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Identifying sources of fibre in Chinese handmade papers by phytoliths: A methodological exploration

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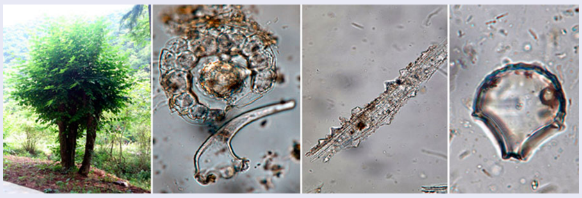
ABSTRACT
This paper proposed phytoliths as promising for identifying and distinguishing sources of fibre in Chinese handmade papers. For an initial methodological exploration, two types of Raw Xuan (unprocessed Xuan paper) and the two plant materials used in making them—namely rice straw and bark from blue sandalwood (*Pteroceltis tatarinowii Maxim.*)—were collected. The dry ashing method was used to extract phytoliths from Raw Xuan and its plant materials.

The results can be summarized as follows. First, phytoliths characteristic of rice (*Oryza sativa*) were abundant in both rice straw and Raw Xuan. By looking for rice phytoliths, it is possible to tell whether or not rice straw fibre is used in a particular paper. Second, hair cell phytoliths were observed in considerable quantities in blue sandalwood bark, but absent in the examined papers. Heat experiments showed that phytoliths in blue sandalwood were resistant to long-term heat and they would unlikely be eliminated when exposed to the heat in papermaking (with heat source barely above 200°C). It is hypothesised that they dissolved while cooked in an alkaline pH (limewater). Further studies are necessary to understand whether phytoliths in blue sandalwood—while cooked in limewater—undergo morphological changes and, if yes, how.



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Fibre identification; Chinese handmade paper; Xuan paper; Blue sandalwood; Phytoliths; Dry ashing

Statement of significance

Historic handmade papers, as well as artefacts made from them, are housed worldwide and studied globally. The technologies to manufacture these papers usually have their origin in China or East Asia, which has been known for hand papermaking traditions and distinctive raw materials and technological choices for a long time. Fibre identification, in many technical studies of historic handmade papers, receives close attention for strategic and practical considerations—e.g., it discloses human's exploitation of plants and directs the decision-making in conservation treatment (when necessary). Conventional approaches to fibre identification that involve chemical analysis or microscopic examination have both strengths and weaknesses. Therefore, for better fibre identification, it is necessary to consistently test, adjust, or change analytical approaches that are currently available. It is also important to explore new ideas and try new methods for the same purpose. Phytoliths are present in all plants, plant structures and organs; and more importantly, they can be family-, genus-, or species-specific. By examining phytoliths in handmade papers, it is possible to distinguish, or even identify, plant sources of fibre.

Introduction

Over the past two decades, multi-analytical studies have been increasingly carried out on papers handmade in pre-1949 China, for the purpose of conservation (e.g., Brown et al. 2017; Gong, Bo, and Gong 2014; Shi and Li 2013; Tsai and van der Reyden 1997; Wang et al. 2014), dating (He et al. 2010; Helman-Ważny 2016; Li et al. 2009) or assessment of authenticity (Li et al. 2017), and exploration of applicable and reliable new, analytical methods (e.g., Li 2010; Liu 2015; Yang, Guo, and Gong 2011). Some (e.g., Gong, Bo, and Gong 2014; Helman-Ważny 2016; Li et al. 2017; Shi and Li 2013) pay close attention to fibre identification and see it as crucial to understanding the manufacture of Chinese handmade

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papers more fully. Conventional approaches to fibre identification include chemical analysis and microscopic examination of fibres. Both approaches have their strengths and weaknesses. Historical records (Pan 2002; Tsien 1973), as well as patterned changes of plant use over time that are revealed by 493 fibre identification results (Li 2018), suggest that overall a limited number of plant species were most intensively exploited for Chinese hand papermaking. As plants produce phytoliths in abundance and many phytoliths have diagnostic shapes and sizes, it is hypothesized that phytoliths can serve as indicators for distinguishing—or even identifying—the plant materials used in Chinese hand papermaking. To test this hypothesis, Xuan paper, a traditional handmade paper, and the two plant materials it is made from, were sampled and studied for phytoliths that they contain.

Background

Phytoliths as indicators for identifying and distinguishing plants

By its most widely accepted definition, phytoliths are microscopic pieces of silica, formed by the deposition of solid silica—from groundwater and in a soluble state—in living plants (Piperno 1988, 11–13). Phytoliths are composed mainly of non-crystalline silicon dioxide, with a certain amount of water. Additional elements—such as aluminium (Al), sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg)—can coexist with silicon and oxygen in phytoliths, in minor or trace quantities (e.g., Anala and Nambisan 2015; Kamenik, Mizera, and Řanda 2013).

Phytolith researchers have agreed that phytoliths occur, often in significant quantities, in all plants, plant structures and organs (e.g., Piperno 2006, 5, 15; Rovner 1983; Shakoor, Bhat, and Mir 2014). Phytoliths vary in shape and size. The shape and size of a phytolith depends mainly on the species of the plant that produced it, but also on the type of cells that deposited silica from which the phytolith is formed, and the location of these cells (Wang and Lu 1993, 16–20). Such variations are sometimes family-, genus-, or species-specific (Piperno 1988; Wang and Lu 1993, 48–141). Even if the shape and size are not characteristic enough, the phytolith assemblage—i.e., the combination, abundance, and relative frequency of some or all phytoliths—makes it still possible to distinguish one plant from another (Rovner 1983).

Phytolith analysis refers to a procedure in which phytoliths are extracted from samples and studied for their morphology, in the hope of identifying and distinguishing their plant source(s). Since the 1970s, phytolith analysis has been extensively applied to sites and material remains all over the world. It has greatly advanced our knowledge about human-landscape interactions and man's exploitation of plants in prehistoric and historic times. In particular, phytolith analysis sheds light on paleoenvironment and paleoecology, (pre-)historic farming activities, human and animal diet and health, dress and adornment, tool use in food and non-food related activities, and burial rituals (e.g., Gorham and Bryant 2001; Rovner 1983; Wu et al. 2017). In short, phytolith analysis is a useful and reliable tool for identifying and distinguishing plant materials.

Chinese hand papermaking: over 2000-year exploitation of plants

Conventionally, 105 AD is considered as the year of the invention of paper (e.g., Biermann 1996, 1; Hunter 1974, 48–63; Tsien 1973; Vickerman 1995, 8–9; Wang and Li 1980; Yang and Yang 2002). However, archaeological findings of paper fragments dated to the Western Han (202 BC—9 AD) refute this notion and instead suggest a papermaking history of more than 2000 years in China (e.g., Collings and Milner 1990; Li 2016; Pan 1964, 1998, 2011, 2002). Nevertheless, it is true that shortly after 105 AD paper became easily obtainable in China, most famously known for writing and painting purposes.

Historically, Chinese papermaking demonstrated strong variations in technologies and materials through time and across space (Li 1983; Tsien 1973). Regarding the use of plants in the over 2000-year papermaking history, the sources of fibre consistently increased and diversified. In the meanwhile, certain sources of fibre gradually replaced others and became the dominant papermaking raw materials (Li 1983; Li 2018). Overall, Chinese papermaking has a few distinctive technological features. First, it uses non-wood plants exclusively as sources of fibre (Pan 1998, 8–11). Second, it involves a complicated pulping procedure, which relies heavily on the papermaker's hand labour and takes years to finish (Wang 2006, 417–425). Last but not least, all materials used in pulping and for papermaking are natural—fibre, water, sunlight, lime, plant extracts, and the like.

Despite the long history of papermaking in China, sources of fibre—especially in the early stages—are restricted to a limited number of, albeit diverse, species. Table 1 lists the plants exploited as sources of fibre in pre-1949 Chinese papermaking (Pan 1998, 143–146; Wang 1999, 129–145, 151–182; Yi 2015). Based on historical records and 493 published fibre identification results, Table 2 identifies five papermaking periods, highlights the plants exploited most intensively for papermaking, and summarises key characteristics—along with related developments—of paper production in each papermaking period (Li 2018; Pan 2002,

Table 1. Plant sources of fibre exploited for hand papermaking in pre-1949 China.

Chinese name	English name	Latin name	Genus	Family+	Plant parts used for papermaking
da ma 大麻	Hemp*	Cannabis sativa	Cannabis	Cannabaceae	Stem
zhu ma 苎麻	Ramie*	Boehmeria nivea (L.) Gaud.	Boehmeria	Urticaceae	Stem
ya ma 亚麻	Flax*	Linum usitatissimum	Linum	Linaceae	Stem
huang ma 黄麻	Jute*	Corchorus capsularis	Corchorus	Tiliaceae	Stem
gou 构	Paper mulberry tree*	Broussonetia papyrifera (L.) L'Hér. ex Vent.	Broussonetia	Moraceae	Inner bark
sang 桑	Mulberry plant*	Morus alba	Morus	Moraceae	Inner bark
san ya pi 三桠皮	Mitsumata	Edgeworthia chrysantha	Edgeworthia	Thymelaeaceae	Bark
chen xiang 沉香	Chinese eaglewood tree	Aquilaria agallocha Roxb.	Aquilaria	Thymelaeaceae	Bark
bai rui xiang 白瑞香	Winter daphne	Daphne papyracea Wall. ex Steud.	Daphne	Thymelaeaceae	Bark
lang du gen 狼毒根	Root of *lang du**	Stellera chamaejasme	Stellera	Thymelaeaceae	Root
mu fu rong 木芙蓉	Cottonrose hibiscus	Hibiscus mutabilis	Hibiscus	Malvaceae	Bark
mu fang ji 木防己	Cocculus orbiculatus	Cocculus orbiculatus (L.) Candolle	Cocculus	Menispermaceae	Bark
yue gui 月桂	Bay tree	Laurus nobilis	Laurus	Lauraceae	Bark
qing tan 青檀	Blue sandalwood*	Pteroceltis tatarinowii Maxim.	Pteroceltis	Ulmaceae	Inner bark
mao zhu 毛竹	Moso bamboo*	Phyllostachys edulis (Carrire) J. Houzeau	Phyllostachys	Poaceae	Stem
dao cao 稻草	Rice straw*	Oryza sativa	Oryza	Poaceae	Whole stalks
mai cao 麦草	Wheat straw*	Triticum aestivum	Triticum	Poaceae	Whole stalks
ku zhu 苦竹	Bitter bamboo*	Pleioblastus amarus	Pleioblastus	Poaceae	Stem
ci zhu 慈竹	Omei mountain bamboo*	Bambusa emeiensis	Bambusa	Poaceae	Stem
huang zhu 黄竹	Yellow bamboo*	Dendrocalamus membranaceus Munro	Dendrocalamus	Poaceae	Stem
zi teng 紫藤	Chinese wisteria	Wisteria sinensis	Wisteria	Fabaceae	Bark
lei gong teng 雷公藤	Threewingnut	Tripterygium wilfordii	Tripterygium	Celastraceae	Bark

*Plants whose phytoliths have been reported (in this study and others published elsewhere by previous researchers). See: Chen et al. (2017), Olivotto (1996), Wang and Lu (1993: Figures 1-19).
+The plant families listed here all produce phytoliths of different shapes and sizes in varying quantities. See: Piperno (1988), Wang and Lu (1993).

Table 2. Principal sources of fibre, production of handmade papers and related developments from Han to Qing dynasties.

Papermaking Periods	Principal sources of fibre used in papermaking	Key aspects of production of handmade papers, and related developments
Han dynasties 202 BC–220 AD	Hemp; ramie	Papermaking began in China. Fibre was sourced mainly from hemp and ramie but also from paper mulberry tree. Other plants such as mulberry tree were exploited for papermaking less frequently.
Jin dynasty and Northern and Southern dynasties 265–589 AD	Hemp; paper mulberry tree; mulberry plant; plants of the genus *Cocculus* or *Illigera*	After Jin dynasty, paper was made from bast fibre—i.e. fibre from the inner bark of mainly dicotyledonous plants—on a much larger scale than before. Regional papermaking centres were established in both South and North China. Pi Zhi (bast paper) was the dominant type. Making papers from mixed fibre sources (e.g., hemp and bast fibres) was well established and became a common practice. By no later than 6th century AD, paper mulberry trees were cultivated in the middle and lower reaches of the Yellow River in North China for papermaking.
Sui-Tang period 581–907 AD	Hemp; paper mulberry tree; mulberry plant; plants of the genus *Cocculus* or *Illigera*; winter daphne; cottonrose hibiscus	By the end of Tang dynasty, sources of fibre were far more diverse than ever before. At least six different families of plants were exploited. Certain plants—such as hemp, mulberry and paper mulberry plants—were cultivated to serve the papermaking. Papermaking was widespread, from the centre to the periphery. Bamboo fibre was used in papermaking for the first time (but only sporadically).
Song-Yuan period 960–1368 AD	Paper mulberry tree; mulberry plant; moso bamboo; rice straw	Paper made from hemp fibre was rare and used only in certain regions of North China. Bast fibre was still the dominant plant materials. Papers made from bamboo fibre—or sometimes a mixed pulp of bamboo and bast fibres—were widely used in writing and printing. Rice straw fibre was introduced into papermaking, and paper made from rice straw fibre was used as wrapping and toilet papers. It was common to use plant extracts in papermaking to facilitate the formation of paper sheets, those with larger dimensions in particular. First time in human history, bast papers were made to serve the manufacture of fiat money.
Ming-Qing period 1368–1911 AD	Moso bamboo; paper mulberry tree; blue sandalwood; rice straw; wheat straw	Paper was manufactured in more regions and in larger quantities, with a better quality and for more uses. Papermaking techniques were described in detail in books. About the same sources of fibre were used as in the Song-Yuan period. The most intensively exploited fibre was sourced from bamboo and less from dicotyledonous plants. Xuande paper made in Jiangxi Province from paper mulberry fibre, and Xuan paper made in Anhui Province from blue sandalwood and rice straw fibre, represents the most sophisticated papermaking techniques in the Ming and Qing dynasties, respectively.

75–281; Wang 2006, 84–381, 1999, 129–145, 151–182; Yi 2015).

Applying phytolith analysis to Chinese handmade papers: An exploratory study with Xuan paper

In studies of handmade papers manufactured in China and elsewhere, the current prevailing analytical approaches to fibre identification involve using (1) chemical/physical techniques and (2) microscopic examination (e.g., Greaves 1990; Isenberg 1967; Wang 2006; 1999). Chemical/physical techniques with instruments usually provide the more precise information on the type(s) of fibre in a paper sample and—if there is more than one type present—the proportion of each. The downside is that such analyses are expensive and require more paper samples, generally amounting to 0.2 g or greater (Shui, Lin, and Zhang 2007, 810; Isenberg 1967, 215–216). This makes them impractical for studying ancient papers that are usually too precious for massive destructive sampling. Microscopic analysis can be undertaken with considerably less paper, with or without sampled fibres being stained (Isenberg 1967, 223–245; Ilvessalo-Pfäffli and Marja-Sisko 1995; Wang 1999). However, to obtain reliable results, it requires high levels of training and expertise in microscopy, papermaking and pulping, and fibre morphology (Greaves 1990).

Given the above facts, for better fibre identification, it is necessary to consistently test, adjust, or change analytical approaches that are currently available. It is also important to explore new ideas and try new methods for the same purpose. The present study was launched exactly for the latter consideration. It hypothesises that phytoliths can serve as potential indicators for identifying and distinguishing the plants used in making Chinese handmade papers. The widespread presence of phytoliths in plants (see discussions in *Phytoliths as indicators for identifying and distinguishing plants*), as well as the diverse species of plants for papermaking (see discussions in *Chinese hand papermaking: over 2000-year exploitation of plants* and information in Table 1), forms a basis for this study.

Xuan paper and the plant materials from which it is made were chosen for this exploratory study. Xuan paper is a type of Chinese handmade paper and it may have its origin in the town of Jing (now known as Jingxian County) in Anhui Province of south China. It is soft and fine in texture and has been used in Chinese calligraphy and painting since its invention. For centuries, Xuan paper has been manufactured by blue sandalwood bark (*Pteroceltis tatarinowii Maxim.*, a species unique to China) and rice straw (Cao 1993; Mullock 1995).

Xuan paper was chosen mainly for two reasons. First, in present-day southern Anhui Province, Xuan paper is still being produced following Chinese hand papermaking traditions, using about the same materials and techniques as initially used several hundred years ago (Fang, Wu, and Lu 2008). It is therefore clearly understood how Xuan paper is manufactured, using what exact plant materials. Second, blue sandalwood and rice straw are grown widely in southern Anhui, making them easy to be sampled. In an exploratory study, the fact that the sources and types of phytoliths are clear would make phytolith identification much easier.

Materials and Methods

Raw Xuan and its two plant materials

Raw Xuan—the newly formed sheets of Xuan paper that undergo no further processing—was used in the experiment (Cao 1993, 92). Raw Xuan was chosen over Processed Xuan because phytoliths found in this type of Xuan paper would be ideally from plant materials and not have been affected by post-processing.

Raw Xuan and its plant materials used in this study were sourced from a modern Xuan paper mill—*Qian Nian Gu Xuan*, literally *thousand-year-old Xuan*—in present-day Jingxian County, southern Anhui. At this mill, Xuan paper is made in a very traditional way. For instance, pulping and papermaking rely heavily on hand labour and use no commercial chemicals such as sodium hydroxide or alum (Mr. Yikui Lu, the mill owner, personal communication, June 30th, 2008). The only alkaline material used is locally procured lime (CaO) (Fang, Wu, and Lu 2008). Lime has been widely used in Chinese papermaking since probably as early as the Eastern Han (25–220 AD). As one of the standard procedures, plant materials needed be soaked or cooked in limewater to prepare them into pulp (Wang 2006, 95). This is also the case with papermaking at *Qian Nian Gu Xuan*.

The samples comprised: (1) two types of Raw Xuan —*jing pi* and *te jing pi*. Both are made from a mixture of blue sandalwood fibre pulp and rice straw fibre pulp, but in different proportions. *jing pi* is a paper in which blue sandalwood fibre pulp and rice straw fibre pulp are mixed in a ratio of approximately 3:2; while in *te jing pi* the ratio is higher than 4:1; and (2) plant materials—blue sandalwood bark and *liao cao* (rice straw cooked in limewater for pulping). Figure 1 shows blue sandalwood growing in southern Anhui and *liao cao* exposed to strong sunlight after cooked in limewater.

Dry ashing for phytolith extraction and identification

The dry ashing method was used to extract phytoliths from the plant materials and Raw Xuan. This includes

Figure 1. a. the *Qian Nian Gu Xuan* mill; b, blue sandalwood growing all over the mountains around the mill. The blue sandalwood bark examined in the present study was peeled from one of these trees; c, blue sandalwood bark and rice straw (*liao cao*), both having been cooked, are laid out on weathered rocks on hillsides around the mill, where exposure to the sun allows natural bleaching to occur.

four main steps: (1) samples were cut off and then fully cleaned in distilled water, including 0.2 g of blue sandalwood bark or *liao cao*, and 0.2 cm by 0.2 cm Raw Xuan (both *jing pi* and *te jing pi*); (2) all samples were placed in porcelain crucibles, ignited in a muffle furnace and heated at 500 °C for six hours; (3) samples were cooled down, and a proper amount of ashed samples were then mounted on microscope slides using Canada Balsam; and (4) the samples were observed under an Olympus BX51 polarized light microscope, at 500× magnification. Phytoliths were photographed when a particular type was found. For a description of the dry ashing method, see Wang and Lu (1993:39-40).

The present study adopted a simplified version of the dry ashing method, compared to those described elsewhere (Piperno 1988, 126–127; Wang and Lu 1993, 39–40). In particular, the ashed samples were not washed in hydrochloric acid (HCl) or in nitric acid (HNO3) before mounted onto the slides. It was so done because, unlike soil or sediment samples, Raw Xuan and its plant materials are much cleaner. Acid washing is not necessary. In microscopic examination carried out later, the phytolith morphology was examined without difficulty. At least with Raw Xuan and it plant materials, the sample preparation described here worked well (Li 2010:24).

One more thing worth mentioning is that paper samples for phytolith analysis are small in terms of both size (each sample measuring 0.2 cm by 0.2 cm) and weight (about 0.15 mg per sample) in this study. It is therefore considerably less than paper samples required for instrumental chemical analysis (1 g or so) or for microscopic examination of fibres (0.2 g or greater) (Shui, Lin, and Zhang 2007, 810; Isenberg 1967, 215–216).

Phytolith extraction and identification was carried out, between June and August 2008, in the sample preparation laboratory at the Department of Scientific History and Archaeometry (now renamed as the Department of Archaeology and Anthropology) in University of Chinese Academy of Science, Beijing, P.R. China. All types of phytoliths noticed in samples were documented photographically for their morphological characteristics. A morphological comparison was then conducted between them and those reported for plants such as mulberry, paper mulberry, hemp, moso bamboo, rice and wheat. Rice phytoliths have been widely reported, and there are well-established criteria for identifying them (Chen 1997; Pearsall et al. 1995). Phytoliths in blue sandalwood were not reported before the phytolith extraction and identification experiment was carried out (in 2008).

Table 3. Major types of phytoliths in Raw Xuan and its plant materials.

Types of phytoliths	Observed in blue sandalwood	Observed in *liao cao*	Observed in *jing pi*	Observed in *te jing pi*
Hair cell	Present	Absent	Absent	Absent
Hair base	Present	Absent	Absent	Absent
Hook-shaped hair	Present	Absent	Absent	Absent
Rice husk multi-cell	Absent	Present	Present	Present
Double-peaked husk cell	Absent	Present	Present	Present
Fan-shaped bulliform	Absent	Present	Present	Present
Dumbbell-like cross-shaped	Absent	Present	Present	Present

Results and Discussion

Phytoliths of different types are present both in the plant materials and Raw Xuan. Major findings are discussed below (see Table 3 for a summary of phytoliths found in the examined plant and paper samples).

Rice phytoliths in rice straw and Raw Xuan

Phytoliths from rice (*Oryza* L.) have been studied since the earliest days of phytolith research (Piperno 2006, 72). The following types of phytoliths are accepted as characteristic of *Oryza* L. and used as the basis for identifying rice as a plant: (1) rice husk multi-cell and double-peaked husk cell phytoliths, which form in the epidermis of rice husk and are unique to the genus *Oryza*; (2) cross-shaped short phytoliths, which occur parallel to each other along their long axes and have multiple thick ridges; and (3) bulliform phytoliths that are fan-shaped, with flared edges. Both cross-shaped short phytoliths and bulliform phytoliths are formed in rice leaves (Harvey and Fuller 2005, 743; Piperno 2006, 73–74; Saxena et al. 2006).

As Figure 2 shows, in *liao cao*, the most distinctive *Oryza* phytoliths are noticed—that is, double-peaked husk cell and rice husk multi-cell (see Figure 2 a–d). In addition, fan-shaped bulliform and dumbbell-like cross-shaped phytoliths were found in considerable quantities. These four phytolith types were also observed in *jing pi* (see Figure 2 e–h) and *te jing pi* (see Figure 2 i–l).

Point-shaped, facetate, rondel, elongate and tracheal phytoliths were also present—although very uncommon—in *liao cao* and the paper (*jing pi* and *te jing*

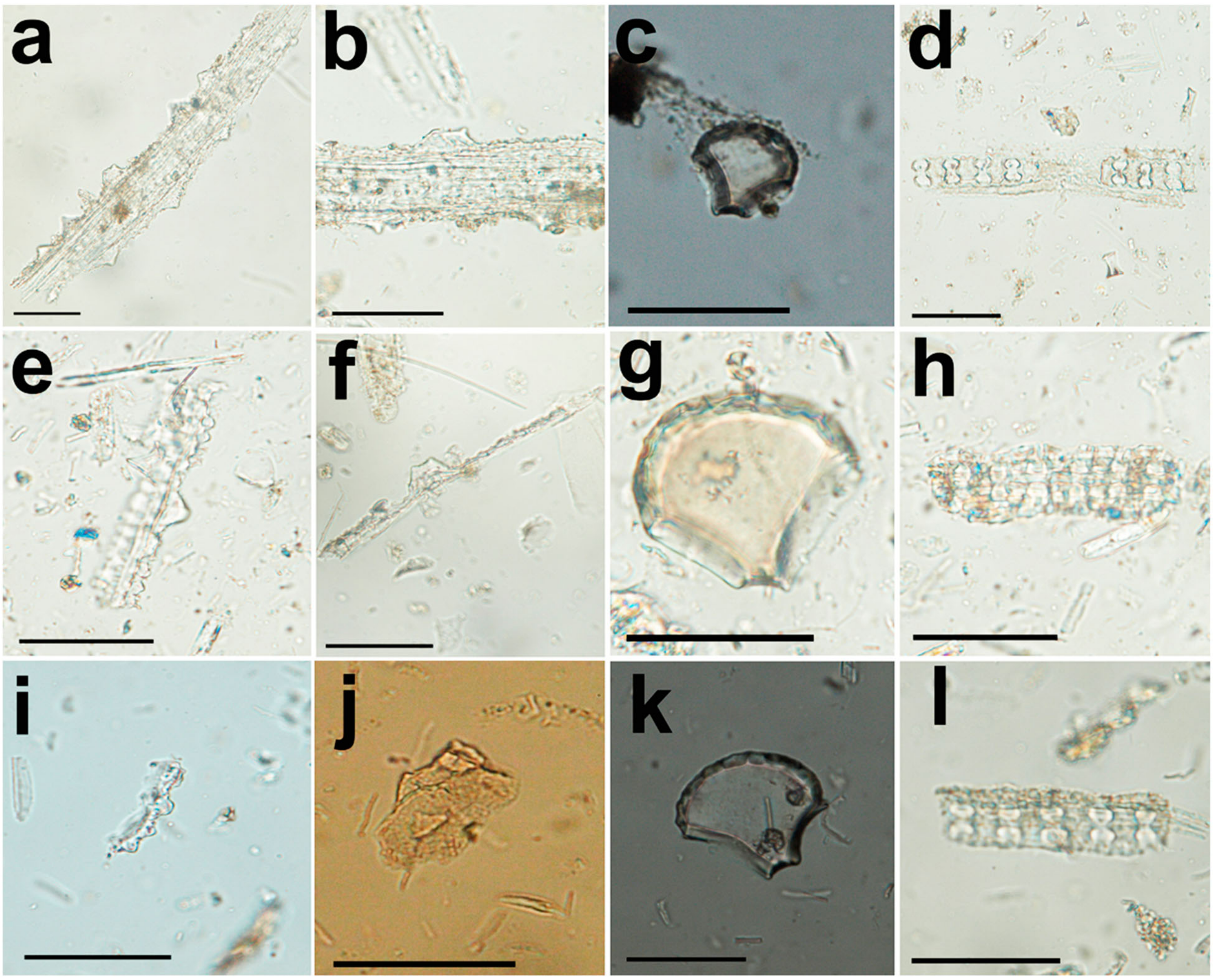

Figure 2. Characteristic rice phytoliths observed in *liao cao* (a to d) and Raw Xuan—*jing pi* (e to h) and *te jing pi* (i to l). a, e, i: rice husk multi-cell; b, f, j: double-peaked husk cell; c, g, k: fan-shaped bulliform; d, h, l: dumbbell-like cross-shaped. Scale bars = 50 μm.

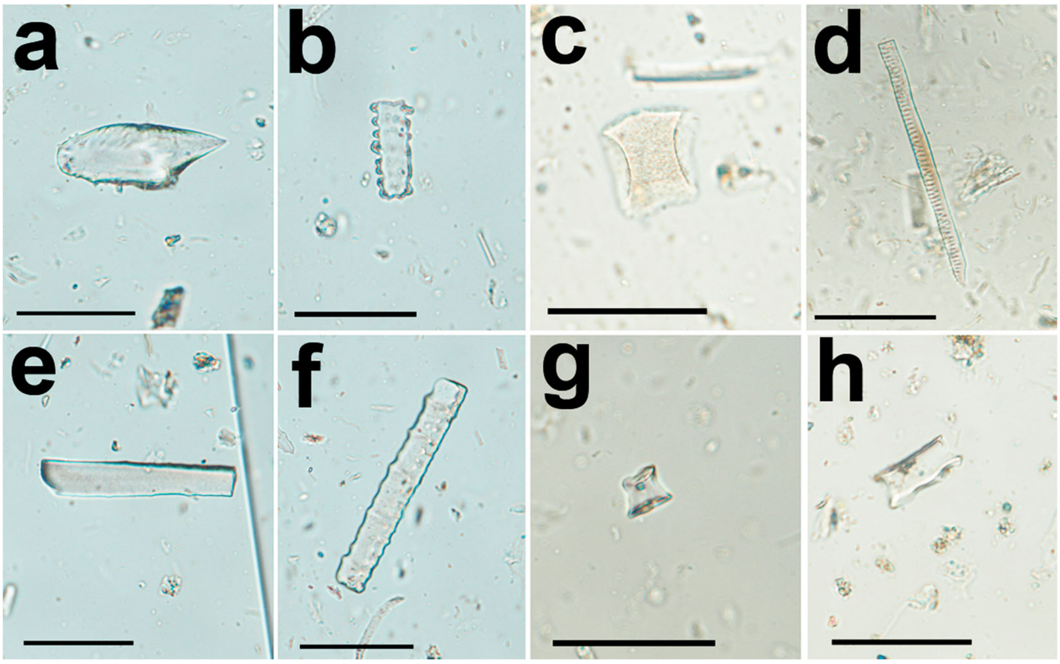

Figure 3. Other types of phytoliths observed in *liao cao* and Raw Xuan. a: point-shaped; b: unidentified; c: facetate; d: tracheal; e, f: elongate; g, h: rondel. Scale bars = 50 µm.

pi) (see Figure 3). These phytoliths presumably come from grasses or seeds and were introduced prior to the formation of paper sheets. Noticed in both *liao cao* and Xuan paper, these phytoliths were very likely transferred from *liao cao* to Xuan paper. Unfortunately, none of them is distinctive enough to suggest a particular kind of grass or seed, because many plants share phytoliths of these types.

Given the findings reported above, a close correlation between phytoliths in *liao cao* and those in Raw Xuan can be established. Three points can be made: (1) Phytoliths from rice straw survive the paper-making process; (2) Both *liao cao* and Raw Xuan contain phytoliths characteristic of rice (*Oryza* L.); and (3) although rice straw pulp differs in terms of proportion between *jing pi* (40%) and *te jing pi* (20%), rice phytoliths are consistently present and easily recognizable. This indicates that one can conclude the presence of rice straw fibres in a particular handmade paper by examining the paper for rice phytoliths.

Phytoliths in blue sandalwood bark were absent from Raw Xuan

Figure 4 shows the types of hair cell phytoliths found in blue sandalwood bark. Figure 4a shows hair cells; Figure 4b shows a hair base phytolith, the epidermal cells from which hair cells originate; and Figure 4c shows a non-segmented hair, a simple, hook-shaped form without noticeable substructure and surface decoration (Piperno 2006, 40). All these types of phytoliths are present in large quantities in blue sandalwood bark (and in its leaves as well, although not shown here).

It must be pointed out that hair cell phytoliths are abundant in *Asteraceae*, *Boraginaceae*, *Cucurbitaceae*, *Dilleniaceae*, *Moraceae*, *Ulmaceae*, *Urticaceae*, and other plant families (Piperno 2006, 39). In this regard,

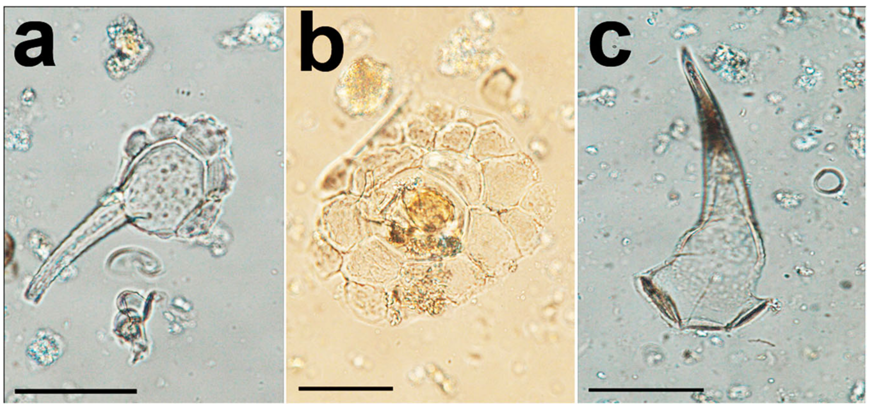

Figure 4. Phytoliths observed in blue sandalwood bark. a, hair cell; b, hair base; c, hook-shaped hair. Scale bars = 50 µm.

they are not diagnostic of blue sandalwood. Nevertheless, the morphological differences between hair cell phytoliths and rice phytoliths are significant. It would be theoretically sound to use phytoliths as the basis for the presence of fibres other than rice straw in Xuan paper, should hair cell phytoliths be observed.

Surprisingly, however, hair cell phytoliths were not found in Raw Xuan. How to interpret this fact?

According to the author's field visit at the *Qian Nian Gu Xuan* mill in June 2008, blue sandalwood bark and rice straw are repeatedly cooked in limewater preparatory to pulping. This process is key to the making of Xuan paper because it removes the outer bark of blue sandalwood and softens the fibres of blue sandalwood bark and rice straw (Fang, Wu, and Lu 2008). It usually takes about *two years* to prepare freshly peeled barks of blue sandalwood into bast fibre pulp. During this period of time, blue sandalwood barks are cooked for *more than ten times*, *ten to twelve hours each time* (Fang, Wu, and Lu 2008). This is much longer than the time it takes to prepare rice straw into *liao cao*—three months or so.

In brief, two factors may account for the absence of hair cell phytoliths in Xuan paper: cooking at high temperature for longer time; or cooking in an alkaline pH.

Heating blue sandalwood barks at high temperatures

Phytolith researchers differ in their opinions on how heat influences phytolith morphology. Some suggest that phytoliths—after being heated for hours at 700 °C—show no (major) changes in physical and chemical properties (Wang and Lu 1993, 4). Others report that phytoliths broke into indistinguishable bodies when heated at 600 °C. A recent study shows that phytoliths in different plant families—when heated in Muffle furnace for hours—undergo morphological changes at different temperature ranges (Wu, Wang, and Hill 2012).

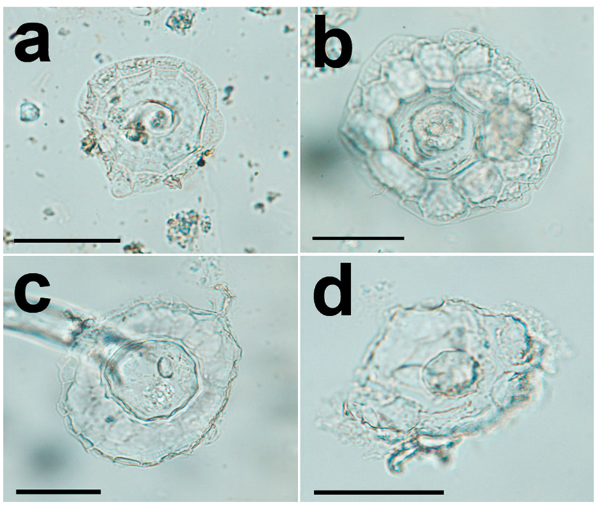

Figure 5. Phytoliths in blue sandalwood barks that were heated a, at 500 °C for 6 hours; b, at 500 °C and 600 °C, for 6 hours at each temperature; c, at 500 °C, 600 °C and 700 °C, for 6 hours each; d, at 500 °C, 600 °C, 700 °C and 800 °C, for 6 hours each. Scale bars = 50 μm.

In June 2009, a heat experiment was carried out to test how high temperature would impact the morphology of phytoliths in blue sandalwood. Samples of blue sandalwood barks were heated in a Muffle furnace in four stages: at 500 °C for six hours, then at 600 °C for another six hours, at 700 °C for another six hours, and at 800 °C for a further six hours. After each stage, the ashed sample was examined under microscope for phytoliths present in it. The results are shown in Figure 5.

The experiments argued that long-time exposure to heat *alone* did not explain why blue sandalwood phytoliths were absent in Xuan paper. Three lines of evidence lead to this argument. First, phytoliths in blue sandalwood—after repeatedly heated at 500 to 600 °C—undergo little or no changes in morphology. In the last two stages of experiment (heated at 700 and 800 °C), phytoliths in blue sandalwood show morphological changes—for example, hair base phytoliths start to have blurred edges, see Figure 5d. But overall, their morphological features are recognizable. Second, the same types of phytoliths—hair cell, hair base, and hook-shaped hair—survive all heat experiments. By the last stage of heat experiments, they are still found in quantities. Clearly, phytoliths in blue sandalwood are resistant to heat. Lastly, the temperature for cooking at the *Qian Nian Gu Xuan* mill is never higher than 200 °C (Mr. Yikui Lu, personal communication, June 30th, 2008).

Based on the information above, it is concluded that, throughout the manufacture of Xuan paper, phytoliths in blue sandalwood are unlikely to be eliminated as a consequence of being heated at around 200 °C.

Alkaline pH as an alternative explanation? A hypothesis

As previously discussed, long-term exposure to heat alone does not explain the complete absence of blue sandalwood phytoliths in Raw Xuan. An alternative explanation could be that blue sandalwood phytoliths are eliminated while cooking in an alkaline pH. This hypothesis is proposed mainly on two considerations.

Firstly, case studies report or caution the adverse effect of alkaline ambient on phytoliths. For example, Krauskopf (1956) points out that at pH 9 and above, phytoliths dissolve rapidly (Rovner 1983). IIer (1979) argues that phytoliths are 'susceptible to dissolution under strongly alkaline conditions (Mulholland and Rapp 1992)'. Recently, Cabanes, Weiner and Shahack-Gross (2011) demonstrate that phytoliths dissolve in an alkaline pH condition (pH = 10), despite that their stability differing between phytolith assemblages (Cabanes, Weiner, and Shahack-Gross 2011).

Secondly, at *Qian Nian Gu Xuan*, blue sandalwood bark and rice straw are cooked in limewater, an alkaline ambient. Lime is used in large quantities to prepare fibre pulp in this mill (Fang, Wu, and Lu 2008). Xuan paper produced at the mill—Raw Xuan in particular—has a pH of greater than 7. Tang (2011) reports a pH of 8 for Xuan paper sampled from the *Qian Nian Gu Xuan* mill (Tang 2011, 160). Evidently, an alkaline ambient is consistently noticed in the manufacture of Xuan paper.

In chemical terms, phytoliths are mainly hydrated silica ($SiO_2 \bullet nH_2O$), and silicon dioxide is an acid oxide that can react with alkaline substances. Therefore, it would not be surprising that, while blue sandalwood and rice straw are cooked in limewater, their phytoliths undergo morphological changes, decrease or in some cases dissolve completely. Blue sandalwood phytoliths are missing from Xuan paper likely due to the latter, extreme scenario. On the other hand, phytoliths in rice straw are not (much) affected. This is because of their stronger stability in an alkaline pH condition and/or the much shorter cooking time that rice straw undergo (Fang, Wu, and Lu 2008).

Admittedly, it remains so far a hypothesis. To test the hypothesis, systematic sampling and controlled experiments are needed to help understand whether phytoliths in blue sandalwood and rice straw—while cooked in limewater—undergo morphological changes and, if yes, how.

Conclusions

Phytolith analysis is hypothesised as promising for identifying and distinguishing sources of fibre in papers manufactured following Chinese hand papermaking traditions. To test this, some initial attempts were made by looking for and comparing phytoliths in both Xuan paper and its two plant materials—blue sandalwood bark and rice straw. The following conclusions can be drawn from this exploratory study:

(1) Phytoliths characteristic of rice (*Oryza* L.) were abundant and could be easily identified in both *liao cao* and Xuan paper. One can confirm the use of rice straw fibre in a handmade paper—whether it is Xuan or other paper, should rice phytoliths be noticed in the paper. Rice phytoliths are diagnostic and can easily be transferred to papers. Their complete absence in a paper suggests fibres sourced from plant materials other than rice straw.

(2) Hair cell phytoliths are found in significant quantities in blue sandalwood bark, but were absent from Xuan paper. Heat experiments suggested that long-term exposure to heat alone is not a direct causal factor for the absence of blue sandalwood phytoliths. An alternative explanation could be that blue sandalwood phytoliths reacted with hot limewater and dissolved completely. Further work will need to be carried out to test this hypothesis.

Finally, two additional points are worth noting regarding the application of phytolith analysis to handmade papers.

First, more papers—when destructive sampling is allowed—and their plant materials should be studied to confirm that phytoliths are not only widely present in handmade papers but can serve as indicators for fibre identification purpose. Besides Xuan paper, there are many other Chinese handmade papers—modern or historic, which are famously known to be made from hemp, mulberry/paper mulberry, bamboo, wheat straw, or root of *Stellera chamaejasme*.

Following the study presented here, a recent publication reports that phytoliths are widely present in modern Chinese handmade papers made from mulberry, hemp, and root of *Stellera chamaejasme*. For the purpose of fibre identification, the authors suggest that different phytolith assemblages help distinguish between papers made from different plant materials (Chen et al. 2017). This latest application of phytolith analysis, again, suggests the potential of phytoliths for fibre identification by demonstrating the widespread presence of phytoliths in papers made from different sources of fibre (bark of tree, root, rice stalks). Additionally, it discloses to us some important information: it is a common phenomenon to find phytoliths in handmade papers, but the degrees to which phytoliths can survive and be detected do vary (for instance, some phytoliths are preserved quite well while others not). In short, a more thorough analysis of more diverse samples is desired.

Second, as more plant materials for papermaking and more handmade papers are studied for phytoliths present in them, constructing a reference collection of phytoliths specifically for plants used in papermaking may become possible and necessary. Standards or criteria need to be specified—or outlined at the very least—to help understand how a particular type of phytoliths can be related to certain plant species and in what degrees of confidence.

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References

Anala, R., and Padma Nambisan. 2015. "Study of morphology and chemical composition of phytoliths on the surface of paddy straw." *Paddy and Water Environment* 13 (4): 521–527.

Biermann, Christopher J. 1996. *Handbook of Pulping and Papermaking*. San Diego, CA: Academic Press.

Brown, Natalie, Dirk Lichtblau, Tom Fearn, and Matija Strlič. 2017. "Characterisation of 19th and 20th century Chinese paper." *Heritage Science* 5: 47.

Cabanes, Dan, Steve Weiner, and Ruth Shahack-Gross. 2011. "Stability of phytoliths in the archaeological record: A dissolution study of modern and fossil phytoliths." *Journal of Archaeological Science* 38 (9): 2480–2490.

Cao, Tiansheng. 1993. *Zhongguo Xuanzhi*. Beijing: Zhongguo Qinggongye Chubanshe. (in Chinese).

Chen, Baozhang. 1997. "Zhiguishi fenxi yu zaipeidao qiyuan yanjiu." *Zuowu Xuebao* 23 (1): 114–118. (in Chinese).

Chen, Wen, Xiumin Xia, Yan Wu, Wenhua Zhou, and Jilong Shi. 2017. "New application of phytolith analysis in paper identification." *Journal of Beijing Institute of Graphic Communication* 25 (2): 1–5. (in Chinese).

Collings, Thomas, and Derek Milner. 1990. "A new chronology of papermaking technology." *The Paper Conservator* 14 (1): 58–62.

Fang, Xiaoyang, Dantong Wu, and Yikui Lu. 2008. "Research and investigation about Qiannianguxuan Xuan paper at Anhui province Jing County." *Journal of Beijing Institute of Graphic Communication* 16 (6): 1–8. (in Chinese).

Gong, Yuxuan, Xiaojian Bo, and Decai Gong. 2014. "Wuweishi Bowuguan guancang Zangwen Dazangjing de jiance fenxi yu baohu yanjiu." *Zhongguo Zangxue* 2014 (3): 176–179. (in Chinese).

Gorham, L. Dillon, and Vaughn M. Bryant. 2001. "Pollen, phytoliths, and other microscopic plant remains in underwater archaeology." *International Journal of Nautical Archaeology* 30 (2): 282–298.

Greaves, Philip H. 1990. "Fibre identification and the quantitative analysis of fibre blends." *Coloration Technology* 20 (1): 32–39.

Harvey, Emma L., and Dorian Q. Fuller. 2005. "Investigating crop processing using phytolith analysis: The example of rice and millets." *Journal of Archaeological Science* 32 (5): 739–752.

He, Qiuju, Tao Li, Ruiting Zhao, Yuling Li, and Fang Shao. 2010. "Non-destructive in-situ characterization of pigments on a portrait of Chinese Taoism figure." *Sciences of Conservation and Archaeology* 22 (3): 61–68. (in Chinese).

Helman-Ważny, Agnieszka. 2016. "More than meets the eye: Fibre and paper analysis of the Chinese manuscripts from the Silk Roads." *Science & Technology of Archaeological Research* 2 (2): 127–140.

Hunter, Dard. 1974. *Papermaking: The History and Technique of an Ancient Craft*. New York, NY: Dover Publications, Inc.

Ilvessalo-Pfäffli, and Marja-Sisko. 1995. *Fiber Atlas: Identification of Papermaking Fibers*. Berlin, New York: Springer-Verlag.

Isenberg, I. H. 1967. *Pulp and Paper Microscopy*. Appleton, Wisconsin: The Institute of Paper Chemistry.

Kamenik, J., J. Mizera, and Z. Řanda. 2013. "Chemical composition of plant silica phytoliths." *Environmental Chemistry Letters* 11 (2): 189–195.

Li, Wei. 1983. "The distribution and changes of China's paper industry in different historical periods." *Geographical Research* 2 (4): 72–83.

Li, Tao. 2010. *Technical Investigation of Ancient Chinese Paper Based Materials with Non-destructive Chemical Methods*. Unpublished Ph.D. dissertation, Beijing: University of Chinese Academy of Sciences. (in Chinese)

Li, Xiaocen. 2016. "Gansu Tianshui Fangmatan Xihan mu chutu zhi de zaiyanjiu." *Kaogu* 2016 (10): 110–114. (in Chinese)

Li, Tao. 2018. "Temporal change of raw materials of fiber used in ancient Chinese papermaking and its implications." *China Pulp and Paper* 37 (1): 37–45. (in Chinese).

Li, Tao, Jinxin Ji, Zhong Zhou, and Jilong Shi. 2017. "A multi-analytical approach to investigate date-unknown paintings of Chinese Taoist priests." *Archaeological and Anthropological Sciences* 9 (3): 395–404.

Li, Tao, Jilong Shi, Xiaoyang Fang, and Changsui Wang. 2009. "The application of Raman spectroscopy, phytolith and starch analyses to research of paper-based materials." *Journal of Beijing Institute of Graphic Communication* 17 (6): 6–10. (in Chinese).

Liu, Chang. 2015. *Study on Chinese Traditional Handmade Paper Image Analysis*. Unpublished Ph.D. dissertation, Beijing: University of Science and Technology of Beijing.

Mulholland, Susan C., and George Rapp, Jr. 1992. "Phytolith systematics: An introduction". In *Phytolith Systematics: Emerging Issues*, edited by George RappJr., and Susan C. Mulholland, 1–13. New York, NY: Spinger Science + Business Media, LLC.

Mullock, Hilary. 1995. "Xuan paper." *The Paper Conservator* 19 (1): 23–30.

Olivotto, Yolanda Margaret Deirdre. 1996. *Phytolith analysis as a means of cellulosic fibre identification: Silica bodies and calcium oxalate crystals in Agave genera (cantala, maguey and sisalana, sisal), Boehmeria nivea (L.) Gaud (ramie), Cannabis sativa L. (hemp), Corchorus capsularis L. (jute), and Musa textilis Nee (abaca, or Manila hemp)*. Upublished Master thesis, Edmonton, Alberta: University of Alberta.

Pan, Jixing. 1964. "Shijie shang zuizao de zhiwu xianwei zhi." *Wenwu* 1964 (11): 48–49. (in Chinese).

Pan, Jixing. 1998. *Zhongguo Kexue Jishushi: Zaozhi Yu Yinshua Juan*. Beijing: Kexue Chubanshe. (in Chinese).

Pan, Jixing. 2002. *Zhongguo Gudai Sida Faming: Yuanliu, Waichuan Ji Shijie Yingxiang*. Hefei: Zhongguo Kexue Jishu Daxue Chubanshe. (in Chinese).

Pan, Jixing. 2011. "Review of debates concerning paper history during the last 30 years in China." *The Chinese Journal for the History of Science and Technology* 32 (4): 561–571. (in Chinese).

Pearsall, Deborah M., Dolores R. Piperno, Elizabeth H. Dinan, Marcelle Umlauf, Zhijun Zhao, and Robert A. Benfer, Jr. 1995. "Distinguishing rice (*Oryza sativa* Poaceae) from wild Oryza species through phytolith analysis: Results of preliminary research." *Economic Botany* 49 (2): 183–196.

Piperno, Dolores R. 1988. *Phytolith Analysis: An Archaeological and Geological Perspective*. San Diego, CA: Academic Press, Inc.

Piperno, Dolores R. 2006. *Phytoliths: A Comprehensive Guide for Archaeologists and Paleoecologists*. Lanham, Maryland: AltaMira Press.

Rovner, Irwin. 1983. "Plant opal phytolith analysis: Major advances in archaeobotanical research." *Advances in Archaeological Method and Theory* 6: 225–266.

Saxena, Anju, Vandana Prasad, I. B. Singh, M. S. Chauhan, and R. Hasan. 2006. "On the Holocene record of phytoliths of wild and cultivated rice from Ganga Plain: Evidence for rice-based agriculture." *Current Science* 90 (11): 1547–1552.

Shakoor, Sheikh Abdul, Mudassir Ahmad Bhat, and Showkat Hamid Mir. 2014. "Phytoliths in plants:A review." *Research & Reviews: Journal of Botanical Sciences* 3 (3): 10–24.

Shi, Jilong, and Tao Li. 2013. "Technical investigation of 15th and 19th century Chinese paper currencies: Fiber use and pigment identification." *Journal of Raman Specroscopy* 44 (6): 892–898.

Shui, Siyu, Mingkuan Lin, and Jingyuan Zhang. 2007. *Guoneiwai Zaozhi Fenxi Jianyan Shiyong Fangfa*. Beijing: Zhongguo Biaozhun Chubanshe. (in Chinese).

Tang, Ying. 2011. *Stabilisation of Natural Colourants and Lignocellulosic Textiles*. Unpublished Ph.D. dissertation, Wellington: Victoria University of Wellington.

Tsai, Feiwen, and Dianne van der Reyden. 1997. "Analysis of modern Chinese paper and treatment of a Chinese woodblock print." *The Paper Conservator* 21 (1): 48–62.

Tsien, Tsuen-Hsuin. 1973. "Raw materials for old papermaking in China." *Journal of the American Oriental Society* 93 (4): 510–519.

Vickerman, Kathrine D. 1995. *Papermaking: Then and Now. A History of Hand Papermaking from Its Beginning, Plus a Process for Using Natural Fibers to Make Papers*. Educational Resources Information Center (ERIC).

Wang, Juhua. 1999. *Papermaking Raw Materials of China: An Atlas of Micrographs and the Characteristics of Fibers*. Beijing: Zhongguo Qinggongye Chubanshe. (in Chinese).

Wang, Juhua. 2006. *Zhongguo Zaozhi Gongcheng Jishushi*. Taiyuan: Shanxi Jiaoyu Chubanshe. (in Chinese).

Wang, Huanhuan, Aimin Cheng, Qinglin Ma, Zhitao Wang, and Changsui Wang. 2014. "Identifying the pigments of a Ming dynasty water-and-land painting." *Dunhuang Research* 2014 (5): 119–124. (in Chinese).

Wang, Juhua, and Yuhua Li. 1980. "Cong jizhong hanzhi de fenxi jianbie shilun woguo zaozhishu de faming." *Wenwu* 1980 (1): 78–85. (in Chinese).

Wang, Yongji, and Houyuan Lu. 1993. *Zhiwu Guisuanti Yanjiu Ji Yingyong*. Beijing: Haiyang Chubanshe. (in Chinese).

Wu, Y., X. Guo, W. Wang, X. Chen, Z. Zhao, X. Xia, and Y. Yang. 2017. "Red pigments and Boraginaceae leaves in mortuary ritual of late Neolithic China: A case study of Shengedaliang site." *Microscopy Research and Technique* 80 (2): 231–238.

Wu, Yan, Changsui Wang, and David V. Hill. 2012. "The transformation of phytolith morphology as the result of their exposure to high temperature." *Microscopy Research and Technique* 75 (7): 852–855.

Yang, Haiyan, Jinlong Guo, and Decai Gong. 2011. "Study on the relationship between morphological characteristics of the fibers of ancient paper and papermaking technologies." *China Pulp and Paper* 30 (2): 32–35. (in Chinese).

Yang, Dongchen, and Jianguo Yang. 2002. "Zhi de faming he gongyi gaijin." *Wenbo* 2002 (5): 47–50. (in Chinese).

Yi, Xiaohui. 2015. "Fibrous raw material taxonomies of Chinese ancient paper and traditional handmade paper." *China Pulp and Paper* 34 (10): 76–80. (in Chinese).