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# A multi-analytical approach to identify red colorants on woodblock prints attributed to Suzuki Harunobu

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## Abstract

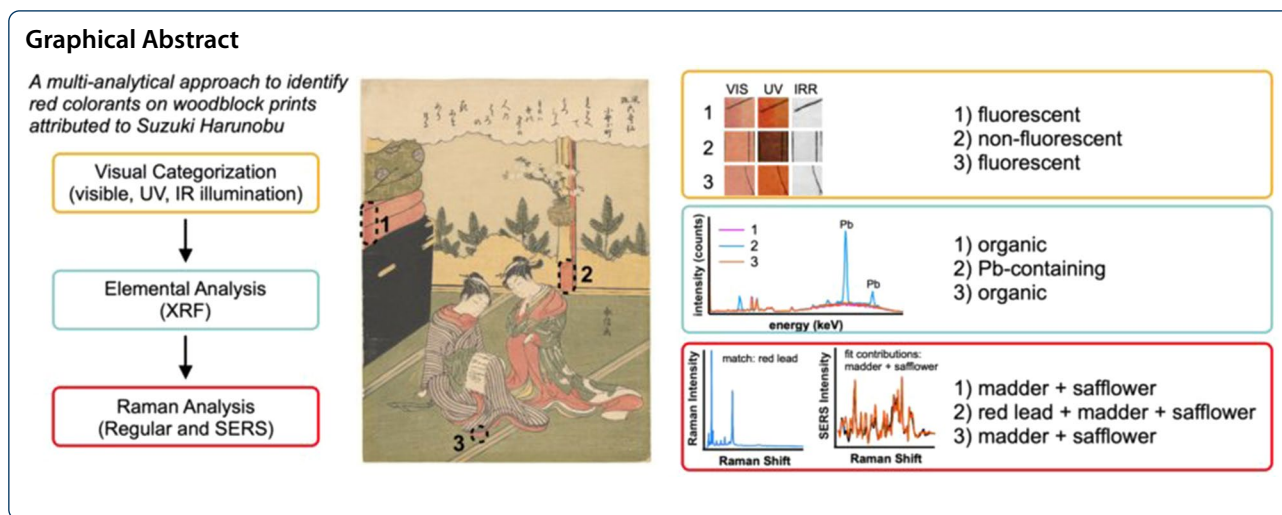
Red organic dye identification is an important topic for conservation of Japanese *ukiyo-e* prints. Of particular interest are the works of Suzuki Harunobu, who was working at the inception of full-color printmaking. These prints were made on thin *kōzo* paper and woodblock printed with semi-transparent to opaque regions of dye(s) and/or pigment(s) mixed with binder. This study used imaging analysis, X-ray fluorescence (XRF), Raman, and surface-enhanced Raman spectroscopies (SERS) to identify the red dyes and pigments on Harunobu prints in the collection of the Portland Art Museum. Through image analysis (visible, UV, and IR illuminations), 23 prints were categorized by appearance. XRF results provided identification of vermilion and ochre pigments, and identified color fields that contained lead. Raman analysis allowed the identification of red lead, and SERS was used to identify both safflower and madder dyes. This work is expected to contribute to the body of knowledge regarding the red dye and pigment palette and mixtures in use in the mid- to late eighteenth century, in the critical early years of full-color printmaking.

**Keywords:** SERS, Red chromophores, Japanese prints, Harunobu, Microsampling

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## Introduction

Edo-period (1603–1868) Japanese woodblock prints are widely recognized for their richly decorated scenes, evocative color application, and technically skillful production. During the Edo period the practice of color woodblock printmaking evolved from two- and three-color images to full-color brocade (*nishiki-e*) prints. These brocade prints were popularized in part by the prolific artist Suzuki Harunobu (c. 1725?–1770). Harunobu drew inspiration from classical literature, poetic conceits, and scenes of everyday life in the city of Edo, now Tokyo, often as reimagined well-known themes in humorous or clever designs. Harunobu was the most prolific and recognized artist working during the critical early years of full-color printing, a pivotal moment in the technical and aesthetic development of *nishiki-e*.

Woodblock prints were produced through a highly collaborative process utilizing the skills of master artisans, overseen by a publisher [1–4]. In simple terms, the design created by an artist (e.g., Harunobu) was transferred to woodblocks by specialized carvers. The key-block together with separate woodblocks for each color would be used by printers to produce the final image. These prints were produced on *kōzo* paper, which is notable for its long, thin fibers, typically sized with *dōsa*, a mixture of animal hide glue and alum. Natural organic dyes and/or mineral pigments, often mixed with rice paste as a smoothing agent, were applied in thin layers that became tightly incorporated with the fibrous paper network. The color palette of full-color *nishiki-e* was extensive but derives from a fairly restricted set of colorant sources, and studies have suggested that dyes or pigments from the same color family were often mixed to achieve the desired tone [5–9]. It should be recognized

that previously hide glue was erroneously cited as a colorant binder [10], and it should be clarified here that the presence of hide glue on *ukiyo-e* is the exclusive result of sizing with *dōsa* and that the historical literature cites the typical use of rice starch as a smoothing agent [1–4].

Red colors were relatively limited, deriving primarily from three mineral (vermilion—mercuric sulfide, red lead—lead(II,IV) oxide, and ochre—mixed iron oxides) pigments and three organic (safflower, sappan, and madder) dye sources [11]. The color-contributing compounds for safflower, sappan, and madder are carthamin, brazilein, and alizarin/purpurin, respectively. Herein, “colorant” will refer to pigment(s), dye(s), or mixtures of two or more in the form that they were applied to prints. The light and humidity sensitivity of organic dyes is well-established in preservation literature [11–15] and their fugitive nature has prompted the modern implementation of strict exhibition lighting regimes to prolong their vibrancy [16]. Definitive identification of colorants used on Japanese prints can inform lighting recommendations and therefore positively impact their accessibility and long-term care.

Many studies have been conducted to analyze colorants on Edo-period prints [7–9, 17–20] and the state-of-the-art techniques have recently been summarized in the literature [21–23]. Non-destructive methods toward pigment/dye identification include imaging under various sources of illumination [e.g., infrared (IR), visible or ultraviolet (UV) light] [7, 24], X-ray fluorescence spectroscopy (XRF) [17, 19], fluorescence spectroscopy [5, 6], and fiber optic reflectance spectroscopy (FORS) [7, 20, 25–28]. These methods, however, provide incomplete molecular information on their own and are best suited to multi-analytical studies.

Micro-destructive techniques such as gas or liquid chromatography-mass spectrometry have been used to provide complete identification of organic colorants [26, 29–33]. These techniques, however, rely on acquisition of a small sample, such as a fiber or cross-section from the work of art being analyzed. While these techniques have been successfully used on fibers as small as 2–5 mm in length [26, 29, 30], sampling fibers is highly reliant on the condition of prints (e.g., fibers that are already raised), the location of the sample area within the print, and with agreement between conservation and curatorial specialists. Given that *kōzo* paper derives its strength from its long-fibered network, sampling from such papers is warranted only with acceptable justification. Therefore, minimally invasive sampling methodologies [e.g., gel extractions or mechanical collection [10, 34], sub-millimeter lengths of fiber [9]] have been used to enable access to analytical tools beyond those non-invasive instrumental techniques that are better attuned to characterizing pigments from less delicate substrates. These minimally invasive sampling methodologies also permit analysis from small (less than 1 mm diameter) and centrally-located color blocks.

Raman spectroscopy provides comprehensive molecular identification of the analyte by probing bond vibrations in the dye or pigment molecule. Raman analysis, however, can be complicated by inherent fluorescence of some dyes. Therefore, surface-enhanced Raman spectroscopy (SERS) has been used in the analysis of red organic dyes, which are often fluorescent [35–40] and SERS has previously been applied to Edo period prints [9, 18, 19].

The work presented herein summarizes a survey of the Suzuki Harunobu prints at the Portland Art Museum with the objective of identifying the dyes and pigments used in red, orange, and pink color fields. These prints were non-invasively analyzed by imaging under visible, UV and IR light, stereomicroscopy, and XRF. Subsequently, seven prints were selected for minimally invasive sampling, wherein microscopic red colorant particulate was collected from the surface of the prints using a soft mechanical hydrogel collection apparatus. The microscopic red colorant particles were analyzed by Raman and SERS and the SERS spectral data were analyzed with a custom-built genetic algorithm (GA) to identify colorant components [10]. The micro-sampling and SERS data analysis techniques have previously been evaluated and determined to be minimally invasive and do not permanently alter the work sampled [10]. By comparing the results across the collection, patterns in color selection were observed.

The results in this paper comprise the palette of red colors used on Harunobu's works in the collection of the Portland Art Museum.

### Harunobu prints analyzed

The collection at the Portland Art Museum includes 32 prints designed by or attributed to the artist Suzuki Harunobu; the majority of those were accessioned nearly a century ago [41]. Therefore, these prints have a long history of protective care and regular condition reporting. Additionally, the prints in the Portland Art Museum's collection are notable for examples of early calendar prints and rare impressions, some being the only known extant impression. Identification of the dyes and pigments used in this collection will inform the conservation community on the printing practices employed in the earliest years of "full-color" woodblock printing (ca. 1765–1770) and on the technical use of color in the period prior to the known introduction of other red colorant sources (e.g., cochineal, eosin) [19].

A total of 23 prints attributed to Suzuki Harunobu were examined. All 23 prints were imaged and analyzed by XRF. Seven prints were selected for micro-sampling and Raman/SERS analysis; a total of 21 microsamples were collected, accounting for 16 color fields. Full visible light and UV light illuminated images of sampled prints are provided in the Additional file 1: Figs. S1–S7. One fiber was collected and analyzed by FTIR, Raman, SERS, and Electrospray ionization-Mass Spectrometry (ESI-MS). A complete list of the prints examined is provided in Table 1.

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Figure 1: Suzuki Harunobu (Japanese, 1725–1770), *Renshi*, from the series *Fūryū goshiki-zumi* (*A Stylish Version of Five Colors of Ink*), ca. 1768, color woodblock print with embossing on paper; *chūban nishiki-e*, image: 11 5/16 in × 8 5/16 in; sheet 11 3/8 in × 8 9/16 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.71.

Figure 4a (deep red): (DETAIL) Suzuki Harunobu (Japanese, 1725–1770), *Fumi yomu danjo* (*Couple Reading a Letter*), 1765/1770, color woodblock print on paper; *chūban nishiki-e*, image/sheet: 10 3/8 in × 7 3/4 in, Gift of Judith P. Benson. Portland Art Museum, Portland, Oregon, 1995.60.4

Figures 4a (red brown) and 6a (left): (DETAIL) Suzuki Harunobu (Japanese, 1725–1770), *Kyōdai no shūgetsu* (*Autumn Moon of the Mirror*), from the series *Zashiki hakkei* (*Eight Views of the Parlor*), ca. 1766/1768, color woodblock print with embossing on paper; *chūban*



**Table 1** (continued)

PAM Acc. No.	Title	Date	Location <sup>a</sup>	Visible light appearance	UV light appearance <sup>b</sup>	IRR absorbance	Unique XRF results <sup>c</sup>	Particle diameter (µm)	Raman results	SERS results
32.75	Ono no Komachi, from the series <i>Fūryū rokka sen</i> (The Fashionable Six Poetic Immortals)	ca. 1768	Red post	Red–orange	Non-FL	Very weak	Pb	7.03 (5.28), 7.58 (5.20)	Red lead	Safflower + madder
32.77	<i>Sanseki</i> (The Three Evening Poems): <i>Teika, Jakuren, and Saigyō</i>	ca. 1770	Clock table CF inner kimono Pink veranda Sky	Red–orange, discolored Medium red Pink Pink	Non-FL FL Non-FL FL	Discoloration weak None None None	Pb NIE Ca NIE	4.62 (2.27)	NR	Safflower (+ madder)
32.78	<i>Hibun</i> (A Secret Missive)	1767/1768	Wood panel Railing	Opaque red Red–orange	UV-Abs Non-FL	Abs Discoloration: weak	Fe Pb	4.28 (1.29)	NR	safflower + madder
32.79	<i>Fukurokuji no atama o soru yūjo</i> (Courtesan Shaving the Head of Fukurokuju)	ca. 1769	Maple leaves Decking RF outer kimono God's head	Medium red Red–orange Medium red Pale pink	Non-FL Non-FL FL Non-FL	None None None None	Ca, Pb Pb NIE Ca			
32.81	<i>Kaminari</i> (Thunder)	1766/1770	Red lantern base Flags	Opaque red Pink	UV-Abs Min-FL	Weak None	Fe NIE			
32.82	<i>Yayoi</i> (The Third Month), from the series <i>Fūzoku shiki porary</i> (Versions of the Poetic Immortals in the Four Seasons)	ca. 1769	Red ground	Dark red	FL	Weak	Ni			
32.83	<i>Ishiyama no shūgetsu</i> (Autumn Moon at <i>Ishiyama</i> ), from an untitled series of <i>Omi hakkei</i> (Eight Views of <i>Omi</i> )	ca. 1768/1769	Red table Lower garments Light wall Baseboard	Opaque red Medium red Pink Pink	UV-Abs FL Non-FL Non-FL	Weak None None None	Fe NIE Pb Pb	9.29 (2.54) 3.10 (3.17) 3.31 (0.89)	NR NR NR	Madder No colorant ID Safflower + madder

**Table 1** (continued)

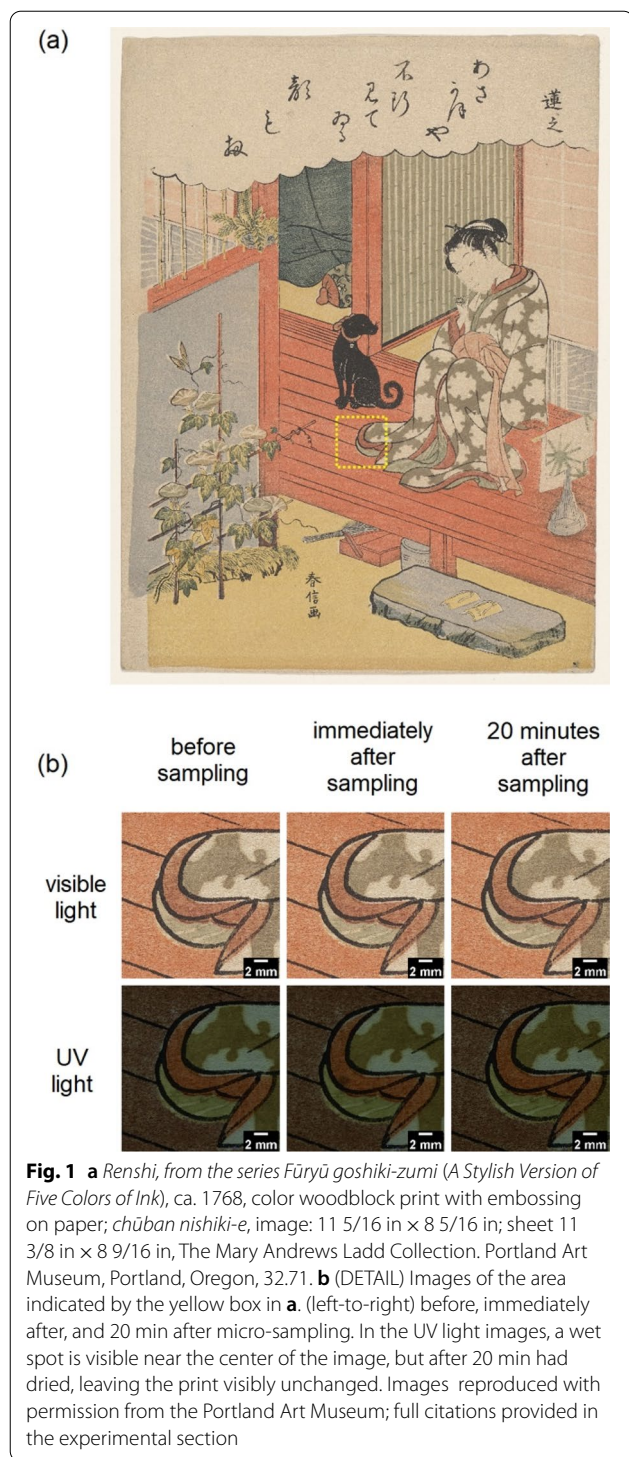
PAM Acc. No.	Title	Date	Location <sup>a</sup>	Visible light appearance	UV light appearance <sup>b</sup>	IRR absorbance	Unique XRF results <sup>c</sup>	Particle diameter (µm)	Raman results	SERS results
32.84	<i>Kyōdai no shūgetsu</i> (Autumn Moon of the Mirror), from the series <i>Zashiki hakkei</i> (Eight Views of the Parlor)	ca. 1766/1768	Lion's mane <i>susuki</i> seedheads RF inner kimono	Opaque red Medium red Medium red	UV-Abs FL FL	Weak Very weak None	Fe NIE NIE	7.26 (5.77)	NR	Safflower
32.87	<i>Jakuren</i> , from the series <i>Sanseki</i> (Three Evening Poems)	ca. 1765/1766	Outer kimono	Medium red	FL	None	NIE			
32.88	<i>Ogi no seiran</i> (Clearing Weather of the Fan), from the series <i>Zashiki hakkei</i> (Eight Views of the Parlor)	ca. 1766/1768	Red wall panel LF kimono	Opaque red Pink	UV-Abs FL	Weak None	Fe NIE			
32.89	<i>Sugaraku no kenka</i> (Children Quarreling over a Sugaraku Game)	1768–1770	Red wall panel LF kimono Front figure kimono Bucket	Opaque red Pink Medium red Orangey-pink	UV-Abs FL FL Min-FL	Weak None None None	Fe NIE NIE NIE			
32.90	<i>Yamabe no Akahito</i> , from an untitled series of <i>Hyakunin</i> (One Hundred Poets, One Poem Each)	1767/1768								
32.93	<i>Little peachling: calendar print</i> for 1765	1765	Inner kimono Peach blossom	Brown-pink Brown-pink	Non-FL Non-FL	None None	NIE NIE			
32.96	<i>Admiring the Reflection in a Water Basin</i>	1768/1769	Woman's inner kimono	Pink	Min-FL	None	Ca			

**Table 1** (continued)

PAM Acc. No.	Title	Date	Location <sup>a</sup>	Visible light appearance	UV light appearance <sup>b</sup>	IRR absorbance	Unique XRF results <sup>c</sup>	Particle diameter (µm)	Raman results	SERS results
35.39	<i>Gi</i> (Righteousness), from the series <i>Gajo</i> (The Five Confucian Virtues)	1767	RF kimono Lacquered stand Sake cup	Medium red Medium red Medium red	FL Non-FL FL	None Very weak None	NIE NIE NIE	12.13 (14.61) 4.52 (3.14)	NR NR	Safflower + madder Safflower + madder
82.2	<i>Ide no Tamagawa: Yamashiro no meisho</i> (The Ide Jewel River: A Famous Place in Yamashiro Province), from the series <i>Fuzoku Mu Tamagawa</i> (The Six Jewel Rivers in Popular Customs)	ca. 1769/1770	Pink screen RF inner kimono	Pink Medium red	Min-FL FL	None Very weak	NIE NIE	14.07 (16.39)	NR	Safflower
1995.60.4	<i>Fumi yomu danjo</i> (Couple Reading a Letter)	1765/1770	Blanket edge Red seal LF kimono	Opaque red Opaque red Red-orange	UV-Abs UV-Abs Non-FL	None None None	Fe, Zn, Hg Fe, Zn, Hg Zn, Pb			
2016.18.1	<i>The Departure</i>	1768/1769	Futon	Medium red	FL	None	NIE	7.29 (3.54); 14.07 (16.39)	NR	Safflower + madder

<sup>a</sup> LF left figure, RF right figure, CF center figure<sup>b</sup> FL fluorescent; Min-FL minimally fluorescent; Non-FL non-fluorescent; UV-Abs absorbing of UV light<sup>c</sup> Elements that are identifying or much higher than the average signal for that element; NIE no identifying elements





*nishiki-e*, image/sheet: 10 1/2 in × 7 9/16 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.84.

Figure 5a: (DETAIL) Suzuki Harunobu (Japanese, 1725–1770) *Renshi*, from the series *Fūryū goshiki-zumi*

(*A Stylish Version of Five Colors of Ink*), ca. 1768, color woodblock print with embossing on paper; *chūban nishiki-e*, image: 11 5/16 in × 8 5/16 in; sheet 11 3/8 in × 8 9/16 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.71.

Figure 6a (second-from-left) and 7a (left): (DETAIL) Suzuki Harunobu (Japanese, 1725–1770), *Koshikibu no Naishi* (*The Koshikibu Handmaid*), from an untitled series of *Hyakunin isshu* (*One Hundred Poets, One Poem Each*), 1767/1768, color woodblock print with embossing on paper; *chu chūban nishiki-e*, image/sheet: 10 7/8 in × 8 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.69.

Figure 6a (second-from-right): (DETAIL) Suzuki Harunobu (Japanese, 1725–1770), *The Departure*, 1768/1769, color woodblock print with embossing on paper; *nishiki-e*, image: 11 1/4 in × 8 1/8 in; sheet: 11 5/16 in × 8 9/16 in, Museum Purchase: funds provided by the Asian Art Council and Asian Art auction proceeds. Portland Art Museum, Portland, Oregon, 2016.18.1

Figures 6a (right) and 7a (left): (DETAIL) attributed to Suzuki Harunobu (Japanese, 1725–1770), *Ishiyama no shūgetsu* (*Autumn Moon at Ishiyama*), from an untitled series of *Ōmi hakkei* (*Eight Views of Ōmi*), ca. 1768/1769, color woodblock print on paper; *chūban nishiki-e*, image/sheet: 10 1/4 in × 7 3/4 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.83.

Figure 7a (center): (DETAIL) Suzuki Harunobu (Japanese, 1725–1770), *Gi* (*Righteousness*), from the series *Gojō* (*The Five Confucian Virtues*), 1767, color woodblock print with embossing on paper; *chūban nishiki-e*, image: 10 7/8 in × 8 1/16 in; sheet: 11 3/8 in × 8 1/16 in, Bequest of Winslow B. Ayer. Portland Art Museum, Portland, Oregon, 35.39.

Figure 8a: Suzuki Harunobu (Japanese, 1725–1770), *Ono no Komachi*, from the series *Fūryū rokkasen* (*The Fashionable Six Poetic Immortals*), ca. 1768, color woodblock print with light embossing on paper; *chūban nishiki-e* image: 11 7/16 in × 8 7/16 in; sheet: 11 7/16 in × 8 1/2 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.75.

Figure 8b: Suzuki Harunobu (Japanese, 1725–1770), *Koshikibu no Naishi* (*The Koshikibu Handmaid*), from an untitled series of *Hyakunin isshu* (*One Hundred Poets, One Poem Each*), 1767/1768, color woodblock print with embossing on paper; *chu chūban nishiki-e*, image/sheet: 10 7/8 in × 8 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.69.

Figure 8c: Suzuki Harunobu (Japanese, 1725–1770), *Kyōdai no shūgetsu* (*Autumn Moon of the Mirror*), from



the series *Zashiki hakkei (Eight Views of the Parlor)*, ca. 1766/1768, color woodblock print with embossing on paper; *chūban nishiki-e*, image/sheet: 10 1/2 in × 7 9/16 in, The Mary Andrews Ladd Collection. Portland Art Museum, Portland, Oregon, 32.84.

## Results and discussion

### Effects of micro-sampling on papers

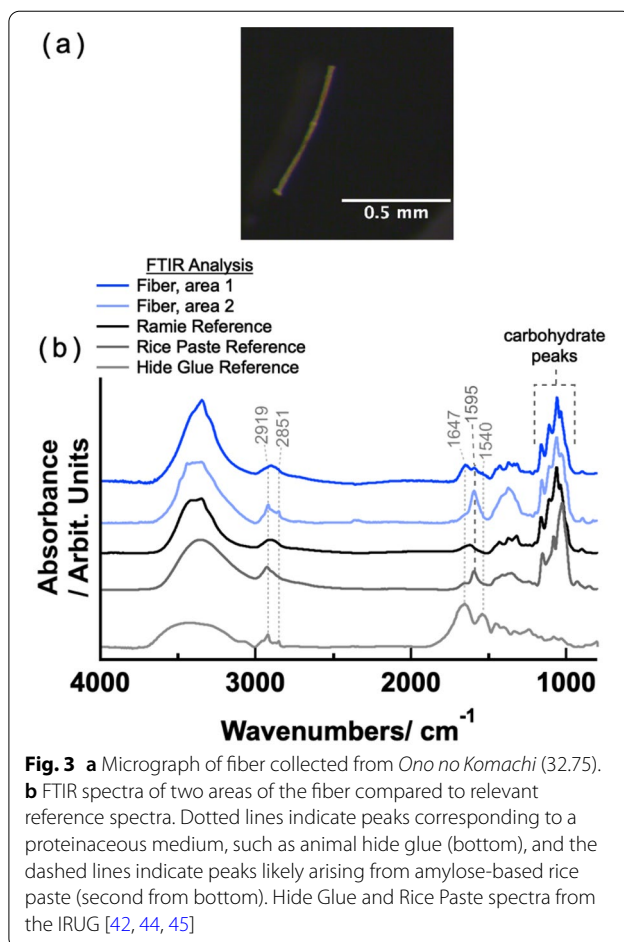
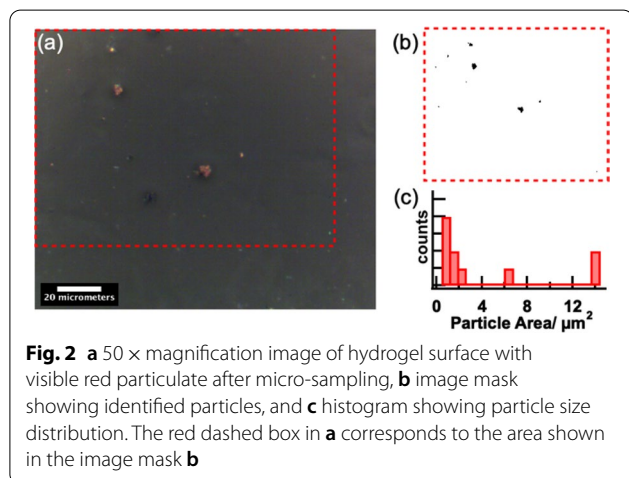
Photo-documentation was used to assess any visible effects of the hydrogel sampling process on the prints. Preliminary demonstrations on mock-up prints indicated that wetting from the water-equilibrated hydrogel may occur, but that the effect was temporary and became invisible once the sampled area dried [10]. A representative example is shown in Fig. 1 along with magnified views of an area before and after micro-sampling. In Fig. 1b, a wet spot with an area of  $1.7 \pm 0.2 \mu\text{m}^2$  is barely discernable by eye. After 20 min the wet spot was not visible under visible or UV light illumination.

### Particle size analysis

Raman microscope images were collected of each hydrogel after sampling and the size distribution of collected particles was evaluated. The average particle sizes for each sample area are included in Table 1. Figure 2 shows an example of a microscope image and the subsequent processing for particle counting. The collected samples from the seven prints ranged from single grains of colorant to larger pieces of glue-bound colorant and average particle diameters ranged from 2.60 to 36.97  $\mu\text{m}$ , much smaller than can be sampled through standard scalpel or needle collection methods.

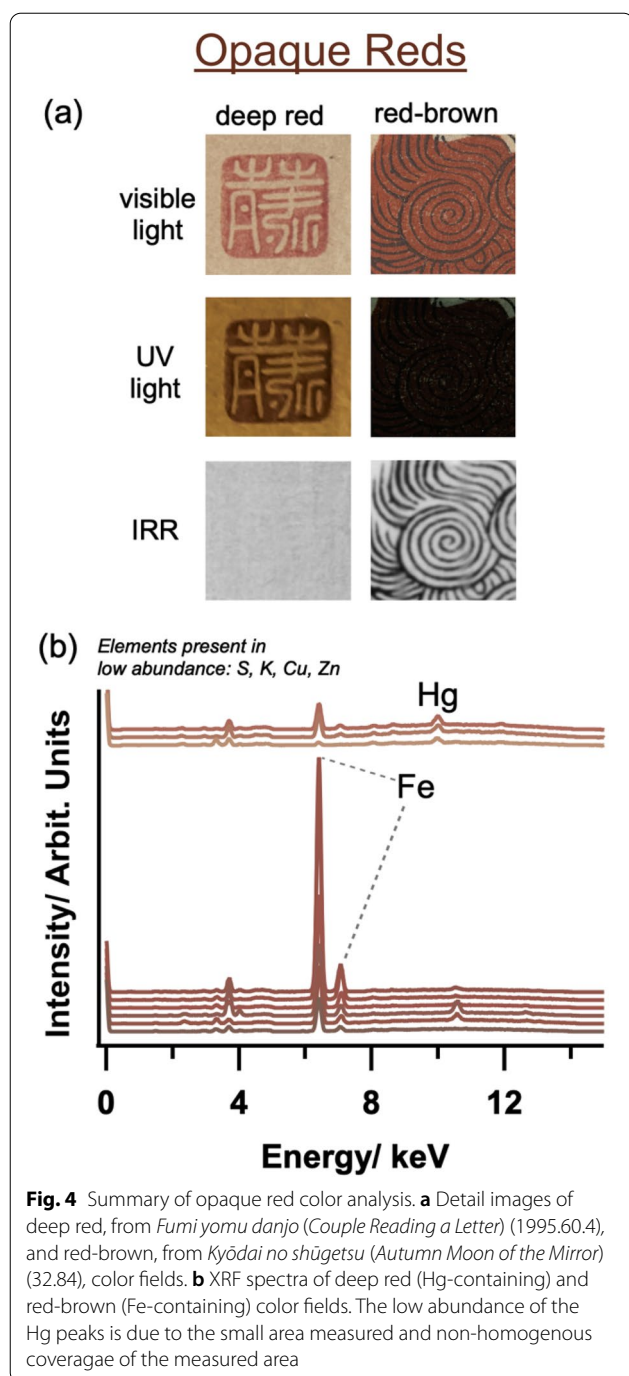
### FTIR analysis of substrate

A micrograph of a single fiber that was collected from *Ono no Komachi (32.75)* is shown in Fig. 3a. This fiber



was raised from the surface and near the edge making sampling possible without detriment to the rest of the print. The fiber was analyzed by FTIR to gain insight into the paper substrate and binding medium. Two FTIR spectra collected from different areas of the fiber are shown in Fig. 3b, along with relevant reference spectra. From 800 to 1500  $\text{cm}^{-1}$  the fiber spectra are nearly identical to a reference spectrum of Ramie [42], a bast fiber in the same class as *kōzo*. Differences arise in the region from 1500 to 1700  $\text{cm}^{-1}$ . In the spectrum of fiber area 1, a weak peak at 1647  $\text{cm}^{-1}$  and a small shoulder at 1540  $\text{cm}^{-1}$  are present, correlating to the Amide I and Amide II peaks in animal hide glue, respectively [43, 44]. In the same region of the spectrum for fiber area 2, a strong peak that correlates with the reference rice paste spectrum [45] is present at 1595  $\text{cm}^{-1}$ .

In both spectra, a peak centered at 2900  $\text{cm}^{-1}$  correlates to the bulk carbohydrate (paper), but the asymmetry of the peak is diagnostic. In fiber area 1, shoulders were observed at 2876, 2939, and 2963  $\text{cm}^{-1}$ ; the second sample spectrum has stronger peaks at 2851 and 2919  $\text{cm}^{-1}$  and a shoulder at 2950  $\text{cm}^{-1}$ . These peaks



and shoulders correlate to hide glue spectral bands at 2852, 2922, and 2957  $\text{cm}^{-1}$ . Similarities of FTIR spectra to a carbohydrate reference (i.e., Ramie fiber) account for the bulk of the signal, consistent with the *kōzo* substrate. Characteristic bands suggest the presence of both proteinaceous animal hide glue and amylose-based rice paste. These findings are consistent with the literature regarding woodblock printmaking [1–4],

which indicate *dōsa* (hide glue) sizing on the paper and rice paste used in smoothing the consistency of colorants prior to application. Because of the thin layer of colorant on the fiber and their low molecular extinction coefficients in IR, no peaks associated with the red dyes were detectable.

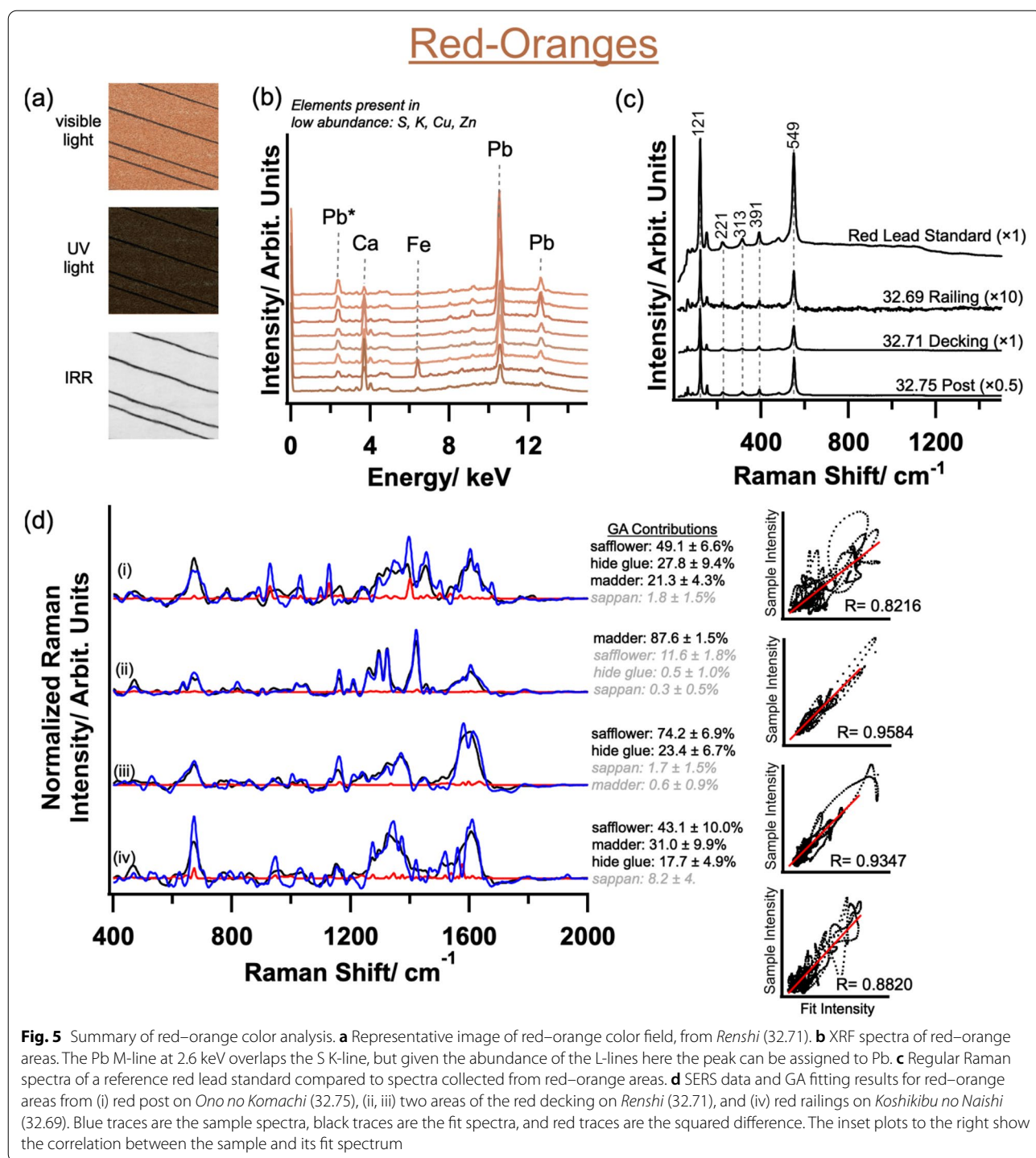
#### Colorant identification

Red areas throughout the Harunobu prints in the collection were first evaluated by non-invasive and non-destructive means. Based on their visible light characterization, those reddish areas are grouped as “opaque reds”, “red–orange”, “medium-reds” and “pinks”. Recently, a thorough study was released analyzing the multimodal imaging appearances of reference dyes and pigments used in *ukiyo-e* [24]. That report acknowledged the limitations of reflective imaging. The red dyes and pigments of interest in our work (i.e., vermilion, red lead, red ochre, safflower, madder, and sappan) reflect IR light, making characterization difficult. With regard to UV-induced luminescence, the previous work demonstrated that both madder and safflower luminesce, whereas inorganic pigments and sappan did not. Reference images from the literature, as well as our own images of lab-produced printed papers (provided in the Additional file 1: Figure S8) were used in the analysis of the Harunobu prints.

Selected areas from the “red–orange”, “medium-red”, and “pink” areas were micro-sampled for analysis by Raman and subsequent SERS. The SERS data was interpreted through spectral matching with a self-built GA with a library of standard SERS spectra prepared and measured to mimic the museum samples as closely as possible. The GA library contained 54 standard spectra: 8 of hide glue, 10 of safflower, 16 of sappan and 20 of madder; because protein glue signal is strongly enhanced by SERS (and was observed in nearly every colorant reference spectrum) the algorithm was designed to account for any signal from the *dōsa* sizing. Rice starch references did not produce SERS spectra with clear peaks (in fact, cellulose has been used as a SERS substrate, for its lack of signal [46]), and thus rice starch spectra were not included in the spectral library. Full dye characterization and reference spectra are presented in the Additional file 1: Figure S9 and Tables S1–S4. The capabilities of this algorithm were fully described in previous publication [10]. The full results of colorant analysis on the Harunobu samples are summarized in Table 1.

#### Opaque reds

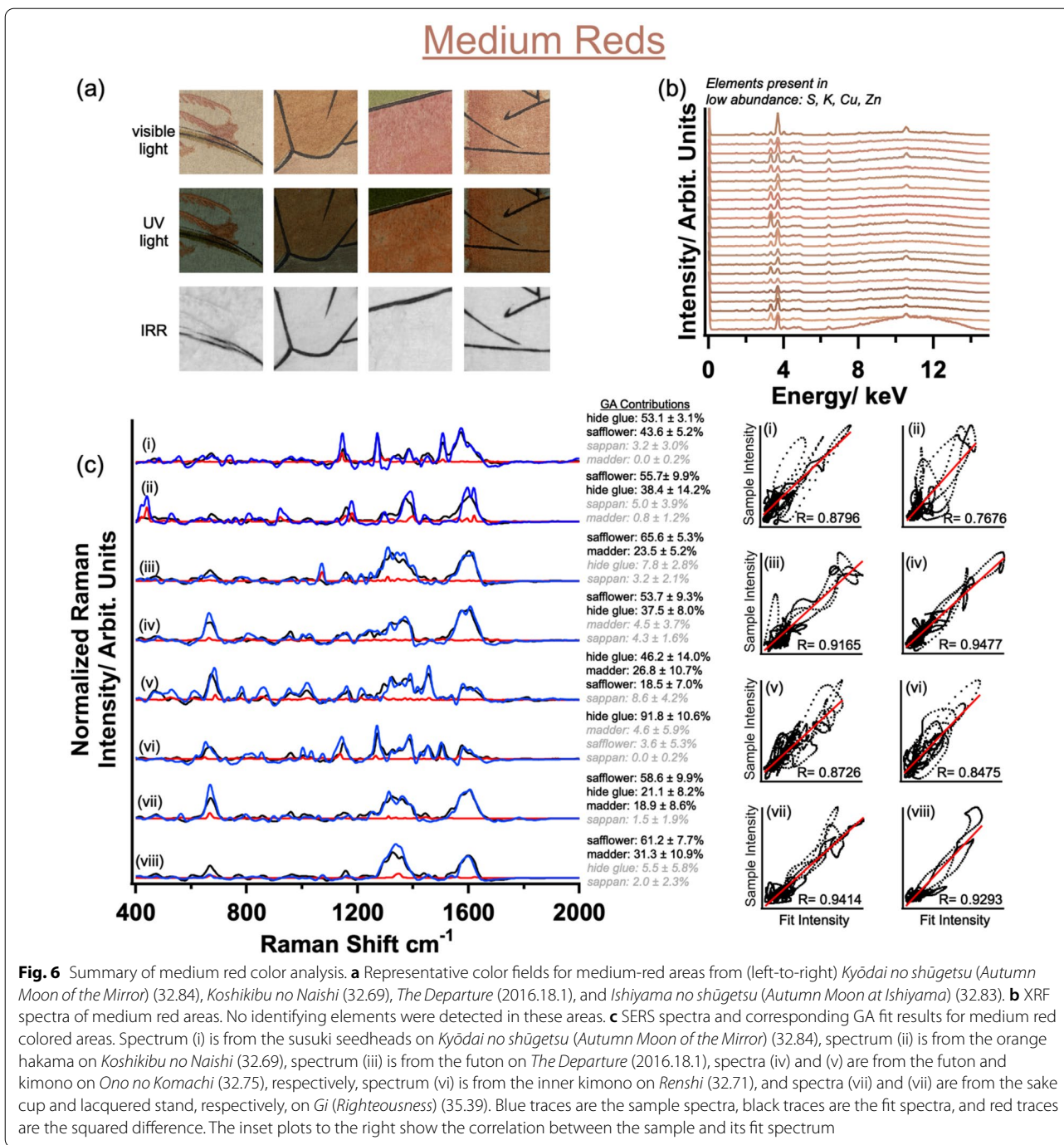
Nine areas presented visually as deep red or red-brown with high opacity. An example of each subcategory is shown in Fig. 4a. Under UV light, these areas did not



fluoresce, and with IRR imaging, only a slight absorption was observed. These imaging results agree with the reference images of inorganic red colorants provided in the previously published study [24]; in that work, the absorption of IR light by inorganic colorants

was not significant, although some absorption was visible in the images of red ochre. XRF spectra of opaque reds are shown in Fig. 4b. Spectra of the deep-red areas all showed evidence of mercury (Hg), indicating the presence of vermilion-based colorant. Spectra of the





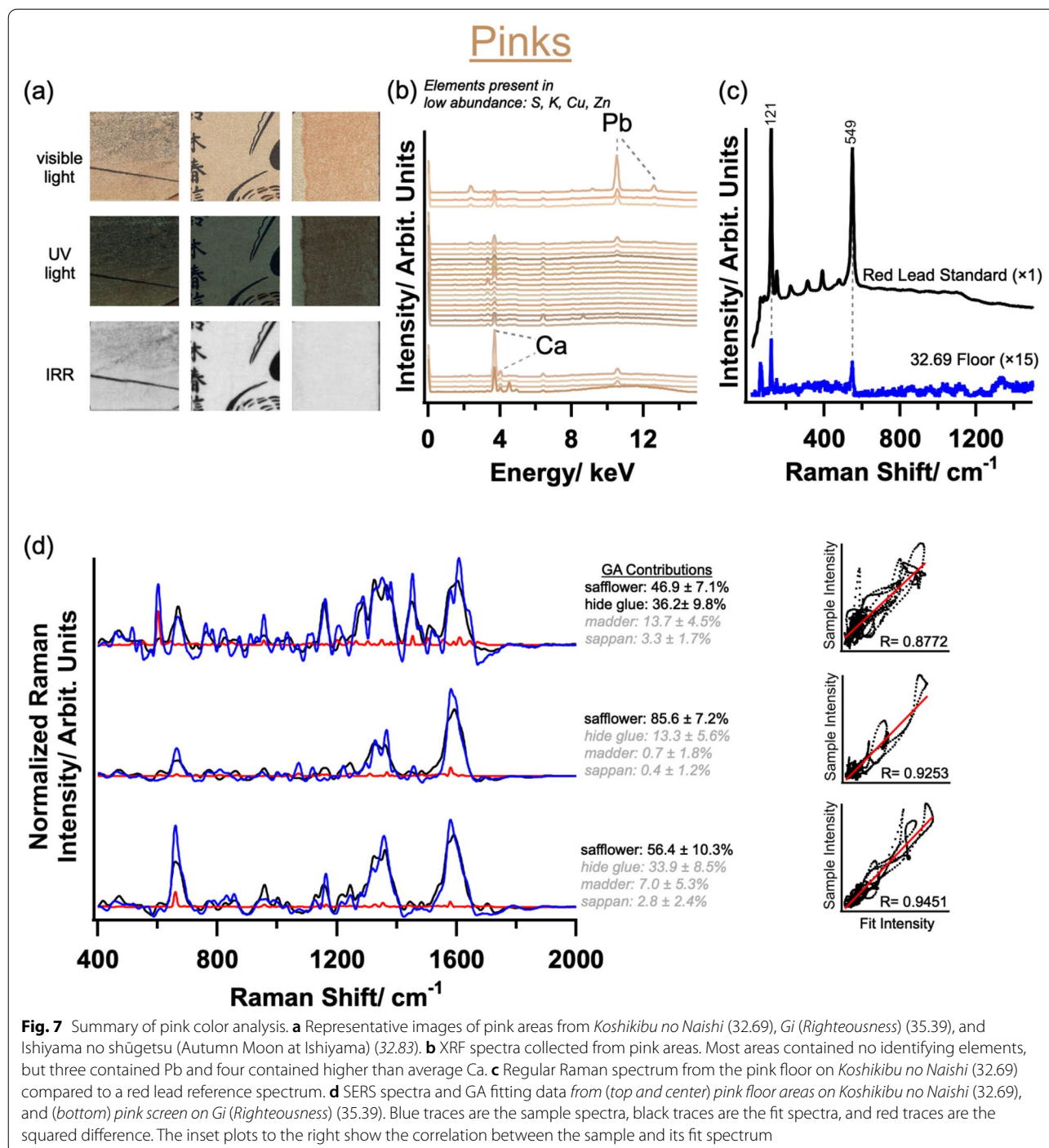
red-brown areas showed high intensity iron (Fe) peaks suggesting that these areas were printed with ochre-based colorants.

Vermilion was only present in three areas on two of the twenty-three prints analyzed—twice in seals on the print and only once as part of the image. Ochre appeared more regularly in the collection, but was observed only on periphery features of the image—never on a central

figure. In all instances, ochre was used to color the image of a hard surface (e.g., tables, cabinets, railings, rocks, mirrors).

#### Red–orange

Eight areas across seven prints were visibly bright red–orange; an example of this color can be seen in Fig. 5a. The red–orange colorant predominantly but not exclusively



appears on architectural features made of wood. Of the eight areas examined by XRF, six are wooden structures, such as decks, railings, or door frames. One remaining area depicts maple leaves and shows evidence of overprinting on the blue-gray background; the final area is a kimono on the only print to also feature vermilion in the image coloration [*Gi (Righteousness)* (35.39)].

These areas appeared less opaque than the deep red areas under UV light. This could be due to less effective absorption of the UV light source, or due to minimal fluorescence arising from the presence of an organic dye. IRR images revealed minimal absorption of the pristine colorants, but areas of discoloration



(blackening) were absorbing of IR light. The XRF spectra for red–orange areas (Fig. 5b) indicate that these areas contain lead, likely found as red lead. However, XRF does not allow differentiation between various lead-based pigments; and other molecular techniques such as Raman would be required to confirm the presence of red lead. In addition to the presence of lead, above-average calcium was present in the measurement of one area and a small amount of iron was present in one area.

Three red–orange areas were micro-sampled and analyzed by Raman and SERS spectroscopies. The resultant Raman spectra (shown in Fig. 5c) revealed that indeed red lead was used in these areas. SERS spectra and results of analysis by GA for these three samples are presented in Fig. 5d. The SERS analysis of all three samples revealed safflower and madder dye contributions. Together, these data indicate the red–orange colorants are three-component mixtures of red lead, safflower, and madder. Such a range of colorants was apparently needed to produce the specific red–orange shade and relative opacity observed in the prints.

### Medium-reds

On 22 areas across 16 prints, color fields ranging from dark pink to red were identified, which are grouped together here as “medium-reds”, comprising a significant portion of the areas of interest in this collection. The majority of these 22 areas were located on textiles, such as kimono, pillows, and futons. Only four medium-red areas represent non-fabric elements. Examples of these color fields are shown in Fig. 6a.

All areas, but one (which absorbed UV light), fluoresced red under UV illumination. In previously published work [24], the fluorescence of Western madder appeared a bright orange, while Indian Madder fluoresced a more red–orange color—likely due to different abundance of alizarin and purpurin in the different plant species. Meanwhile, safflower fluoresced a very bright orange, which appeared overall lighter than the two madder species. For comparison, our reference prints using extracts from Western madder and safflower (Additional file 1: Figure S8) fluoresced reddish and orange, respectively, and the fluorescence faded significantly with UV aging of the papers. Thus, the variety of fluorescence



observed across the Harunobu prints cannot reliably be used to identify colorants due to the species- and aging-dependence of colorant fluorescence. Six areas showed very slight absorption of IR light, making the colorant discernable from its surroundings in IRR images. Although the previous work cited no significant absorbance of IR light by red dyes, the images included in that work suggest safflower may absorb IR light slightly more than the other dyes [24].

Figure 6b shows XRF spectra from medium-red areas, nine of which were selected for microsampling. From the XRF data, no unique or identifying elements were detected in these areas. Fluorescence dominated the regular Raman spectra and therefore did not aid in identifying these medium-red colors. Representative SERS spectra for these samples are shown in Fig. 6c. The GA analysis identified safflower and madder colorants, both alone and in mixtures; and in one case a dye could not be identified.

Four of the nine micro-sampled areas were determined to be colored with a mixture of safflower and madder dyes by SERS. These were *The Departure* (2016.18.1) futon, *Ono no Komachi* (32.75) kimono, and *Gi (Righteousness)* (35.39) sake cup and lacquered stand. Notably, the sake cup and lacquered stand featured in *Gi (Righteousness)* (35.39) were printed with two visually-distinct red colorants in close proximity, though the colorant determination was the same. The printer might have prepared the safflower and madder mixtures in different concentrations of hue and opacity. It is also possible that another, unidentified dye or pigment was mixed with or overprinted to produce the darker color observed on the lacquered stand—such mixtures have previously been observed [6].

Using microsampling and SERS/GA, two areas were determined to be colored with safflower dye only. One, depicting seedheads of the *susuki* (miscanthus grass), was printed in the same shade of medium-red found in the kimonos on the same print, *Kyōdai no shūgetsu (Autumn Moon of the Mirror)* (32.84). The other area identified as safflower, the orange *hakama* trousers on *Koshikibu no Naishi* (32.69), is visually a brighter orange than appears elsewhere. XRF analysis of this area suggests a small amount of arsenic and sulfur (collected at higher excitation energy, parameters and spectrum provided in the Additional file 1: Figure S10), which may be evidence of overprinting an orpiment base layer. Use of orpiment and overprinting has previously been identified in works by Harunobu [5]; however, orpiment was not detected by microsampling, as this collection method is more likely to collect loosely-held surface particulates.

The lower garment of the figure in *Ishiyama no shūgetsu (Autumn Moon at Ishiyama)* (32.83), which is an extremely close visual match to the seedheads and kimonos in *Kyōdai no shūgetsu (Autumn Moon of the Mirror)* (32.84), was determined to be colored with madder dye by SERS/GA. This determination illustrates that preparation and aging of these colorants has rendered visual and optical analyses insufficient for exact identification. The final area, the kimono on *Renshi* (32.71) is visually consistent with the reds on *Ishiyama no shūgetsu (Autumn Moon at Ishiyama)* (32.83) and *Kyōdai no shūgetsu (Autumn Moon of the Mirror)* (32.84), but dye identification was not successful. Particulates collected by microsampling the kimono contained relatively high proportions of hide glue from the paper sizing, while the proportion of colorant was below the detection limit.

While the SERS/GA analysis and identification methods produce spectral matches to the Harunobu prints, verification of the dye identity for one color block was done using ESI–MS. From *Ono no Komachi* (32.75) the futon was identified by SERS as containing safflower, though visual similarities to the previously mentioned red areas (including an area on the same print) suggest the colorant is likely a safflower and madder mixture. This futon area was the source of the fiber sample analyzed by FTIR (“FTIR analysis of substrate” section) and, here, for results verification by ESI–MS because that area had a few raised fibers that could be removed without marring or substantially weakening the rest of the print. ESI–MS provided high-resolution mass spectrometry, though given the small fiber sample, was performed without a chromatographic separation step to maximize the signal. For this study, standards of *kōzo* paper, rice starch paste, hide glue, safflower, sappan and madder dye extracts, respective mock prints, as well as synthetic alizarin and purpurin were analyzed. The results of the ESI–MS analysis for the Harunobu fiber revealed 43 ion fragments that match to safflower standards and 30 ion fragments that match to madder standards (or synthetic chromophores). A portion of these fragments with proposed structures are presented in the Additional file 1: Table S5. The presence of both safflower (as identified in this area by SERS) and madder (identified in a similarly appearing area on the same print by SERS) verify the accuracy of the SERS with GA analysis technique. Sappan was not detected by either SERS or ESI–MS techniques.

### Pinks

Twenty areas on thirteen prints appeared pale pink, ranging from pale pink-tan to more opaque true pinks. Representative images of sampled areas are shown in



Fig. 7a. Light pink areas appear primarily in depictions of architectural surfaces, e.g., flooring or walls, or screens. It seems that pale pinks were not commonly used on central figures, perhaps because their usage would de-emphasize the primary subject(s).

Only three pink areas displayed strong fluorescence under illumination by UV light. All other pink areas were minimally fluorescent (ranging from pink to dusty rose) or not fluorescent under UV illumination. The IRR images reveal one area that was more reflective of IR light than the paper and two areas that showed IR-absorbing black discoloration. The XRF spectra for these areas are displayed in Fig. 7b. Potassium, calcium and sulfur were detected in most measurements and are only indicative of a colorant at higher levels (e.g., elevated calcium in four areas may indicate a white calcium carbonate pigment). Three areas revealed detectable levels of lead, though the intensity of the lead signal in the pinks was much less than in the red–orange areas mentioned previously. Most of the measured pink areas revealed no color-identifying elements.

Five areas were microsampled from four pink regions from prints in the collection. SERS/GA analysis identified safflower dye in three samples (Fig. 7d); one sample also contained madder dye. In one case [*Koshikibu no Naishi* (32.69), floor], red lead was identified (as shown in Fig. 7c) as a mixture with safflower. Two other areas that showed presence of lead [*Ishiyama no shūgetsu (Autumn Moon at Ishiyama)* (32.83), light wall (no colorant identified) and baseboard (safflower and madder)] likely contain small amounts of red lead or lead white, but these two possibilities could not be definitively identified. The last pink area, the screen on *Gi (Righteousness)* (35.39), was visually different from the other areas analyzed, with more opacity, but still a light appearance; this area was colored with safflower, a dye typically regarded as light and transparent in appearance. The lack of inorganic elements in the XRF and in some cases, abundance of calcium, suggests that organic reds were mixed with *gofun*, a calcium carbonate pigment from seashells, to produce these light shades. GA analysis for the last pink sample rendered no dye identification.

#### Summary and comparison to a published study

Figure 8 provides example prints with colorant identifications. This work contributes more findings on the material composition of works attributed to Harunobu; such works have been studied previously in the collection at the Museum of Fine Arts, Boston (MFA) [5]. Like the MFA study, the data herein show that red lead and ochre were used regularly; our data suggest that red lead was regularly mixed with organic colorants. Additionally, our work suggests that the use of red lead and ochre was

reserved for peripheral objects and architectural details within the image. While vermilion was available and identified here, the use of it was sparse—primarily for finishing details (e.g., seals).

The MFA study also identified the prevalent use of madder, alone and in mixtures with safflower or sappan. The suggested practice of color-mixing and use of madder were likewise confirmed in our study; however, questions remain as to the historical use of madder as a printing ink. While these results identified madder used in the Portland Art Museum's collection of prints, this limited investigation cannot address, but may encourage, larger historical inquiry around the production and sourcing of identified madder.

Though the literature has regularly cited sappan as a commonly used dye in *ukiyo-e* printing [5, 7, 11, 17, 24], few studies present evidence of the use of sappan on *ukiyo-e* prints [5, 6]. The results presented herein show an absence of sappan colorant. Given the extreme pH and photosensitivity of brazilin [47, 48], the primary color contributing compound in sappan, its color production may have been less reliable than safflower and madder.

In one case, this study encountered an orange area identified as safflower, which we propose to be a red layer (of safflower) overprinted on yellow (likely orpiment, given the presence of arsenic by XRF). Yellow colorants overprinted with red have been previously noted, with examples of primarily inorganic mixtures (e.g., red lead, orpiment, and iron oxide), primarily organic (e.g., safflower over turmeric), or inorganic–organic overprinting (e.g., madder and sappan over orpiment) [6]. One question remains regarding the use of tinting pigments to produced pink shades. In three of the four pink areas analyzed herein, lead was detected by XRF, but was only definitively identified as red lead in one instance. Further investigations of the remainder of the printing palette are needed to clarify these questions.

#### Conclusions

In this work, red inks on a collection of eighteenth-century woodblock prints by the artist Suzuki Harunobu were evaluated through a multi-analytical methodology. The results of this survey suggest that in the discrete period of 5 years in which Harunobu was designing full-color prints, a wide range of red colorants were in use. These analyses revealed the use of ochre, vermilion, red lead, safflower, and madder colorants; these colorants were used in single colorant, as well as in two- and three-colorant mixtures. Surprisingly, no evidence of sappan use was identified. The results of this work provide definitive molecular identifications of colorants on the full-color prints of Suzuki Harunobu. This work further explores the use of AABLS and GA to interpret SERS

data, underscoring the relevance of these data interpretation methods to identify dye mixtures in low concentrations. The imperfect fitting of the experimental SERS data to the GA reference library demonstrates the oft-unacknowledged variability of SERS spectra and provides an unbiased way to interpret data.

## Experimental

### Materials

Glycerol, polyacrylic acid (PAA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, sodium salt, 50% w/v), *N,N'*-methylenebis(acrylamide) (MBA), silver nitrate, and hydroxylamine hydrochloride were purchased from Millipore-Sigma (St. Louis, MO). Potassium persulfate (KPS), potassium metabisulfite (KMBS), lead (II, IV) oxide, and sodium hydroxide were purchased from Thermo-Fisher (Waltham, MA). Dow SYLGARD™ 184 Silicone Encapsulant (PDMS) was purchased from Ellsworth Adhesives (Germantown, WI). Methanol and formic acid were HPLC grade quality and provided by the Bioanalytical Mass Spectral Facility at Portland State University. All chemicals were used as received. All aqueous solutions were prepared using water filtered through an ion-exchange column (measured resistance greater than 18 M $\Omega$ ).

### Hydrogel synthesis

AMPS-co-PAA hydrogels were synthesized previously reported in the literature [49]. Final weight ratios of components were 18.3% AMPS, 11.2% PAA, 8.1% glycerol, 0.3% MBA, and 0.02% each KPS and KMBS. The gels were allowed to rest in the mold overnight to ensure polymerization was complete, and then removed and equilibrated in deionized water to remove excess reactants. Hydrogels were synthesized and stored for several months and only required a fresh deionized water equilibration before use.

### Silver nanoparticle syntheses

Silver nanoparticles (AgNPs) were synthesized according to optimization of published methods [50]. AgNO<sub>3</sub> (1.00 × 10<sup>-4</sup> M) and NH<sub>3</sub>OH (1.50 × 10<sup>-4</sup> M in 3.33 × 10<sup>-4</sup> M NaOH) solutions were freshly prepared before beginning synthesis. To synthesize nanoparticles, 90 mL of NH<sub>3</sub>OH·HCl and 10 mL of AgNO<sub>3</sub> were mixed under N<sub>2</sub> sparging. After mixing, the solutions were allowed to react for 5 min. Aliquots of 1 mL were then centrifuged at 5000 rpm for 5 min at 4 °C to concentrate the AgNPs. 950  $\mu$ L of supernatant were removed and 50  $\mu$ L of fresh deionized water was added to the remaining pellet. Concentrated AgNP solutions were stored in the dark at 4 °C until ready for use.

## Methods

### Micro-sampling process

Micro-sampling was performed using a hydrogel-assisted micro-sampling device [10]. This handheld assembly uses a small (1 cm<sup>2</sup>) piece of hydrogel loaded into an open-ended plastic cup. Before assembly, the hydrogel was equilibrated in the museum environment (50% RH, 21 °C, 1 h) and excess moisture was wicked away using a KimWipe. The open end of the cup was covered with low density plastic film, which has an approximately 1 mm<sup>2</sup> pinhole. The other side of the cup was sealed using custom molded PDMS stoppers, providing a clear line of sight down the center of the cup, through the hydrogel, and to the pinhole. The apparatus was placed on the surface of the print for 70 s, then lifted vertically before inverting and storing in a sealed container for analysis. The size and shape of the microsampling apparatus provide an easy, low-risk means of collecting microscopic particulate from very small and/or central areas of the prints. A carefully managed workflow (e.g., staggered gel equilibration and imaging times) can allow for sampling of up to 5 areas per hour.

### Preparation of samples for ESI-MS

Madder, saffron, and safflower dye solids (described in the Additional file 1) as well as synthetic alizarin and purpurin were each placed in 5 mL glass vials and dissolved in 750  $\mu$ L of a DMSO/formic Acid 1:1 (v/v) solution. These solutions were sonicated for 30 min, followed by heating in a dry bead bath at 80 °C for 30 min. After heating, 750  $\mu$ L of a methanol/water 1:1 (v/v) solution was added to the extraction vessel; the final extracts were colored and clear. Dye extracts were then transferred to autosampler vials for injection into the ESI-MS system.

Strips of mock prints (approximately 30 × 10 mm, preparation described in the Additional file 1) were prepared for injection in a similar fashion as the dye solids, but with total final extract volume of 200  $\mu$ L. Samples collected from *Ono no Komachi* (32.75) were approximately 2 mm in length and less than 20  $\mu$ m in diameter. They were treated similarly to the mock prints, with volumes scaled down for a final volume of 50  $\mu$ L. All samples were tightly capped and analyzed within 24 h of extraction.

### Instrumental analyses

#### Imaging

White light and UV illuminated images were collected with a Canon 7dmarkII camera with an EF 50 mm F/2.5 lens, Max-Max XniteCC1 and Kodak Wratten 2E filters. VioStorm WildFire VS-60 lights were used for UV illumination with GoldenThread OLT 0.50 $\times$  and UV Innovations Target UV and UV gray cards for color balancing. RAW images were color balanced using CaptueOne software (v10.2.1).

Infrared reflectography images of the Harunobu prints were collected using the Opus Apollo infrared camera with Apollo software (Opus Instruments, Norwich, UK).

All additional Image processing was performed using FIJI (ImageJ 1.53c) [51].

#### **XRF spectroscopy**

XRF spectra were collected from unique red, orange and pink-colored areas, as well as from a blank area of paper, when possible. Prints were raised from their mats by placing low-density foam under the print. The spectra were collected with a Tracer III-SD handheld XRF spectrometer (Bruker, Billerica, MA) using a 0.025 mm Ti filter, 15 kV excitation voltage, 25.8  $\mu$ A current, and 60 s integration time.

Sixteen paper spectra were averaged and a threshold for elemental presence was established according to (1) a signal-to-noise ratio (SNR) greater than 10 and (2) signal greater than two and a half standard deviations above the blank paper average.

#### **FTIR**

FTIR analysis was performed using a Nicolet Continuum FTIR microscope with a Nicolet iS10 infrared spectrometer (Thermo Fisher Scientific, Waltham, MA) and 50  $\mu$ m nitrogen cooled MCT/A detector. The sample was prepared for analysis by pressing onto a diamond window. All data were collected using Omnic software (v8.3.103) and spectra were collected in transmission mode from 650 to 4000  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  spectral resolution and 128 scans averaged. Data were compared to reference spectra from the IRUG database [42, 44, 45].

#### **Raman spectroscopy and SERS**

Raman spectroscopy and SERS were performed directly on the hydrogel surface where particles had been collected. Spectra were collected on a LabRAM HR Evolution spectrometer with 100  $\times$  100 cm motorized stage and motorized z-axis control (Horiba, Kyoto, Japan). Parameters for all spectra were 633 nm laser, 600 lines/mm grating, 300  $\mu$ m confocal hole, and 50  $\times$  objective. Raman spectra were collected over the range of 18–2000  $\text{cm}^{-1}$ . Laser power, acquisition time, and number of scans were optimized for each sample, with a typical acquisition consisting of 2 s integration and 10 scans with 1–25% laser power; the described parameters provided spectral resolution of 4  $\text{cm}^{-1}$ . Care was taken to avoid sample burning; and despite this, evidence of amorphous carbon was seen by the presence of D and G bands in the SERS Raman spectra; the source of amorphous carbon is unknown—though possibilities include adventitious carbon, fine *sumi* particulates, and fractional organics degradation from the excitation laser. Observations of amorphous carbon presence in SERS for dye identification has been previously

observed on historical materials [52], and which did not prevent successful dye identification.

After collecting Raman spectra, 2  $\mu$ L AgNPs were drop cast over the pinhole in the micro-sampling assembly. Excess water was allowed to absorb into the hydrogel for approximately 5 min, forming a thin film of Ag on the surface of the sample particulate. SERS measurements were collected using the Raman spectrometer and parameters previously described; SERS spectra were collected over the range of 400–2000  $\text{cm}^{-1}$ . Measurements were collected in situ (i.e., from the surface of the hydrogel apparatus). Typical SERS parameters were 5 s integration and 30 scans; laser power was optimized for each sample and ranged from 1 to 25%. Baseline correction was performed using an AutoAdaptive Baseline Subtraction algorithm. The AABLS algorithm was allowed to optimize over 50 iterations to remove non-diagnostic signals from dye fluorescence and amorphous carbon presence. (50–81 iterations yielded the same results). Representative spectra before and after baseline subtraction are shown in the Additional file 1: Figure S11.

#### **Particle size analysis**

Images of the hydrogel surfaces were collected using the 3MP iDS camera with CMOS sensor connected to the Raman microscope. The images were then color processed, converted to binary and particles were measured using the Analyze Particles function in FIJI. The minimum particle diameter for measurement was defined as 3 pixels wide, corresponding to 0.3  $\mu\text{m}^2$  at 50  $\times$  magnification, and 1.5  $\mu\text{m}^2$  at 10  $\times$  magnification.

#### **ESI-MS**

Electrospray Ionization Mass Spectrometry (ESI-MS) spectra were collected using a Vanquish UHPLC system coupled to a Q Exactive orbitrap mass spectrometer equipped with an electrospray ionization source (Thermo Fisher Scientific, Waltham, MA). The source was operated in negative mode with a resolution of 70,000 and a full MS scan range from 66.7 to 1000 m/z. Sheath gas flow rate was 35, spray voltage was 3.00 kV, capillary temperature was 320  $^{\circ}\text{C}$ , S-lens RF level was 50, and auxiliary gas heater temperature was 350  $^{\circ}\text{C}$ .

Sample extracts were directly injected without separation using the Vanquish UHPLC auto-injector. The mobile phase had a constant flow of 0.300 mL/min and consisted of a constant 50:50 ratio of (A) methanol and (B) 0.15% formic acid in water. Solvent blank and equilibration steps were performed between each sample run. The sampler module was held at 20  $^{\circ}\text{C}$  and the direct injection column compartment was held at 40  $^{\circ}\text{C}$ .

Raw data was visualized in and exported from Thermo Scientific Xcalibur software using the Qual Browser extension (Thermo Fisher Scientific, Waltham, MA). Data was imported to and processed in Igor Pro v8.04 (Wavemetrics, Lake Oswego, OR).

### Abbreviations

AgNPs: Silver nanoparticles; AMPS: 2-Acrylamido-2-methyl-1-propanesulfonic acid; ESI-MS: Electrospray ionization-mass spectrometry; FTIR: Fourier transform infrared spectroscopy; GA: Genetic algorithm; KPS: Potassium persulfate; KMBS: Potassium metabisulfite; IRR: Infrared reflectography; MBA: N,N'-methylenebisacrylamide; PAA: Polyacrylic acid; PAM: Portland Art Museum; PDMS: Polydimethylsiloxane; SERS: Surface enhanced Raman spectroscopy; UV: Ultraviolet; XRF: X-ray fluorescence spectroscopy.

### Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-022-00731-4>.

**Additional file 1: Figures S1–S7.** Visible and UV illuminated images of Harunobu prints during microsample collection. **Figure S8.** Lab-prepared reference prints illuminated under (top) visible and (bottom) UV light. **Figure S9.** Average spectra derived from standards in the library used for GA fitting. **Figure S10.** XRF spectrum collected from the orange hakama trousers on Koshikibu no Naishi (32.69). **Figure S11.** Examples of SERS data before (black) and after (blue) subtraction of the fitted baseline (red) with the AutoAdaptive baseline subtraction technique with 50 iterations. **Table S1.** Average experimental Raman shifts for bulk hide glue, glue printed on kozo, and aged glue on kozo compared to average literature values and previously published vibrational assignments. **Table S2.** Average experimental Raman shifts for fresh safflower, fresh safflower ink, and aged safflower ink compared to average literature values and previously published vibrational assignments. **Table S3.** Average experimental Raman shifts for fresh sappan, fresh sappan ink, and aged sappan ink compared to average literature values and previously published vibrational assignments. **Table S4.** Average experimental Raman shifts for fresh madder, fresh madder ink, and aged madder ink compared to average literature values and previously published vibrational assignments. **Table S5.** Comparative ESI-MS analysis of Harunobu fibers from Ono no Komachi (32.75) to reference standards.

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### Author contributions

LNK curated, processed, and analyzed data, produced figures, performed computational work, wrote, and edited the original manuscript. TKQ curated and processed data and edited the original manuscript. DD curated, processed, and analyzed data and edited the original manuscript. SS and JK conceptualized the project, handled prints, oversaw the sampling process, and edited the original manuscript. TLC conceptualized the project, supervised, curated, and analyzed data, acquired funding, and edited the original manuscript. All authors have read and approved the final manuscript.

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### Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

### Declarations

#### Competing interests

The authors declare no competing interests.

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