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Characterisation and durability of contemporary unsized Xuan paper

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Abstract In China, Xuan paper has been the paper of choice as artwork support and for conservation, for several centuries. However, little is known about its material properties, especially given the many grades of sized and unsized Xuan paper. In addition, there is a lack of information on its degradation. In this research, a selection of contemporary unsized Xuan papers was investigated, representing diverse raw materials. Seven out of twelve contemporary unsized Xuan papers were determined to be approximately neutral and contain $> 2\%$ alkaline reserve, indicating good durability. Viscometry was used to determine the degree of polymerisation (DP) as none of the samples gave significant reactions to the phloroglucinol spot test. The average DP of ten contemporary unsized Xuan papers is ~ 1700, excluding two papers that have presumably been sun-bleached, and that exhibit significantly lower DP. Using X-ray fluorescence, it can be demonstrated that Ca and Si are the dominant elements and interestingly, Ca content is directly correlated with ash content and with alkaline reserve. Accelerated degradation was performed at two sets of environmental conditions, i.e. 90 °C, 30% RH and 60 °C, 70% RH, and the established degradation rates agreed with the Collections Demography model of paper degradation meaning that degradation of Xuan papers proceeds in the same way as other types of paper. This research gives fundamental insights into contemporary unsized Xuan papers, which exhibit good stability during accelerated degradation despite the low starting DP in the context of the samples used in this study. Our findings may inform methods of Xuan paper production, selection of Xuan paper for conservation purposes, as well as preventive conservation of Xuan paper-based artefacts.

Keywords Xuan paper · Material property · Paper durability · Conservation

Introduction

Xuan paper is a traditional Chinese handmade paper often used for Chinese calligraphy and painting, and is the preferred paper type for conservation of paper-based artefacts, with the reputation of being the "paper king lasting over a thousand years" (Zhang 2018). In addition, the process of its manufacture was declared as intangible cultural heritage of humanity by UNESCO (2009). It is believed that Xuan paper

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originated in the Jing county, Anhui province (China) and has been produced since the Tang dynasty (618–907 CE) (Mullock 1995). The diversity of Xuan paper products provides artists and conservators with a choice of diverse sizing, thickness and weight, as well as patterning (Needham and Holorenshaw 1974). In 2012, ~ 800,000 kg of Xuan paper was produced in paper mills in the Jing county alone (Yao et al. 2012). The paper is widely understood to be of excellent quality and durability; however, scientific evidence for this is conspicuously missing, which is what this research is aiming to address.

The raw materials used in Xuan papermaking are mostly bark fibres of blue sandalwood (*Pteroceltis tatarinowii*), growing in calcium-rich soil, and rice straw (*Oryza sativa*) growing in silica-rich soil (Tsai and Van der Reyden 1997). It has been shown that inorganic minerals precipitate within and between plant fibres, the formations being called 'phytoliths' (Tsai and Van der Reyden 1997; Li 2018). It is thought that the long blue sandalwood fibres constitute the backbone of Xuan paper, while the short rice fibres provide softness (Zhao et al. 2018). A higher content of blue sandalwood is used for 'superior quality' papers and is used for artworks due to more suitable physical properties (Tsai and Van der Reyden 1997; Li 2018). With respect to raw material use, three grades of Xuan paper are available commercially (Mullock 1995; Tsai and Van der Reyden 1997; Wu et al. 2016):

- 'Extra-pure' (特净皮, Tè Jìng Pí), > 80% blue sandalwood,
- 'Pure' (净皮, Jìng Pí), 50–60% blue sandalwood,
- 'Cotton-like' (棉料, Mián Liào), 20–30% blue sandalwood.

Blue-sandalwood fibres may be replaced by other fibres to cut the cost of paper production, leading to imitation Xuan paper (Tsai and Van der Reyden 1997). A typical example is 'Gou Pi' paper (构皮纸, Gòu Pí) made of paper mulberry bark fibre (*Broussonetia papyrifera*) and straw fibre in various proportions. Xuan paper is further classified into unsized paper called 'raw' Xuan paper (生宣, Shēng Xuān), and sized paper called 'ripe' Xuan paper (熟宣, Shú Xuān) (Dong and Zhu 2018). The 'ripe' paper is treated with a solution of bone glue and potassium aluminium sulfate [$KAl(SO_4)_2$] (Tsai and Van der Reyden 1997; Wu et al. 2016; Dong and Zhu 2018). Alum allows gelatine to bond with paper fibres and fill in fibre gaps leading to a hydrophobic surface suitable for some techniques of brushwork painting (Catcher et al. 2017). Unsized Xuan paper is used for freehand brushwork due to better water absorbance (Wu et al. 2016). Traditional Chinese paper mounting and conservation treatments are based on centuries of practice (Catcher et al. 2017). All categories of papers can be used as mounting and conservation materials for traditional Chinese painting and calligraphy, as long as raw materials and properties of the backing papers and of the artefacts are consistent (Mullock 1995; Wu et al. 2016), e.g. Xuan paper is often used as a backing paper to offer mechanical support for aged or damaged artefacts also made of Xuan paper (Tsai and Van der Reyden 1997). It is also commonly used as lining in repairs of tears and creases (Yao et al. 2012; Catcher et al. 2017). Wheat starch is the most frequently applied glue, often liberally, also as surface sizing, leading to conserved objects becoming a mixture of starch and fibres (Catcher et al. 2017).

Traditional Xuan paper production is manual and takes 1–2 years (Yao et al. 2012). The process significantly differs from western papermaking and includes manual fibre preparation steps such as: steaming, soaking, boiling, rinsing, bleaching using sunlight and beating. The resulting sheets are highly homogeneous (Mullock 1995; Tsai and Van der Reyden 1997; Song 2017). According to traditional practice, blue sandalwood bark is only collected during winter in order to obtain particularly soft fibres. During cooking, lime [mixture of CaO, $Ca(OH)_2$, $CaCO_3$], and sodium carbonate ($NaCO_3$) are added successively to remove non-cellulose materials, e.g., lignin, pectin and wax substances (Tsai and Van der Reyden 1997). A natural dispersing agent, kiwi fruit juice, is used during sheet formation to separate fibres in the pulp evenly, and slightly alkaline stream water is used for washing and pulping throughout (Tsai and Van der Reyden 1997; Yang et al. 2018). From the 1950s on, mechanical production gradually took hold, and chemicals began to be used to reduce the duration of the overall process. Since sun bleaching traditionally takes more than half a year (Yao et al. 2012), it was replaced by calcium or sodium hypochlorite bleaching [$Ca(ClO)_2$ or NaClO].

Unlike the well-studied western paper where significant research has been carried out over the

past decades (Zou et al. 1996a, b; Kočar et al. 2005; Liu et al. 2017), systematic scientific research on Xuan paper is quite limited. Tsai and Van der Reyden (1997) studied unsized Xuan papers and Gou Pi papers, in which phytoliths were observed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS) (Tsai and Van der Reyden 1997). A method for differentiation of straw types in unsized 'extra-pure' and 'pure' Xuan paper on the basis of phytoliths has been proposed (Li 2018). Ink absorbance of unsized 'extra-pure' Xuan paper was studied, demonstrating that fibre density and distribution, as well as fibre surface roughness have an effect (Wu et al. 2016). Photo-degradation was studied using three 'cotton-like' Xuan papers by exposing them to UVA radiation, which led to a decrease in blue fluorescence and reflectance, and therefore yellowing (Tang and Smith 2013), unfortunately the authors do not indicate whether the studied samples were sized or unsized, lignin-containing or lignin-free. Since alum sizing on 'ripe' Xuan paper leads to acidification, it has been suggested that this paper should not be applied in conservation or painting (Xu 2008). While research on Xuan paper has been published, mechanical tests were often used, showing high measurement uncertainties (Yeh and Munn 2005), and crucial information is sometimes missing that would allow comparisons, e.g. dates of production are not always clear (Chen et al. 2002, 2003).

Therefore, in this study, samples were comprehensively evaluated using methods conventionally used in paper research (Strlič and Kolar 2005), including fibre identification using microscopy, identification of starch and lignin, determination of pH and degree of polymerization (DP), ash content, alkaline reserve, and elemental analysis using X-ray Fluorescence (XRF). Decrease in DP during degradation was used to calculate the rate of degradation (Zou et al. 1996a), based on the Ekenstam equation, the validity of which was established for many types of paper (Ekenstam 1936; Zou et al. 1996a; Strlič and Kolar 2005; Liu et al. 2017; Coppola et al. 2018). Using diverse paper samples of all grades, from various paper mills in the Jing county, Anhui province, we systematically explored the properties and stability of Xuan paper with the aim to better understand this material of such extraordinary importance in Chinese art and conservation.

Methodology

Samples

Sixteen Xuan paper samples were provided by the Centre of Cultural Heritage Conservation, Sichuan Museum. These papers include three grades of Xuan and Gou Pi papers, produced by three paper mills. An information card was attached to almost all papers, declaring the grade, date of production, paper mill, and fibre furnish, as shown in Table 1. All papers had chain and laid lines. All but three papers are of recent production, with one being 70–80 years old and two being 30 years old at the time of research.

Fibre furnish

On the basis of the standard (ISO 9184-3 1990), fibre furnish using the Herzberg stain was conducted to explore particularly the insufficiently described sample No. 12. GP1, GP2 and XP12 with declared fibre composition were used as references for comparison. All samples were observed with an optical microscope (Brunel Microscopes Ltd, Wiltshire) equipped with a DSLR camera (Canon EOS 1100D, Tokyo) under transmitted light.

Spot tests for starch and lignin

Iodine test was used to detect starch (Isenberg 1967). The reagent was produced using 0.5 g of I_2 (Sigma Aldrich, Dorset) and 1 g of KI (Sigma Aldrich, Dorset), dissolved into 10 mL of deionised water (Millipore, Molsheim). One drop of the resulting solution was dropped on three spots of each paper sheet. No colour change was assessed for starch-free paper.

Following phloroglucinol spot test on the basis of TAPPI T 401 om-15 (2015), a saturated solution of phloroglucinol (Sigma Aldrich, Dorset) in 20% HCl (Sigma Aldrich, Dorset) was used to test for lignin presence on three spots of each sample with reddish colouration being interpreted as lignin presence. This preliminary test is essential for viscometric determination of DP as only papers with low lignin content can be dissolved in the cupri-ethylenediamine (CED) solution.

Table 1 Data as declared by the manufacturers of 16 Xuan (XP) and Gou Pi (GP) papers as used in this research

No	Sample	Date (m/y)	Paper mill	Size (cm)	Grade	Raw materials (Tsai and Van der Reyden 1997)
1	XP1	09/2011	Hong Xing	138 × 68	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
2	XP2	03/2018	Wang Liu Ji	138 × 68	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
3	XP3	05/2018	Wang Liu Ji	138 × 68	Pure	50–60% blue sandalwood bark, 50–60% rice straw
4	XP4	06/2018	Wang Liu Ji	138 × 68	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
5	XP5	06/2014	Hong Xing	138 × 68	Extra-pure	80% blue sandalwood bark, 20% rice straw
6	XP6	1989	Xiao Ling	138 × 68	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
7	XP7	08/2018	Xiao Ling	153 × 84	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
8	XP8	08/2018	Xiao Ling	153 × 84	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
9	XP9	07/2018	Xiao Ling	180 × 97	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
10	XP10	07/2018	Xiao Ling	248 × 129	Cotton-like	20–30% blue sandalwood bark, 70–80% rice straw
11	GP1	07/2018	Xiao Ling	248 × 129	NXP	Mixture of paper mulberry and rice straw
12	No.12	~1940–1950	N/A	N/A	N/A	N/A
13	GP2	06/2018	Xiao Ling	138 × 68	NXP	Paper mulberry
14	XP11	1989	Xiao Ling	138 × 68	Pure	50–60% blue sandalwood bark, 50–60% rice straw
15	GP3	12/2012	Hong Xing	180 × 97	NXP	Mixture of paper mulberry and straw
16	XP12	04/2009	Hong Xing	180 × 97	Extra-pure	80% blue sandalwood bark, 20% rice straw

The product information card of paper No. 12 was lost, and its date of approximate age was estimated by the conservators. All sheets are single-layered. NXP represents 'not Xuan paper'

Water and ash contents

All samples were put into crucibles and placed in a muffle furnace (Aurodent, Celje) to dry, for 3 h at 105 °C to determine water content (%). According to the standard (ISO 2144 2015), after incineration at 900 °C for 1 h, the residue weight represents the ash content (%). Triplicate determinations were carried out, with the average coefficients of variation (CV) for water and ash content being 2.7% and 5.2%, respectively.

Alkaline reserve

Following the standard ASTM D4988-96 (2006), 0.5 g of a sample and 10 mL of standardized 0.1 M HCl (prepared from 37% HCl, Sigma Aldrich, Dorset) were mixed in preparation for titration with standardized 0.1 M NaOH (Sigma Aldrich, Dorset), where methyl red (Sigma Aldrich, Dorset) was used as indicator. The carbonate content of paper was calculated in % of dry paper weight. Each sample was analysed twice, with the typical CV being 4.3%.

pH

The standard cold extraction procedure (TAPPI T 509 om-11 2011) was applied to measure pH, modified to reduce sample size (Strlič et al. 2004). 1.0 ± 0.1 mg of a sample was extracted in 100 µL of deionised water (Millipore, Molsheim) and soaked overnight. A Mettler Toledo SevenGo pro™ pH/Ion Meter (Mettler Toledo, Columbus) with a micro-combined glass electrode (Mettler Toledo Inlab® Micro 51343160, Columbus) were used to perform the measurements. Triplicate measurements were carried out, with the average uncertainty at 0.1 pH unit.

Degree of polymerisation (DP)

On the basis of the standard (ISO 5351 2010), intrinsic viscosity of samples was determined. A sample,~20–30 mg, was dissolved in 10 mL of deionised water (Millipore, Molsheim) mixed with 10 mL of CED solution (1 M, Merck, Darmstadt). The amounts of cellulose were corrected according to individual contents of water and ash. At least three repeated measurements were performed to calculate the average flow time for an individual sample. The

limiting viscosity number was calculated using the Wetzel-Elliot-Martin equation and DP was calculated using the Mark-Houwink-Sakurada equation: $DP^{0.85} = 1.1[\eta]$. Triplicate determinations were conducted per paper sample to obtain the uncertainty ($< 2\%$). This low uncertainty is not dissimilar to that of Whatman No. 1 filter paper (Maidstone, Kent), which was confirmed to be $< 1\%$ (n=5) (Strlič and Kolar 2005), indicating high homogeneity of the samples.

X-ray fluorescence (XRF)

The sample set was examined using a handheld portable XRF spectrometer (Olympus Delta Premium, Tokyo), with X-rays generated in an air-cooled Mo-tube and an acceleration voltage of maximum 50 kV. All the measurements were performed with a total acquisition time of 200 s. The "mining plus" mode with calibration using Cal Check Coupon (Innovative XRF Technologies, Woburn) was used to obtain elemental contents (in weight percent) and corresponding instrumental errors (light elements of atomic number < 12 cannot be detected). Four layers of a sample were used in a measurement, and three spots were randomly measured for each paper sample. The results were averaged, with the relative uncertainties of measurements for elements of interest per paper sheet at 3.0% for Ca, 6.0% for Si, 2.3% for Cl, 3.9% for Fe.

Accelerated degradation

Thermal degradation experiments were carried out using a Vötsch Climate chamber (model VC0018, Balingen-Frommern) at 2 sets of environmental conditions: 90 °C and 30% RH for 10, 20, 30 and 40 days and 60 °C and 70% RH for 28, 56, 84 and 112 days. Four paper samples were selected for these experiments: three grades of Xuan paper (XP3, XP5 and XP10) and 1 Gou Pi paper (GP1).

Photodegradation experiments were carried out using Suntest CPS+(Atlas, Linsengericht) for 20 and 40 h for two cotton-like Xuan papers, XP1 and XP10. Since all the filters were removed during the irradiation, the samples were exposed to the entire light spectrum emitted by the xenon bulb (185–2000 nm) without temperature and relative humidity control. The degraded samples were stored at room conditions (20 ± 1 °C, $50 \pm 10\%$ RH) in the darkness for 1 day before any measurements, and no further pre-treatment was carried out. Due to good homogeneity of all samples, only one DP data point per paper sheet was measured after degradation.

Colorimetry

The CIE $L^*a^*b^*$ colour space (Mclaren 1976) enables colour quantification using the L^*, a^*, b^* coordinates referring to lightness from black (0) to white (100), green (−) to red (+) and blue (−) to yellow (+), respectively. Before the spectrodensitometer (X-rite 500, Grand Rapids) was used, calibration was conducted using the white standard (spectrodensitometer accessory), and the instrument accuracy was assessed using a standard colour checker (X-rite, Grand Rapids). Measurements were taken on ten random spots using four layers of each paper sample using the CIE D65 standard illuminant and 10° observer (ISO 5631-2 2015), with average measurement uncertainties of L^*, a^*, b^* at 0.3, 0.1 and 0.2 unit, respectively.

Results and discussion

Fibre analysis

Fibre furnish plays an essential role in water absorbance of Xuan paper: Wu et al. (2016) show that higher amounts of blue-sandalwood fibres lead to a decreased contact angle. Cross-sectional images and images taken by SEM and atomic force microscopy (AFM) of extra-pure Xuan paper show a densely overlapping fibre web, and voids and pores on fibre surfaces, leading to better ink dispersion laterally and longitudinally (Tang and Smith 2013; Wu et al. 2016). Prior to fibre identification of sample No.12 without fibre identification data, the fibre furnish of three reference papers was determined: GP1, GP2 and XP12. Using routine fibre furnish techniques, fibres of paper mulberry are dyed reddish, are long and thin with even, fine cross-markings (Ilvessalo-Pfäffli 1995), as shown in GP1 and GP2, Fig. 1. The membrane enveloping paper mulberry fibres is another characteristic feature (Ilvessalo-Pfäffli 1995; Helman-Ważny 2014). This membrane can become separated as a ribbon-like structure or torn and washed off during papermaking. It was

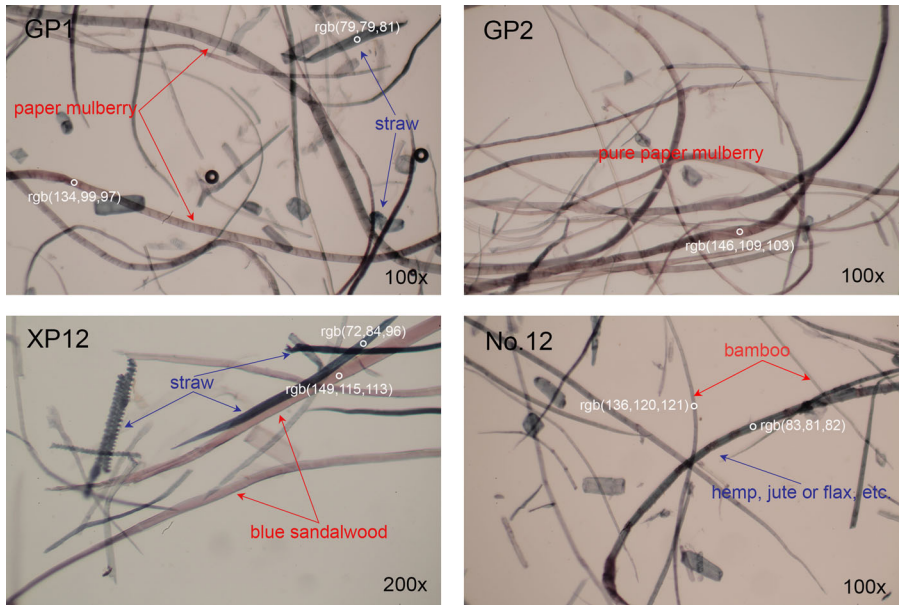

Fig. 1 Fibre morphology of GP1 (100×), GP2 (100×), XP12 (200×) and No. 12 (100×), in which GP1 (mixture of paper mulberry and rice straw), GP2 (pure paper mulberry) and XP12 (mixture of blue sandalwood and rice straw) were used as reference papers for fibre identification of No.12. Fibre areas within white circles were detected by colour picker to obtain corresponding RGB coordinates

rarely found in the reported examples (Helman-Ważny 2014), as well as in the Gou Pi papers in this study. Straw fibres are dyed bluish, are short and ribbon-shaped with pointed ends, associated with small bluish parenchyma cells in a barrel-like structure (GP1, Fig. 1) or epidermal cells in a sawtooth-shape (XP12, Fig. 1) (Collings and Milner 1978; Ilvessalo-Pfäffli 1995). In XP12, the elongated reddish fibres without obvious cross-markings are attributed to blue sandalwood (Ilvessalo-Pfäffli 1995). The identified fibres in the three examined papers are consistent with the corresponding product information.

The fibres in sample No.12 show different features. The long and pointed fibres are likely bamboo, while another type of fibres in slightly wider and irregularly shape with horizontal striations and cross-markings indicate hemp, flax or jute (No. 12, Fig. 1), i.e. *Ma* group fibres (麻, Má, the joint name of hemp, jute, and flax etc.) (Collings and Milner 1978; Ilvessalo-Pfäffli 1995; Han et al. 2019). Red, green, and blue (RGB) coordinates were determined by colour picker (Adobe Photoshop CC 2019) for dyed fibres of GP1, GP2, XP12 and No. 12 within the white circles in Fig. 1.

Paper properties

Material properties are of significance to fitness-for-use of paper, and were thus characterised using a number of established techniques. Ca and Si are the main elements found in all samples, as shown by the results of XRF analyses (Table 2), which is in line with previous research (Tsai and Van der Reyden 1997; Chen et al. 2003; Tang and Smith 2013; Wu et al. 2016).

A comparison between the sum of Ca and Si contents and ash content shows a good correlation for the unsized Xuan papers (Fig. 2a, R^2=0.93); however, it is Ca that has the primary role in this correlation (Fig. 2b, R^2=0.96). Previous research established that micron-sized particles containing high amount of Ca are spread evenly among the fibres of cotton-like Xuan paper (Tang and Smith 2013). Given that Si is associated with straw (Tsai and Van der Reyden 1997; Li 2018), the absence of Si in both No. 12 and GP2 suggests that straw may not have been used as a raw material, which supports the above results of fibre identification. The content of transition metals is low (e.g. Fe), while Cu could not be determined, indicating that metal-catalysed degradation is unlikely (Area and Cheradame 2011). The presence of Cl indicates chemical bleaching used in the course of paper production (Yang et al. 2018).

Table 2 Average elemental contents (%) of interest as obtained using XRF and corresponding standard deviations as determined for three analysis

No	Sample	Ca	Si	Cl	Fe
1	XP1	39.0±2.4	21.0±2.3	11.1±0.5	0.3±0.0
2	XP2	32.1±0.9	25.3±2.7	17.3±0.2	0.2±0.0
3	XP3	16.6±0.4	14.6±1.2	10.3±0.2	0.2±0.0
4	XP4	36.6±0.5	20.7±0.1	13.1±0.1	0.2±0.0
5	XP5	39.3±4.5	16.9±3.3	11.7±0.1	0.3±0.0
6	XP6	52.8±1.0	21.7±0.1	10.2±0.2	0.4±0.0
7	XP7	8.9±0.3	8.7±0.4	10.3±0.1	0.2±0.0
8	XP8	9.0±0.3	7.2±0.8	9.7±0.0	0.2±0.0
9	XP9	9.5±0.2	9.0±0.4	10.7±0.6	0.2±0.0
10	XP10	13.6±0.1	8.5±0.3	10.8±0.6	0.2±0.0
11	GP1	10.3±0.1	7.0±0.3	10.3±0.0	0.2±0.0
12	No.12	30.9±0.7	ND	26.7±0.1	0.2±0.0
13	GP2	29.5±0.9	ND	36.8±0.5	0.1±0.0
14	XP11	43.8±0.8	23.9±0.4	16.4±0.1	0.4±0.0
15	GP3	8.7±0.2	9.8±1.2	15.8±1.5	0.2±0.0
16	XP12	33.3±0.5	17.9±0.6	13.1±0.0	0.2±0.0

ND indicates content below limit of detection

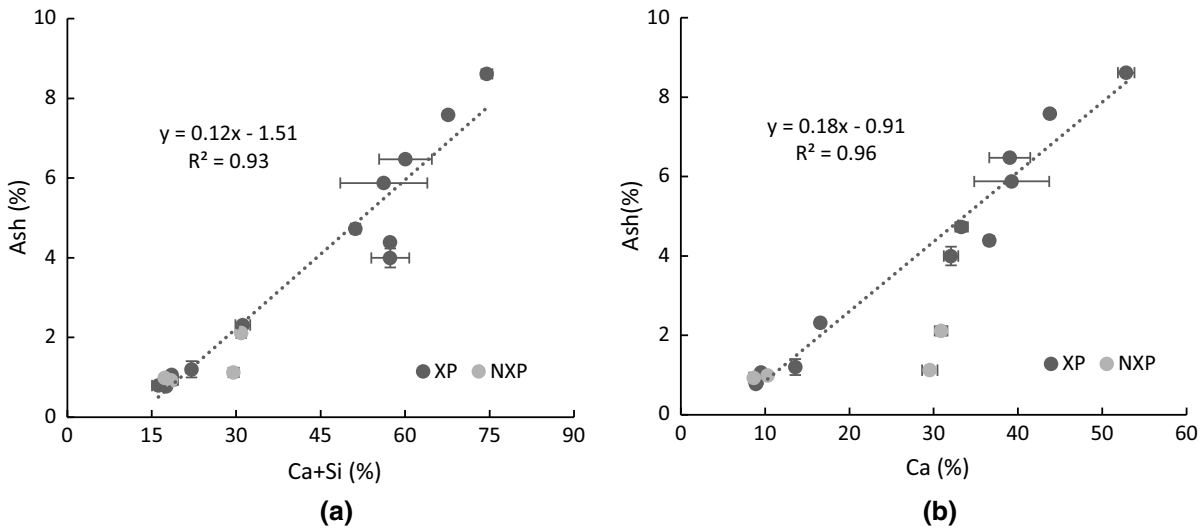

Fig. 2 Comparison between ash content and **a** sum of amounts of Ca+Si; and **b** amount of Ca only, obtained from XRF results. The dotted lines are regressed using 12 Xuan paper samples. NXP represents 'not Xuan paper'

While in our sample set, potassium is measurable in only one Gou Pi paper (GP3) at 3.4% and this element was not detected in the rest of samples, the study of Tang and Smith (2013) associated high quantities of potassium with cotton-like Xuan papers. However, their research does not indicate if the studied samples are sized "ripe" or unsized "raw" Xuan papers and it would not be surprising for potassium to be detected in $KAl(SO_4)_2$-sized papers. As GP3 does not contain Al, we cannot conclude that it was sized.

Table 3 Selected material properties of the sample set. All of the papers are starch-free and none gave a significant reaction to phloroglucinol test

No	Sample	Fibre identification	AR (wt%)	Water (%)	Ash (%)	pH	DP
1	XP1	Blue sandalwood and straw	4.79±0.02	4.25±0.05	6.47±0.05	7.9±0.1	2040±30
2	XP2	Blue sandalwood and straw	1.96±0.03	3.76±0.06	4.00±0.24	7.8±0.0	2040±20
3	XP3	Blue sandalwood and straw	0.89±0.09	3.85±0.09	2.31±0.04	8.0±0.0	1400±20
4	XP4	Blue sandalwood and straw	2.50±0.00	3.74±0.18	4.39±0.07	7.8±0.0	1680±20
5	XP5	Blue sandalwood and straw	4.95±0.02	3.80±0.13	5.88±0.06	7.7±0.0	1530±10
6	XP6	Blue sandalwood and straw	4.71±0.03	3.65±0.08	8.61±0.08	7.8±0.1	830±10
7	XP7	Blue sandalwood and straw	0.19±0.07	4.10±0.08	0.78±0.05	7.7±0.0	1810±10
8	XP8	Blue sandalwood and straw	0.20±0.00	4.33±0.10	0.79±0.08	7.3±0.1	1830±15
9	XP9	Blue sandalwood and straw	0.24±0.11	3.97±0.20	1.06±0.06	6.8±0.1	1600±15
10	XP10	Blue sandalwood and straw	0.12±0.03	3.76±0.06	1.20±0.20	6.5±0.1	1930±25
11	GP1	Paper mulberry and straw	0.10±0.01	4.56±0.14	0.99±0.09	6.4±0.1	1950±20
12	No.12	Bamboo and *Ma* group	2.13±0.09	4.55±0.24	2.11±0.12	7.4±0.1	2090±30
13	GP2	Pure paper mulberry	0.22±0.02	4.51±0.09	1.12±0.04	6.5±0.1	2560±15
14	XP11	Blue sandalwood and straw	2.45±0.04	3.78±0.04	7.59±0.08	7.4±0.1	800±10
15	GP3	Paper mulberry and straw	0.36±0.05	4.31±0.14	0.93±0.13	6.8±0.1	1140±10
16	XP12	Blue sandalwood and straw	2.75±0.07	4.01±0.12	4.73±0.04	7.9±0.1	1420±10

All the measurements were carried out in triplicate except alkaline reserve, which was carried out in duplicate. The results are presented with standard deviations. AR represents alkaline reserve calculated as wt% of $CaCO_3$

From the data in Table 3, a significant variation in alkaline reserve can be observed, ranging from 0.10% to 4.91%. While the permanent paper standard ANSI/NISO Z39.48-1992 (R2009) states the necessary amount of alkaline reserve as 2% $CaCO_3$, higher alkaline reserves generally represent better acid-resistance ability (Strlič and Kolar 2005). Although in our sample set, five contemporary unsized Xuan papers and three Gou Pi papers do not reach the permanent paper standard, this may not be a significant issue as e.g. European rag papers with 0.5% alkaline reserve (Strlič and Kolar 2005) have survived conservation planning horizons of 500 years or more. As shown in Fig. 3a, the alkaline reserve is significantly correlated with the content of Ca (R^2= 0.80), indicating that most of the alkaline reserve in Xuan papers is in the form of $CaCO_3$. Ca is likely introduced into paper due to the use of lime and surface water in the process of papermaking or chemical bleaching (Tsai and Van der Reyden 1997; Li 2018).

Most papers are approximately neutral, the average pH being 7.3, which is consistent with the reported pH of Xuan paper (Chen et al. 2002; 2003; Yeh and Munn 2005). The papers are homogeneous, as testified by the small measurement uncertainties (Table 3). Given the absence of transition metals, the approximately neutral pH and the available alkaline reserve, it is possible that unsized Xuan paper degrades slowly compared to sized Xuan paper. The curve describing the dependence of pH on alkaline reserve levels off at pH 8 (Fig. 3b), which is close to the pH of a saturated $CaCO_3$ solution (Strlič and Kolar 2005).

As evident from the data in Table 3, DP varies from ~800 to ~2000. Two observations are worth stressing: (1) the homogeneity of the papers is significant as the DP within a sheet of paper varies only 1% on average; and (2) the DP is generally and for some samples significantly lower than the DP of contemporary western papers with average DP > 2000 (Stephens et al. 2008). While the low starting DP is undoubtedly the consequence of material processing, two papers with particularly low DP of ~800 stand out, XP6 and XP11. This cannot be the consequence of raw materials use as the rest of the sample set contain similar fibres, and neither can it be related to natural degradation during dark storage:

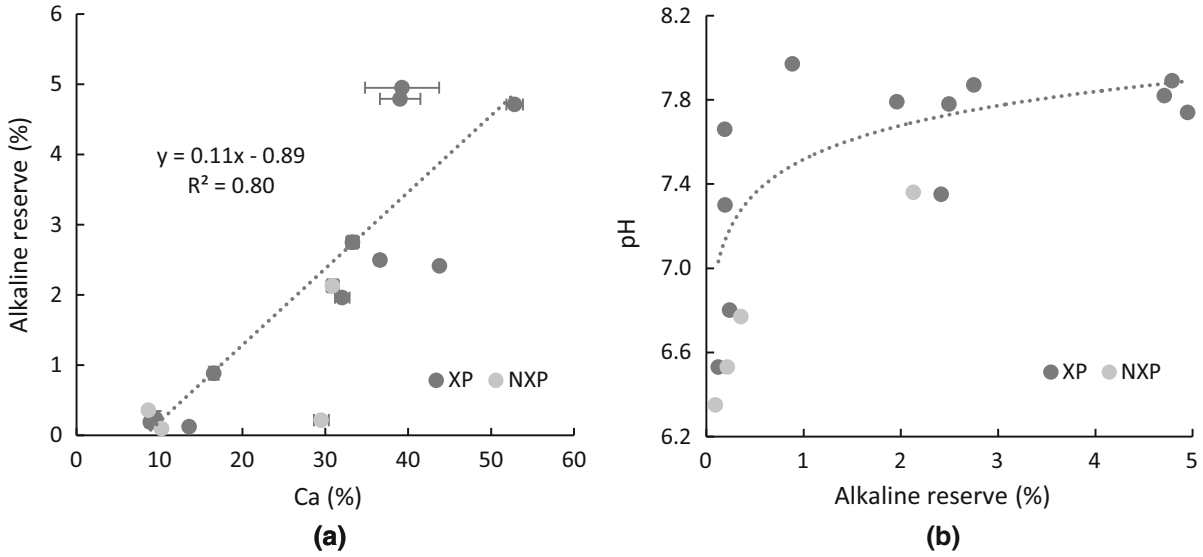

Fig. 3 Comparisons of the alkaline reserve with **a** Ca content and **b** pH of the papers in the sample set. The dotted lines are regressed using 12 Xuan paper samples. NXP represents 'not Xuan paper'

using the dose–response function for paper (Strlič et al. 2015), it can be calculated that a paper with pH 7 and starting DP of 2000 would take ~ 400 years to degrade to DP 800 at room conditions (20 °C, RH 50%). Having the traditional production process in mind, we hypothesise that the two highly degraded cotton-like Xuan papers, i.e. XP6 and XP11, were degraded in the process of sun bleaching. We therefore explored the stability of a selection of samples during photodegradation to see its rapid loss of DP could occur as a consequence.

Accelerated degradation

Photo degradation

As mentioned in the Introduction, it has long been the belief of Chinese artists and curators that extra-pure Xuan paper is a particularly durable type of paper (Tsai and Van der Reyden 1997; Tang and Smith 2013; Wu et al. 2016). While mechanical properties could be used to explore this claim, their measurements are often associated with significant uncertainties (Yeh and Munn 2005; Lichtblau et al. 2008; Brown et al. 2017), therefore, measurements of DP were used instead, as is customary in degradation experiments (Zou et al. 1996a; Strlič and Kolar 2005; Liu et al. 2017; Coppola et al. 2018).

Two recently produced cotton-like Xuan papers with high DP, i.e. XP1 and XP10 were photodegraded using a xenon light source with UV included in order to imitate photodegradation under sunlight. During the 40-h experiment, the DP decreased by 51% (XP1, DP decrease from 2040 to 1010) and 44% (XP10, DP decrease from 1930 to 1090), demonstrating the potentially severely damaging effects of sun-bleaching during traditional production of Xuan paper.

Given that papers were exposed to far UV region, photolysis in the presence of oxygen could lead to photooxidation (Launer and Wilson 1949). UVA-induced degradation of cotton-like Xuan papers was previously shown to generate hydrogen peroxide (H_2O_2) and superoxide radical ions ($O_2^{\cdot-}$) (Tang and Smith 2013), which are known to play a significant role in cellulose oxidative degradation (Kočar et al. 2002, 2005). Both direct photolysis and photooxidation might lead to increased lightness and decreased b^* in the two Xuan papers (Fig. 4a, b); although error bars in Fig. 4b are substantial, a trend towards higher brightness is observed during the experiment. This corroborates previous findings that paper without optical brighteners, such as the unsized Xuan papers in this study, tend to become brighter when exposed to daylight (Pastorelli et al. 2019). The low observed DPs of several Xuan papers in addition to XP1 and

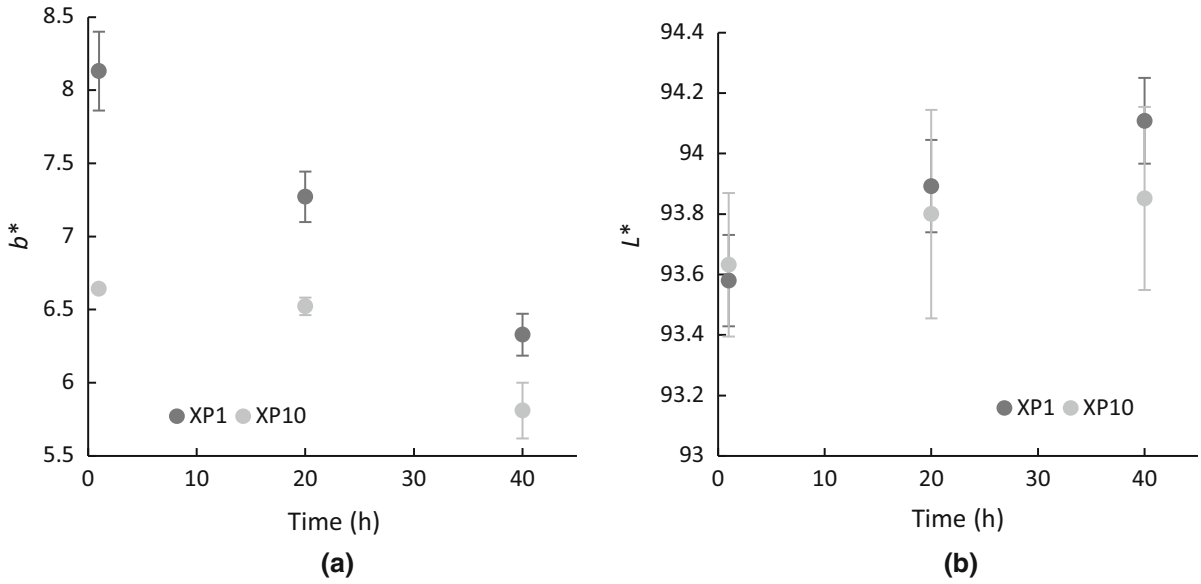

Fig. 4 The colour coordinate b^* (**a**) and L^* (**b**) of XP1 and XP10 during the 40-h photodegradation experiment

XP10 suggest that sun bleaching may not have been entirely replaced by chemical bleaching in the twentieth century.

Thermal degradation

In order to explore whether the dose–response function as developed for western paper can be applied to Xuan papers as well, two accelerated thermal degradation experiments were carried out at 90 °C, 30% RH and 60 °C, 70% RH. A selection of three Xuan papers (extra pure: XP5, pure: XP3, and cotton-like: XP10) and one Gou Pi paper (GP1) were used to investigate their degradation and explore the above claim of exceptional durability.

The data in Table 4 demonstrates that the generally accepted Ekenstam equation (Zou et al. 1996a; Area and Cheradame 2011) can be used to describe the kinetics of degradation of the selected papers, as proper linear regressions of Δ(1/DP) against time can be established at both combinations of degradation conditions. Sample XP5 (extra-pure Xuan paper) seems to have the lowest rate of degradation followed by XP3 (pure) and XP10 (cotton-like), however, sample GP1 has similar properties.

The Xuan paper follows the same principles of degradation as western paper is demonstrated in Fig. 5, where the rates of degradation of the four paper samples are overlaid on the plot as published in Strlič et al. (2015). This proves that the rate of Xuan paper degradation principally depends on pH, T and RH, as is the case for many other cellulosic fibrous materials e.g. textiles (Oriola et al. 2015).

Table 4 Changes in 1/DP over time (day^{-1}) and the corresponding linear regression data describing the degradation of four papers: XP3 (pure Xuan paper), XP5 (extra-pure Xuan paper), XP10 (cotton-like Xuan paper), and GP1 (paper-mulberry paper)

Condition		XP3	XP5	XP10	GP1
90 °C, 30% RH	$k_{1/DP} \times 10^{-6}$ (day^{-1})	10.1	5.5	7.3	6.3
	R^2	0.97	0.98	0.99	0.95
60 oC, 70% RH	$k_{1/DP} \times 10^{-6}$ (day^{-1})	1.0	0.2	1.6	0.8
	R^2	0.94	0.96	0.9	0.94

k represents the corresponding rate constant

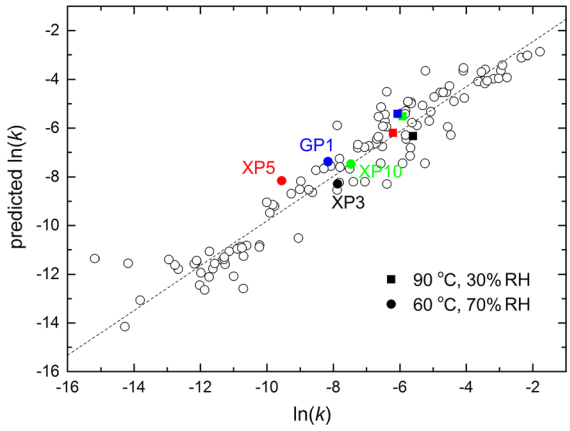

Fig. 5 Comparison of ln(k), where k is in year^{-1}, measured in this study and those predicted by the 'Collection Demography' model (the fitted dashed line) established using European papers (hollow symbols) (Strlič et al. 2015). The solid circles and squares are associated with the two sets of degradation conditions as indicated. The degradation rates for the four tests are superimposed, i.e. XP5 (extra-pure Xuan paper), GP1 (paper-mulberry paper), XP3 (pure Xuan paper) and XP10 (cotton-like Xuan paper)

From the data in Table 4, it could be concluded that fibre composition might also play a role, as samples with a higher proportion of blue sandalwood (e.g. XP5) exhibit lower rates of degradation than samples with low amounts of these fibres (e.g. XP10). However, based on the limited sample set such a conclusion would be premature and further research needs to be carried out using more extensive sample sets to separate out the effect of sample pH, which is known to have a dominant effect on the degradation rate.

These results demonstrate that the degradation of raw (unsized) Xuan paper can be conveniently described using the same dose–response function as has been developed for European paper meaning that its degradation behaviour is similar. Given that the pH of the sample papers is mostly neutral to slightly alkaline, and that the content of transition metals is low, the observed rates of degradation are low, compared to samples of the same age but are acidic sized e.g. sized Xuan paper (Xu 2008) or papers with a high content of iron (Liu et al. 2017). Therefore, the low starting DP of most Xuan papers must be associated with the processing methods used during papermaking and we hypothesize that sunlight-induced bleaching could be the cause of extensive degradation of the most degraded samples in the test set. However, this would need to be experimentally verified in the future.

Conclusions

Following extensive characterisation and degradation experiments, material properties and stability of contemporary unsized Xuan and closely related non-Xuan papers were established using a representative sample set of 16 papers. The following conclusions can be reached:

- While blue sandalwood and rice straw are the main raw materials of contemporary unsized Xuan papers, paper mulberry, bamboo and bast fibres were identified in imitation Xuan papers.
- Elemental analysis using XRF has shown that Ca and Si are dominant and that Ca is mainly associated with both ash content and alkaline reserve. Transition metals were not present in significant quantities indicating that metal-catalysed oxidation is not a significant degradation pathway.
- Most contemporary unsized Xuan papers are neutral or mildly alkaline and contain significant alkaline reserves, which indicates suitable degradation stability. The papers are highly homogenous with average uncertainty of DP determination of 1%, although generally, the starting DP of most papers is low, which could indicate that some of the current papermaking practices may be the cause. Based on photodegradation experiments it can be hypothesised that the two cotton-like Xuan papers exhibiting significantly low DP have been sun-bleached.
- In the context of the sample set used in this research, the applicability of Ekenstam equation was validated based on changes in DP during thermal degradation, and degradation rates were calculated. In addition, the degradation rates of the studied Xuan and Gou Pi papers can be described using the 'Collection Demography' model used to describe European paper degradation, meaning that the general paper degradation principles apply to Xuan papers as well.

Given the popularity of Xuan paper in Chinese paper conservation practice, the results demonstrate that from the material point of view unsized Xuan

paper have similar properties to other types of papers. Although its starting DP can be low, it is usually neutral to mildly alkaline, contains no appreciable amounts of transition metals and has a proper alkaline reserve, and models predict long lifetimes during dark storage. We can thus confirm that the paper is deserving of its reputation as the "paper king lasting over a thousand years" (cf. Introduction). Our research also indicates that for preventive conservation management of unsized Xuan paper-based artefacts, the existing degradation models can be used. However, since in Chinese paper conservation practice Xuan paper is often used with liberal amounts of starch, our future research focuses specifically on the effect of starch on the overall stability of the resulting composite material.

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