

The Metropolitan Museum of Art Bulletin

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SUMMER 2009



**Scientific Research
in The Metropolitan Museum of Art**



Edited by Marco Leona

The Metropolitan Museum of Art, New York

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This publication was made possible through the generosity of the Lila Acheson Wallace Fund for The Metropolitan Museum of Art, established by the cofounder of *Reader's Digest*.

The Metropolitan Museum of Art Bulletin

Summer 2009

Volume LXVII, Number 1

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The Metropolitan Museum of Art Bulletin (ISSN 0026-1521) is published quarterly by The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, NY 10028-0198. Periodicals postage paid at New York NY and additional mailing offices. POSTMASTER: Send address changes to Membership Department, *The Metropolitan Museum of Art Bulletin*, 1000 Fifth Avenue, New York, NY 10028-0198. Four weeks' notice required for change of address. The *Bulletin* is provided as a benefit to Museum members and is available by subscription. Subscriptions \$30.00 a year. Single copies \$12.95. Back issues available on microfilm from National Archive Publishing Company, 300 N. Zeeb Road, Ann Arbor, MI 48106. Volumes I–XXXVII (1905–42) available as clothbound reprint set or as individual yearly volumes from Ayer Company Publishers, Suite B-213, 400 Bedford Street, Manchester, NH 03101, or from the Metropolitan Museum, 66-26 Metropolitan Avenue, Middle Village, NY 11381-0001.

Printed and bound in the United States of America

Publisher and Editor in Chief: John P. O'Neill

Editor of the *Bulletin*: Sue Potter

Production: Christopher Zichello

Design: Antony Drobinski

Cover: In the center, an inscription panel from the Nur al-Din Room, Damascus, Syria. Inscribed in Arabic: "In its towers are assembled splendor and generosity / It is strengthened by Muhammad, the abode of noble qualities. / [In the] year [A.H.] 1119 [A.D. 1707]" (see figs. 1, 80, pages 5, 44). Behind the panel, a cross section of a sample of paint taken from the Nur al-Din Room at the microscope under normal (top) and ultraviolet (bottom) illumination (see also figs. 2, 3, page 6). To identify the original appearance of painted works of art, Museum scientists take microscopic samples that are then mounted in synthetic resins and polished as cross sections. All the paint layers are thus revealed in the sequence in which they were applied. Microscope examination and imaging in normal and ultraviolet illumination selectively highlight differently painted layers. Microanalysis by infrared spectroscopy is then used to identify the different resins and binding media.

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Director's Note

Over the years the Metropolitan Museum has put in place one of the largest teams of conservators and scientists in any art museum in the world. Though the work of these professionals is not often immediately perceptible by our visitors, it is essential to our mission to collect, preserve, study, and exhibit works of art that represent the broad spectrum of human achievement. During the past thirty years separate departments were created at the Metropolitan for the conservation of paintings, textiles, works on paper, and objects. In 2005, recognizing the need to coordinate and expand scientific support for art historical and conservation research, the Museum established the Department of Scientific Research under the direction of Dr. Marco Leona.

A staff of ten scientists with backgrounds in chemistry, biology, geology, and engineering collaborate with curators and conservators on art historical studies, conservation research, and conservation treatments. One aspect of their work entails the characterization of materials found in art objects and the technology used to make them. The department also conducts research directed toward an understanding of how objects deteriorate and the methods that can be employed to prolong their lives, and it plays a critical role in the establishment of proper climate and lighting in the galleries and storage areas of the Museum to ensure the best environment for our collections.

From the reinstallation of the Leon Levy and Shelby White Court, to the reopening of the Wrightsman Galleries, to the current reinstallation of the Islamic Galleries, the work of

the Department of Scientific Research has been a key component of the Museum's efforts to present our collections in ways that enrich visitors' experience. Microscopic residues of paint on the Roman sculptures discovered and identified through advanced analytical techniques have enabled us to reconstruct their original appearance. Painstaking analyses have allowed the French period rooms to be reinstalled in a way that accurately shows their original decorative schemes. Thanks in part to the extensive analytical efforts of our scientific staff, one of the most striking spaces in the Museum, the eighteenth-century Nur al-Din Room from Damascus whose dedicatory inscription graces the cover of this issue of the *Bulletin*, will soon reopen to the public, now with its exquisite painted designs much clearer. Not only are the department's studies regularly published in professional journals, but the results are also being incorporated into gallery labels and audio guide texts.

All this would not have been possible without the generous support of several individuals and foundations. The Museum is grateful to David H. Koch; Tony Evnin; Shelby White; The Andrew W. Mellon Foundation; the Sherman Fairchild Foundation, Inc.; The Leon Levy Foundation; The Camille and Henry Dreyfus Foundation, Inc.; The L. W. Frohlich Charitable Trust; and the National Science Foundation for their commitment to scientific research in art history and art conservation.

Thomas P. Campbell
Director

The Materiality of Art: Scientific Research in Art History and Art Conservation at the Metropolitan Museum

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Marco Leona

A chasm is often imagined to be separating art and science: left brain and right brain are engaged in an endless battle, as if they were not—in the preciously small cranial space they share—both occupied in driving the same human. So art is the realm of creative expression and of intangible values, while science is the dry domain of measurable quantities and inescapable conclusions: if x , then y . No one apparently bothered to discuss this idea with Leonardo, with Rembrandt or Vermeer, or with the countless artists from five continents and five thousand years of human history whose work is represented in the collections of the Metropolitan Museum.

Irrespective of their aesthetic qualities or their role as documents of past periods and civilizations, works of art are also complex technological objects. Materials and techniques employed in artistic production, past and present, often reflect the highest level of scientific achievement of the time. The materiality of works of art, the fact that they are composed of certain materials chosen and structured by artists to obtain a certain effect—in short, that they exist as physical objects—is the foundation of collecting, studying, exhibiting, and preserving art. Objects exist in time and evolve with time.

The closer look at art afforded by scientific investigation is a necessary and valuable complement to art historical analysis, and it is an essential component of preservation and conservation efforts. Technical and scientific investigation of works of art has a long history at the Metropolitan. In 1880, the year the

Museum took up residence in its new home on Fifth Avenue, a controversy erupted over the authenticity of the thousands of Cypriot antiquities it had acquired in 1874 from the collection amassed by General Luigi Palma di Cesnola (who had been appointed director of the Museum in 1879) first during his stint as American consul to Cyprus in the 1860s and continuing into the 1870s. The Museum responded by creating a commission, led by Frederick Barnard, that after “microscopic, chemical, and other examinations of the surfaces,” concluded that the questioned works of art were indeed authentic.¹ During the following decades the Metropolitan repeatedly sought the help of scientists to develop and evaluate conservation treatments. In the 1920s Columbia University’s Colin G. Fink, one of the leading electrochemists in the United States, worked as a consultant on several projects at the Museum. (Tellingly, his acceptance speech for the prestigious Perkin Medal was entitled “Chemistry and Art.”) In 1932 one of Fink’s graduate students, Arthur H. Kopp, was the first chemist to be hired by the Museum. Kopp died tragically in a laboratory fire in 1938, putting an end to the direct presence of scientists in the Museum for at least thirty years.

The modern history of chemistry at the Metropolitan Museum starts in the late 1960s, when Pieter Meyers was hired to work on applying neutron activation analysis and neutron autoradiography to the study of metal objects and paintings. Scientific research in paintings conservation was begun by E. René de la Rie in the mid-1970s. In the years follow-

ing, each of the conservation departments (for paintings, paper, objects, and textiles) added scientists and instrumentation. The Metropolitan was the first art museum in the United States to install a scanning electron microscope (SEM), in 1981, and a Raman microscope, in 2001. In 2005 the Department of Scientific Research was established. The department today employs ten scientists whose backgrounds span chemistry, biology, geology, and engineering and a number of whom have combined advanced degrees in the sciences with graduate training in art conservation.

At the Metropolitan, scientists work in close collaboration with curators and conservators, contributing to art historical studies, conservation research, and conservation treatments. Scientists examine works of art, identify their constituent materials and manufacturing techniques, study aging and degradation mechanisms, and monitor environmental conditions in the galleries and storage areas of the Museum.

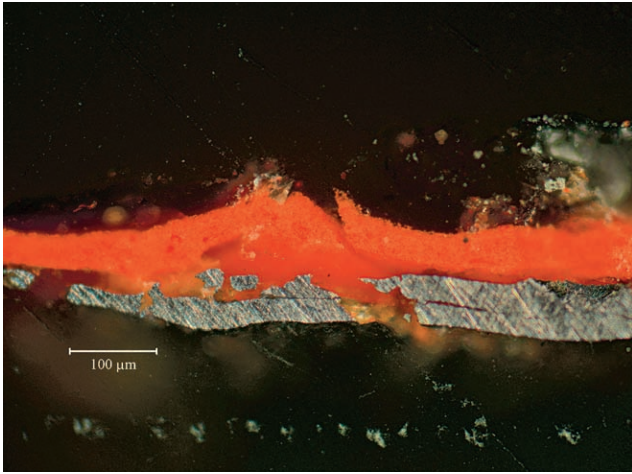
Scientific research on the components, structure, and degradation of works of art is a technically complex endeavor. Substantial technical constraints drive the work of museum scientists: Because art is irreplaceable, analyti-

cal investigations must be noninvasive, or at least require only minimal sampling. Monitoring and testing must be nondestructive. Conservation treatments must be reversible. All of which requires scientists not only to adopt the most advanced scientific technology, but also sometimes to develop it in house. To identify materials, study artists' techniques, and characterize degradation phenomena, the Museum's Department of Scientific Research employs fiber optics reflectance and fluorescence spectroscopy, Raman and infrared microspectroscopy, variable pressure electron microscopy, nuclear magnetic resonance spectroscopy, gas chromatography–mass spectrometry, high performance liquid chromatography, X-ray diffractometry, X-ray fluorescence spectroscopy, and a variety of other methods.

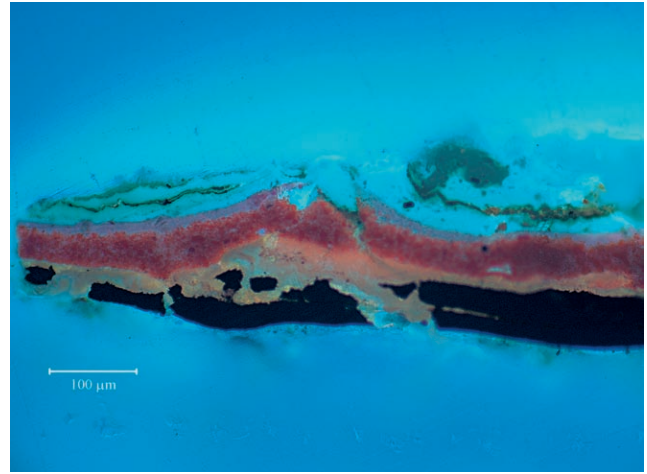
Over the last five years the Department of Scientific Research has provided technical support and advice for Museum exhibitions, construction and reinstallation projects, conservation treatments, and acquisitions. The analysis by optical microscopy and infrared microspectroscopy of cross sections of paint from the Nur al-Din Room (figs. 1–3), an Islamic interior from Damascus dating from the early eighteenth century, for example,



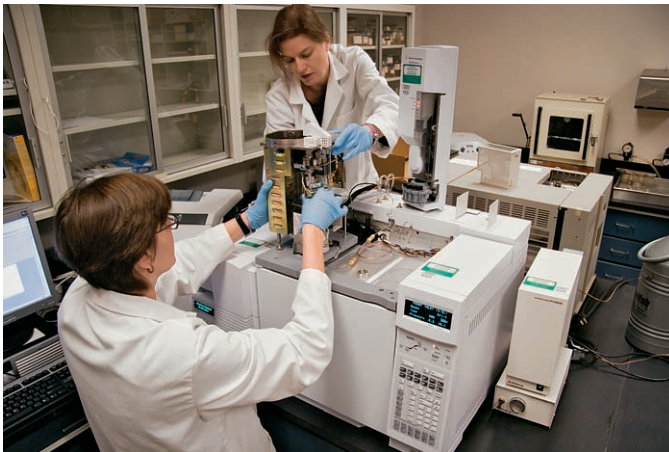
1 • Inscription panel from the Nur al-Din Room (see also fig. 80). Damascus, Syria. Inscribed in Arabic: “In its towers are assembled splendor and generosity / It is strengthened by Muhammad, the abode of noble qualities. / [In the] year [A.H.] 1119 [A.D. 1707].” Wood, colors, gold; 10½ x 37⅜ in. (26.6 x 95.5 cm). The Metropolitan Museum of Art, Gift of the Hagop Kevorkian Fund, 1970 (1970.170)



2 · Cross section of a sample taken from the Nur al-Din Room (see fig. 1) under the microscope in reflected light, showing the succession of paint layers: from the bottom, tin leaf, a yellow glaze, a vermilion paint layer, the pink colorant used to trace the outline of the flower, and, finally, a varnish topcoat. The sample, taken from the pink outline of a red flower near the edge of a panel, was embedded in polyester resin, and the resin block was polished to reveal the layers.



3 · Microscopic image shown in fig. 2 enhanced with ultraviolet illumination. Different paint layers can be easily distinguished because of their characteristic fluorescence. Knowing the sequence in which the painted decoration was applied and understanding how later varnishes may have affected its appearance and structure are essential to treating a work of art.



4 · Julie Arslanoglu (left) and Adriana Rizzo (right) using gas chromatography–mass spectrometry, the standard technique for identifying organic materials in paints or varnishes. Microscopic samples removed from a work of art are treated with appropriate reagents to break them down into smaller molecules and also make them more volatile, so that they can be carried in a flow of gas through a capillary column, where they are separated according to their chemical structure and properties. The separated molecules are then injected into a mass spectrometer, a detector that identifies each component by its molecular weight. Each paint or varnish can be recognized by the chemical identity of the individual components and their ratios in the sample. The distribution of fatty acids, for example, can distinguish different drying oils (such as walnut and linseed oil) from each other, and the presence of specific resin acids can lead to the identification of tree resins in a varnish.



5 · Raman microspectroscopy being used to identify the pigments in a reverse-painted glass paten attributed to Hans Wertinger (German, d. 1533) and dated 1498 (free-blown glass with paint and metallic foils, diam. 14½ in. [36.9 cm]; The Metropolitan Museum of Art, The Cloisters Collection, 2008 [2008.278]). This technique can be used in a noninvasive way, without removing a sample from the object. A laser beam is focused on an area of the object (or a microscopic sample) through high magnification. The materials in the object interact with the laser beam, scattering it in all directions. Most of the light is scattered without changes, but a small number of photons undergo Raman scattering and can be detected at a longer wavelength than the original laser beam. The entity of the wavelength shift and the pattern of shifts (the spectrum) are characteristic of each molecule or crystal in the area of the object hit by the laser beam. In this case, the analysis was accomplished through a relatively thick layer of the glass, as the painted decoration was applied to the underside of the bowl.



6 · Mark Abbe, Annette de la Renta fellow, using fiber optics reflectance spectroscopy to analyze an Early Hellenistic grave stele from the late 4th to the early 3rd century B.C. (Greek, Ptolemaic, found in 1884 in a tomb near Alexandria; painted limestone, h. 29 in. [73.6 cm]; The Metropolitan Museum of Art, Gift of Darius Ogden Mills, 1904 [04.17.1]). Reflectance spectroscopy, a completely noninvasive technique, measures the amount of light scattered by an object at specific wavelengths of light. If the light interval investigated corresponds to the range of wavelengths perceived by the human eye (ca. 400–700 nanometers), the measurement results in the objective characterization of the color of an object. This information is helpful in monitoring and quantifying the fading of colorants and can sometimes be used to identify pigments and dyes. In this instance, the pink area of the tombstone was shown to have been painted with an organic dye mixed with a blue pigment, a detail that points to the artist's understanding of color science. Madder lake, the pink colorant obtained from plant root extract, has a yellow cast; adding a small quantity of a blue pigment neutralizes the yellow tint and gives a cooler and more appealing tone.



7 · Nondestructive elemental analysis by X-ray fluorescence spectroscopy of a Roman statue of an old market woman dated to A.D. 14–68 (marble, h. 49⁵/₈ in. [126 cm]; The Metropolitan Museum of Art, Rogers Fund, 1909 [09.39]) in the New Greek and Roman Galleries. The X-rays interact with the materials in the object, leading to electronic transitions that result in the reemission of X-rays by the object. The characteristic X-ray emission of the object (its X-ray fluorescence) is used to determine its elemental composition. In this case, a microscopic residue of blue pigment was found to contain copper, an indication that a pigment such as azurite or Egyptian blue was originally used in this once polychrome sculpture. Further tests with Raman microspectroscopy or other techniques will be used to confirm the identification.

allowed conservators to identify the original decoration of the rooms so that their installation in the Museum would be historically accurate. Similar investigations have been conducted on the French period rooms, during the reinstallation of the Wrightsman Galleries, and on several polychrome sculptures featured in the forthcoming catalogues of the Chinese and the Italian and French medieval sculpture collections at the Metropolitan. In many cases these investigations were complemented by gas-chromatographic analysis (fig. 4), a technique used to identify the paint binding medium (drying oil, resin) or the varnish. Raman microspectroscopy (fig. 5) has been used in situ, directly on works of art, to identify pigments in drawings, prints, and paintings and to study complex deterioration phenomena such as the corrosion of daguerreotypes and the formation of lead soaps in linseed oil paintings

(see the article in this issue of the *Bulletin* by Silvia Centeno and Dorothy Mahon, conservator, Paintings Conservation Department).

The scope of the department's work can also sometimes be significantly broader, with projects spanning several years. The reinstallation of the Greek and Roman galleries occasioned an investigation into the polychrome decoration of classical sculpture that is still ongoing. Nondestructive and minimally invasive techniques (in some cases developed ad hoc) were used to detect the extremely small remains of the pigmentation that originally covered the sculptures in the Leon Levy and Shelby White Court. Initial work by fiber optics reflectance spectroscopy (fig. 6) was followed by more in situ analyses by X-ray fluorescence spectroscopy (fig. 7) with a portable machine that can be used in the galleries for nondestructive analysis of microscopic



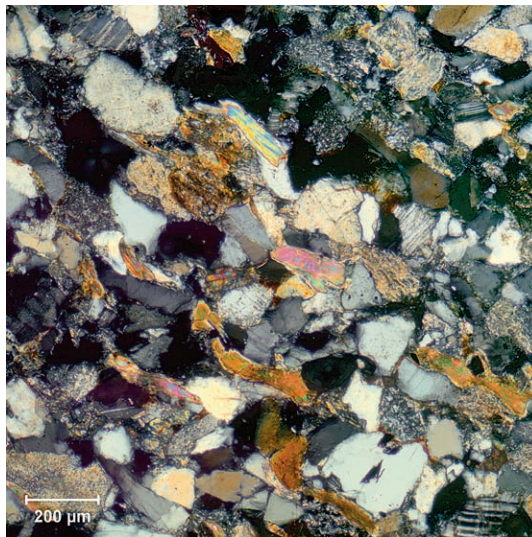
8 • Grave stele with a soldier and two girls. Greek, Ptolemaic, second half of 3rd century B.C. Found in 1884 in a tomb near Alexandria. Painted limestone, h. 16½ in. (41.9 cm). The Metropolitan Museum of Art, Gift of Darius Ogdan Mills, 1904 (04.17.4)

details and finally by microsampling and analysis with electron microscopy and X-ray diffraction. The information collected using these techniques is essential to understanding ancient artistic practices. X-ray diffraction allowed us to identify a rare mineral, mimetite, that was used as a yellow pigment on a Ptolemaic tombstone from Alexandria, Egypt (fig. 8). Because mimetite is found only in the silver mines at Laurion, near Athens, and has seldom been used as a yellow pigment, we can infer that the painter of the tombstone must have been from Athens, where he would have had a chance to encounter it.

In their article in this issue Tony Frantz, Mark Wypyski, and their coauthors from the Objects Conservation Department, Dorothy Abramitis and Linda Borsch, describe the unexpected occurrence of another unusual mineral in a group of ancient pieces of jewelry, many of which were acquired as part of the Cesnola Collection and so are among the first objects to enter the Museum's collection. By using electron microscopy and X-ray diffraction techniques, scientists were able to identify the distinctive green beads that characterize the jewelry—previously described as glass—as variscite, an aluminum phosphate. The green

mineral could have been used either as an imitation of emerald or for its own intrinsic properties. Its discovery in ancient Roman jewelry points to a complex tradition of stone mining and carving and adds to our knowledge of ancient jewelry technology.

The importance of the connection between raw materials (and their sources) and finished works of art is evident in the ongoing study of stone materials in Khmer sculpture that is the subject of Federico Carò's article. By using petrographic analysis, a technique whereby microscopic stone fragments are thinned to the point that they become transparent and are then examined under a microscope to identify the constituent minerals and the fabric of the stone (fig. 9), we have been able to correlate specific monuments in Cambodia to specific types of sandstone. Our results supplement the scarce information that accompanies most Khmer sculptures in Western collections and may help to establish their provenance based on materials analysis. In the current phase of the project the scope of the investigation has been expanded to include the exploration of quarry sites in Cambodia (see fig. 10)



9 • Petrographic thin section of a sample of sandstone from a quarry site in Cambodia. A small sample of stone is cut, ground, and polished to a thickness of approximately 30 micrometers. At this thickness the rock sample becomes transparent, and it can be examined under a microscope in transmitted light. The shape and optical characteristics of the individual mineral grains are an indication of the stone's origin.



10 • Federico Carò at an ancient stone quarry site in Cambodia. The steps and terraces cut in the rock outcropping show where blocks of stone were extracted for use in monumental buildings or in sculpture.

11 • Velichka Kontozova and Felix Deutsch, visiting scientists from the University of Antwerp, Belgium, setting out air samplers on the roof of the Asian Wing of the Museum. To evaluate the air quality in the Museum, the concentration of pollutants and particulates is measured both inside the galleries and outdoors, and the results are compared.

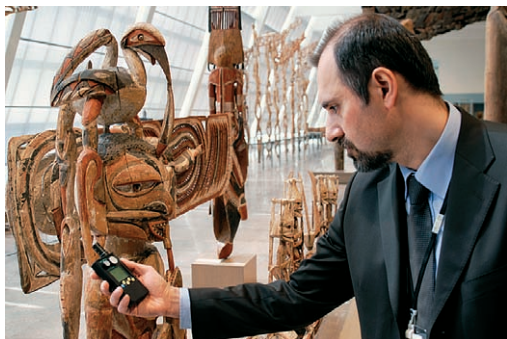
12 • Marco Leona uses a handheld monitor to measure light levels and the amount of ultraviolet light in the New Galleries for Oceanic Art.



cesses. And by applying this technique to a large number of objects from a variety of cultures and periods (examples of which are not in short supply at the Museum) one can build a database of elemental markers that can be used to establish the period of manufacture of a glass object. In his article in this issue Mark Wypyski recounts how this approach restored a questioned Renaissance pendant to its rightful historical place.

The work of the Museum's scientists is not limited to the scientific analysis of works of art. In collaboration with art conservators we investigate corrosion and deterioration phenomena, study conservation treatments and materials, and monitor the Museum environment to ensure that it meets the highest standards. In 2006 we carried out an air quality survey (fig. 11) to investigate the levels of pollutants and particulates in the galleries and in the showcases. Materials used to build exhibition and storage cases are tested to make sure they will not release corrosive vapors. (Even the small amounts of organic vapors normally released by wooden furniture, for example, could accumulate over time in museum showcases, leading to unacceptable conditions.) Light levels on works of art must be carefully evaluated (see fig. 12) and protective filtering applied to reduce the effect of ultraviolet radiation. Climatic conditions in the galleries are monitored and recorded to ensure that the proper range of temperature and relative humidity values is maintained.

Testing materials used in conservation treatment and developing new solutions for tasks such as consolidating and readhering broken parts of a damaged work of art (either



with the aim of mapping the sources for the stone used in Khmer buildings and statuary.

The department's studies on glass technology share a similar focus on chemical analysis to establish the age and origin of works of art. Electron microscopy can be used to quantify accurately the elemental composition of very small fragments from glass objects. Some of the identified elements can in turn be used as markers for specific raw materials and pro-



13 • To determine the best adhesive and pinning system to conserve a damaged marble sculpture, George Wheeler conducted exhaustive mechanical tests on sample blocks. In the foreground here is a scale model obtained by computer-aided machining following 3D laser scanning of the original sculpture: Tullio Lombardo (Italian, ca. 1455–1532), *Adam*, ca. 1490–95 (marble, h. 6 ft. 3½ in. [1.92 m]); The Metropolitan Museum of Art, Fletcher Fund, 1936 [36.163]). The virtual model was used for mechanical calculations and the scale model to test conservation approaches. In the background is the Instron tensile stress tester used to measure the strength of each adhesive and pinning combination.

in response to accidental damage or to replace older restorations) constitute another area of study for Museum scientists. As the Museum prepares to reassemble Tullio Lombardo's *Adam*, an Italian fifteenth-century lifesize marble sculpture that was damaged in 2002, we have thoroughly investigated methods and materials for joining marble, which has traditionally been accomplished with a variety of glues, mortars, and metal pins. Research scientist George Wheeler prepared test samples by adhering marble blocks with several modern synthetic adhesives and various types of reinforcing pins made from such advanced materials as fiberglass, carbon fiber, titanium, and high-performance steels (figs. 13, 14). The mechanical strength of the resulting bond was determined by subjecting the samples to increasing loads with a tensile stress tester (fig. 15). Thermoplastic acrylic resins were found to provide excellent adhesion, and modern composite pins were eventually selected because they outperformed traditional metal pins.

Sometimes our investigations require us to develop new analytical techniques. Julie Arslanoglu and Julia Schultz describe in their article how immunological techniques developed in the biomedical field, for example, have been adapted for the analysis of works of art. Using antibody reactions, proteinaceous substances in paint binding media—egg white or egg yolk, casein, collagen from cow, rabbit, or deer hides—can be distinguished with great sensitivity and extremely high specificity even when only small samples are available.



14 • Marble blocks of standard size and shape used for mechanical testing



15 • Marble test sample at the breaking point in the Instron tensile stress tester

The analysis of dyes, the coloring compounds extracted from plants and insects since antiquity and synthesized from coal tar derivatives starting in the 1850s, is an example of a challenging problem that required a unique and art specific solution. Tracing the use of organic colorants offers a way to follow trade routes, identify relationships between archaeological objects, and authenticate and attribute works of art. The concentrations of organic colorants in artistic and archaeological objects are very low, however, and the lack of analytical techniques of adequate sensitivity has until now significantly hindered the study of ancient dye technology.

Scientists at the Metropolitan Museum have successfully applied surface-enhanced



16 · Fragment of a mummy shroud. Roman, late 2nd–3rd century A.D. Linen, paint; ca. 11¼ x 9⅞ in. (28.5 x 25 cm). The Metropolitan Museum of Art, Museum Accession (x.390). To identify the pigment used for the flesh tones, a microscopic sample (see fig. 17) was removed from the shroud with a tungsten needle. Analysis with techniques such as X-ray fluorescence spectroscopy and visible reflectance spectroscopy hinted at the possibility that a dye extracted from a plant could have been used for the pink pigment. To identify which dye, surface-enhanced Raman scattering was used (see fig. 18). This highly sensitive technique requires such a small sample that the impact on the object is minimal.

17 · Sample of the shroud fragment in fig. 16 being treated with acid vapors in a microscale reaction chamber. Because of the small size of the sample (approximately 25 micrometers), all operations were conducted under a microscope using dedicated microtools.

18 · Tatyana Teslova, Metropolitan Museum/City College of New York intern, analyzing a sample of the shroud fragment in fig. 16 with a Raman spectrometer designed specifically for The Metropolitan Museum of Art. The sample is treated with silver nanoparticles. As the dye molecules migrate from the sample to the surface of the silver nanoparticles, their Raman response is enhanced over a million times due to particular electronic properties of the silver nanoparticles. With this method the pink dye was identified as madder lake.

Raman scattering, a technique based on the ability of silver nanoparticles to amplify electromagnetic radiation, to the detection of dyes in microscopic samples from works of art. We have thus been able to identify some of the earliest examples of the use of dyes, from samples as small as 25 micrometers wide (a human hair is on average 100 micrometers in diameter). Using this technique, the pink pigment in a Roman mummy shroud was identified as madder lake (figs. 16–18). Madder lake is obtained by extracting the colorant contained



in the root of the madder plant with alkali and precipitating it with alum, an aluminum salt. (Lake is the technical term for an organic dye absorbed on an inorganic base, in this case alumina.) That the root of the madder plant contains a beautiful pink colorant is not immediately evident, for the root is in fact orange-brown. Fermentation is necessary to break down the dye compound in the root so that it can be extracted by acid-base reaction. Only when the extract is treated with alum does the dye precipitate as a pink pigment. This knowledge of complex chemical and biochemical phenomena was not exclusive to alchemists or specialized workers, for it was exploited by artists themselves, who were quite interested in the technical details. Very often it was the artists who prepared the pigments, using the instructions in manuals and treatises devoted to selecting the best materials and turning them into resplendent colors.

When scientific research is applied to art, it brings us the same sense of wonder that we often feel in the presence of a masterpiece: How did they know? How could this have been done?

The Chemistry of Aging in Oil Paintings: Metal Soaps and Visual Changes

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Silvia A. Centeno and Dorothy Mahon

As soon as an artist applies oil paint to a canvas or other support, complex chemical and physical processes start to take place as the paint changes from a viscous medium to the cross-linked network that constitutes the dry paint film. The composition of the pigments and the oil medium, whose main function is to bind the pigment particles together, and other additives in the paint mixture considerably affect the drying process. Environmental conditions such as light, temperature, relative humidity, and the presence of pollutants play a key role in how paint films age. Understanding these processes is crucial for determining why a painting looks the way it does and whether the surface texture, opacity, and depth of tone of a paint layer are as the artist intended or have changed over time. Before any conservation treatment begins the condition of a work of art is given careful consideration, and during that process questions may arise.

A case in point is John Singer Sargent's *Madame X* (fig. 19). An examination of the portrait in 1996 revealed passages of a curious texture in the hair and velvet bodice consisting of minute raised bumps that scatter the light (see fig. 20). This prompted further investigation to determine whether this effect was intended by the artist or if it was due to natural aging, earlier conservation treatments, or environmental conditions.

Madame X, a portrait of the American-born Madame Pierre Gautreau (née Virginie Avegno), has been in the Metropolitan's collection for nearly a century. In January 1916 Sargent wrote to his friend Edward Robinson, then the director of the Museum, offering to sell the painting

to The Metropolitan Museum of Art for the modest price of £1,000 (then the equivalent of \$4,762, which would be about \$97,200 today). When it was displayed at the Paris Salon of 1884, *Madame* *** (as it was called then) was denounced by critics and the public alike as offensive, ugly, and an affront to decorum. Despite the scandal, Sargent refused to cede to the demand of Madame Gautreau and her family that he withdraw the painting from the Salon. He repainted the gown's right strap, which originally fell suggestively off the sitter's shoulder, and kept the painting for himself. Over the years he lent it to several exhibitions, the last being the 1915 Panama-Pacific International Exposition in San Francisco, where it was when he wrote to Robinson in early 1916. "I suppose," he told Robinson, "it is the best thing I have done." And by that time the critics agreed.

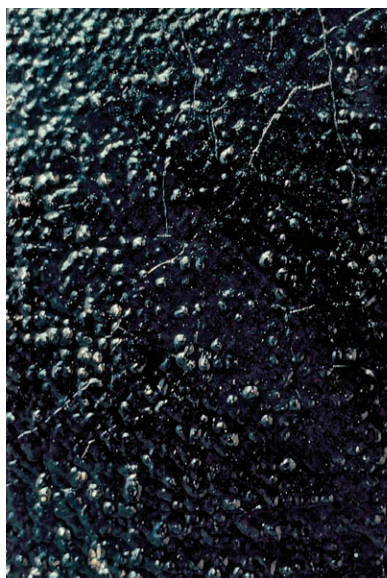
To determine the cause of the textured passages in *Madame X*'s hair and dress, several microscopic samples approximately one-tenth of a millimeter in diameter were taken from the edge of an old loss or crack so as to avoid further damage to the painted surface. These minute paint samples were mounted in a synthetic resin and polished to allow the cross section—or layer structure—of the paint film to be examined under high magnification. In order to obtain insight into an artist's working methods and materials, the Museum's laboratories frequently perform chemical analysis of samples mounted in cross section using a range of microanalytical techniques. Analysis can also help to clarify questions regarding suspected visual alterations of paintings.

Sargent prepared the canvas support of *Madame X* with a light, dull pink ground consisting of lead white (basic lead carbonate) tinted with particles of red iron oxide bound in an oil medium. Inspection of a microscopic sample of the paint film and the ground preparation revealed that the surface texture is caused by irregular lumpy inclusions,

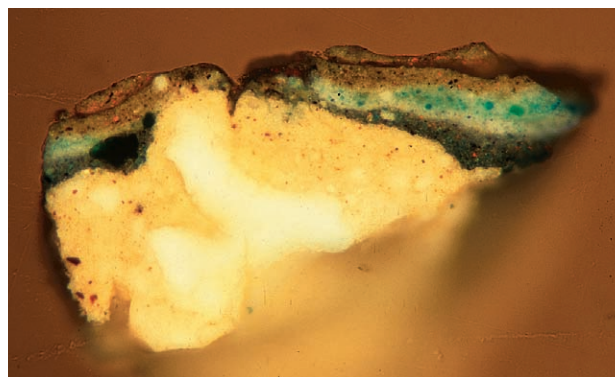
on the order of 10 to 20 micrometers in diameter, in the ground layer (fig. 21). Analysis of the lumpy inclusions by Raman microspectroscopy² revealed that they are composed of lead soaps that result from the reaction over time of the lead white in the ground with fatty acids that are components of the oil binder.³



19 · John Singer Sargent (American, 1856–1925). *Madame X* (*Madame Pierre Gautreau*), 1883–84. Oil on canvas, 82 1/8 x 43 1/4 in. (208.6 x 109.9 cm). The Metropolitan Museum of Art, Arthur Hoppock Hearn Fund, 1916 (16.53)



20 · Detail of *Madame X* (fig. 19) showing the surface texture of rounded protrusions resulting from the formation of lead soaps in the ground layer as it aged



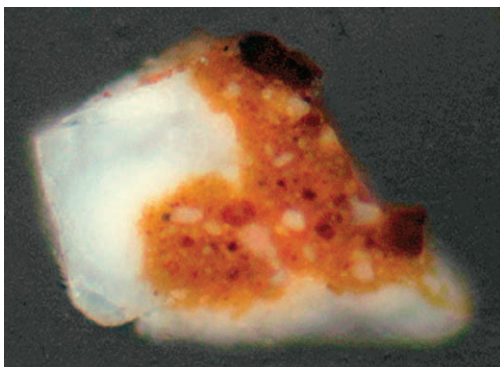
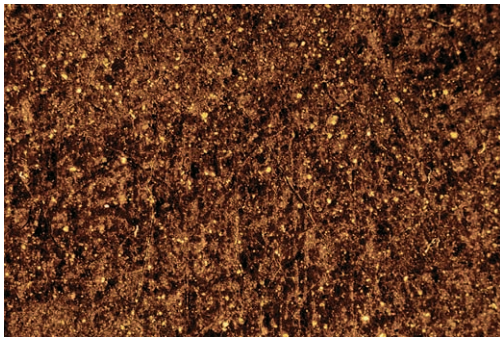
21 · Cross section of a paint sample removed from the background at the right in *Madame X* (fig. 19). A white aggregate of a lead soap measuring approximately 10 to 20 micrometers in diameter is visible in the ground layer as it starts to break through the sequence of paint layers. Original magnification 200x

Heavy metals from pigments such as lead white, lead tin yellow, red lead, and zinc white that are present in the ground preparation or paint layers of oil paintings may react with the free fatty acids in the oil binding medium to form organic salts called soaps. The process of metal soap formation, or saponification, in oil paintings was first characterized in 1997 by researchers in the Netherlands during an investigation associated with the conservation of Rembrandt van Rijn's *The Anatomy Lesson of Dr. Nicolaes Tulp* in the Royal Picture Gallery Mauritshuis, The Hague. More widespread than first suspected, this not yet fully understood process has since been observed in numerous works of diverse origins that date from the fifteenth to

the twentieth century and were painted on a wide range of supports that include paper, canvas, wood, and copper.⁴ The saponified regions often grow into aggregates that swell and sometimes protrude through the paint surface.⁵ The lumpy aggregates can form in the ground layer as well as in the paint layers. The protrusions may be distributed throughout the entire paint surface or they may manifest more prominently in certain areas, such as in the dark brown hair and deep black bodice in *Madame X*.

22 · Guercino (Giovanni Francesco Barbieri; Italian, 1591–1666), *Samson Captured by the Philistines*, 1619. Oil on canvas, 75¼ x 93¼ in. (191.1 x 236.9 cm). The Metropolitan Museum of Art, Gift of Mr. and Mrs. Charles Wrightsman, 1984 (1984.459.2)

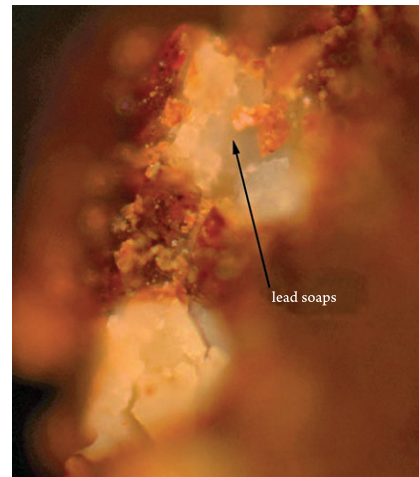
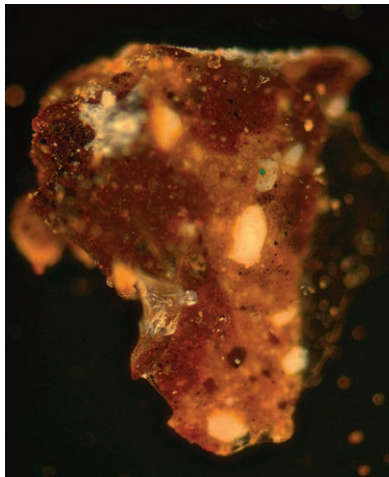




23 · Detail of Guercino's *Samson Captured by the Philistines* (fig. 22) photographed with raking light, showing the presence of coarse lead white pigment particles mixed with a more finely divided ochre pigment in the textured paint surface on Samson's right leg

24 · Cross section of a paint sample removed from a surface protrusion in Samson's leg in Guercino's *Samson Captured by the Philistines* (fig. 22), showing a coarse lead white pigment particle, approximately 20 to 30 micrometers in diameter, surrounded by more finely divided ochre and lead white particles. The ground layer is missing in this cross section. Visible illumination; original magnification 200x

Examination of several paint samples from *Madame X* demonstrated that in this case the aggregates of lead soap were forming throughout the ground layer. The sample removed from the yellow ochre background revealed that the lead soap aggregate is just beginning to push through to the upper paint layer in that area, though the deformation of the paint surface is still barely perceptible, while in the hair and bodice the deformation of the surface is clearly visible (fig. 20). Why the soap lumps are more prominent on the surface in specific passages of paint is not known, but it has been proposed that the reactive fatty acids may originate in the paint layer where the soap lumps are forming or that they may migrate from adjacent paint layers.⁶ Depending on their



25 · (left) Top view of a microscopic sample removed from the bumpy surface at the lower right in Guercino's *Samson Captured by the Philistines* (fig. 22), showing coarse lead white pigment particles mixed with more finely divided ochre pigment. Visible illumination; original magnification 100x

26 · (right) Bottom of the sample in fig. 25, showing white areas, approximately 20 micrometers in diameter, containing lead soaps that resulted from the reaction of the lead white pigment with fatty acids from the oil binder. Visible illumination; original magnification 100x

degree of absorbency, pigments prepared in an oil medium require differing amounts of oil binder to produce paint with good working properties. Carbon-based black pigments, for example, tend to absorb the oil binder, so paint formulations containing these pigments generally require a larger proportion of the binder.

It is possible that in *Madame X* the dark, oil-rich paint layers containing carbon black provided a quantity of free fatty acids that allowed the saponification to proceed at a faster rate. In addition, medium-rich paint containing dark brown and black pigments dries at a slower rate than paint containing pigments such as lead white. A thin, slow-drying paint film could thus remain susceptible to plastic deformation during the development and growth of the lumpy lead aggregates. Conversely, the surface manifestation of the lead soaps may be suppressed where the overlying paint film is much thicker or contains a faster-drying paint formulation.

Not all protrusions on the surfaces of oil paintings are due to the formation of heavy metal soaps. For example, microanalysis of two samples removed from the roughly

textured paint surface of Guercino's *Samson Captured by the Philistines* (figs. 22, 23), which was painted in 1619 for the papal legate to Ferrara, Cardinal Jacopo Serra, showed that the lumps forming the remarkably grainy texture visible throughout the surface are in fact coarse particles of lead white surrounded by more finely divided ochre pigment particles (figs. 24, 25). Chemical analysis of the materials deep within the paint layer in the second sample, however, revealed that some of the lead white particles are in fact undergoing a saponification process (fig. 26). The presence of lead soap formation in just one sample taken from such a large painting dating to the seventeenth century attests to the widespread occurrence of the phenomenon in oil paintings.

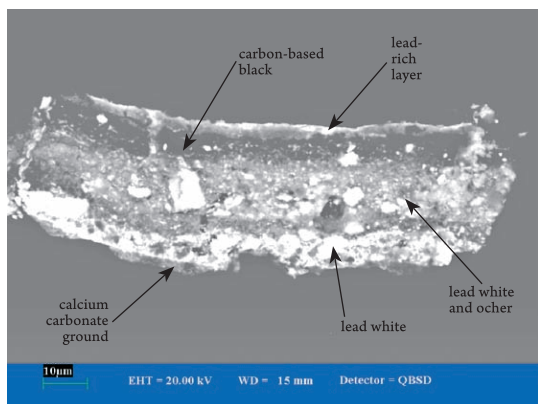
As was the practice of many painters during the Baroque period, Guercino painted *Samson Captured by the Philistines* on a dark brown prepared ground. His thinly painted composition was built up in scumbles, or light semiopaque mixtures, over the dark ground to achieve the dramatic lighting so characteristic of the Baroque. The value relationships of many paintings of this period have shifted considerably, the dark ground becoming more dominant as the upper paint layers grow more transparent over time. The result is an increased contrast between the light and dark passages. It is possible that one of the causes of this growing transparency is the saponification throughout the paint layers of pigments containing heavy metals.

Another manifestation of the degradation process associated with heavy metal soap formation in oil paintings is the development of white hazy surface deposits.⁷ This type of disruption, often described as blooming or efflorescence, can have a marked effect on the visual appearance of a painting, particularly when it forms on top of dark passages of paint. Such was the case with a *Portrait of a Woman* by the seventeenth-century Dutch artist Jan van Ravesteyn (figs. 27–29), a member of the painters' guild in The Hague who painted portraits exclusively. *Portrait of a Woman* is painted on an oak panel support that was prepared



with a calcium carbonate ground, a typical construction in seventeenth-century Holland. The removal of the varnish revealed that the chalky appearance, resulting from a cloudy bloom distributed throughout the surface (see figs. 27, 28), was not entirely due to the poorly saturating and deteriorated varnish.

Examination of the paint film on Van Ravesteyn's painting with a stereobinocular



27 · (opposite, top) Van Ravesteyn's *Portrait of a Woman* (fig. 29), before treatment

28 · (opposite, bottom) Detail of Van Ravesteyn's *Portrait of a Woman* (fig. 29) showing the white haze on the surface of the painting before cleaning

29 · (above) Jan van Ravesteyn (Dutch, ca. 1572–1657), *Portrait of a Woman*, 1635. Oil on oak panel, 26 $\frac{7}{8}$ x 22 $\frac{7}{8}$ in. (68.3 x 58.1 cm). The Metropolitan Museum of Art, Gift of Henry Goldman, 1912 (12.202)

30 · (left) Scanning electron microscope (SEM) image of a cross section removed from the black costume of the sitter in Van Ravesteyn's *Portrait of a Woman* (fig. 29), showing a carbon-based black layer below a lead-rich layer approximately 2 to 3 micrometers thick that resulted from the formation of lead soaps. Original magnification 2200x

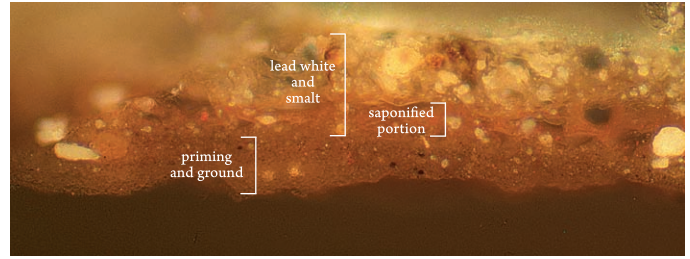


31 • Meyndert Hobbema (Dutch, 1638–1709). *Village among Trees*, 1665. Oil on oak panel, 30 x 43½ in. (76.2 x 110.5 cm). The Frick Collection, New York, Henry Clay Frick Bequest (1902.1.73)

microscope showed a thin layer of an insoluble white crystalline material attached to the surface. A minute sample removed from a deep black passage on the sitter's right arm was mounted as a cross section and analyzed by Raman microspectroscopy and scanning electron microscopy using energy dispersive X-ray spectrometry (SEM-EDS). In this sample (fig. 30), over the calcium carbonate ground preparation is a layer containing mainly lead white, followed by a layer containing a mixture of lead white and iron ochre, over which a paint layer containing a carbon-based black pigment was applied.⁸ In the scanning electron microscope image of this sample cross section, the higher contrast of the very thin layer of white material, approximately two to three

micrometers thick, that lies over the black paint layer suggests that it contains heavy metals. Further analysis revealed that this layer is rich in lead, calcium, and phosphorus.

The elemental analysis of *Portrait of a Woman* suggests that the disturbing white hazy deposit is due to the formation of lead soaps resulting from the dissolution of the lead white in the underlying layers and the migration of the altered lead through the paint layers. In this case a likely source of the free fatty acids necessary for the formation of the lead soaps is the oil-rich, carbon-based black layer. Similar thin, lead-rich white hazy deposits on dark oil paint films have been observed in other seventeenth-century Dutch paintings and have been characterized as the result of the migration of lead



32 · (left) Detail of Hobbema's *Village among Trees* (fig. 31), showing the dark pores of the wood grain throughout the sky

33 · (above) Cross section of a sample removed from the sky in Hobbema's *Village among Trees* (fig. 31). Visible illumination; original magnification 200x

soaps throughout the paint layers and their deposition on the paint surface.⁹

A painting in the Frick Collection by the Dutch seventeenth-century landscape painter Meyndert Hobbema, *Village among Trees* (fig. 31), required conservation treatment to correct an aesthetically disturbing condition. Throughout the entire sky the pores of the oak grain were visible as inky black marks (fig. 32). Notes in the well-maintained conservation records at the Frick Collection attribute this condition to various causes. A 1938 report declares that there is no preparatory layer on the panel, and in 1947 another conservator stated that the ground had become transparent with age, noting that this is frequently the case with Dutch seventeenth-century paintings on oak panel.

Examination of the Frick panel with the aid of a stereobinocular microscope reveals, however, that the support is in fact prepared with a type of thin white ground commonly used for Dutch seventeenth-century paintings. Further examination by polarizing light microscopy and analysis by Raman microspectroscopy and SEM-EDS of a sample mounted in cross section that was removed from the sky at the upper right (fig. 33), an area where a darkened pore of the wood grain is visible, revealed a gray-brown, medium-rich priming layer on top of the cal-

cium carbonate ground, followed by an uppermost layer that contains a mixture of lead white and the blue pigment smalt. The detection of lead soaps in a portion of the top paint layer indicates that the severe localized darkening is caused by an increased transparency resulting from metal soap formation.¹⁰ An understanding of the phenomenon helps us to recognize that this aspect of the painting's appearance was unintended by the artist and is instead a consequence of aging. The change is not reversible and can be corrected only by precise retouching.

The formation of heavy metal soaps does not take place in all oil paintings containing potentially reactive materials. What factors trigger or exacerbate the process and whether it can be arrested or prevented is not yet understood. Various theories have suggested that the phenomenon may result from peculiarities inherent in the artists' materials and techniques, from conservation procedures, or from paintings' exposure to environmental conditions such as high relative humidity and temperature.¹¹ An investigation to explore those theories and add to our understanding of the formation of metal soaps in oil paintings is currently under way in the Department of Scientific Research at The Metropolitan Museum of Art. As usual, it will require the close collaboration between scientists, curators, and conservators that is essential to increasing our knowledge of the magnificent works of art entrusted to our care.

Roman Variscite Beads: In Situ Analysis by X-ray Microdiffraction

•
Tony Frantz, Dorothy H. Abramitis,
Linda Borsch, and Mark T. Wypyski

Accurate characterization of materials found in works of art and archaeological objects contributes to our understanding of cultural history and technological development. The discovery of a particular material in one context may prompt the search for its occurrence elsewhere, allowing us not only to define a geographic and temporal range in which that material was used but also to map trade routes connecting different societies. While such investigations are sometimes undertaken on prominent icons of art history, many—if not most—museum studies are based on more prosaic works.

Beginning in the late 1990s, during the reinstallation of the Metropolitan Museum's Greek and Roman collection, we examined and analyzed an assortment of green jewelry beads in an effort to identify the materials from which they were made and possibly gain insight into their origin. While our investigations showed that most of the beads were accurately catalogued as either glass or varieties of beryl, including emerald, we were surprised to discover a number of objects in the collection, including a gold necklace, pendants, and several earrings, that incorporate beads made of variscite, a relatively rare aluminum phosphate mineral. On making these discoveries, we wondered if we had fortuitously stumbled upon one of Pliny the Elder's *smaragdi*, his term for the twelve types of prized green gemstones known to the ancient world (*Naturalis historia* 16.62–79). Other examples of variscite beads have been excavated from well-documented Roman sites in Europe, and recent studies have used several methods, including X-ray diffrac-

tion, X-ray spectrometry, and Raman microspectrometry, to identify the minerals represented.¹² At the Metropolitan we have expanded on this work by using in situ X-ray microdiffraction and other noninvasive methods to analyze the beads from the collections in the Department of Greek and Roman Art.

Among the pieces of jewelry found to incorporate variscite beads are three pairs of earrings, a single earring, and a necklace (figs. 34–38). The earrings came to the Museum in 1874 as part of the Cesnola Collection of antiquities from Cyprus.¹³ The necklace was acquired in 1920, probably in Rome.¹⁴ The beads on these pieces are all elongated octagonal prisms approximately $\frac{1}{8}$ inch (.3–.4 cm) wide and $\frac{1}{8}$ to $\frac{3}{8}$ inches (.3–1 cm) long. When they are examined under low-power magnification the beads appear to

34 • (top) Pair of earrings. Roman (Cyprus), 2nd century A.D. or later. Gold, glass, variscite; h. of each $\frac{3}{4}$ in. (2 cm). The Metropolitan Museum of Art, The Cesnola Collection, Purchased by subscription, 1874–76 (74.51.3961, 3962)

35 • (center left) Pair of earrings. Roman (Cyprus), 3rd century A.D. Gold and variscite, h. of each $1\frac{1}{8}$ in. (3.5 cm). The Metropolitan Museum of Art, The Cesnola Collection, Purchased by subscription, 1874–76 (74.51.3948, 3949)

36 • (center right) Earring. Roman (Cyprus), 3rd century A.D. Gold, carnelian, variscite; h. $1\frac{1}{8}$ in. (4.1 cm). The Metropolitan Museum of Art, The Cesnola Collection, Purchased by subscription, 1874–76 (74.51.3950)

37 • (bottom) Pair of earrings. Roman (Cyprus), 2nd century A.D. Gold and variscite, diam. $\frac{7}{8}$, $1\frac{1}{8}$ in. (2.2, 2.7 cm). The Metropolitan Museum of Art, The Cesnola Collection, Purchased by subscription, 1874–76 (74.51.3907, 3906)

38 • Necklace. Roman, 3rd century A.D. Gold, emerald, variscite; l. $17\frac{1}{8}$ in. (43.5 cm). The Metropolitan Museum of Art, Rogers Fund, 1920 (20.239)





be similar in color and mineral texture, with inclusions, veins, and concentric growth bands typical of many heterogeneous mineral specimens. The facets of the beads, some of which bear parallel striations from filing and polishing, were clearly produced by working massive polycrystalline material rather than being the natural planar sides of single crystals such as typically occur on emeralds, amethysts, and other gemstones. X-radiographs of the beads indicate that they were drilled continuously from one end, unlike many harder gemstones from antiquity that have been found to have biconical drill holes.¹⁵

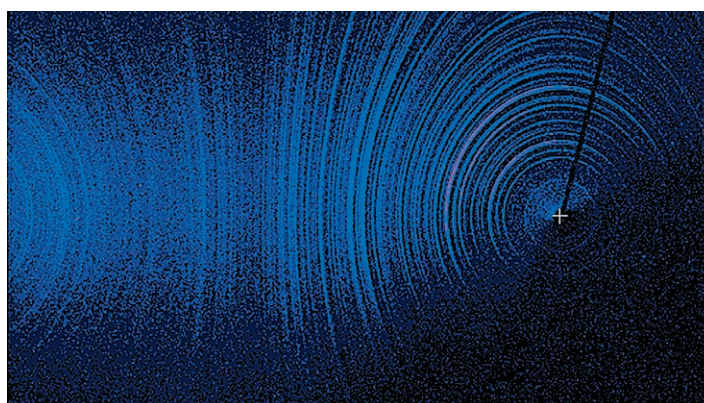
Because the beads are small, intact objects, every effort was made to determine their composition and structure without sampling or using other invasive techniques. To achieve this goal we used X-ray microdiffraction together with variable-pressure scanning electron microscopy and energy dispersive X-ray spectrometry, as these methods are well suited to the nondestructive characterization of small crystalline objects. The only preparative treatment applied prior to the analytical work was a judicious cleaning of the beads with acetone to remove any adventitious oils or other hydrocarbons that might interfere with imaging in the electron microscope. Using a Rigaku Dmax/Rapid instrument, X-ray microdiffraction analysis was performed on corners of the beads that appeared free of obvious accretions. Each bead was carefully positioned using non-adhesive polyethylene blocks to align a protruding corner of the octagonal prism with the X-ray beam (figs. 39, 40).¹⁶ For comparison, nondestructive X-ray diffraction analysis was performed on the flat surfaces of several beads using a Philips PW1835 open-architecture diffractometer.¹⁷ This approach—which has proven useful for the investigation of surfaces on larger objects—was found to be less satisfactory than the microdiffraction method for the small beads involved in this study, most likely because of the difficulty in accurately and reproducibly positioning the bead surfaces on the diffractometer axis.¹⁸ Secondary electron images and energy dispersive (EDS) X-ray spectra were acquired directly from the surfaces

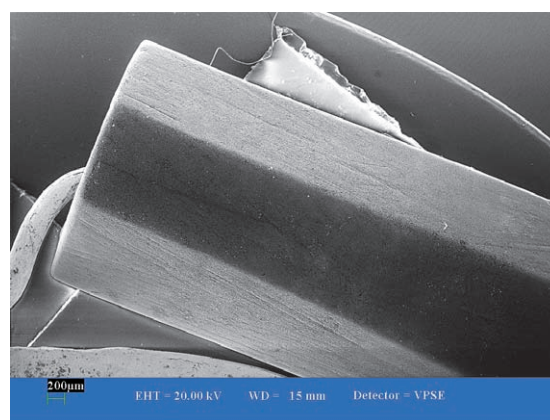
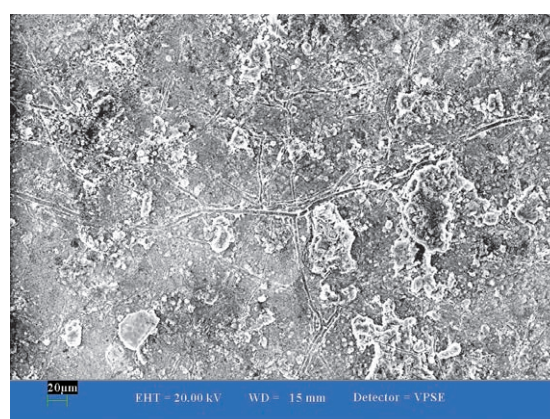
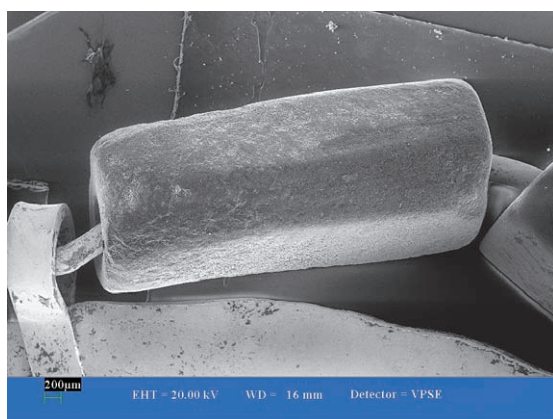
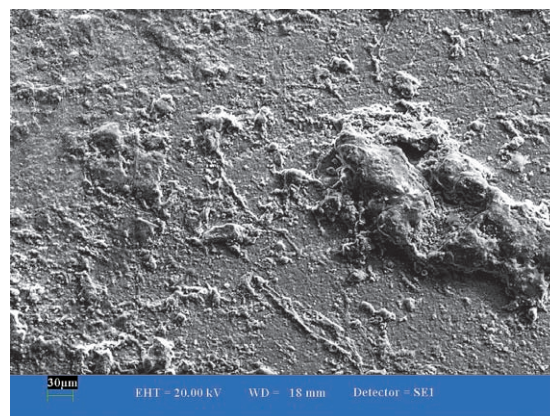
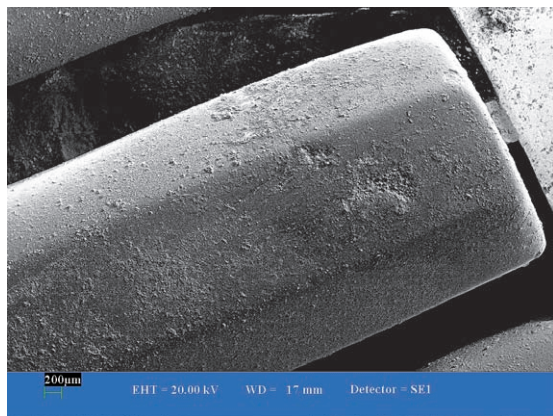
of the beads using a LEO 1455VP variable-pressure scanning electron microscope.¹⁹

The secondary electron images revealed that the surfaces of the beads vary widely. Many have adherent deposits suggestive of the calcareous or siliceous accretions often acquired when objects have been buried in soil (figs. 41–43), and in several instances what appeared to be casts of plant rootlets were visible at high magnification (fig. 44). Other beads are notably free of such deposits (fig. 45). Also, while some beads show distinct parallel striations

39 • Configuration for in situ X-ray microdiffraction analysis of jewelry beads on the Rigaku Dmax/Rapid instrument. The gold earring (fig. 37, left) is held securely without adhesives in a polyethylene block.

40 • Diffraction pattern obtained from the corner of bead no. 4 on a Roman gold earring (fig. 37, left) as recorded by Rigaku Dmax/Rapid imaging plate. Despite shadowing in the lower right quadrant from the body of the bead, the pattern can be accurately integrated with respect to line positions and intensities.





(clockwise from bottom image, left column)

41 · Scanning electron microscope (SEM) variable-pressure secondary electron image of bead no. 4 on a Roman earring (fig. 37, left), a pitted and heavily weathered variscite bead with soil accretions

42 · Scanning electron microscope (SEM) high-vacuum secondary electron image of bead no. 2 on a Roman earring (fig. 36). All three of the variscite beads on this earring bear tenacious soil accretions over their entire surfaces.

43 · Scanning electron microscope (SEM) high-vacuum secondary electron image of soil deposits on bead no. 2 on the same Roman earring shown in figs. 36 and 42

44 · Scanning electron microscope (SEM) variable-pressure secondary electron image of soil deposits on bead no. 2 on the same Roman earring shown in figs. 36, 42, and 43, showing a network of casts of plant rootlets

45 · Scanning electron microscope (SEM) variable-pressure secondary electron image of bead no. 2 on a Roman earring (fig. 37, left), a relatively clean and unweathered variscite bead that preserves parallel striations from cutting and polishing

46 · Scanning electron microscope (SEM) variable-pressure secondary electron image of twist-fabricated gold wire on a Roman earring (fig. 37, left), showing spiral seams of component strands

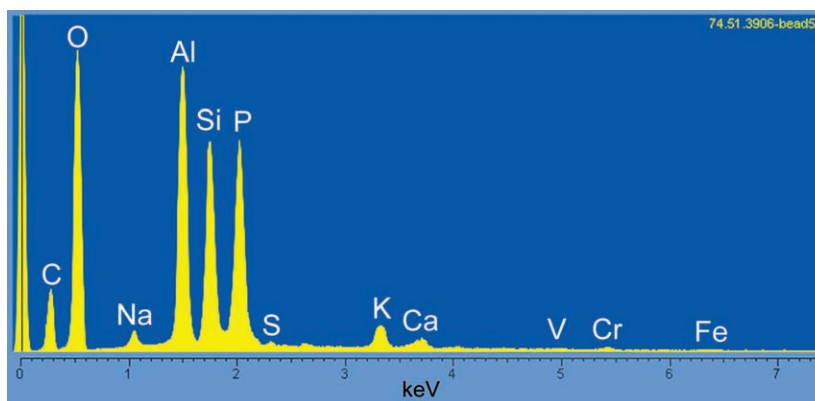
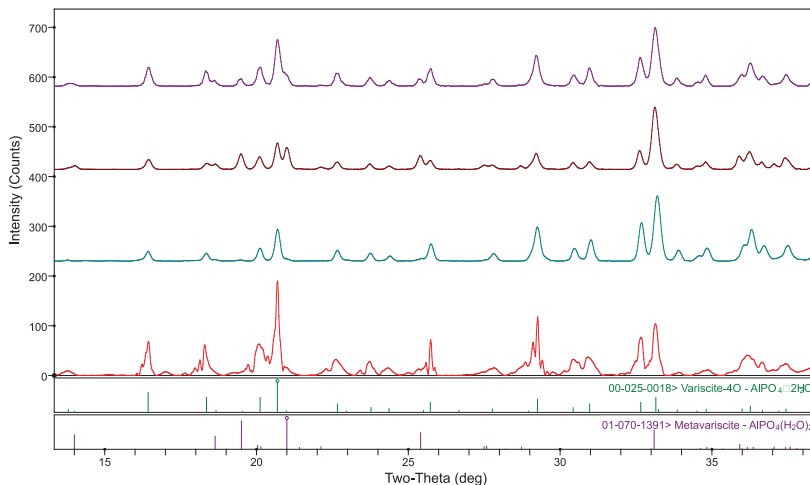
47 · Partial X-ray diffraction patterns obtained via microdiffraction (top three) and diffractometry (fourth from top) from four beads, together with (at bottom) stick patterns for variscite and metavariscite

48 · Energy dispersive (EDS) X-ray spectrum obtained from the surface of bead no. 5 on a Roman earring (fig. 37, left). The strong aluminum (Al) and phosphorus (P) peaks are attributed to variscite, while the silicon (Si), potassium (K), sodium (Na), calcium (Ca), and carbon (C) peaks likely derive from calcareous and siliceous deposits acquired while the bead was buried in soil.

that were most likely made with cutting and polishing tools (see, for instance, fig. 45), the surfaces of others have a uniformly smooth, frosted texture.

Although none of the objects in this study have a documented excavation history, all appear to have a reasonable claim to ancient manufacture or, at the very least, to being free of conspicuous anachronisms that might render them suspect as modern reproductions or forgeries. EDS analysis of the gold in the jewelry shows it to be a gold-silver-copper alloy that resembles in composition many other gold objects having plausible pedigrees for an origin in classical antiquity. In addition, the necklace is made from twisted wire, the earrings are manufactured of sheet metal and cut or twisted wires (fig. 46) joined with a gold-silver-copper solder, and both the beads and the gold in all the objects studied appear to have an extent and type of wear, deterioration, and accretionary material consistent with an origin in antiquity. The disparity in the texture and condition of beads found on the same object (see figs. 41, 45) might suggest either that the object was reconstructed in modern times or that beads made in other, perhaps earlier, contexts were reused in antiquity. Based on the evidence cited here, we are inclined to favor the latter, although the issue remains unresolved.

The X-ray microdiffraction analyses of the beads showed that they were composed predominantly of variscite and its polymorph, metavariscite (fig. 47).²⁰ Given the extent of surface deposits and weathering observed on the beads, no attempt was made to quantify their elemental composition. EDS spectra



obtained from the flat surfaces, however, show that aluminum and phosphorus are major components, often accompanied by significant amounts of silicon, calcium, and carbon (fig. 48). This is consistent with the diffraction results, as well as with the visual evidence of likely carbonate and soil accretions on most of the beads. The spectra are notably free of significant peaks for copper and iron.²¹

Not surprisingly, without the benefit of magnification and other analytical aids, correctly identifying green archaeological materials that have been buried in soil has been difficult. Prior to this study, the beads on the necklace and several of the earrings had been incorrectly catalogued as glass or chalcedony. The pitted surface of several of these beads—now identified as variscite—superficially resembles the weathered appearance of ancient glass. (A similar observation was reported with respect to beads excavated at the Roman site at Grange

Farm, Gillingham, Kent, England, that have been identified as variscite.)²² Glass beads of a similar shape were frequently used in Roman jewelry, most likely as an inexpensive imitation of emerald, the deep green, gem-quality variety of beryl that could be fashioned into simple beads by drilling lengthwise through naturally occurring hexagonal crystals. Although variscite is generally opaque, the beads made from it may have been produced with a similar imitative intent.

Variscite and its polymorph, metavariscite, are hydrous aluminum phosphate minerals ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$). These are secondary minerals of widespread, albeit rare, occurrence in heavily weathered bauxitic and lateritic soils, where they are commonly thought to have been formed by reaction of phosphatic waters with aluminum-rich rocks either on or near the earth's surface.²³ Variscite often occurs as veins like those found in the Can Tintorer mines near Barcelona (fig. 49), which are known to have been worked since the Neolithic period and have frequently been suggested as likely sources for the earliest variscite beads and other ornamental objects excavated from sites in Western Europe.²⁴ The sources for the variscite used in our beads may include these or other mines on the Iberian Peninsula that are evidenced to date from Roman times as well as possible local occurrences in Italy or Cyprus. Specifying this assignment rests partly on the matching of trace-element compositions between source material and finished object, an approach that relies heavily on samples unaffected by surficial accretions or chemically altered by contact with groundwater.²⁵ Modern methods of analysis such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) may well offer the possibility of minimally invasive microscopic sampling for testing objects without visible damage.

A striking feature of our variscite beads is their common shape—an elongated octagonal prism—which they appear to share with other known variscite beads on classical jewelry in other collections.²⁶ Whether this uniform shape reflects a common workshop origin or simply a widespread tradition of

design remains unknown. The heterogeneous texture and polymineralic nature of the beads clearly indicate that they were cut from large specimens of the mineral rather than being derived from naturally occurring single crystals.²⁷ Beads of comparable size and shape to ours have been discovered at Roman sites in Britain²⁸ and in the Zamora province of Spain.²⁹ The proximity of these sites to known historical mining sources of variscite suggests a plausible genetic association for the beads, if not the jewelry to which they belong. Further specification, however, necessarily awaits a more extensive geochemical study.

As Andrew Middleton and his colleagues at the British Museum have suggested, the scarcity of reported occurrences of variscite in Roman contexts may derive from the ease with which the material is mistaken for weathered glass.³⁰ Our work supports this hypothesis and, at the same time, adds to the database of confirmed instances of the mineral from this period. For others who might wish to pursue similar studies in their collections, X-ray microdiffraction offers important advantages over traditional film-based powder diffraction methods because it offers the capability for nondestructive in situ analysis of beads and other small objects as well as significantly more rapid data collection and interpretation. These advantages should encourage the search for occurrences of variscite in other collections and thereby add to the information available to help identify sources of the mineral, trade routes, and even the workshop practices of ancient Roman craftsmen.

49 • Specimen of variscite from the Can Tintorer mine near Barcelona



Khmer Stone Sculptures: A Collection Seen from a Material Point of View

•
Federico Carò

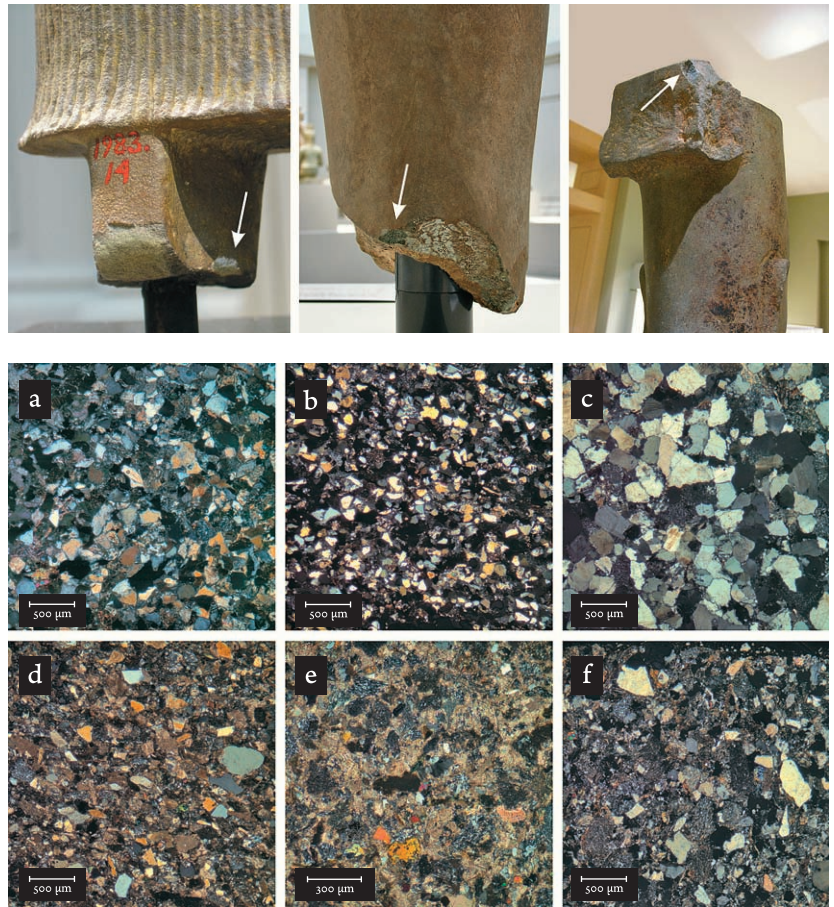
Petrographic analysis can unveil essential clues for reconstructing the function and provenance of stone artifacts and the techniques used to create them. This analytical tool can be especially helpful for integrating and enriching iconographic and stylistic considerations of Khmer sculpture and architecture.³¹ Toward that end, the Department of Scientific Research at the Metropolitan, in collaboration with John Guy, curator in the Department of Asian Art, has undertaken a petrographic study of Khmer sculptural production of the pre-Angkor (ca. sixth to ninth century) and Angkor (ca. tenth to thirteenth century) periods that will be of help to specialists who are investigating the context and provenance of Khmer stone sculptures from different perspectives.

The substantial collection of Khmer art at the Metropolitan comprises pre-Angkor and Angkor freestanding sculptures and architectural elements from Thailand and Vietnam as well as Cambodia. Like the works gathered in Phnom Penh at the National Museum of Cambodia and in Paris at the Musée Guimet, these objects not only illustrate the birth and evolution of the different Khmer styles, but they also record the changes in the sculptural artistic medium through time and across geographic areas. Fifty-four Khmer sculptures from the Museum's collection have been analyzed to date, together with samples from sculptures from the National Museum of Cambodia and other museums. Under memorandums of understanding signed between the Metropolitan Museum and the National Museum of Cambodia, and with the Authority for the Protection and Management of Angkor and the Region of Siem Reap (APSARA) of

Cambodia, new sculpture and quarry samples have recently been added to this study, the aim of which is to provide a comprehensive database of Khmer stone materials that has the potential to develop even further with future contributions from scientists at other museums that have holdings of Khmer sculpture.

In their primary studies of the sandstones of Angkor Wat, Edmond Saurin (in 1954) and Jean Delvert (in 1963) raised cardinal questions about the geological sources of Khmer stone materials. After almost two decades of civil strife in the region, scientific studies of sculptural media resumed in the early 1980s. In 1998 a Japanese research team led by Etsudo Uchida published a study of the stone building materials of Angkor monuments. Pierre Baptiste and his coauthors included sculptural stones in their survey of the Musée Guimet collection in 2001, as did Janet Douglas in the study of twenty-nine sculptures from the National Museum of Cambodia published in 2004 and 2007. Qualitative petrographic descriptions of Cambodian stone sculptures can be found as an appendix in some monographs and museum catalogues. All these studies, though they use different classification systems, describe the same three main types of sandstone: feldspathic arenite, quartz arenite, and graywacke.

The study of a rock with a petrographic microscope requires that a small fragment of material be mounted on a glass slide and polished down to the thickness of about 30 micrometers (thirty thousandths of a millimeter). Such preparation allows scientists to recognize each single mineral or assemblage of minerals that makes up the stone. So as to minimize the physical intrusion on works of art, sample



50 · White arrows indicate areas on sculpture from which fragmentary samples were taken.

51 · Micrographs showing the overall composition and texture of (a) feldspathic arenite; (b and c) fine and medium quartz arenite; (d and e) litho-feldspathic graywacke with different calcite content; and (f) litho-feldspathic graywacke rich in volcanic rock fragments

fragments are chiseled from areas already affected by previous breaks or losses, generally located at the backs of arm or leg joints or on the bottom edges of architectural elements (see fig. 50). When possible, such samples include both the exposed surface and the fresh stone interior so that the weathering of the sculpture can also be assessed. With the aim of describing and unambiguously classifying each sample of rock, the maximum number of detrital grains that make up the framework of the stone in each thin section were counted and each grain classified and measured by means of a micrometric eyepiece using a polarized light microscope. All the analyzed stone samples from the Khmer collection at

the Metropolitan are sandstones, clastic (fragmental) sedimentary rocks composed of a framework of sand-size grains of older rock (clasts) set in a silty or clayey matrix and united by a cementing material.

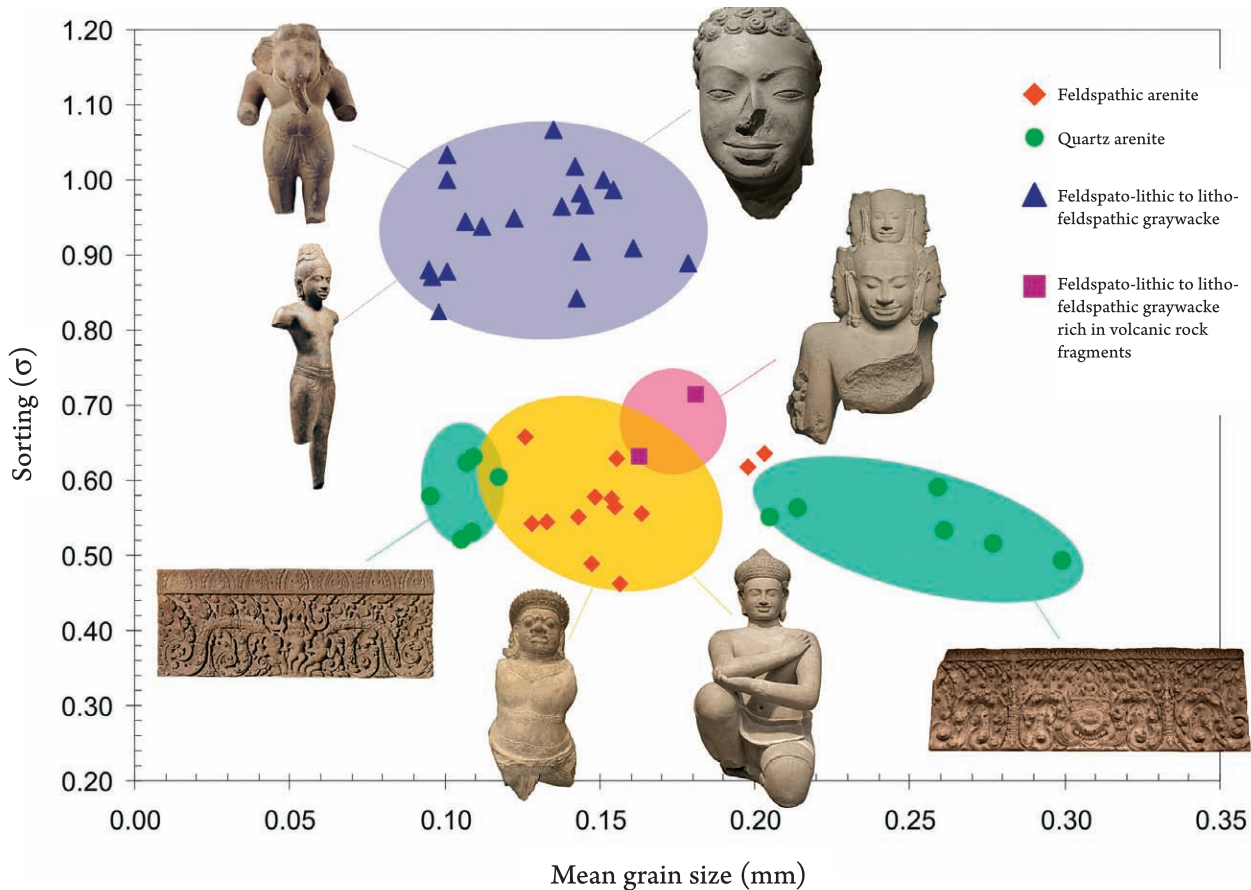
Many schemes of sandstone classification exist, and none of them are universally accepted by all scientists. For the purposes of this review, we have adopted the schemes proposed by F. J. Pettijohn (1954) and by P. Gazzi (1966) and W. R. Dickinson (1970). Pettijohn divided sandstones into two texturally different classes: those with less than 15% of matrix, called arenites, and those with more than 15% of matrix, called wackes. Although this scheme has been criticized, it seems to be the most workable for the samples studied at the Metropolitan, and it allows a sharp visualization of the works of art. Using Pettijohn's criteria, more than half the objects in the Museum's collection are carved from arenites, and the rest are graywackes, a term used in this circumstance

in its general sense of dark gray, immature sandstone with significant matrix content. By using the Gazzi-Dickinson classification it is possible to further detail the nature of the stones present in the collection on the basis of the detrital grain composition. Some 90% of the studied pieces are carved from two types of arenites and two graywackes.

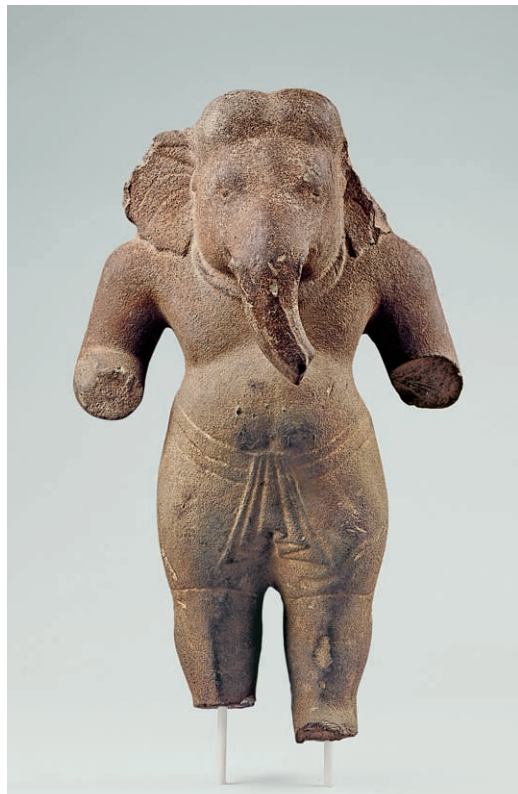
The first type of arenite present in the collection is feldspathic arenite, or sandstone where feldspar is an important detrital constituent that, together with quartz, makes up about 90% of the rock.³² This sandstone is characterized by a yellowish gray color and a granular texture (see figs. 57, 58). It is usually easy to distinguish the natural bedding, or stratification, of the stone, especially when the surface of the sculpture suffered more or less intense weathering. Examination of the stone under the petrographic microscope (fig. 51a)

shows a framework of fine, slightly rounded to angular grains—mostly mono-, poly-, and microcrystalline quartz and alkali feldspar—that are moderately well sorted (varied in size) and cemented by clay minerals, with a preponderance of chlorite. The rock fragments that make up 10% or less of the total framework are mostly chert, quartzite, micaceous schist, and phyllite (metamorphic rocks); intermediate to acid volcanoclasts (volcanic rocks); and subordinate siltstone and shale (sedimentary rocks).

The second arenite is classified as quartz arenite, or arenite with more than 75% quartz. This sandstone often exhibits a light reddish or pinkish gray color (caused by the diffuse film of hematite coating the grains and interstices) and a compact, crisp surface appearance (see figs. 59–61). Microscopically, it can be described as having very fine to medium moderately well sorted grains composed mostly of slightly



52 · The Metropolitan Museum of Art’s collection of Khmer sculpture classified according to the textural and compositional characters of the stone material, showing examples of sculpture carved from each type of stone



53 · Head of a Buddha. Angkor Borei, Cambodia, second half of 6th century. Feldspato-lithic graywacke, h. 24 in. (61 cm). The Metropolitan Museum of Art, Gift of Doris Wiener, 2005 (2005.512)

54 · Standing Ganesha. Cambodia, pre-Angkor period, Prasat Andet style, second half of 7th century. Litho-feldspathic graywacke, h. 17¼ in. (43.8 cm). The Metropolitan Museum of Art, Rogers, Louis V. Bell and Fletcher Funds, 1982 (1982.220.7)

55 · Standing Shiva. Cambodia or Vietnam, pre-Angkor period, Prasat Andet style, late 7th–early 8th century. Litho-feldspathic graywacke, h. 24 in. (61 cm). The Metropolitan Museum of Art, Rogers Fund, 1987 (1987.17)

rounded to angular mono- and microcrystalline quartz cemented by kaolinite (fig. 51b, c).³³

Graywacke sandstones are distinguished by their dark grayish to dark greenish color, remarkable compaction, and, in some cases, highly polished finish (see figs. 53–55, 62). The graywackes in the Museum study are compact, fine-grained, and immature sandstones with a variable content of quartz, feldspar, and lithic fragments. They are mostly of two types, which have compositions varying from feldspato-lithic to litho-feldspathic and which differ as to the type and the relative abundance of rock fragments in the framework grains.

The framework of the most common graywacke is poorly sorted and slightly variable in composition (fig. 51d, e). Quartz is present as slightly rounded to very angular mono- and polycrystalline grains, chert, and quartzite grains, which together form more than half the total volume of the rock. Feldspar grains are alkali feldspar and plagioclase, and vary from 20 to 40% of the entire framework.³⁴ The content of rock fragments in the framework varies and reflects a metamorphic-volcanic provenance for the sandstone.³⁵ The matrix is composed of a fine-grained clay-sized assemblage of chlorite and illite, with subordinate calcite, quartz, iron oxides, and heavy minerals.³⁶ Calcite is present as interstitial cement, together with chlorite, and can vary noticeably in abundance.

The framework of the second type of graywacke is generally coarser, with a relatively high proportion of feldspar grains and rock fragments (fig. 51f). Quartz never exceeds 30% of the total framework. The matrix is abundant and rich in small feldspar laths (thin, narrow,



56 · The sandstone outcrop near Koh Ker known as Ang Khna, where evidence of quarrying of massive monoliths can still be seen. The quarry subsequently became a sacred place when the vertical surfaces were carved with deities and friezes, possibly by hermits.

57 · Kneeling male attendant. Cambodia, Angkor period, Khmer style of Koh Ker, ca. 921–45. Feldspathic arenite, h. 30¼ in. (76.8 cm). The Metropolitan Museum of Art, body: Gift of Douglas Latchford, in honor of Martin Lerner, 1992 (1992.390.2); head: Gift of Raymond G. Handley and Milla Louise Handley, 1989 (1989.100)

58 · Guardian deity. Cambodia, Angkor period, Khmer style of Koh Ker, ca. 921–45. Feldspathic arenite, h. 38¾ in. (98.5 cm). The Metropolitan Museum of Art, Gift of Doris and Harry Rubin, in memory of Ralph Konheim, 1987 (1987.308)





59 · Lintel with carved figures. Cambodia, Angkor period, Khmer style of Koh Ker, ca. 921–45. Quartz arenite, 20 1/4 x 49 in. (51.4 x 124.5 cm). The Metropolitan Museum of Art, Fletcher Fund, 1936 (36.96.6)



60 · Lintel with Shiva on Nandi. Cambodia, Angkor period, Khmer style of the Baphuon, 11th century. Quartz arenite, 23 1/2 x 54 in. (59.7 x 137.2 cm). The Metropolitan Museum of Art, Gift of The Kronos Collections, 1996 (1996.473)



61 · Lintel with a mask of Kala. Cambodia or Thailand, Angkor period, Khmer style of the Baphuon, ca. first quarter of 11th century. Quartz arenite, 23 x 67 in. (58.4 x 170.2 cm). The Metropolitan Museum of Art, Gift of R. Hatfield Ellsworth, in honor of Florence and Herbert Irving, 1994 (1994.94)

elongated plagioclase crystals). Among the accessory minerals, hornblende is the most common and characteristic. The most distinctive feature of this graywacke is the abundance of igneous intermediate to basic brittle volcanic rock fragments (up to 90% of the total rock fragments), which easily break down into pseudomatrix (matrix formed by the mechanical compaction and squeezing of soft clasts, or fragments, in the framework). The relatively fresh volcanic grains suggest that the sediment was not transported very far after it eroded from preeminently volcanic rocks.

The petrographic characterization of the stone materials sheds new light on the Khmer sculpture in The Metropolitan Museum of Art. The study reveals that it is possible to group the sculptures according to strong petrographic similarities (fig. 52). Integrating these results with stylistic considerations, which will be the subject of a future joint study with curatorial colleagues, and comparing them with other published petrographic data about stone usage in Cambodia will add to our ability to contextualize them.

Most of the pre-Angkor sculptures in the Museum, which date from the sixth to the ninth century and represent a diversity of styles and iconographies, were made from similar stone material worked with consummate skill. These early Khmer works originating from the southern provinces of Cambodia (see, for instance, figs. 53–55) are carved from feldspato-lithic to litho-feldspathic graywacke that displays a generally well preserved, dark grayish to dark greenish, sometimes highly polished surface. This sandstone was rarely used for buildings, although a similar type of stone has been found in the early sanctuary of Ta Keo, built in the late tenth to early eleventh century.³⁷

The Angkor statuary in the collection, on the other hand, is mostly made from feldspathic arenite.³⁸ This type of stone—also called arkose, gray or green sandstone, or gray to yellowish brown sandstone—occurs extensively in architectural elements of the Angkor period,³⁹ and it has been also identified in most of the Angkor sculptures collected in the Musée Guimet and the National Museum of Cambodia.⁴⁰ Feldspathic arenite, which constitutes the main subhorizontal tablelands of the Lower to Middle Jurassic Age in northern Cambodia,⁴¹ seems to have been the preferred material for statuary in the highly centralized Angkor kingdom from the tenth to the sixteenth century.⁴² This sandstone forms the shallow bedrock of the region around Koh Ker (fig. 56), some sixty miles northeast of Angkor, which served as the capital of the Khmer empire for a brief time during the reigns of King Jayavarman IV and his son Harshavarman II (928–44). The bedrock could have provided an adequate supply of sandstone for the massive buildings and myriad sculptural works created in the Koh Ker style, exemplified by two male figures in the Metropolitan’s collection, one a kneeling attendant, the other a guardian deity (figs. 57, 58).

Technical rather than geographic or historical motivation seems to have influenced the choice of quartz arenite as a medium. As examples dating from the early tenth to the eleventh century in the Museum’s collection attest (see figs. 59–61), this particular stone appears to have been the favorite material for architectural elements, particularly those carved with intricate detail, in several different pre-Angkor and Angkor styles.⁴³ Quartz arenite was used as well for lintels, columns, and other Angkor architectural fragments of different periods in the Musée Guimet’s collection.⁴⁴ The petrographic data collected on Angkor architecture by Uchida and his coworkers reveal that similar stone, which Uchida calls red sandstone, has been found in the finely carved architectural elements of Banteay Srei, the Angkor temple devoted to the Hindu god Shiva that was consecrated in 967, and in the pillars of the South Kleang in Angkor Thom,



62 · Bust of Hevajra. Cambodia, Angkor period, Khmer style of the Bayon, late 12th–early 13th century. Feldspato-lithic graywacke, h. 52 in. (132.1 cm). The Metropolitan Museum of Art, Fletcher Fund, 1936 (36.96.4)

which also dates to the late tenth century.⁴⁵ Similar examples can be recognized in architectural elements scattered throughout various sites in northern and southern Cambodia.

The markedly immature sandstone rich in volcanic rock fragments appears to have played a specific and short-lived role in Angkor sculptural production. It was used for the sculptures in the Metropolitan that reflect the Khmer style of the Bayon (see fig. 62), the sumptuously decorated Mahayana Buddhist temple that King Jayavarman VII (r. ca. 1180–ca. 1230) built at the center of his capital at Angkor Thom. This supports Douglas and Sorensen’s hypothesis that feldspato-lithic graywacke was predominantly used for sculpture created during Jayavarman VII’s reign.⁴⁶

The Neptune Pendant: Renaissance Jewel or Nineteenth-Century Invention?

•

Mark T. Wypyski

The discovery of a large group of drawings in the Victoria and Albert Museum in London in 1978 was to have a profound impact on the study of Renaissance-period decorative objects. The drawings were identified as by Reinhold Vasters (1827–1909), a German silver- and goldsmith with a reputation for working in medieval- and Renaissance-style decoration. They had been sold as part of Vasters’s estate at an auction house in Aachen in 1909 and ten years and two owners later were presented as a gift to the V&A. The drawings were a set of designs for rock crystal and silver-gilt objects—cups, dishes, plaques, crucifixes—with gold and enamel mounts, as well as Renaissance-style gold jewelry set with gems and decorated with painted enamel. In a 1979 article Charles Truman speculated that rather than simply being records of Renaissance objects, at least some of the drawings may have been designs by Vasters for original pieces done in the Renaissance Revival style.⁴⁷ This revelation prompted the re-examination of decorative arts collections throughout Europe, and a number of objects previously unquestioned as sixteenth- and seventeenth-century originals came to be viewed with skepticism because of their similarity to Vasters’s designs.

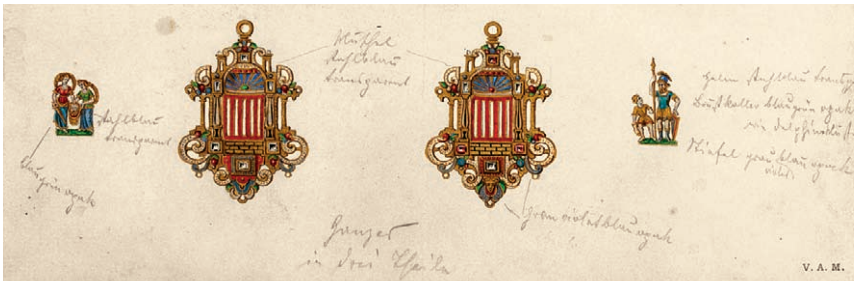
In 1984–85 Yvonne Hackenbroch, then curator emeritus at The Metropolitan Museum of Art, published a study matching decorative objects in the Museum’s and other collections to Vasters’s drawings.⁴⁸ One of these designs was for a type of jewelry that Hackenbroch considered “a true Vasters invention”: a double-sided pendant with two figural scenes placed back to back, each set in a kind of canopied niche, or tabernacle, and flanked by columns. Sculptural

pendants of this sort, according to Hackenbroch, traditionally have flat backs in order to hang correctly when worn. And, she continued, in genuine sixteenth-century examples the different layers are connected with nuts and bolts, rather than being soldered together (“a laborsaving shortcut,” in Hackenbroch’s words) as in the Vasters design.

Hackenbroch was able to link a double-sided pendant in the Walters Art Museum, Baltimore (fig. 63), directly to a design by Vasters (fig. 64). Based on Vasters’s drawing, Hackenbroch reassigned the pendant, which had until then been thought to date to the 1500s, to the late nineteenth century. Her reevaluation was not entirely a surprise, for the Walters pendant had been owned by the storied dealer and collector Frédéric Spitzer (1815–1890) and was included in the sale of his collection in Paris in 1893. Even before the turn of the century it had become clear that alongside the authentic works of art in Spitzer’s vast collection were many objects that had been either restored or made to order in Renaissance style. As Hackenbroch noted, Spitzer is known to have hired a series of artists in Paris, Cologne, Aachen, and elsewhere who made him “old things” (this was reported in 1909 by Stephan Beissel in his book on forged works of art, *Gefälschte Kunstwerke*) and to have “engaged gifted designers and craftsmen, specialists in their own right, [to] study great collections of religious and secular art [and] furnish sketches as points of departure for ingenious repairs or new settings of old fragments.” Recent scientific analysis of the Walters double-sided pendant appeared to confirm that it was indeed produced no earlier than the nineteenth century.⁴⁹



63 · Reinhold Vasters (German, 1827–1909), designer. Double-sided pendant with Judith and her maid with the head of Holofernes and David and Goliath, ca. 1870–90. Gold, enamel, pearls, rubies, diamonds; h. 2 1/8 in. (5.3 cm). The Walters Art Museum, Baltimore (44.424)



64 · Reinhold Vasters. Design for a double-sided pendant, ca. 1870–90. Victoria and Albert Museum, London (E.2847-1919)

Because of its close similarity to the Walters pendant and the drawing for it, Hackenbroch also ascribed a double-sided pendant in the Metropolitan Museum’s collection (fig. 65) to Vasters and dated it to about 1870–90. In the Museum’s pendant two scenes, one with Neptune and the other with Neptune and his wife the Nereid Amphitrite in their chariot drawn by hippocamps, are set back to back in an architectural setting nearly identical to the tabernacle of the Walters pendant. Hackenbroch grouped the two pendants with other nineteenth-century versions of designs by

Flemish goldsmith Erasmus Hornick (who worked in Germany during most of his career and died in Prague in 1583) that had been published in a set of engravings in Nürnberg in 1565. With the aim of either confirming or denying its connection to Vasters, the Metropolitan pendant was subjected to the same type of analysis the Walters jewel had undergone.

Renaissance jewelry usually combines gold, precious stones, and pearls, but it is also commonly decorated with colored enamels. In order to provide objective evidence to help distinguish between authentic Renaissance-period pieces



65 · (above) Double-sided pendant with Neptune and Neptune and Amphitrite. Probably Italian, 16th century, with 19th-century additions. Gold, enamel, jewels, pearls; h. 2 $\frac{3}{8}$ in. (6.7 cm). The Metropolitan Museum of Art, Bequest of Benjamin Altman, 1913 (14.40.665)

66 · (right) Pendant with Prudence. French, ca. 1550–60. Gold, chalcedony, enamel, rubies, emeralds, a diamond, and a pearl; h. 3 $\frac{1}{4}$ in. (8.2 cm). The enameled gold back of the pendant is of 19th-century origin, after a design by Étienne Delaune. The Metropolitan Museum of Art, Gift of J. Pierpont Morgan, 1917 (17.190.907)

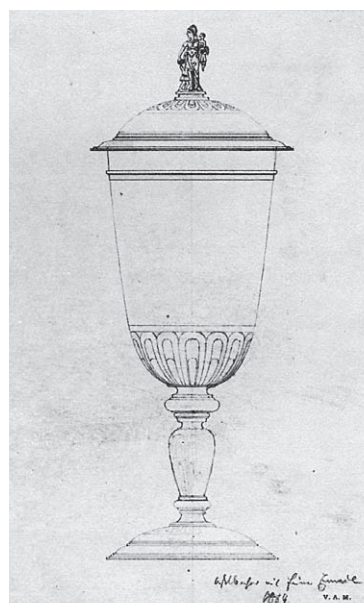
and later pieces done in Renaissance style, the enamels were analyzed on a number of objects in the Metropolitan Museum. This created a reliable database against which other objects could be compared. Tests were conducted, on the one hand, on enameled gold jewelry that has been authoritatively dated to the sixteenth and seventeenth centuries, including a pendant with Prudence that was made in France in about 1550–60 (fig. 66). Enameled gold objects from the eighteenth and nineteenth centuries, including some known to have been designed by Vasters (see figs. 67–70), were also analyzed.⁵⁰



Quantitative chemical analyses of the enamel compositions on the objects were performed in the scanning electron microscope using energy dispersive and wavelength dispersive X-ray spectrometry (SEM-EDS/WDS). This type of compositional analysis, often referred to simply as X-ray microanalysis, is used for all sorts of inorganic materials, such as metals, ceramics, and glass. Because the analysis is usually done on extremely small samples, it is a highly useful technique for the

examination of works of art. As this is a non-destructive technique (i.e., the material being analyzed is not consumed or destroyed), X-ray microanalysis can also be carried out noninvasively directly on the surface of an object, without removing any sample. Surface analysis is limited, however, to objects that fit into the microscope chamber (see figs. 71 and 72). And for vitreous materials a properly prepared sample is usually preferable, as the results of surface analysis can be affected by various factors,

67 · Reinhold Vasters, designer. Covered cup with Charity finial. Rock crystal, enameled gold; h. 10½ in. (26.7 cm). The Metropolitan Museum of Art, Bequest of Benjamin Altman, 1913 (14.40.661a,b)



68–70 · Reinhold Vasters. Three designs for a rock crystal covered cup with Charity finial, ca. 1870–90. Victoria and Albert Museum, London



the most important being deterioration, which alters the chemical composition of the surface.

Enamels are made from glass that is ground up and applied to a metal substrate, where it is fused in place. Analysis of enamels reliably dated to the sixteenth through the nineteenth century identified distinct differences in the overall compositions of Renaissance enamels from the sixteenth and seventeenth centuries and later pieces from the eighteenth and nineteenth centuries. The colorants (metal ions

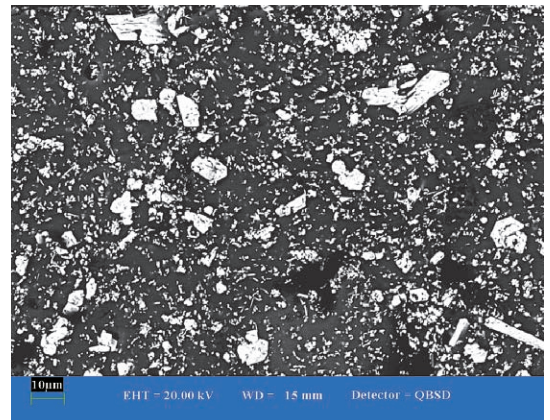
such as copper and cobalt) and the opacifiers (crystalline inclusions in the glass matrix that serve to inhibit the transmission of light, rendering it opaque) used in the two groups of objects also differed (see fig. 73).

The translucent enamels used during the Renaissance generally have soda-silicate, or sodium- and silicon-based, compositions, and they also usually contain relatively large amounts of potassium; relatively small amounts of other glass-forming elements

71 · (left) Pendant (fig. 65) being placed into the chamber of a scanning electron microscope (SEM) for surface analysis of enamels

72 · Scanning electron microscope (SEM) micrograph showing the figure of Neptune on the pendant (fig. 65). The brighter areas are the exposed gold, while the gray areas are white opaque enamel over the gold. Original magnification 36x

73 · Scanning electron microscope (SEM) micrograph of tin oxide crystals in Renaissance-type opaque white enamel. Original magnification 1500x



such as aluminum, magnesium, and calcium; and little if any lead. Translucent red enamels tend to differ somewhat from most of the other colors in that they often contain small amounts of lead, less sodium, and more potassium. Opaque Renaissance enamels all contain significant amounts of lead; white crystalline tin oxide is present in the whites, blues, and turquoise, while green and yellow enamels contain yellow crystals consisting mainly of lead, antimony, and tin.

The colorants in the enamels from the sixteenth and seventeenth centuries are the same metallic oxides used throughout the early history of glassmaking. Blue enamels are colored with cobalt and usually also contain iron, nickel, arsenic, and bismuth, probably unintentional additions from the cobalt ore. So-called black enamel, actually a very dark blue or purple-blue that appears black in reflected light, also contains large amounts of cobalt, usually along with large amounts of manganese, which produces the purple color. Green enamels are colored by the addition of relatively large amounts of both copper and iron (the iron adds a yellow color that serves to shift the bluish color produced by copper alone toward a more true green). Red enamel is also colored with copper, but in a red reduced-oxide form.

In contrast, the overall compositions of enamels from the eighteenth and nineteenth centuries are generally lead-potash-silicate (consisting mainly of lead, potassium, and silicon) or lead-alkali-silicate (containing relatively large amounts of both sodium and potassium). These enamels also typically contain extremely low levels of other common glass-forming elements such as magnesium and calcium. Differences are also seen in the colorants and opacifiers. Blue enamel continued to be colored by cobalt, as it does to this day, but apparently by the eighteenth century a purified form of cobalt was available that no longer contained significant amounts of other elements like arsenic and bismuth. Also during the eighteenth century antimony replaced copper as a colorant in red enamels, and a lead-arsenic compound gradually replaced tin

oxide as the white opacifier. In the nineteenth century green enamel began to be colored with chromium oxide, although it usually contained large amounts of copper as well, and other innovations included the use of uranium as a yellow colorant and the introduction of fluoride-based opacifiers.

The initial examination of the Metropolitan's Neptune pendant (fig. 65) involved the microsampling of several different color enamels from areas of previous loss or damage for quantitative X-ray analysis. This revealed that the translucent colors have soda-based compositions, with oxides of copper as the main colorants in the green and red enamel and cobalt in the blue. The opaque white, blue, and green enamels are also soda-based but contain large amounts of lead as well. The white and blue are opacified with white tin oxide crystals, while the opaque green contains yellow crystals consisting of lead, antimony, and tin and is also colored with a large amount of copper. Both shades of blue contain cobalt as the main colorant, together with significant amounts of bismuth, arsenic, and nickel. All of these enamel samples appeared to be consistent with the compositions of securely dated sixteenth- and seventeenth-century enamels.

To gain a more complete view of the enamels present and to analyze areas where it was not possible to take samples, the surfaces of both sides of the pendant were also examined in the scanning electron microscope (SEM). It soon became apparent that the situation was more complicated than the analysis of the enamel samples had indicated. When the areas from which the samples had been taken were analyzed in the SEM, the initial quantitative results were confirmed. In other areas on both sides of the pendant, however, some of the enamels were found to have lead-potash-based, rather than soda-based, compositions. Green enamel was found that contains chromium as well as copper as a colorant, and red that contains a large amount of antimony but no copper. The high-lead blue enamel also contains cobalt but has no detectable bismuth, and the white has a large amount of arsenic but no tin. These are all characteristics not of Renaissance



74 • Pendant with the Risen Christ(?) flanked by two figures. German or French; Renaissance medallion with frame and chain added in the 19th century by Reinhold Vasters. Gold, enamel, green quartz, rubies, diamonds, pearls; h. 4 in. (10.2 cm). The Metropolitan Museum of Art, Gift of George Blumenthal, 1941 (41.100.30)

enamels but instead of enamels from the nineteenth century. The columns in the architectural framework around the figure of Neptune, for example, are enameled with Renaissance-type white, while the columns on the pendant's other side have the more modern lead arsenate white. The enamel on the bases and the shell-shaped decoration under the figures on both sides is modern; that on the surrounding architectural framework and the niches above the figures is the Renaissance type.

Renaissance and modern enamels have been found on different parts of the same object in other jewels in the Museum's collection. One example is a small pendant with three figures

(fig. 74) that was thought to have been made in Europe during the Renaissance but has a frame that corresponds exactly to another of Vasters's designs in the Victoria and Albert Museum (E.3024-919). X-ray microanalysis confirmed that the enamel on the surrounding border and suspension chain of the pendant is modern and that the enamel on the central medallion is of the Renaissance type. Vasters may have added the framework and chain simply to restore a damaged piece, or his aim might have been to embellish an old piece either to make it appear more valuable or to conform to current fashions or the current view of what a Renaissance piece should look like.

The mix of old and new enamel on the Museum's Neptune pendant means that it too may have a Renaissance origin, as was originally thought before the discovery of the Vasters drawings. Unlike the Walters double-sided pendant, which matches the Vasters design nearly exactly and on which all of the enamels tested were found to be typical of those used in the nineteenth century, the Neptune pendant is probably a restored Renaissance piece, or possibly a pastiche of several different pieces, at least some of which are either wholly modern or were renamed in the nineteenth century. Though it is not completely an original design by Reinhold Vasters, it may have been restored or altered by him. In addition to being a designer of revivalist silver- and goldwork, Vasters also had a reputation as a restorer. At a young age he even worked for the treasury of Aachen Cathedral, where, in the spirit of the historicism of the period, damaged pieces were replaced by replicas or fitted with new parts that were visually indistinguishable from the originals.

Combining technical study with art historical, stylistic, and documentary research can help to reveal the origins of works that lack a firm provenance, as is the case with so many objects in American collections. Scientific analysis may serve to support or deny conclusions based on other evidence, or it may even give rise to an entirely new interpretation and open up new avenues for investigation.

Immunology and Art: Using Antibody-based Techniques to Identify Proteins and Gums in Binding Media and Adhesives

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Julie Arslanoglu and Julia Schultz

Works of art are combinations of materials and cultural influences that vary over time and according to style, taste, region, and artist. Throughout history a great variety of natural products have been used in art, but one of the most common applications of organic materials has been as binding media and adhesives. Mixed with pigments they form the basis for paints, as adhesives they allow solid joints in furniture or repairs to flaking paint, and as varnishes they supply protective coatings for paintings, wood, and other decorative surfaces. Natural binding media and adhesives used in art are made from animal and plant materials. Eggs, milk, and animal glues (made from bones, skin, or fish bladders)—composed primarily of the proteins ovalbumin, casein, and collagen—can not only be found in works of art but have also been used to conserve art. Plant gums such as gum tragacanth, cherry gum, and gum arabic, known as polysaccharides, have been used mainly as binding media for watercolors.

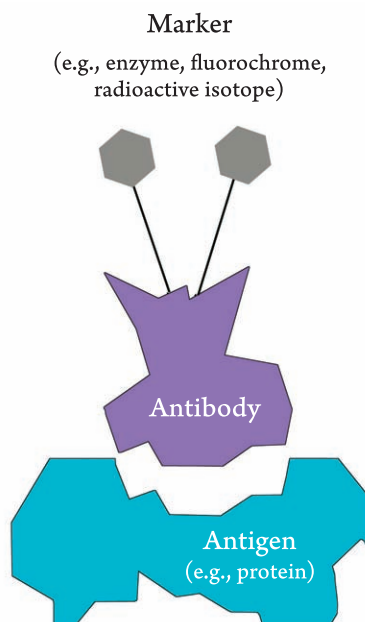
Natural materials, which can be used individually or in combination, are actually complicated chemical mixtures whose composition can alter over time due to human intervention (e.g., conservation treatments), environmental conditions (heat, light, humidity, biodeterioration), and interaction between the components of the mixture. Correctly identifying the organic material in a work of art and understanding its current composition can not only explain phenomena like flaking paint or the growth of microorganisms but also help scientists and conservators devise treatments for halting and preventing such deterioration and determine the best way to display or store an

object in order to preserve it. Knowing the binding media, coatings, or adhesives an artist employed can often reveal his or her working practices and techniques and might also in some cases facilitate authenticating, dating, and determining the regional provenance of an object.

Analyzing the binding media and adhesives on works of art presents special challenges. The organic material can be encased in a complex solid matrix, such as pigment, and its concentration in that matrix tends to be very low. The original organic material may itself be a complex mixture or have become so via the migration of binding media between layers during conservation treatment with adhesives or coatings. In addition, the materials have usually been modified by aging, biological activity, or conservation treatments. And finally, that a sample of the material is required in order to identify proteins and gums dictates that the analytical techniques be both sensitive and specific. One of the main concerns of art-focused scientific analysis is how to obtain information either without a sample or by taking the smallest possible representative sample.

Current analytical methods for the investigation of binding media and adhesives in works of art have limitations. With Fourier transform infrared spectroscopy (FTIR), for example, materials can be classified only into broad categories such as proteins, resins, oils, gums, or waxes. Chromatographic methods such as gas chromatography–mass spectrometry (GC/MS) can identify the material more specifically (collagen, gum tragacanth, linseed oil, or beeswax, for example), but the confident identification of proteins or polysaccharides is

75 • Antibodies made against specific antigens (e.g., collagen, casein, ovalbumin) recognize and bind unambiguously to three-dimensional surface features of the target antigen. They form an antigen-antibody complex. In order to make this complex visible, the antibody can be labeled with a marker, commonly an enzyme, a fluorochrome, or a radioactive isotope.



reduced if the sample is very degraded, part of a complicated mixture, or has been contaminated by an external protein or gum source. Immunological or antibody-based techniques originally developed in the fields of medicine and biotechnology provide an alternative approach. Their acute specificity and high sensitivity allow scientists to verify the presence of gums and to identify and distinguish between proteins such as ovalbumin, casein, and collagen, even in complicated mixtures or in the presence of microbiological contamination.

Immunological techniques take advantage of an organism's immune response to the presence of foreign molecules, or antigens (*antibody-generators*). When the human body is suffering from the flu or any other infection, for example, the immune system mounts an attack by producing antibodies that bind unambiguously to the antigens (the proteins that reside in viruses or bacteria) to form an antigen-antibody complex. In studies of organic materials in art, the antigens are the proteins or gums in the samples taken from the object, recognizable by their specific antibodies, which have been commercially prepared by the immunization of suitable mammals. For analytical purposes, in order to make the antigen-antibody complex visible, the antibody can be labeled with an enzyme,

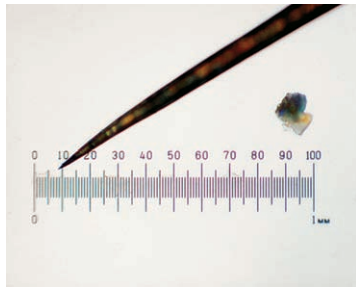
fluorochrome, or radioactive isotope, called a "reporting system." The complexes can then be visualized and measured according to the reporting system by color, fluorescence, or radioactivity (see fig. 75).

In medicine, antibody-based techniques are applied to pregnancy, drug, and HIV tests; identification of blood types; and the diagnosis and treatment of cancer and other diseases. But they have also found their way into more diverse applications such as the characterization of fungal infestation for preservation of historical monuments or the identification of bacteria and dry rot in art.⁵¹ Recent research has also successfully demonstrated the use of immunological methods in the field of conservation science for the identification of proteins and gums in works of art.⁵² In particular, the enzyme-linked immunosorbent assay technique (ELISA) offers great potential in the field of conservation science, since it requires minimal sample handling, is highly sensitive, and is less affected than other methods by protein and gum degradation or contamination. Once the technique is established, ELISA is reasonably straightforward and relatively inexpensive and does not require sophisticated instrumentation. But the major benefit of ELISA is its ability to screen simultaneously for several closely related binding media in a single sample and to specifically identify the components of the mixture (see fig. 76).

ELISA procedures developed for biotechnology do not take into consideration the challenges presented by samples from works of art. It is unrealistic to suppose that an ELISA procedure developed in a medical laboratory to detect a specific disease marker would give optimal results for detection of ovalbumin in, for example, a paint sample from a polychrome sculpture. The feasibility of using immunological methods for the detection and characterization of natural binding media in works of art is not simply a matter of transferring the technology to a different field. The state of degradation and the age of the binding media, interference from pigments and other impurities, biodeterioration, and the efficiency of the extraction method



a



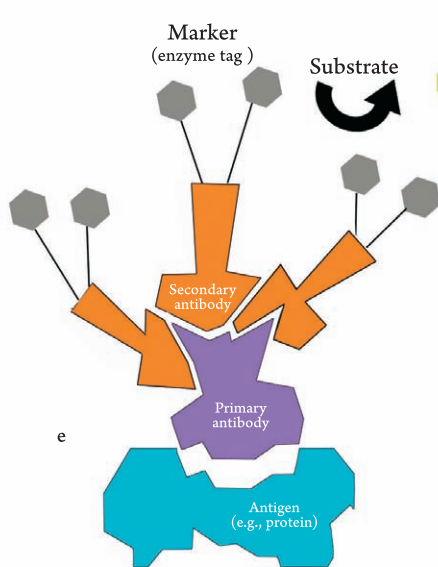
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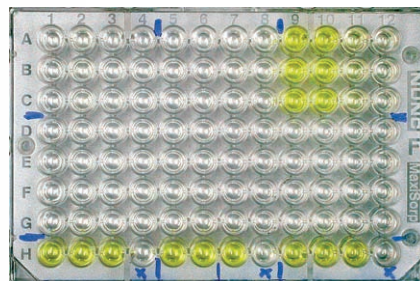
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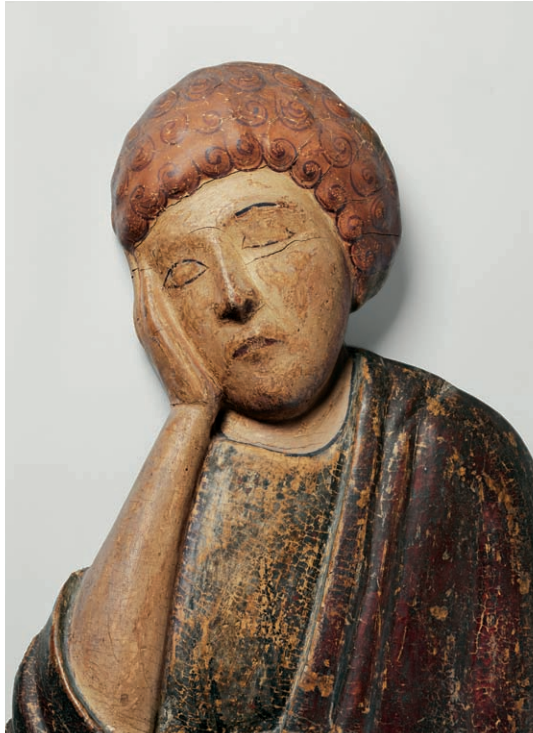
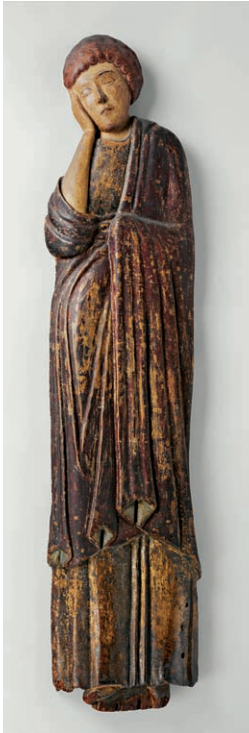
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can all impact the immunological response. These factors can interfere not only with the correct interaction of antibodies or proteins and gums but also with the ability of the detection system to produce a positive response. Furthermore, ELISA is a system of multiple steps and compounds in which each step influences others in the system. Although the ELISA technique has worked well in some cases, previous studies have shown that immunological methods require further research and optimization before they can be used as a reliable analytical tool in art conservation science. During the last two years the Department of Scientific Research at the Metropolitan has been adapting immunological methods, in particular ELISA, with the aim of developing a broad method for reliable and reproducible assays that will allow screening for the most common proteins and gums used in works of art from a single sample in a single experiment. After the parameters for the ELISA protocol and materials were determined, the technique

76 • The ELISA procedure: (a) A small sample is taken from the object in order to answer a specific question. (b) The sample size available for analysis ranges from 30 to 150 micrograms, depending on the nature of the sample, which can be as small as the periods in this text. (c) The proteins and gums in the sample are extracted into an aqueous solution. (d) The unknown sample (antigen) is applied to a MicroWell plate, where the antigen binds to the bottom of the well. (e) The antigen (sample) is then incubated with a solution of specific antibody, which can bind unambiguously to three-dimensional surface features of the antigen. For signal amplification a second solution of antibody is added and incubated. This antibody is linked to an enzyme, and in the final step an appropriate colorless compound (substrate) is added and is converted by the enzyme to yield a detectable colorimetric signal (see Crowther 2001). (f) If the target proteins or gums are present and the concentration is high enough, the wells turn color; otherwise they remain colorless. (g) The results can be observed with the naked eye but are more accurately measured with a spectrophotometer, which measures the optical density (the amount of light absorbed) at a particular wavelength for the colored reaction.

was extensively tested and evaluated on samples from replicas before it was applied to works of art.

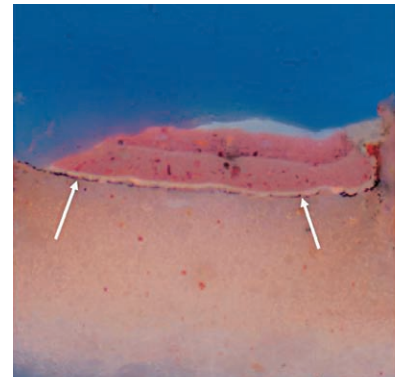
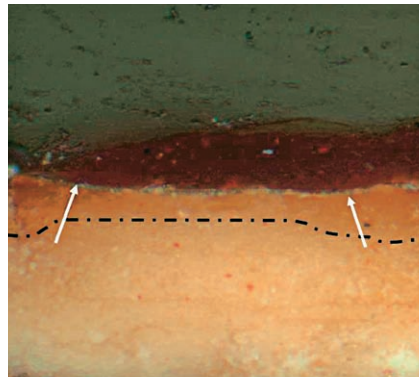
The ELISA method proved invaluable in the study of *Saint John*, an Italian polychrome statue from a late thirteenth-century Crucifixion group at The Cloisters (fig. 77). The figure was carved from red pine that was covered with canvas and gesso and painted. The garments are gilded with tin foil, or tin leaf, and glazed



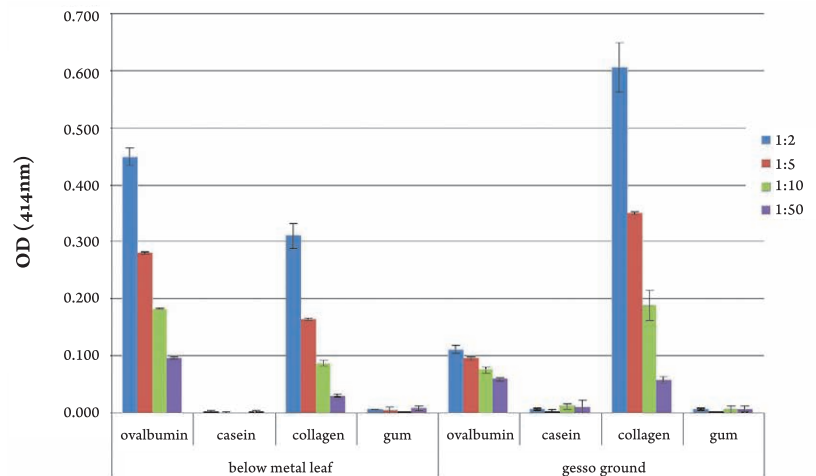
77 · *Saint John* (with detail). Italy, late 13th century. Red pine covered with canvas, gesso, and tin foil and painted with oil glazes; h. 57½ in. (146.1 cm). The Metropolitan Museum of Art, The Cloisters Collection, 1925 (25.120.215)

with oil-resin coatings. In polychrome sculptures the gesso layer is a foundation layer, usually composed of chalk or gypsum combined with animal glue (collagen).⁵³ If the gilding is burnished, the leaf would have been applied either on an additional bole layer (clay-glue mixture) or directly on the gesso with animal glue or egg white (ovalbumin), which is called ground-gilding.⁵⁴ As part of his research on Italian medieval sculpture to be included in a forthcoming catalogue of the collection,⁵⁵ Jack Soutanian, conservator in the Department of Objects Conservation, wanted to determine the nature of the adhesive saturation of the

78 · Cross section of a sample of layers of gesso, paint, gilding, and glazes on *Saint John* (fig. 77) in normal (left) and ultraviolet (right) illumination. In normal illumination a slight saturation of the gesso immediately beneath the metal leaf layer is visible (outlined by the black dotted line), indicating that an adhesive was used for the application of the leaf. Above the thick gesso layer is a very thin layer of tin leaf (indicated by white arrows in both photographs) that is barely visible under normal illumination but can be clearly seen as a thin, dark layer under ultraviolet illumination. Various oil-resin coatings lie on top of the tin leaf. Original magnification 200x



79 · ELISA result for the identification of the binding medium on *Saint John* (fig. 77). On the left is the result for a scraping of the gesso layer and the gilding adhesive immediately below the metal leaf. On the right is the result for a scraping of only the gesso layer beneath those two layers. In order to confirm the presence of the antigen, four dilutions were prepared from each sample, one for each antibody: ovalbumin (egg), casein (milk), collagen (animal glue), and polysaccharides (gums). Both ovalbumin and collagen are clearly present in the first sample, while only collagen is present in the second. Thus the binder for the gesso is animal glue and the adhesive for the gilding is egg.



Sample and target molecules

gesso layer he observed just beneath the gilding on the *Saint John*, which is typical of ground-gilding.

A sample containing all the layers of gesso, paint, gilding, and glazes was taken from the sculpture. Examination of a mounted cross section of the sample under the microscope showed a slight saturation of the gesso immediately beneath the metal leaf layer (fig. 78), confirming that an adhesive may have been used for the application of the leaf. Attenuated total reflectance (ATR)-FTIR microspectroscopy of the cross section could verify the presence of protein in the gesso and in the upper saturated area but could not provide specific information about its identity. It did, however, exclude an oil or a resin as a binding adhesive. Indirect ELISA testing for collagen, ovalbumin, casein, and gum was proposed.⁵⁶ ELISA can easily identify mixtures of binding media but only gives information on the protein and gum content of the whole sample. Because the gilding adhesive did not form a distinct layer that could be clearly separated from the gesso or the gilding layer, the sample for analysis was a mixture of the two materials. A scraping from the gesso layer immediately below the gesso saturated with adhesive was also sampled for comparison, so that the binder of the gesso could be distinguished, if appropriate, from the gilding adhesive. The ELISA analysis clearly showed that collagen (animal glue) is the binder for the gesso and that ovalbumin (egg) is the adhesive for the gilding (fig. 79).

The indirect ELISA method was also applied to the examination of the Nur al-Din Room (fig. 80), a winter reception room from an upper-class Syrian house with inscriptions dating it to 1707. The wooden panels of the room are ornamented with pastiglia, or raised designs made of gesso, mainly in floral patterns or poetic inscriptions in Arabic. The literature suggests that animal glue and egg, as well as gums, may have been used as binding media for the pastiglia and the different paints. The possibility that mixtures of proteins and gums may be present makes these materials ideal candidates for ELISA analysis. Two different samples were taken, one from the pastiglia

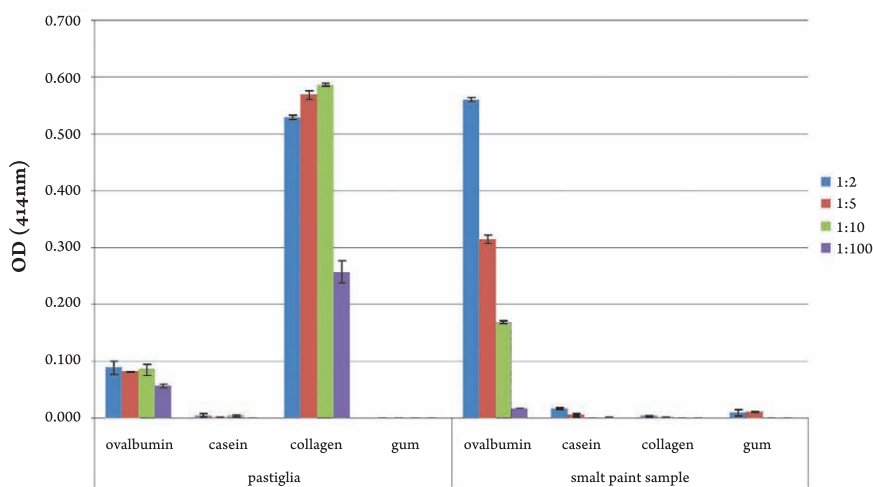
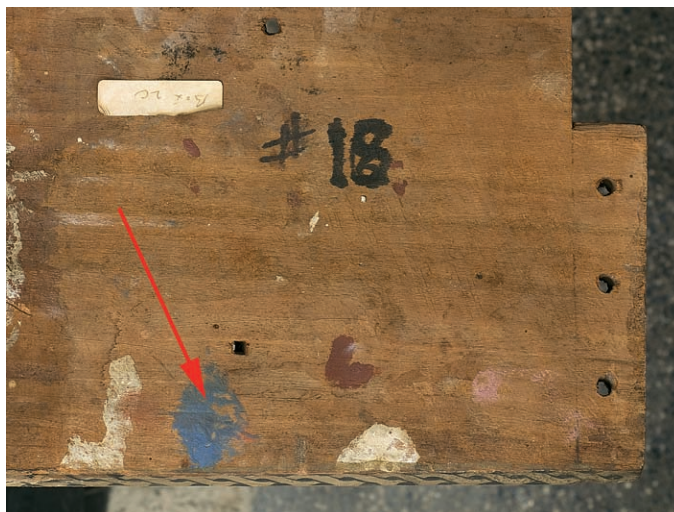
underlying paint layers on a panel on the ceiling and the other, a blue smalt paint sample, from the protected back of an inscription panel (fig. 81). The samples were tested for ovalbumin, casein, collagen, and gum (fig. 82). The result for the pastiglia shows the presence of two different proteins: collagen is the main binding medium, yet traces of ovalbumin were also detected. That the binding medium was a mixture of proteins cannot be excluded, but it is more likely that the ovalbumin migrated or penetrated from other paint layers or was introduced during a former consolidation or

80 • Nur al-Din Room. Damascus, Syria; dated A.H. 1119/ A.D. 1707 in an inscription. Wood, marble, stucco, glass, mother-of-pearl, ceramics, tile, stone, iron, colors, gold; h. 22 ft. ½ in., w. 16 ft. 8½ in. (6.72 x 5.1 m), d. from inside front entrance to back wall 26 ft. 4¾ in. (8 m). The Metropolitan Museum of Art, Gift of The Hagop Kevorkian Fund, 1970 (1970.170)





81 · To test for ovalbumin, casein, collagen, and gum, samples were taken in the Nur al-Din Room (fig. 8o) from areas of the pastiglia on a panel of the ceiling (left) and from a patch of smalt paint on the protected back of an inscription panel (below).



Sample and target molecules

82 · ELISA result for the identification of the binding medium in pastiglia and smalt paint from the Nur al-Din Room (fig. 8o). From each sample, four dilutions of the extraction were prepared for each antibody: ovalbumin (egg), casein (milk), collagen (animal glue), and polysaccharides (gums). Both collagen and ovalbumin are clearly present in the pastiglia sample, while only ovalbumin is present in the smalt paint. This result suggests that the ovalbumin traces found in the pastiglia are a result of migration or penetration from the smalt layer above. Thus, the binder for the pastiglia is animal glue (collagen) and the binder for the smalt paint is egg (ovalbumin).

restoration. The result for the protected smalt paint clearly shows that ovalbumin is the only binding medium present (which means that the ovalbumin in the pastiglia is likely to have come from the paint layers above).⁵⁷ The results are significant because they clearly demonstrate that different binding media were selected for different pigments and different types of paint.

Antibody-based techniques are clearly poised to take a significant and complementary role in the analysis of works of art in the near future. Already the ELISA technique has proven to be an effective and useful analytical

tool, its greatest asset being the unambiguous identification and differentiation of proteins and gums, even in mixtures, in a single experiment on a relatively small sample. In the Department of Scientific Research ELISA is being used to analyze a broad range of art samples in order to ensure the reliability of the technique, and ongoing research designed to ameliorate limitations such as sample extraction, pigment interference, and degradation state will continue to improve our ability to apply the ELISA technique to works of art and interpret the results.

Notes

- 1 I am greatly indebted for this information to Larry Becker and Deborah Schorsch, whose detailed article on the history of objects conservation at the Museum is forthcoming in fall 2009.
- 2 In Raman microspectroscopy the sample material is irradiated with a laser beam, and the radiation that is scattered from this sample is collected and analyzed in the spectrometer. From the analysis of the number and the energy of the photons scattered it is possible to get information about the molecular structure and other properties of the compounds that make up the sample. A Raman spectrum is generally a fingerprint of the materials.
- 3 Raman spectra were recorded with a Renishaw System 1000 spectrometer, using 785 and 514 nm lasers. The laser beam was focused on different areas of the cross sections using x50 objective lenses, allowing spatial resolution in the order of 2–3 micrometers. Powers in the order of 1–5 mW were used, with accumulation times between 10 and 100 seconds. Identification of the materials was done by comparing the spectra of the unknown compounds with those of reference compounds.
- 4 See Noble et al. 2000; Boon et al. 2002; Noble, Boon, and Wadum 2002; Higgitt, Spring, and Saunders 2003; Keune 2005; and Noble, Van Loon, and Boon 2005.
- 5 The heavy metal soaps may further react, presumably with carbon dioxide from the environment, to form lead carbonates, often rich in chlorides, and zinc carbonates—a process called mineralization. Red particles of the lead oxide minium have also been observed in some cases in association with the lead-containing saponified areas. The mechanisms of these soap mineralization reactions have still to be fully elucidated. See Boon et al. 2002 and Keune 2005.
- 6 Noble, Boon, and Wadum 2002; Keune 2005; Noble, Van Loon, and Boon 2005.
- 7 Noble, Van Loon, and Boon 2005; Van Loon 2008.
- 8 Energy dispersive X-ray spectrometry (SEM-EDS) showed that the carbon-based black layer contains (in atomic percents) 98% carbon, .3% calcium, and .1% phosphorus, along with 1.5% lead and .2% copper, allowing the presence of a bone black or ivory black pigment to be ruled out (see Winter 1983). Bone black has been reported to undergo a light-induced deterioration process catalyzed by lead ions in which a white layer is formed on the surface of the black paint (see Van Loon and Boon 2004). SEM-EDS elemental analyses were carried out using an Oxford Instruments INCA analyzer equipped with a Link Pentafet high resolution Si(Li) SATW X-ray detector attached to a LEO Electron Microscopy model 1455VP variable-pressure scanning electron microscope. Analyses were performed under high vacuum conditions at an accelerating voltage of 20 kV in both uncoated and carbon-coated sample cross sections. SEM-EDS analyses were carried out by Mark T. Wypyski.
- 9 Van Loon 2008. Lead soaps present on the dark paint surface may mineralize by reacting with particulates and pollutants in the environment, as well as with other paint components, to form lead sulfates, lead chlorides, lead carbonates, or more complex salts. The thinness of the whitish top layer in Van Ravesteyn's *Portrait of a Woman* prevented its analysis by Raman microspectroscopy. It is not possible to determine by EDS alone whether the lead in the thin whitish deposit is present as a soap or if the soap has mineralized to form inorganic salts. Likewise, it is not possible to identify the nature of the phosphorus- and/or calcium-containing compounds in this layer or to determine the role of calcium in the soap formation and mineralization process.
- 10 Noble, Van Loon, and Boon 2005. Raman bands characteristic of lead soaps were observed in the top paint layer containing a mixture of lead white and smalt. It has been reported that when smalt degrades potassium is leached from the pigment particles and migrates into the paint matrix, where it forms potassium soaps, and also to the paint surface (Spring, Higgitt, and Saunders 2005). This process has been demonstrated in artificially aged samples and deserves further investigation in Hobbema's *Village among Trees* and other works with a similar composition showing visual alterations.
- 11 Noble, Van Loon, and Boon 2005; Van Loon 2008.
- 12 Middleton et al. 2007; Sanz Minguez, Campano Lorenzo, and Rodríguez Marcos 1990.
- 13 Karageorghis 2000, pp. 290–91, no. 483; Oliver 1966, p. 283, fig. 28.
- 14 Richter 1924, p. 35, fig. 6.
- 15 For example, as shown in Gwinnett and Gorelick 1981.
- 16 All analyses were with Cu K α radiation and a 300 μ m (micrometer) collimator. In most cases, simultaneous oscillation about two axes of the goniometer during an exposure time of twelve minutes was found sufficient to capture all Bragg reflections with reasonable continuity of the Debye rings.
- 17 Scans were made between 5° and 90° 2 θ using Cu K α radiation, a .02° step size, and a continuous scan rate of 1.2° per minute.
- 18 Our initial diffraction data prompted us to consider using Raman microprobe spectrometry as a complementary analytical approach in view of its rapid and nondestructive capability for distinguishing members of the variscite group (Frost et al. 2004). As other workers have similarly reported, however, our efforts to acquire useful spectra from the often pitted and weathered surfaces of the beads were heavily compromised by high background fluorescence and scattering under a wide range of analytical conditions (Middleton et al. 2007).
- 19 EDS analyses were performed using an Oxford Instruments INCA Energy 300 energy dispersive X-ray spectrometer microanalysis system integrated with the LEO 1455VP variable-pressure scanning electron microscope. The SEM was operated at an accelerating voltage of 20 kV. Imaging and analyses were done both under standard high vacuum with the secondary electron detector and in the low-pressure mode with a chamber pressure of approximately 100 pascals, with images taken using the variable-pressure secondary electron detector.
- 20 Based on unrestricted searches of the International Centre for Diffraction Data (ICDD), Powder Diffraction File 2 (PDF-2) database, release 2006. Of the several file patterns for variscite in the database, that listed for the 4O polytype (00-025-0018) was consistently found to provide the best overall match with the patterns obtained from the beads.
- 21 This is consistent with the absence of evidence in the diffraction patterns for either the iron-bearing end-member of the variscite-strengite series or the related aluminum phosphate mineral, turquoise, to which variscite is visually similar.
- 22 Middleton et al. 2007.
- 23 Anthony et al. 2000.
- 24 Camprubí et al. 2003; Harrison and Orozco Köler 2001; Querré, Herbault, and Calligaro 2008.
- 25 Querré, Herbault, and Calligaro 2008.
- 26 Middleton et al. 2007, p. 31; Sanz Minguez, Campano Lorenzo, and Rodríguez Marcos 1990, figs. 2, 3, 6.
- 27 That complete diffractometer-based powder patterns are obtained from the sides of the prisms without rotation also supports this conclusion.
- 28 Our beads are dissimilar in size and shape to and compare only in a generic way with the variscite beads excavated from the Roman site at Grange Farm in Kent and recently published by researchers at the British Museum (Middleton et al. 2007), but the article refers to several other beads having octagonal cross sections that have been discovered in Roman Britain.
- 29 Sanz Minguez, Campano Lorenzo, and Rodríguez Marcos 1990.
- 30 Middleton et al. 2007.
- 31 See Delvert 1963 and Douglas 2004.
- 32 See Pettijohn 1975.
- 33 Other accessory minerals are altered alkali feldspar, which in some samples can be as much as 20% of the total framework; muscovite flakes; and layered opaque minerals, mostly ilmenite and fine-grained hematite. If chert grains are excluded, the rock fragments are poorly represented only by small, elongated grains of micaceous schist. The heavy mineral fraction is almost absent.
- 34 Feldspars are often albitized or altered to sericite, while calcite replacement of feldspars as well as of quartz and lithic fragments is abundant. The content in muscovite and biotite is generally minor, and can vary up to 6% of the total framework, with biotite generally prevailing over muscovite. Accessory minerals are epidote, sphene, apatite, zircon, clino- and orthopyroxenes, amphiboles, tourmaline, and magnetite.
- 35 Metamorphic rock fragments are micaceous schist, phyllite, shale, and rare chlorite schist. Volcanic rock fragments have variable dimensions, from a few tenths of a micrometer up to one millimeter. They consist of andesitic to rhyolitic volcanoclasts in different proportions. Carbonate rock fragments include micritic to spathic calcite grains and can vary widely in abundance, up to as much as one-third of the total volume of lithic grains.
- 36 Close observation can reveal frequent pseudomatrix resulting from the breakdown of less competent volcanic and sedimentary lithic fragments.
- 37 See Delvert 1963 and Uchida, Ogawa, and Nakagawa 1998.
- 38 A similar stone used for Angkor statuary has been described by Delvert 1963; Uchida, Ogawa, and Nakagawa 1998; Baptiste et al. 2001; and Douglas 2004.
- 39 See Delvert 1963 and Uchida, Ogawa, and Hirari 1995.
- 40 Baptiste et al. 2001, Douglas 2004.
- 41 Phan 1991, United Nations 1993, Sotham 1997.
- 42 It must be noted that other types of stone have been used for Angkor-style statuary, as was confirmed by this petrographic study. During the early stages of the Angkor empire sculptures in the styles of Kulen (800–875), Preah Ko (875–900), and Bakheng (900–925) were carved from the same graywacke as was used during the pre-Angkor period, while some sculptures in the style of Banteay Srei (ca. 976) were realized from a different, green to bluish graywacke. According to the existing petrographic data, Baphuon-style (eleventh-century) sculptures of reduced size were specifically carved from a very fine, compact, immature sandstone.
- 43 The ongoing petrographic study at the Metropolitan Museum includes lintels dating from the seventh to the twelfth century. Among the studied samples, quartz arenite dominates, although some lintels are carved from feldspathic arenite.
- 44 Baptiste et al. 2001.
- 45 Uchida, Ogawa, and Hirari 1995.
- 46 Douglas and Sorensen 2007.
- 47 Truman 1979.
- 48 Hackenbroch 1984–85.
- 49 Drayman-Weisser and Wypyski 2005.
- 50 Wypyski 2000, 2002, 2007.
- 51 Möhlenhoff 2002, Rolfes 1991, Leupold 2006, Reichmann 2003.
- 52 See Hodgins 1999; Heginbotham, Millay, and Quick 2004; and Mazurek 2006.
- 53 Cennini 1960, pp. 67–71.
- 54 Nadolny 2006.
- 55 Castelnuovo-Tedesco and Soutanian 2010.
- 56 The indirect ELISA is used in order to amplify the signal. A second antibody is added to the system. The unlabeled primary antibody binds to the antigen, and the enzyme-conjugated secondary antibody binds to the primary antibody. Thus the primary antibody acts as an antigen (target molecule) for the secondary antibody.
- 57 Further ELISA analysis of a sample from paint adjacent to the pastiglia was shown to contain both ovalbumin and collagen. The identification of this paint binding medium as egg is confirmed by the egg binding medium identified in the protected smalt paint sample. However, the presence of collagen in this particular paint sample can most likely be attributed to conservation treatment, since no pastiglia was present in the paint sample analyzed.

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Authors' Acknowledgments

Silvia A. Centeno and Dorothy Mahon would like to acknowledge Mark T. Wypyski, research scientist in the Museum's Department of Scientific Research, who carried out the SEM-EDS analyses, and Winifred Murray, who contributed to the examination and carried out the conservation treatment of Jan van Ravesteyn's *Portrait of a Woman* in fulfillment of course requirements for her Certificate of Advanced Study at the Conservation Center, Institute of Fine Arts, New York University. They are also indebted to Petria Noble, head of conservation, Royal Picture Gallery Mauritshuis, The Hague, for her contribution to groundbreaking research on the soap formation process and her continuing generous advice on this topic.

Tony Frantz, Dorothy H. Abramitis, Linda Borsch, and Mark T. Wypyski thank Carlos A. Picón, curator in charge, and Christopher S. Lightfoot, curator, Department of Greek and Roman Art, for facilitating access to the jewelry discussed in their paper; Jamie Newman, Department of Earth and Planetary Sciences, American Museum of Natural History, New York, for providing the sample of variscite from Barcelona; and Paul Lachenauer of the Museum's Photograph Studio for photography of the jewelry and variscite sample. The X-ray microdiffraction instrument referenced in this paper was acquired jointly by the American Museum of Natural History, The Metropolitan Museum of Art, and Columbia University with the support of the National Science Foundation and The L. W. Frohlich Charitable Trust.

Federico Carò, whose research is supported by an Andrew W. Mellon Fellowship at The Metropolitan Museum of Art, is grateful to a number of Museum staff members for their support, comments, and suggestions, including John Guy, curator, and Kurt Behrendt, assistant curator, Department of Asian Art; Donna Strahan, conservator, Department of Objects Conservation; and Paul Lavy, J. Clawson Mills Fellow. He thanks the many people and institutions in Cambodia whose cooperation has made this project possible, in particular Hab Touch, director of the National Museum of Cambodia, for giving him permission to study samples obtained from their collections, and Bertrand Porte, stone conservator with the École Française d'Extrême-Orient (EFEO), for his support in the sampling campaign at the National Museum of Cambodia. He is

indebted as well to Bun Narith, director general, and Khun-Neay Khuon, deputy director general, Authority for the Protection and Management of Angkor and the Region of Siem Reap (APSARA), for supporting the project, and to Im Sokrithy, also of APSARA, for his valuable and constant help in the surveying of Khmer quarries. Special thanks go to Sieng Sotham, director of the Department of Geology, Ministry of Industry, Mines and Energy in Phnom Penh.

Mark T. Wypyski would like to thank Clare Vincent, associate curator in the Department of European Sculpture and Decorative Arts, for her help with his article on the Museum's Neptune pendant and the long-term study of Renaissance enamels.

Julie Arslanoglu and Julia Schultz, Andrew W. Mellon Conservation Fellow, wish to thank Jack Soutanian Jr., conservator, Department of Objects Conservation; Adriana Rizzo, assistant research scientist, Department of Scientific Research, and Akiko Yamazaki-Kleps, assistant conservator, Department of Paper Conservation, for their contributions. The authors also thank Crtomir Tavzes, Institute for Wood Technology of Ljubljana, Slovenia, and New York University students Matthew Van Auken, Scott Breitingner, and Margaret Bezrucyk for their contribution to the ongoing ELISA project at the Metropolitan.

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