Indigo*

Both before and after the introduction of Prussian blue in China, azurite and indigo were the dominant blue pigments. Both were common in the Song and Yuan paintings studied in this research (see chap. 1), although these are not their earliest known occurrences in Chinese art. Azurite and indigo continued to predominate in the later Ming and Qing dynasties, although the use of the two blues differed. Indigo as the sole blue pigment was found only in paintings that were not portraits, both before and after the early eighteenth-century introduction of Prussian blue. Azurite as the sole blue colorant was found mostly in landscapes and paintings of genre subjects. It appears less frequently than indigo, however, and only one example of azurite as the sole blue colorant in a portrait was identified. Overall, after the advent of Prussian blue, where there was only one blue colorant, it was generally not found in portraits but in other types of painting: azurite in seven paintings; indigo in forty-eight paintings; smalt in one painting. In portraits, the use of more than one blue colorant was common.

Both azurite and indigo were identified in 88 of the 159 paintings studied that were dated to the eighteenth century or later. No paintings were found that had Prussian blue and indigo without also including azurite, although Prussian blue was identified in the same painting with azurite as the only other blue pigment in three paintings.

Four paintings used only Prussian blue as a blue pigment, but ten paintings employed other blue pigments in the same painting. Five of the paintings used Prussian blue in blue-, purple-, and green-colored areas. Eleven of the fourteen Qing dynasty paintings with Prussian blue, seven of them portraits, did not contain indigo (see table 3.6).

Artists who have been identified as using Prussian blue include possibly a court painter as well as independent artists, both professionals and scholar-painters. The majority are by unknown artists. The artist Luo Qing (mid-late nineteenth century) has an unknown background. In addition, unidentified studio painters of portraits used Prussian blue. While painters of portraits employed many of the same

colorants as painters of landscape and genre paintings, painters of portraits used more colors with thicker applications of colorants.

With the exception of *Small Birds and Morning Glories* (F1980.152) (see fig. I.2), a painting of contested date, Prussian blue was used in a thin layer in other types of paintings, while in portraits thick layers of Prussian blue alone or with other colorants were seen, especially to create decorations in splendid robes and carpets. Color usages in portraits differ from usages in other Chinese painting types: the portraits employ pigments not often found in other types of paintings (see chap. 4). All portraits in this study that contained Prussian blue date to the mid-nineteenth through the twentieth centuries, and utilized Prussian blue in one or more of the following colors: blue, purple, green, and red-brown (see table 3.6). Three of these used both indigo and Prussian blue with other blue colorants. The concurrent use of indigo and Prussian blue in portraits in this study differed from the practice seen in other painting types. Unlike the three portraits that contain both indigo and Prussian blue, no landscape or genre painting was found to contain both indigo and Prussian blue.

Indigo was not found as blue in portraits after Prussian blue began to be used in China. Although Prussian blue did not replace indigo, the latter was used more frequently for purple and green than as blue when Prussian blue was employed as blue. Unlike indigo, azurite remained widely used in portraits, and there is no clear evidence for Prussian blue replacing it.

#### *Painting Techniques Using Blue Colorants*

Blue colorants were employed in specific ways in Chinese paintings, and one in particular pertains to outlines. Carbon ink, which varies in color from black to brown to blue, was generally the primary medium for drawing outlines, and it was also sometimes used to paint objects. In this study, carbon black ink outlines, also called ink skeletons, were created with elegant brushstrokes for figures and for the traditional subjects of landscapes such as birds and flowers. Gold outlines were also observed, as in *Landscape: Bullock Carts Forging a Mountain Stream* (possibly Qing dynasty) (F1909.245f). Instead of using full color, the sensitive and delicate ink outlines allowed painters to describe subjects with nuance, with other colors filling in the inked outlines. Paintings that lack carbon ink outlines are called “boneless.” A variety of outline drawing styles was observed (Wang 1995; Briessen 1962),



**Figure 3.16.** *An Eagle on a Blue Rock in the Sea*, Qing dynasty, 1644–1912. Album leaf; silk; 33 × 22.6 cm (13 × 8<sup>7</sup>/<sub>8</sub> in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Gift of Charles Lang Freer, F1914.59a. The rock is painted with azurite blue but thin areas appear green. The yellowish tone of the underlying paper or silk may account for the green color.

and sometimes carbon black ink was found under a thin layer of color, as in *A Hundred Birds Worship the Phoenixes* (see fig. 3.1).

Several books on Chinese painting mention a special style called indigo style, in which indigo is the main color (Briessen 1962). In this style, indigo was used instead of carbon black ink to paint landscape elements such as sky and water throughout the painting. Indigo was also often found with yellow as green. *The Mustard Seed Garden Manual of Painting* describes the mixture of indigo and rattan yellow (gamboge) as producing three kinds of green: deep green (*shen lü*), intense green (*nong lü*), and fresh green (*nen lü*) (Sze 1956). A mixture of red and indigo produced lotus green (*lian qing*) (Sze 1956) (see app. 4).

The application of colors as extremely thin layers was observed in many paintings, and where the substrate was a dark brown or light beige, a background color that may be due to either dyed or aged silk or paper may affect the FORS spectra (see app. 3). For example, in *An Eagle on a Blue Rock in the Sea* (Qing dynasty, 1644–1912) (fig. 3.16), the rock was painted with azurite blue, but in thin areas it appears green. The yellowish tone of the underlying silk or paper may account for the green color, but it is not known if this effect was purposeful because it was not possible in this study to determine if the brown color of the silk was formed by dyeing or aging.

Verso painting using azurite and white is a well-known technique for deepening the color in paintings on silk (Hayashi and Hakozaiki 1994). *The Mustard Seed Garden Manual of Painting* explains, “Azurite was also used on the back, giving a painting a wonderful richness” (Sze 1956, 44). The technique was observed during conservation treatment of several portraits at the Freer Gallery of Art and Arthur M. Sackler Gallery (Lee et al. 2003). For example, azurite was applied on the verso of the painting *Portrait of Oboi* in the area of the robe (see fig. 3.4). It was also found on the reverse of the paper support in *Peach Blossom Spring* (1690s–early 1700s) (F1957.4). Azurite is generally utilized for blue verso painting rather than another blue colorant, although it is hard to observe except during conservation treatments. In this study, verso painting was assumed to exist even when FORS did not show an azurite spectrum if XRF confirmed the presence of copper and there were no possible copper pigments in the area of the painting undergoing examination. Azurite was also used in other techniques, such as below an indigo wash, and under red, as in *Portrait of Oboi* (see fig. 3.4).

### *The Introduction and Use of Prussian Blue in Japan with Comparison to China*

While there have been few scientific examinations documenting the occurrence of Prussian blue and other colorants in Chinese paintings, the many studies of Japanese paintings and prints in the Edo (1603–1868) and Meiji (1868–1912) periods offer information concerning the arrival of Prussian blue in Asia and enable comparisons of its use in China and Japan.

Prussian blue was known in Japan in the eighteenth century. It is mentioned in Hayashi Moriatsu’s 1721 painting manual *Painting Methods* (Gasen) and in a 1763 catalog for an exhibition of new products by Hiraga Gen’nai, *Study of Plants, Minerals, and Animals for Use in Chinese Medicine* (Butsurui Hinshitsu) (Katsumori 2007; Katsumori 2008). Prussian blue also appears in pigment collections assembled by Japanese scholars and collectors of the time (Kato et al. 2007; Katsumori 2007; Kuchitsu 2008). Ships traveling from Europe to Asia may have supplied some of the pigment via the captain’s private trade (M’Culloch 1847), and several cargo lists from the late eighteenth and early nineteenth centuries include Prussian blue (Kato et al. 2007; Katsumori 2007).

The earliest known use of Prussian blue in Japanese paintings is from the 1760s. It is seen in a soapfish in a painting (1765–66) from the series *Colorful Realm* by Itō Jakuchū (1716–1800) (Hayakawa and Ota 2010), one of a series of thirty painted between 1757 and 1766 and the only one containing Prussian blue. Elisabeth West FitzHugh’s study of the Japanese collection in the Freer Gallery of Art (2003) found that one of the paintings by Miyagawa Chōshun (1682–1752) contained Prussian blue, but the date of the painting is uncertain. Another early use of Prussian blue was seen in an area of a Japanese painting by Ikeno Taiga (1723–1776), painted in the 1760s (Leona and Winter 2003); although the painting was extensively restored, the area analyzed was believed to be unrestored. Marco Leona and John Winter (2001; 2003), who, like FitzHugh, studied Japanese paintings, also found Prussian blue in a Nagasaki painting by Nanreisai (1771–1836) dated to 1817, as well as in three paintings from the late eighteenth century. In another study Prussian blue was found in a map dated to 1781–91 of administrative land division in Ryukyu, the relay station for the trading between China and Japan (Takagi and Shimoyama 2002). The source for this Prussian blue is not known but is not likely

to be China at this early date, although later in the nineteenth century Japan did import Prussian blue from China (Sasaki 1985; Miyashita 1995). Prussian blue imported as an insoluble powder may have been mixed with animal glue, the binder traditionally used in paintings in both China and Japan.

In Japan, as in China, the occurrence of Prussian blue increased in the nineteenth century. Using FORS, Marco Leona and John Winter (2003) documented that 46 of the 139 Japanese paintings they examined contained Prussian blue. Occurrences were heavily weighted toward later paintings.

In contrast to Chinese paintings, in which Prussian blue was found mainly in portraits and rarely used as the main or sole colorant for blue, Japanese paintings generally employed Prussian blue as one of the main colorants for blue and sometimes the only blue. Japanese paintings also used Prussian blue in large areas, similar to usage seen in Chinese portraits. In Japan, Prussian blue appeared to supplement the use of indigo and azurite, not to replace them (Leona and Winter 2003), while in Chinese portraits indigo was often absent in the presence of Prussian blue. Investigation by Leona and Winter (2003) found that of 97 Japanese paintings that used only one blue colorant, 12 had only Prussian blue as blue, while 85 had indigo only; 33 paintings used both indigo and Prussian blue in the same painting; and 26 contained indigo and Prussian blue in separate design elements. Of 60 paintings with indigo or Prussian blue in a mixture with other colorants, 5 used Prussian blue with yellow as green, while 48 utilized indigo in green.

In addition to traditional Japanese painters, those of the Nagasaki school and Dutch-style painters such as Wakasugi Isohachi (1759–1805) and Araki Jyogen (1765–1824) also used Prussian blue. Nagasaki, the only port open to foreign trade (and solely to the Dutch and Chinese) during the Edo period, is where Prussian blue from Europe most likely arrived in Japan. Prussian blue was also used in the Tōhoku region of Honshū, where Dutch-style painters of the Akita school were located and where it was found in an Akita school European-style painting (Katsumori 2008; Kuchitsu 2005; Kuchitsu 2008). For Japan, it has been assumed that there was a relationship between the diffusion of European painting techniques and the reception of the new blue color, Prussian blue. Several publications on paintings in other collections mention that Prussian blue was found in “traditional Japanese-style”

paintings executed by the Japanese group of Dutch-style painters who were close to Dutch scholars before it became popular in oil paintings and prints (Katsumori 2007; Kuchitsu 2008). Oil painting techniques, not popular at this time, were identified in only one Chinese portrait in this study—*Portrait of Mother Mujia* (see fig. 3.15), in which the only blue identified in the painting was Prussian blue. In comparison, it is interesting to note Prussian blue was also used as blue in oil paintings in Japan.

The use of Prussian blue was especially notable in Japanese *ukiyo-e* prints (Leona and Winter 2003), which Henry Smith (1998) described as a “blue revolution.” The print artist Katsushika Hokusai (1760–1849), for example, employed Prussian blue as early as 1829; by the end of 1830 it had gained in popularity to the extent that by the end of 1831, traditional blues in prints were being replaced (Matsui et al. 2005). The physical and chemical characteristics of Prussian blue proved more suitable for printing than the traditional blues (Smith 1998; Shimoyama and Matsui 2006). Moreover, with increased imports from China (Sasaki 1985; Miyashita 1995), the price of Prussian blue declined, perhaps also explaining its prevalence. In both China and Japan, the artworks in which Prussian blue was concentrated—prints and portraits—were produced by professional groups. In Chinese portraits, however, Prussian blue was used with other blues, while in Japanese prints it largely replaced other blues.

## Conclusions

Indigo and azurite were the dominant blue pigments in Chinese painting and their dominance continued after the introduction of Prussian blue in the eighteenth century. They were found alone, together, in paintings with Prussian blue, and, in the case of azurite, in the same painting with Prussian blue as the sole additional blue pigment.

In this study, Prussian blue was seen with increasing frequency in Chinese paintings of the nineteenth century. It was found more often in portraits than in other types of paintings and was used in blues and in other colors, especially purple and green. Prussian blue did not entirely replace either indigo—which was commonly used throughout the Qing dynasty—or azurite. Indigo blues are still commonly found in paintings after the beginning of the nineteenth century. Similarly, studies of Japanese paintings have found Prussian blue was most often employed as a



blue and that indigo continued to be used after the introduction of Prussian blue.

This study found preferential Prussian blue use in Chinese portraits. Portraits are referred to as a type of “folk” painting by Yu Feian (1988), other types of which have been found to contain Prussian blue (see chap. 4). In Japan, as in China, Prussian blue has been observed more frequently in a particular art form, and in the case of Japan, especially in prints.

The properties of the Prussian blue pigment may explain its preferential use in Chinese portraits and Japanese prints. Not only could it produce a very bright blue, but the small, uniform particle size made it advantageous for green mixtures where indigo (also a pigment with a fine particle size) was traditionally used. Where indigo’s dull blue color made it less than ideal for some of the details in the portraits, azurite, with its brighter blue, was used. By varying particle size, azurite could produce blues from light to dark, as seen in the wave and cloud decoration of the dragon robes in Chinese portraits. Prussian blue, with its bright color and small uniform particle size, could be substituted for azurite in these areas by varying the amount of pigment in a single layer (pigment loading). This same ability to vary shades of color using differing amounts of pigment combined with the bright colors attainable made Prussian blue attractive for Japanese prints, creating shades of color in the landscapes and sky. In addition, as the cost of Prussian blue declined over the course of the nineteenth century, there may have been an economic incentive for its choice. In some cases the Chinese and Japanese paintings in which Prussian blue is used incorporate elements borrowed from European-style paintings, such as chiaroscuro or linear perspective. These European techniques are thought to be associated with the use of Prussian blue by Japanese painters such as those from the Akita school, but this does not appear to be the case in the Chinese paintings.

In China, Prussian blue did not replace indigo or azurite in paintings: it was used in the same way that those pigments were used for blue, purple, and green. In this study, the highest frequency of the occurrence of Prussian blue was found to be in portraits. Although Prussian blue was identified in just 14 of the 159 Chinese paintings examined from the eighteenth century and later, they are evidence of the spread of Prussian blue in the nineteenth century in China.

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# 4

## Colorants and Painting Techniques in Portraits from the Arthur M. Sackler Gallery

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### Introduction

The portrait collection at the Arthur M. Sackler Gallery consists of eighty-five portraits, mainly from the Qing dynasty (1644–1912), originally collected by Richard G. Pritzlaff in the 1930s and 1940s. One related portrait from the Freer Gallery of Art collection has been included in this study. The portraits examined include ancestor portraits, commemorative portraits, both formal and informal, and “beauty paintings.”

Ancestor portraits were painted for use in veneration of the sitter after his or her death and were usually created close to the time of death or as a matched pair after a spouse’s death. They were on occasion copied at a later date to replace damaged portraits. The museum’s collection includes not only ancestor portraits but also images of members of the Qing imperial court in garden or architectural settings that were made and displayed prior to the sitter’s death. These commemorative portraits were not used for ancestral rites but were often painted

at a significant or auspicious moment during the sitter’s life. They can be informal or imitate the traditional poses and strictures of ancestor portraits. It is believed that portraits of unknown women, often called “beauty paintings,” may have been painted in the same portrait workshops where traditional portraits were painted (Stuart and Rawski 2001).

Not all sitters can be identified. For those that are identified, portraits can sometimes be dated from the sitter’s life dates, but the practice of making later copies often makes dating difficult. In any case, a sitter’s life dates can provide an antedate, before which the painting cannot have been painted (Stuart and Rawski 2001; Priest 1943).

Even though a firm date for a portrait may not always be available, portraits still provide valuable information on the introduction of imported materials. By combining identification of the pigments used in the portraits with likely dates of creation, a timeline for the use of imported pigments in portraits in China can be proposed. The colorful decorative motifs in the robes of sitters required both multiple



**Figure 4.1.** *The Qianlong Emperor as Manjushri, the Bodhisattva of Wisdom*, imperial workshop, emperor's face painted by Giuseppe Castiglione (Lang Shining, 1688–1766), mid-18th century. Thangka; silk; 113.6 × 64.3 cm (44 $\frac{3}{4}$  × 25 $\frac{5}{16}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment and funds provided by an anonymous donor, F2000.4. Detail of the center of painting (a), showing the emperor's face. While lac dye was identified throughout most of the painting, FORS indicates cochineal is present in the emperor's lips.

colors and many shades of the same color, most notably in the popular cloud and wave pattern elements. The authors' earlier study of the colorants in Chinese paintings, including five portraits, documented the presence of a few modern and synthetic pigments, notably emerald green, synthetic ultramarine, and Prussian blue (Giaccai and Winter 2005). This study expands on the previous work to examine the import of modern and synthetic pigments into China and their use in Chinese painting.

All the paintings examined in this study were painted with the traditional animal glue binding medium found in Chinese paintings. More than thirty paintings were analyzed, the majority of which are allegedly portraits of the Qing dynasty imperial lineage. Other than *The Qianlong Emperor as Manjushri, the Bodhisattva of Wisdom* (mid-eighteenth century)

(fig. 4.1), there is no evidence that portraits in this collection were painted by the imperial painting academy.

### Workshop Practices

Previous chapters included works by Chinese scholar-painters. These scholars regarded themselves as amateurs, although more recent studies suggest that there was often some exchange of money or goods between scholar-painters and the collectors of their works. Regardless of their employment status, there is a distinct difference between the scholar-painters and the professionally trained painters of portraits, as the latter are more likely to have been taught different methods using colored paints, particularly

the mineral pigments applied in thick, opaque paint layers.

The portraits described here are undoubtedly the product of professionally trained studio painters and were once thought of as “low status as anonymous paintings by professional artisans” (Stuart and Rawski 2001, 31). The professional workshops creating portraits have been a topic of investigation, although much remains to be learned about them. Portraits were typically painted by two or more artisans using a multistep approach (Stuart and Rawski 2001). In some portraits the body was painted first, and only when the painting was ready to be purchased was the face filled in by another artist who specialized in faces; often this artist was the head of the studio. One of the paintings studied here, *The Qianlong Emperor as Manjushri, the Bodhisattva of Wisdom* (see fig. 4.1), is thought to have had the face of Qianlong painted by the Italian Jesuit missionary Giuseppe Castiglioni (Lang Shining, 1688–1766), while the rest of the painting is the work of one or more artists in the imperial workshops.

Robes, headdresses, and jewelry all indicate the rank of the portrait’s subject. Published manuals showing details of the costume and jewelry for different ranks and court garments helped guide the portraitist in the correct details of the sitter’s outfit (Claypool 2012). These status indicators mean that the portraitist had little artistic freedom to change the colors or details of the sitter’s costume. These restrictions may have reduced the incentive to change pigments or add to a pigment palette, especially if a particular method for painting certain details was believed to have been perfected. If new pigments were significantly cheaper, however, an economic incentive may have prevailed.

Because official ranks could be changed posthumously, portraits were sometimes revised to reflect the new rank (Stuart and Rawski 2001). Overpainting was also, on occasion, a deliberate deception once a portrait was no longer used ceremonially and entered the art market. An example from the Sackler’s collection is *Portrait of Qing Court Lady* (eighteenth–early twentieth centuries) (S1991.92) where a rank badge was painted over the original surcoat design to increase interest by future purchasers.

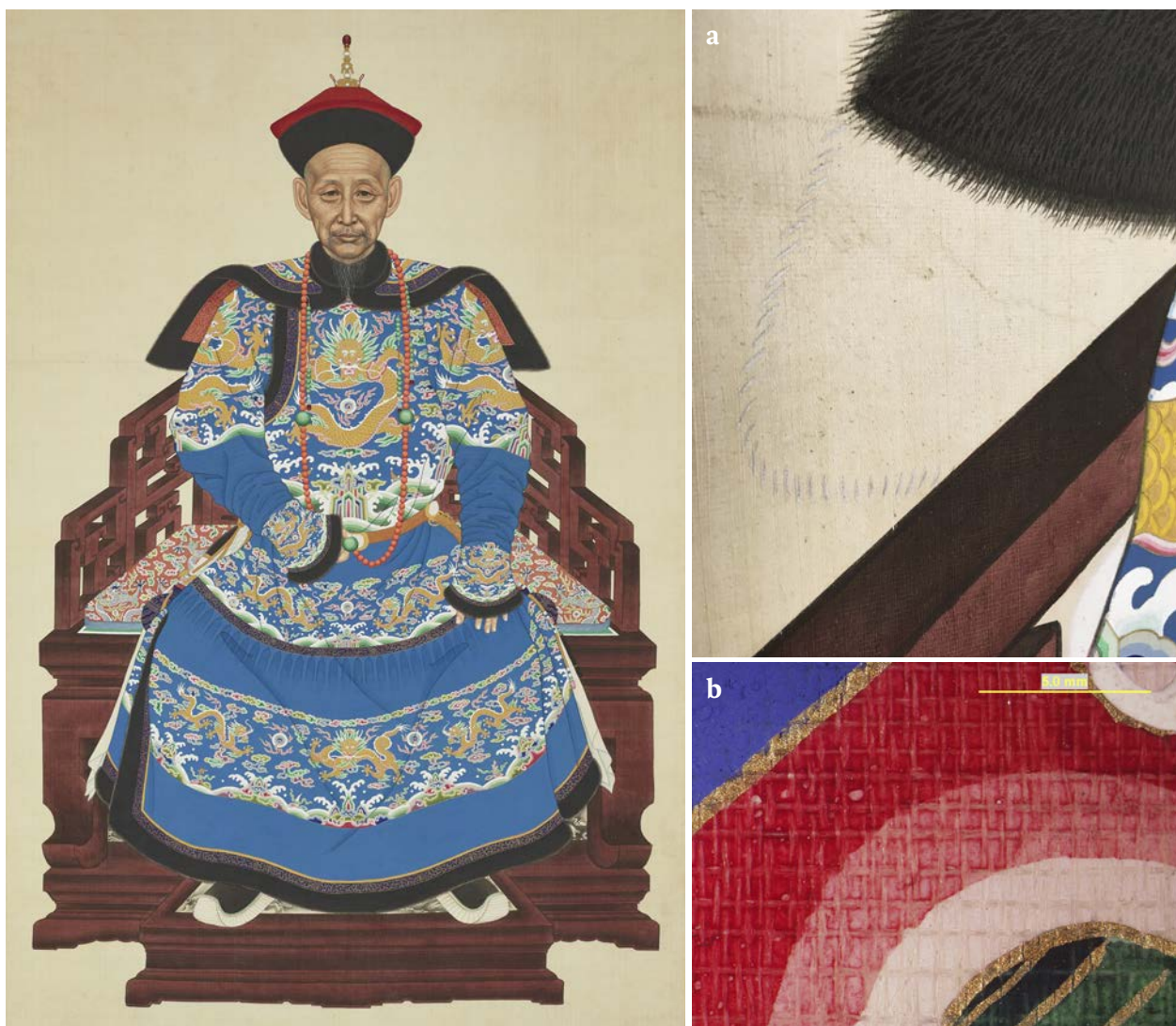
While the sitter’s clothing was prescribed by sartorial codes for station and position in life, chairs, carpets, and other material objects or props provided more opportunity for variety. A chair made of expensive rosewood, for example, was a symbol of luxury but not necessarily part of the sitter’s everyday furniture. Carpet designs, especially, gave plenty of room for license, painted in a variety of colors and hues that



**Figure 4.2.** *Portrait of Yinxiang, the First Prince Yi (1686–1730), 1905.* Hanging scroll; silk; 186.7 × 121.9 cm (73½ × 48 in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.84. Yellow pigment in this robe is pararealgar, an arsenic sulfide.

was rivaled only by the cloud designs of the robes. Often the carpets were painted to imitate the knotted carpet designs in common use during the Ming dynasty (1368–1644) but not necessarily continued in use during the Qing dynasty. More than any other part of the portrait, the details of the setting around the sitter tend to represent the studio in which they were painted. Workshops had their own conventions for the background furniture, carpets, and props, and these were used in many paintings. Thus the furniture has been used by Jan Stuart and Evelyn Rawski to link a few portraits to the same workshop (Stuart and Rawski 2001, 97–99).

Because the furniture, carpets, and props—and even the bodies—were conventional and often generic in nature, they could be painted earlier, even



**Figure 4.3.** *Portrait of the Sixth Prince Yi*, 1905. Hanging scroll; silk; 185.3 × 119.7 cm (72<sup>15</sup>/<sub>16</sub> × 47<sup>7</sup>/<sub>8</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.86. Detail of fur on the robe (a), showing stencil marks where the robe was changed from the portrait of the First Prince Yi (see fig. 4.2). Detail of the lower robe decoration on the sitter's left (b), showing layers of cochineal shading over lead white and cochineal base paint.

much earlier, before the sitter was known. In some cases, stencils were used to generate an outline of various elements in the design, and it could then be filled in with paint, awaiting the addition of a face or costume details. Stencils were reused, and it is possible to identify works from the same workshop by their common motifs. For example, the portraits of the First, Sixth, and Seventh Prince Yi (1905, 1905, 1911) (figs. 4.2–4.4) were made using the same stencil for the sitter and the chair, although slight changes can be observed in the *piling*, a wide collar, among the three sitters (fig. 4.3a).

### Pigments Identified in Portraits in the Arthur M. Sackler Gallery

The methods of using colored pigments are very different in portraits from methods used by scholar-painters in the paintings discussed in chapters 1–3. Scholar-painters are known for using color sparingly, and often in thin washes of color. In contrast, colored pigments cover significantly more of the painting surface in portraits and appear to be present in both larger quantities and with a broader range of hue. Whereas ink is a predominant painting medium in scholar-paintings, in



**Figure 4.4.** *Portrait of the Seventh Prince Yi*, 1911. Hanging scroll; silk; 184 × 120 cm (72<sup>7</sup>/<sub>16</sub> × 47<sup>1</sup>/<sub>4</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.102.

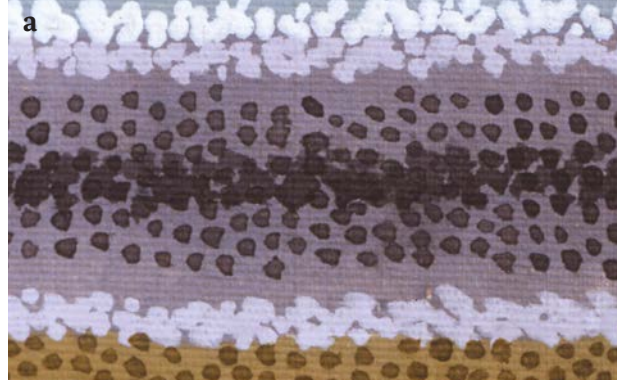
portraits it is used only in outlines and in black design features. The formal ancestor and commemorative portraits examined in this study had many thick layers of paint made with inorganic or mineral pigments and thin washes of organic pigments to modulate shades of color, while the informal portraits mostly had thin layers of both mineral and organic pigments.

Complete pigment identifications made in the course of this research are given in appendix 5. Yellow, green, and brown paints were not fully characterized for these paintings, but where they were identified the results can be found in the appendix.

#### *White Pigments*

Lead white was used as the only pigment for white in the portraits. In four paintings other white pigments were identified, but they were fillers or toners in other colors. For example, the only portrait in which zinc white was found was *Portrait of Daisan* (eighteenth–nineteenth centuries) (S1991.74), where it was used with lac dye in areas of flesh such as the face and hands, while white regions of the painting used lead white. This finding suggests that the zinc white was part of a “flesh tone” mixture in the workshop or utilized by the particular artist who painted the face and hands.





**Figure 4.5.** *Portrait of a Qing Courtier, Possibly Jing Shou* (d. 1889), late 19th century. Hanging scroll; silk; 184.9 × 100.5 cm (72<sup>13</sup>/<sub>16</sub> × 39<sup>7</sup>/<sub>16</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.135. Detail of the carpet border (a), showing light, medium, and dark purple shades.

### Red Pigments

Every portrait examined that had red paint areas showed the use of cinnabar/vermilion. Red lead was less frequently identified, found in only three portraits. The thin washes of red or pink in the portraits examined were consistently confirmed to be insect dyes. Lac dye was prevalent in the older portraits, with cochineal added to the palette as it became available (see chap. 2). In some portraits both lac dye and cochineal were used together or in different areas of the painting, presumably due to multiple artists working on the portrait in the workshop setting as well as due to different colorants being used in different colors, for example, lac dye in the purple areas and cochineal in the organic red and pink areas. Both lac dye and cochineal were used in mixtures with a blue pigment to make purple colors. Wooden chairs often had a red colorant within the brown pigment mixture, most often lac dye, not cochineal.

In total, cochineal was identified in ten portraits. In all but two portraits, lac dye was also detected. For example, in *Portrait of a Qing Courtier, Possibly Jing Shou* (d. 1889) (late nineteenth century) (fig. 4.5), lac dye was used in shading in the carpet and seat cushion, whereas cochineal is found in the necklace beads. The two portraits in which cochineal was used without lac dye, *Portrait of a Qing Court Lady* (mid-late nineteenth century) (S1991.117) and *Spurious Portrait of the Jiaqing Empress* (ca. 1920–48) (S1991.98), are atypical of most of the paintings in the study: both were works on paper, one possibly made specifically for export.

### Orange and Yellow Pigments

Orange-toned realgar or related arsenic sulfides were the most common deep yellow mineral pigments present in the portraits examined. Identified by x-ray diffraction (XRD) as realgar and pararealgar (all  $\text{As}_4\text{S}_4$ ), they were used as the thick yellow pigment and often applied for yellow robes (see fig. 4.2). This frequent use in portraits contrasts with the limited use of arsenic sulfides in the paintings by scholar-painters examined in this study and/or elsewhere (Winter 2008, 23; Schafer 1955).

The Chinese painter Yu Feian (1889–1959) cites arsenic sulfides as a pigment used by “folk artisans,” a category in which he includes the painters of portraits as well as of other genres (Yu 1988). His book *Chinese Painting Colors*, first published in 1955 and translated into English in 1988, reports his research not only into the colors used in twentieth-century China but also into those employed in the

past, compiling information from ten different painting manuals dating from the Tang dynasty (618–907) through the eighteenth century. He states (1988, 44) that the arsenic sulfide pigments were often made by the painters themselves. There is no record of arsenic sulfides having been sourced from outside of China either as pigment or raw materials for painters to further refine. Realgar occurs as a mineral in parts of China and would likely have been available to Chinese painters (Golas 1999; Watson 1923). Note that the pigments found in the portraits are not the same arsenic sulfides identified in Chinese paintings from Dunhuang (chap. 1; Waley 1931, xlvi), where the bright yellow pigment orpiment ( $\text{As}_2\text{S}_3$ ) was used.

Most of the lighter yellow colors in the portraits were made with gamboge. Gamboge was also used in the dark green washes in combination with a blue colorant, either indigo or Prussian blue. Arsenic-based dark yellow pigments and gamboge were not used interchangeably in the paintings examined; most paintings that used realgar or a related pigment also employed gamboge.

### Green Pigments

In addition to the deep green color made by mixing gamboge with either indigo or Prussian blue, a broader range of green hues was rendered with malachite, the synthetic pigment emerald green, or copper trihydroxychloride. Malachite is the most common green mineral pigment mentioned by Yu Feian and the historic painting manuals he consulted, and was the most common green pigment identified in the portraits, appearing in twenty of those studied.

Emerald green most frequently refers to copper acetoarsenite, although it can also encompass the earlier but less stable pigment copper hydrogen arsenite, also known as Scheele's green. Both copper hydrogen arsenite and copper acetoarsenite were first manufactured in the early nineteenth century in Europe (Fiedler and Bayard 1997) and were in use as a painting pigment in European paintings within a few years. Several sources indicate that emerald green was not widely available (or used) in China until the 1850s (Wise and Wise 1998). Yu Feian (1988, 30) suggests that its relative scarcity is due to limitations in trade prior to the end of the First Opium War in 1842. Emerald green appears in seven portraits in the Arthur M. Sackler Gallery collection dated to the mid-late nineteenth century, in almost every case with at least two of the other three nontraditional pigments identified in the study—cochineal, Prussian blue, and synthetic ultramarine.



**Figure 4.6.** *Portrait of an Elderly Couple*, 19th–early 20th centuries. Hanging scroll; canvas; 158.1 × 119.8 cm (62¼ × 47⅞ in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program, and partial gift of Richard G. Pritzlaff, S1991.128. Smalt was the primary blue pigment, although blue details of the red seat cover are azurite.

Rather than simply being added to the palette, in the portraits emerald green appears to have displaced the other copper greens entirely. None of the paintings with emerald green contain malachite or any other green mineral pigment. While malachite was never identified in any of the portraits with emerald green, about half of the paintings with emerald green did use the related copper carbonate pigment azurite elsewhere in the painting. In the portraits of the First, Sixth, and Seventh Prince Yi (see figs. 4.2–4.4) the emerald green areas also contained barium sulfate, presumably as a filler or extender.

The green pigment in two paintings, *Portrait of an Elderly Couple* (nineteenth–early twentieth centuries) (fig. 4.6) and *Portrait of Yang Hong (1381–1451)* (ca. 1451) (fig. 4.7), was neither malachite nor emerald green but atacamite; these appear to be outliers (see further discussion in the case studies below). Atacamite is copper trihydroxychloride, a copper



**Figure 4.7.** Portrait of Yang Hong (1381–1451), ca. 1451. Hanging scroll; silk; 218.6 × 126.9 cm (86<sup>1</sup>/<sub>16</sub> × 49<sup>15</sup>/<sub>16</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.77. The green pigment is atacamite.

compound that can be found in mineral form or made synthetically (Lei 2012). As discussed further below, the copper trihydroxychloride pigment from *Portrait of an Elderly Couple* appears synthetic.

### Blue Pigments

The most variety in pigment use observed in the portraits was among the blue pigments. Azurite, smalt, indigo, Prussian blue, and synthetic ultramarine were all identified, and most of the portraits used at least two blue pigments. In older paintings these were generally azurite and indigo, although *Qing Courtier in a Winter Costume* (nineteenth–early twentieth centuries) (S1991.125) used smalt and indigo (see fig 3.12). The thick blue pigment used to paint the dark blue dragon robes in traditional portraits was found to be azurite or azurite-based in all but three of the paintings in which smalt was identified.

Smalt was the primary pigment used to paint the robes in both *Qing Courtier in a Winter Costume* and *Li Yinzhi (1629–1664)* (eighteenth–nineteenth centuries) (S1991.104) (see fig. 3.11). For the latter, although smalt was used for the dragon robe, azurite was clearly employed in other areas of the painting. In the northern Chinese *Portrait of an Elderly Couple* (see fig. 4.6), smalt was also used for the robes worn by the husband and wife as well as for the darker blue pigments in the vases in the background. While in some cases smalt appears to have been a deliberate choice to produce a lighter colored robe for the sitter, in this painting it was the primary mineral blue pigment and was mixed with lead white to provide a pale blue color for the husband's robe, although small amounts of azurite were identified elsewhere in the painting. Smalt appears to have been imported into China since the Ming dynasty (1368–1644) and most commonly used from the sixteenth through the nineteenth century (Xia et al. 2019). Its use as a paint pigment declined when the cheaper synthetic ultramarine became available (Watson 1923).

Prussian blue was identified in eight portraits, in three of which indigo was also used in separate areas (see chap. 3 for further discussion of Prussian blue). In his discussion of pigments, Yu (1988, 30) mentions “blue (made in Germany),” likely a reference to Prussian blue, although possibly to synthetic ultramarine.

Synthetic ultramarine was found in eight portraits. In most of these, azurite and either indigo or Prussian blue were also used. In one case, *Portrait of a Qing Court Lady* (S1991.117), ultramarine was used only sparingly as bright blue in a small area of the bead motif, while two other major blue colorants were

much more heavily utilized: Prussian blue in blue shading, azurite and Prussian blue in the blue robe, and Prussian blue in green and purple mixtures.

Synthetic ultramarine was discovered in 1828 and, due to its low cost, was soon traded worldwide as both an artists' pigment and as a general blue colorant in, for example, laundry bluing (Plesters 1993; Odegaard and Crawford 1996). Over the course of the nineteenth century, synthetic ultramarine was introduced into the paint palette for portraits and gradually replaced both azurite and smalt. Of the seven paintings containing synthetic ultramarine, only two also used azurite whereas five used Prussian blue. Synthetic ultramarine did not replace indigo as it was commonly used in the fashion of a “thick” or mineral-based pigment.

### Hues and Tonal Variations

The lack of a pure purple inorganic pigment in the traditional palette generally meant that indigo and lac dye were mixed to produce purple shades and could be combined with lead white to create a thick paint layer when desired. In later paintings, purple areas that were created using nontraditional materials were identified, including various combinations of lac dye, cochineal, indigo, and Prussian blue. In some cases, different color combinations were found within the same painting, perhaps reflecting different pigment combinations used by artists within the same workshop or the use of premixed colors whose pigment composition changed from time to time. For example, in *Spurious Portrait of the Jiaqing Empress* cochineal was mixed with ultramarine, rather than indigo, to make purple. *Portrait of Lady Hejia, Secondary Wife of Prince Zaizhi* (mid–late nineteenth century) (S1991.65) also had some unusual pigment mixtures containing ultramarine. In addition to ultramarine used alone for a bright blue color, it was employed in one of two different dark greens identified on the painting: the brighter dark green was a mixture of ultramarine with emerald green, and the duller dark green was a combination of Prussian blue with gamboge. Dark blue areas were painted using ultramarine in a mixture with cinnabar/vermillion and a Prussian blue wash.

Deepening of hue was regularly carried out through layering—the application of thin washes over a previous paint layer, often a thick paint layer. Layering was found with all the common thin paint washes used in portraits and has been used with both traditional colorants and newer additions to the palette: lac dye, cochineal, indigo, Prussian blue, and gamboge.

The layering of thin organic colorant washes over a thicker base layer of color to modulate hue can be seen in the drapery modeling in robes but is best viewed in the cloud designs of dragon robes. In *Portrait of the Sixth Prince Yi* (see fig. 4.3b) two additional layers of cochineal were applied over a lead white and cochineal mixture, making a light, medium, and dark pink stepped deepening of color, mimicking the stepped colors found in the damask designs of the original robes. In a few cases ultramarine was also used as a thin wash layer. *Portrait of Ser Er Chen* (mid-late nineteenth century) (S1991.57) and *Spurious Portrait of the Jiaqing Empress* contained ultramarine as a wash over azurite, shading regions of the robe.

In addition to layering, different hues were also sometimes achieved by mixing pigments with varying amounts of lead white. For example, the pale blue of the robe of the male sitter in *Portrait of an Elderly Couple* was achieved with a mixture of smalt and lead white. In *Portrait of a Qing Courtier, Possibly Jing Shou (d. 1889)* (see fig. 4.5), the lightest blue color was made of a mixture of azurite and lead white (Giaccai and Winter 2005).

With some mineral pigments, different hues can be achieved by grading the pigments, taking advantage of natural variations in color that occur as the pigments are ground from coarser (darker) to finer (paler) particle sizes (Winter 2008, 94–96; see also app. 4). In *Portrait of a Qing Courtier, Possibly Jing Shou (d. 1889)*, while the palest blue shade was unusually made with a mixture of lead white and coarse azurite, a medium shade of blue was obtained using finely ground azurite, and a darker shade of blue was made with larger particles of azurite (Giaccai and Winter 2005).

Although emerald green also becomes progressively lighter as the particle sizes become smaller (Fiedler and Bayard 1997)—a fact known by Yu Feian (1988, 45)—in the portraits where emerald green was used, it appears that this characteristic was not always used to advantage. In *Portrait of a Qing Court Lady* (S1991.117) the lightest green colors were obtained by the addition of lead white, not by more finely grinding the emerald green used in the medium green shades. The dark green shades were achieved by a wash of Prussian blue and gamboge over the emerald green underlayer.

#### *Case Studies of Some Portraits*

*The Qianlong Emperor as Manjushri, the Bodhisattva of Wisdom* (see fig. 4.1) is not an ancestor portrait but is addressed briefly here as a lifetime portrait of the

Qianlong emperor. The Jesuit missionary and painter Giuseppe Castiglione, also called Lang Shining, spent many years at the imperial court and, based on stylistic comparisons, is believed to have painted the face of the emperor in this thangka-inspired painting. A lead-based white, cinnabar/vermilion, red lead, organic yellow, malachite, and azurite were all identified in the painting. Fiber optics reflectance spectroscopy (FORS) indicates cochineal was used by Castiglione in the face of the Qianlong emperor, while other areas were painted with lac dye.

*Portrait of Yang Hong (1381–1451)* (see fig. 4.7) was painted significantly earlier than the other portraits in this study and can be dated to the Ming dynasty, approximately 1451. While many design features changed between this portrait and the Qing dynasty portraits that constitute the majority of this study, the pigments used in the painting are typical of those that were still employed by portrait painters in the traditional palette three hundred years later. The major colorants identified were hydrocerussite, cinnabar/vermilion, lac dye, red lead, atacamite, azurite, and indigo. The green pigment used in the painting was atacamite, which was not as commonly used as malachite in the Qing portraits but has been identified in a later portrait in the study. Similarly, red lead was not commonly used in Qing portraits but did not fall completely out of use.

*Portrait of an Elderly Couple* (see fig. 4.6) was painted on canvas in north China during the nineteenth or early twentieth century. Unlike many of the portraits in this study, it depicts individuals not associated with the imperial court through genealogy or professional position. This portrait uses atacamite as the green pigment rather than the more frequently identified malachite. From polarized light microscopy (PLM) it appears that the green pigment particles have a rounded shape more characteristic of synthetic copper trihydroxychloride (Lei 2012). In addition, a medium blue smalt pigment was used rather than a dark blue azurite for the robes of the two primary figures. Smalt was also present in the dark blue areas in the carpet and vases, but a few small dark blue areas in the red textile behind the female sitter were found to contain azurite, not smalt. In areas where a thin blue wash was needed, such as for the folds in the robes, indigo was used.

Two of the portraits studied may have been made or modified for sale to foreign clients. *Spurious Portrait of the Jiaqing Empress* may have been produced specifically for sale to foreign customers wanting an ancestor portrait in the early

twentieth century although, as more is learned about portraits of the two empresses dowager of the late Qing dynasty, curators are also considering the possibility that this portrait was made at the court, although not as early as the Jiaqing era (1796–1820). This portrait contains almost the full range of imported nontraditional pigments, including cochineal, emerald green, and synthetic ultramarine, as well as traditional pigments such as lead-based white, cinnabar/vermillion, and azurite, so it must date to the mid-nineteenth century or later. *Portrait of a Qing Court Lady* (S1991.92) was modified in the early twentieth century by a repainting of the dragon surcoat over the original eighteenth-century portrait. In the overpainted areas, synthetic ultramarine was identified, whereas azurite was used in the original areas of the portrait.

## Discussion

Consideration of the pigments that have been identified as a whole, rather than on individual paintings, builds understanding of the traditional palette used by portrait painters and the ways this palette changed over time. As new pigments were introduced to China, they became incorporated into the painters' palette at a speed that appears to be related to cost of the pigment in China. The identification of new pigments in a portrait can be used to assist in dating the painting and as additional evidence to group portraits to the same workshop. The adoption of new pigments by portrait painters aligns with their adoption by painters of architecture, painters of paintings for export, and other professional painters. Scholar-painters were, however, less likely to use the new pigments.

### *European Colorants and Their Relationship to the Traditional Palette*

Of the colorants used in portraits discussed above, the pigments lead white, cinnabar/vermillion, lac dye, arsenic sulfides, organic yellows (presumably gamboge), malachite, azurite, indigo, and smalt are consistent with the traditional palette of the scholar-painter. While red lead and smalt have been used for centuries in Chinese paintings and were identified in a few portraits, they were not common pigments in the Qing portraits studied. The rarity of red lead and smalt in the portraits accords with the palettes identified in other Qing paintings examined as part of the larger study presented in this volume. Arsenic sulfide pigments, although often described in painting

manuals, were rarely found in scholar paintings in the Freer and Sackler, but the deep yellow or orange colorant realgar and associated arsenic sulfides were identified in the majority of the portraits.

New colorants found in portraits painted in the nineteenth century include cochineal, a dye indigenous to the Americas, as well as new synthetic colorants. Invented and introduced in Europe, synthetic pigments identified in the Qing dynasty portraits (but not the earlier Ming dynasty portrait) include Prussian blue (1704), emerald green (1814), synthetic ultramarine (1828), and zinc white (1834). Their presence in the portraits is evidence that these pigments became available in China in the mid-late nineteenth century, confirming statements by Yu Feian (1988, 30) that there was increased import of European pigments after the First Opium War, specifically in the Xianfeng reign beginning in 1851. Although there are few other studies of Chinese portraits, He Qiuju and coauthors (2010) also identified emerald green and synthetic ultramarine in the pigments used in a Chinese Daoist portrait from the mid-late nineteenth century.

In general, modern European colorants appeared to be additions to the Chinese palette rather than replacing traditional colorants. Many paintings that contain new nontraditional materials also contain their traditional counterparts. For example, most of the paintings with cochineal also contain lac dye. In some cases, the traditional and the new pigments were used in different manners or for different design elements, suggesting that the workshops distinguished between these new pigments and traditional ones, either with the same artist choosing different colorants in different instances or with different artists preferring the modern colorant over the traditional colorant, although both were available in the same workshop. The one exception appears to be emerald green, which completely replaced malachite in the portraits in which it was identified. As Yu (1988, 30) explained, emerald green's bright color, ease of use, and low cost were the primary reasons it replaced malachite. However, neither ultramarine nor Prussian blue appears to have completely replaced azurite's role in portraits. Likewise, indigo continued in use, although fewer indigo blues were seen in portraits after the nineteenth century.

### *Pigments and Dating*

It can be very difficult to date formal portraits because the pose and props are often conventional, dress is traditional, and portraits of long-deceased

ancestors were sometimes commissioned (see fig. 4.2) (Stuart and Rawski 2001). But art historians can use the presence of modern pigments to narrow the date range of a particular painting. Although modern pigments may not have been used immediately after their invention, the date of their invention does provide an antedate, before which the painting could not have been painted. Antedates can be useful in identifying ancestor portraits that were commissioned many years after the subject's death. Emerald green and synthetic ultramarine were quickly adopted for use in paintings, and their presence dates a painting, to no earlier than the mid-to-late nineteenth century.

The date ranges of three portraits in this study can be narrowed down by pigment identifications. *Portrait of a Qing Courtier* (S1991.105) and its paired painting *Portrait of a Qing Court Lady* (S1991.117), as well as *Portrait of Lady Hejia, Secondary Wife of Prince Zaizhi*, are stylistically dated to the nineteenth century, but pigment identifications indicate they were painted in the mid-nineteenth century or later, when emerald green and synthetic ultramarine were more commonly found in China. Similarly, while *Portrait of Ser Er Chen* is stylistically dated to the eighteenth or nineteenth century, its use of synthetic ultramarine over azurite to create shading indicates that it was painted in the mid-late nineteenth century.

#### *Pigments and Attributions to Workshops*

Four sets of paintings examined were related either by being part of a matched pair or by having enough motifs in common that they were identified as originating from the same workshop. Examination of the pigments found in the portraits can be used to support these associations.

The set of three portraits of the Princes Yi (see figs. 4.2–4.4) have been identified by Stuart and Rawski (2001) as likely to have been painted by the same workshop. The portraits of the First Prince Yi (see fig. 4.2) and Sixth Prince Yi (see fig. 4.3) date to 1905, while the portrait of the Seventh Prince Yi (see fig. 4.4) was painted in 1911. In the portrait of the Sixth Prince Yi the outline from a stencil is visible (see fig. 4.3b), and identical measurements in the features of the portrait of the Seventh Prince Yi suggest that the stencil was reused in 1911 (Stuart and Rawski 2001). Moreover, the pattern used in the seat cushions of all three portraits is identical, and the colors are the same in the first two portraits, while in the third portrait different colors were used. For example, a cloud pattern that is green-colored in the first two portraits is pink in the third portrait. All three

portraits use nontraditional pigments. Although azurite was predominantly used for the large areas of blue in the dragon robe in the later portrait of the Seventh Prince, the blue dragon robe of the Sixth Prince features an unusual mixture of emerald green and ultramarine. The portraits of the First and Sixth Princes have calcium carbonate used in combination with hydrocerussite (lead white) in at least one area. All three paintings also use an atypical mixture for purple: in the portraits of the First and Sixth Princes cochineal is combined not with indigo but with Prussian blue. In the later portrait of the Seventh Prince, lac dye with a small amount of cochineal was combined with Prussian blue in various purple areas.

Three additional pairs of paintings can be identified by their motifs and pigments. One pair depicts husband and wife: *Portrait of a Qing Courtier* and *Portrait of a Qing Court Lady* (S1991.117). The second pair uses the same furnishings, as well as being similar in size and depicting family members: *Portrait of Princess Shouzang (1829–1856), Fifth Daughter of Emperor Daoguang* (mid-nineteenth century or later) (S1991.122) and *Portrait of a Qing Courtier, Possibly Jing Shou (d. 1889)* (see fig. 4.5). The third pair depicts unrelated men but the setting includes the same furniture and carpets, suggesting the portraits were commissioned separately but came from the same workshop: *Man, "A Manchu Noble"* (Qing dynasty) (S1991.108) and *Portrait of Oboi* (mid-eighteenth–early twentieth centuries) (S1991.93).

The husband and wife pair—*Portrait of a Qing Courtier* and *Portrait of a Qing Court Lady* (S1991.117)—is interesting because the dark blue robes of both figures are painted in azurite augmented with emerald green, a pigment composition not found in any other portrait examined. However, in some samples of pink colors in *Portrait of a Qing Courtier*, a small amount of lac dye was identified along with cochineal by high-performance liquid chromatography (HPLC). This mixture was not found in *Portrait of a Qing Court Lady*, possibly because the small samples did not allow for identification of the small amounts of lac dye observed in the primarily cochineal mixture, or because different artists with slightly different paint palettes painted the two portraits, even in the same workshop.

Although the second pair of portraits—*Portrait of a Qing Courtier, Possibly Jing Shou* and *Portrait of Princess Shouzang*—generally contain the same colorants, a few additional colorants, such as indigo and cochineal, were used in *Portrait of a Qing Courtier, Possibly Jing Shou* but not in *Portrait of Princess*

*Shouzang*, suggesting that the portraits were painted at separate times even though they depict members of the same family. In *Portrait of a Qing Courtier, Possibly Jing Shou*, light purple shades were obtained with lac dye, Prussian blue, azurite, and lead white, while the medium and dark purple shades were made with lac dye and indigo (see fig. 4.5a). In *Portrait of Princess Shouzang*, all the purple shades were created using lac dye and Prussian blue. More discussion of the pigments used in this pair are given in the study by Jennifer Giaccai and John Winter (2005).

The third pair—*Man, “A Manchu Noble”* and *Portrait of Oboi*—use a similar, albeit typical, paint palette, but the portraits of unrelated men have had significantly different histories after leaving the workshop and one painting is in considerably worse condition.

### *Comparison to Pigments Used in Other Qing Dynasty Artworks*

The results described above indicate that a handful of nontraditional pigments were added to the palette of the portrait painters. While cochineal was used by scholar-painters (see chap. 2), Prussian blue, synthetic ultramarine, and emerald green were rarely identified in scholar-paintings (see chap. 3). The new European pigments were said to be used by the professional artists whom Yu Feian (1988, 43) describes as “folk artisans,” those who painted portraits, designs on architecture, sculpture, lanterns, and other “colored” paintings.

In recent studies, these new European pigments have been identified in painted architecture (Hu et al. 2013; Zhu et al. 2016; Cheng et al. 2007; Shen et al. 2006; Mazzeo et al. 2004; Li et al. 2013; Wang et al. 2010). While these studies found extensive use of the traditional pigments—including lead white, calcium carbonate white, mercury sulfide, red and yellow iron oxides, red lead, malachite, atacamite and botallackite (both copper trihydroxychloride), azurite, indigo, and smalt—they also identified the more modern pigments emerald green, synthetic ultramarine, and Prussian blue. Studies of cross-sections have also shown that emerald green and synthetic ultramarine replaced traditional pigments in later restorations (Lei et al. 2017). Emerald green appears quite frequently in painting of architectural features, in particular in restorations and in painted figurines (Wang et al. 2010). It was identified in a decorative Gate of Correct Conduct wall painting (*Zhendu Men*, Palace Museum, Peking [now Beijing], restored after 1889) (Cheng et al. 2007); in the restoration of Hall of

Martial Valor (*Wuying Dian*, Palace Museum, Peking, restored after 1869) (Shen et al. 2006); in the restoration of the Drum Tower in Xi’an, a Ming dynasty monument with several restoration campaigns (Mazzeo et al. 2004); and in late nineteenth-century statues (Jin et al. 2010) and other architecture (Zhu et al. 2013).

The palette used for portraits and architecture can be compared to the palette used in the colorful paintings made for export out of China. Elisabetta Polidori’s (2007) study of Chinese paintings made for export and collected between 1769 and 1787 found no Prussian blue and only one organic red pigment, not further identified, although in this era cochineal and Prussian blue were in regular use throughout Europe. She did identify the traditional palette on these paintings: lead white, mercury sulfide, red iron earths, red lead, gamboge, malachite, azurite, and indigo. Later paintings for export, however, did incorporate synthetic European pigments. In their study of nineteenth-century paintings for export, on both pith paper and scrolls, David Wise and Andrea Wise (1998) identified the use of emerald green starting in the 1850s. In addition to emerald green, they found malachite, copper chlorides (possibly copper trihydroxychloride), and synthetic copper carbonates as well mixtures of the various green pigments. They also identified lead white, mercuric sulfide, red lead, and smalt. Additional studies of Chinese pith paintings from the nineteenth century confirmed the use of lead white, calcium carbonate, mercury sulfide, carmine red, red lead, gamboge, malachite, emerald green, azurite, indigo, Prussian blue, synthetic ultramarine, and iron oxide (Carlson et al. 2005; Otieno-Alego 2000). A study by Sotiria Kogou and coauthors (2015) of two sets of paintings for export—twenty collected in the eighteenth and nineteenth centuries by diverse collectors and twenty-six paintings commissioned in China between 1817 and 1831—identified a number of pigments similar to those found in the portraits in the present study, including lead white, cinnabar/vermilion, red iron-based earths, red lead, lac dye, and cochineal (with cochineal identified more frequently than lac dye), realgar, yellow iron-based earths, gamboge, one incidence of chrome yellow, malachite, one incidence of copper trihydroxychloride, azurite, indigo, Prussian blue, and one instance each of smalt and synthetic ultramarine. The authors noted that no Prussian blue was present in the set of paintings commissioned between 1817 and 1831, and it is also of note that no emerald green was identified in any of the forty-six



paintings examined. A recent x-ray fluorescence (XRF) study of Chinese paintings for export identified a dark yellow arsenic-based pigment, possibly the same arsenic sulfide pigment used for the portraits, as well as the co-occurrence of emerald green and barium sulfate in green areas on the paintings (Wang et al. 2018). The combination of emerald green and barium sulfate was also found in the portraits of the First, Sixth, and Seventh Princes Yi (see figs. 4.2–4.4), suggesting that the barium sulfate may have been an extender added during manufacture.

The shared palette of the portraits, painted architecture, and paintings for export and the use of the nontraditional pigments Prussian blue, emerald green, and synthetic ultramarine strengthen Yu's grouping of these painters based on painting style and color choices. Yu (1988, 43) describes these professional artists having a "unique style of color" and explains that they researched pigments that would be inexpensive, convenient to use, and remain unchanged over time. He discusses the uses of imported blue and green pigments, implying that they were employed by painters of all genres including scholar-painters. It appears, however, that in the second half of the nineteenth century in China nontraditional pigments were used primarily by professional painters, not scholar-painters.

## Conclusions

While cochineal and Prussian blue appear to have slowly infiltrated the palette of portrait painters, by the time synthetic ultramarine and emerald green were introduced in the mid-nineteenth century, modern pigments seem to have been fully embraced in portraits. Their use is likely to have been concurrent with, and not unrelated to, the end of the First Opium War, when trade was greatly increased and the door was opened to many of the newly invented modern pigments. Some of the imported materials were treated as additions to the existing palette, for example synthetic ultramarine, while others seem to have replaced original pigments, as when emerald green replaced malachite.

The introduction of new pigments into the Chinese painting palette appears to have occurred first in portraits as well as in other, more functional types of painting, such as architecture and paintings for export. In Qing portraits, there was the occasional use of smalt, common use of cochineal by the mid-late eighteenth century, common use of Prussian

blue by the nineteenth century, and the introduction of synthetic ultramarine and emerald green by the mid-late nineteenth century. Zinc white, barium sulfate, and gypsum have been identified, but as fillers or extenders in colored areas rather than as white pigments. The Qing portraits also use arsenic-based pigments, although only as deep yellow pararealgar or similar arsenic sulfide pigments, not bright yellow orpiment.

Identification of the pigments used in a painting can be helpful in dating portraits. Although no pigment can provide an exact date for a portrait, use of newer pigments can provide an antedate. In addition, when, how and where a pigment was used can suggest groupings of portraits likely to have been painted in the same studio at a similar time. Although pigment use cannot be considered definitive proof, it can certainly lend support to groupings suggested by carpet designs and props.

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# 5

## The Introduction of Nontraditional Pigments and Dyes into the Chinese Palette

Blythe McCarthy and Jennifer Giaccai

### Introduction

Pigments used by artists throughout the long history of Chinese paintings were determined by availability and reinforced by tradition. Ready sources of pigments such as azurite, malachite, and cinnabar/vermillion led to their prevalence in Chinese paintings, while those with more restricted sources such as natural ultramarine and smalt found more limited use. As new pigments became available via trade, they were gradually added to the Chinese painter's palette.

### Pre-Ming Use of Pigments in Portable Paintings

A small group of pigments was observed in Song dynasty (960–1279) paintings and continued in use through the Qing dynasty (1644–1912), as detailed in previous chapters. These include lead white, cinnabar/vermillion, red lead (less common), malachite, azurite, and red, yellow, and brown iron oxides—all minerals with sources in China. In addition to the

mineral pigments, organic colorants were also used in China. The organic blue colorant indigo was present in portable paintings starting in the Song dynasty, and gamboge and lac dye were increasingly in use during the Yuan dynasty (1279–1368), perhaps due to the greater reach of its Mongol rulers. At its height, the Yuan dynasty borders encompassed three times the land of the Southern Song dynasty (1127–1279) China, and its rulers maintained relations with the three western khanates of the Mongol Empire, which may have allowed freer trade of pigments.

Two religious paintings from Dunhuang are the earliest paintings in the study, and they exhibit a palette slightly different from that of the other Song dynasty paintings analyzed. They are the only Song dynasty paintings in this study to contain an insect dye, presumably lac. In addition to the pigments seen in the other Song dynasty paintings, they also contain natural ultramarine and orpiment, as well as the copper trihydroxychloride pigment atacamite as the green pigment instead of malachite, all pigments that were absent or uncommon in the other paintings from the Song dynasty. These differences as well

as analyses of four other portable paintings from Dunhuang (Delbourgo 1980; Mysak et al. 2011) suggest that there may have been a regional palette for paintings in western China, in particular the area around Dunhuang, a city in northwestern Gansu province near the Mogao Caves. A stop on the Silk Road, it had an international population that was heavily involved in trade and was not always under Chinese control. Analyses of pigments from wall paintings share a set of pigments similar to those found in the Dunhuang paintings. However, the wall paintings exhibit a wider variety of white pigments, including gypsum, kaolin, talc, and calcium and magnesium carbonates, perhaps due to the availability of these materials from the components used for the plaster substrate.

The palette for paintings from Dunhuang is defined by the availability of pigments in the area. This use is characterized by the presence of orpiment, natural ultramarine, and/or atacamite. While azurite is a copper carbonate that, together with malachite, had many possible sources in China, natural ultramarine is much rarer, with a source in Afghanistan that would have been more easily obtained in regions in western China such as Dunhuang. Thus regional availability may explain why natural ultramarine is found in this study only in the two works from Dunhuang and one other work associated with western China.

Copper trihydroxychloride pigments (mainly atacamite) that appear to be synthetic are also commonly found in wall paintings (see chap. 1). While the similarity of pigments in portable paintings and in wall paintings from Dunhuang supports the idea of a regional palette, the copper trihydroxychlorides are not limited to wall paintings in Dunhuang but have also been found in a wall painting and sculptures from Buddhist sites in the north China provinces of Shaanxi and neighboring Shanxi (Cauzzi et al. 2013; Egel and Simon 2013; Twilley and Garland 2011; Webb et al. 2007; Lei 2012). Chapter 1 describes copper trihydroxychlorides that were also found in two other religious paintings and an album leaf painting of a secular subject, *Bird on an Apricot Branch* (see fig 1.6), opening the possibility of broader distribution. The use of copper trihydroxychloride pigments thus extends east in this early period in religious paintings, perhaps following northern trade routes or the Buddhist monks as they progressed across China. This pigment has continued in use in China, as its identification in four of the later period paintings studied shows (see app. 5). It is worthwhile noting that this

pigment may be more common than suggested by appendix 5, as many of the analyses of copper green pigments were carried out only with x-ray fluorescence (XRF) and it is necessary to use additional techniques to unequivocally distinguish between malachite and atacamite. Further studies are needed to determine if the production or trade of this pigment was associated with Buddhist monasteries, how it was distributed, and the extent of its use in terms of date and geography.

## Painting Manuals

The early painting manuals discussed in chapter 1 mention many of the pigments found in the paintings discussed in this volume. The information overlaps, and in some cases—perhaps many cases—later manuals have borrowed from earlier ones, preserving the texts to the present (Franke 1950). The number of painting manuals increased tremendously in the Ming (1368–1644) and Qing dynasties and were consumed by those seeking, as Jong Phil Park (2011, 11) puts it, “cultural capital.” These instructional manuals provided a way to obtain painting skills outside the earlier system of tutors used by the scholar-painters. Their simplicity and mechanical nature were not appreciated by the critics of the time, who did not consider that they led to true art. Many of the manuals from this period are not available in Western languages to date; however, we have compiled the terminology on pigments from manuals available in English translation in appendix 4. This appendix also includes information from a mid-twentieth-century publication by Yu Feian, *Chinese Painting Colors* (Zhongguo hua de yan liao yan jiu) and its 1988 English translation by Jerome Silbergeld and Amy McNair. Yu Feian collated details of pigments collected from a large number of painting manuals produced from the Tang dynasty (618–907) through the late eighteenth century. He added commentary based on his experiences as a classical scholar-painter and on his discussions with professional painters of other painting genres, such as portraits, lanterns, and New Year’s paintings.

The information in the manuals on pigments and their use does not always agree with what scientific analysis has identified in paintings. To date, the green pigment atacamite has not been specifically associated with any pigments mentioned in the early painting manuals; however, examination of the terms from painting manuals for green pigments shows the

level of confusion that might be experienced by the twenty-first-century reader. In addition to the terms “first green,” “second green,” and “third green,” which refer to malachite ground in increasingly smaller particle sizes that are increasingly lighter in green color, Yu Feian (1988, 58) also mentions that “branch green” and “flower green” are even paler grinds of malachite than “third green.” In *The Mustard Seed Garden Manual of Painting* it becomes clear that “grass green” appears to be a mixture of indigo and gamboge (Sze 1956, 43), such as the mixtures discussed in chapters 1 and 3. However, other terms from various painting manuals, for example “lacquer green,” “flower-and-leaves green,” “Southern green,” “greasy green,” “paste green,” “peacock green,” and “granulated green,” are not described in a way that makes their chemical composition clear (see app. 4). Copper trihydroxychlorides have been described in texts from Dunhuang as “green salt” or “copper green,” and Lei Yong (2012), in a review of the pigment, differentiates between natural pigments and a synthetic version appearing during the Five Dynasties period (907–79), but neither the term “green salt” nor a pigment with its description has yet been found in other painting manuals. It is, however, mentioned as a pigment in the technical manual *T'ien-kung k'ai-wu: Chinese Technology in the Seventeenth Century* (Tiangong kaiwu) (Song 1966, 287). Yu (1988, 28) says that one of the five shades of green used in Dunhuang murals is a man-made pigment that he refers to as “verdigris,” but this is likely a copper trihydroxychloride.

The yellow pigment orpiment is frequently mentioned in painting manuals, but in this study it was found only in the two paintings from Dunhuang. The dearth of orpiment may be due to loss following degradation, as it is known to photodegrade to white friable degradation products (Keune et al. 2016). It is more likely, however, that orpiment just was not used as frequently as other yellow pigments, such as gamboge and iron oxide. Most of the paintings reported in appendix 5, table A5.2, were studied with the intent to determine the presence or absence of imported blue and red pigments; the yellow regions often went unstudied. Thus later occurrences of orpiment in the Ming and Qing dynasties are possible, and they will be investigated in an upcoming study.

A different arsenic sulfide pigment, pararealgar, and related dark yellow pigments are commonly identified in nineteenth-century portraits. Yu Feian (1988, 44) states that realgar was made by the artists themselves. Man-made arsenic sulfides have been identified in Japanese woodblock prints (Luo et al. 2016; Zaleski

et al. 2018; Vermeulen and Leona 2019), and its manufacture in seventeenth-century China is described by Song Yingxing (Song 1966, 212), while its manufacture and use as a painting pigment are also mentioned in the early twentieth century (Watson 1923, 509).

## Trade Patterns and New Pigments

Beginning in the sixteenth century, increased trade with Europe and the Americas introduced nontraditional colorants to China. They may have been brought by missionaries, offered as tribute at the capital, or imported through trading centers in southern China such as Canton (today Guangzhou), which was the main port for trade with the West from the mid-eighteenth to the mid-nineteenth century. In 1842, the treaty following the end of the First Opium War opened China more broadly to foreign trade. By the late nineteenth century imported pigments were widely available in China, as evidenced by their use in paintings.

### *Spain and the Adoption of Cochineal*

Following the arrival of the Spaniard Hernán Cortés in Mexico in 1519, the red dye cochineal quickly made its way to first Spain and then during the sixteenth century more broadly to Europe (Serrano 2016). Spain, which held a monopoly on the trade in cochineal, attempted to establish a trade relationship with China but was rebuffed in Macao by the Portuguese, who had held the only sanctioned trade relationship with China since the 1500s (Sousa Pinto 2008). The Spanish thus shipped cochineal to Asia via the Manila Galleon that traveled the Pacific Ocean from Mexico to the Philippines. By the 1580s, cochineal was included in the cargo (Phipps 2010, 40). From Manila the cochineal was shipped to Canton. Despite evidence of knowledge of cochineal in China (there is documentary evidence that the Kangxi emperor (1654–1722) was introduced to cochineal as a source of red dye by the early eighteenth century) (Phipps 2010, 40; Donkin 1977), very little cochineal may have been available to Chinese dyers and painters. In Canton, at least twenty-eight ships (English, French, Dutch, Danish, and Swedish) took on cochineal in 1765 (Lee 1951, 212), suggesting that much of the cochineal arriving from Manila may have been reexported.

In addition to trade of the cochineal insects, the early trade in cochineal may have also involved the dyeing of silk either in Canton or in another port city outside of China, with the dyed silk then

traded back to Europe (Lee-Whitman 1982; Van Dyke 2016, 78–79). Sino-Portuguese silks dating to the seventeenth century, whose designs and technical aspects combine Asian and European methods, have been the object of recent study, although their cochineal-dyed threads may be later eighteenth-century, possibly European, additions (Claro and Ferreira 2020).

Although the British attempted to acquire cochineal from areas not controlled by the Spanish in commercial amounts, Spain continued to control the majority of the trade. After Mexico achieved independence in 1821, the Spanish monopoly was broken and cochineal was more widely available and at a lower cost due to greater competition both in and outside Mexico (Salinas 2018; Donkin 1977).

Despite the presence of dye from American cochineal in sixteenth-century silks in Europe, Chinese textiles dyed with cochineal prior to 1800 are rare, perhaps nonexistent (Phipps 2010, 40). The presence of cochineal in European textiles combined with scientific analyses of pigments suggest that New World cochineal was in use in European painting as early as the sixteenth or seventeenth century (although questions remain about the validity of the identification of a New World species) (Serrano 2016, app. 3, table 7). In this research it was not identified in paintings earlier than the late eighteenth century, except for possibly in *Small Birds and Morning Glories* (F1980.152), a painting of contested date (see fig. I.2). The delay in the adoption of cochineal in China is likely associated with the monopoly held by the Spanish who did not have direct trading access to China, the large demand in Europe, cost and other barriers during this period when China closely regulated foreign trade.

### *Qing Regulations and the Adoption of Prussian Blue*

The majority of the Prussian blue identified in this study is found in paintings dated to the mid-nineteenth century or later with one possible exception: *Small Birds and Morning Glories*. According to Kate Bailey's (2012) analysis of documents of that time, there is evidence for a Prussian blue factory operating in Canton from ca. 1827 to 1842, perhaps increasing supply while reducing cost and explaining the increased use seen in the paintings. This time frame coincides with a reduction of the cost of Prussian blue in Japan due to increased imports from China occurring after 1824 (Smith 2005). It is interesting to note that 1842, the year the factory is said to have closed, is also the date of the treaty ending the First Opium War.

As in this study Prussian blue was seen in paintings from the late nineteenth into the twentieth century, Chinese production of Prussian blue likely continued at different locations. Indeed a factory in Canton is mentioned in 1875 by the Archdeacon of Hong Kong in a description of a walk in Canton (Bailey 2012).

### *End of Qing Regulations and the Introduction of Modern European Pigments*

In Europe, during the nineteenth century more and more artists turned to colormen for their painting supplies instead of preparing their own paints. This shift spurred development of an array of new pigments as can be seen in the catalogs of European and American colormen of the time (Carlyle 2001). By the mid-nineteenth century some of these pigments begin to be found in Chinese paintings, primarily in portraits. Pigments identified in nineteenth-century works in addition to Prussian blue include emerald green, synthetic ultramarine, and zinc white (always with other colors). Their presence in the portraits is evidence these pigments became available in China in the nineteenth century, confirming assertions by Yu Feian (1988, 30) that there was increased import of European pigments after the First Opium War.

Modern chromium-based pigments, also invented and used as artists' pigments during the nineteenth century in Europe, were found in two twentieth-century Chinese paintings analyzed for this volume. It is notable that no chromium pigments were identified in any of the portraits analyzed, despite the presence of emerald green, Prussian blue, and artificial ultramarine. Chromium pigments may be rare in Chinese paintings because they, like cobalt and cadmium pigments, were available only as artists' materials, while synthetic ultramarine, Prussian blue, and emerald green pigments were also traded for other uses, such as laundry bluing and insecticides (Fiedler and Bayard 1997; Plesters 1993).

In a painting with chrome yellow, *Bean Vines and Insects*, forgery of Qi Baishi (ca. mid-twentieth century) (F1980.163), a red synthetic azo dye was also present. The spectrum of the dye appears to be similar to the dye Ponceau 2R, developed in the late nineteenth century, identified in Japan in prints dating from 1889, and continuing in use in artists' materials today (Cesaratto et al. 2018). A different red azo dye has been identified in combination with Prussian blue in a painted Chinese lantern from the 1930s (Kelley 2021). Yu classified lantern painters as "folk" or professional painters, the same category he used for portrait painters.

Trade of colorant materials also went from Asia to Europe: gamboge, a colorant found in both European and Asian paintings, is from Southeast Asia. Its presence in the Economic Botany Collection of the Royal Botanic Gardens, Kew, and in the records of British colormen provides evidence of its trade westward for use by European artists. Chinese ink sticks are also offered for sale in nineteenth-century European watercolor catalogs.

#### *Availability of the New Pigments in East and Southeast Asia*

The European pigments found in Chinese paintings in this study were also identified in paintings and other painted works from throughout Asia, with dates of introduction and use similar to those seen in China. These works provide further evidence of the pigments' availability in Asia.

Unlike Prussian blue, which was not used in paintings in East Asia for at least a century after its invention in 1704 (with the possible exception in this study of *Small Birds and Morning Glories*), synthetic ultramarine quickly came into use after its discovery in 1828. Due to its low cost, synthetic ultramarine was soon traded worldwide as both an artists' pigment and as a general blue colorant in other commercial goods (Plesters 1993; Odegaard and Crawford 1996). It has been identified as a late Qing addition in the Mogao Caves (Wang 2000) as well as in many of the Chinese paintings made for export and in painted architecture studies mentioned in chapter 4. In the Polynesian Islands, synthetic ultramarine was used as a blue pigment, although in that locale it is theorized that it was sourced from laundry bluing rather than specifically traded as a paint pigment (Odegaard and Crawford 1996).

In Thailand, Prussian blue was introduced in the early nineteenth century, and emerald green and synthetic ultramarine in the late nineteenth century (Mass et al. 2009). They were used in murals (Prasartset 1996), banner paintings (Giaccai 2008), and manuscripts (Burgio et al. 1999; Huang 2006; Eremin et al. 2008). In Thai paintings, barium sulfate was also used in the late nineteenth century, but it has not been identified as used for white paint in the Chinese portraits examined in chapter 4, only to lighten the color or as an extender in emerald green paints. In Korea, shamanic paintings used emerald green and other copper-arsenic greens from the mid-nineteenth century on (Oh et al. 2015).

Unlike the findings for the Chinese paintings examined in this study, in South and Southeast Asia chromium yellows appear to have been used as early

as the nineteenth century. Chromium yellow and orange pigments were found in nineteenth- and twentieth-century Thai manuscripts (Huang 2006; Burgio et al. 1999) and in nineteenth-century Indian paintings and painted sculpture (Agrawal 1971; Wheeler et al. 2011).

In Tibet many modern pigments were not used until the twentieth century. It has been proposed that the delayed use in Tibetan painting was due to lack of access, but in Japan, even after trade with countries outside of Asia made imported pigments accessible at the end of the Edo period (1603–1868), the adoption of modern pigments other than Prussian blue in Japanese paintings was rare. In a study of five hundred *ukiyo-e* school paintings from the mid-late nineteenth century, Elisabeth West FitzHugh (2003) found only five instances of synthetic ultramarine and a single instance of emerald green. A notable early use of Prussian blue in Japan occurred in a soapfish in *Colorful Realm* by Itō Jakuchū (1765–66) (Hayakawa 2012); no other part of the extensive *Colorful Realm* painting series or any other part of the hanging scroll containing the soapfish used Prussian blue, so this occurrence appears to have been a specific use of a rare quantity of this pigment. Prussian blue seems to have entered into more common use in Japanese paintings after its introduction into woodblock prints in the 1820s (Smith 2005).

### **Pigments and Their Use**

Rather than replacing a traditional colorant, modern European colorants often are additions to the pigments available from which a painter could choose. In many of the paintings in which artists used new, nontraditional pigments, the traditional pigment counterparts were also employed. Many of the paintings where cochineal was identified also contained lac dye. When both dyes were found in the same area of a painting, one was used as a component in a mixed pigment and the other as an overlaid wash, to deepen the color or create shading, similar to the use of a glaze in oil painting techniques.

In Western oil and watercolor technique, lac and cochineal are found as lake pigments. But as discussed in chapter 2, Chinese literature sources do not mention lakes or processes for their preparation, suggesting that these red colorants in China were used as water-soluble dyes rather than insoluble laked pigments. However, analysis of the paintings using fiber optics reflectance spectroscopy (FORS) points to the



possibility of a dye–alum salt complex that could have formed either from the reaction of the dye with an alum sizing layer or with alum added during painting (see app. 2). The insect dyes could have inadvertently produced alum-stabilized insect dye pigments due to the method of application in Chinese paintings. Similar FORS spectra for the insect dyes are also observed in purples, where insect dyes are mixed with a blue colorant. In purples, lac was generally found with indigo and cochineal with Prussian blue, although there were exceptions.

Prussian blue was used in the manner of both azurite and indigo. Azurite is considered one of the “thick colors,” along with malachite and white pigments, according to Yu Feian (1988, 9), and is distinct from the thinly applied colors. It is interesting that Prussian blue appears to be used both as a thick color and as a thin wash, as its properties make variations in color and effect possible. In portraits, when Prussian blue was used in robes where azurite was traditionally used, its high tinting strength was a critical factor in its selection. When Prussian blue was utilized in place of thin washes of indigo or in mixtures with reds (in purples) or gamboge (in greens), its fine particle size, a characteristic it shares with indigo, became important (see chap. 3).

Both Prussian blue and synthetic ultramarine provided bright colors even when small quantities were used. Although of a relatively small particle size, synthetic ultramarine appeared to be used more frequently as a “thick” color. Yu Feian (1988, 30) explains that the bright color, ease of use, and low cost were the primary reasons newer pigments were substituted for traditional ones.

One new pigment that appears to have replaced a traditional one is emerald green. None of the paintings that used emerald green also contained malachite or another copper-based green as a pigment.

## Conclusions

Writing in 1955, Yu Feian (1988, 80) advocated “assimilating foreign nutrients” to advance painting practice. The introduction of new pigments into the Chinese painting palette seems to have occurred regularly throughout the history of Chinese paintings, long before the twentieth century. During the Yuan dynasty, gamboge augmented the use of iron oxide yellow colorants and lac dye became more commonly used. Although cochineal was identified in Chinese paintings dating to the early eighteenth century, it did

not become more common until the nineteenth century, and it appears to have been distinguished in use from lac dye.

As new synthetic pigments were invented in Europe and imported into China during the Qing dynasty, their first uses were identified in portraits as well as in architecture, paintings for export, and wallpapers; only later did they appear in scholarly painting (see chap. 4). Use of the new pigments was dependent on availability in China, and the professional painters using the new pigments would have been cognizant of their cost compared with traditional pigments, especially when large amounts of pigment were needed, as in the portraits examined in this study. In Qing portraits there was frequent use of cochineal by the mid–late eighteenth century, common use of Prussian blue by the nineteenth century, and the introduction of synthetic ultramarine and emerald green by the mid–late nineteenth century. Zinc white and barium sulfate have been identified, but only in colored areas and not as white paints, suggesting that they were employed as bulking agents in premixed paints rather than added by the painters themselves. The portraits also saw the use of a deep yellow arsenic sulfide pigment, thought to be locally manufactured.

New pigments continued to be imported, and by the twentieth century, in addition to continued use of the traditional colorants and those added during the Qing dynasty, new pigments such as titanium white, chrome yellow, and azo reds also came into use in Chinese paintings.

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# Appendix 1

## Analytical Methods

### Painting Selection

The paintings investigated in this study are from the collections of the Freer Gallery of Art and the Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C. The Museum System (TMS) database of the collection was used for the initial selection of paintings, mainly from the Song (960–1279), Yuan (1279–1368), Ming (1368–1644), and Qing (1644–1912) dynasties. All paintings examined in this study were painted in the traditional Chinese method, similar to watercolor but with a proteinaceous binder, except for one oil painting, *Portrait of Mother Mujia*, a portrait (S1991.137). In total, 232 paintings were analyzed in this study but not all the colors in every painting were analyzed.

### Methods

The analysis methods used in this study were generally noninvasive, with samples for specific identifications taken if necessary. The same sample was generally used for multiple techniques. The examination protocol was based on a survey of the colored areas using stereomicroscopic examination, followed by the first two methods described below, both of which are noninvasive. Careful examination of paintings under a microscope was done to document the colors, particles, and thickness of paint layers for the painted areas as well as the condition of background supports. In cases where the layer was too thin or damaged for sampling, the identification was based

on analysis by FORS and XRF and by examination, if necessary, under infrared.

The instrumental details and analytical parameters are given below, listed in the order in which they were performed, beginning with two noninvasive methods. Not all methods were used on each sample.

**Fiber optics reflectance spectroscopy (FORS).** This technique was applied in the visible and near infrared region to characterize colorants, in particular organic dyes as these cannot be identified with XRF. See appendixes 2 and 3 for the FORS characterization of the red insect dyes and indigo, respectively.

FORS in the visible and near infrared region (300–800 nm) was carried out using a Cary 50 ultraviolet-visible spectrophotometer (Varian Analytical). Measurements were taken with the addition of either a fiber optics reflectance probe (Leona and Winter 2001) or a fiber optics probe/remote detector attachment (Giaccai and Winter 2005). A scanning rate of 30 nm / min. and a data interval of 1 nm with a baseline correction were used. Either a white diffuse reflectance reference standard, Spectralon Calibrated Reference Standard #SRS99-010, Labsphere (more information available at [www.labsphere.com](http://www.labsphere.com)), or silk or paper supports of the painting were used for the background. Details of the method are given in Leona and Winter (2001; 2003, as well as app. 2 and 3).

**X-ray fluorescence (XRF).** X-ray fluorescence spectroscopy was undertaken using an Omega 5 Museum and Industrial Object Analyzer, a modified Spectrace 6000 spectrometer manufactured by Data Acquisition and Control. XRF was performed in air for 200 s live time, at 35 kV to identify the presence of inorganic colorants.

The spot size ranged from 3 mm<sup>2</sup> to 1 cm<sup>2</sup>. Current varied to a maximum of 99 mA as needed, according to the nature of paint examined. XRF identified elements heavier than argon and supplied evidence for the identification of most inorganic pigments.

**Fourier transform infrared spectroscopy (FTIR).** A microscopic sample was compressed with a diamond cell, and FTIR spectra were collected in transmission using a Nicolet Nexus 670 Fourier transform infrared spectrometer with the addition of a SpectraTech IR-Plan Advantage microscope. Dry air was fed through the spectrometer and microscope to minimize the interference from water vapor and carbon dioxide. Data were acquired over the range 650–4000 cm<sup>-1</sup> at 2 cm<sup>-1</sup> intervals for 512 or more scans. A clean area of the diamond cell was used for background collection. Happ-Genzel apodization was used. Data were analyzed using Omnic software versions 6.0a–7.3 (Thermo Nicolet).

**X-ray diffraction (XRD).** This technique used Gandolfi cameras (a modified Debye-Scherrer technique) on a standard Philips x-ray generator operated at 40 kV and producing copper K $\alpha$  radiation. This technique identified crystalline inorganic pigments. XRD patterns were collected for some samples with Debye-Scherrer cameras on a Philips x-ray generator #2600. A microscopic sample was mounted on the tip of a glass fiber with rubber cement diluted with toluene, and a Gandolfi x-ray camera was used. Conditions were Cu-K $\alpha$  radiation at 40 kV, and 20 mA.

**Polarized light microscopy (PLM).** A Leitz Orthoplan rotating stage microscope was used to study removed samples by standard methods. This technique was especially useful in the case of mixtures. Samples were mounted on slides with Meltmount ( $n_D = 1.662$ ). A Nikon Eclipse E600 polarizing microscope with Olympus DP70 digital camera was also used to examine slides.

**Scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS).** A FEI Company XL-30 microscope with EDAX Phoenix energy dispersive analysis system was used to determine element identification and particle shape on selected samples. Particle mounts were prepared and carbon-coated prior to analysis under vacuum. Conditions were adjusted for the specific sample.

**High-performance liquid chromatography (HPLC).** All separations were performed on an Agilent 1100 HPLC with a binary pump system with diode array (DAD) and fluorescence (FLD) detection. For postcolumn derivitization a Pickering 5200 PCD was attached between the DAD and FLD. Separations were

performed using a Wakosil RSC18 column (100 mm  $\times$  2.1 mm I.D.) with a flow rate of 0.300 mL/min, at 38 °C. A gradient elution was used with the mobile phase consisting of A: 90% v/v 10 milli-Molar (mM) oxalic acid (aq)/10% v/v acetonitrile; B: 90% v/v acetonitrile /10% v/v 10 mM oxalic acid (aq). Oxalic acid was used in the mobile phase as it was found to significantly reduce tailing and band broadening, which were a problem for the laccaic acids. The gradient program was modified as the column aged, isocratic elution with 10% B up to 5 minutes, followed by a steep gradient to 75% B to intentionally co-elute laccaic acids A and B. This method was developed at the Freer to decrease the detection limits of the laccaic acids (Cole et al. 2006). The following wavelengths were monitored: (1) 500 (BW 16), ref. 650 (BW 50); (2) 490 (BW 16), ref. 650 (BW 50); (3) 285 (BW16), ref. 650 (BW 100). BW stands for bandwidth, used both for the peak being monitored and for its reference. Peak locations and bandwidths are given in nanometers.

Laccaic acids are known to break down with heated acid extraction (Balakina et al. 2006; Novotna et al. 1999). For samples from these paintings, which are typically only the dye in gelatin, they were simply dissolved in 1:1 3N HCl: MeOH (Wouters and Verhecken 1989) without heating and centrifuged at 4000 rpm for 5 minutes. All solvents were HPLC grade from Sigma Aldrich. For standards, carminic acid, alizarin, and purpurin were purchased from Aldrich, and lac dye was purchased from Kremer pigments.

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# Appendix 2

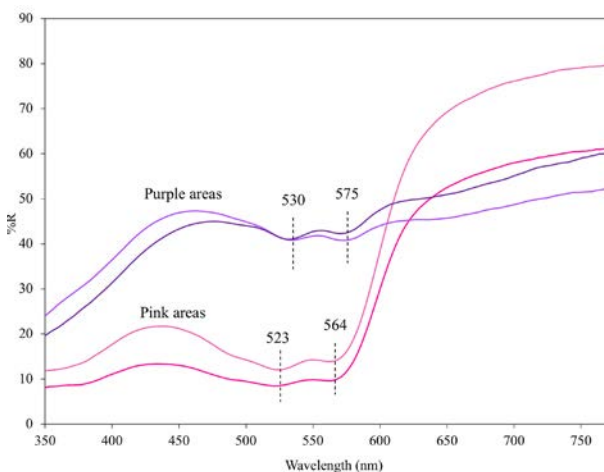
## FORS Identification of Red Anthraquinone Dyes in Chinese Paintings

Christina Bisulca

The red dyes from scale insects (lac dye and cochineal) and from the plant dye madder have closely related chemical structures: they are all anthraquinones with differing functional groups. Differences in the nature and number of these functional groups on the anthraquinone core are responsible for the slight variation in color between these dyes. With fiber optics reflectance spectroscopy (FORS), anthraquinone dyes used on paintings are most easily recognized by the two absorption sub-bands in the visible region (fig. A2.1) of the electromagnetic spectrum. Previous analyses at the Freer Gallery of Art and Arthur M. Sackler Gallery Department of Conservation and Scientific Research found that insect and plant anthraquinones can be distinguished based on the position of these sub-bands (Giaccai and Winter 2005). The bands typically occur at 520–35 nm and 565–75 nm for the insect dyes, and approximately ~515 nm and 545 nm for madders.

As part of the study of red dyes in Chinese paintings, analysis where FORS was followed by high-performance liquid chromatography (HPLC) offered a unique opportunity to validate FORS results. In the vast majority of cases, FORS spectra were recorded on locations prior to sampling

together with the specific application of the dye (application on and nature of substrate, presence



**Figure A2.1.** FORS spectra (normalized) showing two absorption sub-bands in the visible region that indicate an anthraquinone dye. Spectra were taken from color locations indicated in figure A2.2. Areas that were painted with cochineal could be distinguished from those containing primarily lac dye based on absorption sub-band position.



**Table A2.1.** Band positions in FORS for insect dyes in paintings where dye identity is confirmed with HPLC.

Red Dye	Band 1 (nm)	Std	Range	Band 2 (nm)	Std	Range	Number of Samples
Lac dye	532	3	524–40	573	3	566–78	123
Cochineal	525	3	521–30	565	3	560–70	24

std = standard deviation



**Figure A2.2.** Detail of *Portrait of the Seventh Prince Yi*, 1911. Hanging scroll; silk; 184 × 120 cm (72<sup>7</sup>/<sub>16</sub> × 47<sup>1</sup>/<sub>4</sub> in.). Arthur M. Sackler Gallery, Smithsonian Institution, Washington, D.C.: Purchase—Smithsonian Collections Acquisition Program and partial gift of Richard G. Pritzlaff, S1991.102. Detail with yellow arrows showing different purple and pink areas on the robe that were analyzed. See figure 4.4 for the entire painting.

of other pigments, etc.). During the study, spectroscopic differences between the two insect dyes lac and cochineal were noted. Table A2.1 shows the recorded positions of the sub-bands between lac and cochineal in paintings in areas prior to sampling, for a total of 147 samples where the dye identity was confirmed with HPLC. Sub-band positions in lac dye were found to be consistently shifted ~7–8 nm from those in cochineal according to averages in the table. During this study these band positions were used to distinguish between lac dye and cochineal by FORS to locate areas to sample for HPLC or to characterize the dye in cases in which HPLC was not performed, as reported in appendix 5.

Figure A2.2 shows an example where the two dyes were distinguished by FORS in a portrait. This detail

of the chair in *Portrait of the Seventh Prince Yi* (1911) shows locations where both FORS and HPLC were performed. FORS spectra differ significantly in sub-band position between purple and bright pink areas (see fig. A2.1). The purple areas were in a mixture with Prussian blue, causing the absorption into the near infrared (NIR) (~600–800 nm).

Subsequent HPLC identified carminic acid (cochineal) as the major dye component in pink areas and the laccaic acids (lac dye) in purple areas. However, in all purple areas sampled, all samples also contained cochineal as a minor component, although cochineal was not indicated based on FORS analysis alone. In this study, HPLC identified lac and cochineal together in fourteen samples. FORS analysis did not indicate the presence of both dyes; rather FORS spectra were



**Figure A2.3.** *Birds and Flowers*, Hua Yan (1682–1756), 1747. Album leaf; paper; 31.2 × 44.7 cm (12 $\frac{5}{16}$  × 17 $\frac{7}{8}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Purchase—Charles Lang Freer Endowment, F1960.25g. The pink tongue of the bird is a thin wash of lac dye applied directly onto the paper as determined by HPLC.

interpreted to be one or the other dye, typically the major component.

The position of the sub-bands for cochineal align with what has been reported in other studies of this dye as a laked pigment (Fonseca et al. 2019; Bisulca et al. 2008; Vitorino et al. 2015). Lakes are metal-dye complexes formed by precipitating the dye onto an inert particle. One of the more common lakes is created by boiling the dye with alum ( $KAl(SO_4)_2$ ), which forms a dye-alumina complex (Kirby et al. 2007; Clementi et al. 2008). The laking process was done to render the dyes insoluble and also to modify color (Vitorino et al. 2015). In paintings, sub-band position in anthraquinone dyes can also vary depending on the lake preparation (Fonseca et al. 2019) or, in the case of textiles, the mordant (Angelini et al. 2010).

Chinese artists obtained these colorants as the raw dye, and to the author's knowledge there are no historic accounts describing laking processes for these dyes in Asia similar to what is found for

Western materials. However, Yu Feian (1988, 66, 76) recommends a method described by Ze Lang (in 1797) involving the layering of alum washes between paint layers when painting with cochineal to improve color. Asian painting substrates are also typically sized with alum and gelatin (Winter 2008). Even though these processes do not involve boiling and precipitation of the dye as in Western lakes, it would be expected that the dye-salt complex would still form or be present from their original extraction from stick lac, as some historic accounts describe precipitation from solution (O'Connor 1876). A comparison of sub-band positions in cochineal with those determined by Fonseca et al. (2019) indicates that cochineal in Chinese paintings corresponds well with cochineal-alum lake. Band positions for lac dye and its various lakes have not been as well studied.

Instances were found where FORS results deviated from the sub-band averages reported in table A2.1.

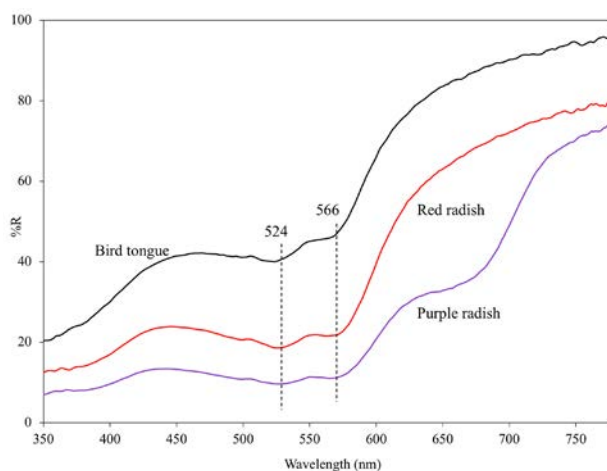


**Figure A2.4.** *Radishes*, Li Shan (1686–ca. 1762), 1730s–40s. Leaf in album *Flowers and Vegetables*; paper; 23.8 × 29.8 cm (9 $\frac{3}{8}$  × 11 $\frac{3}{4}$  in.). Freer Gallery of Art, Smithsonian Institution, Washington, D.C.: Transfer from the United States Customs Service, Department of the Treasury, F1980.169g. The red and purple radishes are thin washes on paper and were found to be painted with lac dye and lac dye and indigo, respectively.

Already noted are instances where more than one dye was present in the mixture. Another common circumstance where band positions differed is where lac dye was applied directly as a thin wash on a paper substrate. In many of these cases, band positions overlapped with those of cochineal, as reported in table A2.1. *Birds and Flowers* (1747) (fig. A2.3) and *Radishes* (1730s–40s) (fig. A2.4) provide two examples in which lac dye was applied directly to the paper substrate. In these cases, the dye was identified as lac dye with HPLC, but in FORS analysis the sub-bands overlapped with that of cochineal at ~525 nm and 565 nm (fig. A2.5). It should also be noted that in some cases the characteristic bands were not present even where a dye was observed visually and subsequently confirmed with HPLC. This situation is

most commonly encountered when dyes are applied over highly absorbing pigments such as cinnabar/vermillion, which masks bands associated with the anthraquinones (Bisulca et al. 2008).

In paintings analysis, most FORS studies have focused on Western paintings in which only laked dyes are used (Fonseca et al. 2019; Clementi et al. 2008; Vitorino et al. 2015). Based on studies of anthraquinones in solution, the position of absorption sub-bands also depends on the local environment (Fabian and Hartmann 1980; Reta et al. 1993; Yoshida and Takabayashi 1968). In the case of Chinese paintings, this environment could include the nature of the substrate (silk vs. paper), the paint binder and its concentration, and the presence of alum or other pigments. Reference paintouts were made with lac dye



**Figure A2.5.** FORS spectra (normalized) of lac dye washes on paper from *Birds and Flowers* (fig. A2.3) and *Radishes* (fig. A2.4). The absorption at ~650 nm is due to the presence of indigo, which was used with lac dye to create the purple color of the radish.

and cochineal for comparison, using both silk and paper substrates. The paint was varied by the presence of alum (1%, 3%, 5%), a gelatin binder (3%, 5%), and other pigments (calcium carbonate).

Unlike laked dyes, the sub-band positions for raw dyes are susceptible to influence of the local environment. This influence is obvious in practice, as the color will change significantly depending on which other materials are present in the paint mixture, in particular in the case of alum and calcium carbonate. When lac and cochineal were present with alum and gelatin (alone or in combination), results were consistent with those in table A2.1. However, in the study of Chinese paintings the presence of alum in paint layers was not determined, so these observations cannot be confirmed. More research on FORS analysis of unlaked dyes and on the effects of the paint preparation used is needed to better understand FORS analysis of East Asian paintings.

These results demonstrate that FORS is a reliable technique for the characterization of anthraquinone dyes. Despite these deviations noted, band positions were often diagnostic, especially in the case of the portraits. This finding indicates a consistency in paint preparation, which is not surprising as these paintings were created in workshops with standardized practices. Moreover, in this study sub-band positions above 530 nm and 570 nm were not found for cochineal. Similar results are reported in other studies (Bisulca et al. 2008; Clementi et al. 2008; Vitorino

et al. 2015), although the position of sub-band 1 can be as high as 540 nm for cochineal lakes prepared with alum and precipitated onto calcium carbonate (Fonseca et al. 2019). It is a reasonable assumption in Asian paintings that where band positions are above 530 nm and 570 nm the dye is lac dye or predominantly lac dye. Although there are some complicating factors—most notably with dye mixtures—FORS is a very sensitive technique for noninvasively discerning between the various anthraquinone dyes and their preparation as used in paintings.

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# Appendix 3

## FORS Identification of Azurite, Indigo, and Prussian Blue in Chinese Paintings

Yae Ichimiya

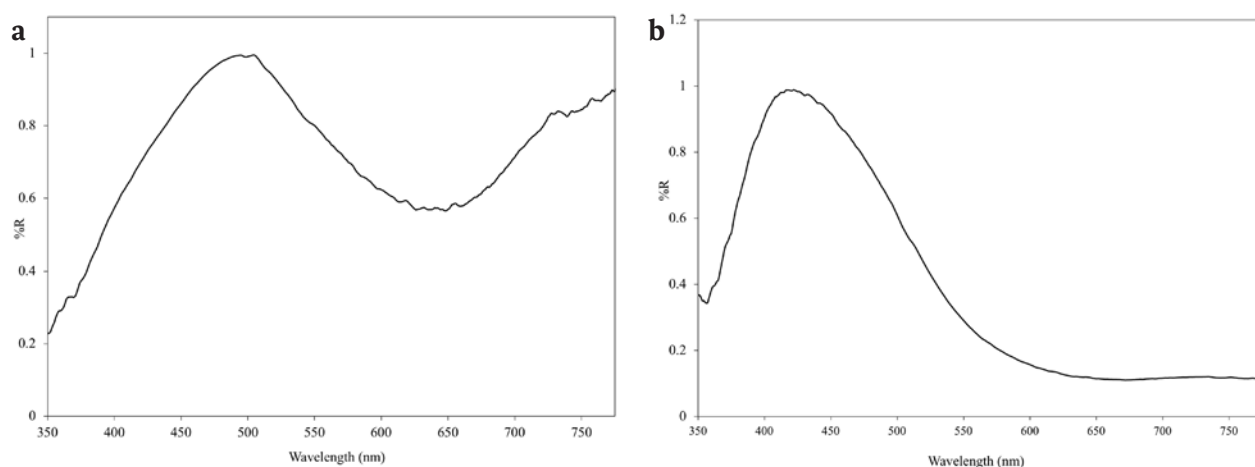
### Introduction

Of the several blue pigments found in Chinese paintings, azurite, a copper carbonate, and indigo, a dye derived from a number of plants, are the two most common. Both are discussed in chapter 3, where the use of the synthetic pigment Prussian blue in Chinese paintings is also described. Studies of Chinese paintings in the Freer Gallery of Art and Arthur M. Sackler Gallery utilized fiber optics reflectance spectroscopy (FORS) in efforts to identify the blue pigments, and it was soon clear that selection of the baseline used in the analysis is important to ensuring valid results with this method. The Chinese paintings study also provided an opportunity to investigate whether it was possible, using FORS, to determine if the blue pigments indigo and Prussian blue were applied as mixtures or consecutive washes. Prussian blue and indigo mixtures also have been investigated by Carole Biron and coauthors (2020) with several noninvasive methods.

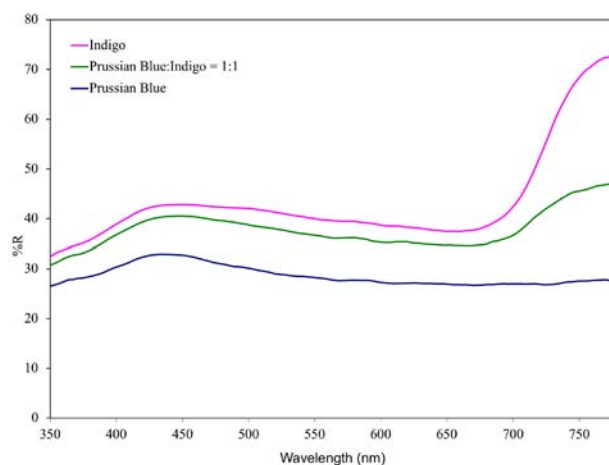
### Effect of Baseline Material Choice

The identification of blue colorants can be affected by the choice of material used for the FORS baseline—in this study, the paper, silk, or a white diffuse reflectance standard—as the color of the underlying aged or dyed support may be visible through the paint layer(s). The significance of the effect depends on the thickness and covering power of the colorants and is especially of note in the analysis of Asian paintings because they often display very thin applications of color.

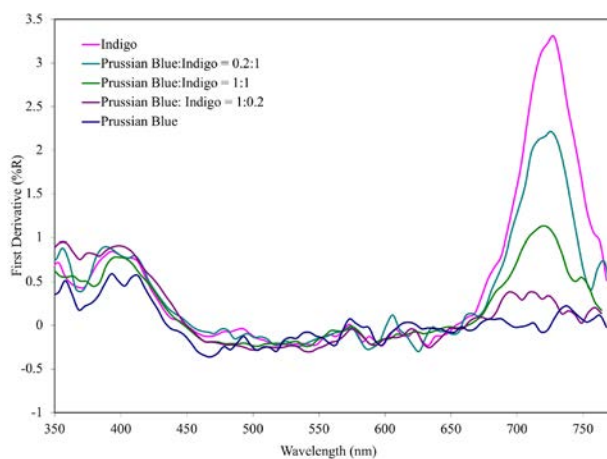
For example, a thin layer of blue colorant in an album leaf, *Landscape with Travelers* (Qing dynasty, 1644–1912) (see fig. 3.9), was examined using two different baselines—a white reflectance standard and the unpainted silk support—and the FORS spectra are shown in figure A3.1. Although the blue pigment was identified as azurite because copper was found with x-ray fluorescence spectroscopy (XRF), the pigment can be misinterpreted as indigo using FORS if a baseline is acquired from a white diffuse reflectance standard. The increased reflectance



**Figure A3.1.** FORS spectra taken of the azurite blue in *Landscape with Travelers* (F1915.36k). In (a), the FORS baseline spectrum was acquired with a white diffuse reflectance standard, Spectralon Calibrated Reflectance Standard #SRS 99-010, Labsphere (more information available at [www.labsphere.com](http://www.labsphere.com)). In (b), a baseline spectrum was acquired using an unpainted area of the silk of the painting support. The increased reflectance in the near infrared (NIR 600–800 nm) in (a) may be misinterpreted as the reflectance from the presence of indigo.



**Figure A3.2.** FORS spectra of Prussian blue, indigo, and a mixture of 1:1 Prussian blue and indigo on unsized paper.

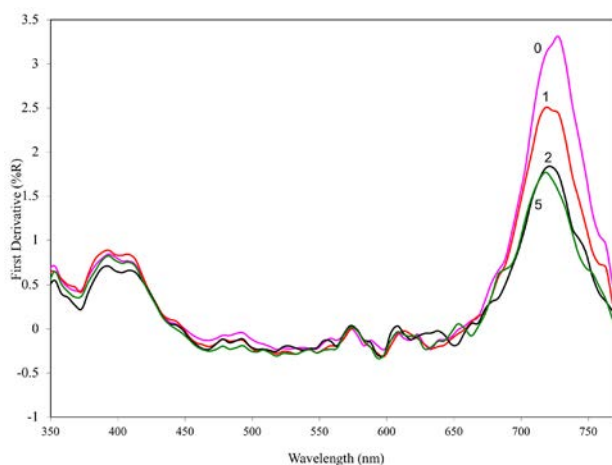


**Figure A3.3.** FORS spectra (1st derivative) of Prussian blue, indigo, and mixtures of Prussian blue and indigo on unsized paper.

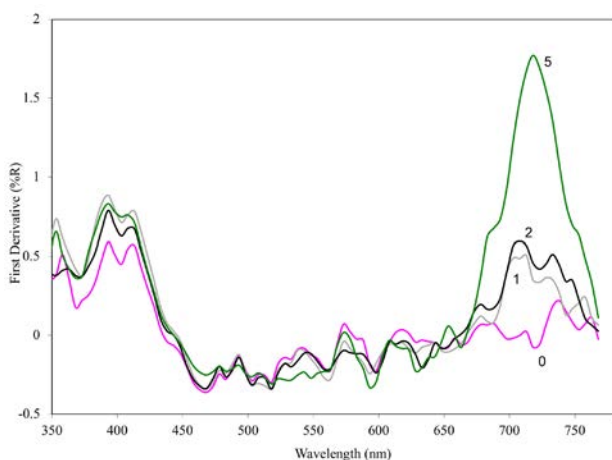
into the near infrared (NIR) from 600–800 nm, as seen in figure A3.1a, when using the diffuse reflectance standard as a baseline may be misinterpreted as the high reflectance that occurs in this region for indigo. Alternatively, using the unpainted support as a baseline adjusts for the color of the support, leaving only the spectrum of the colorant. These experiments suggest that for colorant identification, the analyst needs to carefully consider the selection of baseline material during FORS.

### Paintout Experiments Using Prussian Blue and Indigo Mixtures and Washes

Colors are often used as mixtures or layered over each other. The differences in FORS spectra acquired from indigo and Prussian blue mixtures or layered washes of one pigment over the other were studied by making measurements of modern pigments painted on alum-sized paper substrates. A mixture of indigo and Prussian blue was painted on Chinese paper with sizing (sized both one and two times) as well as on



**Figure A3.4.** FORS spectra (1st derivative) taken of an indigo base and Prussian blue wash(es) on unsized paper. The numbers in the figure indicate the number of brushstrokes of wash over indigo.



**Figure A3.5.** FORS spectra (1st derivative) taken of a Prussian blue base and indigo wash(es) on unsized paper. The numbers in the figure indicate the number of brushstrokes of wash over Prussian blue.

unsized paper. Sample areas were formed of 0, 1, 2, and 5 brushstrokes of wash for each mixture and the individual pigments. The same white reference material mentioned above was used to acquire baseline spectra.

Figure A3.2 shows the FORS spectra for indigo, Prussian blue, and a 1:1 mixture of the two taken from the sample paintouts. The reflectance of the mixture lies between the reflectance of indigo and Prussian blue. The first derivative curves (figs. A3.3–A3.5) of the spectra were used for interpretation as they show more clearly the changes in the near infrared due to

indigo. Because of the characteristic reflectance of indigo in the NIR, a clear change in the reflectance of indigo in the NIR was observed when Prussian blue was mixed with indigo or a wash of Prussian blue was overpainted on indigo. No obvious differences in spectra between sized (spectra not included here) and unsized papers were seen.

Increased reflectance in the NIR was seen to correlate with increased indigo in the mixtures as well as with increased thickness of the upper layer of indigo above the Prussian blue underlayer. The inverse was true for an indigo base with Prussian blue. The NIR reflectance decreased as additional layers of Prussian blue were applied. No significant differences were observed in other parts of the spectra. When Prussian blue and indigo were used together, it was unfortunately not possible to distinguish between application as mixtures or as washes.

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# Appendix 4

## Historical, Modern, and Chemical Pigment Names

Yue Shu, Jennifer Giaccai, Blythe McCarthy,  
Christina Bisulca, and Yae Ichimiya

The following table lists information on Chinese pigment names from the literature as it pertains to the pigments reported in this book. While the table is certainly not complete, it includes sources that are available in English and a select number of additional sources. More details are available in several sources, most notably in Yu Feian (1988) and Winter (2008).

The current English name of each pigment identified on a painting in this study is given in bold, followed by the Chinese name in pinyin, also in bold. The Chinese characters as published in the source are given in the next column, and then the pigment name in Wade-Giles romanization. The scientific identification is given in the next column, together with notes on the identification; chemical compositions are taken from Winter 2008, table 2.1. In the final column are cross-references to the chapters with information on the pigment.

In the table, under each current pigment name are rows of names given in the historical Chinese sources. Under the column head “Sources,” the names of the Chinese authors who mention the Chinese character are given. The final column lists both the Chinese and English bibliographic references. English and Chinese versions of the same original source are separated by semicolons; if the same character was used in multiple original sources, the sources are separated

by periods. For the Chinese version of *Jie zi yuan hua pu* (The Mustard Seed Garden manual of painting), the first initials of each word of the title (*JZYHP*) were used with the year of publication (1868) of printing in the “References” column, as the manuscript is composed of multiple sections written by different authors and two sections, one by Wang Gai and one by Shen Hsin-Yu, include discussions of pigments. Complete bibliographic information appears in the References section at the end of the table. In this section, the original publication date for the Chinese manuscripts is included after the English translation of the title, since that often differs from the publication date of the version used, sometimes by hundreds of years.

For the mineral pigments malachite, azurite, and cinnabar/vermilion, some shades are indicated by an initial character meaning “first” (literally “head”) (頭 *tou*), “second” (二 *er*), or “third” (三 *san*) that precedes the color. The fineness of the particle size progresses from first (the most coarse and darkest) to third (the finest and palest in color). Yu Feian (1988, 56–59) describes grinding and separating pigment particles by size to achieve different pigment grades and colors. Unlike most painters, Ze Lang uses “first” for the lightest shade of red, blue, or green and “third” to mean the darkest shade of these colors.

Chinese characters for the plant sources of dyes (botanical names, etc.) are not included unless they appear to be used also for the colorant. The case of lac dye is especially complicated, and several terms likely represent the stick lac from which the colorant is drawn. They may also represent shellac resin.

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
<b>White pigments</b>					
<b>Lead white</b> <i>Qian fen, qian bai</i>	鉛粉, 鉛白	<i>ch'ien-fen, ch'ien-pai</i>	<b>basic lead carbonate (hydrocerussite)</b> $Pb(OH)_2 \cdot 2PbCO_3$ , <b>lead carbonate (cerussite)</b> $PbCO_3$ . <b>Multiple minerals can be found together.</b>		<b>see chaps. 1–4</b>
Powdered pewter <i>Qian fen</i>	鉛粉	<i>ch'ien-fen</i>	lead white	Wang Fangquan, Wang Gai	Wang 1937, 88. Sze 1956, 41; <i>JZYHP</i> 1868, 1(1): 16a. March 1935, 8.
Ingot white <i>Ding fen</i>	錠粉	<i>ting-fen</i>		Yu Feian	Yu 1988, 10; Yu 2013, 11.
Powder curd <i>Fen ning</i>	粉凝	<i>fen-ning</i>	Franke is uncertain but believes this is lead white.	Wang Yi	Franke 1950, 32; Wang 1621–44, 11: 4b.
Powdered pewter <i>Fen xi</i>	粉錫	<i>fen-hsi</i>	from ground cerussite (lead ore)		Acker 1954, 188n4.
Mandarin white <i>Guan fen</i>	官粉	<i>kuan-fen</i>		Yu Feian	Yu 1988, 10; Yu 2013, 11.
Best lead white <i>Hao fen</i>	好粉	<i>hao-fen</i>		Wang Yi	Franke 1950, 32; Wang 1621–44, 11: 4b.
Lead flower, zinc flower <i>Qian hua</i>	鉛華	<i>ch'ien-hua</i>	Zhang Yanyuan thinks this is the same as <i>huang dan</i> , red lead, but Acker and Yu believe it is lead white. Silbergeld and McNair translate it as “zinc flower” and believe it is zinc white, (see entry under red lead).	Yu Feian, Zhang Yanyuan	Yu 1988, 10; Yu 2013, 11. Acker 1954, 188n4.
Foreign powder, foreign white <i>Hu fen</i>	胡粉	<i>hu-fen</i>	Acker cites Uemura 1933 to identify this as lead white.	Song Yingxing, Yu Feian, Zhang Yanyuan	Song 1966, 256; Song 1637, 3(14): 21b. Yu 1988, 10; Yu 2013, 11. Acker 1954, 188.
Lead white <i>Hui qian ding fen</i>	回鉛定粉	<i>hui-ch'ien-ting-fen</i>		Shen Hsin-Yu	Sze 1956, 582; <i>JZYHP</i> 1868, 3(1): 22a.
Pewter extract <i>Jie xi</i>	解錫	<i>chieh-hsi</i>		Zhang Yanyuan	Acker 1954, 188.
Grated lead white <i>Xiao fen</i>	削粉	<i>hsiao-fen</i>	Franke is uncertain but believes this is lead white.	Wang Yi	Franke 1950, 32; Wang 1621–44, 11: 5a.
<b>Anglesite</b> <i>Liu suan kuang qian</i>	硫酸礦鉛	<i>liu-suan-k'uang ch'ien</i>	<b>anglesite <math>PbSO_4</math></b>		<b>see chap. 1</b>
<b>Calcium carbonate</b> <i>Tan suan gai, fang jie shi mo, fang jie shi, hu fen, ge fen</i>	碳酸鈣, 方解石末, 方解石, 胡粉, 蛤粉	<i>t'an-suan-kai, fang-chieh-shih-mo, fang-chieh-shi, hu-fen, ko-fen</i>	<b>calcium carbonate (calcite)</b> $CaCO_3$		<b>see chaps. 1, 4</b>
White chalk <i>Bai e</i>	白堊	<i>pai-o</i>		Yu Feian	Yu 1988, 9; Yu 2013, 10.
White powder <i>Bai tu fen</i>	白土粉	<i>pai-t'u-fen</i>		Yu Feian	Yu 1988, 9; Yu 2013, 10.
Clamshell white <i>Ge fen</i>	蛤粉	<i>ko-fen</i>		Yu Feian	Yu 1988, 9, 62; Yu 2013, 12, 101. March 1935, 9.
Painting white <i>Hua fen</i>	畫粉	<i>hua-fen</i>		Yu Feian	Yu 1988, 9; Yu 2013, 10.
Pearl white <i>Zhen zhu fen</i>	珍珠粉	<i>chen-chu-fen</i>		Yu Feian	Yu 1988, 9; Yu 2013, 12.
<b>Titanium white</b> <i>Tai bai fen</i>	鈦白粉	<i>t'ai-pai-fen</i>	<b>titanium dioxide</b> $TiO_2$		<b>see app. 5</b>

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Titanium white <i>Tai bai</i>	鈦白	<i>t'ai-pai</i>		Yu Feian	Yu 1988, 62; Yu 2013, 101.
<b>Red-orange pigments</b>					
<b>Cinnabar/ Vermilion <i>Chen sha, zhu sha</i></b>	辰砂, 朱砂	<i>ch'en-sha, chu-sha</i>	<b>mercuric sulfide (cinnabar) <math>\alpha</math>-HgS</b>	<b>In English cinnabar is the mineral and vermilion the man-made pigment. Chinese often does not differentiate between the two words in the same way as English, and man-made vs. mined pigments were not differentiated analytically in this study.</b>	<b>See chaps. 1, 2, 4</b>
Vermilion <i>Zhu sha</i>	朱砂, 硃砂	<i>chu-sha</i>		Shen Hsin-Yu, Wang Gai	Sze 1956, 581; <i>JZYHP</i> 1868, 3(1): 21b. Sze 1956, 38; <i>JZYHP</i> 1868, 1(1): 15a. March 1935, 8.
Fat red <i>Biao hong</i>	膘紅	<i>piao-hung</i>		Yu Feian	Yu 1988, 45; Yu 2013, 3, 40, 106.
Cinnabar <i>Chen sha</i>	辰砂	<i>ch'en-sha</i>		Yu Feian	Yu 1988, 4; Yu 2013, 3.
Pure red <i>Da hong</i>	大紅	<i>ta-hung</i>		Yu Feian	Yu 1988, 45.; Yu 2013, 32.
Ground cinnabar <i>(Dan) sha</i>	(丹)沙	<i>(tan)-sha</i>	Acker's translation lists two items: "cinnabar ( <i>dan</i> ) from <i>Wu-ling</i> " and "finely ground cinnabar." The distinction can be understood as the raw material cinnabar ( <i>dan</i> ) is then ground ( <i>sha</i> means "sand" or "powder") into the pigment.	Zhang Yanyuan	Acker 1954, 187.
Flying vermilion <i>Fei dan</i>	飛丹	<i>fei-tan</i>		Wang Yi	Franke 1950, 32; Wang 1621-44, 11: 5a.
Hibiscus section <i>Fu rong kuai</i>	芙蓉塊	<i>fu-yung-k'uai</i>		Wang Gai	Sze 1956, 38; <i>JZYHP</i> 1868, 1(1): 15a.
Yellow fat <i>Huang biao</i>	黃膘	<i>huang-piao</i>		Shen Zongqian, Ze Lang	Yu 1988, 57, 65; Yu 2013, 107.
Arrowhead <i>Jian tou</i>	箭頭	<i>chien-t'ou</i>		Wang Gai	Sze 1956, 38; <i>JZYHP</i> 1868, 1(1): 15a.
Cinnabar grains <i>Pi sha</i>	疋砂	<i>p'i-sha</i>		Wang Gai	Sze 1956, 38; <i>JZYHP</i> 1868, 1(1): 15a.
Coral red <i>Shan hu mo</i>	珊瑚末	<i>shan-hu-mo</i>		Wang Gai	Sze 1956, 39; <i>JZYHP</i> 1868, 1(1): 15b.
Deep vermilion <i>Yin zhu</i>	銀朱, 銀硃 (Shen)	<i>yin-chu</i>		Shen Hsin-Yu, Song Yingxing, Wang Gai, Wang Yi	Sze 1956, 581; <i>JZYHP</i> 1868, 3(1): 21a. Song 1966, 279, 280; Song 1637, 3(16): 40a. Sze 1956, 39; <i>JZYHP</i> 1868, 1(1): 15a. March 1935, 8. Franke 1950, 31-32; Wang 1621-44, 11: 3a.
Purple acetate <i>Zi fen shuang</i>	紫粉霜	<i>tzu-fen-shuang</i>	vermilion	Yu Feian	Yu 1988, 5; Yu 2013, 4.
Vermilion <i>Zhu</i>	硃	<i>chu</i>		Song Yingxing	Song 1966, 285; Song 1637, 3(16): 42a.

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Red standard, red banner, fat red <i>Zhu biao</i>	朱標, 朱膘	<i>chu-piao</i>	fine pigment floating on top when sizing is added to ground cinnabar, orange-red in tone; also known as “fat red” (朱膘) in reference to grease-like appearance. Wang Fangquan says “bright red.”	Wang Fangquan, Wang Gai, Yu Feian	Wang 1937, 88; Sze 1956, 39; <i>JZYHP</i> 1868 1(1): 15a. March 1935, 8. Yu 1988, 5, 27, 65; Yu 2013, 3, 40, 106
<b>Red lead, minium</b> <b><i>Qian dan</i></b>	鉛丹	<b><i>ch'ien-tan</i></b>	<b>lead tetroxide (minium)</b> <b>Pb<sub>3</sub>O<sub>4</sub></b>		<b>see chaps. 1, 2, 4</b>
Red lead <i>Qian dan</i>	鉛丹	<i>ch'ien-tan</i>		Yu Feian	Yu 1988, 27; Yu 2013, 39.
Yellow vermilion, yellow cinnabar, lead yellow, minium <i>Huang dan</i>	黃丹	<i>huang-tan</i>		Wang Yi, Yu Feian, Zhang Yanyuan	Franke 1950, 32; Wang 1621–44 11: 5a. Yu 1988, 6, 27; Yu 2013, 5, 40. Acker 1954, 188.
Lead flower <i>Qian hua</i>	鉛華	<i>ch'ien-hua</i>	(see entry under lead white)	Zhang Yanyuan	Acker 1954, 187.
Zhang red <i>Zhang dan</i>	漳丹	<i>chang-tan</i>		Yu Feian	Yu 1988, 6, 27; Yu 2013, 5, 40.
<b>Red iron oxide</b> <b><i>Zhe shi, tie hong, yang hua tie hong, yang hua tie</i></b>	赭石, 鐵紅, 氧化鐵紅, 氧化鐵	<b><i>che-shih, t'ieh-hung, yang-hua-t'ieh-hung, yang-hua-tieh</i></b>	<b>ferric oxide (hematite) α-Fe<sub>2</sub>O<sub>3</sub></b>		<b>see chap. 1</b>
Ocher <i>Zhe shi</i>	赭石	<i>che-shih</i>	Yu says <i>zhe shi</i> is red, also called <i>tu zhu</i> , and also known as Dai ocher from its source in Shanxi province. In Sze this is translated into English as umber, but umber generally refers to a brown color, not red. From use in <i>JZYHP</i> , it refers to a bright pigment (i.e., red). Wang Fangquan refers to a dull red or maroon (see entry under yellow iron oxide).	Shen Hsin-Yu, Wang Fangquan, Wang Gai, Yu Feian, Ze Lang, Zou Yigui	Sze 1956, 585; <i>JZYHP</i> 1868, 3(1): 25. Wang 1937, 88. Sze 1956, 43; <i>JZYHP</i> 1868, 1(1): 18b. March 1935, 8. Yu 1988, 5, 54; Yu 2013, 5, 88; Ze Lang 1799, 3: 26a; Zou 1991, 9: 723.
Iron hematite <i>Sha tie</i>	砂鐵	<i>sha-t'ieh</i>		Song Yingxing	Song 1966, 248; Song 1637, 3(14): 15b.
Hematite (ocher) <i>Tu zhu</i>	土朱	<i>t'u-chu</i>	Li equates <i>tu zhu</i> with <i>zhe shi</i> . Although Franke translates <i>tu zhu</i> as umber, Wang Yi uses it for a red pigment.	Li Shizhen, Wang Yi	Franke 1950, 30; Wang 1621–44, 11: 2a; Li 1658, 10: 8a.
<b>Rouge</b> <b><i>Yan zhi</i></b>	胭脂	<b><i>yen-chih</i></b>	<b>can refer to a variety of organic, red, water-soluble colorants and which specific colorant changes over time</b>		<b>see chap. 2</b>
Rouge <i>Yan zhi</i>	胭脂 (Wang Gai), 臙脂 (Shen), 臙肢 (Laufer), 臙脂 (Zhang), 燕支 (Laufer), 燕脂 (Song)	<i>yen-chih</i>	Yu believes rouge obtained from Guangdong is made from lac and that made in Fujian province is either <i>Carthamus tinctorius</i> or madder. March believes it is made from <i>Mirabilis jalapa</i> . Sze believes it is <i>Carthamus tinctorius</i> , <i>Sophora japonica</i> , or <i>Mirabilis jalapa</i> . Laufer gives four botanical sources for <i>yan zhi</i> (see also <i>hu yan zhi</i> below): (1) <i>Carthamus tinctorius</i> , safflower ( <i>hun lan</i> ), (2) <i>Basella rubra</i> , (3) the <i>san liu</i> flower, (4) lac dye. Wang Fangquan calls 胭脂 “( <i>yen tzu</i> ), delicate red or rouge.”	Li Shizhen, Shen Hsin-Yu, Song Yingxing, Wang Fangquan, Wang Gai, Wang Yi, Yu Feian, Zhang Yanyuan	Laufer 1919, 324–28; 8. Li 1658, 15: 44a–b. Sze 1956, 583; <i>JZYHP</i> 1868, 3(1): 23b. Song 1966, 77; Song 1637, 1(3): 52a. Wang 1937, 88. Sze 1956, 583; <i>JZYHP</i> 1868, 1(1): 17a. March 1935, 10. Franke 1950, 30; Wang 1621–44, 11: 2a. Yu 1988, 12; Yu 2013, 14. Acker 1954, 189.
Hangzhou sparrow tongue rouge <i>Hangzhou que she</i>	杭州雀舌	<i>Hang-chou ch'ueh-she</i>		Ze Lang	Yu 1988, 54; Yu 2013, 87.

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Foreign cosmetic or foreign rouge <i>Hu yan zhi</i>	胡燕脂	<i>hu-yen-chih</i>	Li gives two botanical sources for <i>hu yan zhi</i> : (1) lac dye, (2) <i>Basella rubra</i> (Malabar spinach) ( <i>lo kwai</i> )	Li Shizhen quoting Li Xun in <i>Nan hai yao pu</i>	Laufer 1919, 327-8; Li 1658 15: 44a-b.
Purple powder <i>Zi fen</i>	紫粉	<i>tzu-fen</i>	Song refers to this as coming from safflower dregs after dyeing and suggests previous use of <i>zi kuang</i> or mountain pomegranate flowers for rouge.	Song Yingxing	Song 1966, 77; Song 1637, 1(3): 52a.
<b>Lac dye</b> <b><i>Zi jiao, chong jiao</i></b>	紫膠, 蟲膠	<b><i>tzu-chiao, ch'ung-chiao</i></b>	<b>laccic acids</b>		<b>see chaps. 1–4</b>
Red glue/gum <i>Chi jiao</i>	赤膠	<i>chih-chiao</i>	probably stick lac, refers to exudate. Acker translates as red glue; Schafer translates as red gum. Jiao is a general term for an adhesive.	Zhang Yanyuan quoting Zhang Bo	Acker 1954, 189. Schafer 1957, 135.
Ant ore <i>Yi kuang</i>	蟻鉞	<i>i-k'uang</i>	probably stick lac	Zhang Yanyuan	Acker 1954, 189.
Ant lac <i>Yi qi</i>	蟻漆	<i>i-ch'i</i> . Laufer transliterates as <i>yi-tsi</i> .	probably stick lac	Zhang Bo	Laufer 1919, 475; Zhang 1646, 59(2): 2b.
Purple shoots <i>Zi cao rong</i>	紫草茸	<i>tzu-sao-jung</i>		Yu Feian	Yu 1988, 12; Yu 2013, 14.
Purple stem <i>Zi geng</i>	紫梗	<i>tzu-keng</i> . Hirth and Rockhill transliterate as <i>tzi-kōng</i> ; Laufer transliterates as <i>tse-ken</i> .	stick lac	Yu Feian, Zhao Rukuo, Zhou Dagan	Yu 1988, 12; Yu 2013, 14. Hirth and Rockhill 1911, 55. Laufer 1919, 478; Zhou 1465–1620, 103: 11b.
Purple mineral/ore <i>Zi kuang</i>	紫鉞 (Yu, Li, Song), 紫鑛 (Wang)	<i>tzu-k'uang</i> . Laufer transliterates as <i>tse-kun</i> .	stick lac. Song says this was formerly used for rouge, and Sun and Sun in their translation associate it with litmus (a lichen).	Kou Zongshi, Li Shizhen, Song Yingxing, Wang Pu, Yu Feian	Laufer 1919, 478; Kou, 1879, 14: 4b; Li 1658, 15: 44b. Song 1966, 77; Song 1637, 1(3): 52a. Wang 1884, 100: 18b. Yu 1988, 12; Yu 2013, 14.
<b>Cochineal</b> <b><i>Yan zhi chong hong</i></b>	胭脂蟲紅	<b><i>yen-chih-ch'ung hung</i></b>	<b><i>Dactylopius coccus</i>. Coloring agent is carminic acid.</b>		<b>see chaps. 2–4</b>
Carmine, Western red <i>Xi yang hong</i>	西洋紅	<i>hsi-yang-hung</i>	Yu uses this word for cochineal; he uses <i>xi yong mian</i> for chemical red.	Yu Feian	Yu 1988, 13, 15, 30, 31, 45; Yu 2013, 13, 15, 44.
Carmine, foreign red <i>Yang hong</i>	洋紅	<i>yang-hung</i>	Wang Fangquan says <i>yang hong</i> is used to replace <i>yen zhi</i> . Ze uses <i>yang hong</i> for cochineal. Liu (ed. Yu 2013) says that Yu uses “ <i>xi yang hong</i> 西洋紅, carmine” to indicate cochineal; he uses “ <i>yang hong mian</i> 洋紅面” to indicate the cheap chemical red material.	Wang Fangquan, Yu Feian, Ze Lang	Wang 1937, 88. Yu 1988, 66, 70; Yu 2013, 107. March 1935, 10.
<b>Yellow pigments</b>					
<b>Arsenic sulfides</b> <b><i>Xiong huang</i> or <i>ji guan shi, ci huang</i></b>	雄黃 or 鷄冠石, 雌黃	<b><i>hsiung-huang</i> or <i>chi-kuang-shih, tz'u-huang</i></b>	<b>arsenic(II) sulfide (realgar) As<sub>2</sub>S<sub>4</sub>, arsenic(III) sulfide (orpiment) As<sub>2</sub>S<sub>3</sub></b>		<b>see chaps. 1, 4</b>
Realgar, male yellow <i>Xiong huang</i>	雄黃	<i>hsiung-huang</i>	Yu states “made by the painters themselves” about modern portrait painters.	Li Shizhen, Shen Hsin-Yu, Wang Gai	Schafer 1955, 75; Li 1658, 9: 22b. Yu 1988, 44; Yu 2013, 69. Sze 1956, 39, 581; <i>JZYHP</i> 1868, 1(1): 15b, 3(1): 22b. March 1935, 7.

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Female yellow <i>Ci huang</i>	雌黃	<i>tz'u-huang</i>	Zhang identifies as orpiment, also referred to as "yellow of Lin-i and K'un-lun" (林邑崑崙之黃) by Zhang. <i>Linyi</i> is the Chinese name for the country of Champa, now part of Vietnam, so Yu thought this was gamboge (see entry under gamboge).	Zhang Yanyuan	Acker 1954, 188–89. Schafer 1955, 75.
Gold stone <i>Huang jin shi</i>	黃金石	<i>huang-chin-shih</i>		Yu Feian	Yu 1988, 6; Yu 2013, 6.
Cock's comb yellow <i>Ji guan huang</i>	雞冠黃	<i>chi-kuan-huang</i>	high grade of realgar	Wang Gai	Sze 1956, 39; <i>JZYHP</i> 1868, 1(1): 15b. Schafer 1955, 80.
Mineral yellow <i>Shi huang</i>	石黃	<i>shih-huang</i>	Yu treats this as distinct from orpiment and realgar, but his discussion suggests it is an arsenic sulfide.	Song Yingxing, Wang Gai, Yu Feian	Song 1966, 212; Song 1637, 3(16): 47a. Sze 1956, 39; <i>JZYHP</i> 1868, 1(1): 15b. March 1935, 7. Yu 1988, 6; Yu 2013, 6.
<b>Yellow iron oxide</b> <b><i>Yang hua tie huang</i></b>	氧化鐵黃	<b><i>yang-hua-t'ieh-huang</i></b>	<b>goethite <math>\text{HFeO}_3</math>, lepidocrocite <math>\text{FeO(OH)}</math>. Multiple minerals can be found together.</b>		<b>see chaps. 1, 4</b>
Earth yellow, yellow ocher <i>Tu huang</i>	土黃	<i>t'u-huang</i>		Wang Yi, Yu Feian	Franke 1950, 30; Wang 1621–44, 11: 2a. Yu 1988, 7; Yu 2013, 6.
Yellow ocher <i>Zhe shi</i>	赭石	<i>che-shih</i>	(see entry under red iron oxide)	Wang Gai	Sze 1956, 43; <i>JZYHP</i> 1868, 1(1): 18b.
<b>Chrome yellow</b> <b><i>Ge huang</i></b>	鉻黃	<b><i>ko-huang</i></b>	<b>lead chromate <math>\text{PbCrO}_4</math></b>		<b>see chap. 5</b>
<b>Gamboge</b> <b><i>Teng huang</i></b>	藤黃	<b><i>t'eng-huang</i></b>	<b>from genus <i>Garcinia</i></b>		<b>see chaps. 1, 3, 4</b>
Rattan yellow <i>Teng huang</i>	藤黃	<i>t'eng-huang</i>	Wang Fangquan says it is <i>G. morvella</i> [ <i>G. morella</i> ].	Huang Gongwang, Shen Hsin-Yu, Wang Fangquan, Wang Gai, Wang Yi, Yu Feian	Bush and Shih 2012, 263; Huang 1957, 697. Sze 1956, 584; <i>JZYHP</i> 1868, 3(1): 24b. Wang 1937, 88. Sze 1956, 42; <i>JZYHP</i> 1868, 1(1): 16b. March 1935, 9. Franke 1950, 30, 32; Wang 1621–44, 11:2a. Yu 1988, 13; Yu 2013, 15.
Brush-tube yellow <i>Bi guan huang</i>	筆管黃	<i>pi-kuan-huang</i>		Shen Hsin-Yu, Wang Gai	Sze 1956, 584; <i>JZYHP</i> 1868, 3(1): 25a, Sze 1956, 42; <i>JZYHP</i> 1868, 1(1): 17b.
Linyi yellow <i>Linyi zhi huang</i>	林邑之黃	<i>lin-i-chih-huang</i>	(see entry under arsenic sulfides)	Yu Feian	Yu 1988, 13; Yu 2013, 16.
Moon yellow, Viet yellow <i>Yue huang</i>	月黃, 越黃	<i>yue-huang</i>	<i>Yue</i> (越) means "Viet" but was often changed to the homonym <i>yue</i> (月) meaning "moon."	Yu Feian	Yu 1988, 13, 45; Yu 2013, 16, 69.
Zhenla painting yellow <i>Zhenla hua huang</i>	真臘畫黃	<i>Chen-la-hua-huang</i>	Zhenla is in present-day northern Laos and Vietnam.	Yu Feian	Yu 1988, 13; Yu 2013, 16.
<b>Green pigments</b>					
<b>Malachite</b> <b><i>Shi lü, kong que shi</i></b>	石綠, 孔雀石	<b><i>shih-lü, k'ung-ch'üeh-shih</i></b>	<b>basic copper(II) carbonate <math>\text{CuCO}_3 \cdot \text{Cu(OH)}_2</math></b>		<b>see chaps. 1, 3, 4</b>

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Mineral green, stone green <i>Shi lü</i>	石綠	<i>shih-lü</i>		Shen Hsin-Yu, Wang Fangquan, Wang Gai	Sze 1956, 580; <i>JZYHP</i> 1868, 3(1): 21a. Wang 1937, 88. Sze 1956, 38; <i>JZYHP</i> 1868, 1(1): 14a. March 1935, 7.
Flat green <i>Bian qing</i>	扁青	<i>pien-ching</i>	Zhang describes it as “from Wu-ch’ang (Wuhan Hubei)” and as a high-grade malachite. Yu uses the same characters for a blue azurite color (see entry under azurite).	Zhang Yanyuan	Acker 1954, 187.
Official green <i>Guan lü</i>	官綠	<i>kuan-lü</i>	Wang says this is the same as “branch green.”	Wang Yi	Franke 1950, 31–32; Wang 1621–44, 11:3b.
Malachite <i>Kong qing</i>	空青	<i>k’ung-ch’ing</i>		Song Yingxing	Song 1966, 299; Song 1637, 3(18): 58b.
Green flower <i>Lü hua</i>	綠花	<i>lü-hua</i>	palest grade of malachite	Li Kan	Yu 1988, 58; Yu 2013, 96; Li 1921, 1: 15b.
Paste green <i>Ni lü</i>	泥綠	<i>ni-lü</i>	Yu believes this to be malachite.	Fan Chengda	Yu 1988, 8; Yu 2013, 9.
Granulated green <i>Sha lü</i>	沙綠	<i>sha-lü</i>	Yu believes this to be malachite from Tibet and Persia.	Yu Feian	Yu 1988, 9; Yu 2013, 10.
Branch green <i>Zhi tiao lü</i>	枝條綠	<i>chih-t’iao-lü</i>	a pale shade of malachite, lighter than third green ( <i>san lü</i> ) but darker than green flower ( <i>lü hua</i> )	Li Kan, Wang Yi	Yu 1988, 58; Yu 2013, 96; Li 1921, 1:15b. Franke 1950, 32; Wang 1621–44, 11: 3a.
<b>Atacamite and related materials</b> <i>Lü yan tong kuang, lü tong kuang, fu lü tong kuang, xie lü tong kuang</i>	綠鹽銅礦, 氯銅礦, 副氯銅礦, 斜氯銅礦	<i>lü-yen-t’ung-k’uang, lü-t’ung-k’uang, fu-lü-t’ung-kuang, hsieh-lü-t’ung-k’uang</i>	<b>basic copper(II) chloride</b> $\text{Cu}_2\text{Cl}(\text{OH})_3$ . <b>Multiple mineral forms can be found together.</b>		<b>See chaps. 1, 4</b>
Green salt, copper green <i>Tong lü</i>	銅綠	<i>T’ung-lü</i>	Term can also be interpreted (both in English and in Chinese texts) as verdigris or copper acetate, but scientific investigations suggest it is synthetic atacamite.	Lei Yong, Li Shizhen, Song Yingxing, Yu Feian	Lei 2012, 107. Li 1658, 8: 15a. Song 1966, 287; Song 1637, 3(16): 47a. Yu 1988, 9, 28; Yu 2013, 9.
<b>Emerald green</b> <i>Fei cui lü</i>	翡翠綠	<i>fei-ts’ui-lü</i>	<b>copper acetoarsenite</b>		<b>see chaps. 3, 4</b>
Bright “geba” green <i>“Geba” lü</i>	“咯吧”綠	<i>“ko-pa”-lü</i>		Yu Feian	Yu 1988, 45; Yu 2013, 70.
Foreign green <i>Yang lü</i>	洋綠	<i>yang-lü</i>	Yu gives <i>Chanchen</i> (禪臣) and Grumbacher ( <i>Ji pai</i> 雞牌) as sources for foreign green. Note that Grumbacher was established in 1905.	Yu Feian	Yu 1988 45; Yu 2013, 69–70.
<b>Green mixtures</b>					<b>see chaps. 1, 3, 4</b>
Grass or vegetation green <i>Cao lü</i>	草綠	<i>ts’ao-lü</i>	a mixture of indigo and gamboge	Wang Gai	Sze 1956 43; <i>JZYHP</i> , 1868 1(1): 18b. March 1935, 10.
Composite green <i>He lü</i>	合綠	<i>ho-lü</i>	presumed to be a mixture of indigo and gamboge	Rao Ziran	Bush and Shih 2012, 269; Rao 1957, 693.
Old green <i>Lao lü</i>	老綠	<i>lao-lü</i>	a mixture of indigo and gamboge	Wang Gai	Sze 1956, 43; <i>JZYHP</i> 1868, 1(1): 18b. March 1935, 10.
Lotus green <i>Lian qing</i>	蓮青	<i>lien-ch’ing</i>	a mixture of red and indigo	Shen Hsin-Yu	Sze 1956, 585; <i>JZYHP</i> 1868, 3 (1): 26a.



## SCIENTIFIC STUDIES OF PIGMENTS IN CHINESE PAINTINGS

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Fresh green <i>Nen lü</i>	嫩綠	<i>nen-lü</i>	a mixture of indigo and gamboge	Shen Hsin-Yu, Wang Gai	Sze 1956 43, 585; <i>JZYHP</i> 1868, 1(1): 18b, 3(1): 25b. March 1935, 10.
Intense green <i>Nong lü</i>	濃綠	<i>nung-lü</i>	a mixture of indigo and gamboge	Shen Hsin-Yu	Sze 1956, 584; <i>JZYHP</i> 1868, 3(1): 25b.
Deep green <i>Shen lü</i>	深綠	<i>shen-lü</i>	a mixture of indigo and gamboge	Shen Hsin-Yu	Sze 1956, 584; <i>JZYHP</i> 1868, 3(1): 25b.
<b>Unknown green pigments</b>					
Flower-and-leaves green <i>Hua ye lü</i>	花葉綠	<i>hua-yeh-lü</i>		Wang Yi	Franke 1950, 32; Wang 1621-44, 11: 4b.
Peacock green <i>Kong que shi</i>	孔雀石	<i>kung-ch'üeh-shih</i>	Yu says this is from northwest China and the Malay peninsula and "even when broken up into bits and pieces a green color can be produced from it."	Yu Feian	Yu 1988, 9; Yu 2013, 9.
Southern green <i>Nan lü</i>	南綠	<i>nan-lü</i>		Wang Yi	Franke 1950, 32; Wang 1621-44, 11: 4b.
Lacquer green <i>Qi lü</i>	漆綠	<i>ch'i-lü</i>		Wang Yi	Franke 1950, 32; Wang 1621-44, 11: 3a.
Sü blue <i>Su qing</i>	蘇青	<i>su-ch'ing</i>	Franke suggests this may be the same as first green ( <i>tou lü</i> ).	Wang Yi	Franke 1950, 32; Wang 1621-44, 11: 4b.
Greasy (oily) green <i>You lü</i>	油綠	<i>yu-lü</i>		Wang Yi	Franke 1950, 32; Wang, 1621-44, 11: 4b.
<b>Blue pigments</b>					
<b>Azurite</b> <i>Shi qing, lan tong kuang</i>	石青, 藍銅礦	<i>shih-ch'ing, lan-t'ung-k'uang</i>	<b>basic copper(II) carbonate</b> $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$		<b>see chaps. 1-4</b>
Mineral blue, stone blue <i>Shi qing</i>	石青	<i>shih-ch'ing</i>		Shen Hsin-Yu, Wang Fangquan, Wang Gai	Sze 1956, 579; <i>JZYHP</i> 1868, 3(1): 20b. Wang 1937, 88. Sze 1956, 37; <i>JZYHP</i> 1868, 1(1): 13b. March 1935, 6.
Light blue <i>Bai qing</i>	白青	<i>pai-ch'ing</i>	a lighter color than sky blue ( <i>tian qing</i> ), seldom used by artists	Yu Feian	Yu 1988, 8; Yu 2013, 8.
Jade blue <i>Bi qing</i>	碧青	<i>pi-ch'ing</i>	Yu says same as light blue ( <i>bai qing</i> ).	Yu Feian	Yu 1988, 8; Yu 2013, 8.
Flat blue <i>Bian qing</i>	扁青	<i>pien-ch'ing</i>	(see entry under malachite)	Yu Feian	Yu 1988, 7; Yu 2013, 7.
Layered blue <i>Ceng qing</i>	曾青	<i>ts'eng-ch'ing</i>	an older version of the character, 層, is used in the English translation of Yu.	Yu Feian, Zhang Yanyuan	Yu 1988, 7-8; Yu 2013, 7. Acker 1954, 187.
Great blue, pure blue <i>Da qing</i>	大青	<i>ta-ch'ing</i>	coarse azurite. Yu says "same as flat blue."	Yu Feian, Zhang Yanyuan	Yu 1988, 7; Yu 2013, 7. Acker 1954, 189.
Yunnan blue <i>Dian qing</i>	滇青	<i>tien-ch'ing</i>	Yu says "flat blue" from Yunnan province.	Yu Feian	Yu 1988, 7, 71-72; Yu 2013, 7.
Burmese blue <i>Dian qing</i>	甸青	<i>tien-ch'ing</i>	Yu says "flat blue" from Burma.	Yu Feian	Yu 1988, 7; Yu 2013, 7.
Sky blue <i>Kong qing</i>	空青	<i>k'ung-ch'ing</i>	Acker suggests it could be azurite or ultramarine. The location associated with it is "Yüeh-sui" (Xichang, Sichuan). Azurite can be found in Sichuan province.	Zhang Yanyuan	Acker 1954, 187.
Paste blue <i>Ni qing</i>	泥青	<i>ni-ch'ing</i>		Yu Feian	Yu 1988, 71-72; Yu 2013, 120.

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Sky blue <i>Tian qing</i>	天青	<i>t'ien-ch'ing</i>	light blue from refining of layered blue ( <i>ceng qing</i> )	Yu Feian	Yu 1988, 8; Yu 2013, 8.
<b>Indigo</b> <i>Hua qing, dian, dian hua, dian qing</i>	花青, 靛, 靛花, 靛青	<b><i>hua-ch'ing, tien, tien-hua, tien-ch'ing</i></b>	<b>For indigo plants see Han and Cardon. The primary colorant is indigotin. Synthetic indigo was developed in 1880 but it is not currently possible to distinguish natural from synthetic indigo.</b>		<b>see chaps. 1–4. Han 2015, 231. Cardon 2007, 379.</b>
Indigo <i>Dian hua</i>	靛花	<i>tien-hua</i>		Shen Hsin-Yu, Wang Gai	Sze 1956, 42, 584; <i>JZYHP</i> 1868, 1(1): 17b, 3(1): 24b. March 1935, 9.
Formosan indigo <i>Fan zhong qing dai</i>	番中青黛	<i>fan-chung-ch'ing-tai</i>		Li Kan	Yu 1988, 63; Yu 2013, 103; Li 1921, 1: 15a.
Fujian snail shell blue <i>Fujian luo qing</i>	福建螺青	<i>Fu-chien luo-ch'ing</i>		Li Kan	Yu 1988, 63; Yu 2013, 103; Li 1921, 1: 15a.
Guang blue <i>Guang qing</i>	廣青	<i>kuang-ch'ing</i>	indigo, powder form, not lime-soaked	Zou Yigui	Yu 1988, 59, 61; Yu 2013, 97, 100; Zou 1991, 9: 722.
Flower blue <i>Hua qing</i>	花青	<i>hua-ch'ing</i>		Shen Zongqian, Wang Fangquan	Yu 1988, 14, 60; Yu 2013, 17, 98. Wang 1937, 88. March 1935, 9.
Indigo <i>Lan</i>	藍	<i>lan</i>	indigotin	Yu Feian	Yu 1988, 14; Yu 2013, 17.
Indigo <i>Lan dian</i>	藍澱	<i>lan-tien</i>		Song Yingxing	Song 1966, 75; Song 1637, 1(3): 50a.
Shell blue <i>Luo qing</i>	螺青	<i>lo-ch'ing</i>	Both Huang and Rao describe using shell blue as a wash over azurite, suggesting shell blue is indigo.	Huang Gongwang, Rao Ziran, Wang Yi	Bush and Shih 2012, 263–65, 269; Huang 1957, 697; Rao 1957, 693. Franke 1950, 31–32; Wang 1621–44, 1: 4b.
<b>Prussian blue</b> <i>Pulushi lan, Bali lan, yang lan</i>	普魯士藍, 巴黎藍, 洋藍	<b><i>P'u-lu-shih-lan, Pa-li-lan, yang-lan</i></b>	<b>ferric ferrocyanide, inter alia <math>\text{Fe}_4[\text{Fe}(\text{CN})_6]_3</math></b>		<b>see chaps. 2–4</b>
Foreign blue <i>Yang lan</i>	洋藍		likely Prussian blue although not explicitly stated	Yu Feian	Yu 1988, 30; Yu 2013, 45.
<b>Smalt</b> <i>Da qing, hua gan qing, teng zi</i>	大青, 花紺青, 藤紫	<b><i>ta-ch'ing, hua-kan-ch'ing, t'eng-tzu</i></b>	<b>cobalt colored blue glass</b>		<b>see chaps. 3, 4</b>
<b>Ultramarine</b> <i>Qun qing, qing se, qing lan</i>	群青, 青色, 青藍	<b><i>ch'ün-ch'ing, ch'ing-se, ch'ing-lan</i></b>	<b>(lazurite) <math>\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}</math></b>		<b>see chaps. 1–4</b>
Lapis <i>Liu li shi</i>	琉璃石	<i>liu-li-shih</i>	Song discusses this as a gem and says it is produced in the “Western Regions,” suggesting it is natural ultramarine, but also states that it comes in many different colors and that the Chinese are trying to make an artificial version in the manner of ceramic glazes, so it may refer to smalt.	Song Yingxing	Song 1966, 307–08; Song 1637, 3(18): 64a.
<b>Unknown blue pigments</b>					
Buddha blue <i>Fo qing</i>	佛青	<i>fo-ch'ing</i>	same as granulated blue ( <i>sha qing</i> )	Ze Lang	Yu 1988, 8; Yu 2013, 8.
Hui blue <i>Hui qing</i>	回青	<i>Hui-ch'ing</i>	same as granulated blue ( <i>sha qing</i> ) Silbeigeld and McNair note that Hui means Muslim	Ze Lang	Yu 1988, 8, 71–72; Yu 2013, 8, 119–20.

English and Pinyin Name of Color	Chinese Name	Chinese Name (Wade-Giles)	Identification	Sources	References
Old blue <i>Lao qing</i>	老青	<i>lao-ch'ing</i>		Wang Yi	Franke 1950, 30; Wang 1621-44, 11: 2a.
Mao blue <i>Mao er lan</i>	毛兒藍	<i>mao-erh-lan</i>	Yu says "a foreign color ... also called deep indigo" but it is unclear if this refers to chemical composition or the shade of blue.	Yu Feian	Yu 1988, 44; Yu 2013, 69.
Granulated blue <i>Sha qing</i>	沙青	<i>sha-ch'ing</i>	Yu suggests this is a type of azurite, but Silbergeld and McNair believe the source (western parts of China and farther west) suggests it could be ultramarine or smalt.	Yu Feian	Yu 1988, 8, 71-72; Yu 2013, 8.
Deep middle blue <i>Shen zhong qing</i>	深中青	<i>shen-chung ch'ing</i>	possibly azurite	Wang Yi	Franke 1950, 3; Wang 1621-44, 11: 4b.
Tibetan blue <i>Zang qing</i>	藏青	<i>Tsang-ch'ing</i>	Yu classes this with granulated blue.	Yu Feian	Yu 1988, 8, 71-72; Yu 2013, 8, 120.

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# Appendix 5

## Complete Analysis Results

This appendix presents the results of all analytical work for the individual paintings investigated and discussed in this volume. Results are given in three tables: one presents the Song and Yuan dynasty (960–1368) paintings that accompany chapter 1, and two tables show the results for paintings from the Ming dynasty (1368–1644) into the twentieth century. The second table includes results discussed in chapters 2 and 3, while the third table presents results for portraits and relates to chapters 2–4. Within each table paintings are arranged in ascending order by accession number. Accession numbers and titles in boldface are discussed in the text, with the chapter number given after the accession number; if the painting is illustrated, the figure number is given. Relevant table numbers are also noted.

Terms used for colorants reflect the level of certainty of the scientific analysis, and generally multiple techniques were used. The analytical techniques used for each identification are given (for more detail, see app. 1). For some pigments x-ray fluorescence spectrometry (XRF) is sufficient for identification. For example, cinnabar/vermillion is assumed to be present if mercury and sulfur are seen with XRF. Fiber optics reflectance spectroscopy (FORS) can indicate the presence of an insect dye with 100 percent certainty, but less certain is the differentiation between the two insect dyes, cochineal and lac (see app. 2). High-performance liquid chromatography (HPLC) can, however, differentiate the two with absolute certainty. FORS was used to confirm the presence of indigo, often with XRF to show the absence of other blues (see app. 3). FORS together with XRF

was considered positive confirmation of azurite. However, for Prussian blue, Fourier transform infrared spectroscopy (FTIR) was considered necessary for confirmation; likewise FTIR was used to identify gamboge. Either FTIR or x-ray diffraction (XRD) can definitively identify several of the traditional mineral and new synthetic colorants such as lead white, malachite, atacamite, emerald green, azurite, and ultramarine. These methods were used together with polarized light microscopy (PLM) to look for mixtures and document particle shape and accessory minerals to determine if a pigment was natural or synthetic. Colorants discussed in the text have the highest certainty unless it is stated otherwise.

Of note are the terms “lead-based white,” “copper-based green,” “cinnabar/vermillion,” and “cochineal.” The term “lead-based white” has been used where lead has been identified by XRF, but the exact identity of the pigment has not been determined. Where XRD or FTIR determined the presence of lead white (hydrocerussite) or another pigment, the specific pigment name is used. The results from a previous study of lead-based whites (Winter 1981) have been included where the paintings John Winter examined are ones also used in this study.

Similarly, the designation “copper-based green” has been used when the use of XRF has identified copper in a green area of a painting. When positive identifications were found with either XRD or FTIR for a specific pigment such as malachite, atacamite, botallackite, or emerald green (with the addition of arsenic in the XRF spectrum), the specific pigment name was used.

The term “cinnabar/vermilion” has been used for the red mercury sulfide pigment because XRF, the primary means of identifying the pigment in this study, cannot distinguish definitively between the natural (cinnabar) and the man-made (vermilion) pigment.

The term “cochineal” has been used when carminic acid, its primary dye component, was found with HPLC. Although some studies have been able to differentiate between cochineal from the Americas and Armenian cochineal, the sample size combined with the method used did not allow for further specificity.

Trade records and historic documents suggest that the cochineal found in these paintings is most likely American cochineal. For these reasons, the general term “cochineal” was used in this volume.

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**Table A5.1.** Colorants identified in Song and Yuan dynasty paintings.

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1902.224	1178	<i>Luohan Laundering</i>	Lin Tinggui	hanging scroll on panel	silk	hydrocerussite XRD
F1904.341	13th–14th centuries	<i>The Celestial Worthy Taiyi, Who Delivers from Suffering</i>		hanging scroll on panel	silk	hydrocerussite XRD
F1907.139	1178	<i>The Rock Bridge at Mount Tiantai</i>	Zhou Jichang	hanging scroll on panel	silk	hydrocerussite XRD
F1909.244j	12th–13th centuries	<i>Travelers in Snowy Mountains</i>	follower of Liang Kai	fan mounted as album leaf	silk	lead-based white XRF
F1909.245h	possibly Song dynasty	<i>Landscape: A Towering Crag above a River; Trees and a House in the Foreground</i>		album leaf	silk	
F1911.161a	14th century	<i>River Landscape in Mist</i>	formerly attributed to Yan Ciping	album leaf	silk	lead-based white XRF
F1911.209	14th century	<i>Scenic Attractions of West Lake</i>	formerly attributed to Li Song	handscroll	paper	hydrocerussite XRD
<b>F1913.65 (fig. 1.7)</b>	14th century	<b><i>Bodhisattva and Attendants</i></b>		hanging scroll	silk	hydrocerussite XRD
F1914.147a	14th century	<i>Vaisravana, Guardian King of the North</i>	traditionally attributed to Yuchi Yiseng	hanging scroll on panel	silk	hydrocerussite XRD
F1915.17	14th century	<i>Eggplant</i>	traditionally attributed to Qian Xuan	handscroll	paper	hydrocerussite XRD
F1916.50	possibly 14th century	<i>Promenading Ladies</i>	formerly attributed to Zhou Fang	hanging scroll on panel	silk	hydrocerussite XRD; trace calcite XRD XRF
<b>F1916.521 (chap. 1)</b>	14th century	<b><i>Luohan, Holding a Fly Whisk, with Attendant</i></b>	formerly attributed to Wu Daozi	hanging scroll on panel	silk	hydrocerussite, anglesite XRD; trace calcite XRD XRF
F1916.526	12th century	<i>Removing the Saddle, Inspecting the Arrows</i>	traditionally attributed to Zhang Kan	hanging scroll on panel	silk	hydrocerussite XRD
F1917.114	14th century	<i>Portrait of a Woman in White: Lu Meiniang</i>	formerly attributed to He Chong	hanging scroll on panel	silk	hydrocerussite XRD; trace calcite XRD XRF
F1917.183	late 13th–early 14th centuries	<i>Crabapple and Gardenia</i>	Qian Xuan	album leaf mounted as handscroll	paper	hydrocerussite XRD
F1917.334	1345	<i>Ajita, the Fifteenth Venerable Luohan</i>	formerly attributed to Wang Jianji	hanging scroll	silk	hydrocerussite XRD
F1918.6	1345	<i>The Great Luohan, the Venerable Seventeenth</i>	formerly attributed to Guanxiu	hanging scroll	silk	hydrocerussite XRD

Red Colorants	Yellow Colorants	Copper-Based Green	Azurite	Indigo	Ultramarine	Iron-Based Brown
HgS PLM XRF	iron-based yellow PLM XRF	pseudomalachite SEM-EDS XRD	XRD			
HgS XRF	iron-based yellow XRF	malachite XRD	XRD			XRF
HgS PLM XRF	iron-based yellow PLM XRF	malachite XRD	XRD	FORS		
iron-based red XRF				FORS XRF		XRF
		XRF	XRD			
				FORS XRF		
HgS XRF; insect dye FORS	iron-based yellow XRF			FORS		XRF
HgS XRF	iron-based yellow PLM	atacamite PLM XRD	XRD			
HgS XRD	iron-based yellow XRF	malachite XRD	XRD			
insect dye FORS	gamboge FTIR			FORS XRF		
HgS PLM XRF		malachite XRD XRF	XRD			
HgS XRF; lac dye FORS		paratacamite PLM XRD	XRD			
HgS XRF	iron-based yellow XRF			FORS XRF		PLM XRF
HgS PLM XRF						
insect dye FORS	iron-based yellow PLM XRF			FORS PLM XRF		
HgS XRD; red lead XRD; iron-based red XRF; insect dye FORS	iron-based yellow XRF	malachite XRD	XRD			XRF
HgS XRF; hematite XRD	iron-based yellow XRF	malachite SEM-EDS XRD	XRD			

Accession Number	Date	Title	Artist	Format	Support	White Colorants
<b>F1919.107 (chap. 1)</b>	1345	<b>Seated Luohan</b>	formerly attributed to Wu Daozi	hanging scroll	silk	lead-based white XRF
F1919.154	14th–15th centuries	<i>Autumn Foliage and Birds</i>	formerly attributed to Cui Bai	hanging scroll on panel	silk	lead-based white PLM XRF
<b>F1919.163 (chap. 1)</b>	1345	<b>Panthaka, the Tenth Venerable Luohan</b>	formerly attributed to Qian Yi	hanging scroll	silk	hydrocerussite XRD
<b>F1926.1 (chap. 1)</b>	12th–13th centuries	<b>The Buddha Addressing Yamaraja at Kusinagara</b>		handscroll	paper	anglesite XRD
<b>F1930.36 (chap. 5, fig.1.3)</b>	968	<b>Guanyin of the Water Moon</b>		hanging scroll	silk	hydrocerussite XRD (RJG)
F1931.3	14th century	<i>Horses and Grooms Crossing a River</i>	traditionally attributed to Zhao Mengfu	handscroll	paper	
F1935.8	12th–13th centuries	<i>Palace Ladies Bathing Infants</i>	traditionally attributed to Zhou Wenju	fan mounted as album leaf	silk	hydrocerussite XRD
<b>F1935.9 (fig. 1.4)</b>	12th–13th centuries	<b>Palace Ladies and Attendants</b>	traditionally attributed to Zhou Wenju	fan mounted as album leaf	silk	hydrocerussite XRD
<b>F1935.11 (chap. 5, fig. 1.2)</b>	late 10th–early 11th centuries	<b>Ksitigarbha Bodhisattva</b>		hanging scroll	silk	hydrocerussite XRD
<b>F1939.37/ F1960.4 (chap. 1)</b>	late-12th–mid-13th centuries	<b>Palace Ladies Playing Double Sixes</b>	traditionally attributed to Zhou Fang	handscroll	silk	hydrocerussite XRD; anglesite SEM-EDS XRD
F1944.50	13th–14th centuries	<i>Three Horses</i>		album leaf	silk	
F1945.32	1347	<i>Horse and Groom, After Li Gonglin</i>	Zhao Yong	handscroll	paper	hydrocerussite XRD
<b>F1948.10 (fig. 1.1)</b>	ca. 1056	<b>Portrait of Wang Huan</b>		album leaf	silk	cerussite FTIR
F1948.11	ca. 1056	<i>Portrait of Feng Ping</i>		album leaf	silk	lead-based white XRF
F1954.20	mid–late 13th century	<i>Silk Weaving, After Lou Shou</i>	attributed to Cheng Qi	handscroll	paper	hydrocerussite FTIR XRD; trace clays in white FTIR
F1954.21	mid–late 13th century	<i>Tilling Rice, After Lou Shou</i>	attributed to Cheng Qi	handscroll	paper	hydrocerussite XRD; trace clays in white FTIR
<b>F1954.126 (chap. 5, fig. 1.6)</b>	13th–14th centuries	<b>Bird on an Apricot Branch</b>	formerly attributed to Li Zhi	album leaf	silk	hydrocerussite XRD
<b>F1957.14 (fig. 1.5)</b>	14th century	<b>Consort Yang Mounting a Horse</b>	traditionally attributed to Qian Xuan	handscroll	paper	lead-based white PLM XRF
F1959.17	1354	<i>Dwelling in Seclusion in the Summer Mountains</i>	Wang Meng	hanging scroll	silk	
F1992.41	1345	<i>Pindola Bharadvaja, the First Venerable Luohan</i>	formerly attributed to Wu Daozi	hanging scroll	silk	hydrocerussite XRD

## Notes

Identifications labeled (RJG) were performed by Rutherford J. Gettens; identifications labeled (WTC) were performed by W. Thomas Chase.

For F1904.336, 14th century; F1904.337, 14th century; F1916.82, 14th–15th centuries, only the lead-based white pigments were examined, and all were indicated by XRD to be hydrocerussite.

For further information on the paintings, see the online catalog for Song and Yuan dynasty paintings, <https://asia.si.edu/publications/songyuan/>.

Red Colorants	Yellow Colorants	Copper-Based Green	Azurite	Indigo	Ultramarine	Iron-Based Brown
HgS XRF; iron-based red XRF	iron-based yellow XRF		XRD	FORS XRF		
HgS XRF	iron-based yellow XRF	XRF		FORS PLM XRF		XRF
HgS XRF	iron-based yellow SEM-EDS XRF		XRD			
HgS XRF		XRF	PLM XRD XRF			
HgS chemical microscopy (RJG); red lead chemical microscopy (RJG) XRF; insect dye FORS	orpiment XRD	atacamite PLM XRD			natural ultramarine PLM (RJG)	
HgS XRF		XRF		FORS		XRF
HgS PLM XRF		malachite PLM XRD	XRF	FORS		
HgS PLM XRF	iron-based yellow XRF	malachite XRD	XRD			XRF
HgS chemical microscopy (RJG); red lead PLM; insect dye FORS	orpiment XRD (WTC, RJG)	atacamite PLM XRD			natural ultramarine PLM (RJG)	XRF
HgS XRF; red lead XRF; iron-based red XRF	iron-based yellow SEM-EDS	malachite XRD				
				FORS		XRF
HgS XRD; iron-based red XRF; insect dye FORS			XRD			XRF
HgS XRF						
HgS XRF	iron-based yellow XRF; gamboge FTIR SBM	malachite FTIR PLM XRF		FORS XRF		XRF
HgS XRF; iron-based red XRF	iron-based yellow XRF	malachite FORS FTIR XRF		FORS		XRF
insect dye FORS		atacamite XRD	FORS XRF	FORS		
HgS XRF; red lead XRD XRF; insect dye FORS PLM XRF	gamboge FTIR XRF	FORS XRF	PLM XRF	FORS XRF		PLM XRF
HgS XRF				FORS XRF		XRF
HgS PLM XRF; iron-based red PLM	iron-based yellow PLM XRF	malachite XRD	XRD			



**Table A5.2.** Colorants identified in later Chinese paintings.

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1893.32	Ming dynasty	<i>Herons and Water Plants</i>		hanging scroll	silk	lead-based white XRF
F1901.172	17th–18th centuries	<i>Peonies</i>	follower of Yun Shouping	hanging scroll on panel	silk	
<b>F1904.396 (fig. 2.4)</b>	18th century	<b><i>Landscape with Gibbons and Cranes</i></b>	formerly attributed to Qiu Ying	handscroll	silk	lead-based white XRF
<b>F1909.201 (fig. 2.12)</b>	late 17th–18th centuries	<b><i>Autumn Landscape with Birds and Berries and Rabbits</i></b>	traditionally attributed to Yi Yuanji	handscroll	silk	lead-based white XRF
<b>F1909.218 (fig. 3.1)</b>	18th century	<b><i>A Hundred Birds Worship the Phoenixes</i></b>	formerly attributed to Xu Xi	handscroll	silk	lead-based white XRF
F1909.227	18th–19th centuries	<i>Horses and Keepers</i>	formerly attributed to Yan Liben	handscroll	silk	lead-based white XRF
F1909.231	18th century	<i>Hunting Scene</i>	formerly attributed to Wang Meng	handscroll	silk	lead-based white XRF
F1909.239	18th century	<i>Life on the River</i>	formerly attributed to Ma Yuan	handscroll	silk	lead-based white XRF
F1909.245a	Ming dynasty	<i>Landscape: A Man under a Pine</i>		album leaf	silk	
F1909.245c	16th century	<i>Landscape: Pavilions on a Mountain Side; a Stream below</i>	Ma Yuan	fan mounted as album leaf	silk	
F1909.245d	Ming dynasty	<i>Birds and Peaches</i>		album leaf	silk	lead-based white XRF
F1909.245e	Ming dynasty	<i>A Blue Glass Dish Filled with Fruit</i>		album leaf	silk	lead-based white XRF
<b>F1909.245f (chap. 3)</b>	possibly Qing dynasty	<b><i>Landscape: Bullock Carts Forging a Mountain Stream</i></b>		album leaf	silk	
F1909.245i	Ming dynasty	<i>River Landscape: A Pavilion under Pines Built among High Rocks; Distant Mountains</i>		fan mounted as album leaf	silk	lead-based white XRF
F1909.245j	Ming dynasty	<i>Pavilions and People</i>		album leaf	silk	lead-based white XRF
F1909.245k	Ming dynasty	<i>River Scene: A Man Asleep in a Boat—Ducks Swimming by</i>		album leaf	silk	lead-based white XRF
F1909.245l	Ming dynasty	<i>River Landscape: A Pagoda, Foaming Rapids, Distant Hills</i>		album leaf	silk	lead-based white XRF
F1909.245m	Ming dynasty	<i>Landscape: Hillsides, Rocks, Trees, House, and a Boat</i>		album leaf	silk	
F1909.245n	Qing dynasty	<i>A Mother, Child, and Three Maids</i>		album leaf	silk	lead-based white XRF
F1909.245o	Ming dynasty	<i>Mountain Landscape: Crag, Temple, and Pines</i>		album leaf	silk	lead-based white XRF
F1909.245p	Qing dynasty	<i>River Landscape: Houses, Hills, and Distant Mountains</i>		album leaf	silk	lead-based white XRF
F1909.245q	Ming dynasty	<i>River Landscape: A Man Reading in a Boat Moored under a Blossoming Tree</i>		album leaf	silk	lead-based white XRF
<b>F1909.245r (chap. 3)</b>	early 20th century	<b><i>Cat, Rock, and Peonies</i></b>		album leaf	silk	lead-based white XRF
F1909.245s	17th century	<i>Landscape: A Palace between Lake and Mountains</i>		album leaf	silk	

Cinnabar/Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
				FORS	iron-based red XRF; iron-based brown FORS XRF	
	unidentified organic red FORS			FORS		
XRF	lac dye FORS HPLC	XRF	FORS XRF	FORS XRF		
XRF	lac dye FORS HPLC	XRF	FORS XRF	FORS XRF		
XRF	lac dye FORS HPLC		FORS XRF	FORS XRF		
XRF	lac dye FORS	FORS PLM XRF	FORS XRF	FORS XRF		
XRF	lac dye FORS HPLC		FORS XRF	FORS XRF	iron-based red XRF	
XRF	lac dye FORS HPLC		FORS XRF	FORS XRF		
				FORS		
				FORS XRF		
XRF	lac dye FORS HPLC	XRF	FORS XRF	possibly FORS		
	lac dye FORS HPLC	XRF	FORS XRF	FORS	iron-based red XRF	
		XRF	FORS XRF	FORS XRF		
		XRF	XRF	FORS	iron-based red XRF	
XRF			FORS XRF	FORS		
XRF				FORS	iron-based red XRF	
	possible unidentified organic red FORS XRF	XRF	FORS XRF			
	lac dye FORS			FORS		
XRF		XRF	XRF	FORS	possibly red lead XRF	
XRF		XRF	FORS XRF		possibly red lead XRF	
XRF		XRF	FORS XRF	FORS XRF	possibly red lead XRF; iron-based red XRF	
	lac dye FORS HPLC	XRF		FORS XRF		
	lac dye FORS HPLC	XRF	FORS XRF	FORS		titanium-based white XRF
XRF	unidentified organic red FORS XRF	XRF	FORS XRF	FORS XRF		

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1909.245t	Qing dynasty	<i>Peony</i>		album leaf	silk	lead-based white XRF
F1909.245v	15th century	<i>Java Sparrow on a Berry Branch</i>		album leaf	silk	lead-based white XRF
<b>F1909.247a (fig. 3.9)</b>	Qing dynasty	<b><i>Travelers Crossing a Mountain Stream</i></b>	formerly attributed to Fan Kuan	album leaf	silk	lead-based white XRF
F1909.247c	Qing dynasty	<i>River Landscape: Willow and Bamboo—a Bridge across Marshes</i>		album leaf	silk	lead-based white XRF
F1909.247d	Qing dynasty	<i>Landscape: Mountains, Clouds, Trees—a Man in a Boat</i>		album leaf	silk	lead-based white XRF
F1909.247e	Qing dynasty	<i>Landscape: Tea Sipping under Willows</i>		album leaf	silk	lead-based white XRF
F1909.247f	Qing dynasty	<i>Quails and Flowers</i>		album leaf	silk	lead-based white XRF; gypsum FTIR
<b>F1909.247g (chap. 3)</b>	Qing dynasty	<b><i>A House and Garden: A Man Receiving Guests</i></b>	formerly attributed to Chen Juzhong	album leaf	silk	lead-based white XRF
F1909.249a	18th century	<i>A Bird Hovering over Blossoming Branches</i>	formerly attributed to Zhao Boju	album leaf	silk	lead-based white XRF
F1909.249b	18th century	<i>Bees Hovering over Flowers</i>	formerly attributed to Zhao Boju	album leaf	silk	lead-based white XRF
<b>F1909.249c (fig. 2.9)</b>	18th century	<b><i>Quail and Flowers</i></b>	formerly attributed to Zhao Boju	album leaf	silk	lead-based white XRF
F1909.249e	18th century	<i>Red Peony</i>	formerly attributed to Zhao Boju	album leaf	silk	
F1909.249f	18th century	<i>A Blackbird on a Branch; Autumn Leaves</i>	formerly attributed to Zhao Boju	album leaf	silk	lead-based white XRF
<b>F1909.249h (fig. 3.2)</b>	18th century	<b><i>Two Crested Birds on a Branch; Autumn Leaves</i></b>	formerly attributed to Zhao Boju	album leaf	silk	
<b>F1909.398a (fig. 3.10)</b>	Qing dynasty	<b><i>Two Figures amidst Clouds</i></b>	Chen Xiang	album leaf	silk	
F1911.135	Qing dynasty	<i>A Fishmonger and His Customer</i>		album leaf	silk	lead-based white XRF
F1911.161d	Ming dynasty	<i>Approaching the Winter Shore</i>	formerly attributed to Guo Xi	album leaf	silk	
F1911.161f	Ming dynasty	<i>Children Playing in a Garden</i>	formerly attributed to Zhou Wenju	album leaf	silk	hydrocerussite XRD
F1911.161g	17th century	<i>A Soft-drink Peddler and Customers</i>	Jiang Yin	album leaf	silk	lead-based white XRF
F1911.161h	Ming dynasty	<i>Ducklings, Rocks, and Flowers</i>		album leaf	silk	lead-based white XRF
F1911.161j	Qing dynasty	<i>A Moth and a Leafy Branch</i>	formerly attributed to Huang Jucai	fan mounted as album leaf	silk	lead sulfate XRD
F1911.163a	Ming dynasty	<i>Old Scholar Playing the Qin</i>		album leaf	silk	lead-based white XRF
F1911.163f	Ming dynasty	<i>A Tartar, His Horse, and Equipment</i>		album leaf	silk	lead-based white XRF
F1911.163i	17th century	<i>Washing the Elephant</i>	traditionally attributed to Qian Xuan	album leaf	silk	lead-based white XRF
F1911.163j	Qing dynasty	<i>A Horse, Two Men, and a Boy</i>	traditionally attributed to Zhao Mengfu	album leaf	silk	lead-based white XRF
<b>F1911.166c (chap. 3)</b>	early 18th century	<b><i>Two Peasants Crossing a Rocky Ford</i></b>	Qian Yuanchang	album leaf	silk	
<b>F1911.166d (chap. 3)</b>	late 18th–early 19th centuries	<b><i>Morning Bell at Mount Jing</i></b>	Ma Xian	album leaf	silk	lead-based white XRF

Cinnabar/Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
	lac dye FORS HPLC	FORS XRF		FORS		
XRF		FORS XRF	FORS FTIR XRF			
XRF		XRF	XRD	FORS XRF	smalt FORS XRF	
		FORS XRF		FORS XRF		
	lac dye FORS		FORS XRF	FORS XRF		
	lac dye FORS	FORS XRF	FORS XRF	FORS XRF		
XRF	lac dye FORS	XRF	FORS XRF	FORS FTIR XRF		
XRF	lac dye FORS	XRF	FORS XRF	FORS XRF	iron-based brown XRF	
XRF	lac dye HPLC		FTIR XRF	FORS		
	insect dye FORS XRF	XRF		FORS XRF		
	lac dye FORS HPLC	XRF		FORS		
XRF		XRF		FORS		
	lac dye FORS HPLC	XRF		FORS		
XRF		FORS XRF	FORS FTIR XRF	FORS		
XRF					smalt FORS XRF	
		malachite XRD	FORS XRF	FORS XRF		
XRF					iron-based red XRF	
XRF	lac dye FORS HPLC	malachite XRD	FORS PLM XRF	FORS XRF	iron-based yellow PLM SEM-EDS XRF; iron-based brown SEM-EDS XRF	
XRF	lac dye FORS HPLC			FORS		
	lac dye FORS HPLC		FORS XRF			
XRF		malachite XRD			iron-based brown XRF	
XRF	lac dye FORS	XRF	FORS XRF	FORS XRF		
XRF				FORS		
XRF	lac dye FORS	XRF	FORS XRF	FORS XRF		
XRF	lac dye FORS	XRF	FORS XRF	FORS XRF		
XRF		XRF	FORS FTIR XRF	FORS XRF		
XRF		XRF	FORS XRF	FORS XRF	iron-based brown XRF	

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1911.167a	Qing dynasty	<i>Mountain Landscape</i>	traditionally attributed to Yi Yuanji	album leaf	silk	lead-based white XRF
F1911.167b	Qing dynasty	<i>Landscape: Children Playing with a Skipping-Rope</i>	formerly attributed to Su Hanchen	album leaf	paper	
<b>F1911.167c (fig. 3.8)</b>	Qing dynasty	<b><i>An Armed Man Leading a Horse</i></b>	formerly attributed to Chen Juzhong	album leaf	silk	
F1911.167d	Qing dynasty	<i>A Buddha, Two Lions, and Four Attendants</i>		album leaf	silk	lead-based white XRF
F1911.167e	17th–19th centuries	<i>Boats Anchored at the Shore</i>	formerly attributed to Zhao Boju	album leaf	silk	lead-based white XRF
F1911.167h	Qing dynasty	<i>A Supper under Blossoming Trees</i>	formerly attributed to Zhou Wenju	album leaf	silk	lead-based white XRF
<b>F1911.167i (table 3.6)</b>	19th century	<b><i>A Toy-Peddler and Children</i></b>	traditionally attributed to Li Gonglin	album leaf	silk	lead-based white XRF
F1911.167m	late 18th–early 19th centuries	<i>Winter Landscape: Hills, a Lake, Village and Temples</i>	Ma Xian	album leaf	silk	lead-based white XRF
F1911.167n	Qing dynasty	<i>A Luohan Mounted upon a Lion</i>	formerly attributed to Li Gonglin	album leaf	silk	
F1911.167o	Qing dynasty	<i>Mountain Landscape: A House among Rocks and Trees</i>	formerly attributed to Li Songnian	album leaf	silk	
F1911.173	17th–18th centuries	<i>River Landscape in Blue and Green</i>	traditionally attributed to Qiu Ying	handscroll	silk	
F1911.186	Qing dynasty	<i>Traveling in Mountains and Streams</i>	formerly attributed to Guo Xi	handscroll	silk	lead-based white XRF
F1911.188	18th century	<i>Immortals Playing Weiqi on Penglai</i>	traditionally attributed to Leng Qian	handscroll	silk	lead-based white XRF
F1911.222	Ming dynasty	<i>Garden Scene: Melons, Eggplants, Flowers, and Two Weasels</i>		handscroll	silk	hydrocerussite XRD, lead sulfate XRD,
F1911.489	18th century	<i>Two Archers on Horseback</i>		album leaf	silk	
<b>F1911.490 (fig. 2.14)</b>	16th–17th centuries	<b><i>Enjoying a Meal on Board a Boat</i></b>		fan mounted as album leaf	silk	lead-based white XRF
F1911.505a-h	18th–19th centuries	<i>Scenes from the Story of the Western Wing</i>	traditionally attributed to Qiu Ying	album leaf	silk	lead-based white XRF
F1911.514	Qing dynasty	<i>Scenes from the Lives of Famous Men</i>	formerly attributed to Wang Zhenpeng	handscroll	silk	hydrocerussite XRD
F1911.518	Qing dynasty	<i>Illustrations of the Ladies Classic of Filial Piety</i>	formerly attributed to Liu Songnian	handscroll	silk	lead-based white XRF
<b>F1914.59a (fig. 3.16)</b>	Qing dynasty	<b><i>An Eagle on a Blue Rock in the Sea</i></b>		album leaf	silk	
<b>F1915.2 (fig. 3.7)</b>	18th century	<b><i>Spring Festival on the River</i></b>	traditionally attributed to Qiu Ying	handscroll	silk	hydrocerussite FTIR XRD
F1915.16	early–mid-15th century	<i>Central Asians Presenting Tribute Horses</i>	traditionally attributed to Han Gan	handscroll	silk	lead-based white XRF
F1915.36a	Qing dynasty	<i>River Landscape: Houses and Cloudy Mountains</i>	traditionally attributed to Gao Kegong	album leaf	paper	
F1915.36f	17th century	<i>Landscape</i>	traditionally attributed to Tao Cheng	album leaf	paper	
<b>F1915.36k (app. 3, fig. A3.1)</b>	Qing dynasty	<b><i>Landscape with Travelers</i></b>	formerly attributed to Fan Kuan	album leaf	silk	lead-based white XRF

Cinnabar/Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
		XRF	FORS XRF	FORS XRF		
XRF	lac dye FORS		XRF	FORS XRF		
XRF			PLM XRF		natural ultramarine FORS FTIR PLM	
	lac dye FORS	XRF	FORS XRF	FORS		
XRF		XRF	FORS XRF	FORS XRF		
FORS XRF	insect dye FORS	FORS XRF	FORS XRF	FORS XRF		
						Prussian blue FORS FTIR
XRF			FORS XRF	FORS XRF		
FORS XRF	insect dye FORS	FORS XRF	FORS XRF			
FORS XRF	insect dye FORS	FORS XRF	FORS XRF	FORS XRF		
		FORS XRF	FORS XRF	FORS XRF		
FORS XRF			FORS XRF	FORS XRF		
XRF	lac dye FORS HPLC	FORS XRF	FORS XRF	FORS XRF		
	lac dye FORS HPLC	FORS XRF	FORS XRF	FORS FTIR	gamboge FTIR; iron-based brown XRF	
		FORS XRF	FORS XRF	FORS XRF		
XRF				FORS XRF		
XRF	lac dye FORS HPLC	FORS XRF	FORS XRF	FORS XRF		
XRD	insect dye FORS	malachite XRD	XRD	FORS XRF	unidentified organic yellow PLM	
XRF	lac dye FORS	FORS XRF	FORS XRF	FORS XRF		
			XRD XRF			
SEM-EDS XRF	lac dye FORS HPLC	XRF	PLM XRF	FORS XRF	smalt FORS PLM XRF	
XRF	lac dye FORS HPLC	XRF	FORS XRF	FORS	arsenic-based yellow XRF; unidentified yellow FORS	
		FORS XRF		FORS XRF		
				FORS XRF		
			FORS XRF	FORS XRF		

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1915.248	18th century	<i>Palaces on the Shore of a Lake</i>	follower of Qiu Ying	hanging	silk	lead-based white XRF
F1916.92	16th–17th centuries	<i>Ducks on the Autumn Stream</i>		hanging scroll on panel	silk	
F1916.133	ca. 1800	<i>Assemblage of Objects to Celebrate the Chinese New Year</i>		hanging scroll on panel	silk	lead-based white XRF
<b>F1916.593 (chap. 3)</b>	Qing dynasty	<b><i>Lions and Cubs</i></b>		hanging scroll	silk	lead-based white XRF; gypsum XRD
F1917.105	16th century	<i>Luohan and Demon</i>	formerly attributed to Guanxiu	hanging scroll on panel	silk	lead sulfate SEM-EDS XRD
F1918.41	Qing dynasty	<i>River Landscape—Early Snowfall</i>		hanging scroll	silk	lead-based white XRF
F1919.156	15th–16th centuries	<i>Plum Blossoms, Camellias, and Mandarin Ducks</i>		hanging scroll	silk	hydrocerussite FTIR XRD
<b>F1919.167 (fig. 3.5)</b>	Qing dynasty	<b><i>Thousand-Armed Guanyin</i></b>	formerly attributed to Xu Zhichang	hanging scroll	silk	lead-based white XRF
F1952.25	Qing dynasty	<i>Handscroll Entitled “K'o Fang T'u”</i>		handscroll	paper	lead-based white XRF
F1955.20a	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20b	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20e	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20f	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20g	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20h	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	lead-based white XRF
F1955.20i	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20j	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20L	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20n	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
F1955.20o	1729	<i>Landscapes with Poetic Inscriptions</i>	Hua Yan	album leaf	paper	
<b>F1957.4 (chap. 3)</b>	1690s–early 1700s	<b><i>Peach Blossom Spring</i></b>	Shitao	handscroll	paper	
<b>F1960.25a (chap. 3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	
<b>F1960.25b (chap. 3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	
<b>F1960.25c (chap. 3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	lead-based white XRF
<b>F1960.25d (chap. 3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	lead-based white XRF
<b>F1960.25e (chap. 3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	
<b>F1960.25g (chap. 3, fig. A2.3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	lead-based white XRF
<b>F1960.25h (chap. 3)</b>	1747	<b><i>Birds and Flowers</i></b>	Hua Yan	album leaf	paper	

Cinnabar/Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
XRF	lac dye FORS HPLC	FORS XRF		FORS		
	lac dye FORS HPLC	malachite XRD	XRD	FORS		
XRF	lac dye FORS HPLC	XRF	FORS XRF		red lead XRF; arsenic-based yellow in green XRF	
XRF			XRF	FORS	iron-based brown XRF	
XRF		FORS XRF		FORS XRF		
XRF		atacamite XRD	FORS XRF	FORS XRF		
			PLM XRD			
XRF		FORS XRF	FORS XRF	FORS XRF		lithopone retouch XRF
XRF		FORS XRF		FORS XRF	iron-based red FORS XRF	
XRF				FORS XRF		
		FORS XRF		FORS XRF		
XRF						
		FORS XRF		FORS XRF		
		FORS XRF		FORS XRF		
				FORS XRF		
				FORS XRF		
XRF		FORS XRF		FORS XRF		
XRF		FORS XRF		FORS XRF	gamboge FTIR with fiber optics	
microchemical (RJG)		malachite XRD	PLM XRF	FORS XRF		
XRF			FORS microchemical (RJG) XRF	FORS	iron-based red XRF	
XRF		XRF	FORS XRF	FORS		
		XRF	FORS XRF	FORS		
	insect dye FORS	FORS XRF	FORS XRF	FORS		
	insect dye FORS		FORS XRF			
	lac dye FORS HPLC	malachite XRD				
XRF			FORS XRF	FORS		

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1960.25i (chap. 3)	1747	<b>Birds and Flowers</b>	Hua Yan	album leaf	paper	lead-based white XRF
F1960.25j (chap. 3)	1747	<b>Birds and Flowers</b>	Hua Yan	album leaf	paper	
F1964.5a	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5b	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5c	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5d	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5e	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5f	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5g	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5h	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5i	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5j	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5k	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1964.5l	1774	<i>The Poetic Concepts, Inspired by the Poems of Jiang Kui (ca. 1155—ca. 1235)</i>	Luo Ping	album leaf	paper	
F1975.15	mid-18th century	<i>Landscape with Tall Trees</i>	Qian Weicheng	fan	paper	
F1975.16	1871	<i>Maiden in a Bamboo Grove</i>	Zhou Bin	fan mounted as album leaf	paper	hydrocerussite FTIR XRF
F1975.18	18th century	<i>Leisurely Life at a Scholar's Riverside Dwelling</i>	Cai Jia	fan mounted as album leaf	paper	lead-based white XRF
F1980.98	Qing dynasty before 1766	<i>Billowing Clouds in the Pine Valley</i>	Dong Bangda	handscroll	paper	
F1980.116	mid-17th century	<i>A Scholar in his Mountain Studio</i>	Gao Cen	album leaf mounted as hanging scroll	paper	

Cinnabar/Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
XRF		XRF		FORS		
FORS XRF			XRF	FORS		
XRF	lac dye FORS	XRF	XRF	FORS XRF		
				FORS XRF		
				FORS XRF		
	lac dye FORS HPLC			FORS XRF		
XRF				FORS XRF		
XRF	lac dye FORS HPLC					
				FORS		
				FORS FTIR		
XRF	lac dye FORS			FORS XRF		
XRF	lac dye FORS HPLC			FORS XRF		
				FORS XRF		
FORS XRF			FORS XRF	FORS		
				FORS	iron-based red XRF	
XRF	insect dye FORS	XRF	FTIR XRF			
		XRF	XRF	FORS XRF		
		XRF	FORS XRF	FORS XRF		
XRF				FORS XRF	iron-based red XRF	

Accession Number	Date	Title	Artist	Format	Support	White Colorants
<b>F1980.126 (fig. 3.3)</b>	mid-18th century	<b>Palace Ladies and Children</b>	Ding Guanpeng	handscroll	paper	lead-based white XRF
F1980.136i	probably 1652	<i>Pine and Blossoms</i>	Gu Ying	album leaf	paper	lead-based white XRF
<b>F1980.138 (fig. 2.8, fig. 3.6)</b>	1816	<b>Blending Soup in a Metal Tripod</b>	Gai Qi	hanging scroll	silk	lead-based white XRF
<b>F1980.139 (chap. 2, table 2.4)</b>	1832	<b>Zhong Kui and His Assistants under Willows</b>	Fei Danxu	hanging scroll	paper	lead-based white XRF
F1980.142a	early 18th century	<i>Reading the Book of Changes in the Autumn Mountains</i>	Wang Xuehao	fan mounted as album leaf	paper	
F1980.142b	1741	<i>Rice Paddies and Egrets, After a Poem by Wang Wei</i>	Li Shizhuo	fan mounted as album leaf	paper	
F1980.142d	1710	<i>Cabbage</i>	Yang Jin	fan mounted as album leaf	paper	
<b>F1980.142e (chap. 2, table 2.4)</b>	1822	<b>Lady and Maid in a Garden in Moonlight</b>	Gai Qi	fan mounted as album leaf	paper	lead-based white XRF
F1980.142f	1754	<i>Mountain Landscape</i>	Dong Bangda	fan mounted as album leaf	paper	
<b>F1980.142h (chap. 2, table 2.4)</b>	probably 1770	<b>On a Branch of Willow</b>	Yuan Tong	fan mounted as album leaf	paper	
F1980.142i	1838	<i>Orchid and Fungus-of-Immortality by a Torrent</i>	Hu Jiushi	fan mounted as album leaf	paper	
F1980.142j	late 18th–early 19th centuries	<i>Scholar Reading in a Thatched Hut</i>	Dong Gao	fan mounted as album leaf	paper	
F1980.148	early 20th century	<i>Chrysanthemums and Amaranth</i>	attributed to Wu Changshuo	hanging scroll	paper	
F1980.149	early–mid 20th century	<i>Lichees and Chicks</i>	forgery of Qi Baishi	hanging scroll	paper	
F1980.150	1762	<i>Drunken Chung K'uei</i>	forgery of Luo Ping	hanging scroll	silk	lead-based white XRF
<b>F1980.152 (Introduction, fig. I.2, chaps. 2, 3, 5, tables 2.4, 3.6)</b>	possibly early 18th century	<b>Small Birds and Morning Glories</b>	attributed to Jiang Tingxi	fan	paper	hydrocerussite FTIR PLM
F1980.155	1886	<i>Peach Blossom Spring</i>	attributed to Ren Yi	hanging	paper	lead-based white XRF
F1980.156	1828	<i>Vegetables and Fruits</i>	Gu Luo	handscroll	paper	lead-based white XRF
F1980.158	mid–late 19th century	<i>Flowers</i>	Zhao Zhiqian	hanging scroll	paper	lead-based white XRF
F1980.162	late 18th century	<i>Bird on an Autumn Branch</i>	Xu Gang	hanging scroll	paper	
<b>F1980.163 (chap. 5, table 3.6)</b>	mid-20th century	<b>Bean Vines and Insects</b>	forgery of Qi Baishi	hanging scroll	paper	
F1980.165	1864	<i>Scholar Arriving in the Rain</i>	Wang Su	hanging scroll	paper	lead-based white XRF
<b>F1980.168 (fig. 3.13, tables 2.4, 3.6)</b>	mid–late 19th century	<b>Bamboo, Orchid and Rock in a Tub</b>	Luo Qing	hanging scroll	paper	
<b>F1980.169a-i (fig. A2.4)</b>	1730s–40s	<b>Flowers and Vegetables</b>	Li Shan	album leaf	paper	lead-based white XRF
F1980.172	mid-19th century	<i>Lady under a Banana Tree</i>	Fei Danxu	hanging scroll	paper	lead-based white XRF

Cinnabar/ Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
XRF	insect dye FORS	malachite FTIR XRF	FORS XRF	FORS XRF	gamboge FTIR	
	lac dye FORS HPLC			FORS		
XRF	lac dye FORS HPLC	XRF	FORS XRF	FORS XRF		
XRF		XRF	FORS XRF	FORS XRF		carminic acid FORS HPLC
				FORS XRF		
XRF				FORS XRF		
				FORS XRF		
XRF	lac dye HPLC		FORS XRF	FORS XRF		carminic acid HPLC
				FORS XRF		
				FORS XRF		carminic acid FORS HPLC
	lac dye FORS HPLC	XRF		FORS FTIR		
	lac dye FORS HPLC			FORS XRF		
XRF	lac dye FORS HPLC			FORS XRF		
				FORS XRF		barium-based red lake XRF
XRF		FORS XRF	FORS XRF	FORS XRF		
PLM XRF		XRF	FORS XRF		gamboge FTIR	carminic acid FORS HPLC; Prussian blue FORS FTIR XRF
		FORS XRF		FORS XRF		
XRF	lac dye FORS HPLC	XRF		FORS FTIR		
FORS XRF				FORS XRF		
FORS XRF				FORS		
						synthetic organic red HPLC; chrome yellow XRF; Prussian blue FTIR
			FORS FTIR XRF	FORS XRF		barium-based white XRF
						carminic acid FORS HPLC; Prussian blue FTIR
XRF	lac dye FORS HPLC	XRF		FORS XRF	iron-based red XRF	
XRF			FORS XRF	FORS FTIR XRF		

Accession Number	Date	Title	Artist	Format	Support	White Colorants
F1986.8	19th century	<i>Maps of Hainan, the Pescadores, and Taiwan</i>		handscroll	paper	
F1997.40	early 18th century	<i>Map of the Grand Canal</i>		handscroll	silk	hydrocerussite FTIR PLM XRD
F1997.87.2	1945	<i>Grapes</i>	Qi Baishi	album leaf	paper	
F1998.222.2	1919	<i>Cicada on Tree Branch</i>	Wang Zhen	fan mounted as album leaf	paper	
F2000.6	18th century	<i>Four Luohan with Attendants, Tigers, and Suppliant</i>	formerly attributed to Lu Lengjia	hanging scroll	silk	lead-based white XRF
<b>S1987.220 (table 2.4)</b>	1941	<b><i>Morning Glories and Grasshopper</i></b>	Qi Baishi	hanging scroll	paper	
S1990.62	1960	<i>Plum Flowers and a Beauty</i>	Cheng Jiezi	hanging scroll	paper	
<b>S1991.46 (fig. 2.5, table 2.4)</b>	mid-late 19th century	<b><i>Beautiful Ladies Riding</i></b>	formerly attributed to Giuseppe Castiglione	handscroll	paper	lead-based white XRF
<b>S1991.138 (fig. 2.6)</b>	17th–19th centuries	<b><i>Magpies in a Pine Tree, Ducks and Hollyhocks; with Spurious Signature</i></b>		hanging scroll	silk	lead-based white XRF
S1993.43	19th century	<i>Children Playing in the Snow at the New Year</i>		hanging scroll	silk	lead-based white XRF

## Note

The following painting was found to have been heavily overpainted in previous restoration campaigns and so pigment identifications are not reported: F1911.235, Ming dynasty, 15th century.

Table A5.3. Colorants identified in portraits.

Accession Number	Date	Title	Artist	Format	Support	White Colorants	Cinnabar/Vermilion
<b>F2000.4 (chap. 3, fig. 4.1)</b>	mid-18th century	<b><i>The Qianlong Emperor as Manjushri, the Bodhisattva of Wisdom</i></b>	imperial workshop, emperor's face painted by Giuseppe Castiglione	thangka	silk	lead-based white XRF	FORS XRF
<b>S1991.47 (fig. 2.2, table 2.4)</b>	mid-late 18th century	<b><i>Portrait of Hongyan, Prince Guo (1733–1765)</i></b>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.48 (fig. 2.10)</b>	1750s	<b><i>Hongyan, Prince Guo (1733–1765), Reading in a Spring Garden</i></b>		hanging scroll	silk	lead-based white XRF	XRF
S1991.49	1723–1735	<i>Beauty Standing Near a Pot of Orchids</i>		hanging scroll	silk	lead-based white XRF	XRD
S1991.50	mid-18th–19th centuries	<i>Beauty Holding an Orchid (Portrait of Lady Liu)</i>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.57 (chap. 4)</b>	mid-late 19th century	<b><i>Portrait of Ser Er Chen</i></b>		hanging scroll	silk	lead-based white XRF	XRF
S1991.60	early 20th century or possibly late 18th–19th centuries	<i>Emperor Qianlong on Horseback Crossing Gold Tortoise Jade Rainbow Bridge</i>	formerly attributed to Giuseppe Castiglione	hanging scroll	silk	hydrocerussite FTIR	
S1991.61	1767 or later	<i>Portrait of Prince Hongming</i>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.65 (chaps. 3, 4, tables 2.4, 3.6)</b>	late 19th century	<b><i>Portrait of Lady Hejia, Secondary Wife of Prince Zaizhi</i></b>		hanging scroll	paper	hydrocerussite XRD	XRD

Cinnabar/Vermilion	Organic Reds	Copper-Based Green	Azurite	Indigo	Other Colorants	Modern Colorants
		PLM	PLM			
XRF	lac dye FORS HPLC	XRF	FTIR PLM XRF	FORS XRF		
				FORS XRF		
				FORS		
XRF	lac dye HPLC	XRF	FORS XRF	FORS XRF		
			FORS XRF	FORS XRF		carminic acid HPLC; barium chromate XRF
XRF	insect dye FORS		FORS XRF	FORS XRF		
XRF			PLM XRF	FORS XRF	unidentified organic yellow XRF	carminic acid FORS HPLC; emerald green PLM XRF; possibly cobalt blue FORS PLM XRF
XRF	lac dye FORS HPLC	XRF	XRF	FORS		
XRF	insect dye FORS		FORS FTIR XRF	FORS XRF		

Carminic Acid	Lac Dye	Arsenic Sulfides	Copper-Based Green	Emerald Green	Azurite	Indigo	Prussian Blue	Ultramarine	Other Colorants
FORS	FORS		malachite FORS FTIR		FORS FTIR XRF	FORS FTIR			red lead FORS XRF; unidentified organic yellow XRF
FORS HPLC--inpainting?	FORS HPLC	XRF	XRF		XRF	FORS			iron-based red XRF; iron-based yellow XRF; iron-based brown XRF
	FORS HPLC	XRF	FORS XRF		FORS XRF	FORS XRF			unidentified organic yellow XRF
	FORS HPLC	XRF	XRF		PLM XRF	FORS			possibly madder HPLC
	FORS HPLC		XRF		XRF	FORS			iron-based brown XRF
	FORS HPLC		XRF		FTIR PLM XRF	FORS		ultramarine PLM	
	FORS				FORS FTIR	FORS			
	FORS HPLC	XRF	XRF		XRF	FORS XRF			red lead PLM XRF
FORS HPLC	FORS HPLC	pararealgar XRD		PLM XRD XRF	XRF	FORS	FTIR	synthetic ultramarine FORS FTIR PLM XRD	unidentified organic red HPLC; gamboge FTIR; iron-based brown XRF

Accession Number	Date	Title	Artist	Format	Support	White Colorants	Cinnabar/ Vermilion
<b>S1991.74</b> (chap. 4, fig. 2.13)	18th–19th centuries	<b>Portrait of Daisan</b>		hanging scroll	silk	hydrocerussite XRD; zinc oxide XRD	XRF
<b>S1991.77</b> (fig. 4.7)	ca. 1451	<b>Portrait of Yang Hong</b> (1381–1451)		hanging scroll	silk	hydrocerussite XRD	XRF
S1991.80	1806	<i>Portrait of Yinghe</i> (1771–1839)		hanging scroll	silk	lead-based white XRF	XRF
S1991.82	second half 19th century	<i>Portrait of Jalafengge</i> (fl. 2nd half 19th century)		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.84</b> (figs. 2.11, 3.14, 4.2, tables 2.4, 3.6)	1905	<b>Portrait of Yinxiang,</b> <b>the First Prince Yi</b> (1686–1730)		hanging scroll	silk	hydrocerussite FTIR; calcite FTIR; barium sulfate FTIR	XRF
<b>S1991.86</b> (chaps. 2, 3, figs. 2.3, 4.3, tables 2.4, 3.6)	1905	<b>Portrait of the Sixth</b> <b>Prince Yi</b>		hanging scroll	silk	hydrocerussite FTIR; calcite FTIR; barium sulfate SEM-EDS	XRF
S1991.87	mid-18th century	<i>Life Portrait of Yinti,</i> <i>Prince Xun</i> (1688–1755)		hanging scroll	silk	lead-based white XRF	XRF
S1991.88	mid-18th century	<i>Portrait of Yinti,</i> <i>Prince Xun and Wife</i>		hanging scroll	silk	lead-based white XRF	XRF
S1991.90	ca. 1785 or later	<i>Portrait of Guanglu,</i> <i>Prince Yu</i>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.92</b> (chap. 4)	18th–early 20th centuries	<b>Portrait of Qing Court</b> <b>Lady</b>		hanging scroll	silk	hydrocerussite XRD	
<b>S1991.93</b> (chap. 4, fig. 3.4)	mid-18th–early 20th centuries	<b>Portrait of Oboi</b>		hanging scroll	silk	lead-based white XRF	XRF
S1991.95	1731	<i>Portrait of Yinli, Prince</i> <i>Guo</i> (1697–1738)	probably by Mangguri	hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.98</b> (chaps. 3, 4, table 2.4)	ca. 1920–48	<b>Spurious Portrait of</b> <b>the Jiaqing Empress</b>		hanging scroll	paper	lead-based white XRF	XRF
<b>S1991.99</b> (fig. 2.7)	1723–26	<b>The Yongzheng</b> <b>Emperor's Nephew at</b> <b>a Daoist Ceremony</b> <b>for the Recovery of His</b> <b>Father</b>	attributed to Jiao Bingzhen	hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.102</b> (figs. 4.4, A2.2, tables 2.4, 3.6)	1911	<b>Portrait of the Seventh</b> <b>Prince Yi</b>		hanging scroll	silk	hydrocerussite FTIR; barium sulfate FTIR XRF	XRF
<b>S1991.104</b> (chap. 4, fig. 3.11)	18th–19th centuries	<b>Li Yinzu</b> (1629–1664)		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.105</b> (chaps. 2, 4, tables 2.4, 3.6)	mid–late 19th century	<b>Portrait of a Qing</b> <b>Courtier</b>		hanging scroll	paper	lead-based white XRF	XRF
<b>S1991.108</b> (chap. 4)	Qing dynasty	<b>Man, “A Manchu</b> <b>Noble”</b>		hanging scroll	silk	hydrocerussite FTIR	XRF
S1991.109	18th–19th centuries	<i>Portrait of a Qing</i> <i>Courtier, Possibly</i> <i>Yinreng (d. 1725) as</i> <i>Heir Apparent</i>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.117</b> (chaps. 3, 4, tables 2.4, 3.6)	mid–late 19th century	<b>Portrait of a Qing</b> <b>Court Lady</b>		hanging scroll	paper	hydrocerussite XRD	FORS XRF

Carminic Acid	Lac Dye	Arsenic Sulfides	Copper- Based Green	Emerald Green	Azurite	Indigo	Prussian Blue	Ultramarine	Other Colorants
	FORS HPLC	pararealgar XRD			FORS XRF	FORS XRF			unidentified organic yellow XRF; iron- based brown XRF
	FORS HPLC		atacamite XRD		XRF	FORS			red lead XRD; iron- based brown XRF
	FORS HPLC	XRF	XRF		XRF	FORS XRF			unidentified organic yellow XRF; iron- based brown XRF
	FORS HPLC	XRF	XRF		XRF	FORS XRF			unidentified organic yellow XRF; iron- based brown XRF
FORS HPLC	FORS HPLC	pararealgar XRD		FTIR PLM XRF			FORS FTIR	synthetic ultramarine FORS PLM	gamboge FTIR; iron- based brown XRF
FORS HPLC	FORS HPLC	XRF		FTIR PLM SEM-EDS XRD XRF			FORS FTIR	synthetic ultramarine FORS FTIR PLM SEM- EDS XRD	unidentified organic yellow XRF; iron- based brown XRF
	FORS HPLC				FORS XRF				unidentified organic yellow XRF; iron- based brown XRF
	FORS HPLC	XRF	XRF		XRF	FORS			unidentified organic yellow XRF; iron- based brown XRF
	FORS HPLC	XRF	XRF		XRF	FORS			
					PLM XRD			synthetic ultramarine alteration PLM XRD	
	FORS HPLC	pararealgar XRD XRF			FORS XRF	FORS XRF			unidentified organic yellow XRF
	FORS HPLC		XRF		XRF	FORS			unidentified organic yellow XRF
FORS HPLC				XRD XRF	PLM XRF			synthetic ultramarine FORS PLM	unidentified organic yellow XRF
	FORS HPLC	pararealgar XRD XRF	malachite XRD XRF		XRF	FORS			
FORS HPLC	FORS HPLC	XRF		FTIR PLM XRF	FTIR XRF	FORS XRF	FTIR		gamboge FTIR XRF; iron-based brown XRF
	FORS HPLC		XRF		FORS XRF	FORS			smalt FORS PLM XRF
FORS HPLC	FORS HPLC	XRF		FTIR PLM XRF	XRF		FORS FTIR	synthetic ultramarine FORS PLM	unidentified organic yellow XRF
	FORS	XRF	malachite FTIR		XRF	FORS FTIR			
	FORS HPLC				PLM XRF	FORS XRF			
FORS HPLC		arsenic sulfide XRD		XRD XRF	FTIR PLM XRF		FTIR	synthetic ultramarine FORS FTIR PLM XRD	gamboge FTIR; iron- based brown XRF



Accession Number	Date	Title	Artist	Format	Support	White Colorants	Cinnabar/ Vermilion
<b>S1991.119</b> (chap. 3, table 3.6)	19th–early 20th centuries	<b>Portrait of Chinese Woman in a Kingfisher Headdress</b>		hanging scroll	silk	lead-based white XRF	XRF
S1991.121	early 18th century or later copy	<i>Portrait of Lady Guan</i>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.122</b> (chap. 4, table 3.6)	mid-19th century or later	<b>Portrait of Princess Shouzang (1829–1856), Fifth Daughter of Emperor Daoguang</b>		hanging scroll	silk	hydrocerussite FTIR XRD	XRF
<b>S1991.125</b> (chap. 4, fig. 3.12)	19th–early 20th centuries	<b>Qing Courtier in a Winter Costume</b>		hanging scroll	silk	lead-based white XRF	XRF
<b>S1991.128</b> (chap. 3, fig. 4.6)	19th–early 20th centuries	<b>Portrait of an Elderly Couple</b>		hanging scroll	canvas	hydrocerussite FTIR XRF	PLM XRF
S1991.133	18th century	<i>Portrait of an Unidentified Man and His Son</i>		hanging scroll	silk	hydrocerussite XRD	XRF
<b>S1991.135</b> (fig. 4.5, tables 2.4, 3.6)	late 19th century	<b>Portrait of a Qing Courtier, Possibly Jing Shou (d. 1889)</b>		hanging scroll	silk	hydrocerussite XRD	XRF
<b>S1991.137</b> (fig. 3.15, table 3.6, app. 1)	ca. 1890	<b>Portrait of Mother Mujia</b>		hanging scroll	silk	hydrocerussite FTIR XRF	XRF

Note: not all yellow and brown pigments in the portraits were identified as part of this study.

Carminic Acid	Lac Dye	Arsenic Sulfides	Copper- Based Green	Emerald Green	Azurite	Indigo	Prussian Blue	Ultramarine	Other Colorants
	FORS HPLC	XRF	XRF		FTIR PLM XRF		FORS FTIR		
		XRF	XRF		XRF	FORS			unidentified organic red FORS; iron-based brown XRF
	FORS HPLC	pararealgar XRD	atacamite XRD		XRF		FTIR		gamboge FTIR; iron- based brown XRF
	FORS HPLC		XRF			FORS			unidentified organic yellow PLM XRF; smalt FORS FTIR PLM XRF
	FORS HPLC	XRF	atacamite FTIR PLM XRF		XRF	FORS			smalt FORS PLM XRF
	FORS HPLC	realgar XRD	malachite XRD		FORS FTIR PLM XRF	FORS FTIR XRF			gamboge FTIR XRF; iron-based brown XRF
FORS HPLC	FORS HPLC	pararealgar XRD; unidentified arsenic sulfide XRD	malachite XRD		FTIR XRD	FORS FTIR	FTIR SEM- EDS		madder retouch HPLC; gamboge FTIR
		XRF					FTIR		



# Contributors

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