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Applying micro-computed tomography (micro-CT) and Raman spectroscopy for non-invasive characterization of coating and coating pigments on ancient Chinese papers

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Abstract

The coating technique, supposedly invented by Chinese papermakers no later than the 3rd century AD, greatly improved paper sheets' qualities of color, texture, writability, and printability. Alongside the dispersal of papermaking and surface-treatment techniques beyond China, coated papers were manufactured and used in many other regions of the world. Understanding the manufacture of coated papers, therefore, is crucial for perceiving how surface treatments were developed to meet the need for paper with enhanced properties. However, the characterization of coating and coating pigments on ancient Chinese papers has long remained an unsolved issue, and previous studies on this topic have often produced inconclusive results. To explore a non-invasive methodology that can more reliably characterize coated papers and the coating pigment on them, this article presents the results of a pilot study that applied micro-computed tomography (micro-CT) and Raman spectroscopy to samples of three Qing Dynasty (1644–1911 AD) papers and two handmade papers manufactured in China in the 1990s. Micro-CT revealed the coating layer(s) on *Lajian* (waxed coated paper) and *Lengjinjian* (gold-dusted paper) of the Qing Dynasty and characterized the modern raw xuan and bamboo papers as uncoated. Raman spectroscopy, together with handheld X-ray fluorescence analysis, identified the mineral-based pigment in the coating layer, suggesting the use of lead white or kaolin as the coating pigment. Additionally, Raman analysis confirmed the use of other mineral pigments (red lead and cinnabar), beeswax, and organic dyes (gamboge, kermesic acid, and possibly purpurin) in the manufacture of *Lajian* and *Lengjinjian* papers. The combination of micro-CT and Raman spectroscopy, it is therefore suggested, is a practical, more reliable approach for non-invasive investigation of coating and coating pigments on ancient Chinese paper specimens.

Keywords: Coated paper, Coating pigment, Micro-computed tomography, Raman spectroscopy, Handheld X-ray fluorescence analyzer

Introduction

Conventionally, the term "paper" and its Chinese counterpart "*zhi* (纸)" refer to the thin sheets that used plants as sources of fibers and were formed by suspending the pulp on a porous mould [1, p. 3, 2, 3, p. 4]. This particular way of papermaking was invented by Chinese craftsmen in the Western Han Dynasty (202 BC–9 AD), but its

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widespread use across China became evident only after 105 AD [4, 5]. Beginning in the third century AD, the papermaking technology spread from China to the rest of the world [6–8]. Before the papermaking machine was invented in France in 1798 AD [6, 9, p. 16], papermaking activities around the world were heavily hand-based, and many papermakers owed their papermaking technologies to China [6, 7, 9, pp. 5–15, 10–15].

Alongside the dispersal of these Chinese-style papermaking technologies, also transmitted was the paper-treatment practice of coating paper sheets with a fine powder of whitish, inorganic substances, in the hope of modifying or enhancing the color (whiteness and brightness), texture (gloss and smoothness), and certain physical properties (opacity, strength, and ink retention) of new paper sheets [6, 16, pp. 145–146]. It is believed that Chinese craftsmen first practiced this sort of coating treatment no later than the third century AD [e.g., 1, pp. 128–132, 16, p. 146]. A coated paper, as discussed below, is a paper subjected to intentional surface treatment *after* sheet formation by having ground minerals or mineral-based pigments—alone or mixed with other substances—brushed over one or both sides of each sheet [17, 18]. Those ground, often fine-sized minerals are known as the coating pigment. This definition distinguishes a coating pigment from a filler, which refers to the mineral particles often added as opacifiers to the pulp *before* sheet formation [18, pp. 194–195, 19, pp. 26–27].

Characterization of ancient Chinese coated papers: a short review

The first report describing possibly coated Chinese papers was made by Julius Wiesner, an Austrian botanist, in the 1910s. Wiesner, while conducting a microscopic examination of a 2nd century AD Chinese document, noticed an unusual fine-grained mass, which consisted mainly of mineral substances, among the fibers and partly attached to them [20]. Wiesner ascribed most of the grained particles to a "mineral filling," which some interpreted later as the earliest coating pigment [e.g., 1, p. 129]. Elsewhere, Wiesner reported the microscopic identification of gypsum ($CaSO_4·2H_2O$) as a coating pigment on Chinese papers dated between 220 and 589 AD [1, pp. 128–129, 9, 16].

Chinese scholars did not pay attention to ancient coated papers until the 1960s–70s. Pan Jixing examined the papers unearthed from the Hala Hezhuo Tomb (348 AD) in Xinjiang of northwestern China and, viewing them under an optical microscope, he found mineral particles among the fibers on both surfaces of the examined paper. According to Pan, mineral particles are common on papers dated to the third to the fourth century AD [1, p. 129], and their presence on one or both sides of the paper characterizes a single-sided or double-sided coating [21]. Western scholars at this time also showed interest in the coating of ancient Chinese papers. For example, Collings and Milner proposed, based on examinations using atomic absorption spectroscopy (AAS), that gypsum served as the coating pigment on ancient Chinese documents from the Stein Collection [22]. Since completion of these studies, it has been accepted that coated papers were first manufactured in China, over 1000 years earlier than in the West [1, pp. 128–129, 3, p. 194, 8, 23].

Since the 1980–90s, examination methods using the high-resolution scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX) have been widely applied to ancient Chinese papers. Elemental analysis using EDX sheds light on the types, and the relative concentrations, of metal elements on papers' surfaces. Because of this, EDX has often been employed as a standard method for characterizing coating pigments. For example, Wang et al. applied SEM/EDX to a great many Chinese historical (105–1911 AD) document papers, calligraphic works, and Buddhist scriptures and reported the wide application, and the diversity, of coating pigments [16]. Wang et al. also characterized papers as single-side coated or double-side coated based on EDX results [16, pp. 188–190]. Through SEM/EDX analysis of more than 200 ancient paper specimens, Chinese scholars discovered that gypsum, kaolin (with kaolinite, $Al_2O_3·SiO_2·2H_2O$, being the dominant mineral), chalk ($CaCO_3$), or talcum powder ($3MgO·4SiO_2·H_2O$) was most often used as the coating pigment [1, 16, 24]. Using SEM/EDX and the optical microscope, Rischel noticed that most Chinese documents dated to the 10th century AD or earlier were coated with gypsum [25–27].

From the year 2000 till now, an interest in ancient Chinese paper-based materials has continued to grow, and diverse analytical approaches—including those suitable for phase identification—have been used for studying the manufacture and surface treatment of handmade Chinese papers. Using Raman spectroscopy, Li et al. reported that chalk was a coating or filling pigment on paper currencies of the Late Qing Dynasty (manufactured and issued in the 1890s) [28, 29]. On the other hand, Wang et al. reported the X-ray diffraction (XRD) identification of kaolin as the coating pigment on Tripitakas dated between 1271 and 1644 AD [30], and Gong et al. suggested, also based on XRD identification results, that the Western Han papers unearthed at the Xuanquanzhi site in Dunhuang of Gansu Province were coated with diverse whitish pigments, including gypsum, kaolin, and talcum powder [31]. Recently, Clifford pointed out that mica, a whitish coating pigment, played a central role in the manufacture of the 18th-century Chinese wallpapers in British country houses [32]. Table 1 lists the main

Table 1 Representative technical investigations of ancient Chinese coated papers and the main findings (indet = indeterminate)

Analytical approaches	Dates/ages	Function or use	Coating pigment	Data sources
OM	202–8 BC	Paper	Indet.	[33]
	73 BC–5 AD	Paper	Indet.	[34]
	25–220 AD	Documents	Indet.	[35]
	25–220 AD	Documents	Indet.	[36]
	2nd-century AD	Documents	Gypsum	[20]
	94 BC–420 AD	Documents	Talcum powder	[37]
	348–513 AD	Documents	Indet.	[16, pp. 135–139]
	4th–9th century AD	Buddhist scripts	Indet.	[33, 38]
	410 AD	Documents	Indet.	[39]
	645–780 AD	Documents	Indet.	[16, pp. 195–196]
	11th–13th century AD	Buddhist scripts	Indet.	[40]
	1324 AD	Buddhist scripts	Indet.	[41]
	1368–1644 AD	Calligraphy	Indet.	[42]
SEM–EDX	25–220 AD	Documents	Gypsum, chalk	[16, pp. 100–102]
	3rd–4th century AD	Documents	Gypsum	[27]
	~400 AD	Buddhist scripts	Kaolin	[16, pp. 133–134]
	581–907 AD	Buddhist scripts	Kaolin, gypsum, chalk, talcum powder	[16, pp. 188–189]
	581–907 AD	Buddhist scripts	Kaolin, gypsum	[42]
	907–1127 AD	Buddhist scripts	Kaolin	[16, pp. 274–275]
	11th–13th century AD	Buddhist scripts	Chalk, talcum powder	[24]
	1809–1872 AD	Documents	Kaolin, talcum powder	[43]
	1900s	Documents	Chalk	[44, 45]
	1644–1911 AD	Documents	Kaolin	[46, 47]
	1644–1911 AD	Screen wallpaper	Kaolin, chalk	[48]
AAS	400–900 AD	Documents	Gypsum	[22]
Raman	1890s	Paper currencies	Chalk	[28, 29]
	After 1830s	Paintings	Gypsum	[29, pp. 128–131]
XRD	94 BC–420 AD	Documents	Talcum powder	[31]
	1271–1644 AD	Buddhist scripts	Chalk, kaolin	[30]

findings of representative technical studies on ancient Chinese coated papers.

An unsolved issue and the objectives of the present study

Microscopic examination, elemental analysis, and phase identification have undoubtedly contributed to the characterization of coating and coating pigments on ancient Chinese papers. However, to what extent they have helped identify, or distinguish between, coated and uncoated papers has varied from one case study to another, depending on which criteria the investigators have used for determining the presence or absence of a coating layer or pigment. Some investigators have seen the presence of mineral particles among or attached to a paper's fibers as suggesting the presence of a coating treatment on the paper [1, pp. 129–131, 21, 38, 49]. Other investigators have thought that a joint application of microscopic observation and elemental analysis—the latter of which often indicates the types, and the relative abundances, of metal elements—could suffice both to characterize a paper as coated and to characterize the coating pigment used [22, 24–27]. Still others have believed that only phase characterization can reliably identify a paper's coating pigment [28–31, 50]. Uncertainties and ambiguities, therefore, stand out in review of the studies above, and comparisons between the studies are not easily made.

Probably the most noticeable issue that remains unsolved is that each analytical approach—whether the data it provides is microscopic, compositional, or spectrometric—seems insufficient to justify concluding that a coating layer was present, that any such layer present was applied in a specific way, or that some exact mineral was used as its coating pigment [29, 50]. Microscopic examination is a useful yet inconclusive means to identify a coating layer, and it is somewhat simplistic to assume that mineral particles filling spaces between, or attached to, the fibers must be (residues of) the coating pigment [50]. Compositional data may reveal the relative abundance of (especially) inorganic elements on a paper. However, the elemental concentration values are usually obtained from averaging over a small study area, thus only representative of this target area. Furthermore, the detected values may be a result of both sides of paper (since paper is normally thin) and often fail to reflect the compositional difference between the two surfaces of paper or between the surfaces of paper and the fiber layer between them. Spectrometric techniques are ideal for fast, in situ, and accurate phase identification, which is key to the characterization of coating pigment(s); however, without microscopic observation and compositional data, spectrometric techniques alone can hardly reveal, or visually present, how a method of surface coating was practiced. Microscopic, compositional, and spectrometric data, of course, complement each other, but multi-analytical studies as such have, unfortunately, been very few in number.

The present work attempts to tackle this issue of the coating on ancient Chinese papers by jointly applying methods of analysis using optical microscope, handheld X-ray fluorescence analyzer, micro-computed tomography (micro-CT), and Raman spectroscopy to a sample of three ancient and two modern Chinese papers. It is hoped that, through such a multi-analytical and non-invasive investigation, some standard methods can be established for characterizing ancient coated paper and the coating pigment on it, which may eventually lead to a better understanding of the coating practice used in the manufacture of ancient Chinese papers. Related issues of the coating treatment and manufacture of coated papers (such as dyeing and waxing), although not the focus of the present paper, will also be briefly discussed.

The ancient papers to be investigated were sampled from *Lajian* (waxed coated paper) and *Lengjinjian* (gold-dusted paper), both of which are high-quality, specialty papers whose manufacture remains poorly understood. Pan Jixing, on the basis of textual analysis, suggests that waxed yellowish papers, dyed with *huangbo* extracted from the bark of *Phellodendron amurense*, were manufactured in the Tang Dynasty (618–907 AD), implying the use of an early form of *Lajian* as early as the 7th century AD [1, pp. 132–134]. The practice of combining dyeing, coating, and waxing to make *Lajian* was well established in China no later than the 10th century AD, and it remained a popular method for manufacturing high-quality coated papers through the Tang to Qing dynasties (618–1911 AD) [51]. Although it is widely accepted that some standard treatments—e.g., dyeing, coating, and waxing—were used in the production of *Lajian* and its variants, knowledge of how these treatments were applied to the paper sheets remains sparse [51, pp. 145–146]. Not until very recently did technical and experimental studies start to shed light on the manufacture of *Lajian* in the Qing Dynasty, confirming a variety and complexity in the manufacturing techniques utilized [46, 47, 52, 53]. *Lengjinjian* manufacture used many of the same techniques (dyeing, coating, and waxing) employed in the production of *Lajian*; to an extent, *Lengjinjian* was a variant of *Lajian*. *Lengjinjian* was decorated with very thin metal foils or with metal powder; however, *Lajian* barely used metals for decorative purpose [54].

Materials and methods

Ancient and modern Chinese paper specimens

The main aim of this study is to establish a paradigm for characterizing a coated paper and the coating pigment on it. Two groups of paper specimens have been collected for this purpose:

1. Group A consists of three paper specimens, two from *Lajian* (waxed coated paper) and one from *Lengjinjian* (gold-dusted paper). The two *Lajian* paper specimens—one in purple-red and the other in bright yellow—are labeled separately as QP and QY; these specimens, according to the results of fiber analysis (Dr. Zhou Gu, personal communication, 30 December 2018), contains 30% blue sandalwood fiber and 70% rice straw fiber. By contrast, the *Lengjinjian* paper specimen, labeled as QR, is in dark wine red. The three paper specimens were sampled from document papers supposedly used by the royal families of the Qing Dynasty, and they were offered for analysis by the China Printing Museum (Beijing). Figure 1 shows the *Lajian* and *Lengjinjian* paper specimens to be investigated in the present study.
2. Group B consists of two modern Chinese handmade paper specimens, one sampled from raw xuan, which is made from blue sandalwood (*Pteroceltis tatarinowii Maxim.*) and rice straw (with a 6:4 ratio of fibers), and one sampled from a paper made from pure bamboo fibers. Both papers were produced in the 1990s at papermaking mills in South China, following traditional Chinese papermaking techniques and using locally grown plants. By 'raw xuan', it refers to the newly formed sheets of Xuan paper that undergo no further processing. Neither of the raw xuan or bamboo paper received such surface treat-

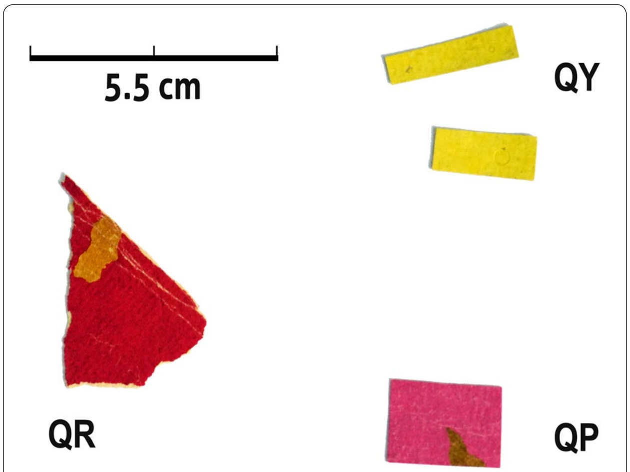

Fig. 1 Three Qing Dynasty paper specimens (QP and QY for Lajian paper, QR for Lengjinjian paper)

ment as dyeing, coating, or waxing. The two handmade papers were kindly offered by Professor Enami Kazuyuki at the RyuKoku University (Japan). The raw xuan paper is labeled as ENA#1, the bamboo paper as ENA#2 (Table 2).

Optical microscope

A Zeiss Axio Imager M2 microscope, which allows for high-quality Differential Interference Contrast (DIC) imaging, was employed for carrying out stereoscopic analysis of the five selected paper specimens.

Micro-CT scanner

Micro-computed tomography (micro-CT) is a three-dimensional (3D) imaging technique ideal for investigating the microstructure of a given sample non-invasively. X-rays, while passing through the examined sample, are absorbed to different degrees by different parts of the sample, depending mainly on the compositional differences in the sample [55, 56]. The varying absorption of X-rays generates different grayscale values on the resultant X-ray tomographic image, by which one can distinguish between, for example, the fibers (organics such as cellulose and lignin) and mineral pigments (inorganics such as chalk, gypsum, and kaolin). In the case of paper-based materials, CT images can complement the examination of a sample's surface(s) by scanning electron microscopy or optical microscope.

Applications of micro-CT to archaeological objects have mainly focused on inorganic materials such as bronze [57], ceramics [58], stone and jade [59], and faience or glass beads [60–63]. Regarding organic-based materials, micro-CT analysis has only recently started to show its power and potential uses. For example, Baumann et al. [55] and Allegra et al. [64] have reported micro-CT investigations for virtual unrolling of parchments and papyri scrolls. Prior to this study, there has been no report of the micro-CT investigation of ancient Chinese papers and paper-based materials.

The main procedures used in our micro-CT analysis may be described as follows: (1) A 2 mm by 2 mm paper specimen was put into a plastic tube, and the tube was then glued onto the sample holder (Fig. 2a). (2) The paper specimen in the tube was scanned with an EasyTom High-Resolution X-ray Micro CT System (RX Solutions, France). Scans were performed with voxel sizes of 3.5 μm, at 50 kV source voltage and 100 μA source current, over a 360° sample rotation. (3) When micro-CT scanning was finished, about 1440 images were collected for each paper specimen, and these were then imported into Amira (Thermo Fisher Scientific, USA) to generate a three-dimensional (3D) digital model showing the 3D structure—in this study, the virtual cross section—of the investigated paper specimen (Fig. 2b).

Handheld X-ray fluorescence analyzer

A handheld XRF (hhXRF) analyzer (Thermo Scientific Niton XL3t 950 GOLDD++) was used for investigating the surface chemical composition of each paper specimen non-invasively. The hhXRF analyzer is equipped with a 50 kV X-ray tube (100 μA, 2 W maximum), an Ag anode target excitation source, and a silicon drift detector (SDD) with an active area of 5 mm^2 fitted with a polymer

Table 2 The paper specimens investigated in this study

Lab. no.	Paper name	Color	Source(s) of fiber	Dates	Possible surface treatment
QP	Lajian	Purple-red	Blue sandal and rice straw	Qing Dynasty (1644–1911 AD)	Waxing dyeing coating
QY	Lajian	Bright yellow	Blue sandal and rice straw	Qing Dynasty (1644–1911 AD)	Waxing dyeing coating
QR	Lengjinjian	Dark wine red	Indeterminate	Kangxi Period (1662–1722 AD) of the Qing Dynasty	Waxing dyeing coating metal foils or powder
ENA#1	Raw xuan	White	Blue sandal and rice straw	The 1990s	None
ENA#2	Bamboo paper	White	Bamboo	The 1990s	None

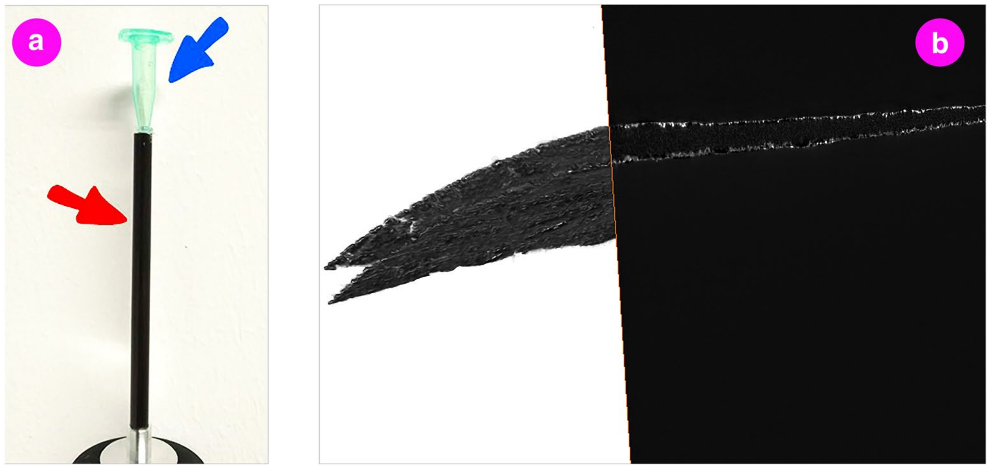

Fig. 2 **a** Positioning of paper specimen for the micro-CT scanning. The red arrow indicates the sample holder while the blue one shows the paper specimen (Lajian QY) in a plastic tube; and **b** a reconstructed paper specimen with a cross-sectional image, with the brighter layers corresponding to the coating layers and the darker layer to the fibers in between

window (MOXTEK AP 3.3 film) that ensures superior X-ray transmission in the low-energy range down to Be Kα. The X-ray beam's focal-spot size is about 3 mm in diameter. All spectra were acquired using a standard metal mode and a 120-s total analysis time. The calibration of the instrument was done by the Fundamental Parameters (FP) method designed by the manufacturer (Niton).

Raman spectroscopy

Raman spectroscopy has been well recognized as a powerful tool for phase characterization and identification, and its applications to paper-based Chinese materials have increased substantially in the past two decades [65]. In the present study, Raman spectroscopy was used to identify the coating pigment as well as other substances (e.g., wax, mineral-based pigment, and organic dyes) in the coating layer, all of these being important to the manufacture of coated papers.

Raman analysis was performed using the DXR 2xi Raman imaging microscope (Thermo Fisher Scientific, USA). A 532 nm diode laser was used as the excitation source. The size of the light spot was 1 μm and the maximum laser power used at the sample was about 3 mW. The spectral resolution was ~ 4 cm^{-1}. The 50 × objective lens was used for positioning. Raman spectra are subject to smoothing but no baseline subtraction. Raman analysis is also applied to modern natural beeswax which was obtained from a Chinese beekeeper. Assignments of Raman peaks for dyes, especially gamboge, the yellow dye which contains α- and β-gambogic acids (namely a mixture of $C_{38}H_{44}O_8$ and $C_{29}H_{36}O_6$), were made with reference to the online Raman Spectroscopic Library at University College London (http://www.chem.ucl.ac.uk/resources/raman/).

Results and discussion

Microscopic observation of the surface of paper specimens

Microscopic observation helps one to understand the undisturbed microstructure of papers [27]. In particular, it shows how the fibers, pigments, and other substances are distributed across a certain area of one's paper specimen.

Figure 3 reveals the information obtained through our microscopic observations, showing that: (1) Lajian QP has a waxy surface on both sides, underneath which whitish particles and fibers are seen. The fibers' morphological characteristics, however, are vague and barely recognizable. (2) Compared to Lajian QP, Lajian QY has a very smooth and dense surface texture, suggesting the presence of a dense coating layer. Fibers are completely invisible. (3) Lengjinjian QR is different from the two Lajian papers mainly in that a large quantity of particles is distributed among the fibers on QR, forming a powdery, loose coating layer. (4) The two modern handmade papers (ENA#1 and ENA#2) show distinctive features compared to the Lajian and Lengjinjian papers: they both are very thin and porous, and their fibers show much clearer micro-morphological characteristics.

Given the microscopic observations described above, the three ancient papers (QP, QY, and QR) retains some features of surface treatment, seen especially by a recognizable coating or waxy layer; the two modern ones (ENA#1 and ENA#2), by contrast, are uncoated.

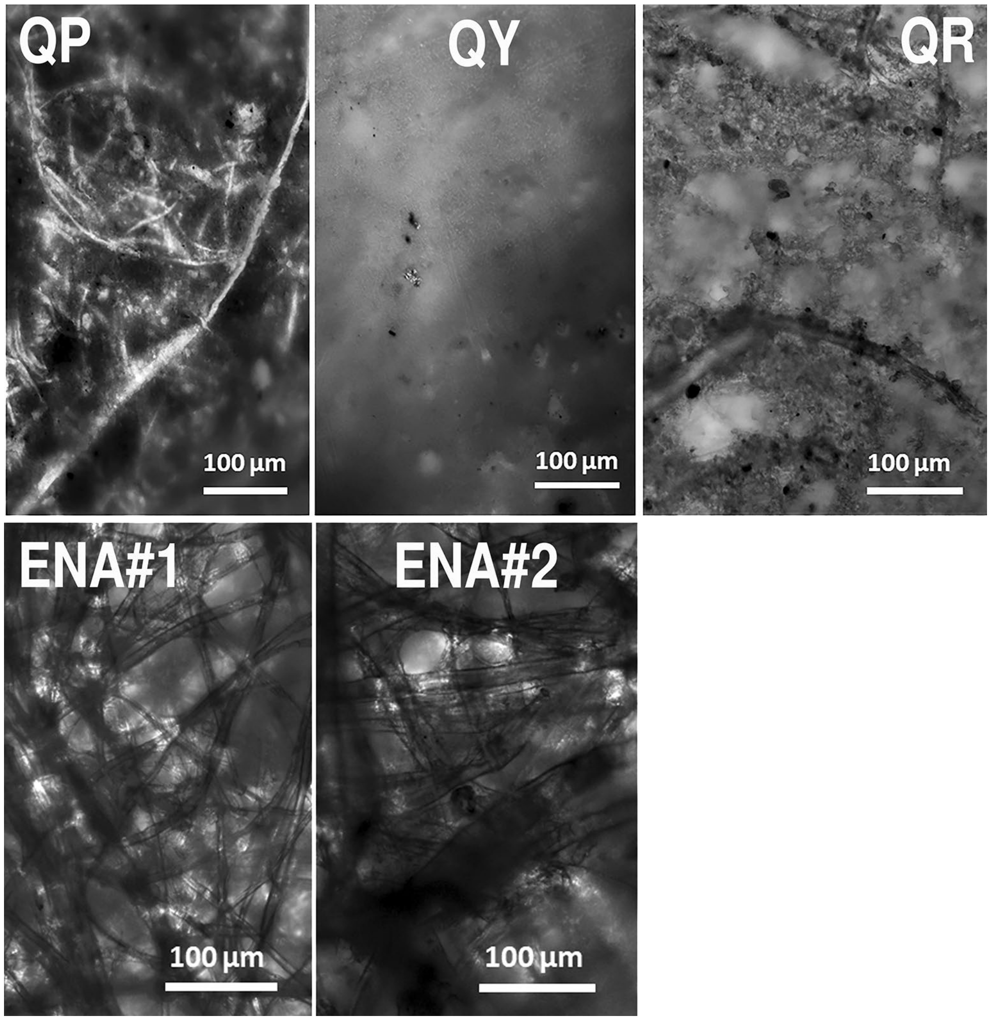

Fig. 3 Microscopic characteristics of the ancient (QP, QY, and QR) and modern (ENA#1 and ENA#2) Chinese papers. Figures cited from Ref. [66], with permission from the publisher

Microscopic observations, however, are unable to identify which coating pigment was used in each case.

Characterization of the coating layer by micro-CT

With micro-CT images, a 3D digital model is generated for each investigated paper specimen and, based on this model, a virtual cross section can be obtained for each specimen. On the cross-sectional image, the darker area, due to the low absorption of X-rays, indicates the fiber layer; while the brighter area, resulting from a relatively high absorption of X-rays, corresponds to the coating layer.

Figure 4 shows the virtual cross sections for the five paper specimens, from which one may conclude that: (1) The three ancient papers all show a layered structure. Each Lajian sample (QP and QY) has a coating layer on each side of the paper, suggesting a double-sided coating. By contrast, Lengjinjian QR shows the coating layer only on one of its sides, implying a single-sided coating. Also noticeable is the more or less tight, evenly distributed layers of the Lajian and Lengjinjian papers, which indicates that their coating treatment was done using heavy and repeated pressing. (2) The two modern papers (ENA#1 and ENA#2) show no layered structure, and each of them has a loose, unevenly distributed fiber layer, which conforms to the expectation that those papers would have received no surface treatment.

Micro-CT results conform well to microscopic observations and, even better, micro-CT analysis offers a straightforward and non-destructive way to identify the presence or absence of a coating layer as well as to distinguish between the coated (QP, QY, and

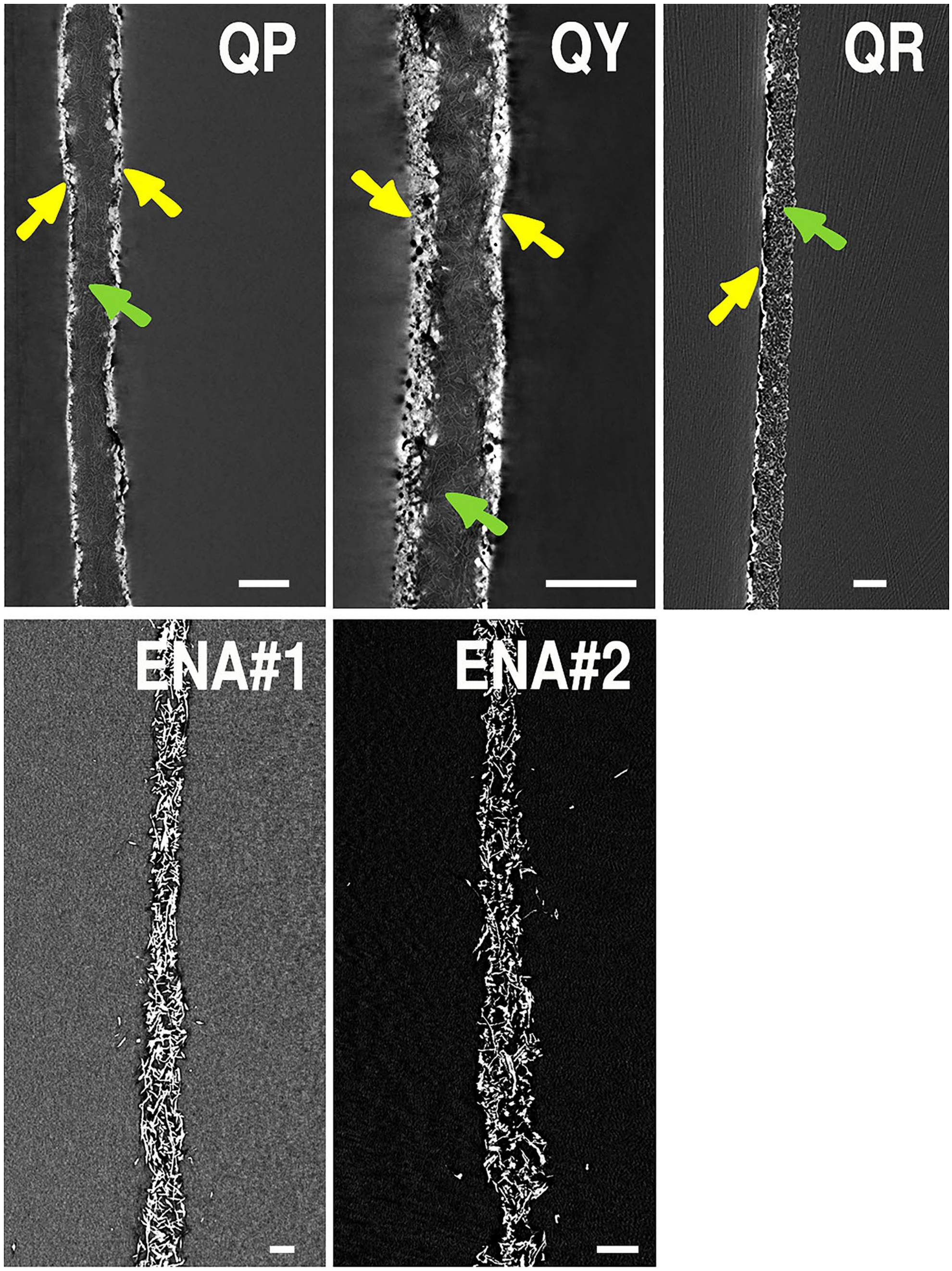

Fig. 4 Virtual cross sections of the five investigated papers reconstructed by micro-CT (the yellow arrow indicates the coating layer while the green arrow stands for the fiber layer). Scale bar = 100 μm. Figures cited from Ref. [66], with permission from the publisher

QR) and uncoated (ENA#1 and ENA#2) papers. Additionally, micro-CT results suggest, through the contrast between the brighter and darker areas seen in the grayscale images produced, the (near) absence of inorganic substances in the fiber layer of each of the three ancient papers (QP, QY, and QR). This observation seems to rule out the presence of large quantities of minerals among the fibers as fillers. In other words, micro-CT may have potential use in concluding the presence, or absence, of fillers (Table 3).

Table 3 Thickness of the coating layer or the fiber layer

Lab. no.	Paper name	The thickness of the observed layers (Mean ± SD, μm)	
		Coating layer (n = 10)	Fiber layer (n = 15)
QP	Lajian	17.3 ± 6.5	117.3 ± 8.0
QY	Lajian	19.3 ± 4.9	77.6 ± 8.3
QR	Lengjinjian	13.8 ± 4.3	101.3 ± 8.0
ENA#1	Raw xuan	0	156.5 ± 29.1
ENA#2	Bamboo paper	0	118.5 ± 19.1

Characterization of the coating pigment by hhXRF

Based on the microscopic observations and micro-CT scanning described above, we determined that the three ancient papers—Lajian QP, Lajian QY, and Lengjinjian QR—retained features of coating. They were therefore chosen for a hhXRF study to reveal the coating pigment used in each case. For each paper, both sides were investigated by hhXRF, and the elemental compositions of their surfaces were compared.

The hhXRF results are shown in Fig. 5. The Lajian papers (QP and QY) are rich in lead (> 90% Pb, wt%) on both the front and the back sides. On the other hand, the Lengjinjian paper (QR) shows high concentrations of mercury (67.0% Hg, wt%) and sulfur (15.6% S, wt%) on the red surface, which distinguishes it from the two Lajian papers.

Although lead or mercury content is high on the three papers, neither metal can be simply designated as the coating pigment, given that all the papers are colored and the coloring pigment(s), if present, might have contributed to the high concentration of lead or mercury. Lajian QY shows a bright yellow color, excluding the possibility that lead found on it exists in the form of red lead (Pb_3O_4), a red mineral pigment. That being said, Lajian QY is more likely to have been coated by a whitish or yellowish lead-based pigment. Lajian QP, on the other hand, is a purple-red paper. The lead on QP may or may not have come from red lead. As for the wine-red Lengjinjian QR, its mercury is attributable to cinnabar (HgS) and, due to the absence of lead on it, lead-based pigments are unlikely to have served as its coating pigment.

In brief, hhXRF results do not suffice to identify any of these paper's coating pigment.

Characterization of the coating pigment by Raman spectroscopy

Raman analysis was applied to both sides of the three ancient papers, in the hope of characterizing phases in the coating layer, which might relate directly to the coating pigment. Seventeen high-quality Raman spectra were collected, of which five were from Lajian QP, seven from Lajian QY, and five from Lengjinjian QR. Raman analysis confirmed that the same pigments or dyes were used on both sides of each examined paper. Here, a "dye" refers to an organic extract from natural plants while a "pigment" to an inorganic colorant.

Figure 6 shows some of the most representative results of the Raman analysis. Given that the examined Lajian and Lengjinjian papers were manufactured and used between the middle 17th and the early 20th century AD, the assignments of Raman peaks and the characterization of phases targeted the pigments and dyes most often used in China during that period [67–69]. At the same time, hhXRF results were taken into consideration in phase identification.

Raman spectra in Figs. 6a, b were obtained from the purple-red Lajian QP, whose surfaces are rich in lead (Pb). In Fig. 6a, Raman peaks are noticeable at 144, 390, 635, 976, 1045, and 1319 cm^{-1}, which do not conform to any single phase. The assignments of these Raman peaks can be given as follows: 144 and 390 cm^{-1} to massicot (β-PbO), an orthorhombic crystal of lead monoxide [70, 71]; 635 and 976 cm^{-1} to lead sulfate ($PbSO_4$) [71]; and 1045 cm^{-1} to lead white ($Pb(OH)_2{\cdot}2PbCO_3$) [72]. As for the Raman spectrum in Fig. 6b, Raman peaks at 120, 140, 222, 310, 383, 477, and 543 cm^{-1} fit well with those of red lead (Pb_3O_4); on the other hand, the broad Raman peak between 1050 and 1090 cm^{-1} indicates the presence of a carbonate group [70]. Given the purple-red color, it would be reasonable to assume that Pb_3O_4 served as the major, if not the only, coloring material. Carbonates are present in the coating layer, and hhXRF results show a high concentration of lead, results which, taken together, indicate the presence of lead white. As for lead monoxide and lead sulfate, they can either be heat-reduced products of lead white [73] or impurities associated with lead white [74]. Relating the Raman results to the hhXRF and micro-CT data, one concludes that lead white was most likely applied to Lajian QP as the coating pigment.

Raman spectra in Figs. 6c, d were collected from Lajian QY, whose surfaces are also rich in lead (Pb) but show a bright yellow color. The Raman spectrum in Fig. 6c shows a noticeable peak at 1050 cm^{-1} as well as two others at 320 and 410 cm^{-1}, results which altogether conform to those of lead white [75], a common white pigment in ancient China. The Raman spectrum in Fig. 6d also shows a strong peak at 1050 cm^{-1}, indicative of lead white. Also, it has Raman peaks at 1434, 1592, 1626, and 2932 cm^{-1}, which fits with the Raman peaks of gamboge that contains α- and β-gambogic acids. Gamboge is a yellow dye extracted from the Garcinia (Garcinia Linn.) tree. Lead

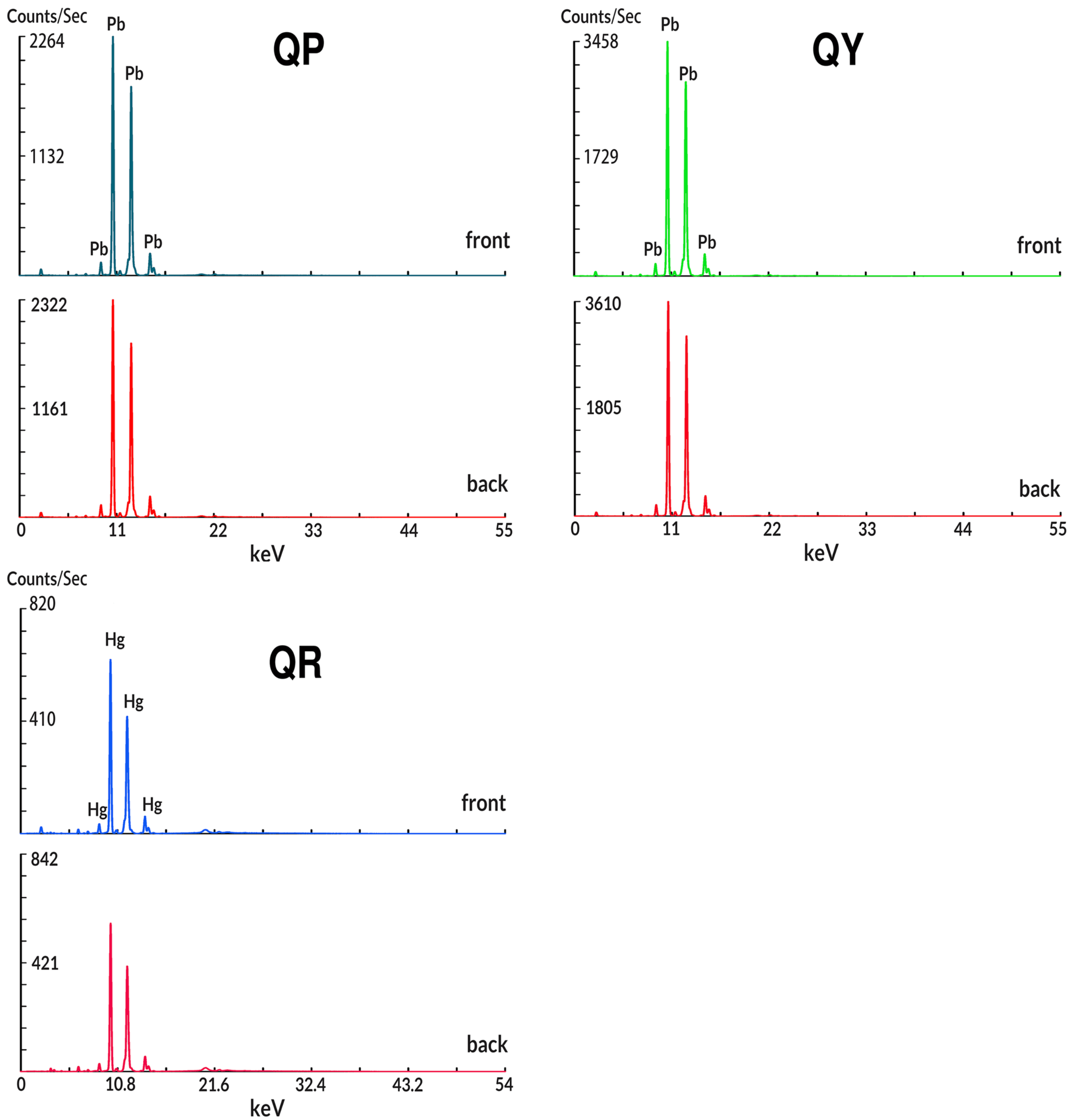

Fig. 5 Major elements detected on the surfaces of Lajian (QP and QY) and Lengjinjian (QR) samples

white is found on both sides of Lajian QY, corresponding to the two coating layers. Gamboge, being an organic yellow dye, does not form a coating layer itself. Therefore, the coating pigment on both sides of Lajian QY, we conclude, was prepared from lead white.

Raman spectra in Figs. 6e, f were obtained from Lengjinjian QR, whose surfaces are wine red. The Raman spectrum in Fig. 6e shows peaks at 144, 195, 397, 514, and 637 cm^{-1}, all attributable to kaolin ($Al_2O_3{\cdot}SiO_2{\cdot}2H_2O$) [29, p. 67]. Kaolin was an important white pigment in ancient China, and its use on wall paintings and painted artifacts began as early as the Western Han Dynasty (206 BC–24 AD) [76, 77] and continued through the Qing Dynasty [78]. Also, kaolin was widely used as a filling or coating pigment in papermaking [18, p. 195]. Thus, the present study proves that kaolin was used as a

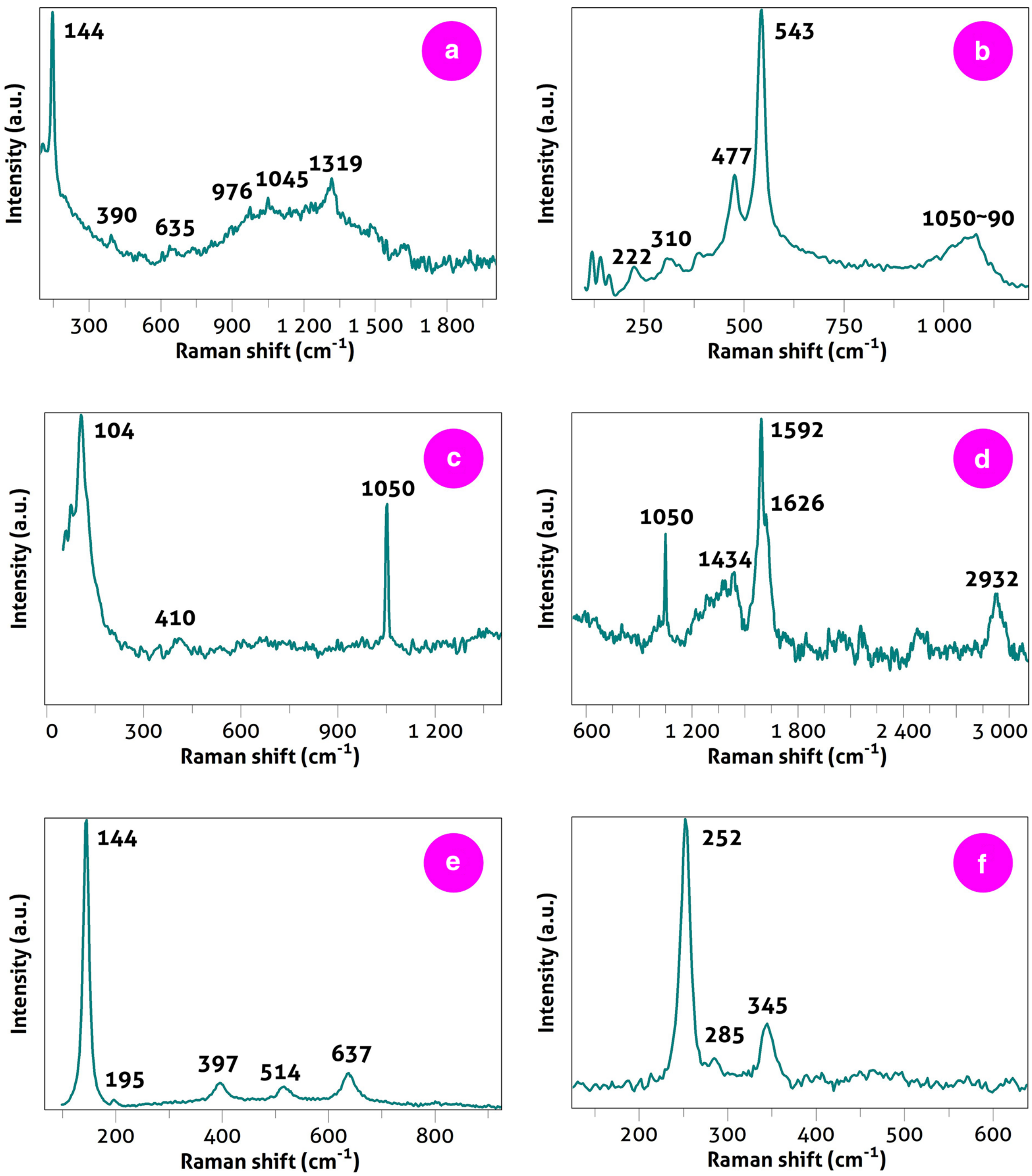

Fig. 6 Raman spectra of pigments and dyes (**a**, **b** from Lajian QP; **c**, **d** from Lajian QY; **e**, **f** from Lengjinjian QR)

coating pigment in the manufacture of Lengjinjian QR. The Raman spectrum in Fig. 6f shows three peaks at 252, 285, and 345 cm^{-1}, which conforms well with those of cinnabar (α-HgS). Cinnabar serves as the major, if not the only, red colorant on Lengjinjian QR, which explains the concentration of mercury indicated by the hhXRF results.

Given the findings above, one may conclude that Raman analysis helps characterize and identify the coating pigment as well as the coloring materials on these three ancient papers. One may also conclude that Raman results are compatible with those of hhXRF and micro-CT analyses.

Two additional issues: waxing and dyeing

Microscopic observations, micro-CT, hhXRF, and Raman results have altogether suggested that (1) The Lajian and Lengjinjian papers were colored or dyed, with Lajian QP having been colored by red lead, Lajian QY by gamboge, and Lengjinjian QR by cinnabar. (2) Both Lajian QP and Lajian QY were coated using lead white as the coating pigment; by contrast, Lengjinjian QR was coated using kaolin as the coating pigment. The coating treatment having now been well understood, two additional issues central to the manufacture of these three papers remain to be explored: waxing and dyeing.

As discussed in "Microscopic observation of the surface of paper specimens", microscopic observations suggest that the manufacture of Lajian and Lengjinjian should also have involved waxing, the purpose of which would have been to form a waterproof layer. Figure 7a shows a Raman spectrum collected from Lajian QY, with strong Raman peaks at 1050, 1134, 1290, 1440, 1465, 2724, 2845, and 2885 cm^{-1}. These Raman peaks fit well with those of natural beeswax we obtained from a Chinese beekeeper (shown in Fig. 7b) or Raman peaks of beeswax (1062, 1129, 1295, 1440, 2723, 2849, and 2881 cm^{-1}) reported elsewhere [71]. It appears, therefore, that beeswax was used for waxing Lajian QY. Beeswax does not appear to have been detectable for Lajian QP and Lengjinjian QR, however.

As for paper dyeing, our Raman analysis confirmed that gamboge was the only coloring material used on Lajian QY. Lajian QP and Lengjinjian QR were colored, respectively, with red lead and cinnabar, but the Raman analysis suggested the presence of organic dyes on these two papers, which would also have contributed to the red color. For example, Fig. 7c shows Raman peaks at 470, 660, 810, 1022, 1316, 1476, and 1607 cm^{-1}, which fit with the characteristic Raman peaks (479, 653, 811, 1028, 1317, 1484, 1603 cm^{-1}) of kermesic acid ($C_{16}H_{10}O_8$), a red dye extracted from Kermes scale insects [79]. Figure 7d, on the other hand, shows Raman peaks at 1206, 1316, and 1412 cm^{-1}, which are usually attributable to the presence of C-C, C-O, NH_2, or ring structures; given these Raman peaks, natural mineral-based pigments, starch, protein, and wax materials are excluded [80, 81]. Purpurin ($C_{14}H_8O_5$), a red dye extracted from madder plants, seems a possible candidate as it shows Raman peaks at 1213, 1277, 1319,

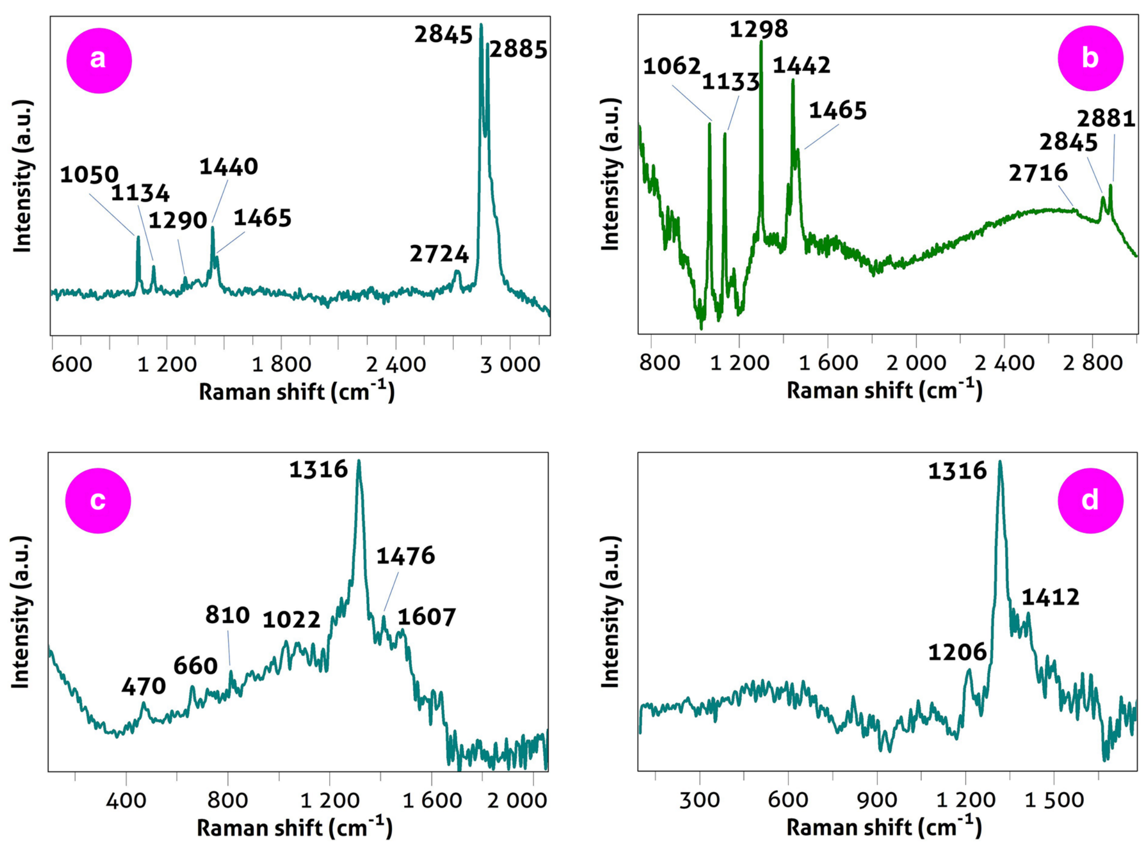

Fig. 7 Raman spectra of (**a**) beeswax identified on Lajian QY, **b** modern natural beeswax, **c** kermesic acid as a red dye on Lajian QP, and **d** purpurin as a possible red dye on Lengjinjian QR

Table 4 Summary of the findings made in the present study

Lab. no.	Paper name	Coating pigment	Wax	Coloring materials (pigment and dye)
		Raman	Raman	hhXRF/Raman
QP	Lajian	Lead white	n.d.	Red lead, kermesic acid
QY	Lajian	Lead white	Beeswax	Gamboge
QR	Lengjinjian	Kaolin	n.d.	Cinnabar, purpurin (?)
ENA#1	raw xuan	None	None	None
ENA#2	bamboo paper	None	None	None

n.d. not detectable, ? uncertain

and 1401 cm^{-1} within 1200 to 1450 cm^{-1} wavelength range [79]. Further analysis will be needed to confirm the red dye on Lengjinjian QR.

Once again, Raman analysis has shown its power to characterize phases (and to then determine waxes, pigments, and dyes) used in the manufacture of coated papers (Table 4).

Discussion and Summary

This study was carried out to establish a methodology that can characterize the coating layer and coating pigment on ancient Chinese papers non-invasively and more accurately. The purpose of this study is twofold: to demonstrate the weakness in the conventional approaches (microscopic observation and compositional analysis); to explore the potential of micro-CT and Raman spectroscopy in studying ancient coated papers.

The study began with microscopic examination of the selected paper specimens, followed by a handheld XRF analysis. Needless to say, both approaches are helpful for retrieving instant information regarding the distribution of fibers and mineral particles as well as the possible composition of mineral particles. However, neither approach can reveal the distribution of the coating layer or identify the coating pigment. By contrast, micro-CT images show—by means of reconstructed cross sections—not only the presence or absence of the coating layer but also the thickness and the distribution pattern of the coating layer. Combined with micro-CT images, Raman analysis provides convincing results when characterizing and identifying a paper's coating pigment. In short, we believe that a combination of micro-CT scanning and Raman spectroscopy can resolve difficulties attending the study of ancient coated papers better than conventional approaches.

As mentioned in "Characterization of the coating layer by micro-CT", we also believe that micro-CT scanning has potential for distinguishing a coating pigment from a filler, the two of which, according to our present knowledge, were often prepared from different minerals or from the same mineral but applied with different contents and thus, importantly, would generate different X-ray absorption spectra. However, without actually cross-sectioning the paper specimen and performing spot tests (such as Raman mapping) on the cross section, it is difficult to confirm the fillers or to compare the coating pigment with the fillers.

Based on the findings of the present study, we can describe the general procedures used in the manufacture of ancient coated papers such as Lajian and Lengjinjian: chosen (dyed) papers were first coated by having finely ground powder of inorganic substances (e.g., lead white and kaolin) brushed over one or both sides of the paper; then, pigments prepared from inorganic materials such as red lead and cinnabar, alone or mixed with organic dyes extracted from natural plants (such as gamboge, kermesic acid, and purpurin), were brushed over the surface of the paper, for the purpose of dyeing or coloring; finally, waxy materials (for example, beeswax) were applied to the paper to form a waterproof layer. Similar procedures have been described elsewhere, in technical studies of ancient Lajian papers [46], as well as in experimental studies on the manufacture of modern Lajian papers [51]. What is new about the present study, however, is that it shows, even with a small sampling, the complexity and diversity in the use of materials for manufacturing Lajian papers. This shows the necessity of carrying out technical studies on a much larger sampling of Lajian and its variants, in order to reveal a fuller understanding of the Lajian manufacture.

Lastly, it is necessary to evaluate the practicality and applicability of the proposed methodology. The advantages are self-evident: (1) in all analyses the sample size can be very small (the smallest paper-specimen size in this study was about 2 mm by 2 mm); (2) there is no need to further compromise the paper specimens; that is, no further cutting or pre-analysis sample preparation is needed for the proposed analyses; (3) performed with care in the course of analyses, no aspect the proposed approach would cause (visual) damage to the investigated samples, nor would the samples be contaminated by such things as organic and inorganic chemicals, dirt, and liquids; (4) the data collection and interpretation are relatively straightforward. Given these advantages, we believe that the proposed methodology (especially the combination of micro-CT and Raman spectroscopy) is ideal for paper fragments that are too small or too precious to allow for destructive sampling or analysis. At the same time, this methodology's ability to work with paper fragments—which, unlike whole ancient documents of great value, may readily be transported to a testing site—might reduce concerns arising from the low portability of micro-CT scanners and Raman spectroscopy equipment.

Conclusion

A multi-analytical, non-invasive study was carried out on three ancient (two Lajian and one Lengjinjian) and two modern (raw xuan and bamboo paper) Chinese handmade papers, with the goal of addressing one central question: whether a paper was coated or not and, if it was coated, how its coating layer and coating pigment might be correctly characterized and identified. To approach that goal, microscopic observations, surface elemental analysis, micro-CT imaging, and Raman spectroscopy were applied to the selected paper specimens.

The results show that neither microscopic observation nor elemental analysis suffices to characterize the coating layer or the coating pigment. They also show that micro-CT imaging is a more reliable tool for identifying and characterizing the coating layer, and that Raman spectroscopy is a more accurate technique for identifying the phases in the coating layer. The combination of micro-CT and Raman spectroscopy could serve as a better solution to the difficulties of investigating the coating treatment on papers. Besides that, Raman spectroscopy has shown its power in identifying other substances (such as wax, pigments, and dyes) that might have been used in the manufacture of coated papers.

In sum, the present study provides a novel, practical approach for non-invasively characterizing ancient Chinese coated papers.

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Abbreviations

OM: Optical microscope; SEM/EDX: Scanning electron microscope/elemental dispersive X-ray spectrometry; hhXRF: Handheld X-ray fluorescence analyzer; AAS: Atomic absorption spectrometry; micro-CT: Micro-computed tomography; Raman: Raman spectroscopy; XRD: X-ray diffraction.

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Authors' contributions

TL and CL conceptualized the experiments, interpreted the data, and wrote early drafts of the manuscript. TL carried out the microscopic examinations and hhXRF analysis; CL carried out the micro-CT analysis; and D. Wang performed the Raman analyses. All authors read and approved the final manuscript.

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Availability of data and materials

All data supporting the conclusions of this article can be obtained from the corresponding authors upon reasonable request.

Competing interests

The authors declare that they have no competing interests.

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