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Characterizing the age of ancient Egyptian manuscripts through micro-Raman spectroscopy

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We report the first in-depth, systematic study of the Raman spectra of black pigments on ancient Egyptian papyri with well-specified dates from the 4th century BCE to the 10th century CE. The observed spectra are all characteristic of carbon black, but the shapes of the spectra change systematically with the manuscript date, a striking observation given the time span represented. We conclude that the pigments for these papyri were manufactured by using similar processes. We attribute these experimentally observed changes to chemical degradation, possibly the result of the oxidation of both amorphous carbon and crystalline aromatic carbon within these pigments. This investigation offers new insights into the ink materials used in ancient Egypt and provides a possible basis for a new nondestructive means for estimating the dates of ancient papyri. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: pigment; carbon; Egyptian papyri; ancient manuscript

Introduction

One of our most important sources for understanding the culture and history of the ancient world are Egyptian papyri, because they preserve whole classes of texts that otherwise rarely survive from antiquity, such as literary manuscripts, personal correspondence, contracts, petitions, census declarations, property declarations, and tax receipts.[1] These documents are also important in that many of them bear precise dates and locations, providing a useful complement to other forms of ancient evidence, such as archaeological stratigraphy, art historical styles, or paleography, from which historians can construct only relative chronologies or approximate geographies.[2,3] Spectroscopy offers the opportunity for nondestructive characterization of materials. In particular, micro-Raman spectroscopy has been extensively used to identify the chemical composition of selected pigments on manuscripts,[4–11] including ancient Egyptian papyri,[12–14] through determination of the characteristic vibrational frequencies of molecular entities making up the pigment. However, the nature of the Raman scattering process can also provide additional details about the character and structure of materials within a chosen microscopic region, especially for carbon-based pigments.

The general Raman spectrum for carbon black materials is well known,[15–21] comprised of two distinct features: a broad peak near 1350 cm^{-1} designated traditionally as the D band and a narrower peak near 1585 cm^{-1} designated as the G band. The G band arises from the in-plane stretching of the sp^2 carbon for carbon-based aromatic structures, the E_{2g} optical phonons.[22,23] The origin of the D band is more complex[22–24] but has been associated with disorder in the graphitic structure and breaking of the crystal lattice symmetry. The D band is visible when there are vacancies or defects in the graphitic crystal structure, for example at the edges of graphene sheets[25,26] or in amorphous carbon.[21,27]

As part of an ongoing collaboration between Columbia University and New York University, we undertook a detailed investigation of the Raman scattering responses for a number of ancient manuscripts from Columbia University's extensive collection of papyri, which are cataloged according to Advanced Papyrological Information System (APIS) metadata standards. Building on this unique collection, we undertook the first detailed, systematic study of the Raman scattering response for black pigments in ancient papyri of well-specified date, spanning a 1200-year range from the 4th century BCE to the 10th century CE. Through this study, we discovered that the spectroscopic character of the pigments varies systematically with the age of the writing – an unprecedented observation that can provide the basis for a new nondestructive technical methodology to estimate the age of an ancient manuscript.

Experimental

We utilized an inVia Renishaw micro-Raman instrument equipped with a single grating (1800 lines/mm) spectrometer and a Peltier-cooled charge-coupled device to characterize the Raman spectra

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of these manuscripts. All spectra reported here were obtained by using a 633-nm laser focused through a ×50 Zeiss microscope objective lens (NA = 0.75) corresponding to a spot size of approximately 0.5 μm. Because the optical beam examines an ensemble of carbon structures and because we do observe considerable heterogeneity of the observed Raman response, we do note here that the individual experimental spectra may be somewhat dependent on the precise optical geometry. For this reason, we maintained a constant geometry throughout the data reported here.

The low laser power (below 0.5 mW) and short exposure times (75 s) ensure minimal laser-induced effects on the observed spectra, as verified in comparative experiments by using Kremer's 'Furnace Black' pigment (also marketed as 'Lamp Black') on modern papyrus. In particular, for these measurements, spectra acquired at 1 mW for 3 min were not statistically different from experiments at 0.5 mW obtained with much shorter acquisition times. The average height ratio (I_D/I_G) from measurements at 0.5 and 1 mW and the same acquisition time differed by less than 0.5%, less than 1 standard deviation. Temporal fluctuations in temperature and humidity can cause significant movement of papyrus or paper substrates during the time of spectral acquisition. To hold the papyri in focus without damaging them, we clamped the manuscripts between two pieces of matte board, with 2 × 2 cm cutouts on the upper board. When using this methodology, the overall focus on the manuscript, as indicated by the microscope image, remained stable for approximately 2 min.

For comparison purposes, we examined spectra of modern pigment materials. Kremer Pigments (247 West 29th Street, New York, NY 10001, USA) supplied the two carbon black pigments: Furnace Black (denoted here as Lamp Black), item 47250, and 'Fine Charcoal', item 47810. We obtained papyrus sheets from Dick Blick Art Materials (PO Box 1267, Galesburg, IL 61402-1267, USA), item 11239-1001, and gum arabic from acacia tree, item 51198-250G from Aldrich. The gum arabic was dissolved in deionized water to achieve the desired working consistency. Either Furnace Black or Fine Charcoal pigment was mixed into this solution. We fabricated a pen tip by cutting the tip of a cotton swab with a knife, and a new 'pen' was used for each type of ink. We applied the ink directly to new papyrus sheets by using the pen tip. After drying, each papyrus was baked for 24 h at 32 °C to remove solvent and other volatile material. We discovered that changes in the baking temperature or time from these values did not affect the resultant spectra.

For all observed spectra, we subtracted a scaled background spectrum obtained from uninked regions of each document and a linear baseline to isolate the signal deriving from the carbon black ink, following conventional Raman spectral analysis. We fitted each individual spectrum to the appropriate two-peak or three-peak model by using the spectral curve-fitting module of the ORIGIN software package (Origin Pro version 9.0 software from OriginLab, Peak Fitting Module). The analysis routine returns the values of parameters that minimize the sum of the squares of the deviation. The routine also returns for each parameter the standard deviation and the standard error (or standard error of the mean) for the fit. For testing for the dependence of a parameter as a function of document age, we used the linear regression analysis of Excel (Office 2010), which provides a number of statistical parameters including the associated *p*-value for a given linear regression. For *p*-values less than about 0.05 for the fitted slope, we can confidently reject the hypothesis that the parameter is independent of age. Here where we provide errors for fitted values, we report ±1 standard error of the fit.

The two-peak fit with the D peak associated with a Lorentzian and the G peak associated with a Gaussian function were selected on the basis of best fit from preliminary experiments on Kremer Furnace Black. Voigt functions provided the second-best fit when used for both the D and G peaks. The Voigt function represents a mix of a Gaussian and a Lorentzian function. In the case of the D peak, the Voigt function primarily consists of the Lorentzian linewidth, and in the case of the G peak, it mostly comprises the Gaussian linewidth. The other linewidth component in both cases is virtually nonexistent. This further points to why we chose to fit the D peak with a Lorentzian and G peak with a Gaussian.

Basic observations

For this investigation, we selected 17 manuscripts (see Table 1) written predominantly in black ink, with dates either explicitly stated in the manuscript or narrowly defined by textual content. These manuscripts, listed in Table 1, span the date range from 4th century BCE to 10th century CE. All manuscripts originated in the Nile valley or have associations with the Nile valley. Sixteen manuscripts are on papyrus substrates, and one is written on paper. Here, for conciseness, we will use the APIS numbers to designate specific manuscripts, but Table 1 gives standard papyrological citation information.

All 17 manuscripts exhibited the well-known general Raman spectrum for carbon black materials.[15–21] We do not observe

Table 1. Documents from ancient Egypt with well-specified dates used in this study

Document name [a]	APIS no. [b]	Date or range [c]	Place
P.Col.inv. 785	p1905	400–200 BCE	None
P.Zen.Pestm. 32	p61	258 BCE	Fayyum
P.Zen.Pestm. 6	p26	257 BCE	Fayyum
P.Zen.Pestm 12	p40	254 BCE	Fayyum
P.Oxy. 4.797r	p380	103–102 BCE	Oxyrhynchos
P.Col. 10.256	p289	137 CE	Tebtynis (village in Fayyum)
P.Fay. 352	p395	185 CE	Theadelphia (village in Fayyum)
P.Col.inv. 76a	p479	192–193 CE	Tebtynis (Arsinoites nome/ Fayyum)
P.Fay. 42	p386	196 CE	Euhemeria (Arsinoites)
P.Col. 8.228	p263	205–206 CE	Oxyrhynchites
P.Col.inv. 786	p1927	293–294 CE	None
P.Col. 10.284	p317	311 CE	Oxyrhynchos
P.Col. 10 289	p322	331 CE	Oxyrhynchites nome
P.Col. 8.241	p276	432–433 CE	Oxyrhynchites nome
SB 26.16753	p1508	515 CE	Oxyrhynchos
P.Col.inv. 589	p1831	800–900 CE	Hermopolis or Panopolis (possibly)
P.Col.inv. 597	p1839	800–1000 CE	Fayyum

[a]As designated in the Columbia University Libraries' catalog.
[b]APIS is the Advanced Papyrological Information System; data available through the Papyrological Navigator at http://papyri.info.
[c]Where a range is indicated, the midpoint is used for all calculations.

Journal of RAMAN SPECTROSCOPY

any additional distinct features for any of the manuscripts; in particular, we observe no measurable Raman scattering in the 2700 cm^{-1} carbon overtone region or in the 2800–3100 cm^{-1} CH stretching region. Figure 1 shows three typical spectra normalized to the peak intensity near 1585 cm^{-1} obtained from manuscripts dating 800–900 CE, 137 CE, and 258 BCE (red, blue, and black lines, respectively). The figure also indicates the corresponding positions on the manuscripts where we obtained these spectra. This figure illustrates the observed overall spectral shapes and changes in spectral shape with the date or age of the writing on the papyrus. These changes include a decrease in the intensity of the region between the D and G peaks, a decrease in the intensity of the peak at 1350 cm^{-1} with respect to the peak at 1585 cm^{-1}, and narrowing of the two peaks with increasing age. For comparative purposes, Fig. 1 also shows spectra obtained in the same way for two modern reference pigments based on carbon black, Kremer Furnace Black (a soot-based pigment) and Kremer Fine Charcoal (a char-based pigment), that were deposited onto modern papyrus substrates. These two spectra exemplify the considerable variety of spectra found for carbon black materials produced under different manufacturing conditions.

Our process for establishing the spectroscopic baseline assures that the reported spectra are not influenced by Raman scattering or other scattering processes associated with the substrate itself. This is supported by our observation that the spectra obtained from the manuscript on a paper substrate are not materially different from those obtained from manuscripts of approximately the same date on papyrus. Although the inks may include some form of organic binding material such as gum arabic, previous studies have shown that the Raman scattering cross sections for pigment materials are typically far larger than for typical binder materials.[6] In addition, we observe no distinct features in spectral regions associated with strong Raman scattering for gums or other prospective binding materials (including the 2900 cm^{-1} CH stretching region or the 800–1100 cm^{-1} regions).[28] We conclude that our observed spectra are characteristic of the carbon black pigment materials and are not significantly influenced by Raman scattering from the substrate or from binder materials or other organic material within the region of the ink under observation.

Spectral parameter determination

Detailed analyses and spectroscopic assignments for the Raman spectral features of carbon black materials have been the subject of extensive discussion for many years and can be extremely complex, depending on the material's origin and thermal history.[25,29–31] Following much of the literature, we chose two different models that can represent our observed data reasonably closely with a relatively small number of derived parameters. Firstly, because the observed spectra exhibit peak scattering intensity at two different photon energies, we used a simple two-peak model to describe our observed spectra. For this model, we fitted the observed spectra to a Lorentzian-shaped D band and a Gaussian-shaped G band by using a conventional data analysis package (OriginPro). These choices in lineshape function gave better fits to the observed data than other combinations of Lorentzian or Gaussian functions as indicated by the reduced chi squared and the residual sum of squares reported for the fits. The two-peak model thus allows us to characterize the observed shape for each individual spectrum in terms of five separate experimentally derived parameters: G band peak position, G band full width at half maximum (FWHM), D band peak position, D band FWHM, and the peak intensity ratio of the D and G bands: I_D/I_G. Figure 2(a) illustrates a typical observed black ink Raman spectrum obtained from manuscript APIS p380 dated as 103/102 BCE, one of the papyri from the study. The two-peak intensity fit, shown in red in Fig. 2(a) along with a plot of the residuals, matches quite closely the observed spectrum, although the fit is low in the region between the peaks and slightly underestimates the peak heights. This mismatch with the two-peak model is also present in all other manuscripts of this study and has been noted previously in several reports.[17,32,33]

Many researchers have discussed the spectral features of the carbon black two-peak model presented earlier in terms of the D and G bands that are understood in detail for graphite[18,23] and for graphene.[24,26,34] In many practical cases, however, researchers have found it necessary to include additional spectroscopic features in the region near 1550 cm^{-1}.[15,30,35] In particular, Sadezky[30] and many others[35–37] attributed a Raman scattering band near 1550 cm^{-1} to the presence of amorphous carbon compositions containing small aromatic groups and other forms of sp^2 carbon. Building on this extensive spectroscopic literature,

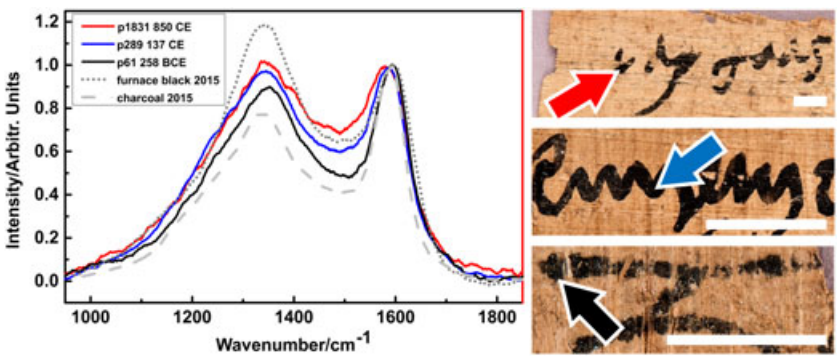

Figure 1. Raman spectral changes as a function of manuscript date. Left panel: example typical Raman spectra of carbon black pigment from three documents: p1831 (red line) from 850 CE ± 50 years, p289 (blue line) from 137 CE, and p61 (black line) from 258 BCE. All spectra were obtained with a 633-nm laser. The spectra are normalized to the G band peak intensity. Right panel: optical micrographs from the three manuscripts (top to bottom: APIS p1831, APIS p137, and APIS p61). The approximate area from which the spectra were acquired is shown by the color-coded arrows. The white bars represent 5 mm in dimension. Also shown are the spectra of the modern pigments Kremer Charcoal (fine) and Kremer Furnace Black illustrating the range of spectra for modern pigments.

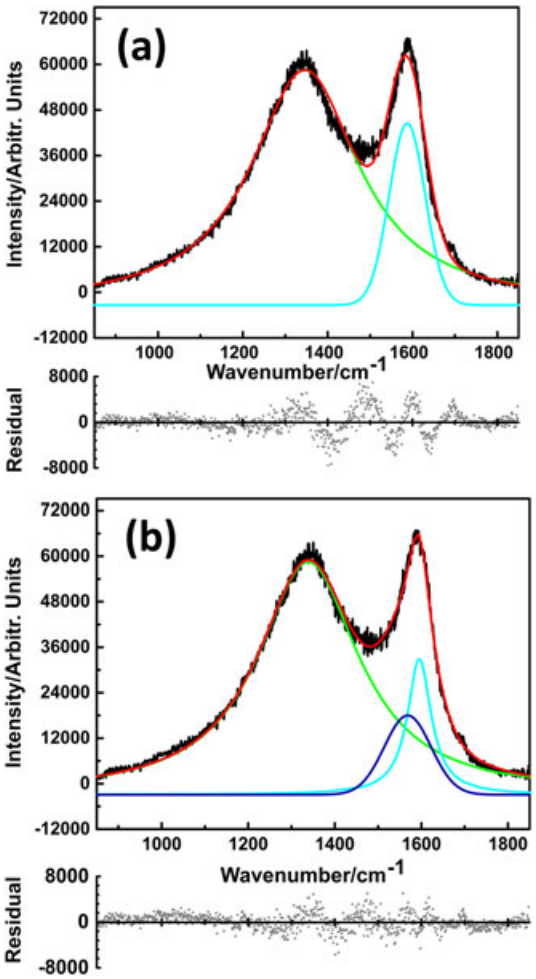

Figure 2. Carbon black pigment Raman spectrum. Typical Raman spectrum (black line) acquired on manuscript APIS p380 with a 633-nm laser. (a) The two-peak model includes the D peak fit with a Lorentzian (green line) and the G peak fit with a Gaussian (cyan line). The total two-peak fit is shown in red. (b) Raman spectral fit using the three-peak model described in the text. The fit (red line) is the sum of D1 peak (green), G peak (cyan), and D3 peak (blue). The residuals are plotted below each spectrum.

we also analyzed our data by using a three-peak model by using the designation D1 for the D band, centered around 1350 cm^{-1}, in the three-peak analysis and adding a hypothetical additional peak, which we will designate D3 following the notation of Sadezky.[30] We used a Gaussian lineshape for the D3 peak and Lorentz lineshapes for the D1 and G peaks following the practice of Sadezky[30] and others.[32,33,38–40] These lineshapes gives better stability and a lower residual sum than other combinations of Lorentzian and Gaussian peaks. The three-peak model provides an eight-parameter description of the observed lineshapes: the widths and peak positions of the D1, G, and D3 spectral peaks and the relative peak intensities I_{D1}/I_G and I_{D3}/I_G. Generally, the additional parameters allow for an improved fit at the cost of complexity and increased uncertainties in values of individual parameters. Figure 2(b) shows the spectral fit using this three-peak model for the same spectrum of Fig. 2(a), which indeed describes the observed spectrum better than the two-peak fit, as indicated by the residual plots, especially in the region between the G and D1 peaks.

We typically acquired 20–40 Raman spectra from different regions of each papyrus to assure an accurate sampling of the ink. We analyzed each individual spectrum by using the two different models laid out earlier. In all cases, we found significant variation in the fitting parameters for individual spectra obtained from any given papyrus. This variation, in all cases, is much greater than the fitting error of each individual spectrum. From this data, we obtain for each parameter not only the average value but also the standard error of the mean (or 'standard error'), which provides the level of confidence that the average value estimates the true mean value for this parameter.[41] In addition, we determined the standard deviation of the experimental points from the average value. The standard deviation provides a quantitative measure of the variations in the value of this parameter from different locations on the manuscript.[41] Because intrinsic variations in the pigments determine the observed standard deviations, these remain invariant, whereas the standard error improves as the number of data points increases. We conclude that the ink pigments as observed with our optical configuration (which remained fixed for all experiments reported here) are heterogeneous on the scale of our measurement resolution (0.5 μm). For every papyrus, we determined the average value, the standard deviation, and the standard error of the mean for each of the five fitting parameters by using the two-peak model and for the eight parameters associated with the three-peak model.

Two-peak analysis results

Following this methodology, we investigated all 17 papyri, obtaining spectral data from various positions on each papyrus to ensure uniform sampling. Figure 3(a) shows the average fitted values for intensity ratio I_D/I_G for all 17 papyri obtained from the two-peak model as a function of the creation date for that manuscript. Vertical error bars in this figure represent ±1 standard error of the mean (red bars) for each of our papyri, while horizontal bars show the uncertainty in date if any. The data of Fig. 3(a) show that for the papyri of this study, the average value of the spectral parameter I_D/I_G decreases with increasing age of writing. Figure 3 summarizes the derived values for all five measured parameters in the two-peak model as a function of the manuscript date. These data demonstrate that each of the spectral parameters exhibits systematic change with writing age. These observations are remarkable, not only in light of the known variations in Raman spectra from carbon black materials derived from different sources[17,30,35,42] (Fig. 1) but also especially so given the time span of the sample set (more than 1200 years), the different provenances of the individual papyri, and inevitable differences in the environmental histories of their survival and storage over centuries.

Regardless of the mechanisms responsible for the observed systematic variation in parameters with age, we may assume that, whatever the functional form, the behavior can be represented by a Taylor series within the time domain of the experiments. Thus, we used conventional linear regression analysis to test for the linear variation of each parameter with the date of writing. This would not assure that the correlation is linear but only that the data can be described as a linear correlation over the range of dates included in this study. In this analysis, we fixed the values of each parameter at the average observed value and the known writing date as shown in Table 1. Figure 3 shows linear least squares fits to these data. The linear regression analysis provides a statistical *p*-value to

Journal of RAMAN SPECTROSCOPY

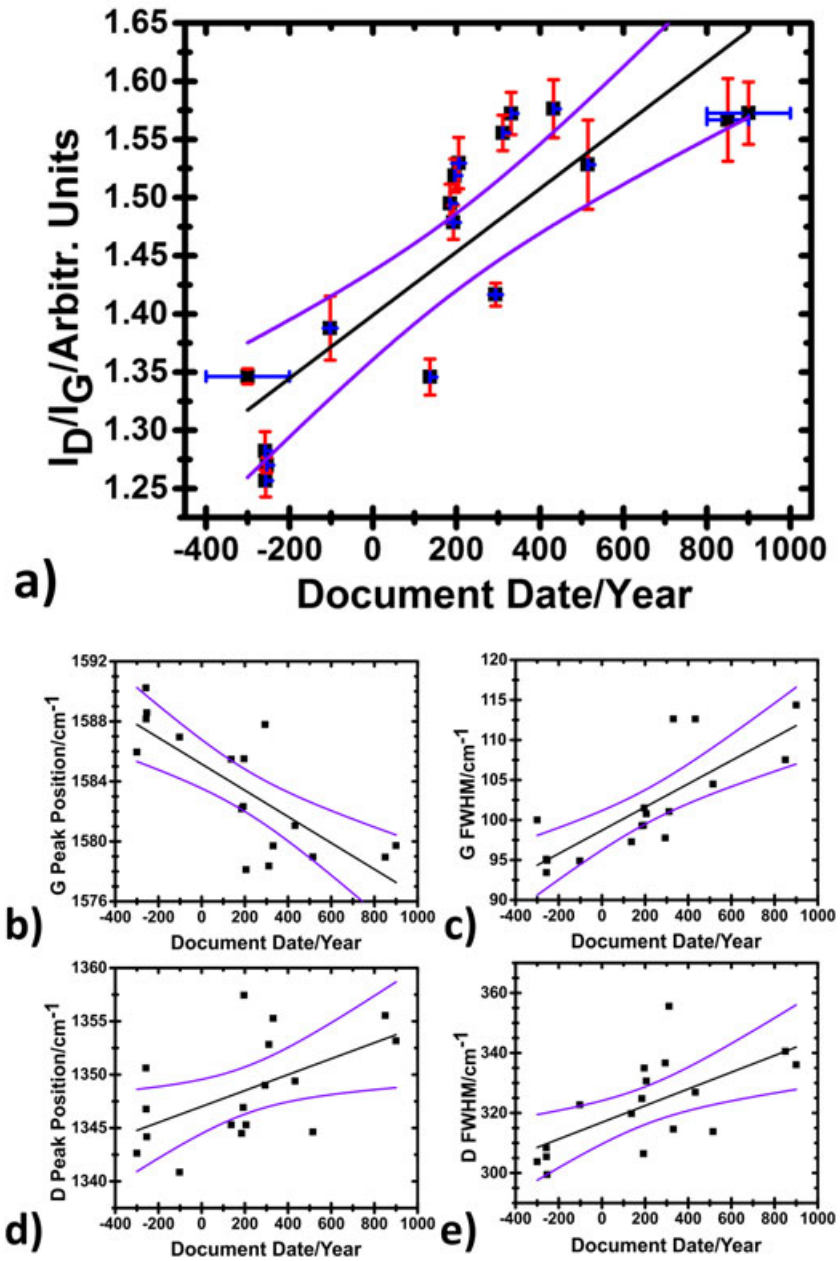

Figure 3. Summary of Raman spectral parameter trends from two-peak fits. (a) The average I_D/I_G extracted from the fits for each of the 17 manuscripts plotted as a function of manuscript date or year. The black line is the linear regression fit with an intercept of 1.40 and a slope of 2.72×10^{-4} year^{-1}. The standard error of the mean for determination of I_D/I_G of each manuscript is shown in red and the uncertainty in date, if any, in blue. Purple lines give the 95% confidence intervals for the mean values. The analysis does not include uncertainty in date or standard error. (b) G band peak position with regression fit intercept of 1585.16 cm^{-1} and slope of −0.00877 cm^{-1} year^{-1}. (c) G band FWHM with regression fit intercept of 98.7 cm^{-1} and slope of 0.0145 cm^{-1} year^{-1}. (d) D band peak position with regression fit intercept of 1347.01 cm^{-1} and slope of 0.00747 cm^{-1} year^{-1}. (e) D band FWHM with regression fit intercept of 316.9 cm^{-1} and slope of 0.02784 cm^{-1} year^{-1}.

test the hypothesis that the observed linear variation is statistically significant.[43] We obtained *p*-values well below the value of 0.05 for all five parameters, confirming that the variation of each parameter with age is statistically meaningful. Figure 3 also shows the 95% confidence bands in purple for estimates of the average parameter values derived from this analysis. These estimates for the mean parameter value coupled with the 95% confidence bands and the *p*-values provide convincing evidence for a significant correlation between these experimentally derived parameters with manuscript age. We conclude that within the 95% confidence limits shown, a linear relationship can describe the estimated average values derived for all five experimentally derived parameters over the date range for this study. These tests assure that these correlations are statistically meaningful.

Surprisingly, we also found that the standard deviations for each parameter across all 17 manuscripts do decrease measurably with increasing manuscript age. Exponential fit of the measured standard deviation for I_D/I_G for example decreases from 0.18 to 0.07 as the document date changes from 900 CE to −300 CE with an exponential time constant of 1260 years. These data show that the pigments of older papyri are decidedly more homogenous than

those of newer ones, as reflected through the standard deviation of the Raman spectral parameters obtained with our experimental geometry, strongly suggesting physical or chemical change in the pigment characteristics with age of writing.

Three-peak analysis results

Within the three-peak model, the inclusion of a D3 peak between the D1 and G peaks changes significantly the values for many of the parameters as obtained with the two-peak model. The three-peak analysis shows that the widths and peak positions of the G and D3 bands are essentially independent of document age within experimental error. The *p*-values obtained from the linear regression analysis, which exceed 0.3 for these four parameters, confirm this independence. The specific values obtained along with the standard errors are G FWHM = 65.9 ± 1.9 cm^{-1}; D3 FWHM = 122.7 ± 1.3 cm^{-1}; G frequency = 1594.8 ± 0.5 cm^{-1}; and D3 frequency = 1554.9 ± 1.5 cm^{-1}. In this analysis the D1 band peak position parameter varies slightly but significantly with the linear correlation as a function of date (years, CE) described by an intercept of 1338.4 cm^{-1} and slope of 0.00702 cm^{-1} $year^{-1}$ with a significant *p*-value of 0.008. Similarly, the D1 FWHM correlation as a function of date is given by an intercept of 288.8 cm^{-1} and a slope of 0.0316 cm^{-1} $year^{-1}$ with a *p*-value of 0.0009. These parameters are in the range of values for various forms of carbon black reported by other researchers who have incorporated D1 into their analysis.[36,37] The observed 38% decrease in I_{D1}/I_G and 52% decrease in I_{D3}/I_G with increasing age (toward earlier dates) for the time domain of our papyri study indicate a significant contribution to the observed total scattering intensity by constituents within the pigment that decay as a function of time. The *p*-values for a linear regression analysis of both parameters (0.01 for I_{D1}/I_G and 0.04 for I_{D3}/I_G) confirm the statistical significance of a hypothesized dependence of these parameters on the manuscript age, although these values are not as definitive as those for the two-peak analysis. Thus, in this interpretation, the spectral parameters for the G and D3 parameters remain relatively fixed, while the D1 band spectral parameters along with the relative intensity parameters I_{D3}/I_G and I_{D1}/I_G dominate the observed changes in the overall spectral shape.

General observations

Because carbon black materials are technologically important, their Raman spectra have been investigated extensively. These studies have firmly established that carbon black materials synthesized under different conditions exhibit dramatically different Raman spectra, depending upon the synthetic methodology, the process parameters, the starting material, and other variables in the process as well as the subsequent thermal history[30,42] (see Fig. 1 for two modern examples). It has long been recognized that Raman spectroscopy is extremely valuable in identifying and characterizing pigments, both ancient and modern, including pigments based on carbonaceous materials. In the case of carbon, interpretation and analysis, however, have been complicated by several factors. Firstly, in part because of the forbidden nature of the characteristic D band, the Raman spectra of graphitic carbon is dispersive – that is the relative intensities, lineshapes, and positions are significantly dependent upon the wavelength of excitation.[18,24,44,45] This makes it difficult to quantitatively compare measurements obtained with excitation at different wavelengths. In our case, we chose 633 nm because this helps assure that the delicate ancient manuscripts will not undergo damage during measurement. Secondly, the novel character of the D band requires an unusual nonsymmetric fundamental lineshape,[24] and in practice, researchers have been forced to analyze the overall spectrum using a variety of lineshape functions with incorporation of as many as ten or more highly overlapping spectral peaks.[37,46,47] This renders the resolution of spectroscopic parameters very much analysis dependent, providing values of specific spectroscopic parameters that are poorly determined.

Despite these difficulties, several researchers have attempted to relate differences in the overall lineshapes of observed Raman spectra for ancient artistic materials to specific types of carbon-based pigments. Thus, Coccato *et al.*[48] undertook an extensive study of the Raman spectra of commercial black pigments and related materials by using laser sources with wavelengths of 532 and 785 nm. This work illustrates the variety in overall spectral lineshapes presented by modern commercial pigments. Although this work provides peak frequencies for these pigments and offers some general guidelines for distinguishing between pigments of different types, direct comparison with the spectra reported here is hindered by the difference in excitation wavelengths. Tomasini *et al.*[11] explored Raman spectra taken with excitation at 514.5-nm wavelength for a series of modern commercial pigments in a study designed to distinguish between modern carbon-based pigments and to extend this approach to the identification of the nature of historical pigments. Using an analysis similar to the two-peak analysis used here, they reported the values of the five spectral parameters for each pigment. Because the excitation wavelength for these studies is different from that used here, we cannot directly compare these results with those reported here. From an analysis of the correlations of the linewidths and frequencies for the D and G bands, they were able to demonstrate that the pigments in one 19th-century wooden sculpture can be associated with a wood-based charcoal, while black pigments for a second sculpture is more likely derived from a bone charcoal.[49] These two studies highlight the utility of Raman spectroscopy for understanding the nature of pigments in historical contexts, but they also demonstrate the need for careful and quantitative experiments.

Ancient primary sources provide virtually no information about the methods of manufacture of black pigments in ancient Egypt nor about the methodology of ink formulation from these pigments. Although we are aware of no primary source descriptions of ink formulation in ancient Egypt, Lucas and Harris[50] speculates as to some possible methods for making carbon-based pigments in ancient Egypt. Wiborg[51] correctly noted that the historian Pliny the Elder reports that the ancient Greeks used soot or char with gum to manufacture black pigments. For our study, the black pigments on each ancient manuscript have experienced a unique history, defined by possible variations in manufacture, processing, storage temperature, and ambient environment. Thus, the observations presented here of systematic variation in the overall spectral shape with age within a disparate collection of papyri from various sites in ancient Egypt written over a 1200-year time span are truly extraordinary. The correlations represented in Fig. 3 strongly

suggest that the pigments used in the manuscripts of this study (and by extension to many or even most papyri produced in the Nile valley of Egypt between the 4th century BCE and the 10th century CE) were manufactured by using similar techniques or processes. Further, these observations also strongly suggest that after the pigments were deposited on the substrate, a unified set of chemical or structural changes has given rise to variations in the details of the Raman spectra that evolve over time, independent of the specific source or origin of each papyrus. These propositions imply that by studying the detailed Raman spectra of carbon inks on papyri with *known* dates from this general period and provenance, we can establish correlations useful for estimating the date of pigment manufacture for a papyrus of an *unknown* date from the same general period and provenance based on its Raman spectra. This assumes that the pigments were used relatively soon after manufacture, a condition implied by the results of this study. However, there will be significant limitations on the confidence for these estimates set by variations in the factors that influence the details of the spectral differences including possible variations in the process of manufacture and environmental history.

Spectral change through chemical degradation processes in carbon pigments

Because the correlations described earlier are without precedent, we seek a reasonable and tenable hypothesis that can explain the observations. One possible explanation for the observed spectral change with age is chemical change within the pigment material. In particular, oxidative processes are known to degrade carbon black materials on laboratory timescales at elevated temperatures.[52,53] Furthermore, amorphous carbon is more reactive than planar, sp^2-bonded, crystalline carbon.[53,54] If earlier assignments are correct,[30] the D3 region corresponds to small aromatic molecules and chains with significant sp^2 content. Thus, we suggest that oxidative processes, over long timescales under ambient conditions, can degrade sp^2 carbon within the amorphous regions, thus reducing these sources of Raman scattering in the D3 spectral region. The consequence of a loss of Raman signal in the D3 for our two-peak fits would be a narrowing of the G and D peaks accompanied by a shift in the peak position of the G peak to higher energy and the D peak to lower energy, in agreement with our results. This picture, then, is consistent with our observations and with known properties of carbon black materials. The observed decrease in the standard deviations of the spectroscopic parameters, including I_D/I_G, from the two-peak analysis provides additional support for the chemical degradation hypothesis. Because the amorphous carbon constituents should oxidize more rapidly than the more stable crystalline regions, oxidation processes would drive the composition of the pigment toward the more stable and uniform crystalline graphitic materials by chemically modifying small aromatic molecules and other sp^2 carbon, leaving a more homogeneous pigment.

Laboratory studies of carbon black oxidation also support the explanation proposed here. Ivleva *et al.*[55] used Raman spectroscopy to study the changes in spark discharge (GfG) soot in an oxidative atmosphere at elevated temperatures. These researchers extracted D3 intensities relative to the G band and found that these intensities decrease rapidly with oxidation time. They attributed this decrease to the oxidation of the amorphous carbon fraction. Their observed changes in spectral peak positions and linewidths with oxidation time mirror closely the spectral changes reported here with increasing manuscript age. For the intensity ratio I_D/I_G, we observe a decrease with increasing age, whereas Ivleva *et al.* reported that this ratio increases with increasing oxidation time. However, the intensity ratio I_D/I_G is highly reflective of the basic dimension of the graphitic crystals, L_a, for graphitic carbon, increasing with decreasing L_a for $L_a >$ about 2 nm but decreasing with decreasing L_a for $L_a <$ about 2 nm.[15,22,25,56,57] Thus, the difference in behavior can be explained in terms of small changes in crystalline dimensions upon oxidation, suggesting that the pigments for the manuscripts reported here are characterized by a relatively small crystallite size. In a related study, Knauer *et al.*[58] observed two different steps in the oxidation of GfG soot: a low-temperature or rapid step in which the amorphous carbon is removed and a higher-temperature, slower step for direct oxidation of the graphitic crystallites. Small crystalline size is further supported by the lack of second-order Raman processes around 2700 cm^{-1}.[56,59] Similar observations have been reported by Su *et al.*[54] for synthetic soots and by Keown *et al.*[60] in studies of oxidation of biomass chars. These laboratory studies of several carbon-based systems demonstrate that oxidation does cause changes in the Raman spectra of carbon black material similar to those observed here, providing additional support for an oxidation hypothesis. Although the detailed chemistries for these oxidative processes at present are not well understood, we note that molecular oxygen is present in the ambient environment for these manuscripts, the timescales for reaction are very long, and ambient temperatures are sufficient to support very slow oxidative degradation.

Discussion

The unexpected discovery of a systematic change in the Raman spectra of ancient Egyptian papyri correlated with the date of writing provides important implications for the study and understanding of ancient Egyptian papyri and indeed all other ancient texts written with carbon ink. Our results suggest that the black pigments of these manuscripts result from manufacturing processes that remained relatively consistent over the 1200-year span of this study. The correlations may also prove useful in estimating manuscript dates in some instances by using statistical methods to determine prediction intervals that account for the spread in the data.[43] However, the observed intrinsic variations (Fig. 3) will place limits on the efficacy of estimation of dates for individual manuscripts. This intrinsic variation may reflect significant differences in individual manuscripts as measured today resulting from variations in thermal and environmental history of individual papyri. Alternatively, the variations could result from individual differences in the pigment manufacture process. Indeed, all of these factors may be operative; they constitute a basis for further study.

Despite these limitations, the evolution of these black pigments with age as observed through micro-Raman spectroscopy (Fig. 1) provides, in principle, a scientific basis for the first truly nondestructive method for dating, even if approximately, of ancient writing by establishing the association of observable spectroscopic parameters with age of writing. Such a methodology, as reported here, could

potentially lead to techniques that would help papyrologists and ancient historians differentiate between genuine ancient documents and modern forgeries.

The recently published description of a manuscript known as the 'Gospel of Jesus' Wife' (or GJW)[61] has renewed interest in the phenomenon of modern forgeries of purportedly ancient works (see Jones[62] for a useful overview, contextualizing the debate over the GJW manuscript). As part of this debate, Krutzsch and Rabin[63] discussed several methods for characterizing ancient writing materials as applied to GJW. With respect to our preliminary description of the raw Raman spectra for the pigments in GJW,[64] they raised some technical questions that we quantitatively clarify here. However, they also questioned the scientific value of characterization of GJW through Raman spectroscopy, concluding that the results are 'not sufficient to support authenticity of [GJW]'. To be very clear, the motivation behind our research is not to authenticate any inks on papyrus as 'ancient'. The methodology reported here (at least in its current state) does not and cannot conclusively demonstrate that a specific carbon ink on a papyrus is in fact ancient. It can, however, show in some cases whether the spectral characteristics of the ink, analyzed statistically, resemble or are compatible with the spectra gathered from documents of an indisputably ancient origin. Moreover, on the basis of the established correlation between the spectral characteristics of ancient inks and their dates of writing (Fig. 3), Raman characterization can suggest approximate date ranges with specified degrees of statistical confidence for manuscripts without known dates (e.g. most literary manuscripts). Such date ranges may then be compared with date range estimates derived from other evidence (e.g. paleography, papyrus construction). In this way, Raman characterization may serve to disprove a hypothesis about authenticity but cannot positively authenticate any particular writing or manuscript as ancient. That said, with respect to suspected modern forgeries, the establishment of the correlation reported here is not a small advance: it provides a quantitative framework within which scholars may weigh the Raman evidence against other classes of evidence when coming to a definitive conclusion with respect to any specific manuscript.

The potential historical importance of a nondestructive technique of dating based on this methodology is not limited to authentication and should not be underestimated: few literary or religious manuscripts (e.g. texts of Homer or the Bible) are explicitly dated in the way that many ancient documents typically are. Techniques based on this methodology could therefore add significantly to our understanding of ancient cultural and religious history by bringing greater – and possibly absolute – chronological precision to texts that currently exist in merely relative chronological relationships to each other.[65,66] Finally, the knowledge gained from such studies may also prove useful to conservators, who may wish to base their evaluations of documents' states of preservation, as well as judgments of the appropriateness of housing and storage environments, on this understanding of the characteristics of oxidation. Translating this exciting concept into practical applications will require careful consideration of statistics and additional experimental investigation.

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