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Short- and long-term effect of radiation damage in cotton paper

The analysis of cultural heritage artefacts with ionizing radiation has rapidly increased in popularity over the last decades - in particular at synchrotron sources - leading to many fascinating new discoveries. However, the damage inflicted to the materials under study during the irradiation is still largely unknown. Organic samples, such as paper, are especially vulnerable to degradation by X-rays. In this work we quantify the radiation damage on a molecular level and show that the chemical reactions triggered promote cellulose degradation and continue to alter the material for several months after the irradiation took place.

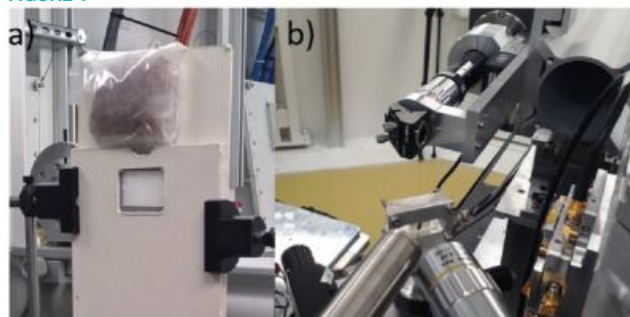
Paper artefacts are an important part of our cultural heritage. Aside from drawings and other paper-based artworks, archival and library material such as private letters and public documents also give us a unique insight into the written heritage of past generations. A large part of this immense cultural heritage treasure is still hidden from the public at large, but is of enormous importance to historians and codicologists. Special care is needed for their conservation as they can easily be destroyed by fire, water damage or attacks from microorganisms and insects. While the composition of paper is complex and varied considerably over the course of history, its basic structural level consists of a network of plant fibers made of cellulose. Cellulose is the most abundant naturally occurring macromolecule on earth. It is a polysaccharide with the chemical formula $(C_6H_{10}O_5)_n$. To understand the fundamental radiochemistry of paper, in this research we used a simple paper (Whatman no. 1), made of cotton linters, which is almost exclusively cellulose (99%).

IRRADIATION

The use of ionizing radiation, and especially synchrotron X-ray, for the analysis of paper artefacts has increased rapidly over the last decades [1]. For example, the use of X-ray fluorescence imaging allows scientists to reveal blacked-out ink writings, thus unearthing information that was beyond reach for centuries [2]. However, when the X-ray photons interact with cellulose, they can break chemical bonds and depolymerize the molecules. This initiates further chemical degradation that can continue on larger timescales than the irradiation duration.

To recreate conditions as close as possible to a real synchrotron experiment, in this study we used the PUMA beamline (Figure 1). The paper samples were irradiated with different X-ray doses using the macro beam ($1 \times 2 \text{ cm}^2$) and with a photon energy of 7.22keV (wavelength 1.7 Å). The effect of paper moisture content was investigated using different silica gels to maintain three different relative humidity levels during irradiation (Figure 1a).

FIGURE 1



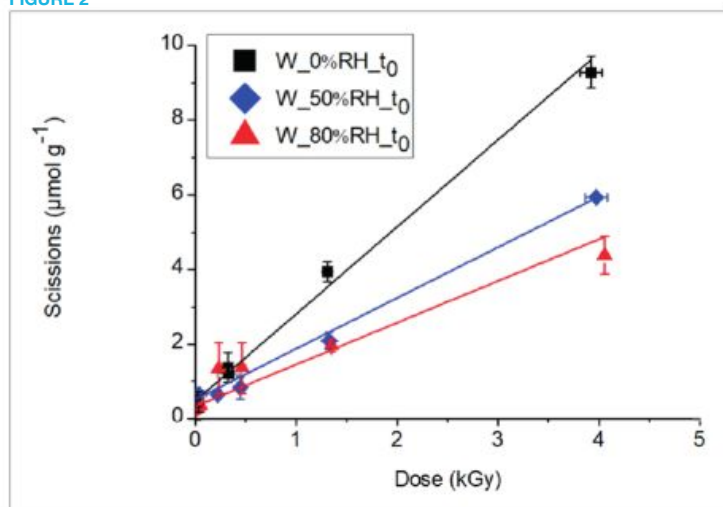
MONITORING THE RADIATION DAMAGE ON THE MOLECULAR SCALE

When evaluating radiation damage, it is important to look beyond macro-scale observations, such as a color change for instance, and focus on the changes incurred in the molecular structure of the material, due to the interaction with photons. To characterize the depolymerization, indicator of hydrolytic scissions of cellulose, and hence molecular length shortening and fiber damage, size-exclusion chromatography (SEC-MALS-DRI) was used. High-performance liquid chromatography (HPLC-FLD-DAD) allowed the quantification of hydroxyl free radicals, which are indicators of the cellulose auto-oxidation phenomena. This approach was complemented by macro-scale observations such as UV luminescence, spectrometry and photography.

SHORT AND LONG TIME SCALES

Our analysis showed that chemical damage happened on the molecular scale during the irradiation, starting from a relatively low dose of 21 Gy. It was observed that the higher the dose of SR-X radiation absorbed by the paper, the greater the depolymerization and the higher the concentration of hydroxyl free radicals. This behavior can be seen in Figure 2, which shows glycosidic scissions as a function of the dose for paper samples irradiated at different relative humidity conditions. The impact of humidity is unmistakable; there is less damage in humid paper than in dry paper.

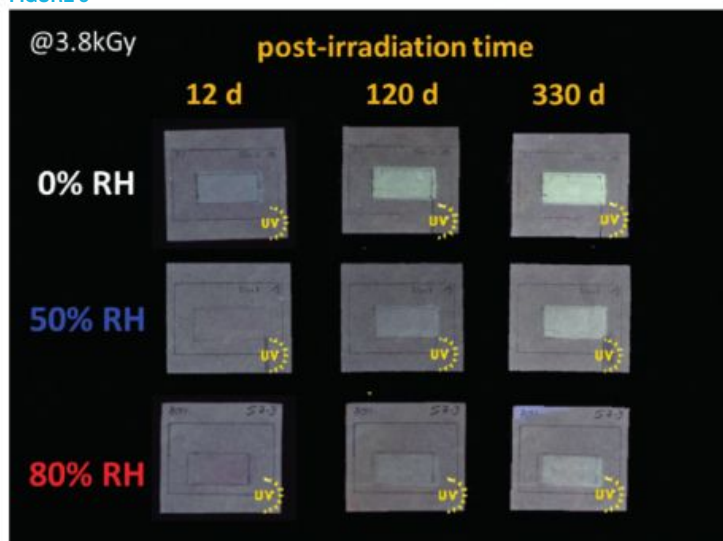
FIGURE 2



To monitor irradiation changes over longer time scales, the samples were stored under controlled thermohygro-metric conditions and the physio-chemical changes were studied over a period of two years. We could show that the UV-luminescence signal and the yellowing of the paper (Figure 3), as well as the depolymerization and the auto-oxidation of cellulose continued increasing over time, indicating that the chemical degradation reactions were still taking place several months after the irradiation. This finding is important for conservators, as it shows that a simple check for macroscopic changes after the irradiation does not preclude potential future harm to the material.

Our results quantify the impact of X-rays radiation to paper samples at both the molecular and macroscopic scale for the first time. Further work is in progress to better understand the effect of natural aging and the impact of additives (sizing, inks, fillers) that are part of real artefacts.

FIGURE 3



PUMA BEAMLINE



Associated publication

Short and long term effects of X-ray synchrotron radiation on cotton paper.



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Captions

FIGURE 1: Experiments on PUMA beamline: a) paper inside a plastic bag with silica gel to maintain a stable relative humidity during irradiation with the macro beam and b) paper irradiation with the micro beam.

FIGURE 2: Glycosidic scissions concentration (S) as a function of SR-X dose. The irradiation took place at different relative humidity levels (0%, 50% and 80%) at room temperature.

FIGURE 3: UV luminescence image of Whatman no. 1 paper samples irradiated on PUMA beamline at 3.8 kGy at various relative humidity levels (0%, 50% and 80%) at room temperature. Luminescence appears in the irradiated area (1x2 cm²) gradually and differently depending on the relative humidity.