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Shine a light on papyrus: monitoring the aging process

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Abstract

The aging behavior of ancient papyri is not entirely understood, although such understanding is crucial for tailored conservation concepts to preserve these precious historical documents for the millennia to come. In a study on accelerated aging, the effect of light on papyrus sheets was studied, and the consequences were monitored by a combination of non-invasive and invasive techniques. Papyrus sheets were aged for two months at 90 °C and 50% relative humidity, with and without the influence of light. Changes at the optical, mechanical, and molecular levels were monitored using CIELAB color measurements, tensile tests, Fourier transform-infrared spectroscopy (FTIR), and size exclusion chromatography—multi angle light scattering (SEC-MALS). Light exposure has severe consequences for the optical and mechanical properties of papyri, reflected by a strong decrease in cellulose chain length and tensile strength. SEC-MALS proved to be the best method to assess the conservation status of papyri due to its clear results and low sample demand. This publication seeks to highlight the effects of light-induced degradation of papyri and to facilitate an understanding of the underlying aging mechanisms, to support in future conservation measures.

Keywords: Papyrus, *Cyperus papyrus* L., Light aging, Conservation science, Restoration, Conservation, SEC-MALS, Tensile test, Method comparison, Light-induced degradation, CIELAB, FTIR

Graphical Abstract

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Introduction

Papyri are among the earliest sources of writing in history [1], displaying invaluable insights into ancient medicine, astronomy, religion, and daily life, especially

regarding ancient Egypt, Greece, and the entire Mediterranean world [2–4]. Therefore, the conservation of these objects is most important for preserving the contained knowledge for many generations to come.

To find the most suitable, tailored conservation treatments, it is necessary to have extensive information on the material characteristics of papyri and their aging behavior. Ancient papyri often appear to be in quite brittle conditions nowadays, having suffered especially from insects, microbial attacks as well as climatic changes with variations in humidity, temperature, light exposure, and general pollution [5, 6]. Those papyri that survived until the present day experienced mostly slow decay processes over centuries and millennia in dark and dry surroundings, being buried in tombs or just in the sand. After excavation, some papyri were presented to the interested public, adding light as factor influencing the deterioration, and stored in magazines around the world, sometimes at higher humidity levels than those of the Egyptian desert, due to different climatic conditions at the locations of the collections and owing to the common practice to store papyri in one room with other objects that require higher humidity levels as, for example, parchment or historic papers [7].

In this study, the aging process of papyri is modeled through accelerated aging at 90 °C and 50% relative humidity (RH) to investigate the effect of light irradiation on papyri and to allow for comparison of the observed phenomena to previous studies [5, 8–10]. These two parameters were chosen to model decay processes of papyri with an emphasis on degradation phenomena occurring after excavation, i.e., the part of natural aging that cannot be entirely avoided but minimized through the choice of suitable storage and presentation parameters (light, heat, and humidity) at magazines and exhibitions. Higher temperatures accelerate the degradation processes which occur naturally, but more slowly, in lignocellulosic material under ambient temperature conditions [11]; 90 °C was chosen to enable the comparison of our results to a significant recent study on the aging of papyri [8]. While natural aging in the Egyptian desert occurred mainly under dry conditions, the comparably high value of 50% RH was chosen to mimic actual storage conditions of papyri in magazines nowadays. While 35% RH was suggested as ideal humidity for the storage of ancient papyri [12], the actual humidity in magazines is often maintained at higher levels, especially if historic paper, parchment and papyri are stored together [7, 12]. Additionally to the influence of temperature and humidity, consequence assessment of irradiation on papyri is essential when the understandable desire of the public to display ancient papyri in museums is considered. The focus on the influence of light is accounted for by two sample sets, one irradiated by a xenon lamp at 1 W/m^2 and one kept in darkness, for a direct comparison. The samples were artificially aged for up to two months. In this way we were able to evaluate the results in the context of previous studies, that used similar time spans [5, 8, 9].

Apart from studying the effects of this accelerated aging treatment and providing extensive material characterization of papyri, the second focus of this study was to provide a comprehensive overview of the methods applicable to analyze these changes in the material. This is of special importance, since there are some accelerated aging studies of papyri in the literature, but with a focus on distinctly different analytical techniques, aging parameters, and even sample material. To give an idea, McGovern [13] focused on tensile properties by determining the folding endurance of papyrus sheets after 72 h at 105 °C. Flieder et al. [5] studied the influence of light, temperature, and humidity but did not apply variations of these parameters in combination. They assessed the results by pH measurements, degree of whiteness, copper number, and zero-span tensile tests. These results are compared to ours and discussed in detail in the Results section. In a recent publication Łojewska et al. [8] used infrared (IR), UV/Vis-spectroscopy, and size exclusion chromatography (SEC) to study the aging behavior of papyri, employing paper as a model substrate for the accelerated aging study. They attempted to choose a model substrate with properties similar to papyri, especially regarding the lignin content. So they chose lignin-rich groundwood paper with respect to a literature source [14], that reported up to double the amount of lignin in papyrus sheets than actually present [15], thereby compromising the suitability of this paper as ideal reference material to study the aging effects of papyri. Apart from that, paper has by design mechanical properties different from papyri, since papyri have a bidirectional orientation, owing to their production in two layers that are pressed together at a 90° angle, whereas the fibers in paper are randomly oriented through pulping and mechanical disintegrating processes in paper production.

Elnaggar et al. assessed the viability of laser cleaning of soiled papyri after accelerated aging for 28 days at 70 °C and 50% RH. Effects of the aging treatment were evaluated using colorimetric measurements, viscometric measurements to determine the degree of polymerization (DP) of the samples, FTIR and SEM–EDX [10].

For the material characterization of ancient and modern papyri, invasive and non-invasive methods should be differentiated, and non-invasive techniques preferred whenever possible, especially if ancient samples are analyzed. Among the techniques with no or minimal sample consumption, spectroscopic techniques (Raman,

Fluorescence, Infrared and UV/Vis) and techniques to study the elemental composition (XRF, SEM–EDX, PIXE) have been commonly applied [8, 16–18]. Techniques that elucidate the elemental composition have proven to be especially useful in the analysis of ancient inks, to distinguish iron-gall inks from carbon inks and to detect trace elements indicative of the archaeological context of the sample [19, 20]. These techniques are less powerful if only the organic writing-ground is analyzed, which is the focus of this study.

Analysis of the organic components of papyri has focused on viscometry and size exclusion chromatography-multi-angle light scattering (SEC-MALS) to determine the chain length of the main constituent, the cellulose [8–10]. To study further properties of cellulose, as for instance the crystallinity, X-ray diffraction and nuclear magnetic resonance spectroscopy (NMR) measurements have been conducted [8, 9]. The monosaccharide composition of hemicelluloses and pectic polysaccharides in *Cyperus papyrus* L. pith has been characterized by different chromatographic methods, applied after hydrolysis [21, 22]. The composition of lignin in ancient papyri and *Cyperus papyrus* L. stems has recently been investigated in detail using NMR and chromatographic methods, such as pyrolysis—gas chromatography/mass spectrometry and degradation followed by reductive cleavage (DFRC) [23–26]. The lignin content of modern and ancient papyri has been analyzed using gravimetric methods, acetyl bromide soluble lignin (ABSL) and thermogravimetric analysis (TGA) [14, 23, 27]. Among these three methods, TGA frequently led to an overestimation of the lignin content, while ABSL is to be preferred over gravimetric Klason lignin analysis in the analysis of historic materials, due to the lower sample requirement of the ABSL method [15].

To choose the most suitable analytical technique to study the aging characteristics of papyri, we referred to the publication of Łojewska et al., who rated the discriminatory power of methods applied in their study as SEC > FS > FTIR > Raman > XRD [8]. In an extensive study to develop dose–response functions for the degradation of historic papers, Pastorelli et al. chose to use viscometric measurements representing cellulose degradation and CIELAB color measurements as most suitable methods to determine a variety of factors influencing paper aging [28]. To obtain profiles of the entire cellulose chains and to study oxidation features along the (hemi-) cellulose chains, we chose SEC-MALS combined with fluorescence markers for carboxyl groups.

To summarize, this study models the degradation process of papyri by accelerated aging, applying 90 °C for two months, with a special focus on the additional effects of strong light irradiation. Since the majority of ancient papyrus objects in Western collections are stored between glass slides, the papyrus samples analyzed in this study were subjected to accelerated aging between glass slides as well. The results are analyzed regarding changes in optical properties (CIELAB measurements and degree of whiteness), mechanical properties (tensile tests), and changes on the molecular level (FTIR spectroscopy and SEC-MALS). For the first time, labeling of the carboxyl groups in papyri, using the 9H-fluoren-2-yl-diazomethane (FDAM) procedure, was performed to monitor oxidative changes. The results were thoroughly compared to the literature, including an in-depth discussion of which methods are beneficial and meaningful for assessing the degradation state of papyri.

Materials and methods

Materials

Unwritten commercial papyrus rolls were purchased from pgi-versand.de (Volkach, Germany).

To account for differences regarding optical changes during the aging treatment between the deliberately yellowed commercial papyri and papyri that did not experience such a color-changing treatment, CIELAB measurements were conducted on native papyrus pith as well, aged under the same conditions. Therefore, stripes of *Cyperus papyrus* L. pith were purchased directly from the farmers at Qaramos, Sharqia Province, Egypt. For the aging tests, the rind was removed using a ceramic knife and slices of dry papyrus pith mounted between glass slides, as it was done in the case of commercial papyrus sheets.

Whatman filter paper No.1 was obtained from Merck KGaA, Darmstadt, Germany and used to determine the aging effects on lignin-free cotton linters paper regarding optical and mechanical changes, for comparison. Whatman paper has been frequently used in aging studies in the literature.

For SEC-MALS analysis, DMAc, LiCl and HCl were obtained at the highest purity available from Sigma-Aldrich, Steinheim, Germany. 9*H*-Fluoren-2-yl-diazomethane (FDAM) for labeling of carboxyl functionalities along cellulose chains was synthesized in our laboratory [29].

Accelerated aging

Light/dark comparison

To study the influence of sunlight, an accelerated aging test was conducted using a Q-SUN Xe-3 test chamber by Q-Lab Deutschland GmbH, Saarbrücken, Germany. Instrument parameters were 90 °C black panel temperature, 55 °C air temperature, and 50% relative humidity (RH). Half of the samples were exposed to light (1 W/m^2), the measured light output at the sample surface

underneath the microscopic slides was on average slightly smaller, 0.98 W/m^2. The samples were aged up to 57 days. The samples were mounted in between two microscope slides to avoid convolving. The transmission spectrum of the slides between 200 and 700 nm is shown in Additional file 1: Fig. S1.

Color measurements (CIELAB color space)

Color measurements were performed on a PCE-CSM 8 spectrometer (PCE Instruments, Meschede, Germany) between 400 and 700 nm as described by Jaxel et al. [30], with a measuring aperture of 8 mm and a 45°/0° illumination/viewing angle. Three spots were measured and averaged for each sample. For the aging studies, three different samples were prepared per time interval, and three spots were recorded on each of them. The same spots were monitored before and after the artificial aging procedure. The results were obtained as L*, a*, and b* values. Lightness, L*, is represented by values between zero and 100, a* represents the color range of green to red, and b* represents the color range between blue and yellow. Delta E is computed as Euclidean distance of the L*, a* and b* coordinates using the CIE76 color difference formula [31].

ISO-brightness

The measurements of ISO brightness were performed according to DIN ISO 2470 [32] on a U-3010 spectrophotometer (Hitachi, Tokyo, Japan). ISO brightness was determined before and after accelerated aging on the same measuring spots.

Fourier transformed infrared spectroscopy (FTIR)

The attenuated total reflection (ATR)-FTIR spectra of the aged samples were recorded on a PerkinElmer Frontier IR single-range spectrometer (PerkinElmer Inc., USA) in the wavenumber range of 4000–500 cm^{-1}. The system was composed of a diamond/ZnSe ATR-crystal and a $LiTaO_3$-detector. The resolution was 4 cm^{-1}. The spectra were baseline corrected using Spectragryph software (Spectragryph Version 1.2.8., Dr. Friedrich Menges, Germany) by setting the coarseness value of the advanced baseline correction function to 25%. The spectra were normalized to unity using the band at 1030 cm^{-1}.

The lateral order index (LOI) was determined according to a procedure for pure cellulose and softwood Kraft pulps [33–35]. The LOI is the ratio of the height of the peak around 1428 cm^{-1} and the height of the peak around 896 cm^{-1}. The height H_{1428} was calculated by drawing a baseline from the local minimum at 1490 cm^{-1} to the local minimum at 1395 cm^{-1}. The obtained baseline ordinate value at 1428 cm^{-1} was subtracted from the maximum absorption at 1428 cm^{-1}. The height H_{896} was determined in the same fashion by a baseline from the local minimum at 915 cm^{-1} to the local minimum at 870 cm^{-1}.

Tensile test

For tensile tests, the Zwick Z020 universal testing machine (Zwick/Roell, Ulm, Germany) was used. The traverse was set to 25 mm. Samples were, on average, 10 mm broad and 0.2 mm thick. Each spot of the aging test was represented by 10 measurements to compensate sample heterogeneity.

Size-exclusion chromatography

Sample dissolution and uronic acid group labeling

The samples were prepared for SEC-MALS following a modified variety of the 9H-fluoren-2-yl-diazomethane (FDAM)-labeling protocol by Bohrn et al. [29], to combine the dissolution of cellulose with group-selective fluorescence labeling of carboxyl groups. 30 mg of papyrus samples were disintegrated for 3 × 20 s in distilled water and left to swell in water overnight. The samples were washed with 0.1 M HCl, acetone, and DMAc. The samples were resuspended in 3 ml DMAc and 1 ml freshly prepared FDAM solution and agitated in a shaking bath at 40 °C for one week. The liquid was removed by suction through a filter paper, and the solid remainder was washed with DMAc, transferred to a dry vial, and agitated in 2 ml DMAc/LiCl (9% m/v) for several days. After dissolution, 0.3 ml of the sample solutions were diluted with 0.9 ml DMAc and filtered through 0.45 µm syringe filters to prepare for SEC-MALS analysis, which was conducted in duplicate.

SEC-MALS

The SEC system was coupled with MALS, refractive index (RI), and fluorescence detectors with automatic injection and four serial columns [36]. DMAc/LiCl was used as an eluant at a LiCl concentration of 0.9% (m/V). Molecular weight distribution and the related polymer-relevant parameters were calculated using the corresponding software programs, based on a refractive index increment of 0.140 mL/g for cellulose in DMAc/LiCl (0.9%, m/V). The following general SEC parameters were used: flow: 1.00 mL/min; columns: four PL gel, mixedA, ALS, 20 µm, and 7.5 × 300 mm plus precolumn; fluorescence detection: excitation: 252 nm, emission: 323 nm; injection volume: 100 µl; run time: 45 min.

Results and discussion

To get an idea of the aging processes in ancient papyri, an accelerated aging setup was chosen for modern commercial papyrus sheets at 90 °C and 50% RH—with and without the influence of light. An almost immediate

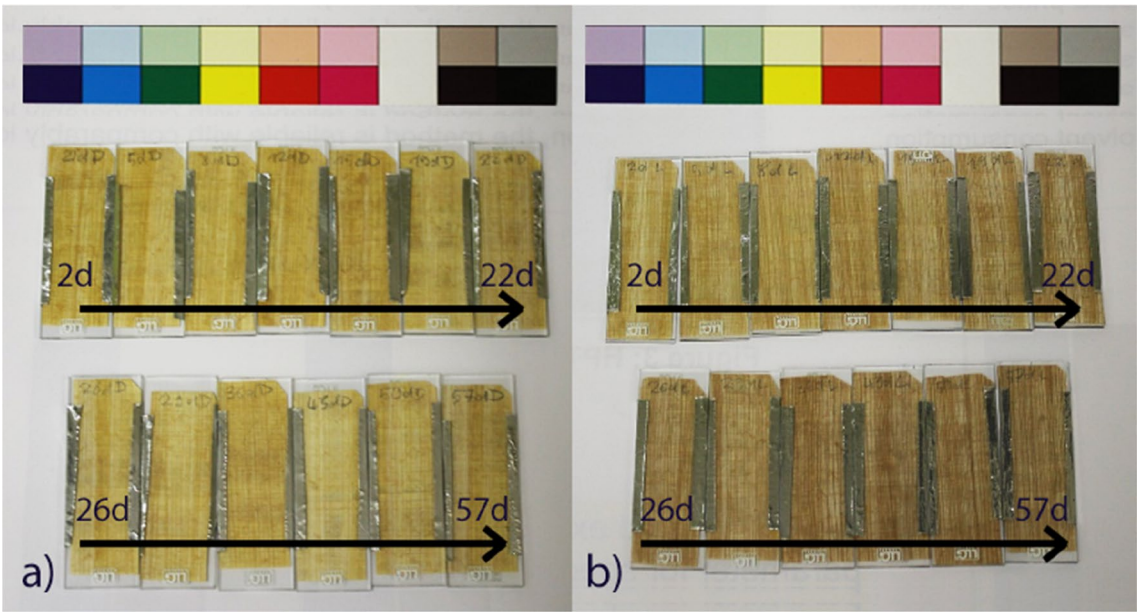

Fig. 1 Comparison of papyrus paper samples aged in the dark (**a**) and under light influence (**b**) for up to 57 days

color change was observed for the samples aged under the influence of light. Thus it was analyzed whether this color change is accompanied by a deterioration of the mechanical properties and an underlying degradation of the main load-bearing element in papyrus tissue, the cellulose chains. CIELAB, FTIR, tensile tests and SEC-MALS measurements were conducted on the aged papyri to monitor the degradation phenomena and to compare the suitability of these methods to monitor the changes.

Already after 2 days, the light-aged samples exhibited a strong color change, which increased with aging time. The samples aged in darkness did not show any significant color changes, not even after two months of aging, as shown in Fig. 1.

Color change

To quantify the color changes, CIELAB measurements were conducted. **L*** expresses the difference in lightness (zero to 100), **a*** the difference in the green–red region **b*** the difference in the blue–yellow region and **Delta E** represents the total color change. **Delta E** values above 2–3 are easily recognized by the human eye.

The color change induced by light irradiation (Fig. 2a) is seen by an increase in Delta E already after two days, then rising with time and reaching a plateau around 10–15 days at Delta E values of 12–13. A small color change is measurable for papyrus samples aged without light, reaching values around 4–5, which should be visible for the human eye but not represent a huge difference in readability of the object. Cotton linter samples showed no measurable color change, neither with nor without light influence during this time span.

The detailed nature of this color change for light-aged papyri is explained in Fig. 2b and c. The strongest factor is a decrease in yellowness over time, reaching a plateau after around 10 days. Lightness declines the same way, but to a slightly smaller extent. Already after 2 days, a small red shift was detected that stayed constant during the aging period.

Commercial papyrus sheets are deliberately yellowed, as we showed in a previous publication [37]. This process can also be watched in a recent video about modern Egyptian papyrus production [38]. To resemble today's appearance of ancient papyri, modern papyrus manufacturers use a chlorine bleaching step after a strong alkaline treatment to adjust the desired color—making it brighter—to resemble the optical appearance of ancient papyri. The alkaline treatment reduces the lignin content from around 16% in native *Cyperus papyrus* L. pith to around 5% in commercial papyrus sheets, as those used in our study [15]. While the alkaline treatment must induce some morphological changes in the papyrus structure, the remaining lignin constituents are still mainly connected via β-O-4′ alkyl-aryl ether bonds, the most common inter-unit linkage in native lignin (66% of all inter-unit linkages in commercial papyrus sheets, vs. 85% in native *Cyperus papyrus* L. pith) [24, 37]. Nevertheless, the alkaline treatment does not alter the distribution and length of cellulose chains in commercial papyri significantly [37].

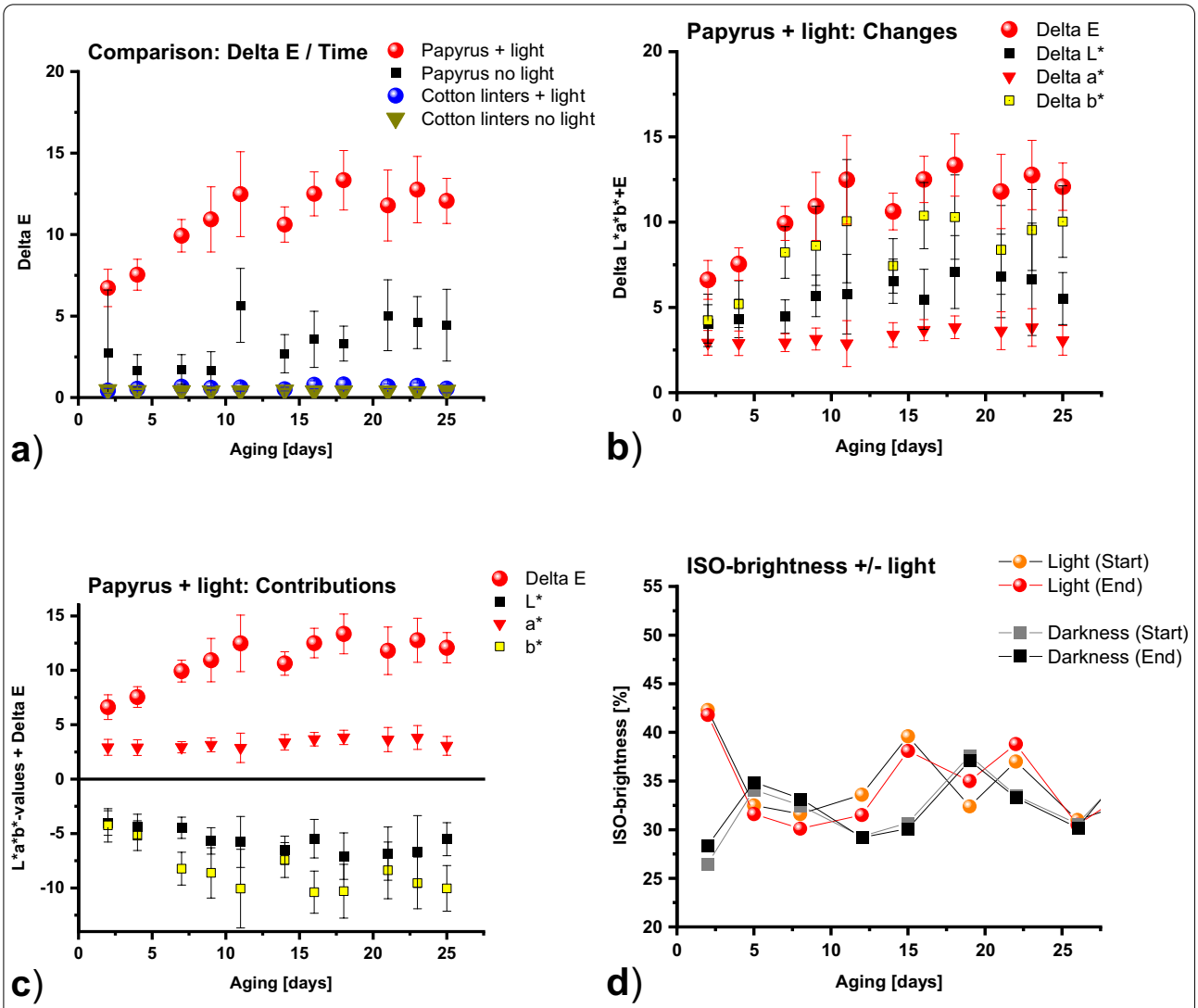

Fig. 2 CIELAB measurements of papyri and cotton linter samples aged with and without the influence of light. **a** Comparison of Delta E for papyrus and cotton linter samples aged with and without light, **b** Delta values for light-aged papyrus samples, **c** Color changes for light-aged papyrus—expressed as difference in L*, a*, and b* and Delta E for comparison, **d** ISO-brightness for papyrus samples aged with and without light influence. Error bars indicate the standard deviation of nine measurements per time step for the CIELAB measurements

The alkaline treatment involved in their production limits the suitability of commercial papyri as model samples to study the degradation patterns of ancient papyri. However, since the profile of cellulose chains is similar to untreated papyri and the general production mode resembles the traditional one—pressing *Cyperus papyrus* L. stripes into two-ply sheets in rectangular orientation without a prior disintegration step as in paper production—the analysis of commercial papyri still presents an acceptable starting point to gain insights into the degradation patterns of ancient papyri. This is especially helpful in the analysis of cellulose chains in papyri, that are otherwise difficult to directly analyze, due to solubility issues resulting from the high lignin content of native papyrus pith [15, 28].

Nevertheless, the alkaline chlorine bleach treatment strongly limits the possibility to transfer results on the yellowing behavior of commercial papyri to papyri produced according to historic descriptions, since a higher pH and bleaching-treatments have strong effects on the mechanism of color change, especially in the case of historic papers [28]. The bleaching treatment employed in modern commercial papyrus production leads to partial chlorination of the residual lignin and extractive compounds [37]. Among these chlorinated compounds, chloro-4-methylphenol, chloro-4-vinylphenol,

chloro-guaiacol, chloro-syringol, and chloro-4-vinylguaiacol were detected as chlorinated lignin monomers using pyrolysis–gas chromatography/mass spectrometry [37]. Papyrus lignin is—in its native state—strongly acylated by p-coumaric and ferulic acids [23]. Both were found to be strongly chlorinated in the commercial sheet, as detectable by combining Py-GC/MS with prior methylation (tetramethylammonium hydroxide, TMAH) to avoid thermal decarboxylation. When chlorinated phenols are irradiated by sunlight or xenon light, phenoxyl radicals are formed, which can couple to biphenyls, among other polyaromatic compounds, as shown in a study irradiating 4-chlorophenol on cellulose [39]. As there are many different chlorinated aromatic compounds in the lignin of commercial sheets, there are manifold and very complex ways for radical fragmentations, reactions, and recombinations to form a variety of chromophores absorbing at different wavelengths, thereby producing the color change observed in the CIELAB measurements.

To account for the different optical properties of papyri produced according to historic recipes, described most detailed in *Naturalis historia* by Pliny the Elder [2–4, 40], native *Cyperus papyrus* L. pith (Fig. 3a) was subjected to the same conditions of accelerated aging as the commercial papyrus sheets and the optical changes were monitored by CIELAB measurements (Fig. 3b).

The general trend of optical changes triggered by accelerated aging is similar for native pith and commercial sheets. All samples showed a slight shift toward the red region with temperature, independent of the influence of light (value a*). Lightness (L*) decreased for all samples with temperature and time. This effect was strongly enhanced by irradiation, being especially prominent for the bleached commercial sample. For native pith, a similar visual effect occurs, but to a lower extent, due to the formation of quinoid compounds from the contained lignin, as described for the photooxidation of wood [41]. This decrease in lightness is almost nonexistent when only heat and no irradiation are applied, both for native pith and commercial sheets (Fig. 3b).

The degree of whiteness measurements did not prove useful in the assessment of color changes of papyri (Fig. 2d). Although the spots of measurement were the same before and after the aging process, differences in whiteness through aging were not detectable due to the optical heterogeneity of the samples. The brightness-measurement norm "ISO 2470-1:2016 is limited in its scope to white and near-white pulps, papers, and boards" [32], which did not allow a straightforward application to yellow and brownish papyri.

To summarize, accelerated aging at high temperatures leads to a red-brown color shift of papyrus sheets. The influence of light on the optical appearance of papyri is strong and is already observable after two days. The main effect is a decrease in lightness and especially yellowness. This effect is strongly pronounced for commercial sheets, which are more yellowish from the start. The major share of light-induced browning of commercial papyri occurs within the first 10–15 days, at elevated temperatures. This indicates that facsimiles produced from commercial papyri can show a strong color change upon a short, first period of light exposure, after which only slight further darkening is to be expected. For native papyrus pith, the same mechanisms of decreased lightness and yellowness can lead to an even "whiter" appearance to the human eye within the analyzed time frame, since dry papyrus pith is significantly less yellow from the start. The perceived browning of papyrus sheets produced according

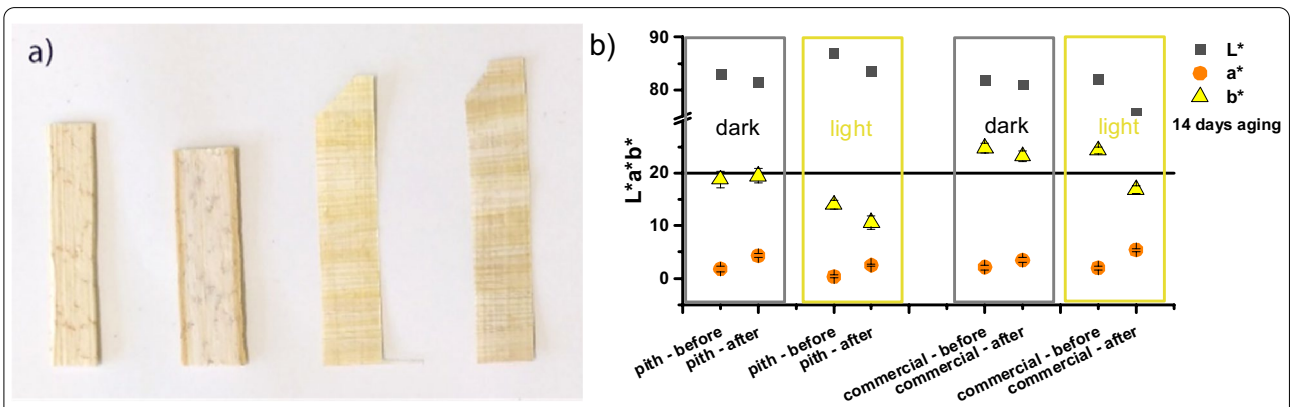

Fig. 3 **a** Papyrus samples aged for two weeks at 90 °C and 50% RH. Left side: untreated *Cyperus papyrus* L. pith from Qaramos, Egypt, aged without and with light. Right side: Commercial papyrus samples aged without and with light. **b** Comparison of CIELAB measurements for pith (left) and commercial papyrus sheets, each time before and after aging—with and without the influence of light. Error bars indicate the standard deviation of nine measurements for each time step

to historic descriptions without any deliberate yellowing step is a process that does not happen within four weeks (even under accelerated aging conditions), but over years and decades. Just to give an example regarding color changes of ancient papyri, one 1200-year-old papyrus fragment showed the CIELAB coordinates: L*: 56, a*: 7.2, b*: 21.0. This may serve just as an orientation, that the major contributing factor to the altered optical properties of ancient papyri, to the state we see today, is a strong decrease in lightness. The yellowness of this particular object is significantly below the yellowness of commercial sheets and slightly above typical values for untreated papyrus pith (Fig. 3). Based on the results shown in Fig. 3 it could be speculated that ancient papyri would appear even less yellow, if they had been exposed to light during the last millennia, which was definitely not the case for most papyri that were usually buried underground without light exposure.

Comparison of our results to literature

To our knowledge, there are two artificial aging studies in the literature addressing the effects of light on papyrus, besides one including dark aging, in a study on the feasibility of laser cleaning for papyri. El-Nahawi [42] irradiated papyri, produced according to Pliny's description for one day with a daylight lamp of 76.400 lx, to study whether Pliny's mention of "drying the fresh sheets in the sun" leads to an increase in brightness. No significant color change was observed, but a small tendency toward decreased lightness (L*) was detected by CIELAB measurements, which showed the same tendency as the results discussed above.

A more extensive accelerated aging study was carried out by Flieder et al. [5].They produced sheets from *Cyperus papyrus* L. plants cultivated at the Natural History Museum in Paris and additionally obtained white and brown sheets from Egypt. Which of these was used for artificial aging is not specified in the publication.

These papyrus sheets were aged for up to six weeks using 80 °C, 65% RH in darkness, as compared to a series irradiated by a 1500 W-Xenon lamp, 25 °C, and 50% RH. The aging behavior was studied by the degree of whiteness, pH measurements, copper number, and a zero-span tensile test. The pH decreased for all aging experiments; the copper number increased mainly for brown papyrus and slightly for light-aged white papyrus. Meaningful results for the zero-span tensile strength were not obtained due to sample heterogeneity.

Concerning the degree of whiteness, the study reported a clear decrease for heat-aged and humidity-aged white papyrus sheets. For the light-aged samples, a decrease in yellow tone after one week of aging was reported. This effect vanished during the subsequent weeks of aging, and the degree of whiteness reached the same values as for unaged papyri.

Compared to our results, the main color change observed may have been due to the combination of light and elevated temperature/humidity. Since the color change we observe for samples aged in darkness is much less severe, the elevated humidity of 65% RH (at 80 °C) may itself be a strong cause of discoloration of papyrus sheets. This is in agreement with the observations of Beny et al. at the National Library of Egypt, who analyzed and discussed "excessive amounts of moisture that caused some papyri to darken," a problem that they accounted for by admitting the least amount of moisture possible [43]. Most likely, Flieder et al. used unbleached papyrus sheets—produced either by themselves or untreated Egyptian samples—where the color change upon light exposure was not as strong as for modern commercial sheets.

Elnaggar et al. assessed the feasibility of laser cleaning on papyri [10]. Within their study setup, model papyrus samples from the Pharaonic village in Giza, Egypt, were subjected to accelerated aging for 28 days at 70 °C and 50% RH; no indication of additional light irradiation was given. After the aging process, they reported a decrease in lightness (L*) from 81.7 to 77.6 and an increase in yellowness (b*) from 20.6 to 23.9. The lightness decrease corresponds well to our data for both commercial sheets and native piths when aged for 25 days without light influence. We detected a trend toward yellowing only for dark-aged pith, but to a much smaller degree. Native pith can be brighter and significantly less yellow than the papyri used in their study [37]. Whether NaOH-yellowed papyri or untreated specimens were analyzed can therefore not definitely be answered by interpreting the published data; a light aging study would bring certainty.

Suitability of FTIR measurements to detect the effects of accelerated aging on papyri

For the public, the optical appearance of an ancient papyrus in museums and collections is the most important feature, since it determines readability and appeal of the object. To determine whether the optical change induced by the artificial aging process leads to other measurable, but invisible changes in the materials' structure, FTIR spectra were recorded.

The FTIR spectra of aged papyri did not show any clear aging-dependent trend for any band. After light-aging for two months, basically the same spectrum is observed as after two days (Fig. 4a, purple and dark blue lines). The entire spectra, also for the samples aged in darkness, are shown in Additional file 1: Fig. S2. There are higher peaks at 1605 cm^{-1}, 1430 cm^{-1}, 1372 cm^{-1} and 1313 cm^{-1} for some samples, but these are generic bands for any

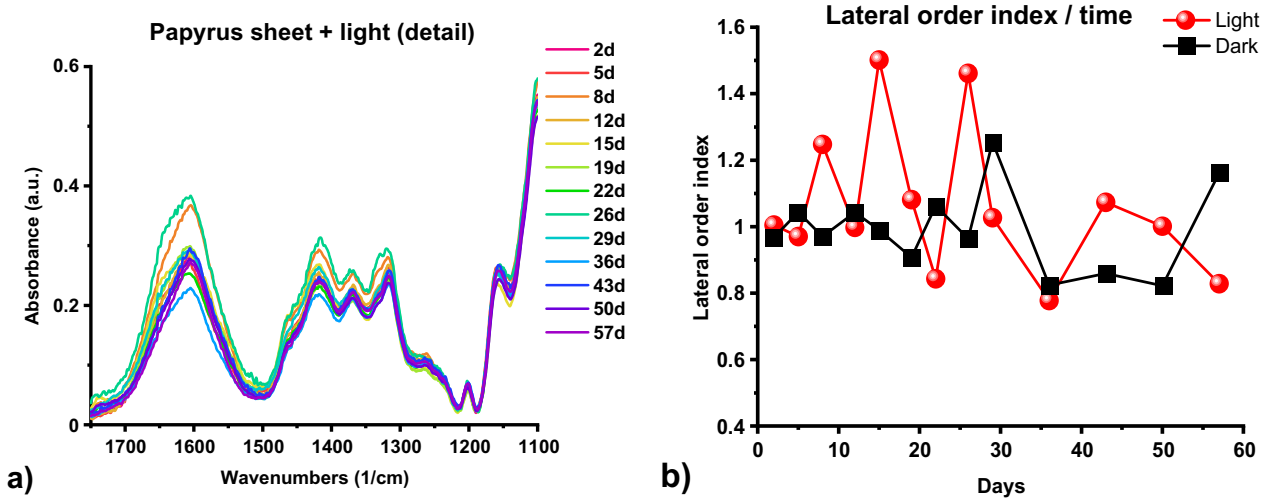

Fig. 4 Analysis of infrared spectra of aged papyri. **a** Detail of the infrared spectrum of light-aged samples, focusing on the area of the expected carbonyl and carboxyl bands. Background was subtracted and all spectra normalized to the highest peak of cellulose at 1030 cm^{-1}; **b** Lateral order index vs. time for aged papyri with and without the influence of light, according to [33–35]

cellulosic material, including isolated nanocellulose from cotton linters [44]. Since they show no trend under the applied aging conditions, we cannot draw a conclusion as to specific oxidations or other features of any constituent of papyri. Note the absence of a band around 1510 cm^{-1}, that represents the stretching vibration of the double bond in the aromatic ring and is sometimes even used for lignin quantification [45].

The lateral order index—depicted in Fig. 4b—is an approach for evaluating changes in the crystallinity of cellulosic samples [33–35]. For papyri aged under the conditions applied in this study, no clear trend was observed, either with or without the influence of light. The observed fluctuation for the analyzed samples can be explained by sample heterogeneity—an effect that might be minimized by measuring the same spots before and after aging. Still, the aging conditions used are most likely too mild to affect the crystallinity indices to a clear, measurable degree.

In the context of our study, FTIR did not prove to be a suitable method for studying the aging process of papyri. Despite being a most valuable analytical method in general, FTIR has difficulties to monitor the aging-related oxidation features of papyri, since aldehyde and keto groups on cellulose form hydrates and hemiacetals/hemiketals that do not contribute to the C=O band in FTIR measurements [46]. Also, papyri contain large amounts of carboxyl functionalities from the start [21], in the form of glucuronic and galacturonic acids in hemicellulose and pectin. Any additional cellulose oxidation must be put in relation to a potential degradation of hemicellulose and pectin in papyri if the entire sample is analyzed without fractionation [47].

Effects on mechanical properties and cellulose degradation

Apart from the optical properties, the brittleness and mechanical stability of papyrus objects is the major concern of conservators who need to assess suitable mounting conditions and the long-term stability of the objects.

To check on the effects of high-temperature aging with and without light, tensile tests of the aged samples were conducted. These were compared to measurements of the degree of polymerization (DP) of cellulose by SEC-MALS. The basic question was whether a decrease in mechanical properties could be detected and, if so, if this was also reflected at the molecular level of cellulose, the main structural compound in plant tissue.

For all mechanical tests (except for stiffness, expressed by E-Modulus), the effect of light-aging is most obvious compared to samples aged in darkness. We see a strong decline in tensile strength, and tensile energy absorption as the work necessary to break the papyrus specimen entirely. The tensile tests showed the same trend for papyri and cotton linters, which contrasts with the optical properties of cotton linters after light aging, which did not change at all (Fig. 2a). While the mechanical properties are governed by the cellulose polymer, the optical properties are determined by UV/Vis absorbing components from lignin and hemicelluloses.

The samples aged in darkness did not show a significant decrease in mechanical properties, even after

being aged at 90 °C for a month. It becomes clear that the tensile properties decrease severely with light-aging time for papyri. Especially for cotton linters, this dependency appears to be linear.

This trend is not or not as strong found for the E-Modulus. This parameter expresses the stiffness of a sample by focusing on the first and therefore elastic part of the stress–strain diagram, as opposed especially to the tensile energy absorption (until the sample is entirely broken)—a parameter that accounts for the plastic deformation of the samples.

McGovern [13] reported tensile strength and E-Modulus values of 32.73 N/mm^2 and 2.69 GPa, respectively, for *Cyperus Papyrus* L. pith test specimen, which were, on average, twice as thick as our test bodies (McGovern: 0.4 mm). These results are in a similar order of magnitude to our values (Fig. 2c). In this publication, a hot press (2.76 MPa, 177 °C, 60 s) was used for comparison. After this treatment, tensile strength increased to 48.95 N/mm^2, E-Modulus doubled, and strain decreased. McGovern also conducted an aging test, heating the samples for 72 h to 105 °C. After this, the folding endurance (double folds) decreased from 12 to 2.5.

Papyri are different from paper in being bidirectionally oriented by production, when two stripes are pressed together in a perpendicular arrangement. At first, one of these layers will bear almost the entire force in the tear direction of the test instrument. This layer—as any part of *Cyperus Papyrus* L. pith—consists of vascular bundles and parenchymatic tissue between them. The vascular bundles are much denser and consist of long cellulose fibrils "glued" together by lignin and hemicellulose. The parenchymatic tissue consists mainly of cellulosic material separated by huge voids, providing the necessary flexibility to ultimately fold the sheets into rolls. Therefore, papyrus paper can be regarded as a "composite" material. It can be imagined that at first the entire force is concentrated on the vascular bundles, which contribute most of the strength and stiffness to the material. These did not seem to be affected severely by the aging conditions, as expressed by the E-Modulus (Fig. 5c).

Once the vascular bundles start to break and the range of plastic sample deformation is reached, it depends on the integrity of the parenchymatic tissue, whether it breaks immediately or is just plastically elongated. It can be concluded that the effect of light harms the parenchymatic tissue especially strong, since it is less dense and therefore exposes more surface area to irradiation than the denser vascular bundles.

For ancient papyri, the strong degradation of parenchymatic tissue is found in a similar fashion, sometimes just leaving a net of vascular bundles of the object, as depicted in Fig. 6.

Integrity of cellulose and hemicellulose

SEC-MALS of the (hemi)cellulose—especially if coupled to labeling of carbonyl and carboxyl functionalities—does not only reflect the loss in mechanical strength on the molecular level, but also provides an in-depth understanding of the chemistry of aging processes in papyri. This is best described by the relative distribution of cellulose and hemicellulose chains regarding their length and changes thereof with aging time. In this study, SEC-MALS of papyri is coupled for the first time with the labeling of carboxyl functionalities to detect differences during the aging process with respect to uronic acids.

Figure 7a and b present the molecular weight distributions of papyrus celluloses, depicting the molecular weight on the x-axis and its relative abundance as the y-axis. Therefore, longer chains are found on the right side of the graph. This is mirrored for the chromatograms in Fig. 7e and f, which show the chromatographic elution in SEC with larger molecules eluting first. The chromatograms for the aged samples in Fig. 7a and b are given in Additional file 1: Fig. S3.

The analysis of papyrus cellulose at the molecular level is usually more sensitive compared to tensile tests, which suffer from larger error margins. This is especially true for anisotropic materials such as papyrus. SEC usually reports molecular changes long before they reach concentrations that can be detected by mechanical testing. Aging under dark conditions yields just a moderate decrease in molar mass (Mw-10%, Fig. 7c), the cellulose part proves rather resistant after two months of heat aging. While the overall molar mass distribution did not change significantly for papyri in darkness, a stronger decrease in the high molecular weight fraction of cellulose was observed when the samples were aged under the influence of light. While the average molar mass seemed to reach a plateau after 15 days (Mw-23%, Fig. 7c), the distribution showed significant changes afterwards (Fig. 7b). Deconvolution of the molar mass distribution data indicates a second high molar mass polymer population (Fig. 7d), indicative of radical-induced degradation. Both fractions (Fig. 7d) show a distinctly different behavior in solution, which is visible from different slopes of molar mass and retention time; the latter corresponds to the hydrodynamic volume of the sample (Fig. 7e). Considering the pristine condition of the non-irradiated samples, the cellulose degradation mechanism of the irradiated papyrus can be explained by radicals formed by the photolysis of the chlorinated lignin compounds or hemicelluloses in the commercial sheets. Radicals lead to cellulose oxidation by H-atom abstraction and the formation of carbonyl and carboxyl moieties throughout the cellulose chain that can result in the formation of chromophores and chain cleavage initiated by light irradiation [49–51].

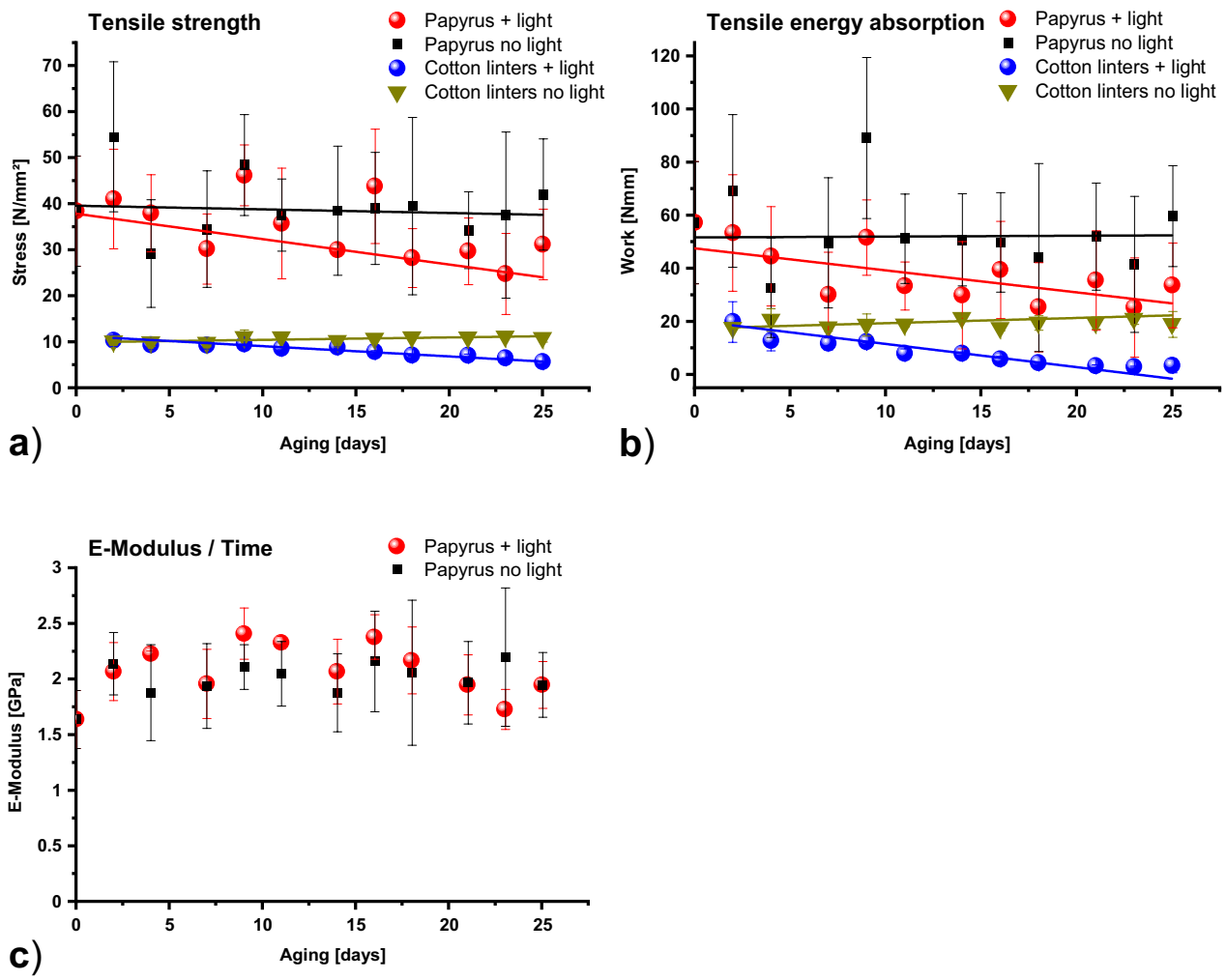

Fig. 5 Aged papyri compared to cotton linters for **a** tensile strength, **b** tensile energy absorption, and **c** E-Modulus. Error bars indicate the standard deviation for ten measurements per time step

Hemicellulose is expected to be found in the low Mw region, contributing to the smaller peak of bimodal distribution. Compared to the larger cellulose peak, the relative amount of the lower Mw region did not decrease. It comprises smaller chains for long-time light-aged samples (Fig. 7b, left part) and increases relative to the cellulose peak (compare Fig. 7e and f, gray lines). This can be explained by the coelution with shorter cellulose fragments. The behavior of light scattering signals with aging time (Fig. 7f) is particularly interesting. There may be different reasons for the drastic change in slope in the hemicellulose fractions, but most likely this effect is connected to an increase in fluorescence induced by chromophore formation from hemicelluloses and smaller fragments [52]. Dark aging does not cause such effects. In line with this observation is the decreasing content of uronic acid groups during aging (Fig. 7c). Papyri naturally contain a significant amount of carboxyl functionalities, with major contributions from glucuronic and galacturonic acids from hemicelluloses and pectin [21]. The stronger loss of uronic acids with light-induced aging can be seen as an indicator of a higher reactivity of the hemicellulose/pectin parts, relative to cellulose, in papyrus during aging.

Comparing the strong immediate degradation of long cellulose chains at light exposure, levelling off after 15 days (Fig. 7c) to the almost linear loss in tensile strength (Fig. 5a), it seems probable that not just the very long cellulose chains determine the mechanical properties of papyri, but the linkages between different structural elements in papyrus tissue. When looking at the microscopic structure of ancient papyri, the parenchymatic tissue is often strongly degraded (Fig. 6 and [53]), whereas the dense vascular bundles are comparably well preserved. It is conceivable that in the case of light aging

Fig. 6 Example of degradation of ancient papyri. Partially, only the vascular bundles remain and form a loose net instead of a closed surface. **b** Depicts a close-up of the document in **a**, where the network-type structure due to degradation is nicely visible. Photos: with kind permission from University Library Leipzig, Papyrus, and Ostraka Collection, P. Lips. inv. 1460 [48]

long cellulose chains are degraded first, also for statistical reasons, whereas the major effects in decreasing the mechanical properties of papyri result from slower, successive cleavage of bonds between lignin, hemicelluloses and resulting deterioration of inter-component adhesion with cellulose. The length of cellulose chains levels off at comparably high values.

Comparison to literature

To the best of our knowledge, there is just one previous report of a SEC-MALS measurement of papyri in the literature. Łojewska et al. [8] analyzed one modern and one ancient papyrus sample, derivatizing the OH-groups of the cellulose chain with phenyl isocyanate and dissolving the molecules in THF. They obtained a DP of 5700 for modern Papyrus paper and 800 for the ancient sample. However, this derivatization method has been shown to affect cellulose integrity by chain shortening and oxidation so that the results might be less reliable.

There are huge differences concerning the calculation and elaboration of cellulose DP depending on the method and solvent. Castro et al. [9] used viscosity measurements in 0.5 M cupriethylenediamine (cuen) to measure the DP. For papyrus stripes, they obtained a starting DP of 590, which decreased to 123 after being exposed to 100 °C for 500 h and to 236 after being exposed to a Xenon arc lamp

(See figure on next page.)

Fig. 7 Top row: Molecular weight distributions of artificially aged papyri without (**a**) and with light influence (**b**), as detected by SEC-MALS. Middle row: **c** Decrease of weight-average molecular weight (Mw) and carboxyl groups (COOH) with aging time. To visualize the degradation of cellulose alone (without the hemicellulose contribution), the chromatograms were deconvoluted and only the Mw of the cellulose peaks (right side of **a** + **b**) was considered. Error bars indicate the standard deviation of two measurements per time step for the amount of carboxyl groups. **d** Different populations of (hemi-)cellulose chains in light-aged papyri. Long chains (red) are degraded and the Mw is shifted to shorter chains lengths (blue). Hemicelluloses are found in the green peak. The chromatogram of an unaged papyrus sample (gray) is shown for comparison. Bottom row: Example chromatograms/RI-signals (gray) of samples aged for 22 d in darkness (**e**) and for 43 d under light influence (**f**). The colored lines in **e** + **f** reflect the fluorescence of the MALS detector, especially for **f** with the light-aged samples

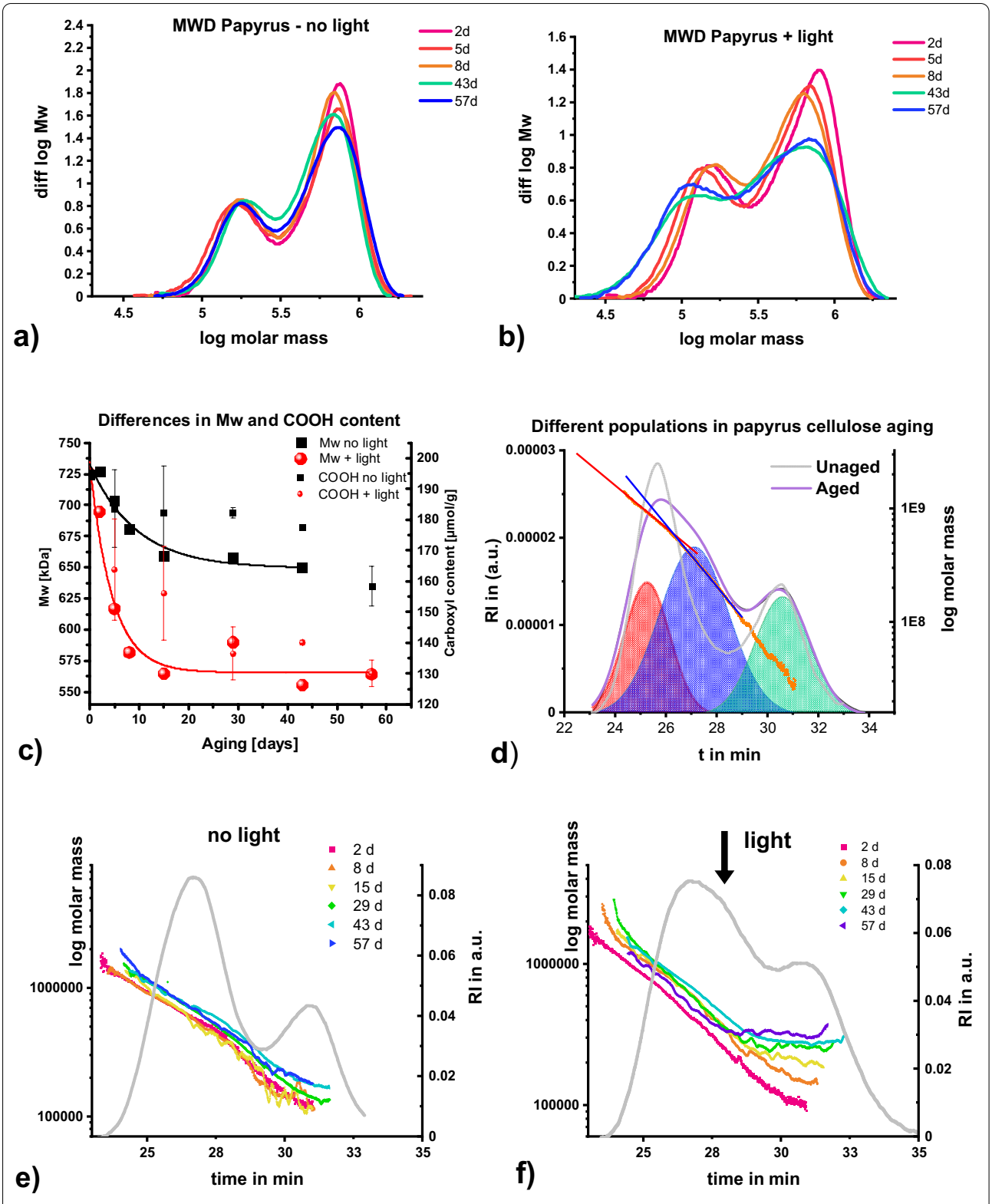

Fig. 7 (See legend on previous page.)

(1000 W/m^2) at 65 °C and 25% RH for 500 h. Elnaggar et al. [10] report a DP of 1547 for non-degraded papyri and an even higher DP of 1768 after accelerated aging for 28 days (70 °C, 50% RH). Not all methods of analyzing cellulose DP are equally suitable for different lignocellulosic materials. In the scope of the TAPPI standard T230 for viscosity determinations it is mentioned, that the method is mainly suitable for bleached cotton and wood pulps, as well as for conventional kraft pulps of up to 4% lignin [54]. Given that native *Cyperus papyrus* L. pith contains around 16% of lignin, around 25% of hemicelluloses and in total less than 50% of cellulose [15, 27], the applicability of viscosity measurements to analyze the degree of polymerization of cellulose in papyrus objects is yet to be confirmed.

For the calculation of DP, we used the weight-average molecular weight (Mw) of the entire distribution of cellulose and hemicellulose [55]. For the relative cellulose Mw decrease with aging time (Fig. 7c) the Mw of the cellulose peak alone was taken, in order to illustrate the strong initial degradation of cellulose chains. The starting DP of papyrus cellulose in our studies was 3000, which stayed constant after aging in darkness, but decreased to 2500 after aging under the influence of light.

Conclusion

Papyri might suffer severely from the influence of light, as shown in this study for commercial papyrus sheets. The effect was not observed under the same humidity conditions in the absence of light. The cellulose degradation is related to radical mechanisms caused by chlorine-containing compounds which were introduced by bleaching of the yellow-colored papyrus sheets to make them appear less yellow. Upon light-aging, a photo-induced color change toward brown appears almost immediately, at least after two days, as clearly detectable by the human eye, but also reflected in CIELAB values. ISO-brightness and FTIR did not provide conclusive information for analyzing this effect.

The color change is accompanied by a strong decrease in tensile strength and tensile energy absorption while maintaining a constant E-Modulus. This indicates that the load-bearing vascular bundles remain largely intact, while the parenchymatic tissue is strongly weakened—an effect commonly observed for ancient papyri as well. At the molecular level, this degradation trend is reflected by a decreasing cellulose DP with irradiation time. SEC-MALS proved to be the most reliable and detailed method for assessing the conservation status of papyri, especially considering the low sample consumption, as it provides accurate molecular data (chain length and oxidation degree) on the molecular level.

Ancient papyri did evidently not experience a chlorine-bleach treatment, as used in the production of modern commercial papyri, although the latter are often regarded as analogous to historic papyrus paper—especially in the production of facsimiles. Therefore, the aging behavior of ancient papyri can follow different pathways and might show degradation patterns different from contemporary commercial papyri, which must be analyzed in detail in the future. The analysis of these model samples showed that papyri might suffer severe consequences from light exposure, at least after certain pretreatments. Therefore, for exhibition purposes, it is recommended to minimize light exposure to ancient papyri and exclude light entirely when papyri are stored. Most definitely, direct exposure to sunlight should be avoided.

Abbreviations

FTIR: Fourier-transformed—infrared spectroscopy; SEC-MALS: Size-exclusion chromatography—multi angle light scattering; RH: Relative humidity; UV/Vis: Ultraviolet/visible light spectroscopy; FDAM: 9H-fluoren-2-yl-diazomethane; DIN: German industry norm; ISO: International organization for standardization; ATR: Attenuated total reflection; LOI: Lateral order index; HCl: Hydrogen chloride; DMAc: N,N-dimethylacetamide; LiCl: Lithium chloride; TMAH: Tetramethylammonium hydroxide; DP: Degree of polymerization; Mw: Weight-average molecular weight; THF: Tetrahydrofuran; Cuen: Cupriethylenediamine; COOH: Carboxyl groups.

Supplementary Information

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Additional file 1: Figure S1. Transmission spectrum of the microscope slides used to mount the papyri during accelerated aging. **Figure S2.** FT-IR spectra of samples aged for up to 57 days with and without the influence of light. **a** Entire spectrum without the influence of light; **b** Entire spectrum with the influence of light; **c** Detail of the spectra (1750–1100 1/cm) aged in darkness. **Figure S3.** Chromatograms of aged samples without (left) and with (right) light influence, expressed as sample concentration (RI) vs. time, normalized to equal peak area. Note the different curve shapes—the "third peak"—for light aged samples after a longer aging treatment.

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Author contributions

FB and DDO performed the measurements. FB, JG, and AP analysed the data. FB wrote the manuscript. TR and AP supervised the project. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

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References

1. Braidwood RJ, Jacobsen T, Parker RA, Weinberg S. Radiocarbon dates and their implications in the near and middle Eastern area, a brief. Mem Soc Am Archaeol. 1951;8:52–3.
2. Ekschmitt W. Das Gedächtnis der Völker: Hieroglyphen, Schrift und Schriftfunde auf Tontafeln, Papyri und Pergamenten. Berlin: Safari-Verlag; 1964.
3. Černý J. Paper & books in ancient Egypt. London: H.K. Lewis & Co Ltd; 1952.
4. Nicholson PT, Shaw I, Press CU. Ancient Egyptian materials and technology. Cambridge: Cambridge University Press; 2000. p. 740.
5. Flieder F, Delange E, Duval A, Leroy M. Papyrus: the need for analysis. Restaurator. 2001;22(2):84–106.
6. Krutzsch M. Materialtechnische Beobachtungen während der Restaurierung. In: Fischer-Elfert H-W, editor. Magika Hieratika in Berlin, Hannover, Heidelberg und München. Berlin: De Gruyter; 2015.
7. Glauert M. Klimaregulierung in Bibliotheksmagazinen. In: Hauke P, Werner K, editors. Bibliotheken bauen und ausstatten. Berlin: Humboldt-Universität zu Berlin; 2009. p. 158–173.
8. Łojewska J, Rabin I, Pawcenis D, Bagniuk J, Aksamit-Koperska MA, Sitarz M, et al. Recognizing ancient papyri by a combination of spectroscopic, diffractional and chromatographic analytical tools. Sci Rep. 2017;7(1):46236.
9. Castro K, Princi E, Proietti N, Manso M, Capitani D, Vicini S, et al. Assessment of the weathering effects on cellulose based materials through a multianalytical approach. Nucl Instrum Methods Phys Res Sect B. 2011;269(12):1401–10.
10. Elnaggar A, Fitzsimons P, Nevin A, Watkins K, Strlič M. Viability of laser cleaning of papyrus: conservation and scientific assessment. Stud Conserv. 2015;60(sup1):S73-81.
11. Arnold RB. ASTM paper aging research program. The book and paper group of the American institute for conservation. 2000. https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v19/bp19-01.html. Accessed Jun 23 2021.
12. BPG Papyrus. Housing—book and paper group wiki. American Institute for Conservation (AIC). 2022. https://www.conservation-wiki.com/wiki/BPG_Papyrus#Housing. Accessed 18 Feb 2022.
13. McGovern JN. Bonding in papyrus and papyrus-like mats. TAPPI. 1982;65(5):159–62.
14. Wiedemann HG, Bayer G. Papyrus: the paper of ancient Egypt. Anal Chem. 1983;55(12):1220A-1230A.
15. Bausch F, Owusu DD, Jusner P, Rosado MJ, Rencoret J, Rosner S, et al. Lignin quantification of papyri by TGA—not a good idea. Molecules. 2021;26(14):4384.
16. Lövestam NEG, Swietlicki E. PIXE analysis and imaging of papyrus documents. Nucl Instrum Methods Phys Res Sect B. 1990;45(1):307–10.
17. Nehring G, Krutzsch M, Rabin I. Tuschenanalyse im P 11702. Arch Für Papyrusforschung Verwandte Geb. 2021;67(2):277–82.
18. Cohen Z, Olszowy-Schlanger J, Hahn O, Rabin I. Composition analysis of writing materials in geniza fragments. In: Jewish manuscript cultures. De Gruyter. 2017. p. 323–38. https://doi.org/10.1515/9783110546422-013/html. Accessed 21 Jan 2022.
19. Rabin I, Krutzsch M. The Writing Surface Papyrus and its Materials 1. Can the writing material papyrus tell us where it was produced? 2. Material study of the inks. In: proceedings of the 28th Congress of Papyrology. Barcelona: Publicacions Abadia de Montserrat; 2016. p. 773–81. https://recercat.cat//handle/2072/359655
20. Christiansen T, Cotte M, de Nolf W, Mouro E, Reyes-Herrera J, de Meyer S, et al. Insights into the composition of ancient Egyptian red and black inks on papyri achieved by synchrotron-based microanalyses. Proc Natl Acad Sci. 2020;117(45):27825–35.
21. Free H. Studies on the cell wall compositions of families in the commelinid monocotyledons, Thesis. ResearchSpace@Auckland; 2013. https://researchspace.auckland.ac.nz/handle/2292/23110. Accessed on 23 Jun 2021.
22. Buchala AJ, Meier H. Hemicelluloses from the stalk of *Cyperus papyrus*. Phytochemistry. 1972;11(11):3275–8.
23. Karlen SD, Free HCA, Padmakshan D, Smith BG, Ralph J, Harris PJ. Commelinid monocotyledon lignins are acylated by p-coumarate. Plant Physiol. 2018;177(2):513–21.
24. Rosado MJ, Bausch F, Rencoret J, Marques G, Gutiérrez A, Rosenau T, et al. Differences in the content, composition and structure of the lignins from rind and pith of papyrus (*Cyperus papyrus* L.) culms. Ind Crops Prod. 2021. https://doi.org/10.1016/j.indcrop.2021.114226.
25. Rencoret J, Rosado MJ, Kim H, Timokhin VI, Gutiérrez A, Bausch F, et al. Flavonoids naringenin chalcone, naringenin, dihydrotricin, and tricin are lignin monomers in papyrus. Plant Physiol. 2021. https://doi.org/10.1093/plphys/kiab469.
26. Lucejko JJ, Colombini MP, Ribechini E. Chemical alteration patterns of ancient Egyptian papyri studied by pyrolysis-GC/MS with in situ silylation. J Anal Appl Pyrolysis. 2020;152:104967.
27. El Ashry EHE, El Kilany Y, El Engebawy A, El Taraboulsi MA. Some chemical data on *Cyperus papyrus* L. the ancient papermaking material. Egypt J Chem. 2003;46(1):181–5.
28. Pastorelli G, Cao S, Cigić IK, Cucci C, Elnaggar A, Strlič M. Development of dose-response functions for historic paper degradation using exposure to natural conditions and multivariate regression. Polym Degrad Stab. 2019;168:108944.
29. Bohrn R, Potthast A, Schiehser S, Rosenau T, Sixta H, Kosma P. The FDAM method: determination of carboxyl profiles in cellulosic materials by combining group-selective fluorescence labeling with GPC. Biomacromol. 2006;7(6):1743–50.
30. Jaxel J, Fontaine L, Krenke T, Hansmann C, Liebner F. Bio-inspired conformational lipophilization of wood for scCO2-assisted colouring with disperse dyes. J Supercrit Fluids. 2019;1(147):116–25.
31. International Organization for Standardization. ISO/CIE 11664-4. ISO. 2019. https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/07/41/74166.html. Accessed 29 Mar 2022.
32. ISO. 2470-1:2016 Paper, board and pulps—measurement of diffuse blue reflectance factor—part 1: indoor daylight conditions (ISO brightness). 2016.
33. O'Connor RT, DuPré EF, Mitcham D. Applications of infrared absorption spectroscopy to investigations of cotton and modified cottons: part I: physical and crystalline modifications and oxidation. Text Res J. 1958;28(5):382–92.
34. Evans R, Newman RH, Roick UC, Suckling ID, Wallis AFA. Changes in cellulose crystallinity during kraft pulping. Comparison of infrared, X-ray diffraction and solid state NMR results. Holzforschung. 1995;49(6):498–504.
35. Odabas N, Amer H, Bacher M, Henniges U, Potthast A, Rosenau T. Properties of cellulosic material after cationization in different solvents. ACS Sustain Chem Eng. 2016;4(4):2295–301.
36. Potthast A, Radosta S, Saake B, Lebioda S, Heinze T, Henniges U, et al. Comparison testing of methods for gel permeation chromatography of cellulose: coming closer to a standard protocol. Cellulose. 2015;22(3):1591–613.
37. Bausch F, Rosado MJ, Rencoret J, Marques G, Gutiérrez A, Graf J, et al. Papyrus production revisited: differences between ancient and modern papyrus production modes. Cellulose. 2022.

38. Business Insider. Meet some of the last papyrus makers in Egypt keeping a 5,000-year-old craft alive. Still standing. 2021. https://www.youtube.com/watch?v=SBdVhvo2UUM. Accessed 23 Jun 2021.
39. Da Silva JP, Vieira Ferreira LF, Da Silva AM, Oliveira AS. Photochemistry of 4-chlorophenol on cellulose and silica. Environ Sci Technol. 2003;37(20):4798–803.
40. Lewis N. Papyrus in classical antiquity. Oxford: Clarendon Press; 1974. p. 174.
41. Pandey KK, Vuorinen T. Comparative study of photodegradation of wood by a UV laser and a xenon light source. Polym Degrad Stab. 2008;93(12):2138–46.
42. El-Nahawi U. Untersuchungen zur Herstellung von Papyrus: Beschreibungen von äußeren und mikroskopischen Merkmalen und Qualität. Master Thesis; Hildesheim: HAWK Hochschule für angewandte Kunst. 2020.
43. Beny A, Hassan M, Said N. Low-budget and ´low tech´ solutions for papyrus conservation and storage at the National Library of Egypt. https://www.researchgate.net/profile/Ana-Beny/publication/265114609_LOW-BUDGET_AND_%27LOW-TECH%27_SOLUTIONS_FOR_PAPYRUS_CONSERVATION_AND_STORAGE_AT_THE_NATIONAL_LIBRARY_OF_EGYPT/links/572f051408ae7441518fa7de/LOW-BUDGET-AND-LOW-TECH-SOLUTIONS-FOR-PAPYRUS-CONSERVATION-AND-STORAGE-AT-THE-NATIONAL-LIBRARY-OF-EGYPT.pdf. Accessed 18 Feb 2022.
44. Kunaver M, Anžlovar A, Žagar E. The fast and effective isolation of nanocellulose from selected cellulosic feedstocks. Carbohydr Polym. 2016;148:251–8.
45. Trafela T, Strlič M, Kolar J, Lichtblau DA, Anders M, Mencigar DP, et al. Nondestructive analysis and dating of historical paper based on IR spectroscopy and chemometric data evaluation. Anal Chem. 2007;79(16):6319–23.
46. Potthast A, Rosenau T, Kosma P, Saariaho A-M, Vuorinen T. On the nature of carbonyl groups in cellulosic pulps. Cellulose. 2005;12(1):43–50.
47. Becker M, Ahn K, Bacher M, Xu C, Sundberg A, Willför S, et al. Comparative hydrolysis analysis of cellulose samples and aspects of its application in conservation science. Cellulose. 2021;28(13):8719–34.
48. Papyrus- und Ostrakasammlung der Universitätsbibliothek Leipzig. P.Lips. inv. 1460. https://papyri.uni-leipzig.de/receive/UBLPapyri_schrift_00273790. Accessed 16 Sep 2021.
49. Coseri S, Biliuta G, Simionescu BC, Stana-Kleinschek K, Ribitsch V, Harabagiu V. Oxidized cellulose—survey of the most recent achievements. Carbohydr Polym. 2013;93(1):207–15.
50. Malešič J, Kolar J, Strlič M, Kočar D, Fromageot D, Lemaire J, et al. Photo-induced degradation of cellulose. Polym Degrad Stab. 2005;89(1):64–9.
51. Ahn K, Zaccaron S, Zwirchmayr NS, Hettegger H, Hofinger A, Bacher M, et al. Yellowing and brightness reversion of celluloses: CO or COOH, who is the culprit? Cellulose. 2019;26(1):429–44.
52. Rosenau T, Potthast A, Zwirchmayr NS, Hettegger H, Plasser F, Hosoya T, et al. Chromophores from hexeneuronic acids: identification of HexA-derived chromophores. Cellulose. 2017;24(9):3671–87.
53. Nielsen I. PAPYRUS structure, manufacture and deterioration. PhD Thesis. School of Conservation, Copenhagen. 1985.
54. TAPPI. Viscosity of pulp (capillary viscometer method) (revision of T 230 om-08). 2013. https://www.tappi.org/content/tag/sarg/t230.pdf. Accessed 18 Feb 2022.
55. Oberlerchner JT, Rosenau T, Potthast A. Overview of methods for the direct molar mass determination of cellulose. Molecules. 2015;20(6):10313–41.

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