SOCIETÀ ITALIANA DI FISICA

SIF

IYL 2015

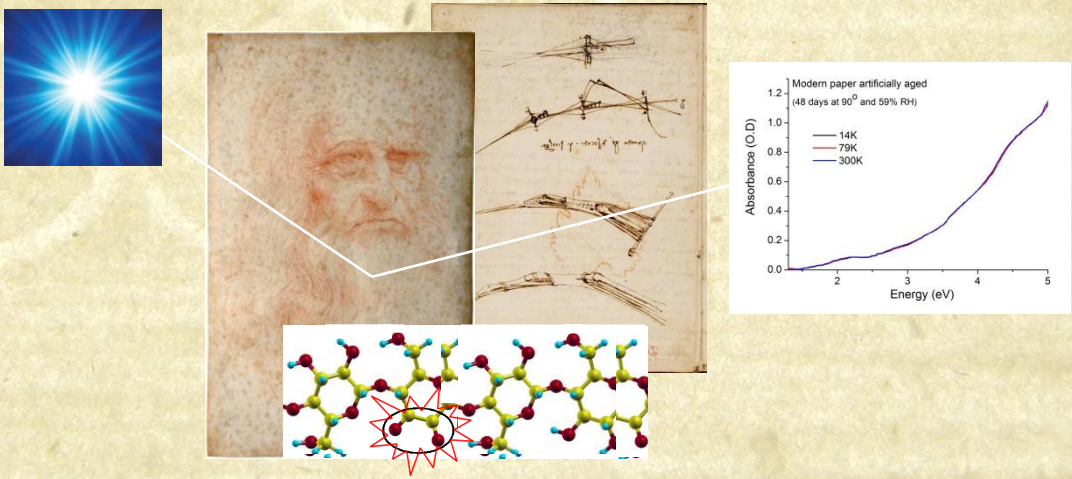
101°

CONGRESSO NAZIONALE

Roma, 21 - 25 settembre 2015

# Optical properties of ancient paper are governed by structural disorder of cellulose

Braidotti M. C., Mosca Conte A., Violante C., Conti C., Fastampa R., Pulci O., Lojewska J., Missori M.




ISCA

UNIVERSITÀ DEGLI STUDI DI ROMA TOR VERGATA

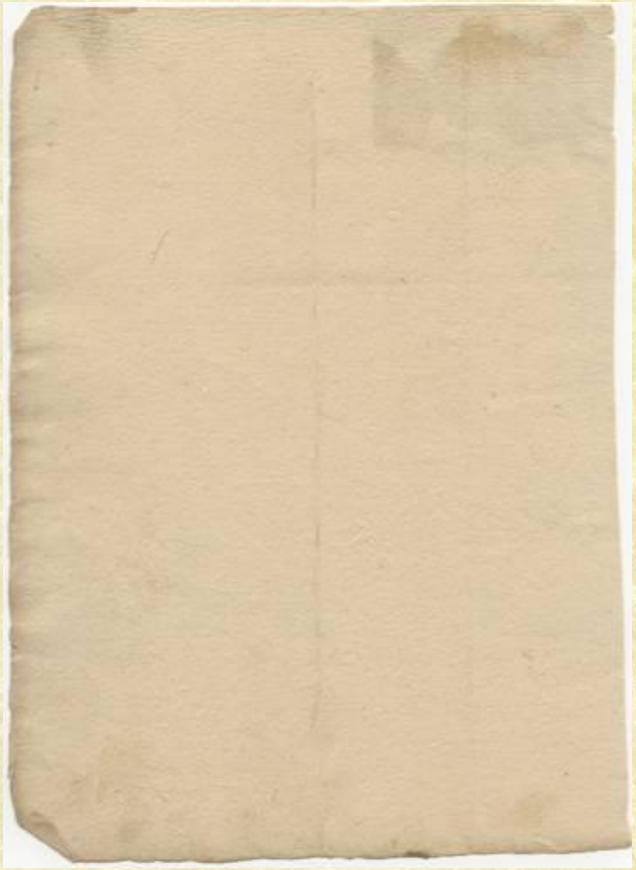
ETSF

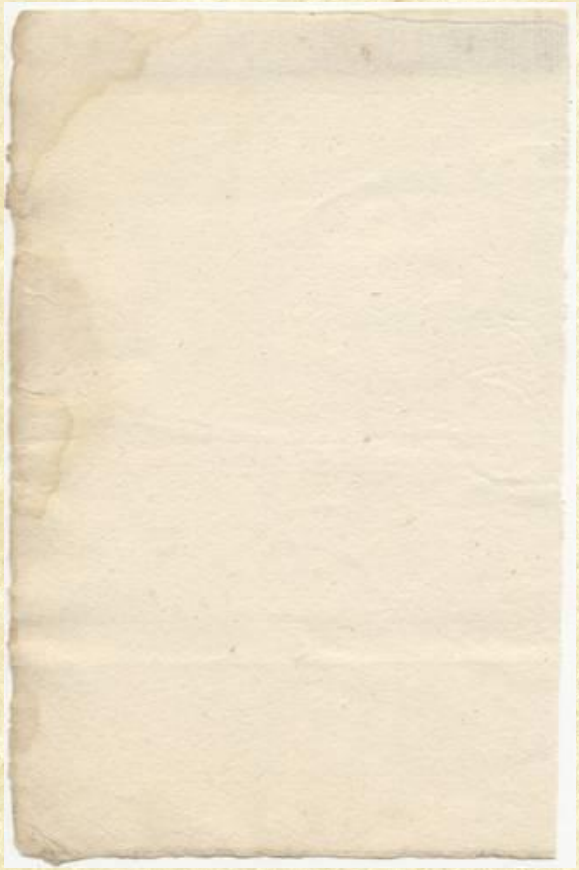
SAPIENZA UNIVERSITÀ DI ROMA

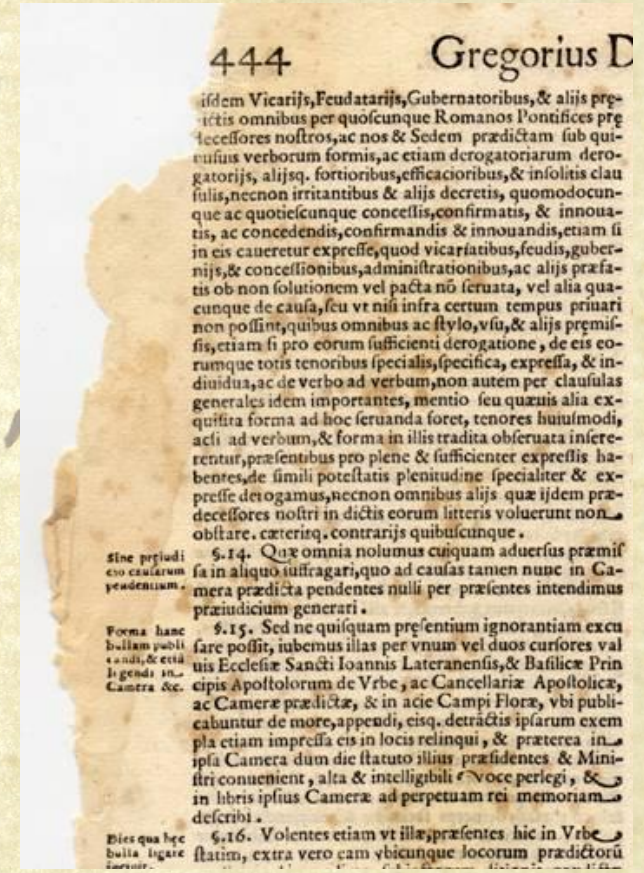
UNIVERSITÀ DEGLI STUDI DE L'AQUILA

JAGIELLONIAN UNIVERSITY IN KRAKOW

# Yellowing of ancient paper

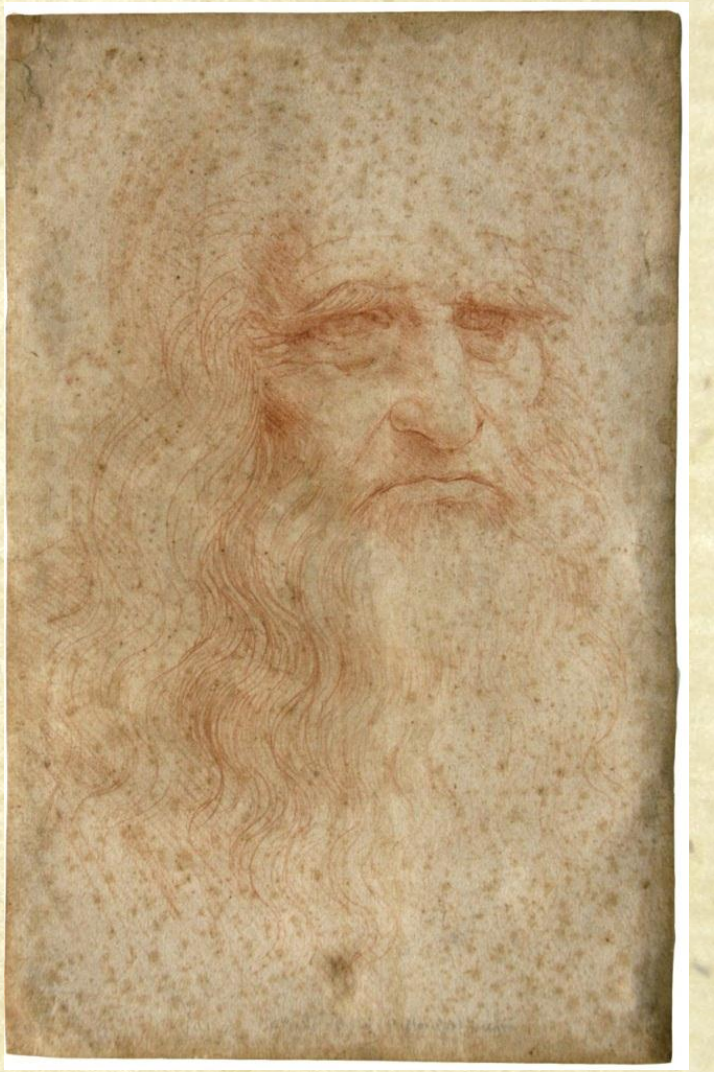






1898


2012

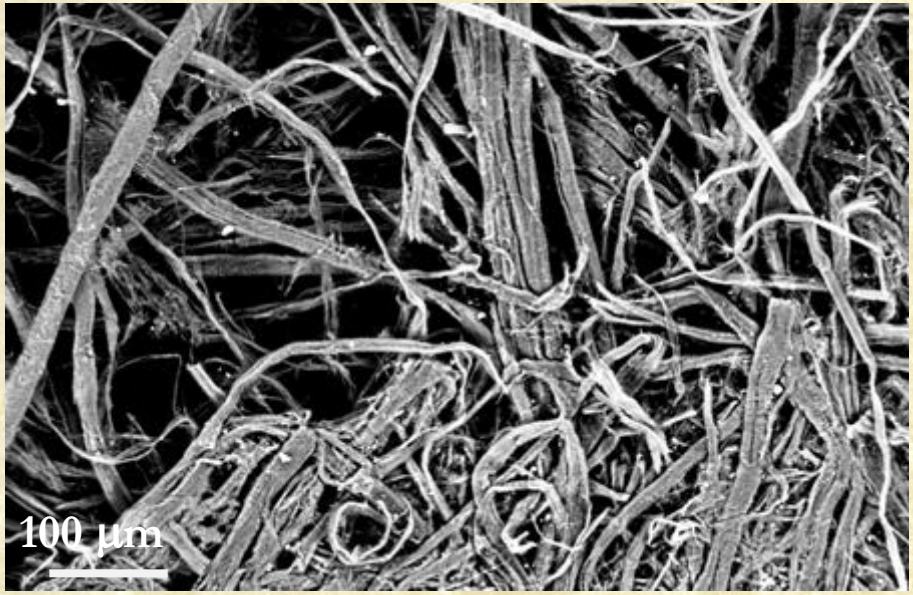


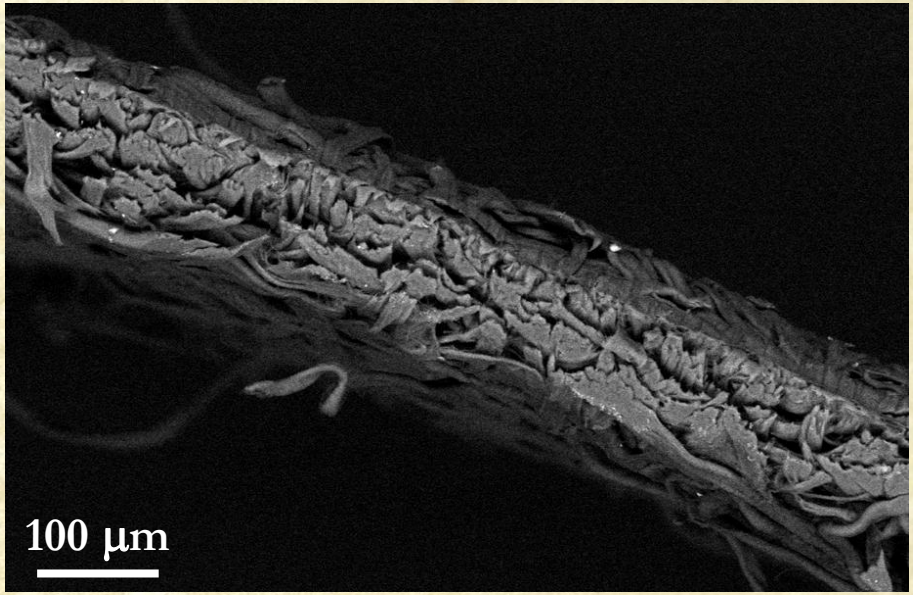
APPLIED PHYSICS LETTERS **104**, 224101 (2014)

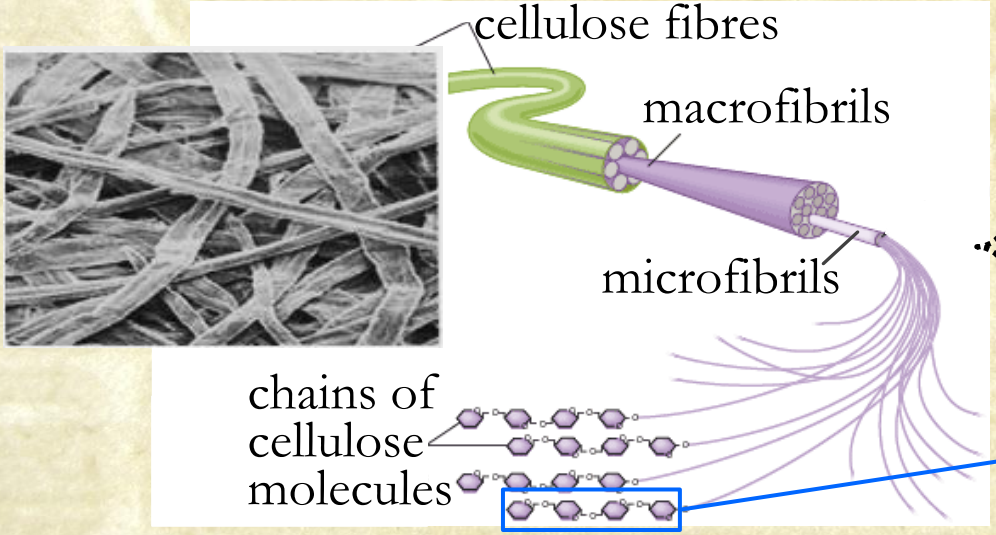
**Visual degradation in Leonardo da Vinci's iconic self-portrait: A nanoscale study**

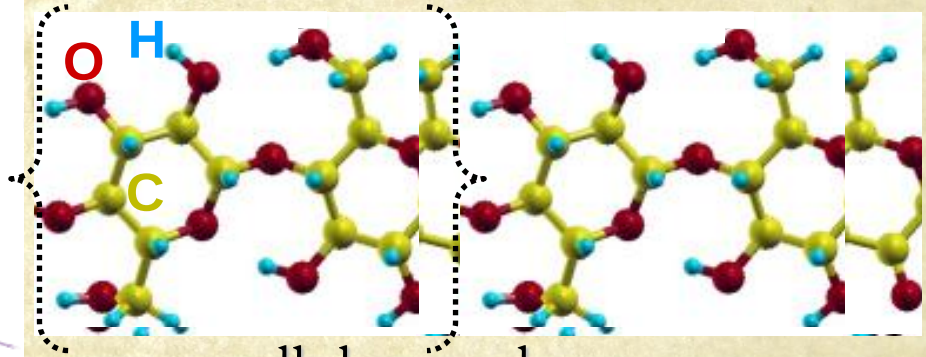
A. Mosca Conte,[1] O. Pulci,[1,2] M. C. Misiti,[3] J. Lojewska,[4] L. Teodonio,[1,5] C. Violante,[1] and M. Missori[5]

# Paper: morphology and chemistry



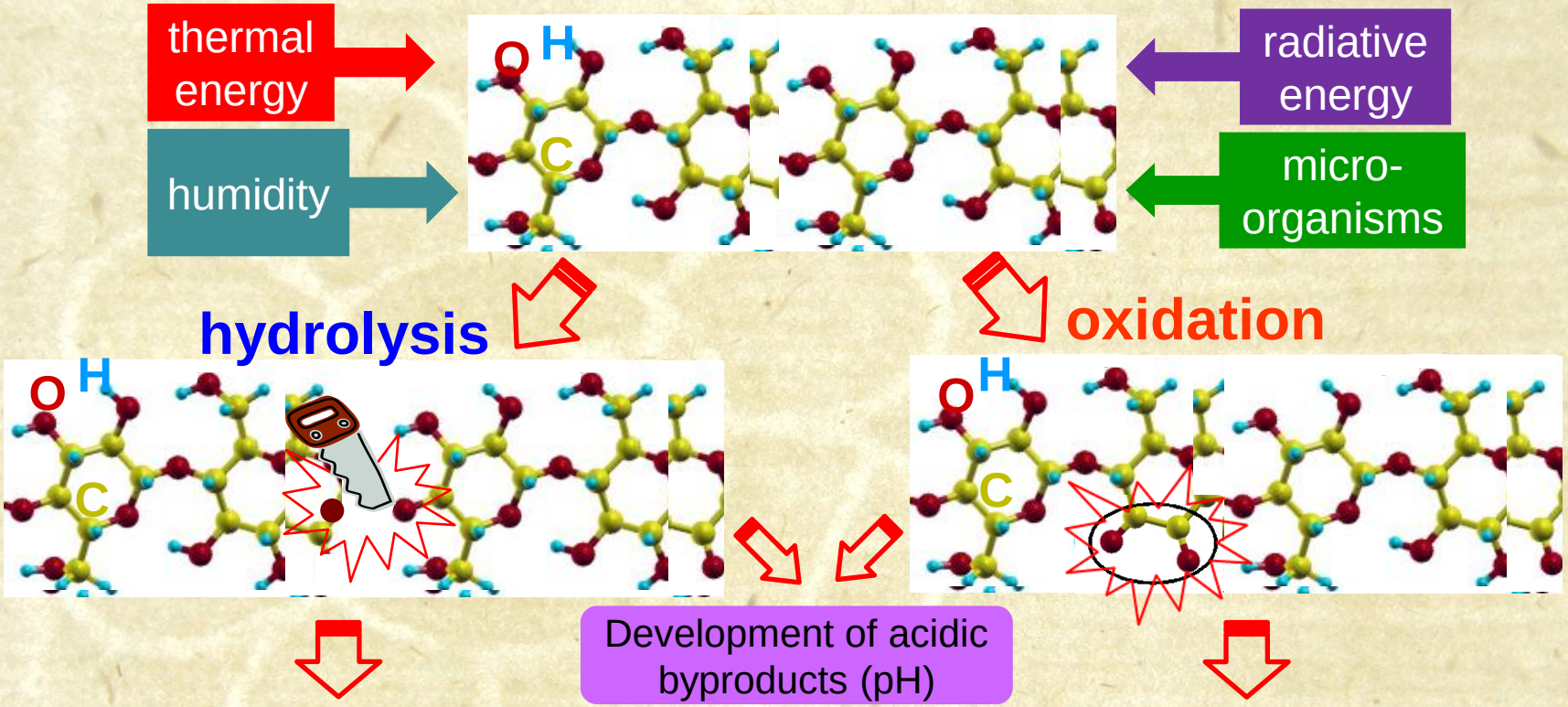




cellulose polymer:

high temporal stability

M. Missori, et al., Phys. Rev. Lett. **97**, 238001 (2006).

# Degradation at the molecular scale




Variations of mechanical and morphological properties

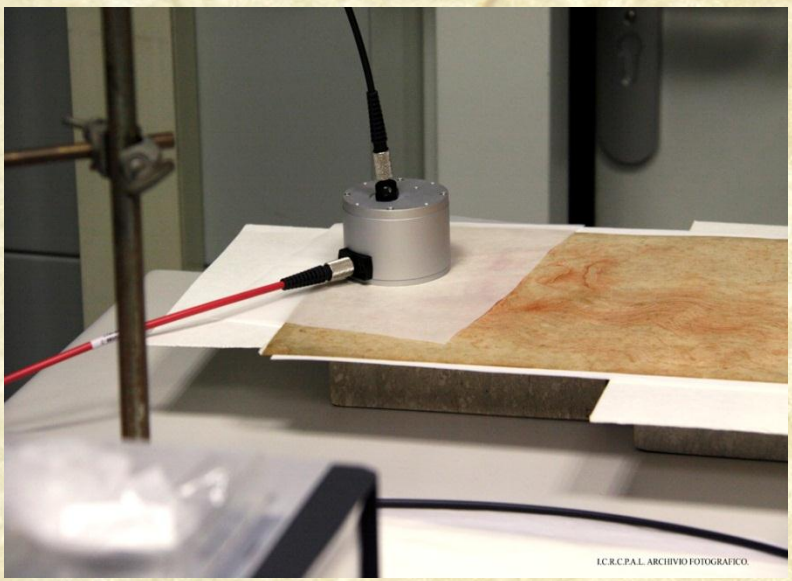
**UV-Vis active oxidized groups (chromophores)**

Variation of optical properties (yellowing)

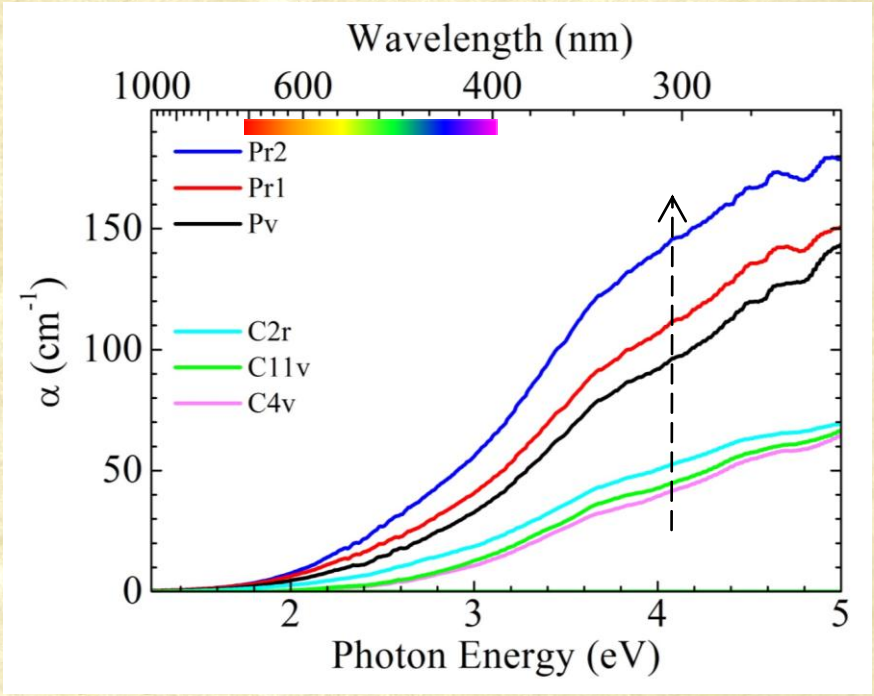
M. Bicchieri, et al., J. of Raman Spectr. **37**, 1186 (2006).

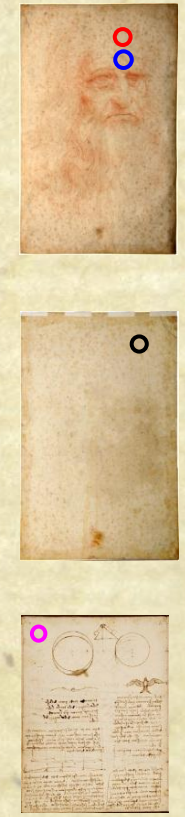
T. Lojewski, et al., Carbohydrate Polymers **82**, 370 (2010).

# UV-Vis spectroscopy of ancient paper




$$\alpha(\lambda) = s_\infty(\lambda)\frac{(1-R_\infty)^2}{R_\infty}$$



PHYSICAL REVIEW B **89**, 054201 (2014)

**Optical response of strongly absorbing inhomogeneous materials: Application to paper degradation**

M. Missori,[1] O. Pulci,[2,3] L. Teodonio,[1,4] C. Violante,[2] I. Kupchak,[5] J. Bagniuk,[6] J. Łojewska,[6] and A. Mosca Conte[2]

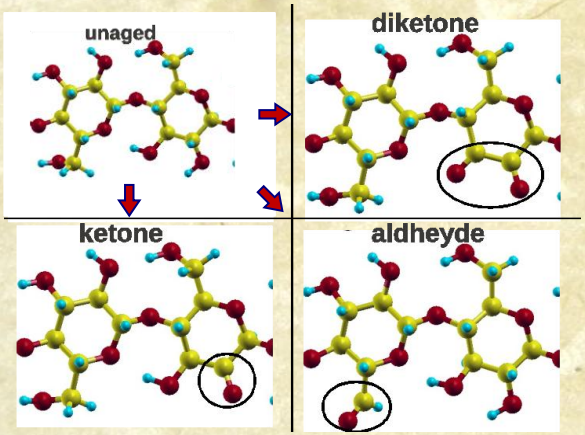
# Theoretical simulations of cellulose UV-Vis absorption

Density Functional Theory (DFT)

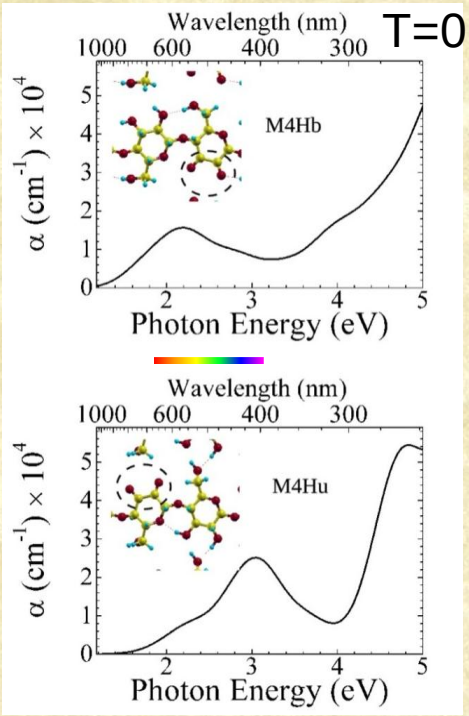
http://www.quantum-espresso.org/

Time-Dependent DFT

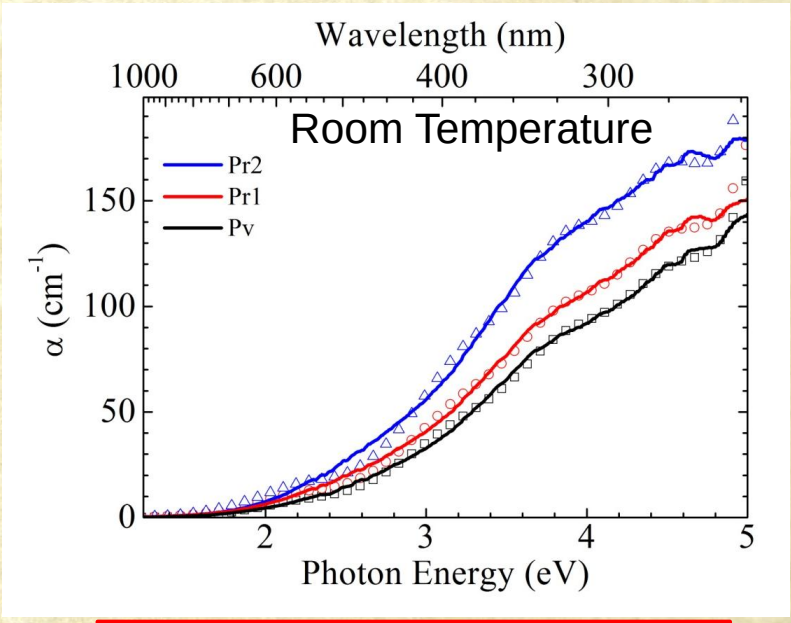
http://dp-code.org




T=0K+smearing




diketones




Chromophores concentration = 6 mmol/100g of cellulose

PRL 108, 158301 (2012) PHYSICAL REVIEW LETTERS week ending 13 APRIL 2012

**Role of Cellulose Oxidation in the Yellowing of Ancient Paper**

A. Mosca Conte,[1] O. Pulci,[1,2] A. Knapik,[3] J. Bagniuk,[3] R. Del Sole,[1] J. Lojewska,[3] and M. Missori[4,*]

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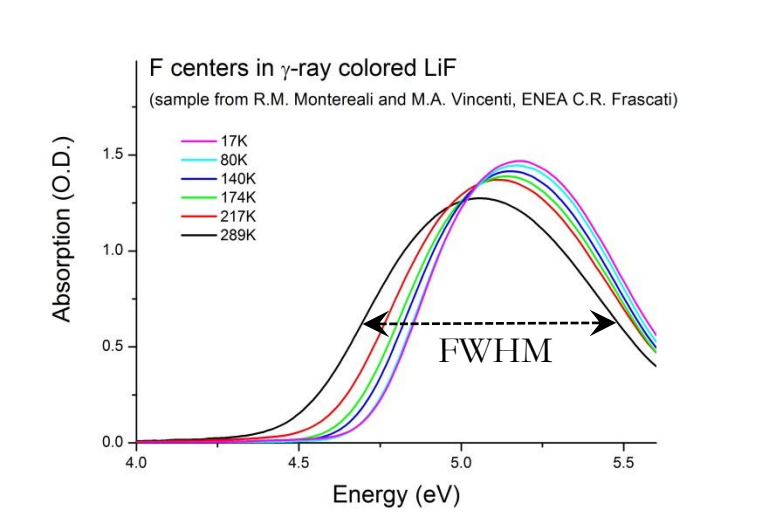
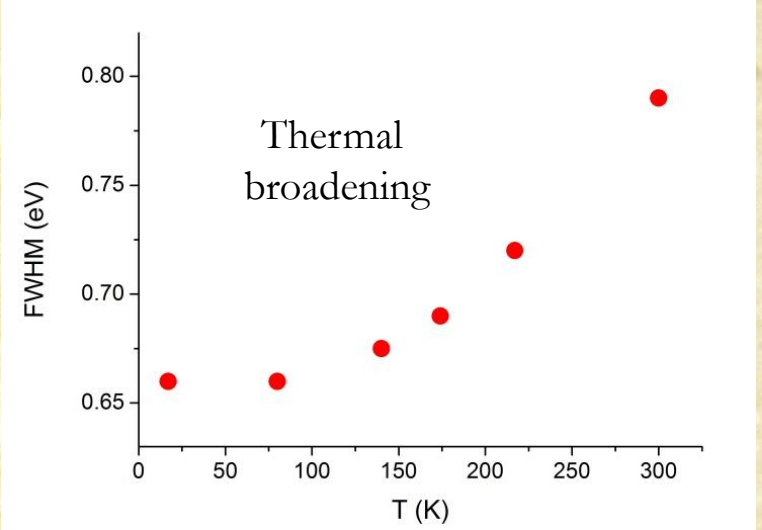
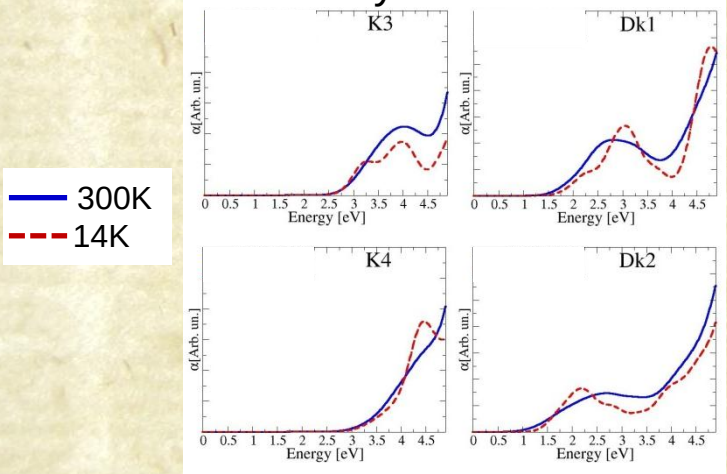
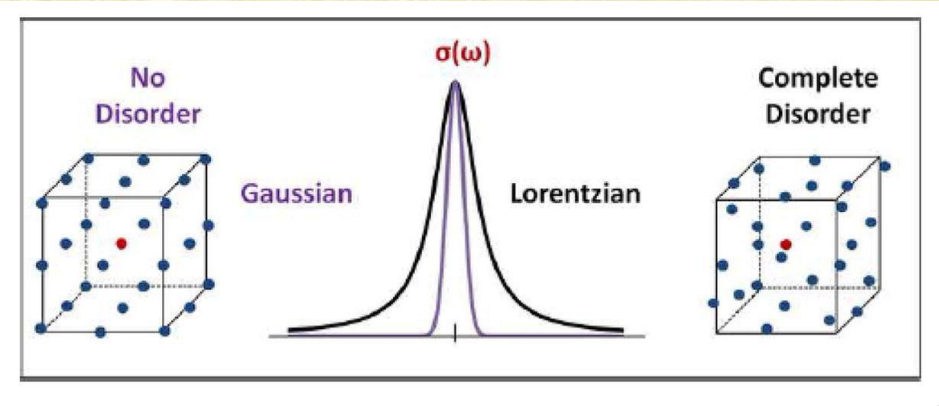
# Temperature effect on spectral line shapes of chromophores in solid




Molecular dynamics simulations

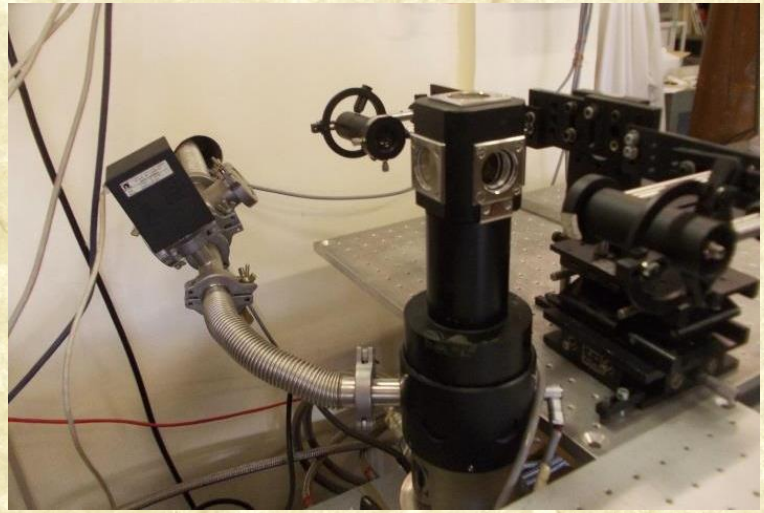


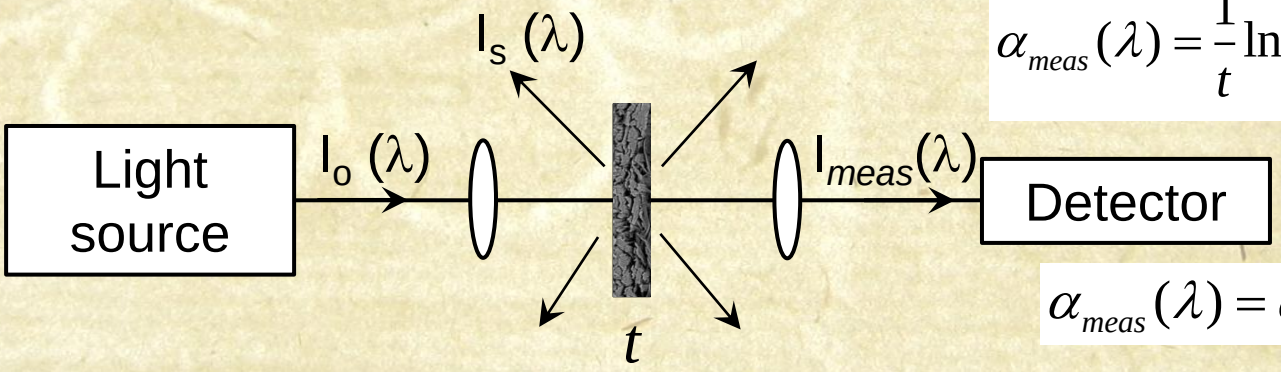




Disorder-induced broadening of the absorption line shape of a chromophore in a solid matrix

Prathamesh M Shenai et al., *Disorder and spectral line shapes in two-level systems*, Chem. Phys. Lett. **582**, 66-70 (2013)

# Experimental set-up for low-temperature UV-Vis spectroscopy of paper






$$\alpha_{meas}(\lambda) = \frac{1}{t} \ln \frac{I_0(\lambda)}{I_{meas}(\lambda)}$$

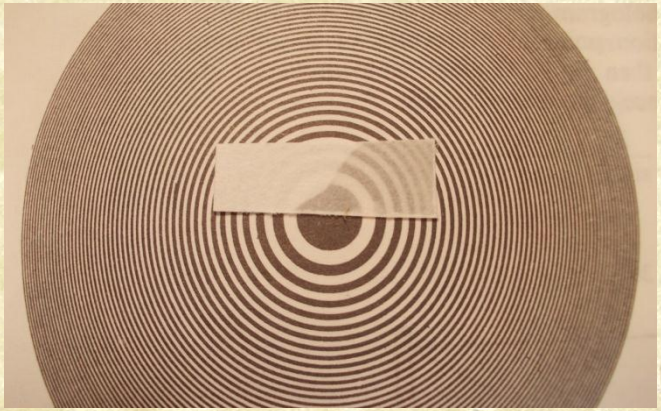
$$\alpha_{meas}(\lambda) = \alpha(\lambda) + \alpha_s(\lambda)$$

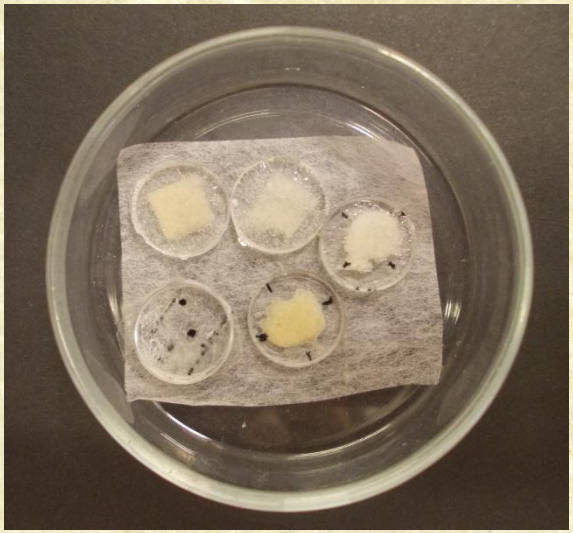
$$\frac{I_s(\lambda)}{I_0(\lambda)} \propto t\sigma(\lambda) \propto t(n_c^2 - n_m^2)^2$$

# Decreasing the scattering of paper

Refractive index of cellulose $n_c \simeq 1.5$ → **refractive index matching** material must be cryogenic, UV transparent, low viscosity → enamel of acrylate polymers ($n_c \simeq 1.46$)

refractive index matching of a paper sample



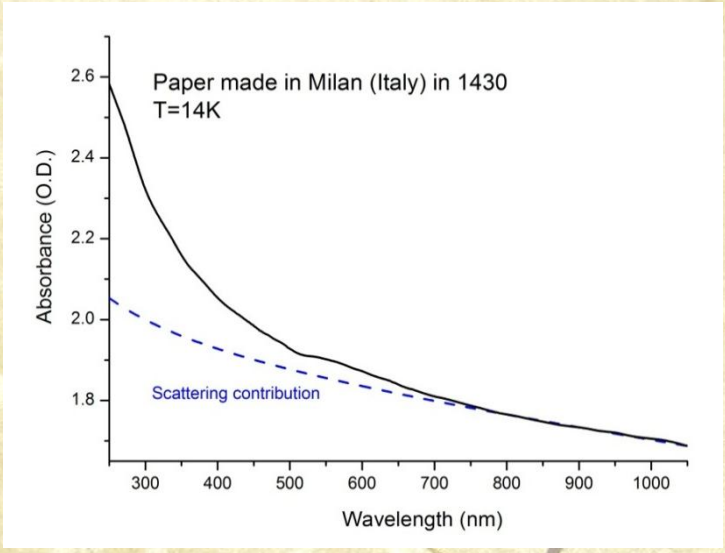


paper samples on a fused silica substrate

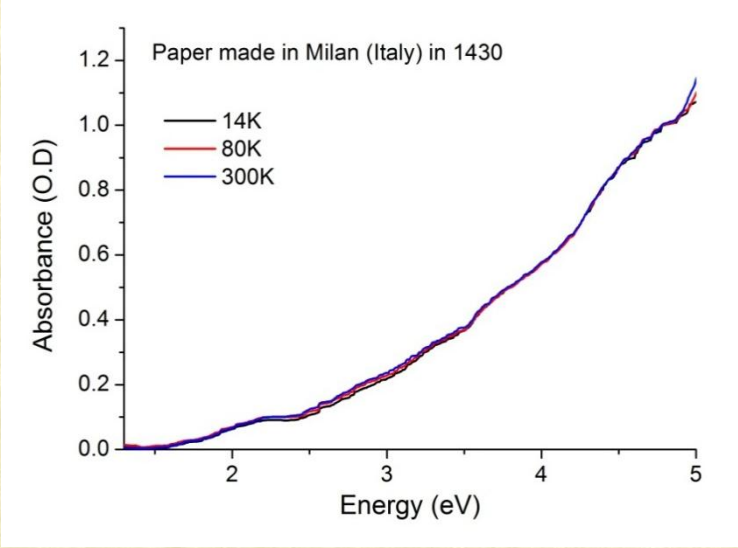
sample mounted on the cryostat cold-finger

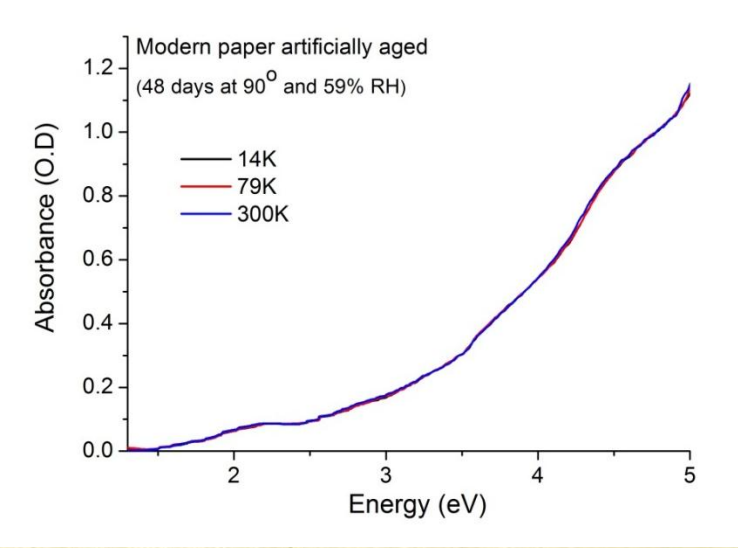
# Experimental results

Absorption and scattering (modeled by a polynomial) contributions of a paper sample




Absorption (subtracted of scattering) vs photon energy



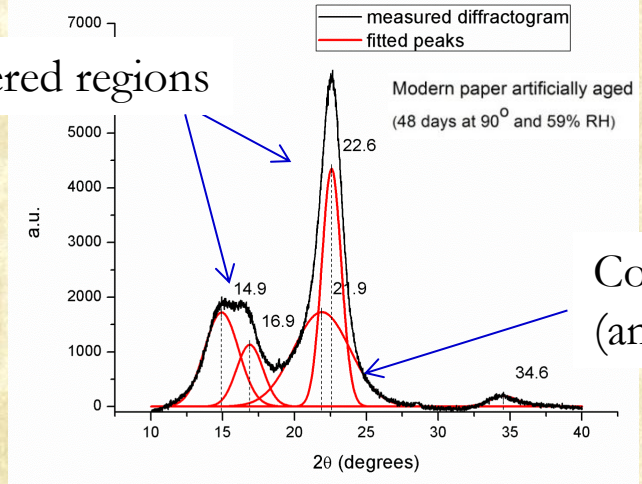

→ tiny differences vs temperature

# Chromophores localized in the disordered regions of cellulose fibers

Cellulose fibers are composed of ordered and disordered regions

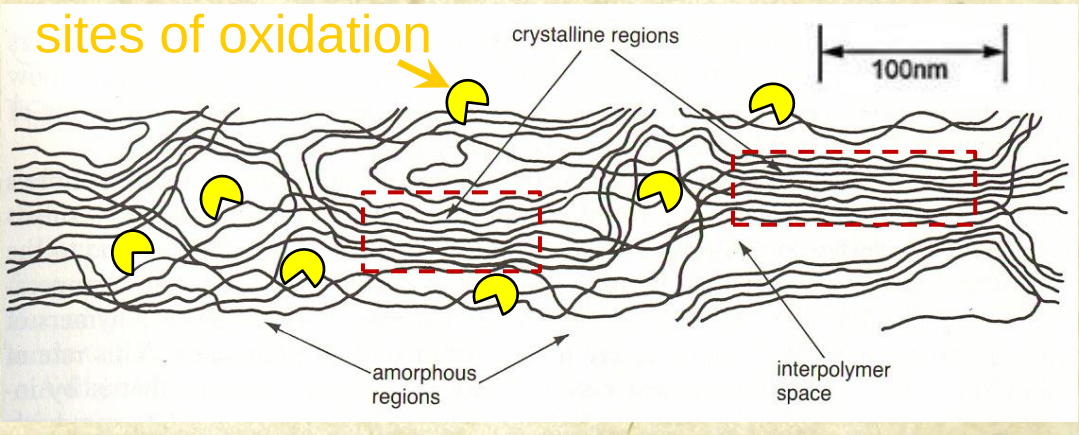
XRD peaks from ordered regions

X-ray diffraction




Contribution of disordered (amorphous) region

Arrangement of cellulose polymers within elementary fibrils of cellulose




Crystalline regions are unaffected by oxidative degradation

# Conclusions

The absorption spectra of paper show negligible modifications as function of temperature (14-300K).

These results can be explained according the following hypothesis:

- dynamic effects due to temperature are negligible with respect to those due to structural disorder;
- chromophores that are relevant for UV-Vis absorption (responsible for yellowing of ancient paper) are localized in the disordered regions of cellulose fibers.

We acknowledge CPU time granted by CINECA, funding from the EC's FP7 grants no. 211956 (ETSF user project 211), CISSCA, ICRCPAL–MIBACT.