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RESEARCH ARTICLE

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Differentiation of pine and oil-based soots in East Asian inks using Raman spectroscopy

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Abstract

East Asian inks are a major component of calligraphy, paintings, and prints in China, Japan, and Korea and are historically made from either pine soot or oil-lamp soot mixed with a proteinaceous binder. Although the inks from the two different soot sources have different properties in East Asian works of art, no non-destructive methods to differentiate them scientifically currently exist. Raman spectroscopy (RS) of carbonaceous materials is commonly used to extract information about their properties and has been applied here to East Asian inks. Soots used in making modern inks were collected from 10 sources in China and Japan and analyzed using RS. RS using 405-, 633-, and 785-nm excitation has been able to differentiate pine soot from oil-lamp soot, also called lampblack. In addition, principal component analysis (PCA) of only 785-nm Raman spectra has been able to discriminate between two different soots used in a 19th-century Japanese woodblock printing of *Kaishien Gaden*. In addition to allowing discrimination between inks on East Asian works of art, these results may be of use to other fields using carbonaceous materials.

KEYWORDS

carbonaceous materials, PAH, PCA, soot, woodblock printing

1 | INTRODUCTION

Raman spectroscopy (RS) has been used to examine the molecular structure of soot and other polycyclic aromatic hydrocarbon (PAH) materials in the fields of combustion, electronic materials, geology, and cultural heritage.[1–8] RS primarily interrogates the PAH molecules that comprise the smallest fragments of soot particles. The PAH molecules are present in stacks and clusters forming primary particles approximately 10–30 nm in size, which themselves aggregate into the final mature soot fractal aggregates in the range of a few hundred nanometers.[9] In East Asia, black pigments are traditionally soot-based suggesting RS would be a useful tool for their analysis. The soot pigment is mixed with a proteinaceous animal skin glue binding medium and dried to form inksticks; in addition, small amounts of many different materials are added for their fragrance, preservative, or mystical properties.[10] In interviews with ink studios by the authors, ink manufacturers discussed the addition of camphor, gold leaf, and bear gall as examples of just some of the additives in inksticks, with camphor being the most common additive. Similar inks are used in Korea, Japan, and China, although the common term in the English-speaking world is "Chinese ink"; in this paper, we will use the term East Asian ink to encompass all the sources of ink and soot examined. East Asian ink is known as *sumi* in Japan, *mo* in China, and *meok* in Korea.

In paintings and calligraphy, significance is often attributed to the soot source in East Asian inks used to create the work of art, with different types of soot ascribed different properties when applied to paper, for example, lampblack inks are believed to have a brownish tint and to be useful in depicting vegetation. As such, it is desirable to differentiate between various East Asian inks used on different parts of a painting, as well as to be able to identify the soot source of the East Asian ink used. Because of the nature of the extremely thin layers of ink used in many paintings and calligraphies, a method for examining East Asian ink that does not involve taking a sample is preferred, or even required. Analysis of the pigments used in East Asian paintings can provide valuable information about the practices of the artist, trade patterns, and provenance.[10]

East Asian inks have been studied by a number of techniques in past studies, most requiring samples.[11–14] A pyrolysis gas chromatography mass spectrometry (Py-GCMS) study on an inkstick was able to identify a number of additives present in inksticks, but gave little information on the soots used.[13] In examinations of soot itself, Swider and Winter studied the zeta potential of the soots before and after transformation into ink and Osawa identified the presence of a small amount of fullerenes in East Asian inks using liquid chromatography.[15,16] Udaka used scanning electron microscopy (SEM) and dynamic light scattering (DLS) to look at fractal aggregate size, demonstrating that pine soots consistently have larger fractal aggregate sizes than traditional lampblacks and that the fractal aggregate size of pine soots will range broadly, depending on the specific method used to manufacture the pine soot.[17] Studies by Zhang et al. support the larger fractal aggregate size of pine soots identified by Udaka.[18] Kim and Eom analyzed the inks used in 15th-century movable metal-type printed books from Korea using field emission-SEM and determined via particle size measurements that both lampblack and pine soot inks were used in printing.[19]

1.1 | Manufacture of soots used in East Asian inks.

The two traditional types of soot used in making East Asian ink are lampblack and pine soot.[10] Lampblack was traditionally made by burning a triglyceride vegetable oil or animal fat (e.g., rapeseed oil, tung oil, and lard) in a wicked flame with a collection bowl placed upside-down approximately 10 cm above the wick. The bowl is occasionally rotated so that soot is deposited on a new location of the bowl, and every few hours, the upper bowl is removed, and the soot is collected to be used for ink.[20] In some larger Chinese ink studios, a new technique has been developed for manufacturing lampblack that uses the same traditional fuel sources but requires much less manpower. This method features a rotating steel drum approximately 10 cm above the wick to capture soot over an approximately 4-m-long row of cotton wicks burning the traditional triglyceride-based fuels. Although the fuel source and soot capturing distance are the same as the traditional lampblack, the modern lampblack is immediately removed from the region of the flame.

Pine soot can be made through a variety of methods, although using the same fuel materials, the resinous branches or roots of *Pinus huangshanensis* or *Pinus densiflora*. Methods for manufacturing pine soot vary more than those for manufacturing lampblack, ranging from methods very similar to those described in the Ming dynasty to more modern methods using non-flammable materials for capturing the soot.[21] Because of concerns about ash or sparks contaminating the product, the fire itself is either shielded or separated from soot collection by a long chimney. Recent methods observed for manufacturing pine soot, most with a historic precedent, include capturing pine soot in a small room containing a shielded flame, capturing soot after a long slanted chimney empties into a large soot collection chamber distant from the flame, or in a series of containers forming a chimney above the flame while simultaneously shielding the soot from sparks.[17]

1.2 | Raman spectroscopy of carbonaceous artists' pigments.

RS has been used for some time to examine works of art non-invasively and is ideal in this context although care must be taken to avoid high laser powers particularly when examining black pigments.[22] Tomasini et al. were able to differentiate between graphite, charcoals, and soot-based pigments and identify them using RS on works of art.[23,24] Coccato et al. addressed RS of carbonaceous artists' materials and gave guidelines for examining different carbonaceous materials with RS.[25] Similarly Lambrecht et al. have proposed using RS to identify different type of archaeological char.[26] Daly et al. used RS combined with principal component analysis (PCA) of the entire Raman spectrum to separate a number of charcoal and black chalk drawing materials.[27] Goler et al. have used the I_D/I_G ratio of soot-based black inks to date Egyptian manuscripts.[28,29]

1.3 | Raman spectroscopy of other carbonaceous materials

After the first RS study by Tuinstra and Koenig to determine the size of microcrystallites in graphite, RS has been used in a wide variety of fields to study the properties of carbonaceous materials.[4,6,30] RS of various carbonaceous materials has been used to examine the properties of extraterrestrial carbons.[31] Amorphous carbon materials in shungite and other carbon-rich minerals have been characterized using RS.[7,32,33] In the field of atmospheric pollution, RS has been used to investigate the carbonaceous materials present, for example, where Catelani et al. found differences in the Raman spectra of atmospheric carbon from urban and non-urban regions.[34,35] RS has been extensively used in the examination of graphenes, carbon nanoribbons, carbon nanotubes, and other novel electronic materials.[5,6,36–42]

In combustion, RS has been used for examining the size of PAH molecules that compose the primary particles of soot for many years.[2,8,43–49] The Raman G band arises from the unbroken graphene-like structure in the center of the PAH molecules, whereas the asymmetric stretch that composes the D band only becomes spectroscopically allowed at the edges of or defects within the graphene plane.[50] By adding additional peaks into the fitting procedure, for example, the D2, D3, and D4 peaks, more complex predictions of soot structures can be studied.[43] In some recent studies, Le et al. used RS to examine the effect of heat treatment on soot structure and have recently been using RS in situ to study soot formation directly in the flame.[44,51]

An additional factor to evaluate in the Raman spectra of soots is the dispersion of peaks. It is widely observed that the position of the D peak shifts depending on the energy of the incident laser used in RS, generally with a slope of approximately 50 cm^{-1}/eV.[52] However, as the degree of disorder in carbonaceous materials increases, the G peak becomes dispersive, whereas in carbonaceous materials with a large graphitic nature, the position of the G peak remains constant regardless of the incident laser energy used in RS.[4–6,53]

Although analysis of East Asian paintings and calligraphy may be a small field, the diversity in flame structures and sooting environments may provide analogs to the PAH materials community. Camphor soot and candle flames have been investigated as a novel electronic material.[54–56] In addition to its use in artwork, East Asian ink has also recently had some interest in the field of new medical technologies.[57] Pine soot may serve as an analog for atmospheric contributions from wood stoves and forest fires.

2 | EXPERIMENTAL

2.1 | Sample soots

Samples of soot used to produce East Asian inks were obtained from 10 workshops and studios in China and Japan, some of which have been actively producing soot and inksticks for hundreds of years. Most workshops visited made both soot and inksticks; however, one workshop exclusively produced soot, whereas a few others exclusively made inks and relied on soots purchased from other sources. In addition, two samples of carbon black obtained from Columbian Chemicals Co. (now Birla) and used in prior ink studies were also examined. A complete list of sample materials can be found in Table 1. Although prior to the advent of carbon black, only traditional lampblack and pine soot can be expected to be used in East Asian inks, carbon black and lampblacks made in a non-traditional manner were also included in this study to allow comparison of traditional and modern materials. Although modern materials may be used in modern works of art, they may also be found in historic works of art with modern conservation treatment.

To prevent static dispersal of soots onto the instrument optics, soots were made into 7-mm diameter pellets by gently compressing with a hand press from Pike Technologies designed for producing samples for vibrational spectroscopy.[58] To provide sufficient data for statistical analysis and determine heterogeneity of the sample, 10–25 spots on each soot sample were examined with RS.

2.2 | Woodblock-printed Japanese books

Four versions of *Kaishien gaden* from the Smithsonian's National Museum of Asian Art (NMAA) were examined using a 785-nm incident wavelength Raman spectrometer manufactured by Wasatch Photonics; see experimental details below. *Kaishien gaden* is the Japanese printing of the famous Chinese painting manual *Jie zi yuan hua pu* written by Wang Gai, first published in 1679, and still in print worldwide. It is commonly translated into English as *The Mustard Seed Garden Manual of Painting*.[59] All four NMAA copies of the woodblock-printed book were published in Kyoto between 1748 and the end of the Meiji period, via two different publishers; see Table 2. The accession number or lab record number indicates the different copies; however, most copies have multiple volumes. For copies 813 and 814, two separate volumes each were analyzed; the different volumes of a single copy were expected to be printed roughly contemporaneously and have been sold and stored in similar conditions over the hundreds of years since printing. *Kaishien gaden* is noted for being one of the earliest books in Japan printed with multiple wood blocks. The key block was used to print the outline of the page, any printed characters, and outlines of the overall structure. Depending on the page, other blocks were then used to add detail in other inks, both with various colors and lighter and darker shades of black.

TABLE 1 Soot sources used with what is known about fuel source and manufacturing.

Sample number	Soot type	Fuel source	Manufacturing method	Source
1.1	Carbon black	Mineral oil		Suzuka-zumi
1.2	Carbon black	Mineral oil		Suzuka-zumi
1.3	Traditional lampblack	Canola oil	Larger particle size	Suzuka-zumi
1.4	Traditional lampblack	Canola oil	Smaller particle size	Suzuka-zumi
1.5	Lampblack	Sesame oil		Suzuka-zumi
1.7	Pine soot	Cut pine branches		Suzuka-zumi
2.1	Lampblack	Vegetable oil		Boku-undo
2.2	Pine soot	Pine		Boku-undo
3.1	Traditional lampblack	Canola	Finest grade	*Kobaien
3.2	Traditional lampblack	Canola	Medium grade	*Kobaien
3.3	Traditional lampblack	Canola	Coarse grade	*Kobaien
4.1	Lampblack	Tung oil with some pig fat	Made in modern fashion	*Tunxi Hu Kai Wen
5.1	Lampblack	Tung oil with some pig fat		Wu Cheng Lin
6.1	Traditional lampblack	Tung oil	Water-cooling oil bowls	*Old Hu Kai Wen
7.1	Pine soot	Pine wood	Stacked chimney style	*Yu Wen Xuan
7.2	Traditional lampblack	Tung oil	Thin wick ~1 mm, bowl not rotated	*Yu Wen Xuan
8.1	Traditional lampblack	Tung oil	Wick soaked in medicinals	*Yu Xuan Zhai
8.2	Pine soot	Pine root	Steel chimney to small room	*Yu Xuan Zhai
9.1	Pine soot	Pine wood	Earthenware chimney to fiberglass tent	*Uchida-shoen
10.1	Pine soot	Pine wood	Shielded flame in steel wire tent	*Kishu-shoen
11.1	Carbon black		Raven 410	*Columbian Chemicals (now Birla)[15]
11.2	Carbon black		Raven 1250	*Columbian Chemicals (now Birla)[15]

Note: Sources marked with * manufactured the soot on-site.

TABLE 2 Locations analyzed in four copies of *Kaishien gaden*.

Accession number/lab record number	Publisher	Volume and page number	Sample locations	# spots analyzed
FSC-GR-780.**812**	Kawanami Shirōemon	2, 8–9	Key block	20
FSC-GR-780.**813**	Kawanami Shirōemon	2, 8–9	Key block	19
FSC-GR-780.**813**	Kawanami Shirōemon	3, 36–37	Key block	19
FSC-GR-780.**814**	Hishiya Magobē	1, 28–29	Key block	17
FSC-GR-780.**814**	Hishiya Magobē	2, 40–41	Key block	20
LRN 9850[60]	Hishiya Magobē	15–16	Key block, intense black	15 key block, 5 intense black

Note that *Kaishien gaden* is separated into multiple parts, each with multiple volumes. The volume and page number followed in Table 2 refer to the volume number assigned by the museum. Although pages 8–9 in volume 2 were examined for both copies 812 and 813, these are from different parts of the book and so were not printed from the same woodblock. In addition, in traditionally bound East Asian books, both the front and back of a page share a singular page number, so the spread visible in an open book refers to the back of one page and the front of the next page. Pages 15–16 refer to one opening view with the back of page 15 and the front of page 16 composing the two halves of the image (Figure 1). In each volume examined, 17–20 spots were analyzed. For

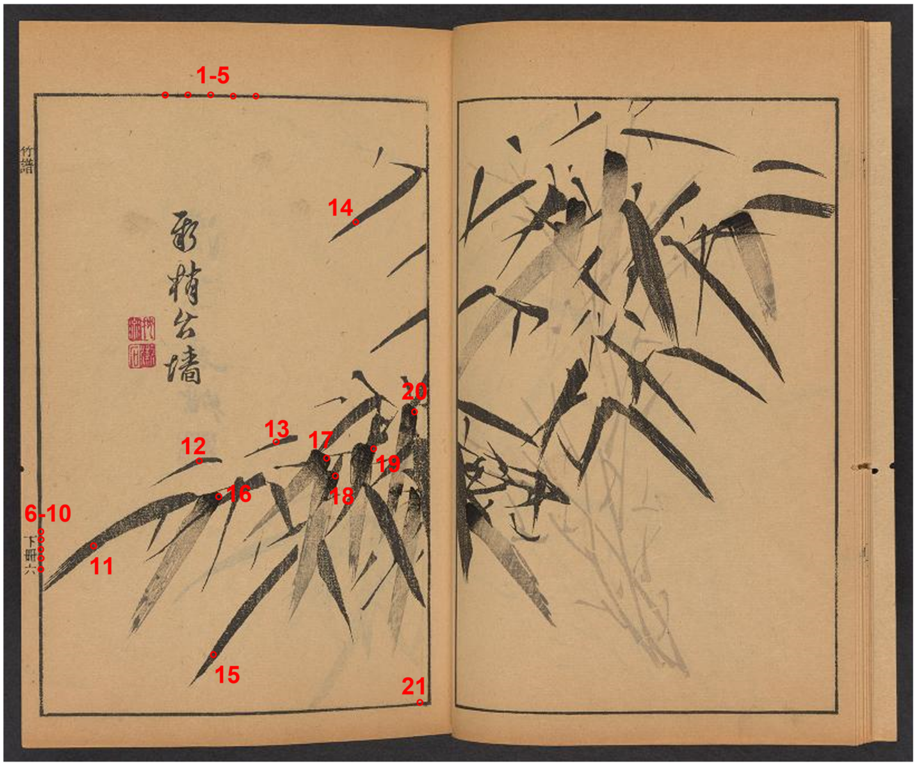

FIGURE 1 Page 15–16 of Volume 2 Part 4 *Kaishien gaden*, copy LRN 9850 with analysis locations annotated. The darker black is visible in locations 16–20; all other locations are from the keyblock. Original, unannotated image courtesy of the Smithsonian Libraries and Archives.

this study, locations were chosen to focus on the keyblock. In the case of copy LRN 9850, a few areas in a separate darker intense black were also observed and analyzed.

2.3 | Raman spectroscopy

Raman spectra were obtained from two different instruments using three different incident wavelengths. A Wasatch Photonics Raman spectrometer with an f/1.3 fiber optic probe with a 785-nm incident laser was used for examining all the soot samples as well as for noninvasive examination of ink on works of art. The Wasatch spectrometer is model WP-785-R-XR-LMMF with a 25-μm slit for 6-cm^{-1} resolution and wavelength calibrated against polystyrene. In addition, RS with a 405-nm incident laser was carried out on a JY Horiba LabRam Evolution Raman microscope at a magnification of 5× using a grating of 300 grooves/mm and a resolution of 4 cm^{-1}. The system is wavelength calibrated against silicon. Spectra were acquired for five co-added 10-s scans in 10–25 different locations on the soot samples. To investigate peak dispersion, four soots were further examined with 633- and 785-nm incident lasers using the same JY Horiba Raman microscope as the 405-nm incident laser spectra.

Because of strong absorption by the samples, laser power was kept low, varying from 0.3 to 3 mW at the surface of the soots depending on the wavelength and individual sample. In all cases, laser power was kept low enough that any background laser-induced incandescence (LII) was minimized, no changes in the Raman spectra over time were observed, and no visible damage to the sample was seen. Although LII is minimized by the use of low laser power, with strongly absorbing samples, it is difficult to completely eliminate.[8] Although not presented here, samples with larger thermal mass, for example, inksticks, were better able to diffuse thermal energy from laser excitation and had lower LII than those samples that had smaller thermal mass. Raman spectra from inksticks also confirmed that the Raman spectra of inks only contained peaks due to soot.

All spectra had baselines subtracted to eliminate the rising or falling baselines present from LII or fluorescence. Both baseline subtraction and D and G peak fitting used the same python code for all samples from a Raman instrument to reduce the possibility of human error during the subtraction and fitting process. A third-order polynomial baseline was fit on either side of the soot peaks and subtracted from data before fitting peaks.[8]

Raman spectra were fit with two primary peaks, the D peak and the G peak, and the results were then analyzed for reproducibility and effectiveness of soot separation and identification. For this study, the minimal two-peak fitting routine first proposed by Ferrari and Robertson was chosen for maximum reproducibility.[4] The D peak is fit with a Lorentzian profile centered at approximately 1345 cm^{-1}, and the G peak is fit with a Breit–Wigner–Fano profile at approximately 1590 cm^{-1}; see Figure 2.

After peak fitting, D and G peak positions, D and G peak widths using half-width at the half maximum (HWHM), and the intensity ratio for the D and G peaks (I_D/I_G) were recorded for each spectrum and used for statistical analysis. It is found that the use of the peak fit results after background subtraction minimized the effect of LII, fluorescence, and noise. LII and noise could not be completely eliminated; therefore, the R^2 value of the fit was calculated, and all soot spectra for which the R^2 value was less than 0.70 were discarded. Inspection of the rejected spectra, generally fewer than 1–2 spectra per sample, showed that poor fits were most commonly due to poor Raman scattering leading to high signal-to-noise ratios or high LII from the sample. Uncertainties in the fit were calculated from the variances using the `uncertainties` and `NumPy` python libraries.[61,62]

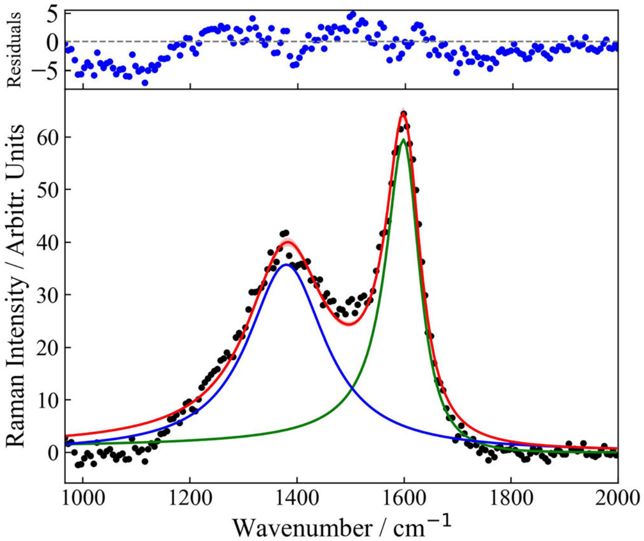

FIGURE 2 Raman spectrum of soot sample 1.2 using 405-nm incident laser after baseline subtraction (black dots) with D peak fit (blue line), G peak fit (green line), and combined fit (red line).

Kernel density estimations (kde) show the population density for the various peak fit parameters and allow multiple curves to be plotted on a single graph for comparison between different soot types and soot sources. The kde were generated in Python using the `matplotlib`, `seaborn`, and `pandas` python libraries.[63–66] Statistical and PCA on the peak fit results from all spectra were performed using `pandas` and the `scikit-learn` Python library.[67] PCA of the 785-nm excitation data captured 82% of the variability with three PCs, whereas the 405-nm excitation data captured 90% of the variability with only two PCs. When 785- and 405-nm data were combined, three components capture 79% of the variability; see Figure S1. In a separate PCA of 785-nm data from the historic inks used in the *Kaishien gaden*, three PCs captured 94% of the variability in the data; see Figure S2.

3 | RESULTS

3.1 | Peak fit results of individual soot samples and soot types

Between 405- and 785-nm incident laser analyses, over 900 Raman spectra were collected and analyzed. Summarizing the peak fit data in correlation plots allows easier comparison between different soot samples and soot types. Histograms in the correlation plots show that there is not a normal distribution curve for the collection of soot samples; however, a correlation plot for a single soot sample shows that individual soot samples trend toward a normal distribution over the fitting parameters (Figure S3). This suggests that the individual samples are generally homogeneous. Overall, individual samples showed smaller standard deviations than soot types (Table 3).

Correlation plots, when colored by soot type, show significant variation within the soot types suggesting that Raman peak fitting parameters alone may not be enough to differentiate between the different soot types; see

TABLE 3 Average and standard deviation of peak fit variables for spectra from Wasatch spectrometer (785 nm inc. laser) for traditional lampblack and pine soot and two specific soots of each type.

Soot sample/type	G peak position/cm^{-1}	G peak HWHM/cm^{-1}	D peak position/cm^{-1}	D peak HWHM/cm^{-1}	I_D/I_G
Traditional lampblack (all)	1588 (±1.4)	43 (±1.5)	1311 (±1.7)	104 (±3.0)	1.56 (±0.20)
3.2	1588 (±1.3)	44 (±1.4)	1311.2 (±0.65)	103 (±1.1)	1.72 (±0.020)
6.1	1588.6(±0.81)	43(±1.4)	1310(±1.5)	103(±1.6)	1.66 (±0.13)
Pine soot (all)	1590 (±1.4)	38 (±2.4)	1310 (±4.9)	103 (±2.8)	1.43 (±0.14)
2.2	1589.6 (±0.20)	35.6 (±0.37)	1304.6 (±0.41)	105.2 (±0.43)	1.538 (±0.012)
10.1	1590 (±1.6)	40 (±1.3)	1313.6 (±0.57)	106.4 (±0.87)	1.518 (±0.015)

Figure 3. In general, pine soots show the most variation in peak fit parameters, whereas the unknown and modern lampblacks group in the tightest cluster. The majority of pine soots have low D peak positions in spectra obtained with 405-nm incident laser light than when excited with a 785-nm incident laser, and smaller G peak widths in spectra from both incident laser wavelengths. Traditional lampblacks frequently, but not always, had a low wavenumber, broad G peak. The Raman data from 405-nm incident laser also showed strong correlations between the two fit parameters for the G peaks and the I_D/I_G peak ratio, observed as diagonal lines in the plot of G-peak width and G-peak position versus I_D/I_G peak ratio. These correlations are non-existent or significantly weaker in the spectra obtained with a 785-nm incident laser.

3.2 | Principal component analysis of soots

Correlation plots are limited to comparing sample information for only two variables at a time. PCA of the Raman peak fit information allowed all the peak fit variables to be taken into consideration. PCA of Raman data from a single incident laser wavelength, either 405 or 785 nm, was able to separate some individual soot samples and soot types; however, there remained significant overlaps of some clusters. PCA from the 405-nm incident radiation Raman spectra were better able to separate soot types and soot samples (Figure S4).

Combining the Raman peak fit parameters PCA of the Raman data from both 405- and 785-nm incident radiation shows better separation than either data set separately; see Figure 4. When categorized by type of soot, traditional lampblacks, and pine soots, the two soot types most likely to be found on historic works of art can be separated using two wavelength PCA. The separation between individual soot samples was not as successful as those by soot type. In some cases, when multiple soot samples clustered together, an explanation may be present. Samples 3.1, 3.2, and 3.3 cluster together, and all three are traditional lampblack soots made in the same factory. Samples 1.7, 2.2, and 9.1 all cluster together, and it is believed that the soot workshop that produces sample 9.1 is a supplier for inkstick workshops 1 and 2. However, many of the lampblack produced by modern or unknown (but likely modern) methods overlap significantly despite being obtained from different sources.

Figure 4 shows that much of the separation between pine soot and the various lampblacks is encompassed in PC 1 with the remainder of the overlap separated by PC 2. Analysis of the loadings plot shows contributions of the individual Raman spectrum peak fit parameters to PC 1 and 2; see Figure 5. The primary negative contributor to PC 1 is the G peak position of the 405-nm Raman spectra, whereas the primary negative contributor to PC 2 is the G peak position in the 785-nm Raman spectra, suggesting that G peak dispersion may contribute to the separation of pine soot from traditional lampblack. However, six of the peak fitting parameters are also positive contributors to PC 1, whereas the D peak widths were positive contributors to PC 2, suggesting that G peak position is not the only difference to be found between traditional lampblacks and pine soots. Examination of the peak fit parameters in Figure 3 further supported that the G peak in traditional lampblacks was not dispersive, whereas for pine soots, the G peak was dispersive.

3.3 | Dispersion of D and G peaks

To examine peak dispersion more closely, two soot samples were selected for further analysis from the pine soots and traditional lampblacks in the study. The JY Horiba Raman microscope was used to examine 10 spots on each soot sample at each of three incident laser wavelengths. The dispersion for the D peaks of all soots averages 40 cm^{-1}/eV, less than the approximately 50 cm^{-1}/eV more commonly observed.[52] The dispersion of the G peaks varies from 1.5 cm^{-1}/eV for the traditional lampblacks to 8.6–10.1 cm^{-1}/eV for the pine soots; Figure 6. This suggests that traditional lampblacks have more ordered regions of PAH molecules, whereas the PAH molecules in pine soots are more disordered.[4,5,53] The more ordered nature of the PAH molecules in traditional lampblack may be a consequence of the periods of heating close to the flame that traditional lampblacks undergo during their manufacture.

3.4 | Application to a work of art

Four copies of *Kaishien gaden* were examined using non-invasive RS with a 785-nm incident laser beam. The four copies were all printed in Kyoto during the 18th and 19th centuries but by two separate publishers. Correlation plots, not shown, show little difference between the peak fit results for the two publishers. Although most of the peak fit results for the *Kaishien gaden* spectra fall within the range of those observed in the modern soots examined above, the average D peak width was significantly narrower (84 ± 8.9 cm^{-1}) than any observed in the modern soots, where the minimum D peak width measured was 95 cm^{-1}. PCA of the *Kaishien gaden* ink data exclusively captured 94% of the variance in the keyblock ink

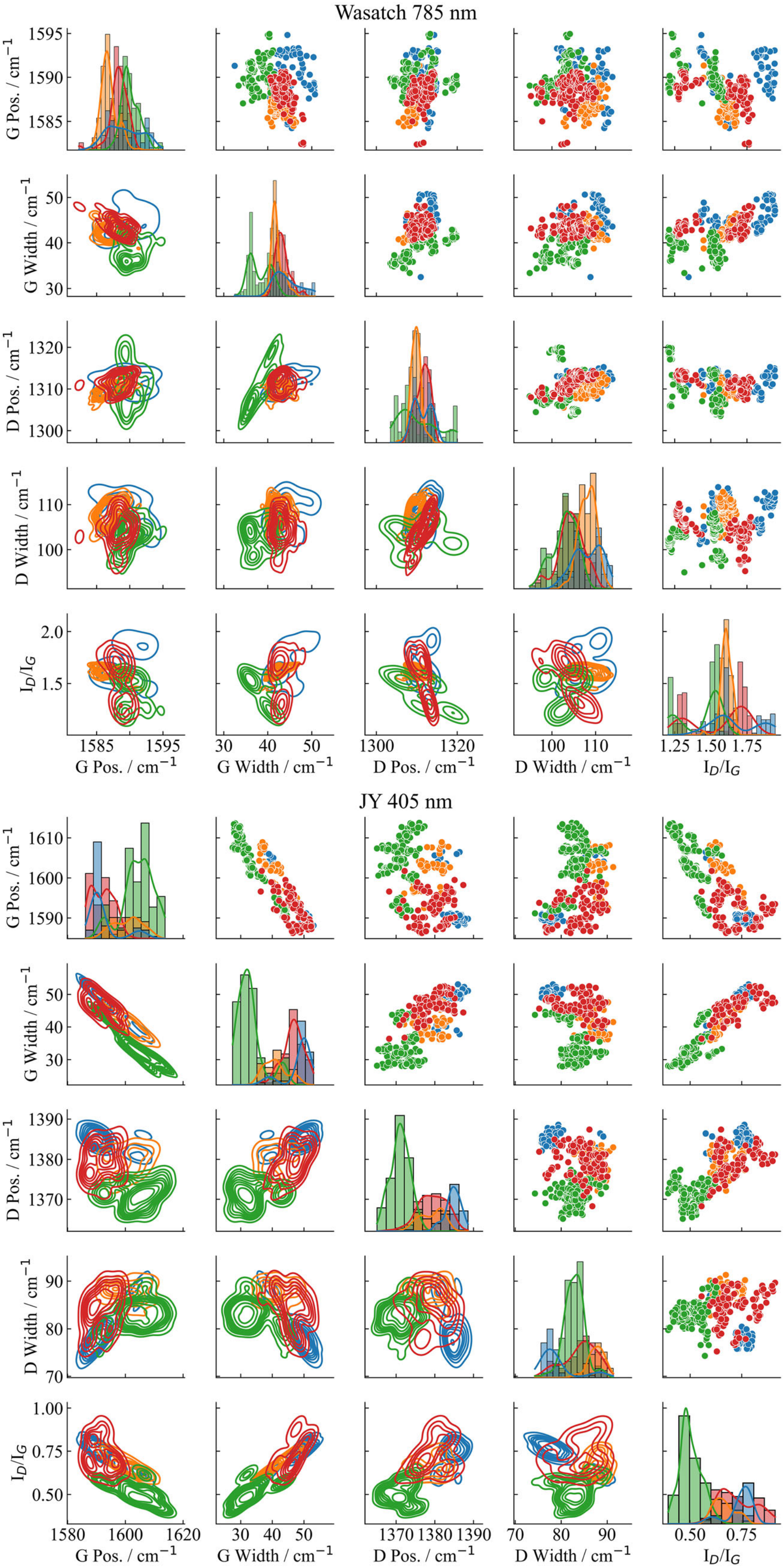

FIGURE 3 Correlation plot of Raman peak fitting parameters for 785-nm Raman spectra (top) and 405-nm Raman spectra (bottom) from all soot samples colored by soot type: carbon black (blue), traditional lampblack (red), unknown lampblacks (yellow), pine soot (green).

used by the two publishers; however, overlap between the two 95% confidence intervals was present and shows that RS with a 785-nm incident laser alone cannot separate the two publishers (Figure 7). Woodblock printers were known to prepare large quantities of ink in advance, and it is possible that the pre-prepared ink

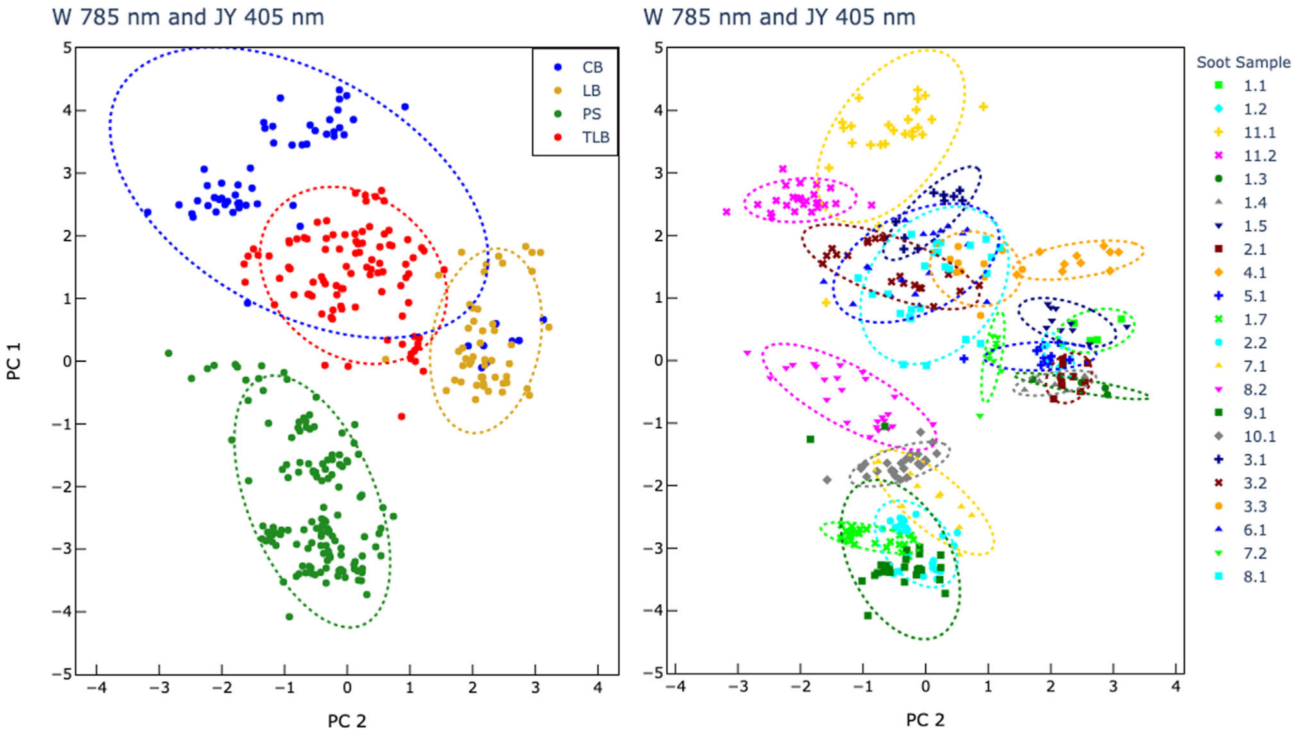

FIGURE 4 PC 1 versus PC 2 plots showing soot types (left) and each soot sample (right) separately. Ellipses are for a confidence level of 95%. Peak fit data from both 785- and 405-nm Raman spectra were used in the principal component analysis.

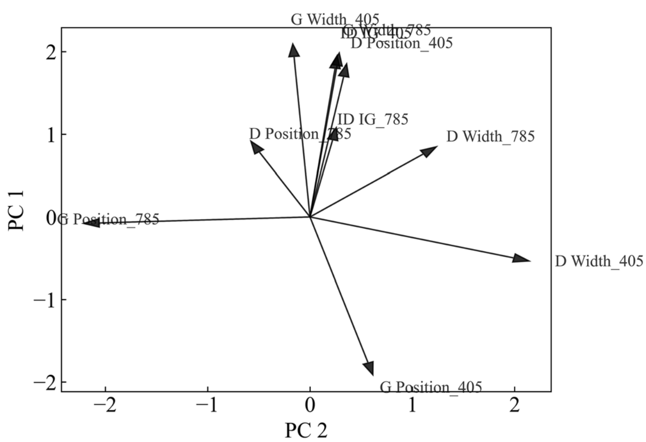

FIGURE 5 Loadings of Raman peak fit parameters to the first two principal components.

could come from different soot sources, which may explain the large spread within and overlap between the different printers in Figure 7.[68]

On pages 15–16 of *Kaishien gaden* (LRN 9850), the woodblock print illustration of bamboo shows three different printing stages using black ink. The key block was used to print the outline of the page and much of the overall structure of the bamboo illustration, whereas a second printing block was used with a very dark rich ink in some areas of the print, particularly at the nodes where the bamboo leaves were attached to the bamboo stems. A third printing block was used with a light grey ink to add depth to the illustration. PCA was used to analyze the Raman spectra from the key block and the dark overlay printing. Unfortunately, the light gray printed areas had a very weak Raman signal, and no usable spectra were obtained in those regions. The PCA between the key block end overlay shows that the two samples can be separated using this technique and suggests that the publisher Hishiya Magobē used a different ink source for the key block versus the rich black overlay (Figure 8).

Goler et al. have identified changes in the Raman spectra of soot-based inks over time.[28,29] In particular, Goler et al. noted peak broadening of the G and D peak widths as inks aged, whereas the inks on the *Kaishien gaden* had narrower D peak widths (84 ± 8.9 cm^{-1}) than those observed from the modern soots. The average width of the G peak (36 ± 2.2 cm^{-1}) could suggest a pine soot was used for printing the *Kaishien gaden* books when compared with the modern soots; however, the variation in D peak width from the modern soots and the difference in trends from those observed by Goler et al. suggest that more studies will need to be performed to better understand the effect on Raman peak characteristics of aged soots and inks before any conclusions can be drawn about the type of soot used in these books.

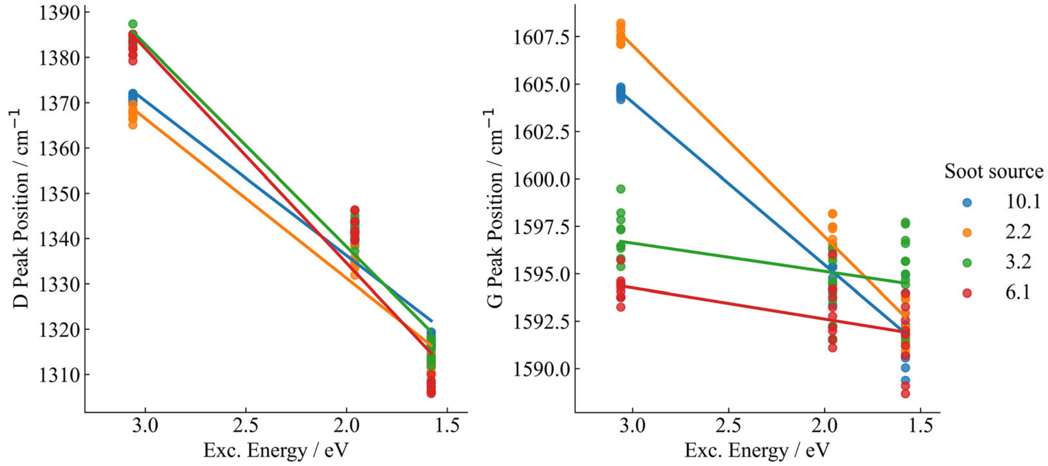

FIGURE 6 Dispersion for the D peak (left) and G peak (right), colored by soot sample for two pine soots (10.1 and 2.2) and two traditional lampblacks (3.2 and 6.1).

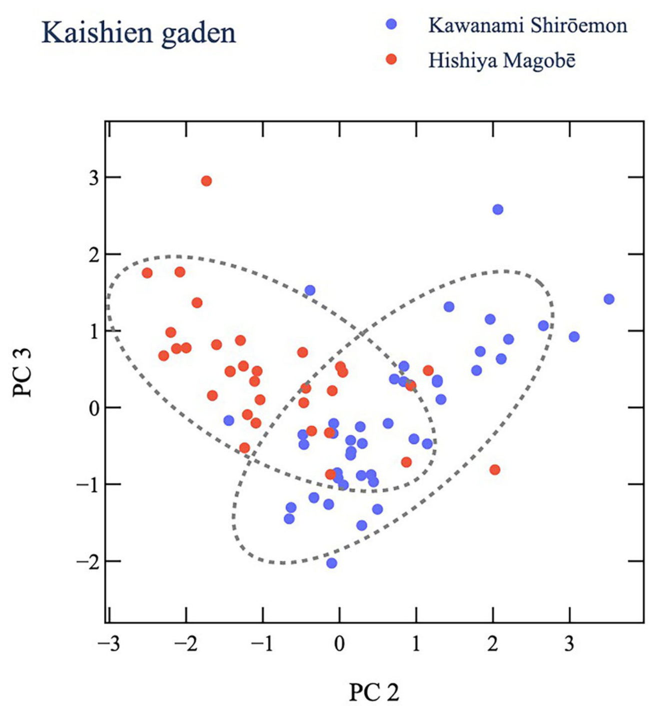

FIGURE 7 PC 2 versus PC 1 showed the best separation of Raman spectra from the keyblock of four editions of Yu Xuan Zhai Kaishien gaden showing two different publishers (Kawanami Shirōemon, blue; Hishiya Magobē, red; 95% confidence ellipse, gray); however, PCA was unable to definitively separate the publishers.

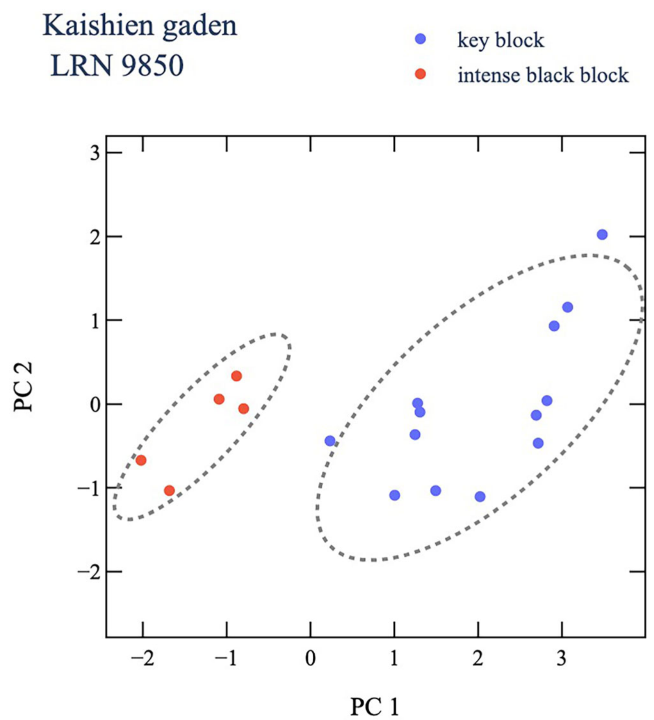

FIGURE 8 PCA of black inks from two different print blocks in a bamboo illustration suggesting different inks are used for the key block and the intense black sumi block.

4 | DISCUSSION

The G peak parameters for pine soots show few prominent trends, but overall, the pine soots have narrower G peaks located at higher energies, particularly when examined with a Raman system with a 405-nm incident laser. For all spectra pine soots have lower I_D/I_G when compared with the other soots examined. Of note, two pine soot samples from two different ink workshops, 1.7 and 2.2, both of which purchase soots rather than make their own, overlapped consistently in every peak parameter with each other and with soot 9.1, suggesting that both ink workshops purchase their pine soot from the same original manufacturer, and suggesting that Raman peak properties may be able to differentiate between some specific samples, not only broad soot manufacturing techniques.

Modern lampblacks often trend consistently with the two carbon black samples purchased from an ink workshop, although not with the two carbon black samples from Columbian. In general, the modern lampblacks show Raman peak parameters in the middle of the range observed for all soots. Using PCA the modern and unknown lampblack cannot be separated from traditional lampblacks, although the larger group of all lampblacks can be separated from the pine soots as in Figure 4.

Although the PCA of the soots does allow separation of the pine soot and traditional lampblack, an easier method for discrimination may be the examination of the G peak dispersion. Almost all the traditional lampblack samples collected have similar Raman spectral parameters: very small positive or even negative G band dispersion and narrow, high wavenumber D peak positions; see Figure 6. During the production of traditional lampblack soot, most of the soot formed is heated over the flame for an additional period of up to 20 min before being rotated away from the flame or being collected, essentially heat-treating the soot after its initial formation. The extended period of heating of the traditional lampblacks may result in fluidity of the soot structure, allowing the PAH molecules to become more ordered, as demonstrated by Pawlyta et al.[69]

The lack of G band dispersion suggests a more graphitic nature for traditional lampblacks, but the wide G peak can be thought contradictory to this conclusion. Ferrari and Basko show that the G peak dispersion and G peak width are smaller for more ordered carbons,[5] and although the traditional lampblacks have no G peak dispersion, the G peak width is large. This effect may be because a two-peak fit does not take into account the presence of a D2 peak; however, Ferrari and Basko also used a two-peak fit when examining G peak dispersion and widths.[5] Lajaunie et al. also found G dispersion decreased with the heat treatment of amorphous carbons.[53]

The partial separation of the aged inks in the four copies of *Kaishien gaden* with PCA suggests that different inks, or different methods of making or storing the inks, were used by the two different publishers. However, the separation of the publishers' inks by PCA is not complete. More study is needed to determine if the separation of inks is maintained over a larger selection of printed works by the publishers. The separation of the intense black printed features demonstrates that the publishers discriminated between the sumi used for the general printing of the key block and the printing of a more distinctive region in the illustration. Comparing the trends in peak fit parameters for Kaishien gaden with those of the modern soots and trends previously identified by Goler et al. suggest that more work is needed to identify the changes in inks over time identified by RS.[28,29]

5 | CONCLUSION

RS shows promise to discriminate between traditional East Asian inks. Modern soots made by the traditional lampblack method can be identified by the lack of G peak dispersion when using two incident laser wavelengths in RS. PCA on a single work of art using only one Raman wavelength may be useful for identifying different soot sources or inks used in different areas of the work of art, although work remains to be done to fully understand the implications of aging on the RS of soot-based inks. Continuation of this research will further investigate the different properties of East Asian inks in works of art to be able to better understand the working methods of artists, calligraphers, and printers throughout East Asia.

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CONFLICT OF INTEREST STATEMENT

The authors know of no conflicts of interest in this article.

DATA AVAILABILITY STATEMENT

Software used for peak fitting is available via GitHub. Upon publication, Raman data can be made available via FigShare.

IMAGE PERMISSIONS

The image used as the base of Figure 1 has been made available by the Smithsonian Institution Libraries and Archives as CC0 or "No Copyright – United States."

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