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An Investigation into the Prevalence and Chemistry of Crystal Formations on the Surface of Iron-Gall Ink: The Preliminary Results

ABSTRACT

The phenomenon of crystal formation on the surface of iron-gall ink has been observed within both manuscripts and drawings, including the work of artists such as Jean-François Millet, Giovanni Domenico Tiepolo, Luca Giordano, Jean-Ignace-Isidore Grandville, and Francisco de Goya. In areas of dense ink application, dendritic networks of white or pale yellow crystals appear on the surface of the ink lines, often rendering those dark passages light and matte in appearance. In the most marked examples, the lightness of these ink crystals can be visually disfiguring, generating aesthetic confusion in much the same manner as darkened lead white.

Despite major initiatives taken over the last decade to better understand the process of iron-gall ink degradation, no systematic research or experimentation has focused on crystal formation. My work examines the prevalence and trends in the occurrence of iron-gall ink crystals found within drawings in the collection of the Department of Prints, Drawings, and Photographs of the Museum of Fine Arts, Boston, and select works from other U.S. collections. Through preliminary instrumental analysis and laboratory experimentation, I am exploring the role of ink composition and environment in the formation of these crystals, and considering the implications on the conservation of these works.

INTRODUCTION

This article addresses the ability of excess inorganic salts within iron-gall ink to form crystals, a condition of natural aging of iron-gall ink that is tangential to the issue of ink corrosion. In areas of dense ink application, networks of white or yellow crystals appear on the surface of the ink

lines, often rendering those dark passages light and matte in appearance. In the most marked examples, the lightness of these ink crystals can be visually disfiguring, generating aesthetic confusion, something akin to the color change that paper conservators have come to associate with darkened lead white. In this Jean François Millet drawing (figs. 1a–b), the crystallization has changed the shadows of the hillside from their original dark color to pale gray.

Though this study has uncovered numerous examples of this condition, statistics indicate that crystallization occurs in less than six percent of the European drawings in the Museum of Fine Arts, Boston (MFA), collection. Crystallization is usually only visible under magnification; however, in rare instances it can be macroscopic. While a few areas of this ink drawing by Goya-follower Leonardo Alenza y Nieto (figs. 2a–b) demonstrate the typical brown, brittle, and blurred appearance of aging iron gall, the majority of the ink lines appear as matte gray dendritic networks of crystals.

LITERATURE REVIEW

A review of iron-gall ink literature revealed that to date this condition has not been the focus of systematic research. In fact, only two articles mention iron-gall ink crystallization. Addressing the issue of side effects caused by aqueous conservation treatments, Reissland made an important distinction between crystals that form as a result of external sources versus inorganic materials that crystallize out of iron-gall ink as a result of natural aging (Reissland 2001). She cites traditional deacidification treatments with calcium and magnesium as potential sources for sulfate salt deposits, though the possibility of salt precipitation also exists with barium hydroxide (Barry 2001) and even phytate treatments (Neevel 2001). Such crystals can be immediately recognized by their indiscriminate deposition over the ink and paper surface. Crystalline material from an external source can also settle on the surface of a work of art through dry deposition. For example,
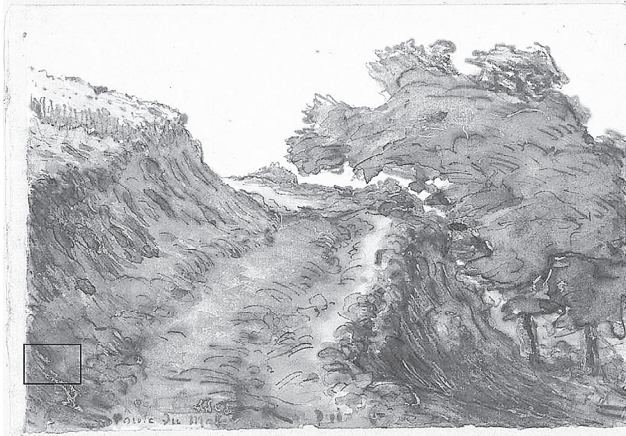
Fig. 1a. Jean-François Millet (French, 1814–1875), *Road from Malavaux, near Cusset*, 1867. Watercolor and pen and brown ink over graphite pencil, 11.2 x 16.2 cm. Gift of Martin Brimmer (76.425). Photograph © 2004 Museum of Fine Arts, Boston.
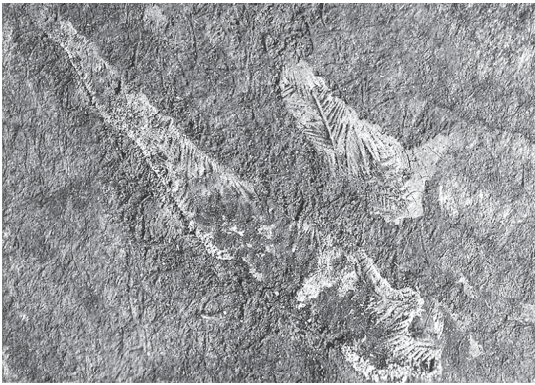

Fig. 2a. Leonardo Alenza y Nieto (Spanish, 1807–1845), Francisco Goya y Lucientes (Spanish, 1746–1828), *Siempre los Mismos*, about 1830–1845. Pen and brown ink, 11 x 18.4 cm. Bequest of Eleanor A. Sayre (2002.423). Photograph © 2004 Museum of Fine Arts, Boston.
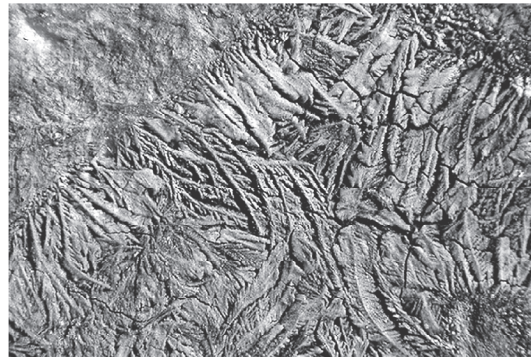

Fig. 1b. Micrograph of the shadows of the lower left hillside in Millet's *Road from Malavaux, Near Cusset* (25x magnification).

Fig. 2b. Micrograph of the area above the head of the central figure in Alenza y Nieto's *Siempre los Mismos* (50x magnification).

artists and scribes sprinkled particulate matter, called *blotting sand* or *pounce,* over the surface of fresh ink to speed up drying prior to the advent of blotting papers (Finlay 1990). Microscopic examination of a seventeenth-century Italian drawing (figs. 3a–b) attributed to a follower of Marcantonio Franceschini revealed remnants of blotting crystals of regular shape superficially adhered to the ink, not integral to the ink matrix.[1] These crystals originating from an external source are distinctly different in appearance from natural iron-gall ink crystals.

A team of German conservators makes the only other published reference to iron-gall ink crystal formations in a 2000 article describing the treatment of a Johann Sebastian Bach manuscript (Fuchs et al. 2000). Theirs constitutes the first attempt to classify iron-gall ink crystals based on physical appearance and hypothesize a chemical source. They suggest that an orange surface crust is symptomatic of an iron oxide; a whitish haze is indicative of manganese, zinc, or aluminum; and a greenish hue betrays the presence of copper. The authors do not specify that this hypothesis was

confirmed through chemical analysis. Despite increasing scrutiny of the aging properties of iron-gall ink, the phenomenon of crystallization is yet to be understood.

PROJECT DESCRIPTION

This project attempts to address the question "what causes iron-gall ink to crystallize?" with three areas of focus. The brown ink drawings within the collection of the Museum of Fine Arts, Boston, were surveyed and examined under magnification to determine the frequency and conditions in which iron-gall ink crystals occur. Laboratory experimentation was performed on fabricated ink samples in order to reproduce the phenomenon of crystallization and establish the role of ink composition and environment in crystal formation. Instrumental analysis is subsequently being conducted to identify the chemical composition of these fabricated ink crystals, as well as to identify the crystalline material within works of art. This article presents the preliminary results of the study.

Fig. 3a. After Marcantonio Franceschini (Italian (Bologna), 1648–1729), *Holy Family with St. Anne and the Child Baptist,* eighteenth century. Pen and brown ink with brush and brown wash, heightened with white gouache, on prepared paper, 28.3 x 20 cm. Gift of Quincy Adams Shaw (94.94). Photograph © 2004 Museum of Fine Arts, Boston.

SURVEY RESULTS

Microscopic examination of nearly seven hundred European drawings from the fifteenth through the nineteenth centuries in the collection of the Department of Prints, Drawings, and Photographs of the Museum of Fine Arts, Boston, unearthed forty-four drawings exhibiting crystals. Thanks to the contributions of colleagues at other U.S. institutions, including the Walters Gallery, Pierpont Morgan Library, and Worcester Art Museum, sixteen additional examples have been added to this growing list. These numbers indicate that the condition is not unique, though neither is it abundant. A chart of the survey results (chart 1) demonstrates that the formation of crystals does not correlate with any one specific time or place of origin. The drawings with crystals span the entire time period under examination and generally reflect the strengths and weaknesses of the MFA collection rather than any genuine trends. However, the survey did reveal the circumstances in which crystals form, morphology of the crystals as they
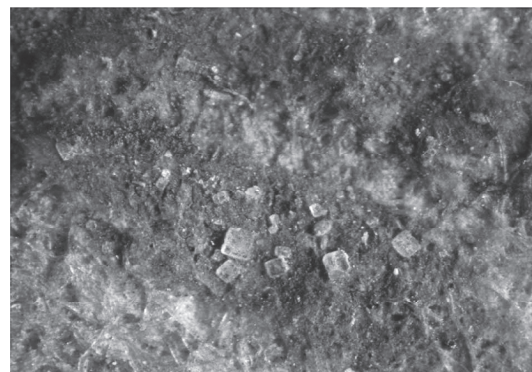

Fig. 3b. Micrograph of the chin of the Virgin in the follower of Franceschini's *Holy Family with St. Anne and the Child Baptist* (50x magnification).

appear under magnification, and color of the crystals relative to the ink.

Crystals most often occur in drawings with heavy ink application. Where crystals appear, a substantial quantity of ink remains atop the surface of the paper, generally in areas of pooled ink at hooks and tails of lines or at the intersection of strokes. Crystals may form along the edges of ink lines, suggesting a pattern of drying resembling a tideline, or, alternatively, can span the entire breadth of the artist's pen or brush stroke.

In terms of crystal morphology, the most distinct crystalline form associated with iron-gall ink is the dendritic network (fig. 4). These complex structures are called dendrites because they resemble branching vegetation, and though they appear delicate, can be quite extensive (Dana 1953). Scanning electron microscopy of a crystalline ink flake reveals that the growth pattern of the crystals in the direction of crystallographic axes is what creates this dendritic structure (figs. 5a–b).
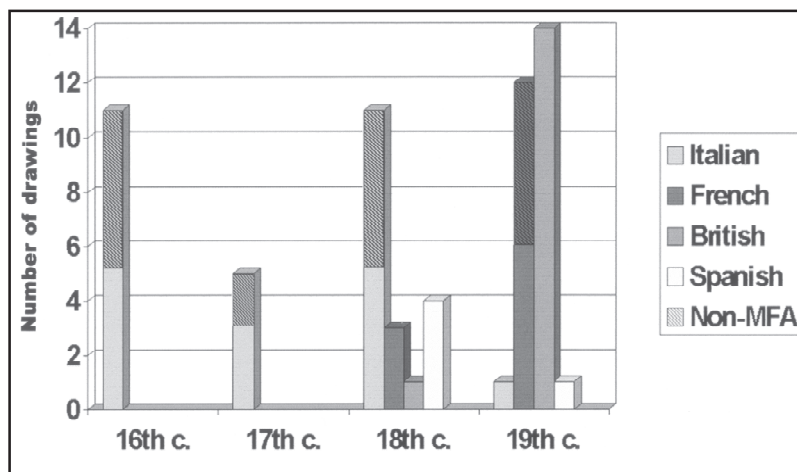

Chart 1. Survey results charting the distribution of drawings with crystals based on the nationality of the artist and the date of execution.
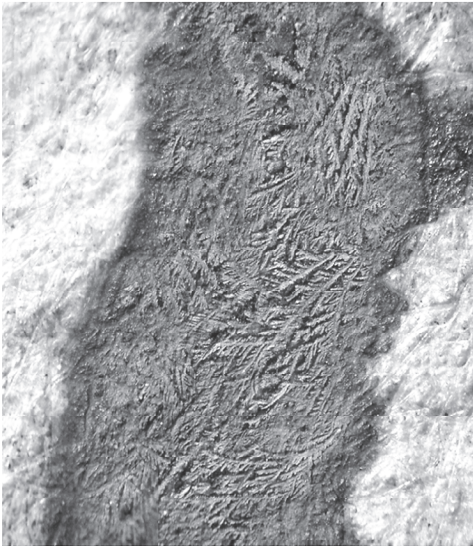
Variations in the morphology of the crystals can be observed in several drawings. For example, crystalline structures that maintain a single dominant crystallographic axis similar to a dendrite, but with truncated branching, actually look like needles. In contrast, crystalline structure may only be visible as a pale surface haze, as seen in this micrograph taken of a Dante Gabriel Rossetti drawing (figs. 6a–b). Though the crystallization is indistinguishable at low magnification, scanning electron microscopy reveals an inherent dendritic structure within the ink. Finally, individual polygonal crystals may also be present, as in the intersection of the dentrites in this micrograph of a Goya-follower drawing (fig. 7). Though the shape of these individual crystals should adhere to exact geometry as dictated by the laws of crystallization, the presence of impurities can distort their form.
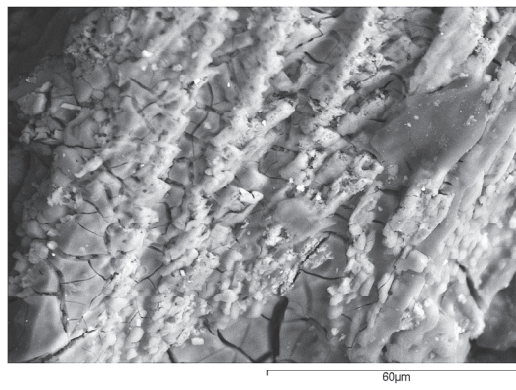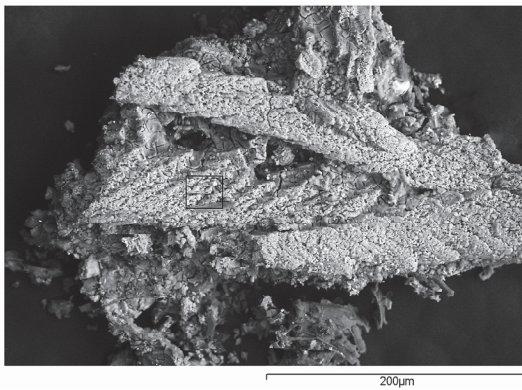
Fig. 4. Micrograph of drapery (18x magnification) in Giovanni Domenico Tiepolo (Italian, 1727–1804), *The Visitation,* after 1770. Pen and brown ink with brush and brown wash over charcoal, 46.4 x 36.2 cm. Bequest of William A. Coolidge, Museum of Fine Arts, Boston (1993.30).

Fig. 5a–b. Scanning electron micrographs of crystalline ink sampled from Théodore Rousseau (French, 1812–1867), *Shepherd and Flock in a Landscape,* mid nineteenth century. Pen and brown and gray wash, heightened with white, 23.5 x 20.1 cm, Print Department Special Fund, Museum of Fine Arts, Boston (64.985). Courtesy of Scientific Research Laboratory, Museum of Fine Arts, Boston.
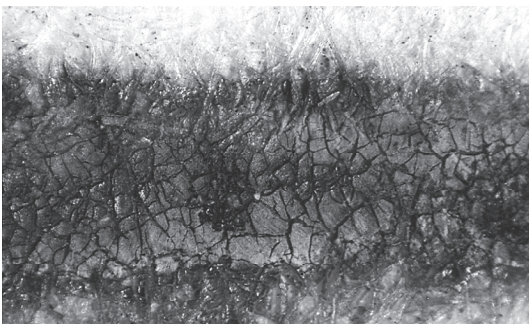

Fig. 6a. Micrograph of the title border (50x magnification) in Dante Gabriel Rossetti (English, 1828–1882), *The Early Italian Poets (study for title page)*, 1861. Pen and brown ink on cream laid paper, 17.5 x 10.9 cm. Print Department Special Fund, Museum of Fine Arts, Boston (58.50).
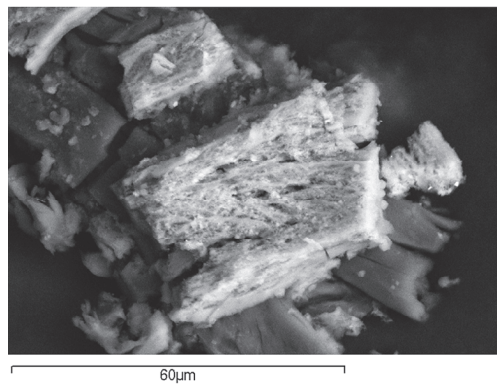
Fig. 6b. Scanning electron micrograph of crystalline ink sampled from Rossetti's *The Early Italian Poets.* Courtesy of Scientific Research Laboratory, Museum of Fine Arts, Boston.

Fig. 7. Micrograph of Alenza y Nieto's *Siempre los Mismos* (50x magnification).

The formation of crystals does not seem linked to any single stage in the iron-gall ink deterioration process. The general color and condition of the ink drawings that exhibit crystals cover the entire range associated with iron-gall ink from relatively fresh, stable, and almost black to burnt, brittle, and brown. The color of the crystals can remain consistent with the general color of the aging ink; or alternatively, they can range in color differing from the ink. Translucent crystals are visible in a few examples, though more commonly, the crystals will appear opaque white or pale gray. Also typical is a variation in color ranging from a greenish yellow to orange. Ink crystals appear as distinct structures in a range of colors; however, combinations of these crystal structures often co-exist on individual drawings, suggesting either a common source that is able to manifest itself in a range of physical forms or heterogeneity of the ink.

SUMMARY OF WORKING HYPOTHESIS

On-going collection of experimental and analytical data in combination with published iron-gall ink research point to three key factors in the formulation of iron-gall ink that may predispose the ink to crystallization: the common use of excess iron sulfate in historic ink mixtures, the inorganic impurities of natural iron sulfate, and the lack of a binding material that might mask the natural tendency of mineral salts to crystallize.

To produce the black ink, iron (II) sulfate heptahydrate reacts with gallic acid extracted from a natural tannin source and upon oxidization forms the black iron (III) pyrogallate ink (Krekel 1999). Though the molecular ratio

for a stable iron-gall ink has been known since 1660, recent research has clearly shown that European recipes throughout the fifteenth through the nineteenth centuries predominately called for 50% more iron sulfate than is required, and an even greater excess was not uncommon (Neevel 1995). To date, laboratory experimentation and analysis of MFA drawings strongly support the theory that excess iron sulfate is the primary player in the crystallization process, though we continue to assess the role of inorganic impurities of the naturally occurring mineral.

The iron sulfate used in the manufacture of iron-gall ink was most often from the natural source, green vitriol. Impurities present within the raw material differed depending on the place of origin. Analysis of two distinct vitriols used widely throughout the fifteenth through the nineteenth centuries indicates that natural iron sulfate consisted of both the ferrous and ferric states accounting for 88% and 53% of the matter. Moreover, impurities of copper, zinc, manganese, aluminum, potassium, and magnesium accounted for as much as 47% of the mineral (Krekel 1999).

The third factor suspected of contributing to the crystallization of iron-gall ink is the binding medium, specifically the quantity of binder relative to iron sulfate within the ink. A review of weight ratios in historic ink recipes (chart 2) demonstrates that one part by weight of gum arabic was by far most commonly recommended for every one part of iron sulfate; however, many recipes suggest far less. In fact, recipes such as Theophilus' guide to the manufacture of metallo-gallic ink in *De encausto* neglect any mention of binding media (James 2001). The impact of varying quantities of binding medium in the aging process warrants consideration. The chemical reaction that produces the black ink complex requires a molar equivalent of iron ions and gallic acid for a balanced equation. Excess iron sulfate or other mineral impurities do not par-
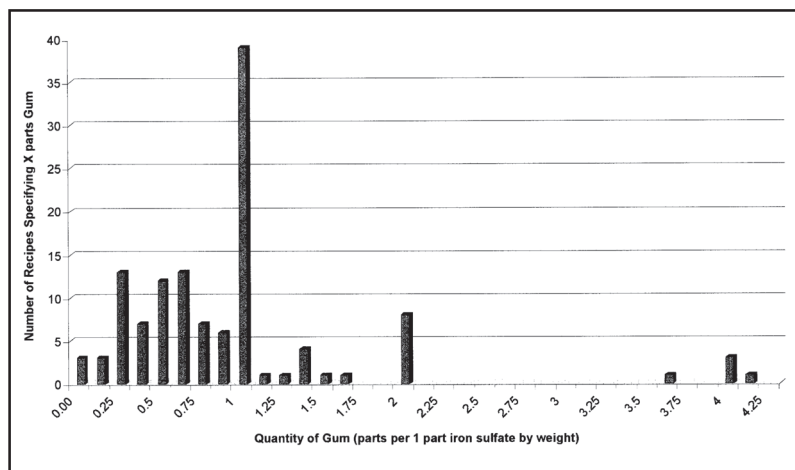

Chart 2. Weight ratios of gum arabic to iron sulfate in 124 published historic iron-gall ink recipes.

ticipate in the actual ink-forming reaction, leaving them free to follow their own preferred reaction mechanism. The addition of a large quantity of binding medium would hold in suspension all components of the ink mixture, and might physically impede any further reaction of those excess salts. Conversely, a relatively small quantity of gum arabic would be ineffective in keeping the components in suspension, and might not inhibit crystallization of the salts out of the ink mixture.

EXPERIMENTAL PROCEDURE

Reference Sample Preparation

A series of experiments was designed with the goal of producing ink crystals under controlled laboratory conditions in order to test the theory that ink containing excess sulfates, particularly iron, and a low concentration of binding medium is predisposed to the formation of crystals upon aging. Four iron-to-gall ratios were selected based on the ratios of historic ink recipes: 100% excess iron sulfate, 50% excess iron sulfate, an "ideal" balanced ratio, and 100% excess of gall. Each of these four inks was separated into five equal portions and a stepwise ratio of gum binder was added: 0, 0.25, 0.5, 1, and 2 parts by weight. The final result was twenty iron-gall inks variants.

Each ink was brushed out onto handmade, rag paper.[2] Hot-pressed, sized paper was selected based on the observation that crystallization most readily occurs when ink remains in concentration on the surface of a drawing substrate. Each paper sample had an experimental counterpart of ink brushed out onto glass microscope slides, allowing concurrent observation of the ink without interference by the support.

Artificial Aging

Several sample sets were subjected to accelerated aging by humidity cycling between 95% and 20% relative humidity at constant temperature of 21°C in desiccator cabinets at the MFA. Five additional sets underwent controlled humidity cycling at elevated temperature in a Tabai Platinous Rainbow PR-26 environmental chamber at the Image Permanence Institute at the Rochester Institute of Technology. Relative humidity was cycled every three hours between 85% and 25% at a constant temperature of 90°C. Exposure times were increased incrementally with each ink set (0, 3, 6, 9 and 12 days) in order to assess crystal growth at regular intervals in the aging process.

RESULTS AND DISCUSSION

When brushed out in sufficient concentration to remain atop the surface of the paper, ink crystals were consistently produced with the laboratory ink recipes that called for an excessive amount of iron (II) sulfate and a small amount of gum binding medium: 100% excess iron (II) sulfate with gum binder ratios of 0, 0.25, and 0.5 parts by weight and 50% excess iron (II) sulfate with gum binder ratios of 0, 0.25 and 0.5 parts by weight. Subsequent fluctuations in temperature and humidity caused the sulfates to deliquesce and subsequently exsiccate to a range of crystalline formations.

Influence of the Ratio of Iron Sulfate to Gum Binder

Remarkably, experimentation revealed that in the presence of sufficient tannin, iron-gall ink will form a uniformly consistent film of black ink even without the addition of a binding medium. However, when excess iron sulfate is present within the ink mixture, a binding medium must be added in order to force the formation of a continuous film. These scanning electron micrographs show three ink samples made from the same recipe, a recipe calling for excess iron sulfate (figs. 8a–f). Note that scanning electron micrographs are not solely topographic in representation, but also indicate relative atomic weight of the component chemical elements through variations in the density of the image. Higher atomic weight elements, in this case concentrations of iron, will appear as lighter, whiter areas. In the sample containing no gum binder (figs. 8a–b), uneven distribution of the unreacted iron sulfate is demonstrated by the pervasive whiteness throughout the micrographs. Concentrations of iron in these areas were confirmed through energy dispersive spectroscopy performed on each sample. The sample containing a relatively small amount of gum arabic (figs. 8c–d) exhibits distinct dendritic patterns, demonstrating that a small amount of binding medium is enough to slow crystal formation and allow complex networks to develop. Once a critical relative amount of binder is reached (figs. 8e–f) a uniform, consistent film is achieved. In this sample, that critical amount is one part by weight gum arabic to one part iron sulfate, the most common ratio called for in historic recipes.

Formation of Crystals upon Aging of Laboratory Inks

Interestingly, artificial aging catalyzed a slow-phase separation as the ink underwent humidity cycling. This collection of scanning electron micrographs depicts the crystalline material as it moves out of the ink suspension. A slow separation of iron salts from the ink matrix was observed with humidity cycling at room temperature (figs. 9a–b). More extreme reactions were noted upon the introduction of heat (figs. 9c–f). The variations in size and shape of the crystalline salts produced through laboratory experimentation highlight the fact that crystal morphology is strongly affected by external conditions.
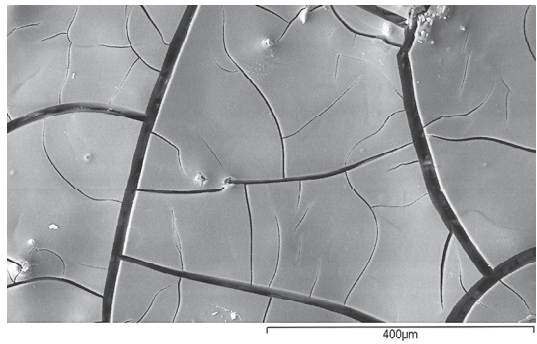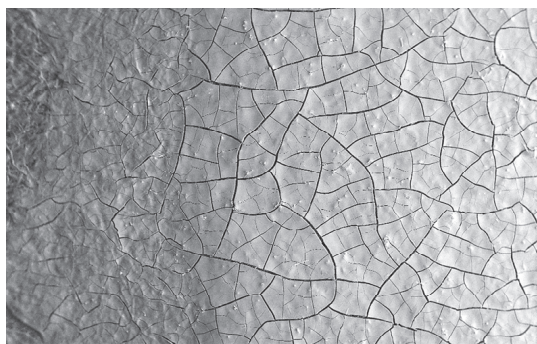
Figs. 8a–f. Scanning electron micrographs of laboratory inks prepared with excess iron sulfate and varying amounts of gum arabic binder. Courtesy of Scientific Research Laboratory, Museum of Fine Arts, Boston.
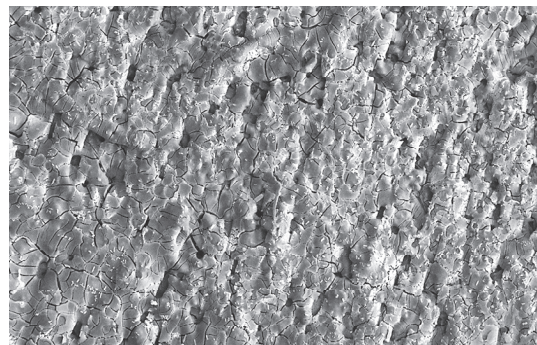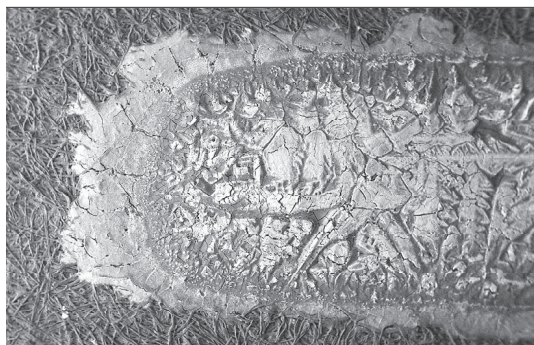
Figs. 8a–b. 1: 1.52: 0 (weight ratio of iron (II) sulfate: gallnuts: gum arabic)

Figs. 8c–d. 1: 1.52: 0.25 (weight ratio of iron (II) sulfate: gallnuts: gum arabic)

Figs. 8e–f. 1: 1.52: 1 (weight ratio of iron (II) sulfate: gallnuts: gum arabic)

Analysis of Laboratory Ink Crystals

Preliminary X-ray microdiffraction analysis of crystals fabricated in the lab yielded patterns strongly matching those of synthetic anhydrous ferric sulfate. Excess ferrous sulfate heptahydrate in the ink mixture can readily undergo oxidation in the presence of moisture to form a basic ferric sulfate. Ferric sulfate can range in color from grayish-white to yellow depending on the degree of hydration. It has also been suggested that ambient relative humidity will cause the iron (II) ions to form iron (III) oxide or iron (III) oxyhydroxide even under acid conditions prevailing in the ink, though the rate and extent of this oxidation reaction depends on the ratios of iron to sulfate ions in the solution (Flynn 1984; Neevel 1999). As we continue our analysis we will evaluate the presence of oxide or hydroxides in contrast to, or combination with, ferric sulfate. The results will be reviewed in light of analyses of samples collected from works of art in order to assess the extent to which crystals created in the lab compare chemically with crystals that have been documented on works of art (figs. 10a–b).

INSTRUMENTAL ANALYSIS OF WORKS OF ART

Utilizing a combination of instrumental techniques, the staff of the MFA Scientific Research Laboratory has begun

Figs. 9a–f. Scanning electron micrographs of laboratory inks after artificial aging. Courtesy of Scientific Research Laboratory, Museum of Fine Arts, Boston.
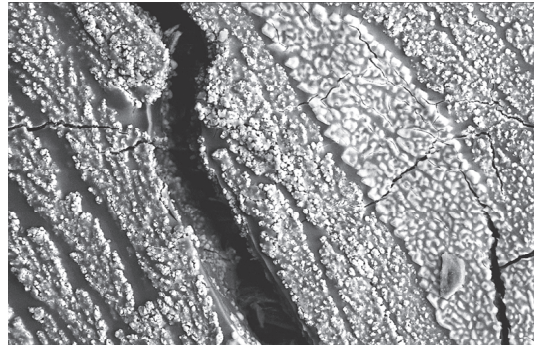
Figs. 9a–b. 1:2.0:0.5 (weight ratio of iron (II) sulfate: gallnuts: gum arabic) after artificial aging by humidity cycling at constant room temperature.
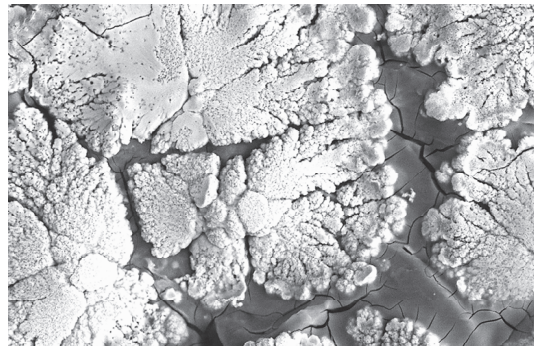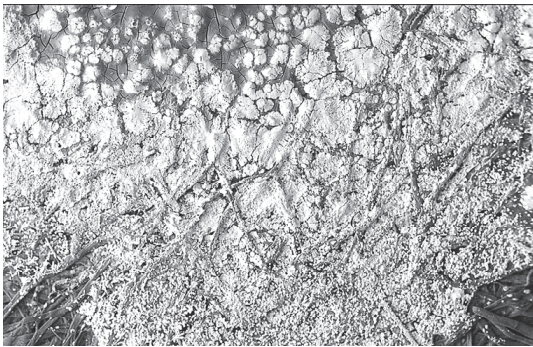
Figs. 9c–d. 1:2.0:0 (weight ratio of iron (II) sulfate: gallnuts: gum arabic) after artificial aging by humidity cycling at elevated temperature.

Figs. 9e–f. 1:1.52:0 (weight ratio of iron (II) sulfate: gallnuts: gum arabic) after artificial aging by humidity cycling at elevated temperature.

analysis to identify the chemical composition of the crystalline material found within several of the museum's drawings. Though definitive chemical identification cannot be presented at this stage in the project, some informative observations can be made about the nature of the crystalline material.

In advance of sampling, initial examination of the artworks is being carried out with X-ray fluorescence spectrometry (XRF), which provides elemental surface analysis with a detection threshold of atomic weight greater than potassium. Though trace elements seem to get lost in the baseline noise, XRF provides strong initial insight into the major heavy metal components present within individual crystal or ink samples. Iron and sulfur are consistently the primary elements detected.

Upon sampling, a combination of instrumental techniques is employed on each sample to most thoroughly analyze the material composition. Scanning electron microscopy (SEM) is capable of magnifying a sample from 30 to 300,000 times, allowing careful inspection of crystal

morphology. In combination with energy dispersive x-ray spectroscopy (EDX), the equipment can simultaneously detect the presence of all chemical elements with an atomic weight of sodium and higher, and give indications of atomic ratios. To date, EDX analysis has shown that the elemental distribution of crystalline areas does not differ greatly from areas of well-formed ink, though the relative quantity of inorganic to organic matter rises significantly where crystals appear. Iron, sulfur, aluminum, calcium, and potassium are consistently present as major and minor elements, while copper, sodium, magnesium, and silica can often be detected in trace quantities. The following percentages indicate the relative quantity of elements present within the crystalline ink samples. Carbon and oxygen have been excluded from the calculations since the samples were not coated nor analyzed in full vacuum. Iron and sulfur range in quantity from 32% to 73% and 14% to 49%, respectively, of the crystalline material. Aluminum, calcium, and potassium account for as high as 11%, 9%, and 13%, respectively, though at times can be present in only trace quantities. The remaining elements detected are consistently lower than 2% of the inorganic composition. In terms of the hypothesis regarding the color of the crystals as indicative of the major chemical component (Fuchs et al. 2000), we have not yet been able to substantiate that correlation. Thus far, EDX results suggest that the quantities of copper, zinc, and manganese within the crystal samples are not significant enough to be considered the source material for crystallization.

Fourier transform infrared (FTIR) microspectroscopy can evaluate the chemical class of compounds present in a sample, and in some instances identify exact organic and inorganic compounds by matching the spectrum of the sample to a known reference material. For this study, multiple spectra were collected for samples from works of art and were compared to each other and to reference sample spectra. In each case, multiple samples removed within each work of art produced very similar spectra, regardless of the color of the crystal. This indicates that the crystals have a fairly uniform major composition and that any variability is below the detection limit of IR spectroscopy. The variation of match correlations within each sample set, two
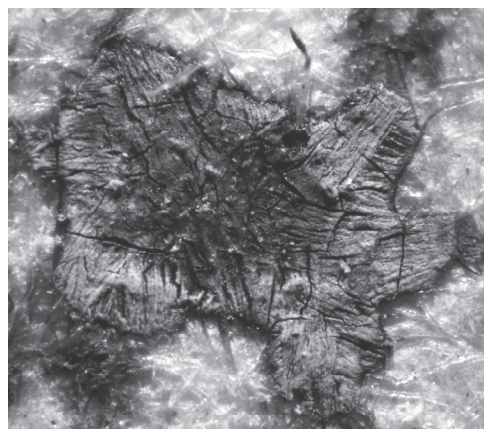

Fig. 10a. Micrograph of George Du Maurier (English (born in France), 1834–1896), *Natural Indignation,* 1854–96. Pen and brown ink, 14.1 x 21.9 cm. Samuel Putnam Avery Fund, Museum of Fine Arts, Boston (63.1260). Image taken at 50x magnification.
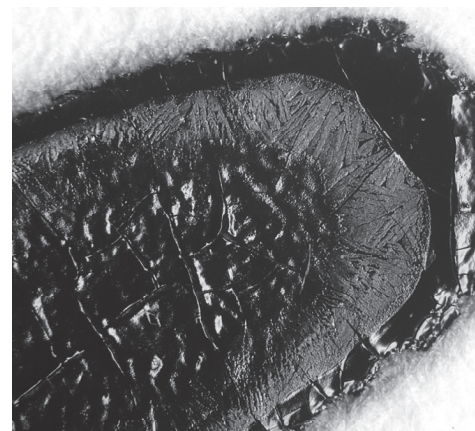

Fig. 10b. Micrograph of laboratory ink (1 iron sulfate: 2 gallnuts: 0.5 gum arabic by weight) after artificial aging by cycling relative humidity at room temperature. Image taken at 50x magnification.

or three samples from a single object, ranges from 100 to 82.

Comparing the spectra for the works of art to each other does not show clear similarities in the spectra except in one case. Interestingly, the crystalline material sampled from a nineteenth century British drawing by John Varley and a 1867 drawing by Jean François Millet produced spectra that were very similar. The variation of match correlations for five samples from these two drawings ranged from 79 to 100, with all but four of the comparisons being over a value of 85. Figure 11 shows the spectra for these two drawings by Millet and Varley along with the best reference material match, an ink composed of iron sulfate, gallnuts, and gum arabic in the relative proportions of 1.0: 2.0: 0.25. When superimposed, the two sample spectra are almost identical. The compositional similarities for samples from these two works of art may imply that the same or similar ink formulas were used.

The reference spectra for ferric sulfate hydrate and ferrous sulfate did not produce good spectra matches for any of the samples from the works of art. However, the major absorption bands in each of the spectra occur in the 1250 to 900 wavenumbers region. As sulfates absorb in this region, it is possible that some form of sulfate, hydrated sulfate, or mixtures of sulfates is present. Other major functional groups that absorb in this region include oxides, hydroxides, and phosphates; although the presence of these compounds is unlikely, they were checked for matches and none were found. Additional work is planned to prepare and analyze more reference materials and mixtures in order to better characterize the composition of the crystals formed in the iron-gall inks. Reference samples are also being collected from commercial chemical sup-
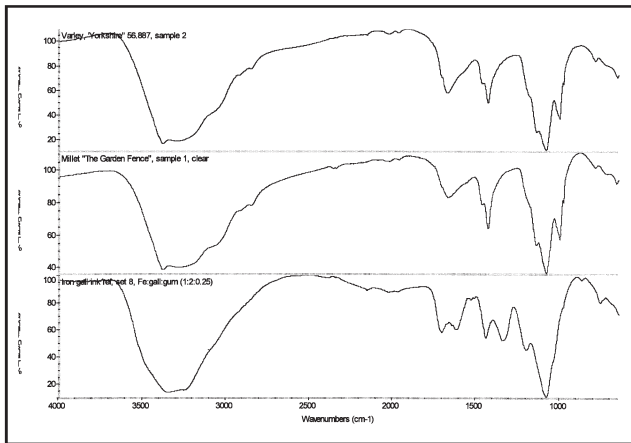
Fig. 11. An overlay of infrared spectra for samples obtained from two drawings as well as for the best matching reference ink containing a weight ratio of 1:2:0.25 (iron (II) sulfate: gallnuts: gum arabic). John Varley (English, 1778–1842), *Yorkshire,* nineteenth century. Pen and brown ink, 7.9 x 23.2 cm. Gift of Colonel Leslie Buswell (56.887). And Jean-François Millet (French, 1814–1875), *Orchard Fence near Vichy; The Garden Fence,*1867. Watercolor and pen and brown ink over graphite, 11.2 x 16.2 cm. Gift of Martin Brimmer (76.424).

pliers as well as from the Mineralogical and Geological Museum at Harvard University in an attempt to make an exact identification.

Additional techniques, which may be utilized in the future phases of this project, include x-ray diffraction (XRD) and Raman spectroscopy. Both techniques can provide exact identification of specific compounds in an unknown material if the reference data is available. MFA scientists are now working on establishing sample preparation techniques for analysis by x-ray micro diffraction available at Massachusetts Institute of Technology, as the reference standards for this technique are the most comprehensive.

The complex data collected from the analysis of crystals sampled from works of art contrast the relatively straightforward data retrieved in the analysis of the laboratory ink samples. Though the laboratory experimentation was successful in physically reproducing the crystallization effect, the chemistry does not as closely resemble that of the naturally aged samples from works of art. This difference may be attributable to the degree of purity of materials used in creating the inks. As previously discussed, the vitriol used in historic inks often contained relatively large quantities of impurities. It is also conceivable that the crystalline material is not one but rather a mixture of compounds, making the isolation of their compositions quite complicated. Finally, the demonstrated sensitivity of these crystals to changes in environment compounds this complexity. Consequently, these preliminary results have underscored the need to combine instrumental techniques and build on

existing reference data in order to most thoroughly characterize the chemistry of iron-gall ink crystals in the future phases of this project.

IMPLICATIONS FOR CONSERVATION

The goal of this first phase of research has been to heighten general awareness of the ability of iron-gall ink to crystallize and enable the reader to recognize shifts in the appearance of aging iron-gall ink upon crystallization. In the future, this project intends to conduct experimentation that will address parameters for safe storage as well as conservation treatment. Specifically, future testing will focus on the effects of common treatments on crystals as well as feasibility of treatment to diminish crystalline growth for those rare cases in which the presence of crystals critically compromises the aesthetic intent of a work of art. In advance of any comprehensive study, the notion of treating these works raises immediate red flags. Ink crystals may consist of inorganic salts that if solubilized during treatment and introduced into the paper matrix could cause undesirable long-term effects.

CONCLUSION

At this stage in the project, it is reasonable to conclude that fluctuating humidity levels throughout the natural aging process lead to the movement of excess inorganic salts out of iron-gall ink. If conditions foster movement to the surface of the ink rather than into the paper substrate, the possibility exists for crystallization. Further research is required to determine precise parameters of fluctuations required for this phenomenon to occur as well as to definitively evaluate the role that ink composition, namely an excess of sulfate minerals in combination with minimal binding medium, plays in the crystallization process. Though preliminary analysis has provided insight into the chemistry of iron-gall ink crystals, further analytical work is necessary for precise identification of crystals that appear on works of art. Also, the implications of conservation treatment on both the formation and dissolution of crystalline iron-gall ink remains to be investigated.

both formally and informally, provided examples and insight into the crystallization phenomenon.

NOTES

1. SEM/EDX analysis of seven crystals yielded consistent results. Ratios of potassium, calcium, and sulfate suggest the chemical composition $KCaSO_4$. Trace amounts of iron, silica, aluminum, magnesium, and sodium detected appear to have superficially transferred from the ink.

2. Cream for Calligraphy antique laid, hard pressed, gelatin sized, 100% cotton, handmade paper manufactured by Twinrocker, Inc. Handmade Paper & Papermaking Supply, P.O. Box 413 Brookstone, IN 47923.

REFERENCES

Barry, C., and J. Fields. 2001. An examination of iron gall ink drawings in the British Museum deacidified with barium hydroxide. In *The iron gall ink meeting*. Newcastle upon Tyne: The University of Northumbria, 83–88.

Dana, E. S. 1953. *Dana's textbook of mineralogy.* 4th ed. New York: Wilson & Sons.

Finlay, M. 1990. *Western writing implements in the age of the quill pen*. Wetheral, Carlisle: Plain Books.

Flynn, C. M. 1984. Hydrolysis of inorganic iron (III) salts. *Chemical Review* 84: 31–41.

Fuchs, R., O. Hahn, and D. Oltrogge. 2000. Geist und Seele sind verwinnt; Die Tintenfrass-Problematick der Autographen Johann Sebastien Bachs. *Restauro* 2: 116–121.

James, C. 2001. The evolution of iron-gall ink and its aesthetical consequences. In *The iron gall ink meeting*. Newcastle upon Tyne: The University of Northumbria. 13–21.

Krekel, C. 1999. The chemistry of historical iron gall inks: Understanding the chemistry of writing ink used to prepare historical documents. *International Journal of Forensic Document Examiners* 5: 54–58.

McArdle, J. V. 1985. Iron compounds. In *Kirk-Othmer concise encyclopedia of chemical technology.* New York: Wiley & Co. 672–673.

Neevel, J. G. 1995. Phytate: A potential conservation agent for the treatment of ink corrosion caused by irongall inks. *Restaurator* 16: 143–160.

Neevel, J. 1999. The behaviour of iron and sulfuric acid during iron-gall ink corrosion. In *ICOM Committee for Conservation Preprints 12th Triennial Meeting, Lyon 29 August – 3 September 1999.* London: James & James (Science Publishers) Ltd. 528–533.

Reissland, B. 2001. Ink corrosion: Side-effects caused by aqueous treatments for paper objects. In *The iron gall ink meeting*. Newcastle upon Tyne: The University of Northumbria. 109–114.

Stecher, P. G., et al., ed. 1968. *The Merck index: An encyclopedia of chemicals and drugs.* 8th ed. Rahway, NJ: Merck & Co., Inc.

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