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Impact of the paper degradation state and constituents on its behavior during and after X-ray exposure

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Abstract

Paper is a complex biopolymer material which contains papermaking additives and often bears inks and other graphic media. Cultural heritage paper-based artefacts are most often deteriorated to some extent. This research explores how intrinsic factors such as constituents and degradation state can impact the modifications incurred in aged papers during and after X-ray examination. To this end laboratory model papers, artificially aged, and 18th and 19th century archival documents, with and without additives (gelatin, calcium carbonate) and iron gallate ink, were exposed to Synchrotron X-ray radiation at doses that were previously shown to incur damage in unaged cotton papers (0.7 to 4 kGy). Glycosidic scissions, hydroxyl free radicals, UV luminescence and yellowing were measured immediately after the irradiation, and were monitored over a period of three years. The depolymerization of cellulose was lower in the aged papers, as well as in the papers containing calcium carbonate and gelatin, than in the unaged fully cellulosic papers. Compared to the papers with no additives, there were more hydroxyl free radicals in the papers with calcium carbonate and slightly less in the gelatin sized papers. UV luminescence and yellowing both appeared post-irradiation, with a delay of several weeks to months, while the intensity of the responses was impacted by the various paper constituents. The papers with iron gallate ink showed limited degradation in the low doses range, most probably due to recombination of the free radicals produced. Doses below 4 kGy did not cause yellowing or UV luminescence of the archival papers within the whole monitoring period. At higher doses (26 to 36 kGy), a slight UV luminescence appeared after 21 months, as well as a slight yellowing after three years, in some of them. No clear correlation between the degradation induced by the irradiation and the constituents in the paper nor its conservation state could be made. The archival papers in good conservation state depolymerized to the same extent as the model papers, while the most degraded archival papers were less impacted than the latter.

34 **Introduction**

35 X-ray analytical techniques are used to examine historic documents and artworks on paper and gain
36 insight into their materials, manufacturing techniques and history (Creagh 2007; Albertin et al.
37 2015; IAEA 2016; Kozachuk et al. 2016; Pouyet et al. 2017). Yet because they are ionizing, X-
38 rays induce changes in organic (as well as inorganic) materials. Cellulose depolymerization,
39 oxidation and changes in the optical properties have been observed under gamma-ray (Ershov
40 1998; Bouchard et al. 2006; Henniges et al. 2013; Bicchieri et al. 2016) and X-ray exposures
41 (Mantler and Klikovits 2004; Kozachuk et al. 2016; Gimat et al. 2020). In quasi-pure cellulose
42 paper, the impact of X-rays has been shown to be proportional to the dose (Gimat et al. 2020).
43 However, due to the large diversity in the components and in the degradation state of historic
44 cellulosic artefacts, the global impact of X-ray photons is difficult to foresee.

45 Paper is made of plant fibers, which besides cellulose, most often also contain other biopolymers
46 such as hemicelluloses and lignin. Additives, fillers and sizing, are usually added to writing and
47 drawing quality papers to enhance usability parameters: e.g. reduce water permeability, increase
48 opacity and enhance brightness. In cultural heritage collections, such papers also often bear media
49 such as inks and pigments. The materials and chemicals used are diverse. In ambient conservation
50 conditions, a number of these additives can impact the paper degradation rate. For instance gelatin
51 (Dupont 2003a) and alkaline minerals (Reissland 1999; Sequeira et al. 2006; Ahn et al. 2012; Poggi
52 et al. 2016) have been shown to decrease the cellulose depolymerization rate, whereas transition
53 metals in inks and pigments promote degradation by producing acids and free radicals (Selih et al.
54 2007; Potthast et al. 2008). If and how additives can impact the radiation-induced degradation of
55 cellulosic paper is still unknown. The presence of absorbing elements, such as iron in the metal-
56 gallate ink or calcium in the fillers could have a shielding effect and decrease the nominal X-ray
57 dose, thereby lowering the degradation impact. Such a shielding effect could also be counteracted
58 by the free radicals formed via the transition metals, which are known cellulose degradation
59 promoters (Emery and Schroeder 1974; Jeong et al. 2014). It has been shown that iron-containing
60 pigments undergo a redox reaction under X-ray radiation (Bertrand et al. 2015; Gervais et al. 2015;
61 Gimat 2016). Moreover, the structural modification of an additive under irradiation can also affect
62 the paper degradation rate. For instance, X-rays were shown to produce defects inside calcium
63 carbonate (Kabacińska et al. 2017), whereas polypeptide chains (e.g. gelatin) were shown to

64 undergo hydrolysis (Moini et al. 2014). Bicchieri et al. have examined the combined impact of the
65 degradation state and certain paper additives on the degradation incurred by ionizing radiation used
66 for mold disinfection (Bicchieri et al. 2016). The authors used gamma-rays at a dose of 3 kGy.
67 They tested cellulose paper Whatman n°1, as well as a commercial permanent paper (with CaCO₃
68 filler and optical brighteners, and sized with alkyl ketene dimers), which they pre-degraded by an
69 acid treatment. The acid treated samples showed less radiation induced depolymerization than the
70 control samples, indicating that the degradation state played a role. The permanent paper yellowed
71 more than Whatman n°1, which was attributed to structural modifications of calcium carbonate and
72 optical brighteners under gamma radiation. To our knowledge, such study has not been conducted
73 using X-rays, nor at lower doses used during synchrotron X-ray examination of cellulosic cultural
74 heritage artefacts. This lack of research motivated the present study, which attempts at better
75 understanding the mitigated impact of X-rays on paper, depending on the fiber deterioration level
76 and on the presence of components other than the fibers.

77 Handmade linen rag papers from the 18th and 19th century and industrially-made cotton linters
78 papers (Whatman n°1) to which various additives were incorporated (gelatin, calcium carbonate
79 and iron gallate ink) were exposed to synchrotron X-ray radiation. The papers, some of which had
80 been previously artificially aged, were irradiated at doses in the range 0.7-4 kGy. The samples were
81 characterized immediately after the exposure using a multiscale analytical procedure developed in
82 a previous study (Gimat et al. 2020), which encompasses the macroscopic (yellowing and UV
83 luminescence) and the microscopic scales (glycosidic scissions and formation of hydroxyl
84 radicals). The changes were monitored over a period of three years.

85

86 **Materials and Methods**

87 **Paper samples**

88 *Laboratory-prepared samples*

89 Two types of paper were used: Whatman n°1 (W), which is a commercial paper made of cotton
90 linters (min. 98% alpha cellulose), and a linen rag paper (R) manufactured using traditional stamper
91 beating at Moulin du Verger papermill (Puymoyen, France). W and R were used either with no

92 further modification (control samples), or upon undergoing various artificial aging treatments (aged
93 samples), in an attempt to approach the molecular degradation state of centuries old cultural
94 heritage papers. Two artificial aging conditions, one predominantly hygrothermal (*hyg*) and the
95 other predominantly oxidative (*ox*), were used to depolymerize and increase the carbonyl content
96 of cellulose. The conditions were adjusted so as to achieve a similar degree of polymerization (*DP*)
97 and a different degree of oxidation in the *hyg* and *ox* samples.

98 *Hyg* aging of W and R (samples called W_*hyg* and R_*hyg*) was performed according to the TAPPI
99 method (TAPPI T573 sp-15 2015). Glass tubes (Wheaton, 35 mm internal diameter (ID) × 147
100 mm, 144 mL) were filled with 4.0 g of paper (dry weight), i.e. 4.23 g of paper conditioned at 50%
101 relative humidity (RH) and 23 °C, based on the value of the equilibrium moisture content (EMC =
102 5.43 %_{wt}) determined with the sorption isotherm. The tubes were hermetically closed and heated
103 at 100 °C in an oven (Memmert UN 55 oven) during 10 days to reach a decrease in *DP* of about
104 50%. During *hyg* aging, both hydrolysis and oxidation occur. The weight-average degree of
105 polymerization (*DP_w*) of cellulose was measured using SEC-MALS-DRI (details in Physico-
106 chemical characterizations section) and the copper number (*N_{Cu}*) was determined using the
107 standard method (TAPPI - T 430 cm-99 1999). The total carbonyl groups concentration was
108 derived from *N_{Cu}* using the following formula proposed by Röhrling: $[CO] = \frac{(N_{Cu}-0.07)}{0.06}$ (Röhrling
109 et al. 2002). *DP_w* for W_*hyg* and R_*hyg* was 1490 ± 2% and 1961 ± 1.6%, respectively. *N_{Cu}* of
110 W_*hyg* was 0.11.

111 Oxidative degradation (*ox*) was carried out by immersing W in an aqueous solution of sodium
112 hypochlorite (0.42-0.62% active chlorine) adjusted to pH 7 with HCl 6 N, during 15 min under
113 gentle stirring. At this pH, NaClO is known to promote enhanced carbonyl groups formation
114 (aldehyde, ketone, and carboxyl groups) on C2, C3 and C6, short chain organic acids as well as
115 considerable glycosidic scissions (Nevell and Zeronian 1985). The samples (called W_*ox*) were
116 abundantly rinsed with milli-Q water until neutral pH of the water, and were dried between blotters.
117 The *DP_w* for W_*ox* was 1352 ± 2% and *N_{Cu}* was 0.42.

118 Some of the W_*ox* samples additionally underwent a reduction treatment with Na(BH)₄ to reduce
119 the carbonyl groups produced during the aging (aldehyde and keton functions) to alcohol groups,
120 and achieve a nearly null *N_{Cu}*. To this end, a solution made with anhydrous Na(BH)₄ (Sigma)
121 (2.91g) dissolved in absolute ethanol (154 mL) was prepared, in which 1.54 g of paper was
122 immersed and left under gentle stirring during 12 hours. After reduction, the papers were

123 abundantly rinsed with milli-Q water until the water reached neutral pH, and were dried between
124 blotters. The samples were called *W_red*.

125 A portion of the W and R control samples were sized by immersing the paper sheets in a 20 g L⁻¹
126 aqueous solution of type B photographic grade gelatin from cattle bone (Gelita type restoration 1,
127 Kind & Knox) at 30 °C during 10 minutes. The sheets were then dried vertically at ambient
128 temperature. The sized samples were named *W_G* and *R_G*.

129 The dry gelatin uptake (UP) of *W_G* and *R_G*, determined as $UP =$
130 $\frac{m_{sized\ paper\ dry} - m_{unsized\ paper\ dry}}{m_{unsized\ paper\ dry}}$, was 4.8% ± 0.2. Dry masses were calculated subtracting the EMC

131 at 23 °C and 50% RH measured according to the standard method (TAPPI T 502 cm-07 1998). The
132 UP value falls in the range of gelatin content in historical papers (Barrow 1972; Barrett 1992) and
133 corresponds to a substantial amount of size in the paper (qualified as with '+' in Table 1).

134 Some of the *W_G* and *R_G* samples were used to apply the second compound of interest: iron
135 gallate ink, also referred to as I (samples called *W_GI* and *R_GI*). The ink was prepared by mixing
136 FeSO₄·7H₂O (Sigma Aldrich, 99%) (40 g L⁻¹), gallic acid monohydrate (Sigma Aldrich, 99%) (9
137 g L⁻¹) and gum Arabic (Sigma Aldrich, G9752) (140 g L⁻¹). The mixture was stirred during 3 days
138 at room temperature. The amount of gum Arabic used was purposely high in order to limit the
139 penetration of the ink inside the paper. The iron sulfate vs gallic acid ratio was adapted from a
140 recipe used in previous work (Rouchon et al. 2011). Large inked strokes (1.5 cm wide each) were
141 applied side by side with a flat-end metal pen ("Plakat", Brause) in order to cover the whole sample
142 surface. This procedure was not intended to replicate a quill pen stroke, but to provide a large and
143 homogeneous inked surface (2×1 cm²). The ink penetrated 30 to 112 microns into the paper, *i.e.*
144 one third to one half of the sheet thickness, as observed with the optical microscope (Fig S1 in the
145 Supplementary data file). The iron content determined by XRF using a previously established
146 calibration curve (unpublished data) was similar in both samples: 97 (± 5) μmol g⁻¹ in *W_GI* and
147 110 (±15) μmol g⁻¹ in *R_GI*, values that are comparable to those in historical documents (36-179
148 μmol g⁻¹) (Rouchon et al. 2011).

149 The third compound added to the papers was CaCO₃ (samples called *W_Ca*). W paper was
150 immersed in a saturated aqueous solution of calcium hydroxide (95%, Sigma Aldrich) (approx. 1.4
151 gL⁻¹) during 1 hour and was dried in ambient air. This was repeated four times successively in order
152 to achieve a high calcium carbonate content. After each bath, the paper sheets were placed between

153 two blotters, and the excess solution was removed by applying a 10 kg Cobb test metal roller once
154 back and forth on the blotters. Then the sheets were dried under weight. The reaction of CO₂ with
155 the air when the paper is removed from the solution converts Ca(OH)₂ to CaCO₃, so-called alkaline
156 reserve (AR). The AR determined according to the standard method (TAPPI T 553 om-00 2000)
157 was $1.18 \pm 0.06 \text{ mol kg}^{-1}$, otherwise expressed as $6.0\% \pm 0.3$ equivalent CaCO₃. Additionally, a
158 commercial permanent paper made of cotton linters, which contained 7.25% precipitated CaCO₃
159 (Krypton parchment, Spixel Inc, formerly Domtar), was used (samples named K). Because it was
160 manually prepared, Ca distribution inside W_Ca was less homogeneous than in K paper (Fig. S2
161 in supplementary data file). All the samples were conditioned prior to use at 50% RH, 23 °C
162 according to the standard method (TAPPI T 402 sp-08 2013).

163

164 *Archival papers*

165 Five archival paper documents from the 18th and 19th century manufactured with linen rags were
166 chosen. They were named DCN, SE, LN1, LN5, and M. They seem to have different gelatin size
167 content, varying from light to strong, and different *DP* (Table 1 and Table S1 in the Supplementary
168 data file). SE is a page from an 18th century printed volume and has a slightly brownish hue, which
169 appears darker in the center inked area of the page, due to natural aging. DCN is a printed decree
170 and has a very faint bluish hue. These two papers seem to have the lowest amount of sizing (Fig.
171 S3 in the Supplementary data file). The three other documents (LN1, LN5 and M) are individual
172 folios of notarial deed documents. M is a blank paper while both LN1 and LN5 are handwritten
173 with iron gall ink. In SE, DCN, LN1 and LN5, only ink-free areas were used, in order to better
174 compare with M. Additionally, to investigate the effect of the iron gall ink on ancient archival
175 paper, the laboratory-made iron gallate ink was applied to some of the M samples using large
176 strokes as previously described for papers W_GI and R_GI, which yielded a homogeneous inked
177 area (sample called M_I).

178

179 **Table 1** Samples characteristics: constituents, aging method, thickness (x), density (ρ), equilibrium moisture content
180 (EMC) at 23 °C and 50% RH (TAPPI T 502 cm-07 1998), weight-average or viscometric-average (*) degree of
181 polymerization (DP_0), pH (TAPPI T 509 om-15 2002), copper number (N_{Cu}) (TAPPI - T 430 cm-99 1999),
182 concentration of total carbonyl groups ([CO]) (Röhrling et al. 2002), ash content (measured at 525 °C) (TAPPI 211
183 om-02 2002), alkaline reserve (AR) expressed as % CaCO₃ (TAPPI T 553 om-00 2000). Standard deviation (STD) is

184 provided when possible. Cot: cotton papers; lin: linen rag pulp papers; ox: oxidative degradation; hyg: hygrothermal
 185 aging; red: reduction treatment; nat. natural aging; Ca: calcium carbonate filler; I: iron gallate ink; Gel: gelatin sizing
 186 (identified with hydroxyproline spot test, with ++: highest size content; +: medium size content; ~: lowest size content
 187 (levels defined with a water drop absorption test) (Fig S3 in the Supplementary data file). n.d. stands for not determined.
 188

Sample	fiber	Additive	aging	x μm	ρ g cm ⁻³	EMC % wt	DP ₀	pH	N _{Cu} / [CO] μmol g ⁻¹	Ash %	AR % _{eq}
W	cot	none	none	170	0.51	5.43	2948±2%	6.90 ±0.02	0.05	<0.1	
W_hyg	cot	none	hyg	151	0.55	5.46	1490±2%	6.2 ±0.2	0.11 / 0.67		
W_ox	cot	none	ox	170	0.53	n.d.	1352±2%	6.73 ±0.02	0.42 / 5.83		
W_red	cot	none	ox/red	170	0.53	n.d.	1431±1.1%	6.41 ±0.05	0.02		
W_G	cot	Gel+	none	170	0.54	6.13	3021±1%	5.70			
W_GI	cot	Gel+, I	none	170	0.62	6.90	2225*	4.21			
K	cot	Ca	none	100	0.68	5.61	2566±2%	8.89		7.6	7.3
W_Ca	cot	Ca	none	170	0.54	5.20	2803±2.2%	8.86		5.4	6.0
R	lin	none	none	160	0.54	5.78±0.18	2980	7.90			
R_hyg	lin	none	hyg	141	0.60	n.d.	1961±1.6%	6.14			
R_G	lin	Gel+	none	160	0.53	6.57	3326±6.8%	7.68			
R_GI	lin	Gel+, I	none	150	0.55	7.21	2290*	5.15			
SE	lin	Gel~	nat	115	0.64	5.46	1000±9.4%	5.90			
LN5	lin	Gel++	nat	125	0.62	5.36	1039±5.7%	4.92		1.1	
M	lin	Gel++	nat	125	0.47	5.75±0.04	1490±12.8%	5.03		1.5	
M_I	lin	Gel++, I	nat	125	0.72	n.d.	702*	n.d.			
LN1	lin	Gel+	nat	165	0.68	5.12	1608±2.3%	5.28		0.8	
DCN	lin	Gel~, Ca	nat	90	0.72	6.01	2869±6.2%	7.61		2.5	

189 X-ray radiation exposures

190 Synchrotron X-ray setup

191 The papers were cut into a few cm² samples, inserted in plastic photography slide frames, and
 192 heated for 2 h at 40 °C (Memmert UN 55 oven) for gentle moisture desorption. They were then
 193 placed 48 h in a climatic chamber at 23 °C and 50% RH for equilibrium moisture regain, after
 194 which they were sealed in LDPE plastic bags where silica gel ProSorb (Atlantis) was added so as
 195 to maintain 50% RH (± 5%). The EMC (23 °C, 50% RH) of the papers was determined according
 196 to the TAPPI test method (TAPPI T 502 cm-07 1998) (Table 1). No moisture leakage was recorded
 197 upon monitoring the RH inside the bags for at least 72 h prior to the synchrotron radiation (SR)
 198 experiment with a temperature/humidity logger (Ibutton® Hygrochron, Measurement Systems

199 Ltd). The bags were themselves sealed with Escal® film also filled with silica gel to stabilize the
200 RH to 50% for transportation from the laboratory to the synchrotron facility.

201 The irradiation was performed on the beamline PUMA (SOLEIL synchrotron, Saclay). A
202 monochromatic beam ($2 \times 1 \text{ cm}^2$) from a double crystal monochromator (DCM) with Si(111)
203 crystals was used at photon energies of 7.22 keV, 12.5 keV or 18 keV. The samples were exposed
204 perpendicular to the beam, inside the LDPE bags. The irradiation duration varied to reach various
205 doses in the range 7 Gy to 4 kGy. The dose D (Gy), *i.e.* the total energy deposited per mass unit of
206 material, was calculated as follows:

$$207 \quad D = \frac{F \cdot E \cdot t}{m} = \frac{I_0 \cdot (1 - e^{-\mu \cdot x}) \cdot E \cdot t}{\rho \cdot \sigma \cdot x}$$

208 with F , the absorbed photon flux (ph s^{-1}); E , the energy of X-ray photons (J); t , the exposure time
209 (s); I_0 , the incident flux (ph s^{-1}); m , the mass of paper (kg); x , the thickness of paper (cm); ρ its
210 density (g cm^{-3}); σ , the beam imprint; μ the linear attenuation coefficient (cm^{-1}), which was
211 determined by measuring the incident and transmitted flux impinging stacked sheets as previously
212 described (Gimat et al. 2020).

213

214 *Laboratory XRF spectrometer*

215 W paper was irradiated using a Micro X-ray Fluorescence Spectrometer (M6 Jetstream, Bruker)
216 with a $100 \mu\text{m}^2$ polychromatic beam (0-50 keV). The beam is produced by an X-ray tube with a
217 rhodium anode (50 kV, 600 μA). The instrument is equipped with a $100 \mu\text{m}$ -thick beryllium
218 window and polycapillary optics are used to focus the X-ray beam. The X-ray detector is a 60 mm^2
219 SDD and has a Peltier cooler. For each energy of the X-ray source, the linear absorption coefficient
220 μ was calculated using the coefficients, density and mass fraction of the most abundant components
221 of paper, namely cellulose, water and air (Fig. S4 in the Supplementary data file).

222 The sample area was scanned in successive spots (area equal to the beam size) in one or repeated
223 cycles. The signal to noise ratio of the XRF spectrum depends on the number of cycles and their
224 duration. Two samples were thus exposed during 1 cycle for 500 ms and 3000 ms per spot and
225 received doses of about 3.5 and 22 Gy, respectively. These doses were chosen to be in the same
226 range as the two lowest doses used in the SR experiment at 7.22 keV (7 and 21 Gy). To study the
227 dose-response reciprocity, one sample was exposed repeatedly for 30 cycles with 100 ms exposure
228 per spot, thus being irradiated to 22 Gy.

229 Physico-chemical characterizations

230 After the irradiation, the samples were kept in the dark at 50% RH and 23 °C until analysis. The
231 analyses were usually performed within 6 days, the latter being the shortest possible duration
232 between the irradiation and the analysis. This allowed for immediate damage assessment. Post-
233 irradiation monitoring was carried out by regularly re-examining the samples.

234 *Molar masses*

235 The molar mass distribution and the number- and weight-average molar masses of cellulose M_n
236 and M_w were determined using Size-Exclusion Chromatography (SEC), except for the inked
237 samples which were analyzed using viscometry. For SEC, paper samples (3-5 mg) were prepared
238 and analyzed as described previously (Dupont 2003b). The precision on M_w was between 0.2 and
239 4.0 RSD%, depending on the samples.

240 S , the glycosidic scissions concentration, was calculated using DP_n , with $DP_n = \frac{M_n}{M_{AGU}} = \frac{N_{AGU}}{N_{molecule_t}}$,
241 where N_{AGU} is the total number of anhydroglucose units, i.e monomers ($M_{AGU} = 162 \text{ g mol}^{-1}$) and
242 $N_{molecule_t}$ is the total number of cellulose molecules at any time t (μmoles). As each glycosidic bond
243 scission increases by one the number of cellulose chains, the increase in the concentration of new
244 chains formed is equal to S . The number of scissions being equal to $N_{molecule_t} - N_{molecule_{t0}}$ and N_{AGU}
245 being equal to $6170 \mu\text{mol g}^{-1}$ of paper, hence $S = 6170 \left(\frac{1}{DP_{n_t}} - \frac{1}{DP_{n_{t0}}} \right) \mu\text{moles g}^{-1}_{\text{paper}}$ (Whitmore
246 and Bogaard 1994).

247 In order to avoid polluting the SEC columns with iron, DP of the gelatin-ink coated samples W_GI
248 and R_GI was measured using viscometry in cupriethylene diamine (CED) (TAPPI T 230 om-19
249 1999) with a capillary viscometer Routine 100 (Cannon-Fenske). Irradiation was carried out four
250 days after the ink application. Due to experimental constraints, the viscometry measurements were
251 carried out 29 days after the irradiation. Before the viscometry analysis, the paper samples were
252 chemically reduced with NaBH_4 (same treatment as described above) in order to avoid solvent
253 induced depolymerization. They were dried between blotters and conditioned at 50% RH and 23
254 °C. The viscometric DP (DP_v) was calculated from the intrinsic viscosity $[\eta]$ using the Mark-
255 Houwink-Sakurada equation, by applying the coefficients proposed by Evans and Wallis (Evans
256 and Wallis 1987) : $[\eta] = 0.91 \times DP_v^{0.85}$. DP_v is assumed to be very close to DP_w as M_v has been

257 reported to be closer from M_w than M_n (Ross-Murphy 1985). This allows to parallel DP_v with DP_w
258 with some confidence. The formula proposed by Dupont et al. (Dupont et al. 2018) was used for
259 the conversion of DP_v to DP_n : $DP_n = 1575 e^{(DP_w/3536)} - 1575$.

260 *Hydroxyl radicals*

261 The paper samples were soaked for 3 minutes in a methanolic solution of TPA (98%, Sigma
262 Aldrich) (1 mM). They were left to dry at ambient temperature for 24 h and conditioned at 23 °C
263 at 50% RH. TPA reacts with hydroxyl free radicals (HO^\bullet) in the paper and produces
264 hydroxyterephthalic acid (HTPA), which accumulates in the paper. HTPA was extracted from the
265 paper (2-3 mg) by soaking during three hours in 300 μ l of phosphate buffer (KH_2PO_4 50 mM pH
266 3.2, 70% water:30% methanol), and was quantified by reverse phase liquid chromatography with
267 UV and fluorescence detection (RP-HPLC/FLD-DAD) according to a previously established
268 method (Jeong et al. 2014). HTPA (μ mol g^{-1}) was calculated with respect to the paper dry weight,
269 subtracting the additives weight, to correlate sample behavior based on their cellulosic content only.
270 In order to ensure the quality of the results, it was verified that no HTPA was formed upon
271 irradiating TPA powder.

272 *Colorimetric and UV luminescence measurements*

273 The diffuse reflectance and UV luminescence of the paper samples were measured with a non-
274 invasive UV-Vis-NIR spectroradiometer (Specbos 1211UV, JETI). For UV luminescence, the
275 excitation was centered at 365 nm (with full width half-maximum FWHM = 20 nm). Measurements
276 were normalized to a blue luminescent certified reflectance standard (USFS-461 Spectralon) to
277 correct for light intensity change with time. The maximum intensity of each UV luminescence
278 spectrum was used to monitor the global intensity change. To calculate the change the following
279 formula was used:

$$280 \quad \Delta I(\lambda_{\max}) = I(\lambda_{\max})[irr] - I(\lambda_{\max})[Ctrl]$$

281 with $I(\lambda_{\max})[irr]$ and $I(\lambda_{\max})[Ctrl]$ the intensities of luminescence at the wavelength maxima
282 measured inside (irr) and outside (Ctrl) of the irradiated area, respectively.

283 A spectrophotometer (Konica Minolta, CM-26d) was used to measure the chromaticity
284 coordinates L^* , a^* and b^* in the CIELAB 1976 system. The variation of the color coordinate b^* ,

285 which spans on the blue-yellow scale, was used to quantify the yellowing expressed as $\Delta b^* = b^* -$
286 b_0^* (positive value).

287

288 **Results and discussion**

289 *Calculation of the X-ray dose*

290 The extent of radiation damage usually depends on the X-ray dose absorbed by a sample. Different
291 papers are expected to absorb X-ray differently, especially when heavy elements are present as the
292 latter increase the absorption. Measuring the X-ray dose is thus essential in order to compare
293 changes in paper samples after irradiation on a common basis. In order to do so, it is necessary to
294 define the linear attenuation coefficient (μ) of each sample for each experimental setup and
295 condition (see synchrotron X-ray setup for dose calculation). μ depends on the sample material, but
296 also on the X-ray energy. For the laboratory instrument micro XRF irradiation, μ of the Whatman
297 n° 1 paper (W) was calculated using the entire energy spectrum of the polychromatic beam (Fig.
298 S4b in the Supplementary data file). For the experiments on PUMA beamline, the values of μ for
299 W were measured at the three energies used for the irradiation. The values decreased with
300 increasing energy: $4.29 \pm 0.07 \text{ cm}^{-1}$ at 7.22 keV, $1.02 \pm 0.06 \text{ cm}^{-1}$ at 12.5 keV and $0.31 \pm 0.031 \text{ cm}^{-1}$
301 at 18 keV. The values for μ of the model and historical papers at 7.22 keV are given in Table 2.
302 Fe in W_GI and R_GI and the calcium carbonate in W_Ca and K both increase the photon
303 absorption. Although they contain a similar amount of calcium carbonate and have a similar pH
304 (~8.9), K has a higher μ than W_Ca. This value (9.56) was also the highest of all. This was
305 explained by the higher paper density as well as smaller and more homogeneously distributed
306 mineral particles. This observation also applies to the iron gallate ink coated papers, where the
307 presence of iron on the surface increases the value of μ . The gelatin in W_G seemed to increase
308 only slightly the value of μ , while the opposite was observed in R_G. The artificially aged samples
309 W_hyg, W_ox, W_red and R_hyg also showed a higher X-ray absorption, which might be due to
310 a slightly higher paper density.

311 The absorption coefficients of the archival paper samples varied from 5.60 (LN5) to 8.18 (DCN).
312 These values could again be related to the paper density, with the higher density papers DCN, MI
313 and LN1 exhibiting the higher μ values. The distribution of the fibers and non-fiber components

314 across the sheets also most probably played a role. DCN displayed the highest μ , which was
 315 attributed to the presence of calcium (Table 1), as well as copper and iron (Table 1, Table S1, Figs
 316 S3 & S5 in the Supplementary data file).

317 These results confirmed that the additives influenced the way paper absorbed X-rays and suggested
 318 that structural parameters such as fiber density may also play a role.

319 **Table 2** Linear attenuation coefficient μ of Whatman n° 1 papers (cot), linen rag papers (lin) and archival papers
 320 (archiv) at 7.22 keV, 50% RH.

Model papers								
cot	W	W_hyg	W_ox	W_red	W_G	W_GI	K	W_Ca
μ (cm ⁻¹)	4.29±0.07	5.32±0.07	5.66±0.14	5.28±0.044	4.76±0.016	7.03±0.036	9.56±0.2	6.89±0.12
ρ (g cm ⁻³)	0.51	0.55	0.53	0.53	0.54	0.62	0.68	0.54
lin	R	R_hyg			R_G	R_GI		
μ (cm ⁻¹)	5.01±0.25	5.69±0.28			4.77±0.07	7.99±0.08		
ρ (g cm ⁻³)	0.54	0.6			0.53	0.55		
Archival papers								
archiv	SE	LN5	LN1	DCN	M	M_I		
μ (cm ⁻¹)	6.66±0.036	5.6±0.23	7.21±0.10	8.18±0.6	5.69±0.030	10.05±0.030		
ρ (g cm ⁻³)	0.64	0.62	0.68	0.72	0.47	0.72		

321

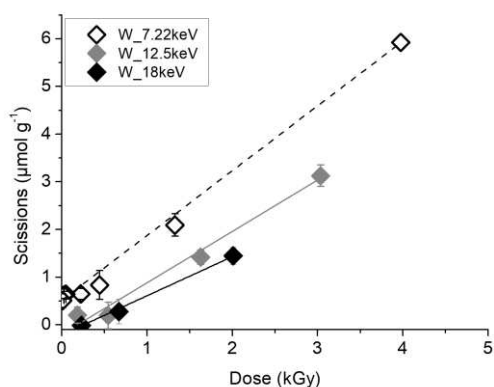
322 *DP and hydroxyl radicals*

323 Impact of the X-ray dose and photon energy

324 A first experiment, carried out with a laboratory Micro X-ray Fluorescence Spectrometer, allowed
 325 assessing the impact of low doses in the range of those usually delivered by these laboratory
 326 instruments. All the unaged W samples, irradiated to a dose up to 22 Gy, had a similar *DP* to the
 327 Control sample (Fig. S6 in the Supplementary data file), indicating that no macromolecular
 328 degradation took place during the irradiation, whether the dose was delivered at once or in several
 329 stages. This is consistent with the lowest observable adverse effect dose (LOAED) for glycosidic
 330 scissions of 0.21 kGy defined in our previous work (Gimat et al. 2020).

331 Exposures to synchrotron X-ray radiation were carried out next to study (i) the variation of the
 332 photon energy and (ii) reach higher doses, similar to those used during spectroscopic examinations
 333 with this type of instrument. Synchrotron X-ray fluorescence experiments usually use energies in
 334 the range of 1 to 20 keV (Glaser and Deckers 2014), sometimes even higher if heavy elements are

335 investigated. To investigate if the degradation was energy dependent, W samples were exposed to
336 three photon energies: 7.22, 12.5 and 18 keV. Fig. 1 shows the glycosidic scissions concentration
337 (S) as a function of the absorbed dose up to 3.9 kGy, at the three energy levels. S increased with
338 the dose in the range of 0 to 6 $\mu\text{mol g}^{-1}$. The impact was very small below the LOAED (0.21 kGy)
339 and was followed by a linear increase from 0.5 kGy upwards. S increased steeply, similarly at 12.5
340 keV and 18 keV. At 7.22 keV, all the values of S were shifted up. A similar energy dependence has
341 been observed for electron beam irradiation (Bouchard et al. 2006) at energies of several MeV.
342 While the photoelectrons created by the X-ray photons in our experiment have much lower
343 energies, it seems like the inverse relation between kinetic energy and cellulose damage remains
344 true in the keV regime. We are not sure why this is the case, but it is noteworthy that the inelastic
345 mean free path (IMFP) varies considerably for electron energies in the range of our experiment
346 compared to the typical average diameter of cellulose fibers. The IMFP for electrons in graphite
347 changes from 9.2 nm at 7.3 keV to 19.5 nm at 18 keV (Shinotsuka et al. 2015). While the exact
348 path lengths in cellulose will likely be slightly different, this shows that it is thus much more
349 probable that a photoelectron produced by 18 keV X-rays escapes the cellulose fibers before
350 causing damage than it is for one produced by 7 keV X-rays. Based on these results, all the
351 following experiments were carried out at 7.22 keV, the most penalizing conditions, to enhance the
352 chances of observing and characterizing damage.
353



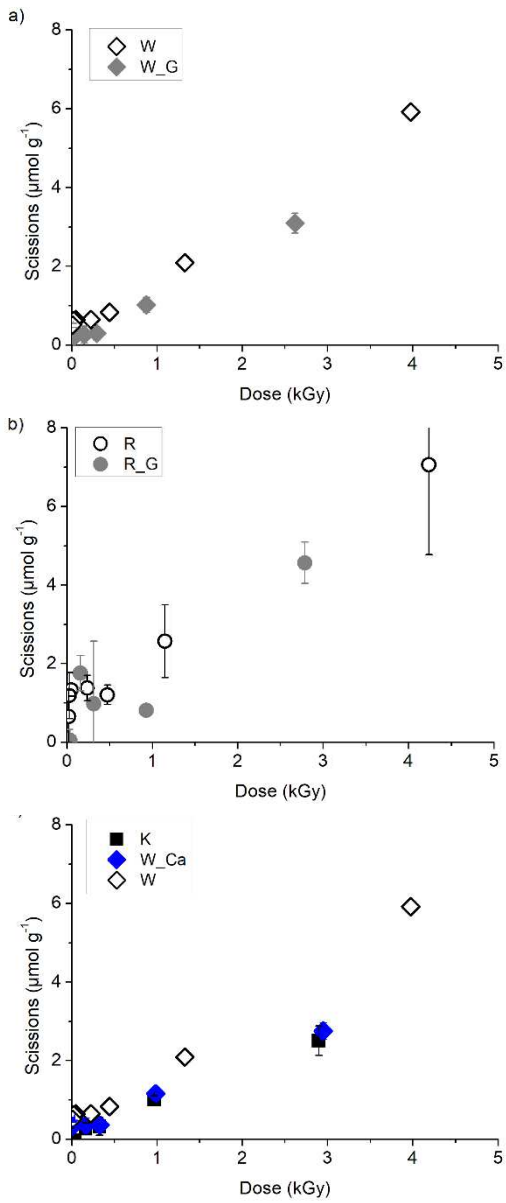
354
355 **Fig. 1** Glycosidic scissions concentration S as a function of the X-ray dose in Whatman no. 1 irradiated at energy
356 levels 7.22, 12.5 and 18 keV at 50% RH

357 Impact of calcium carbonate and gelatin

358 The glycosidic scissions and hydroxyl free radicals concentrations in the unaged papers, in the
359 papers with calcium carbonate and in the papers with gelatin increased in a quasi linear fashion as
360 a function of the X-ray dose, up to $6 \mu\text{mol g}^{-1}$ for W and up to $8 \mu\text{mol g}^{-1}$ for R (Figs. 2 & 3). *S* in
361 W_G was slightly lower than in W Control (Fig. 2a). This observation is consistent with the fact
362 that gelatin size tends to lower the depolymerization rate of cellulose during the degradation
363 induced by aging (Dupont 2003a). Besides gelatin, this could also be partly due to the difference
364 in moisture in unsized vs sized paper (EMC at 23°C of 5.43% and 6.13%, respectively), as moisture
365 was shown to reduce cellulose depolymerization during synchrotron X-ray irradiation (Gimat et al.
366 2020). Because of a larger standard deviations on the data points, this was less clearly established
367 for R and R_G, where *S* values were quasi similar (Fig. 2b) despite the EMC difference (5.78% vs
368 6.57%, respectively) (Table 1).

369 The samples with gelatin (W_G and R_G) produced less hydroxyl radicals than the Control
370 samples (Fig. 3a and 3b). This could be an indication that gelatin was able to scavenge the HO°
371 produced during the irradiation.

372 In both W_Ca and K, *S* increased slightly less as a function of the dose than in W Control, which
373 is especially visible at the high doses, as shown on Fig. 2c. This suggests that calcium carbonate
374 can buffer the acids produced during the X-ray exposure, which is the expected role of the alkaline
375 reserve in paper (Whitmore and Bogaard 1994; Ahn et al. 2013; Rouchon and Belhadj 2016). On
376 the other hand, W_Ca and K showed a larger HO° production than the Control samples (Fig. 3c).
377 This, again, could be due to the pH, as an alkaline medium is known to enhance the lifetime of
378 HO° radicals, and hence the probability that they react with TPA. These results also confirmed
379 previous observations that the HO° concentration did not always correlate directly with the
380 glycosidic scissions concentration, and indicate that other species and mechanisms are involved
381 (Jeong et al. 2014; Gimat et al. 2020).

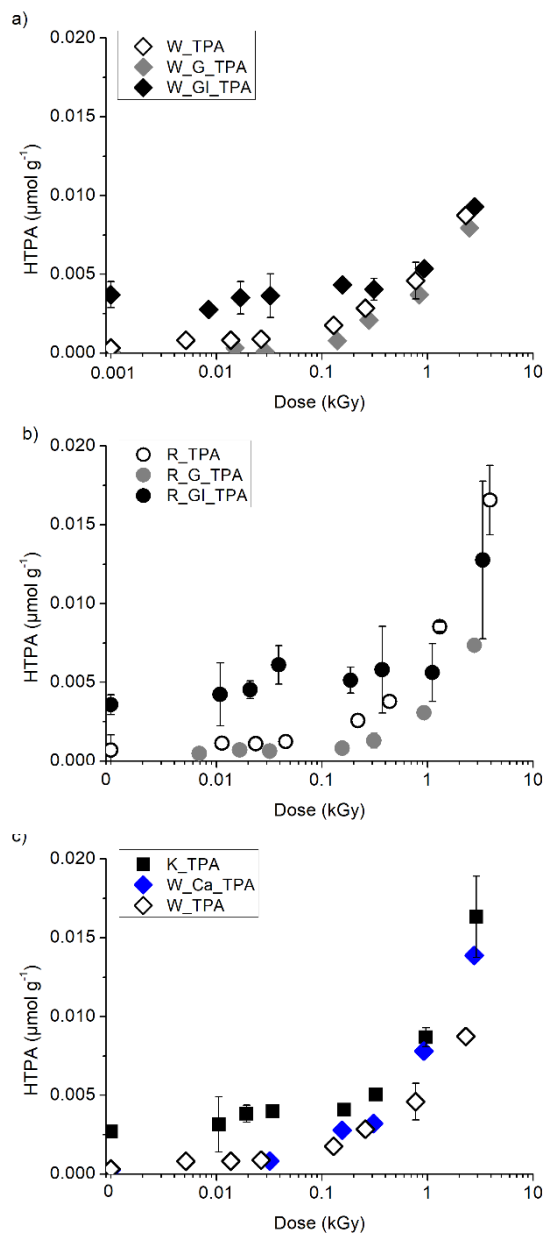


382

383

384 **Fig. 2** Glycosidic scissions concentration (S) in W and R Control papers, papers with gelatin (W_G and R_G) (a, b)

385 and with calcium carbonate (W_Ca and K) (c) as a function of X-ray dose.



386

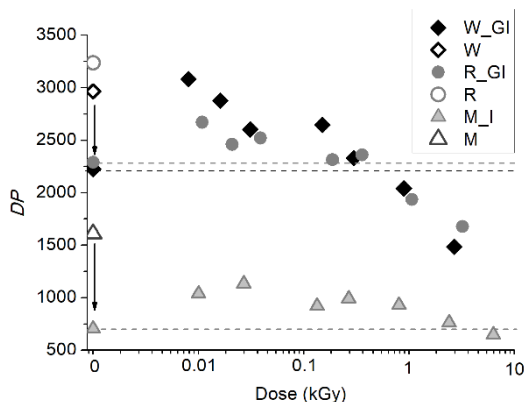
387 **Fig. 3** Impact of gelatin, iron gallate ink (a, b) and calcium carbonate (c) in W and R papers on the HTPA
 388 concentration as a function of X-ray dose. The logarithmic scale is used for easier visualization.

389

390 Impact of the iron gallate ink

391 For the three samples coated with the iron gallate ink (W_GI, R_GI and M_GI), the *DP* of the non-
 392 irradiated samples was considerably lower than that of the Control samples (W, R and M) as

393 represented by the arrows on Fig. 4. This was attributed to strong and almost instant acid hydrolysis
394 and oxidation reactions due to the presence of iron gallate ink, which occurs within the period
395 between sample preparation and analysis (33 days). This has been observed previously (Rouchon
396 et al. 2011, 2016). Indeed, a *DP* loss of 25% and 30% was measured for W_GI and R_GI,
397 respectively, which is consistent with previous observations (Rouchon et al. 2011) for inked
398 Whatman n° 1 where a 24% *DP* loss was recorded within a similar timeframe. A striking
399 observation was made in the low doses range: after irradiation (up to 0.29 kGy for W_GI, 0.36 kGy
400 for R_GI and 2.4 kGy M_GI), the *DP* of the iron gallate ink coated samples was higher than the
401 *DP* of their non-irradiated counterpart (Fig. 4, dashed lines). This was interpreted as having two
402 possible causes. First, it has been shown that iron gallate ink containing papers produce free
403 radicals, such as HO° and other reactive oxygen species (Gimat et al. 2016, 2017). This enhances
404 the chances for free radicals recombination leading to the auto-oxidation termination reactions, and
405 in turn lowers the concentration of radicals accumulated in the paper, thus, preserving cellulose
406 from their attack. Secondly, the crosslinking induced by the recombination of cellulosic radicals
407 could lead to an increase in *DP* which would be measurable if the radicals have high molar mass.
408 This is consistent with the fact that in the low irradiation doses range, HTPA was produced in
409 higher amount in the irradiated ink coated samples W_GI and R_GI than in the Control counterparts
410 W and R (Fig. 3a, 3b), and in similar amount as in non-irradiated W_GI and R_GI. In the higher
411 doses range (from 0.89 kGy for W_GI, 1.1 kGy for R_GI, and 6.3 kGy for M_GI), the samples
412 reached a lower *DP* than the non-irradiated samples, and the HTPA concentration in the samples
413 reached similar levels with and without ink. This was interpreted as an indication that the enhanced
414 scissions induced by the irradiation at the high doses likely exceeded the supposed impact of the
415 free radicals recombination reactions.
416



417

418 **Fig. 4** Viscometric-average degree of polymerization (DP_v) of iron gallate ink coated papers W_GI (a), R_GI (b),
 419 and M_GI (c) as a function of X-ray dose (kGy). The dose is represented on a logarithmic scale for easier
 420 visualization. Control samples without ink or gelatin are represented by the void data points. Arrows represent the
 421 DP drop due to the iron gallate ink. At low X-ray doses, irradiated samples have a higher DP than non-irradiated
 422 control sample (above the dotted lines)

423

424

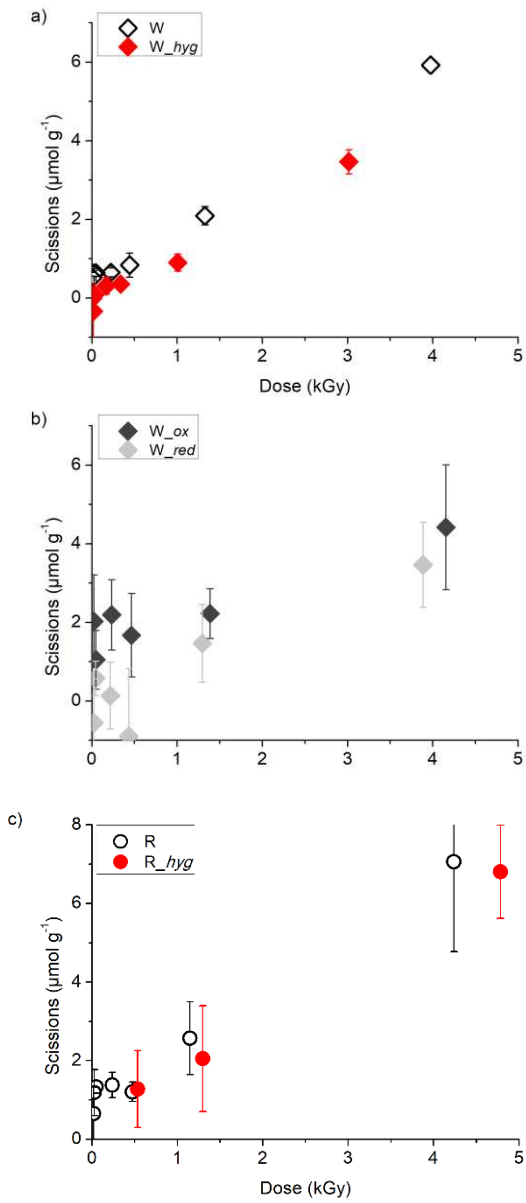
425 Impact of the degradation state

426

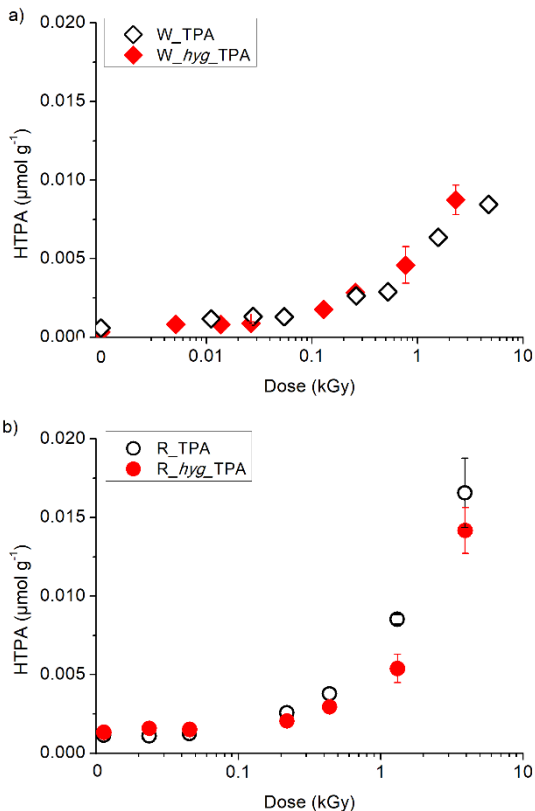
427 The artificially degraded papers (W_hyg, W_ox and W_red) were irradiated at 7.22 keV to
 428 various doses to study if and how the degradation state modifies the impact of the X-rays exposure.
 429 The intent was to possibly extrapolate the results to centuries-old cultural heritage paper. The three
 430 samples had a similar starting DP ($DP_w \approx 1400$, *i.e.* about 50% lower than W) and a different
 431 oxidation state: $N_{Cu} = 0.42$ for W_ox (*i.e.* $5.83 \mu\text{mol g}^{-1}$ total carbonyl groups, as calculated
 432 according to (Röhrling et al. 2002), $N_{Cu} = 0.11$ for W_hyg (*i.e.* $0.67 \mu\text{mol g}^{-1}$ total carbonyl groups)
 433 and $N_{Cu} = 0.02$ for W_red (*i.e.* near-zero carbonyl groups besides the reducing ends) (Table 1).
 434 Figures 5a and 5b show the glycosidic scissions concentration in these samples as a function of the
 435 dose. In W_hyg, S increased linearly with the dose, yet slightly less than in W Control (Fig. 5a).
 436 This suggests that lower DP and/or higher carbonyl groups concentration might lessen somewhat
 437 the impact of X-rays (slight “counter-degradation effect”). For samples that underwent oxidation
 438 (W_ox and W_red), S was in the same range (up to $6 \mu\text{mol g}^{-1}$) as for W and W_hyg at respective
 439 doses (Fig. 5b), yet with higher standard deviations. The main contrast between the two samples is
 440 in the low dose region. In the range –up to 0.5 kGy, while W_red underwent fewer glycosidic
 441 scissions, in W_ox S was higher than in the other samples, with a sharp increase to $1\text{-}2 \mu\text{mol g}^{-1}$ for

442 doses below 1.4 kGy. This indicates that at low doses, a high concentration of carbonyl groups in
443 the paper tended to enhance the X-ray induced depolymerization. In the higher doses range (≥ 1
444 kGy), the depolymerization of all the samples reached the same range, between 4 and 6 $\mu\text{mol g}^{-1}$.
445 The “carbonyl” (“pro-degradation”) effect seemed overridden by the overall stronger
446 depolymerization inflicted by the higher irradiation doses. Fig 6a shows that a similar amount of
447 HO° free radicals was produced in W_hyg and in W, indicating that the free radicals were not fully
448 responsible for the difference in the glycosidic scissions, and that the HO° were not significantly
449 involved in the production of carbonyl groups.

450 Neither a pro-, nor a counter-degradation effect of low *DP* and high oxidation level was observed
451 in the linen rag model papers. *S* extended higher (up to 8 $\mu\text{mol g}^{-1}$) and increased linearly as a
452 function of the dose, yet, in a similar way for the undegraded Control sample and for the degraded
453 R_hyg, despite the *DP* of the latter being 34% lower ($DP_w \approx 1961$) (Fig. 5c). Moreover, above 0.1
454 kGy, slightly less HO° free radicals were detected in R_hyg than in R (Fig. 6b). This, and the large
455 standard deviations on each data point of R samples muddles the interpretations. The extrapolation
456 of the results from a simple machine-made cellulosic paper to a traditional handmade rag pulp
457 paper is not straightforward. The next level of complexity, which was to test the response of
458 archival papers, was thus anticipated as very challenging.



459 **Fig. 5** Glycosidic scissions concentration (S) in aged papers W (a, b) and aged rag papers R (c) as
 460 a function of X-ray dose compared to respective control samples.



461 **Fig. 6** HTPA concentration in control samples, aged W (a) and aged R (b) as a function of X-ray
 462 dose.

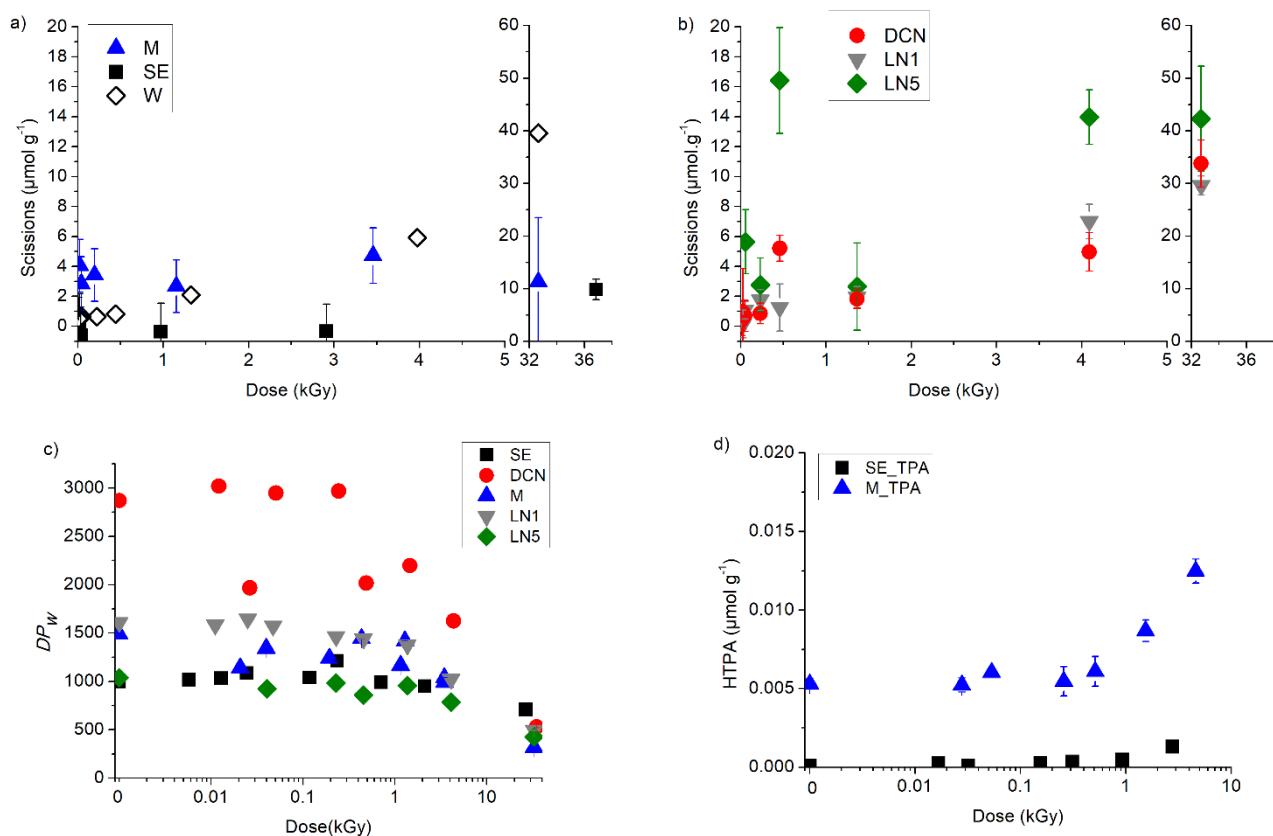
463

464 Archival paper documents

465 For the historic samples irradiated to various doses, *S* values were overall in the same range as
 466 those measured for the model samples. Only LN5 degraded more and showed *S* values at least
 467 twice as high at all the doses tested (Figs. 7a, 7b). However, the depolymerization behavior with
 468 increasing dose was not progressive as observed for the model papers (except for LN1), especially
 469 in the low doses. For instance, SE did not undergo scissions below 3 kGy, and M had a constant
 470 degradation (plateau) response on the whole dose range, with *S* around 3.5 μmol g⁻¹ (Fig. 7a). No
 471 correlation could be made with the *DP* (table 1), the paper constituents or the paper density. All
 472 the papers have similar iron and calcium content, except for DCN which has more calcium due to
 473 the calcium carbonate filler (Fig. S5 in the Supplementary data file). The other possible difference
 474 in composition would be the gelatin content, the latter being a factor that tends to lower the
 475 degradation in the model papers. Unfortunately, the gelatin content of the archival papers was

476 unknown and could not be measured. However, an indirect indication of sizing was given by a
477 water drop absorption test, which showed that M and LN5 were more hydrophobic than DCN (fig.
478 S3 in the Supplementary data file). Even though there can be other reasons for paper
479 hydrophobicity such as reduced porosity for instance, the former two showed higher S than the
480 latter, which would tend to invalidate the aforementioned protective role of gelatin. The differences
481 in S could thus arise from local heterogeneity and to samples' structural parameters such as porosity
482 or constituents' composition. This was not unexpected as in handmade papers the additives are
483 usually not as homogeneously distributed at the microscopic level as in industrial papers.

484 Very high doses, between 32 and 38 kGy, were then tested on the archival papers, as well as on W.
485 The results showed that DCN, LN1 and LN5 were similarly extensively degraded as W, with S
486 comprised between 30 and 43 $\mu\text{mol g}^{-1}$ (Figs 7a & 7b). M and SE resisted surprisingly well, being
487 the least degraded samples, with S close to 10 $\mu\text{mol g}^{-1}$. Despite the different kinetics, most samples
488 approached LODP (Levelling Off Degree of Polymerization) with DP_w W = 345; DP_w M = 318;
489 DP_w LN5 = 426; DP_w LN1 = 495. The least degraded samples were DCN (DP_w = 530) and SE (DP_w
490 = 708) (Fig. 7c). The production of HO° free radicals was measured in SE and M. In SE, HO°
491 concentration was very low, but it was higher in M over the whole dose range reaching a similar
492 amount as in the model papers containing Ca and ink (Fig. 7d). This difference was thus attributed
493 to the slightly higher calcium and iron content in M than in SE (Fig. S5 in the Supplementary data
494 file).



495

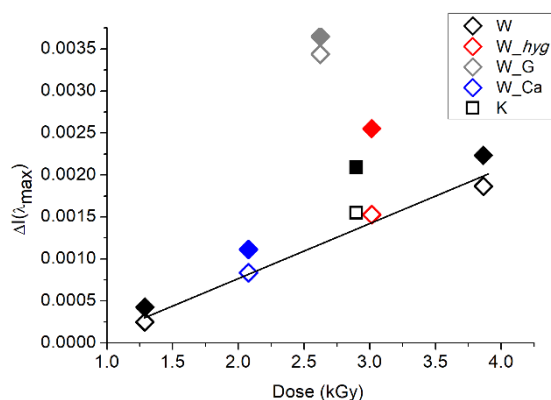
496 **Fig. 7** Glycosidic scissions concentration (S) (a, b), DP_w (c) and HTPA concentration (d) in archival samples as a
 497 function of X-ray dose. Logarithmic scale (c-d) is used only for a better display of the data.

498

499 *UV Luminescence and yellowing*

500 Before the irradiation, all the samples, model and archival papers, exhibited luminescence under
 501 UV when excited at 365 nm, which is a common feature of paper (Fig. S7 in the Supplementary
 502 data file). The model samples W and R exhibited a luminescence maximum λ_{\max} at 432 nm, which
 503 is consistent with previous data (Gimat et al. 2020). The intensity varied depending on the
 504 degradation state, luminophores being produced during the aging, and on the type of additive. For
 505 instance gelatin is expected to show a broad luminescence spectrum with $\lambda_{\max} = 402$ nm (unaged)
 506 and 414 nm (artificially aged at 50% RH and 80° C) (Yova et al. 2001; Duconseille et al. 2016).
 507 After X-ray exposure, no change in the UV luminescence spectral distribution was observed during
 508 the three years monitoring period. The intensity at λ_{\max} [$I(\lambda_{\max})$] of each spectrum was followed

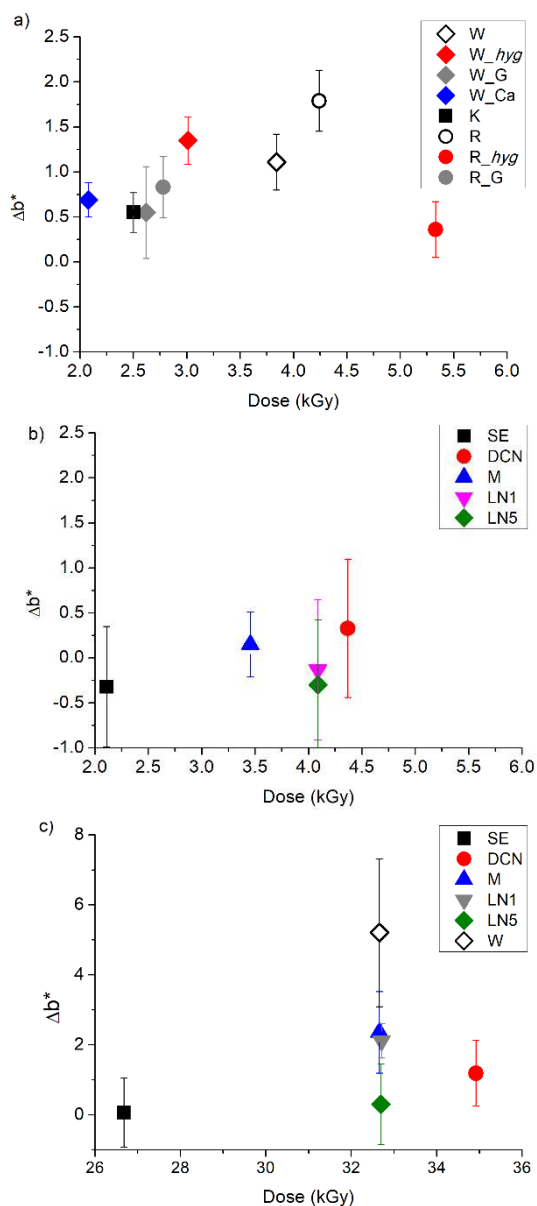
509 over time. After eight months, the area irradiated at 7.22 keV of the model papers (dose range from
 510 2.8 to 4 kGy, depending on the sample) exhibited an increase in the intensity of the UV
 511 luminescence compared to the respective Control samples ($\Delta I(\lambda_{\max})$), as shown Fig. 8 and Fig. S8
 512 (Supplementary data file). All Whatman no.1 model papers (except for the sized samples), showed
 513 luminescence proportionally to the absorbed dose (Fig 8, white marks, linear trendline). The
 514 highest increase in luminescence was observed on the sized samples W_G and R_G with
 515 $\Delta I(\lambda_{\max})_{R_G}$ of 0.0042 and $\Delta I(\lambda_{\max})_{W_G}$ of 0.0036 (R_G data not shown), indicating that a large
 516 quantity of luminophores was produced post-irradiation. These samples were still the most
 517 luminescent samples after 11 months. The luminescence of W_hyg and K grew beyond that of the
 518 other samples between 8 and 11 months. The change in luminescence between unaged and aged R
 519 papers (with no additives) was slower than for unaged and aged W, with a smaller $\Delta I(\lambda_{\max})$ of R
 520 and R_hyg (0.0011 and 0.00015, respectively) compared to W and W_hyg ($\Delta I(\lambda_{\max})$ (0.0022 and
 521 0.0025, respectively).



522
 523 **Fig. 8** $\Delta I(\lambda_{\max})$ of W, 8 months (empty marks) and 11 months (full marks) after X-ray irradiation. $\Delta I(\lambda_{\max})$ is the
 524 subtraction of the luminescence of the non-irradiated area from that of the irradiated area. The black trendline
 525 represents the dose/luminescence response in W Ctrl samples.

526
 527 Colorimetric measurements were carried out three years after the irradiation, on the irradiated areas
 528 and the non-irradiated control samples (Fig. 9). All the model samples showed very small Δb^*
 529 values (Fig. 10a) and a global color change ΔE^* between 0.55 (for K) and 1.87 (for R), i.e. below
 530 the usually accepted level for a just noticeable difference. Among the W samples, the artificially
 531 aged W_hyg had the highest Δb^* (1.35 ± 0.26). The opposite trend was observed with R samples,
 532 where R_hyg had a lower Δb^* than R. This observed behavior difference is all the more valid since

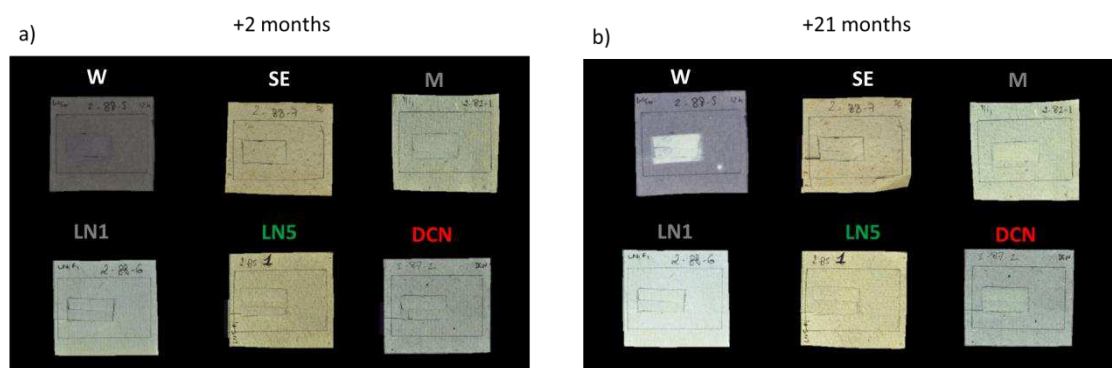
533 the data points for R on Fig 10a correspond to higher doses than for W samples and that R_hyg is
534 the most strongly irradiated sample. This may indicate complex radiochemistry mechanisms of
535 chromophore destruction and chromogens formation. As opposed to the observations after
536 hygrothermal aging of gelatin sized papers (Dupont 2003a; Missori et al. 2006), the irradiation did
537 not modify the yellowing in the gelatin sized papers. This may be related to the radical scavenging
538 properties of gelatin, which could lower the kinetics of cellulose chromophores formation. To sum
539 up, for the model samples, the additive that had the highest impact on luminescence was gelatin.
540 This is most probably due to its own intrinsic luminescence properties and to maybe also to its
541 chromogenic degradation products appearing post-irradiation. Yellowing did not appear to be
542 linked to either the initial conservation state nor to the presence of additives, which indicates
543 complex mechanisms at play of chromogenic structure formation and destruction.
544



545
 546 **Fig. 9** Yellowing increase (Δb^*) of papers measured three years after X-ray irradiation on W and R model papers (a)
 547 and on the archival papers (b, c).
 548

549 The initial UV luminescence spectra of the archival papers showed maxima with different
 550 intensities $I(\lambda_{\max})$ and positions (between 444 nm and 460 nm), which could be due to differences
 551 in the quantity and the type of UV-absorbing groups such as carbonyl compounds, respectively.
 552 This could also be due to a different moisture content, as the latter has been shown to affect the
 553 luminescence properties of paper (Kocar et al. 2005; Castellán et al. 2007). Before irradiation, no

554 correlation between the state of degradation (*DP*) and the intensity of the luminescence of the
 555 papers could be made. Indeed, LN1 and M, both with similar *DP* around 1500, displayed more
 556 intense luminescence than the other historic samples, either more degraded (DP_w LN5 = $1039 \pm$
 557 5.7% , and DP SE = $1000 \pm 9.4\%$) or less degraded (DP DCN = $2869 \pm 6.2\%$). The presence of
 558 additives such as gelatin could not be fully responsible of the luminescence intensity either, as the
 559 latter was not correlated to the hydrophobic properties used as an indication of the gelatin content
 560 (M and LN5 highly hydrophobic, LN1 medium hydrophobic, SE and DCN not hydrophobic)
 561 After irradiation at doses below 4.4 kGy no change was observed on the archival papers. Indeed,
 562 no differences in the UV luminescence (data not shown) nor the yellowing ($\Delta b^* < 1$) were
 563 measured in the irradiated vs the non-irradiated areas (Fig. 9b). At the highest doses tested (26-36
 564 kGy), a slight luminescence appeared on M and DCN twenty-one months after the irradiation (Fig.
 565 10). It thus took almost two years for the luminophores to build up inside the archival papers.
 566 Similarly, as with the model samples, no correlation between the luminescence and the *DP*, or the
 567 glycosidic scissions could be made. A test was made by irradiating M at a very high dose (290
 568 kGy), which induced marginal luminescence, and only after ten months (data not shown).



569
 570 **Fig. 10** Photographs under UV light of W and archival papers exposed to X-ray radiation at doses between 26 and 33
 571 kGy, 1 month (a) and 21 months (b) after the irradiation.

572
 573 Within the high dose range (26-36 kGy), no change was observed for SE and LN5, and the other
 574 archival samples (DCN, M, LN1) exhibited a slight yellowing, with Δb^* of 1.2, 2.4, and 2.1,
 575 respectively (Fig.9c). The strongest yellowing was recorded on W ($\Delta b^* = 5.2 \pm 2.1$).

576
 577 In conclusion, the behavior of historical papers under X-ray is multifactorial and difficult to
 578 predict. This study showed that the response of archival paper to X-ray radiation is very varied, in

579 terms of *DP* losses (the largest being for DCN and LN1), luminescence (M and DCN exhibited the
580 higher luminescence intensity), and yellowing (M and LN1 yellowed the most). These observations
581 led to the conclusion that in the samples with additives and in the aged/degraded samples, optical
582 changes (yellowing and luminescence) were mostly uncorrelated. Moreover, as observed with the
583 model papers, these optical changes were also not directly correlated with the macromolecular state
584 (depolymerization). These observations underline the complex chemistry triggered by the exposure
585 to X-rays.

586

587 **Conclusion**

588 Synchrotron X-ray radiation at energies and doses most often applied for analytical purposes to
589 paper-based cultural heritage has been shown to be detrimental to one-component cellulosic paper
590 (Whatman n°1). However, field situations are complex as historic papers are multiparametric,
591 which interferes with a precise prediction of the effect of X-ray radiation. They usually are
592 degraded to some extent and they contain other constituents besides the biopolymers, such as
593 papermaking additives, ink and their degradation by-products. The present research investigated
594 how these parameters could influence the X-ray radiation-induced degradation when studied
595 separately in model papers. The latter were artificially aged and/or supplemented with additives,
596 which enabled to single out some of the influential parameters. The additives tested were gelatin
597 as sizing agent, and calcium carbonate as filler. Iron gallate ink was applied on some of the gelatin-
598 sized papers, modeling writing/drawing medium. Following the same methodological approach as
599 developed in a previous publication (Gimat et al 2020), the changes were measured immediately
600 after the irradiation at the microscopic level (macromolecular and molecular degradation) and the
601 macroscopic changes embodied by the optical properties (UV luminescence and yellowing) were
602 monitored time-delayed.

603 In the dose range from 0 to 4 kGy, gelatin-sized samples and samples with CaCO₃ underwent a
604 slightly reduced irradiation-induced depolymerization. Surprisingly, up to 0.89-1.1 kGy, the iron
605 gallate ink coated papers had a higher *DP* than the Control samples, which was attributed to a
606 decrease in the free radical initiated autooxidation reactions through radicals recombination and
607 crosslinking. Above these doses, a higher rate of scissions induced by the irradiation prevailed. The
608 production of hydroxyl free radicals was higher in all the samples containing CaCO₃, maybe due

609 to the increased lifetime of HO° at alkaline pH. The depolymerization behavior of the aged model
610 samples was different in the industrially-made (Whatman no 1) and in the handmade papers (linen
611 rags). Higher degradation state (lower *DP*) tended to stabilize Whatman n°1 paper towards X-ray
612 radiation, by lowering the macromolecular degradation. Conversely, the aged handmade paper
613 showed a similar amount of glycosidic scissions as the unaged counterpart. Carbonyl groups in the
614 artificially aged Whatman n°1 papers increased the glycosidic scissions in the low doses range,
615 below 0.5 kGy. Confirming previous results (Gimat et al. 2020), the optical changes appeared with
616 considerable delay, often one year after the irradiation, and could not be directly correlated to the
617 initial *DP* nor to the glycosidic scissions concentration that grew steadily during this post-
618 irradiation period (dark storage, room temperature). As expected, the archival papers made of linen
619 rags had an overall more complex X-ray exposure behavior than the model papers. First, the *DP*
620 was roughly constant in the low doses range below 4 kGy, which led us to increase the irradiation
621 doses. The large dispersion of the data was attributed to the paper macroscopic and microscopic
622 heterogeneity in terms of additives distribution degradation state and microstructure, but also to
623 the presence of multiple possible pro- and counter-degradation constituents in historic papers acting
624 synergistically. At very high doses (26-36 kGy), the archival papers reached the LODP
625 immediately upon irradiation, similarly as Whatman n° 1. No color change or UV luminescence
626 were observed within one year after the exposure at those high doses. After twenty-one months,
627 two archival papers showed a slight UV luminescence, but no clear connection with the
628 depolymerization or with the constituents could be made. These contrasted results indicate that
629 laboratory samples have their limitations to model archival/historic papers and that the
630 radiochemistry at play is rather complex. However, the observation that, overall, the historic papers
631 resisted better the X-ray exposures than modern papers is an important step forward that enables
632 to consider analyzing historic papers with better confidence. This work focused on the paper
633 material in chemical terms. Considering paper microstructure properties in the future may shed
634 more light on the limitations encountered.

635 A significant outcome of this work was to show the importance of carefully choosing the analytical
636 conditions that limit the exposure, thus the dose, when analyzing genuine artefacts using X-rays.
637 This can be achieved either by applying higher energy, or using low exposure times, and always
638 maintaining some humidity, as demonstrated in our previous work. The mid-range relative
639 humidity value recommended for paper-based cultural heritage storage is thus a good compromise.

640 Documenting the exact location of the X-ray photons impact and implementing a long-term
641 monitoring of the eventual changes through regular photographic follow-up under both UV and
642 visible lights are also advisable.

643

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652

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