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Archaeological Chemistry VIII

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Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

Preface

The 12th Archaeological Chemistry Symposium was held as part of the Spring ACS National Meeting in New Orleans, Louisiana, April 7–11, 2013. This volume is a compilation of presentations from the Symposium, the latest in a long tradition that began at the ACS National Meeting in Philadelphia in 1950. The numbering of the symposia is, however, somewhat in question. According to Brill (*1*), "…memories of only the First and Third Symposia remained clear [at the 4th Symposium]… We leave it (with a blush) to the historians…to decide upon the reality of the Second Symposium…"

The symposium consisted of four half-day symposia, an evening poster session, and a keynote address by Dr. A. Mark Pollard, Edward Hall Professor of Archaeological Science and Director of the Research Laboratory for Archaeology and the History of Art at the University of Oxford. We choose four broad categories for the symposia: Pigments, Residues and Material Analysis, X-Ray Fluorescence Spectroscopy, and Isotopes in Archaeology. These categories are by no means comprehensive. Rather, they serve as a snapshot perspective of archaeological chemistry today and are necessarily biased toward our areas of expertise and those of the participants in a chemistry meeting. Notably, studies of ancient DNA and other advances in biomolecular archaeology are underrepresented in this volume.

The papers herein show that archaeological chemistry today is more than the usual studies of trace elements in pottery and lithics, which continue to contribute to our understanding of human behavior in the past. New areas of research include more focus on portability to analyze pigments in situ and artifacts in museums, nascent developments in non- and minimally destructive chemical characterization, new applications of isotopic analyses, and an increasing interest in archaeological biomolecules.

This volume is divided into sections that roughly follow those of the Symposium. The first section, Pigments and Dyes, begins with a review of manuscript pigments by Dr. Mary Virginia Orna, the organizer of the 9th Archaeological Chemistry Symposium and Editor of *Archaeological Chemistry: Organic, Inorganic, and Biochemical Analysis* (*2*). Each of the following sections begins with a review paper from one of our invited speakers. Dr. Valerie Steele, now at the University of Bradford in the Department of Archaeological Science, provides an overview of the state — for better and for worse — of analyses of archaeological residues. Portable X-ray fluorescence instruments are becoming extremely common in archaeological chemistry investigations; Dr. Aaron Shugar of Buffalo State University provides in his chapter some perspectives and warnings against the indiscriminate use of this technology. Finally, Dr. Matthew

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Sponheimer gives an overview of the contributions of stable carbon isotope and trace metal studies in understanding early hominin diets.

The final chapter of the book provides a perspective on the earliest work in archaeological chemistry in the 18th century and brings us up to today's challenges. We find ourselves in Dr. Pollard's text, carrying out our own research "on a wing and a prayer, " as both the solitary chemist supported by her institution in part for the accessible public interest aspect of her research and a scientist within an anthropology department, fighting for funding in this era of sequestration and downsizing. We hope that this volume contributes toward the "open, respectful, meaningful and iterative dialogue across the many disciplinary boundaries" encountered in archaeological chemistry (*3*).

We thank all of the contributors and reviewers for their time and effort. We especially thank technical editor Arlene Furman of ACS Books for her patience and help in producing this volume, and Seth Rasmussen, Tom Strom, and Vera Mainz from the Division of the History of Chemistry (HIST) for all their help in organizing and running the Symposium. HIST and the ACS Divisional Activities Committee provided the majority of the funding for the Symposium, with additional support from the Society for Archaeological Sciences and Bruker Corporation.

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Chapter 1

Artists' Pigments in Illuminated Medieval Manuscripts: Tracing Artistic Influences and Connections—A Review

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For the art historian, chemical analysis of pigments serves two main purposes. It can confirm or deny the alleged attribution or dating of a painting based on comparison with the known painting practices of the artist or period. In addition, the analysis of pigments can have a broader, and perhaps a more profound, importance to the historian as a tool for understanding more about the artistic process itself. This paper reviews the collaborative building of a pigment database, tracing lines of influence and interconnection between medieval centers of manuscript production, clarifying periods of known usage of several important artists' pigments, the difference in pigment usage between Armenian and Byzantine artists, the problems involved with handling manuscripts directly, and anachronistic pigment usage. The technical future of chemical analysis of medieval manuscripts is also discussed.

Introduction

"Color is the most visual, pervasive example of the importance of chemistry to our lives" (*1*). Though medieval artists could not have realized nor expressed this observation since the formal discipline of chemistry would not exist for centuries yet to come, color, for them, was the most visual and pervasive reality in their pursuit of crafting the manuscripts they handed on to us as precious treasures of their era. This paper will review the scientific identification of artists' colors used in manuscripts between the 10th and 16th centuries for the following purposes:

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- To determine or confirm place of origin and date;
- To trace lines of influence between and among painting schools and cultures;
- To recommend conservation & handling practice based on the content;
- To uncover forgeries (de-authentication);
- To specify attributions among different painters in a manuscript.

In addition to these objectives, Robert Feller (*2*) lists two additional ones: objective description of method, and restoration. Although the identification method used and described here consisted of extracting minute samples for analysis by means of X-ray diffraction, infrared spectroscopy and measurement of refractive index, this approach is now questionable in light of the availability of newer, non-invasive techniques that allow the analyst access to the manuscript in situ. The value of these methods will be discussed later in this paper.

The manuscripts described and analyzed in this work came from a variety of Armenian and Byzantine workshops; the dates of their creation range from the early 10th century to the late 16th century.

Pilot Project: The Gladzor (Glajor) Gospel Book of UCLA

The Gladzor Gospel Book (Armenian MS 1, UCLA) has been the subject of very extensive study. Analysis of its palette by X-ray diffraction, Fourier transform infrared spectroscopy and refractive index measurements yielded some rather startling information: virtually all of the pigments used in its manufacture were of mineral origin with the exception of red (madder) lake, which was employed by all five of the artists who worked on the manuscript, and of gamboge, used by the three "apprentice" artists who worked in an atelier other than that of the two master painters (*3*, *4*). A summary of pigment usage by atelier is given in Table I; examples of two of the pigments is shown below in Figure 1.

Madder was derived from the roots of the *Rubia tinctorum* and other members of the *Rubiaceae* family. It has been known from ancient times, having been described by Strabo, Pliny the Elder, Dioscorides and the Talmud. Though most often used as a dye, it could also be used as a pigment if precipitated on a solid substrate such as aluminum hydroxide (*5*). Gamboge was another plant-derived colorant taken from the sap or ooze of trees of the genus *Garcinia*. It, too, was used extensively from ancient times (*6*). Since neither of these organic pigments was used extensively in the manuscript, one could safely say that shielding the work from light would not be a principal concern since mineral pigments are virtually lightfast over indefinite periods of time. Such analyses are enormously helpful to curators and conservators who must control the handling of such precious documents.

Analysis of the Gladzor (Glajor is an alternative spelling) Gospel Book not only yielded helpful information regarding conservation, but also was helpful in specifying attributions among different painters in the manuscript. Differences in the employment of the blue pigments indicated the involvement of two different workshops: one used azurite (basic copper(II) carbonate) and high quality natural

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ultramine, while the other used lesser quality natural ultramarine. The second workshop also used a purple pigment that consisted of a mixture of red lake and ultramarine; this occurred nowhere in the miniatures attributed to the first workshop. Likewise, gamboge, used in the second workshop was not found among the pigments of the first workshop (*4*).

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Table I. Pigments Listed by Atelier as Used in the Gladzor Gospel Book (*3*, *4*)

Hue	*"Master Painter" Atelier*	*"Apprentice" Atelier*
Black	Charcoal black	Charcoal black
Blue	Azurite; Ultramarine	Ultramarine + Ultramarine Ash
Brown	Vermilion mixed with orpiment, gypsum and charcoal black	Vermilion mixed variously with orpiment, gypsum, charcoal black, whiting and hydrated iron oxide
Flesh	Orpiment mixed with realgar	Orpiment mixed with realgar, gamboge, gypsum and anhydrite
Gold	Gold	Gold
Green	Orpiment mixed with azurite or with ultramarine	Orpiment mixed with gamboge or ultramarine plus anhydrite and a trace of vermilion
Magenta	Red lake or red lake mixed with white lead	Red lake
Olive		Gamboge
Orange		Minium or orpiment mixed with minium
Purple		Ultramarine mixed with red lake
Red	Vermilion	Vermilion
White	Calcined bone mixed with quartz	White lead
Yellow	Orpiment	Gamboge, or orpiment mixed with massicot, or realgar mixed with orpiment, gamboge and massicot

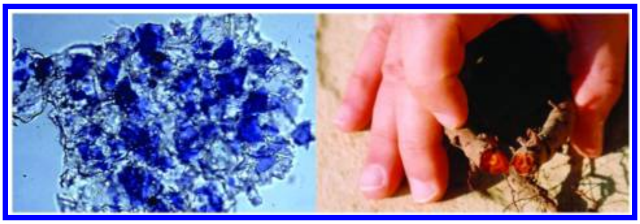

Figure 1. Two pigments found throughout the pages of the Gladzor Gospel Book. Left: A photo-micrograph (130X magnification) of natural ultramarine. (Photograph by M. V. Orna); Right: A broken-open sample of a madder root, Rubia tinctorum (Photograph courtesy of Zvi C. Koren).

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Additional Analyses of Armenian and Byzantine Manuscripts

Such a wealth of information was gathered from this pilot project that it was deemed important to try to gather as much information from other Armenian manuscripts to determine if there was indeed a traditional Armenian palette, and also to compare this palette with manuscripts of different origins, such as Byzantine, Persian, Iranian, etc. origins. Hence, the second phase of the study comprised the analysis of the pigments of manuscripts in the United States and Israel representing four distinct developments in the history of Armenian art: A) manuscripts of Greater Armenia and Melitene in the 10th and 11th centuries; B) manuscripts in the vicinity of Lake Sevan in the 12th to 14th centuries (northeastern Greater Armenia); C) manuscripts in the vicinity of Lake Van in the 14th and 15th centuries (central Armenia) (*7*, *8*) and D) manuscripts of the Armenian Kingdom of Cilicia in the 13th and 14th centuries (*9*). Table II is a summary table of all twenty-four of the Armenian manuscripts analyzed by the Cabelli-Orna-Mathews group (*10*). Figure 2 is an illustration from one of these manuscripts, the monumental Trebizond Gospel, so-named from its find spot, but likely to have been produced in the area of Tsamandos (*11*) in eastern Turkey (*12*). In the pages following the summary, the results of the analyses are given and are compared to Byzantine manuscripts at the University of Chicago (Table III lists the ten manuscripts analyzed by Orna and Mathews (*13*, *14*), nineteen Iranian and eleven Indian manuscripts from the Vever Collection in the Arthur M. Sackler Collection of the Smithsonian Institution (*15*), and eight Persian and three Turkish manuscripts from the Spencer Collection of the New York City Public Library (*16*).

Needless to say, it would be impossible to include the volume of data obtained from these manuscripts in this paper, but some observations on the occurrence of certain common pigments present in them will allow us to draw some conclusions about pigment usage in the greater Middle East during the time period in question. We must realize, of course, that this is a very small sampling of the entire corpus of extant manuscripts of these genres, so any generalizations must be tentative. With these caveats in mind, we have selected certain pigments of each observed hue and listed in Table IV their occurrence on a percentage basis in each of the types of manuscripts described above. Figure 3 is a bar graph of Table IV which affords a basis for visual comparison.

Figure 2. Detail of the Evangelist Luke. Trebizond Gospel, San Lazzaro, Venice 1400/108 and 1925, fol. 299v. Courtesy of the Director, Mekhitarist Monastery of San Lazzaro; photo credit: johndeanphoto.com.

Table II. Armenian Manuscripts

MS No.	*Name*	*Date*	*Origin*
SL 1144/86	Queen Ml'ke Gospel	908-921	Lake Van (east)
W. 537	Gospels of the Priest	966	
St. James 2555†	"Second Ējmiatsin" Gospels	ca. 1000	
SL 887/116	Adrianople Gospel	ca. 1007	Thrace (Greece)

Continued on next page.

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Table II. (Continued). Armenian Manuscripts

MS No.	*Name*	*Date*	*Origin*
SL 1400/108 1925	Trebizond Gospel	mid-11th century	Trebizond
St. James 2556	Gospels of King Gagik-Abas	ca. 1050	
FGA 33.5, 47.2-4	Gospels fragment	1050	Melitene group
St. James 1924	Shukhr Khandara Gospels	1064-66	Melitene group
SL 888/159	Karapet Gospel	ca. 1200	Urfa, Cilicia
Chi MS 949	Red Gospels	ca. 1237	Northern Armenia
FGA 32.18	Baron Vasik Gospel	1250	Hromkla, Cilicia (T'oros Roslin)
FGA 44.17	Gospel of Hohannes	1253	Hromkla; Cilicia
W. 539	Gospel on vellum	1262	Hromkla, Cilicia (T'oros Roslin)
PML 789	Gospels fragment	1296	Eastern Armenia
PML 622	Menologium	1348	Sis, Cilicia; (Sargis Pitsak)
St. James 365	Isaiah Commentary	ca. 1305	Eastern Armenia
UCLA Arm MS 1	Gladzor Gospel Book	ca. 1305	Gladzor, eastern Armenia
MMA 38.171.2	John Incipit Leaf	1300-1310	Eastern Armenia
St. James 2360	Gospels of T'oros Tarōnets'i	ca. 1321	Eastern Armenia
St. James 1794	Khach'en MS by the Monk T'uma	ca. 1327	Eastern Armenia
St. James 1941	Sultaniya Gospels by Awag	1334-1336	Eastern Armenia
W. 543	Khizan Gospels by Khach'atur	1455	Lake Van, Armenia
W. 540	Gospels	1475	Lake Van, Armenia
St. James 135	Hymnal of Martiros Khizants'i	1575	Lake Van, Armenia

FGA = Freer Gallery of Art, Washington, D.C. MMA = Metropolitan Museum of Art, New York, NY. St. James = Monastery of Saint James, Jerusalem. SL = Monastery of San Lazzaro, Venice. PML = Pierpont Morgan Library, New York, NY. W = Walters Art Gallery, Baltimore, MD. UCLA = University of California, Los Angeles: University Research Library, Special Collections. Chi = University of Chicago, Chicago, IL.

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Table III. University of Chicago Special Collections Byzantine Manuscripts Analyzed by FT-IR

MS No.	*Name*	*Date*
46	Haskell Gospels	Late 13th Century
129	Nicolaus Gospels	1133
131	Chrysanthus Gospels	Late 12th Century
232	Greek (Phillipps) Gospels	12th Century
727	Georgius Gospels	Late 13th Century
879	Lectionary of Constantine the Reader	Late 12th Century
948	Lectionary of Saint Menas the Wonderworker	Late 12th Century
965	Rockefeller – McCormick New Testament	Late 12th Century
972	Archaic Mark	Mid-12th Century?
1054	Elfleda Bond Goodspeed Gospels	10th Century

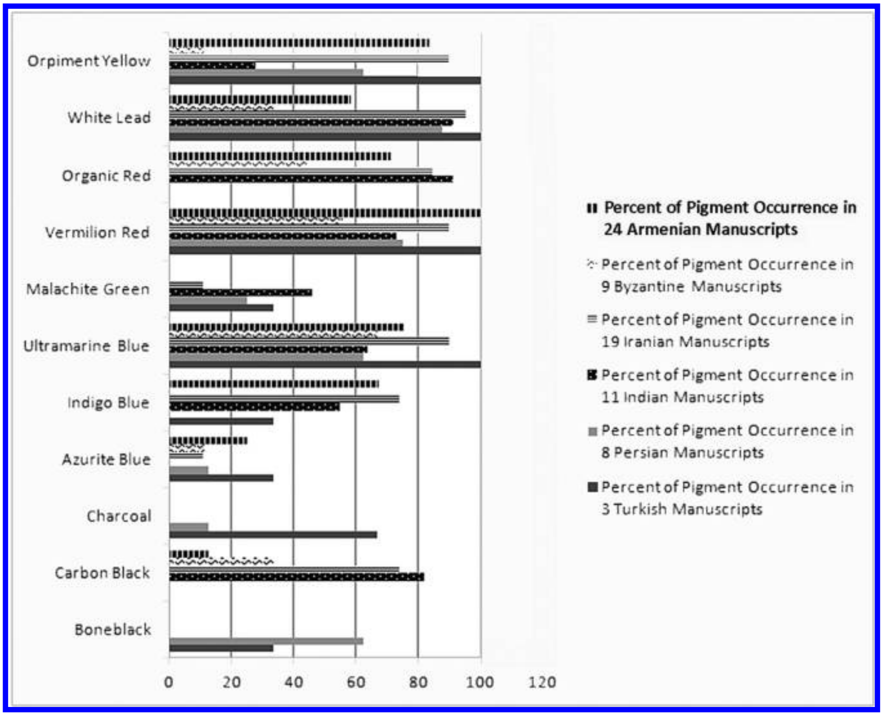

Figure 3. Graphical Representation of the Data in Table IV.

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Table IV. Percent of Pigment Occurrence in Medieval Manuscripts of 6 Different Origins

Pigment	*Armenian (24)*	*Byzantine (9)**	*Iranian (19)*	*Indian (11)*	*Persian (8)*	*Turkish (3)*
Bone-black	0	0	0	0	62.5	33.3
Carbon Black	12.5	33.3	73.7	81.8	0	0
Charcoal	0	0	0	0	12.5	66.8
Azurite Blue	25.0	11.1	10.5	0	12.5	33.3
Indigo Blue	66.8	0	73.7	54.5	0	33.3
Ultrama-rine Blue	75.0	66.7	89.5	63.6	62.5	100
Malachite Green	0	0	10.5	45.5	25.0	33.3
Vermilion Red	100	55.6	89.5	72.7	75.0	100
Organic Red	70.8	44.4	84.2	90.9	0	0
White Lead	58.3	33.3	94.7	90.9	87.5	100
Orpiment Yellow	83.3	11.1	89.5	27.3	62.5	100

* Only nine of the ten Byzantine manuscripts list in Table III are included in this analysis. Chicago MS 972 is discussed separately.

Results and Discussion

At first glance, there seem to be some very clear dividing lines with respect to pigment usage for certain areas. Taking each of the pigments in Table IV, and comparing their usage with alternatives, yields some interesting conclusions.

Carbon Black: Use of this pigment in Armenian and Byzantine manuscripts is moderate, in Iranian and Indian manuscripts, it is the predominant black, and it is totally absent from Persian and Turkish manuscripts. Since both boneblack and charcoal are also entirely absent in the Armenian and Byzantine manuscripts, we can conclude that black was not a very important pigment. Since boneblack is present in the majority of Persian manuscripts, and both charcoal and boneblack are present in the Turkish manuscripts, we conclude that painters in those areas preferred the use of these blacks as opposed to carbon black, possibily because of greater availability of wood and bone in these areas.

Azurite: Azurite, basic copper(II) carbonate, is a blue pigment with a greenish tinge. Its chemical formula is $2CuCO_3 \cdot Cu(OH)_2$. It finds its greatest usage in Armenian and Turkish manuscripts, with moderate usage in Byzantine, Iranian, and Persian manuscripts, whereas it is totally absent from the Indian manuscripts in the cohort. Again, availability may be a factor since azurite deposits throughout Europe have been known since ancient times, but would more than likely have to be imported into the Middle East and beyond. In addition, usage of indigo as a viable alternative blue pigment is very prevalent in almost all of the Armenian, Iranian, and Indian manuscripts.

Ultramarine Blue: Table IV conveys the fact that this blue pigment, obtained from the semiprecious stone lapis lazuli, was almost universally used in the manuscripts examined. While ultramarine, a clathrate compound of polysulfide ions in a silicate cage structure, was highly prized in Europe and cost more than gold, its major deposit was in Afghanistan, a location on the silk road trade route. This can possibly explain its prevalence in Middle Eastern manuscripts since it would not have been an import subject to price hikes of middlemen along the way.

Malachite Green: Malachite, the gemstone as opposed to the organic dye of the same name, is another basic copper(II) carbonate variant with the formula $CuCO_3 \cdot 2Cu(OH)_2$. Curiously, it is totally absent from the Armenian and Byzantine manuscripts examined, but finds moderate usage in the other types of manuscripts. The nearest deposits would have been the Timna Valley, Israel, and the Russian Urals.

Vermilion Red: Evidence of this pigment's almost universal usage is found in Table IV. It is often the most prevalent red pigment in any ancient or medieval sample. Known from ancient times as its natural ore, cinnabar, mercury(II) sulfide, HgS, was also synthesized by heating elemental mercury and elemental sufur together. Large deposits of cinnabar were, and are, found in China and in Almaden, Spain. While it was highly prized as a pigment, its great cost led to the use of lesser red pigments along with it: many of the manuscripts we examined also contain organic red pigments like madder (alizarin) and cochineal (carminic acid) (*14*). The latter has its origin in the "Old World" in the form of a colorant derived from the egg sacs of scale insects of the genus *Kermes*, whereas its "New World" source was the scale insect of the genus *Dactylopius* (*18*).

White Lead: Basic lead(II) carbonate, $2PbCO_3 \cdot Pb(OH)_2$, is another highly prized pigment used from ancient times. It was manufactured by corroding elemental lead with vinegar in the presence of carbon dioxide (often produced by the fermentation of hot horse dung). In the manuscripts we examined, we see its prevalence increase the farther east we go, the Turkish manuscripts being an exception. The Iranian, Indian, and Persian manuscripts examined used only white lead, while silicates are present in the Armenian and Byzantine manuscripts.

Orpiment: This yellow mineral pigment, As_2S_3, enjoyed great usage in Armenian, Iranian, Persian, and Turkish manuscripts, but moderate to little usage in Indian and Byzantine manuscripts. Due to availability, the Indian manuscript painters preferred to employ Indian Yellow, while Byzantine artists preferred to use organic yellow pigments derived from plants. Realgar, As_4S_4, is a red arsenic sulfide often found associated with orpiment in mineral deposits.

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Gypsum is calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$. Anhydrite is its anhydrous form.

Massicot is the yellowish to reddish-yellow orthorhombic form of lead(II) oxide, PbO. The tetragonal form of PbO is called litharge.

Although these analyses have not yielded information enabling the determination or confirmation of the place of origin and date of these manuscripts, we can say at least that the pigments used correspond to the accepted known usage periods, with one exception, as we will see in the next section. However, the analyses have allowed us to take tentative steps toward tracing lines of influence between and among painting schools and cultures; to recommend conservation and handling practice based on the content, and in one instance, that of the Gladzor Gospel Book, to specify attributions among different painters in a manuscript. So, we have shown that virtually all the purposes associated with the scientific identification of the colors used in manuscripts have been fulfilled with one exception: uncovering forgeries. For this, we must return to an anomalous manuscript grouped with the Byzantine manuscripts in Table III.

The "Archaic Mark," Chicago MS 972 (Gregory-Aland MS 2427)

We have deliberately omitted this manuscript from the above analysis because of the occurrence of an anachronistic pigment on many pages of this manuscript. Figure 4 shows two infrared spectra. The bottom spectrum was obtained from a blue pigment from MS 972 (2427); the top spectrum is a reference spectrum of Prussian blue. The band corresponding to the C≡N of ferric ferrocyanide is common to both spectra. Replicate spectra of blue pigments removed from different locations in MS 972 (2427) indicate that the average frequency of this band is 2083 ± 6 cm^{-1}. The ubiquitousness of an iron blue in this manuscript raises doubts about its authenticity. Figure 5 is a detail from folio 34v, the location of the Prussian blue sample from which the spectrum in Figure 4 was derived.

The iron blues are the first of the artificial pigments with a known history and an established date of first preparation. The color was made by the Berlin color makers Johann Jacob Diesbach and Johann Konrad Dippel (1673-1734) in or around 1706 (*17*). Moreover, the material is so complex in composition and method of manufacture that there is practically no possibility that it was invented independently in other times and places (*18*, *19*). This fact, in addition to the evidence indicating that both MS 972 (2427) and a Gospel fragment from the Hermitage Museum, St. Petersburg (*20*), were copies of a late 12th century gospel book in the National Library of Greece, codex 93 (*21*), suggests that these manuscripts originated some time much later than their purported 12th century fabrication. Furthermore, neither of these manuscripts has a geneaology that can be traced prior to 1930, a fact suggesting that their origin very well may be during the flurry of Athenian forgeries that came to the market in the 1920s (*13*).

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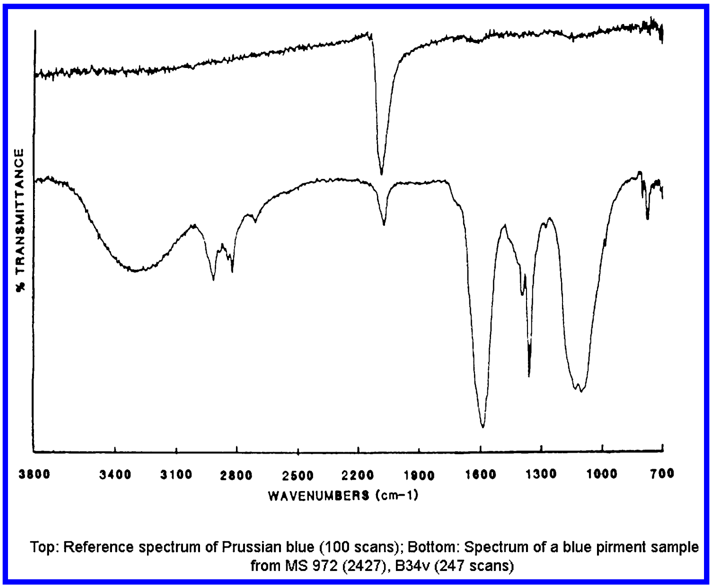

Figure 4. Fourier-Transform Infrared Spectrum of folio 34v, Ms. 972 (2427), the "Archaic Mark.", and Archaeological Chemistry, IV. Reproduced with permission from reference Orna, M. V.; Lang, P. L.; Katon, J. F.; Mathews, T. F.; Nelson, R. S. Applications of infrared microspectroscopy to art historical questions about medieval manuscripts. In Allen, R.O., Ed. Archaeological Chemistry, IV (Advances in Chemistry Series, 220). American Chemical Society: Washington, D.C., 1989; pp. 265-288. Copyright 1989, American Chemical Society (13).

In 2006, the University of Chicago Library and the University of Chicago Divinity School moved to lay to rest once and for all the questions that arose from our study and from some later studies done by Abigail B. Quandt of the Walters Art Gallery by calling for further research (*22*). Thanks to funding provided by an anonymous donor, McCrone Associates, Inc. of Westmont, Illinois, was charged with taking samples of the manuscript, specifically from the parchment, the ink, and a range of paints in the manuscript illuminations, and for all the spectrographic analysis carried out on them. The determined goal was, for the first time, to make a comprehensive chemical examination of all components of the codex (parchment, ink, paints and coatings), utilizing the most current technologies available (*23*).

The McCrone report (*24*) unambiguously reconfirmed our initial finding of Prussian blue, an invention of the early 18th century, in the manuscript. Furthermore, the report documented the presence of additional materials that were incongruent with a 12th date, namely, zinc white (ZnO), not used as a pigment until about 1780, and blanc fixe, a synthetic form of barium sulfate introduced in the 1820s. The report also said that the combination of zinc white and blanc fixe suggested the presence of lithopone, or Orr's white, which was not invented until 1874. These findings alone placed the manuscript, at its earliest, at the latter part of the 19th century. Furthermore, infrared spectroscopy also indicated the presence of cellulose nitrate most likely used as a binding medium; it was only in 1920 that this material became widely available. Finally, almost three months later, the report on the radiocarbon dating of the manuscript parchment gave a calibrated (95% confidence) date range of 1461-1640 (*25*), indicating that the forger(s) used old parchment, but apparently, not old enough!

Figure 5. Folio 34v, Chicago Ms 972 (2427), the "Archaic Mark." The blue pigment in this miniature was analyzed by FT-IR (spectrum above) and found to be Prussian blue. Courtesy Special Collections Research Center, University of Chicago Library.

In a video produced by the University of Chicago and broadcast on 26 October 2009 (*26*), Dr. Margaret M. Mitchell, one of the principal investigators on the Archaic Mark project, announced the results of the investigation. She first stated the importance of the discovery because of all the New Testament manuscripts extant, the Archaic Mark had the highest degree of correspondence with Codex Vaticanus, the oldest complete text of the Gospel of Mark (4th century). She then announced that the manuscript, purchased by the university in 1941, is a modern production that was fabricated between 1874 and the first decades of the 20th century, and would no longer be included in critical editions of the Greek New Testament. However, she also pointed out the value of the data collected insofar as it will help ongoing scholarly investigations into and detection of manuscripts forged in the modern period.

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The Future of Illuminated Manuscript Analysis

All of the examples cited above, including the very recent re-analysis of the "Archaic Mark," were done by extraction of minute particles from the manuscripts, and then subsequent small particle analysis by a variety of means, including X-ray crystallography, Fourier transform infrared microspectroscopy, polarized light microscopy, chemical microscopy, scanning electron microscopy with X-ray fluorescence analyzer and X-ray fluorescence. These methods, though highly sophisticated, are almost universally available to the analytical chemist.

A very promising method that until about a decade or so ago has not been universally available is micro Raman spectroscopy, or Raman microscopy (RM), a method capable of delivering unambiguous results without the necessity of removing small particles from the manuscript, and therefore a method most dear to the heart of any curator of precious manuscripts. Furthermore, according to the doyen of RM, Robin J. H. Clark (*27*), the method can identify mixtures of pigments at high spatial (≤ 1 μm) resolution and down to even picogram quantities, is non-destructive, largely immune to interference, and able to be applied to manuscripts in situ, and even to identifying the reaction products of inorganic pigments that have degraded on the manuscript page (*28*). Difficulties arise when organic pigments are present as they are both prone to photochemical degradation and to fluorescence. A typical RM instrument is shown in Figure 6.

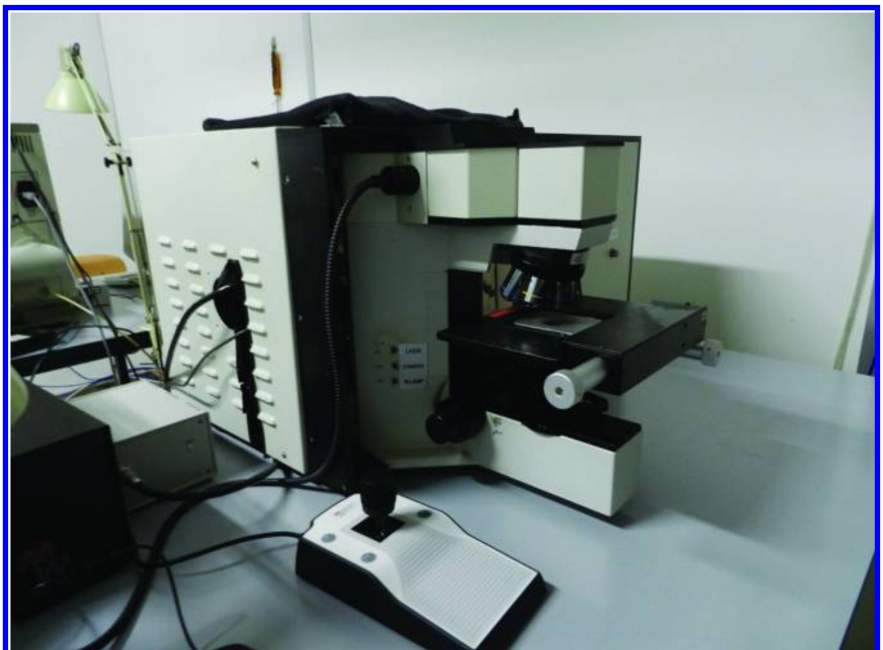

Figure 6. A typical RM Spectrometer (Horiba LabRAM) equipped with EDGE filters, 10, 50 and 100X objectives and telecamera. Courtesy of the University of Modena and Reggio Emilia, Italy. Photograph: M. V. Orna.

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