Investigation of parchment alteration by correlative nonlinear optical microscopy and infrared nanoscopy

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Parchment was the main writing material in the Middle Ages in Western Europe up to the growth of paper production in the 14-15th centuries. Made from an untanned animal skin it was preserved by liming, scraping and drying the skin under tension. Parchment is very sensitive to water, causing in extreme case the denaturation of collagen, its main constituent, to gelatin. The aim of this work is to demonstrate the interest of using two complementary nondestructive techniques, nonlinear optical microscopy and IR nanospectroscopy, to better understand the mechanisms of degradation.

Nonlinear microscopy is an emerging and promising optical technique for the investigation of artworks. The potential of pump-probe microscopy has been proven for the discrimination of pigments in painting [1] and nonlinear optical (NLO) microscopy based on simultaneous detection of two photon excited fluorescence (2PEF) and second harmonic generation (SHG) has been shown to give insight into the structure and the nature of the components of varnishes (binders, fillers, pigments) [2]. This latter technique performs non-invasive three-dimensional (3D) imaging with micrometer-scale resolution based on an intrinsic optical sectioning. A key advantage is probably its multimodal capability with different modes of contrasts that are directly linked to the structural and chemical nature of the materials. SHG signals are specific for non-centrosymmetric structures, with no counterpart in usual (linear) optical techniques. Fibrillar collagen emits strong SHG signals as widely used in biomedical imaging (cornea, skin…).

In this study [3], we show that SHG microscopy provides structural information of the 3D organization of the fibrillar collagen within parchments. Historical parchments at different states of degradation are investigated going from a well-preserved to a gelatinized parchment. We demonstrate that during degradation SHG signals vanish due to molecular and/or macromolecular modifications. We finally apply this investigation to an historic maritime map from the 17th century [3].

Infrared spectroscopy provides information on collagen secondary structure and is used to characterize the parchment gelatinization. To have a better insight into collagen modifications, analysis have to be performed at the fibers (~1-5 µm) or fibrils (~100 nm) scale, therefore infrared technique with a high spatial resolution is required. We report the first results in parchment fibers analysis at the nanometer scale using nanoinfrared spectroscopy (nanoIR, AFM imaging coupled with IR illumination to collect IR spectra with nanometer scale resolution).

The correlation of both NLO microscopy and nanoIR provides morphological and chemical information at different length scales about collagen degradation. NLO microscopy therefore appears as a powerful tool to reveal collagen degradation in a non-invasive way. It should provide a relevant method to assess or monitor the condition of collagen-based materials in museum and archival collections.

[1] T. E. Villafana, W. P.Brown, J. K. Delaney, M. Palmer, W. S.Warren, M.C. Fischer, Proc. Nat. Ac. Sci. **111** (2014) 1708-1713
[2] G. Latour, J.-P. Echard, M. Didier, M.-C. Schanne-Klein, Opt. Express **20** (2012) 24623-24635
[3] G. Latour, L. Robinet, A. Dazzi, F. Portier, A. Deniset-Besseau, M.-C. Schanne-Klein, Scientific Reports (accepted)