

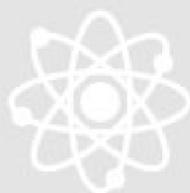
Raman and luminescence spectral imaging of paper natural degradation

Sabina Botti, Francesca Bonfigli, Valentina Nigro, Alessandro Rufoloni, Angelo Vannozzi

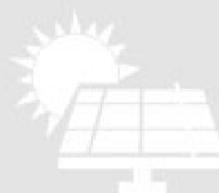
ENEA, Fusion and Technologies for Nuclear Safety and Security Department,
Via E. Fermi, 45, 00044 Frascati, Italy

107° Congresso SIF, 13-17 settembre 2021

Sezione 6



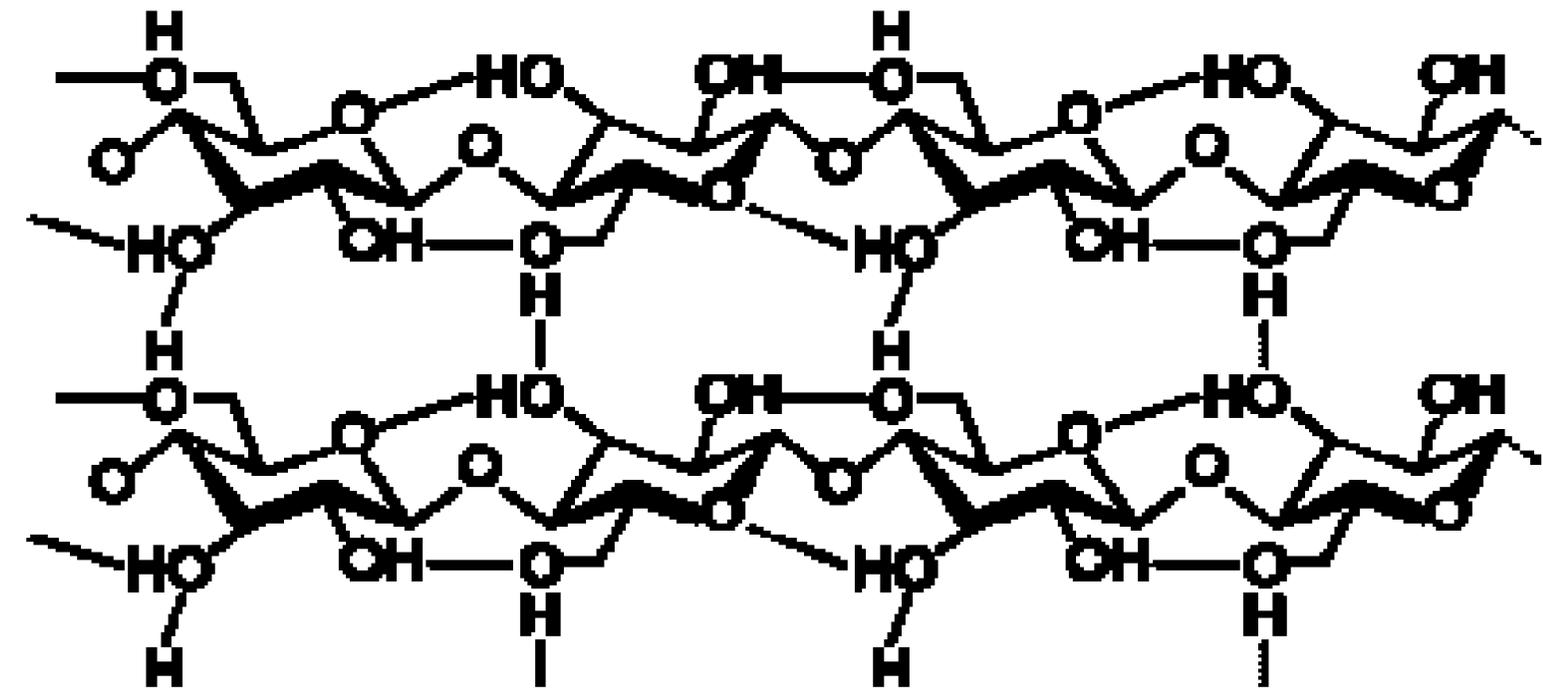
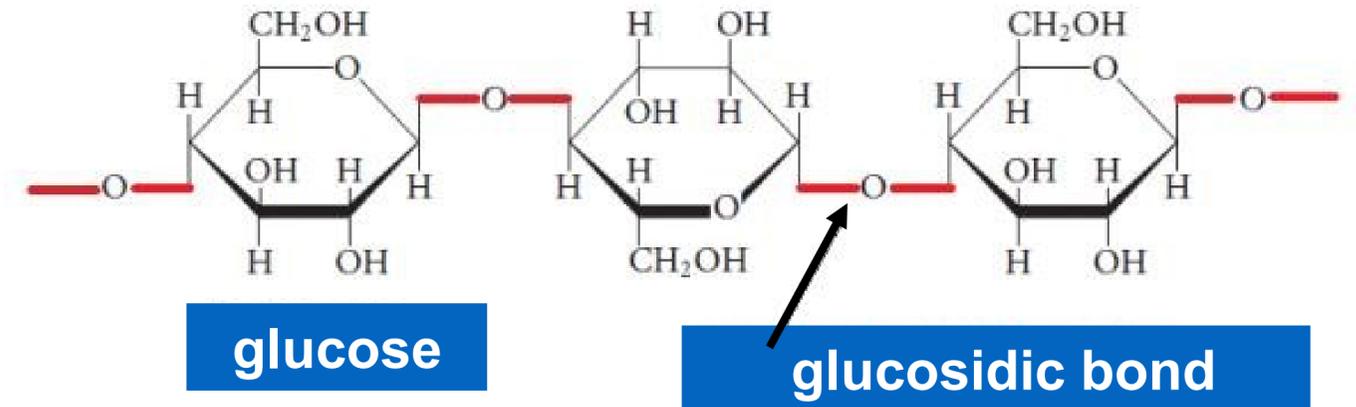
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- The development of suitable scientific approaches for the conservation and restoration of library heritage is of prime importance.
- Due to the restrictions in paper sampling the spectroscopic techniques, intrinsically non – destructive, are gaining large interest to investigate the chemical-physical properties of modern and ancient paper and to monitor the hystorical sample ageing, supplying a guide to conservation and restoration procedure.

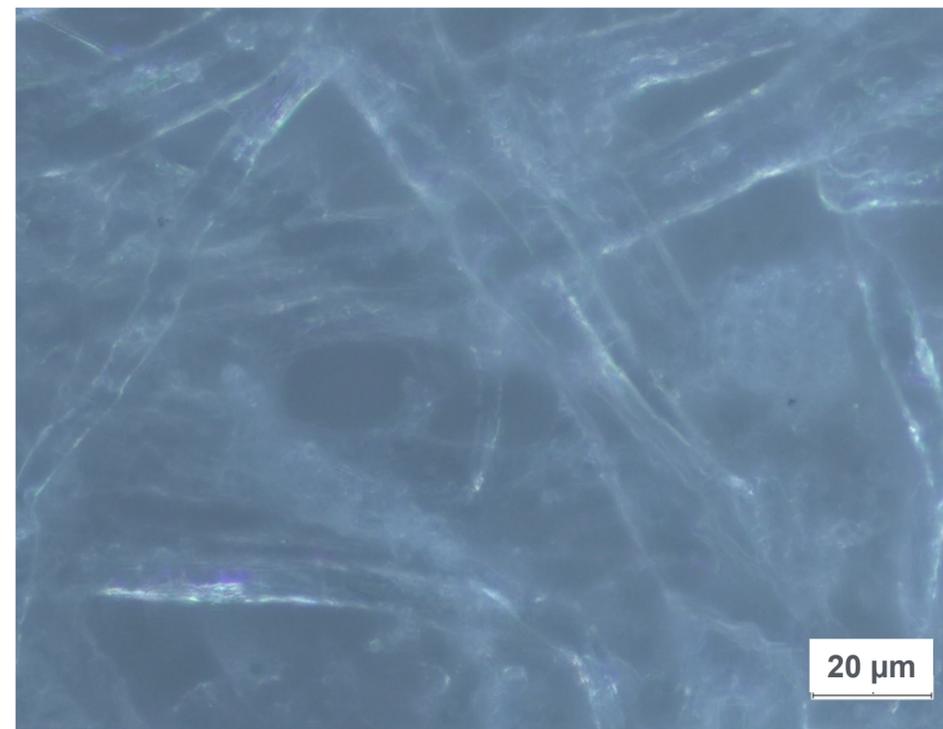
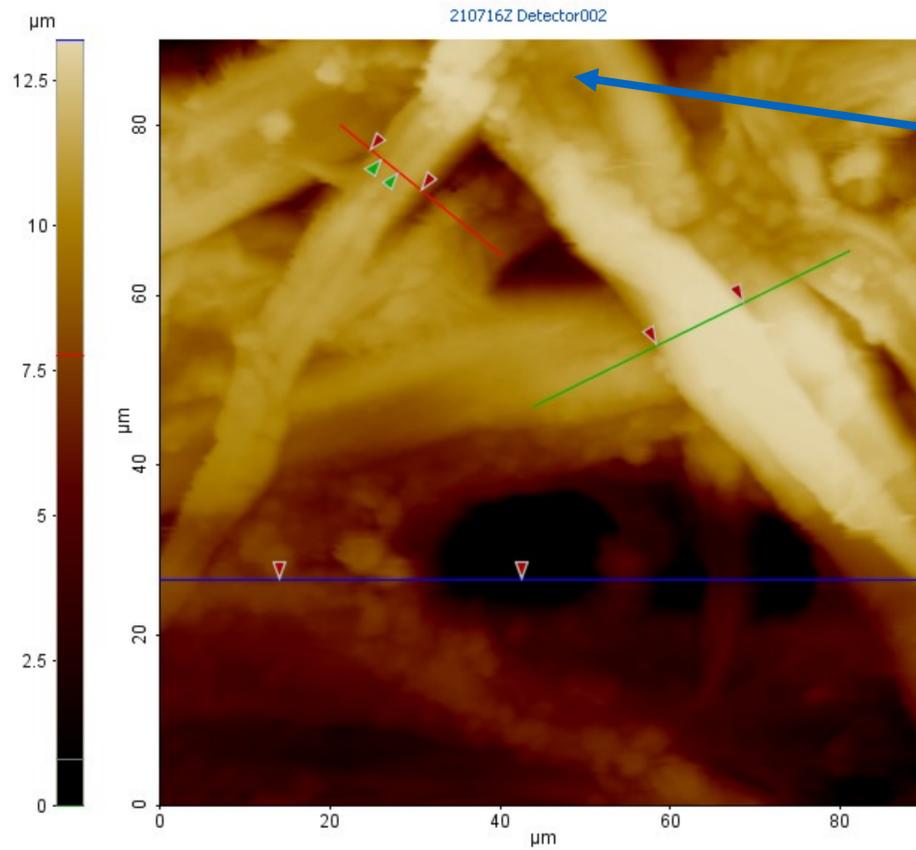
Cellulose chain structure

- Paper is produced by pressing cellulose fibers and drying them together in sheets.
-
- The cellulose is a natural linear polymer of glucose monomers linked by glucosidic C-O-C bonds.
- Cellulose chains are held together by strong hydrogen bonds that promote aggregation of single chains into highly oriented structure.
- In addition to cellulose fibers the paper contains various fillers that are used for bleaching, strengthening...

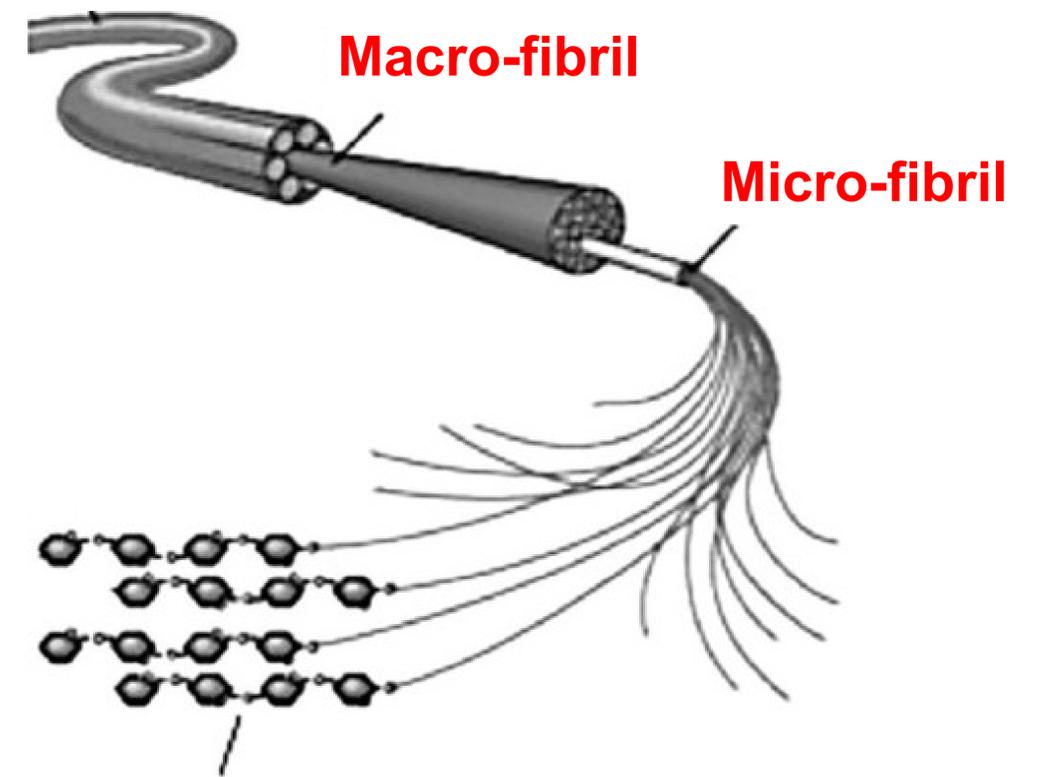


From micro-fibril to fiber

2021 Fabriano paper



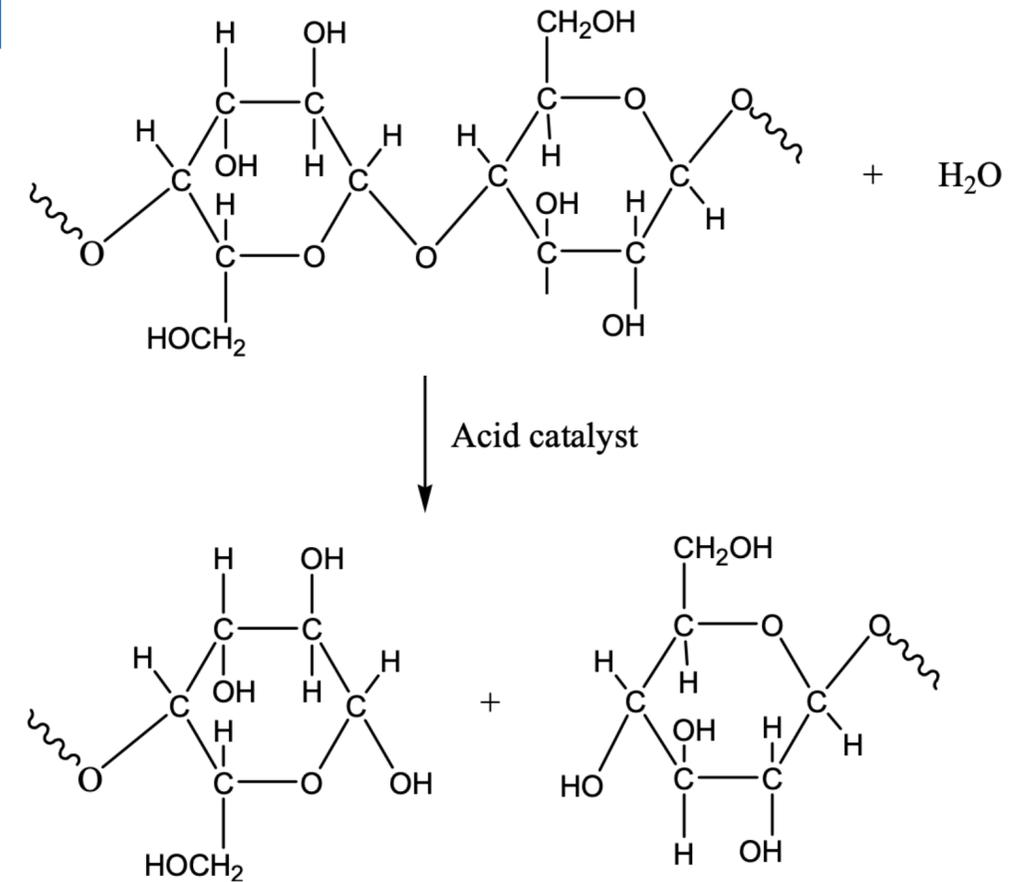
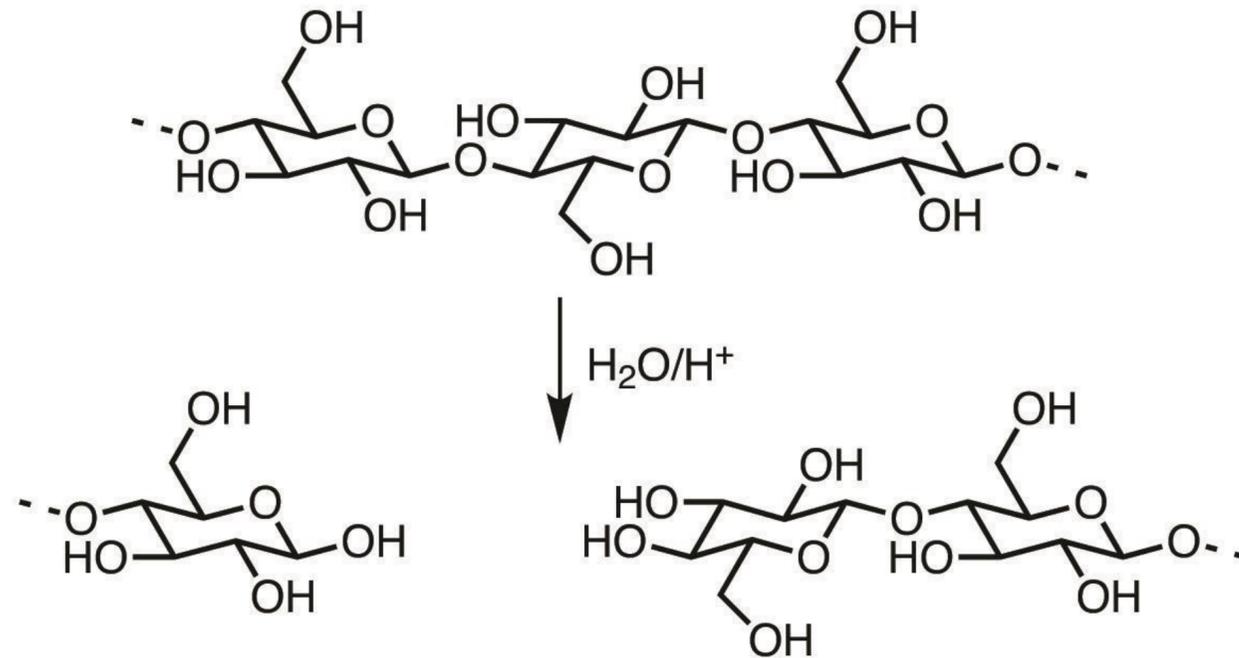
Cellulose-fibers



Cellulose chains

It is widely accepted that the paper ageing is mainly due to the hydrolytic and oxidative mechanisms of cellulose

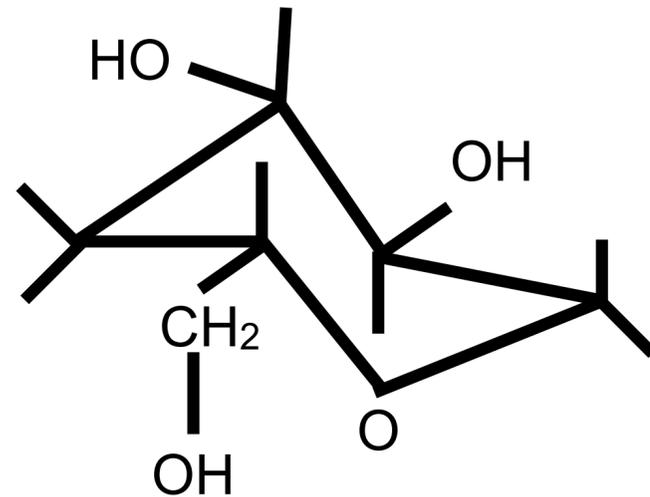
HYDROLISIS



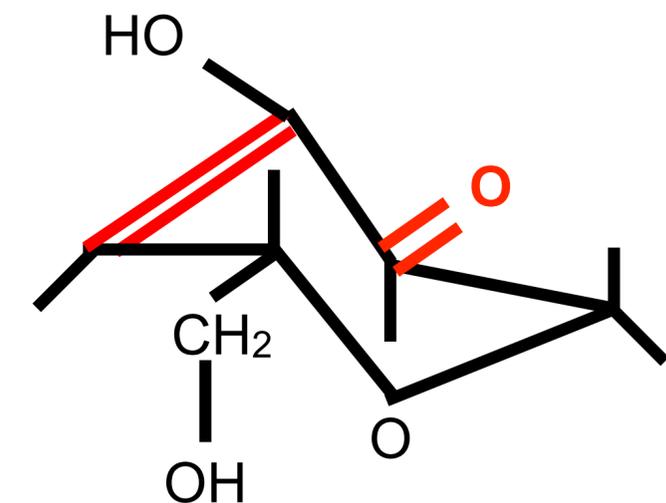
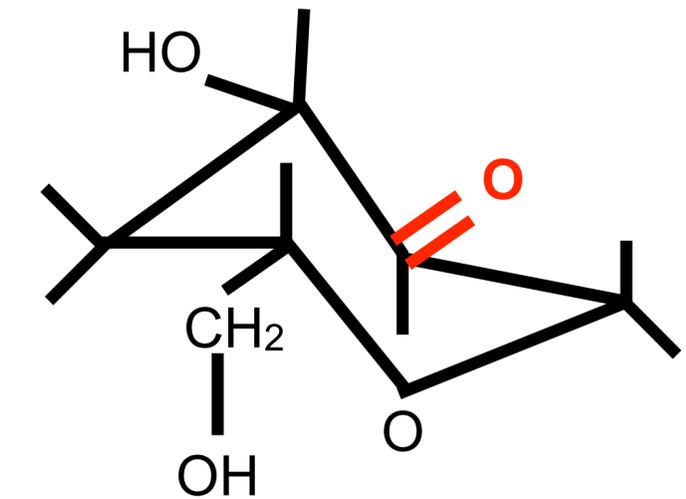
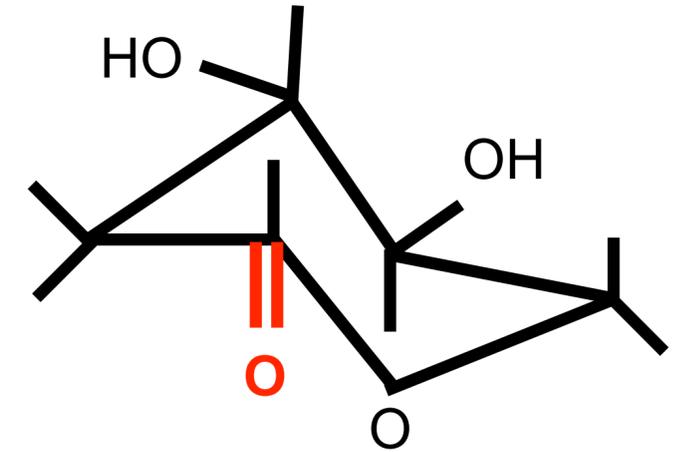
- Acidity catalyzes the cleavage of glucosidic C-O-C bond, shortening the cellulose chain.

- It depends on the presence of additives, pollutants in the ambient, writing media (i.e inks..)

Paper degradation mechanisms: oxydation



- The hydroxyl groups present in the cellulose chain are very sensitive to oxidation.
- The natural oxidative process can be accelerated/artificially induced by light, inks, transition metals, pollutants.
- Oxidative reactions lead to the formation of carbonyl and carboxyl groups. The formation of double and triple C-C bonds is possible as well



METHODS

Technique	Target
<ul style="list-style-type: none">• Raman and luminescence spectroscopy with surface scanning	<ul style="list-style-type: none">• Definition, from spectroscopic fingerprint, of suitable markers to evaluate the paper ageing degree.
<ul style="list-style-type: none">• HR-SEM	<ul style="list-style-type: none">• Paper surface morphology
<ul style="list-style-type: none">• AFM	<ul style="list-style-type: none">• Evaluation of paper surface roughness on selected regions.

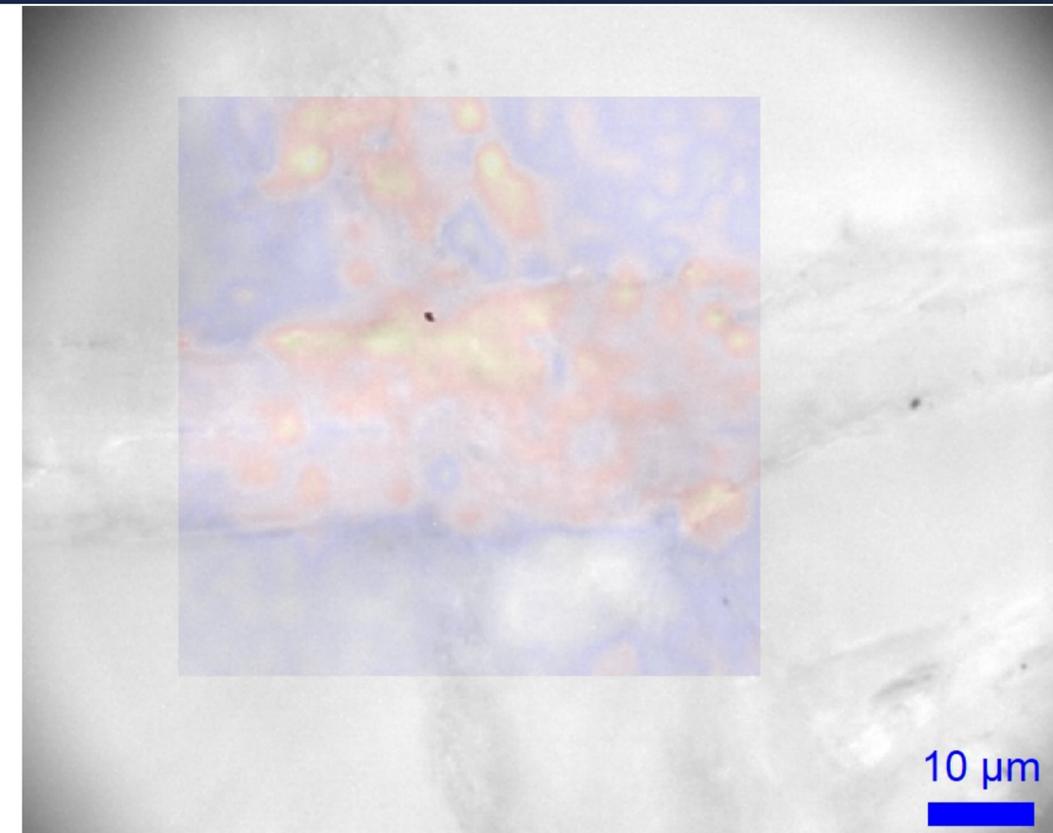
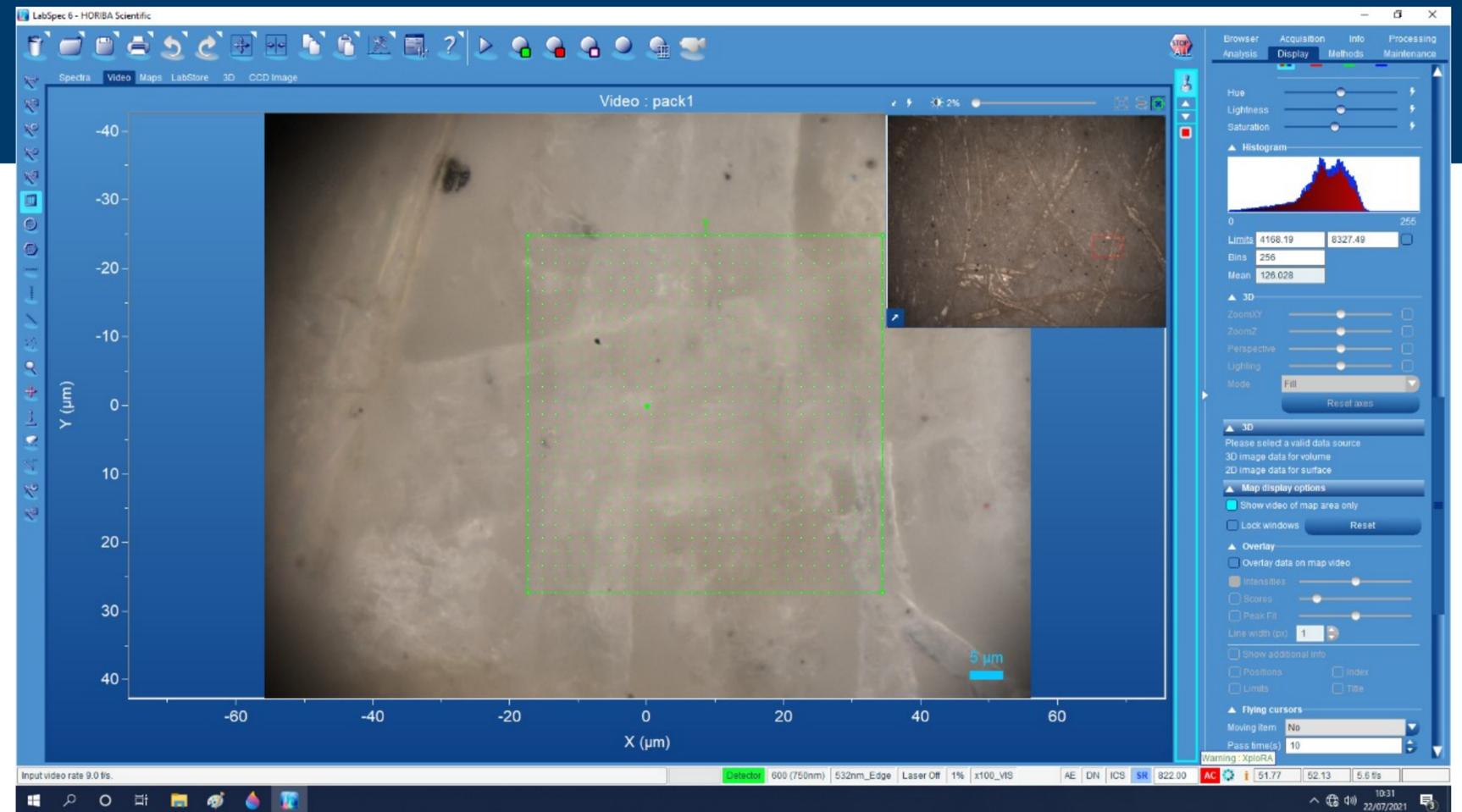
Raman and luminescence spectroscopy

Raman and luminescence spectra were acquired with a confocal Raman spectrometer (Horiba XploRA Plus) at every point of a prefixed grid with 532 nm excitation wavelength.

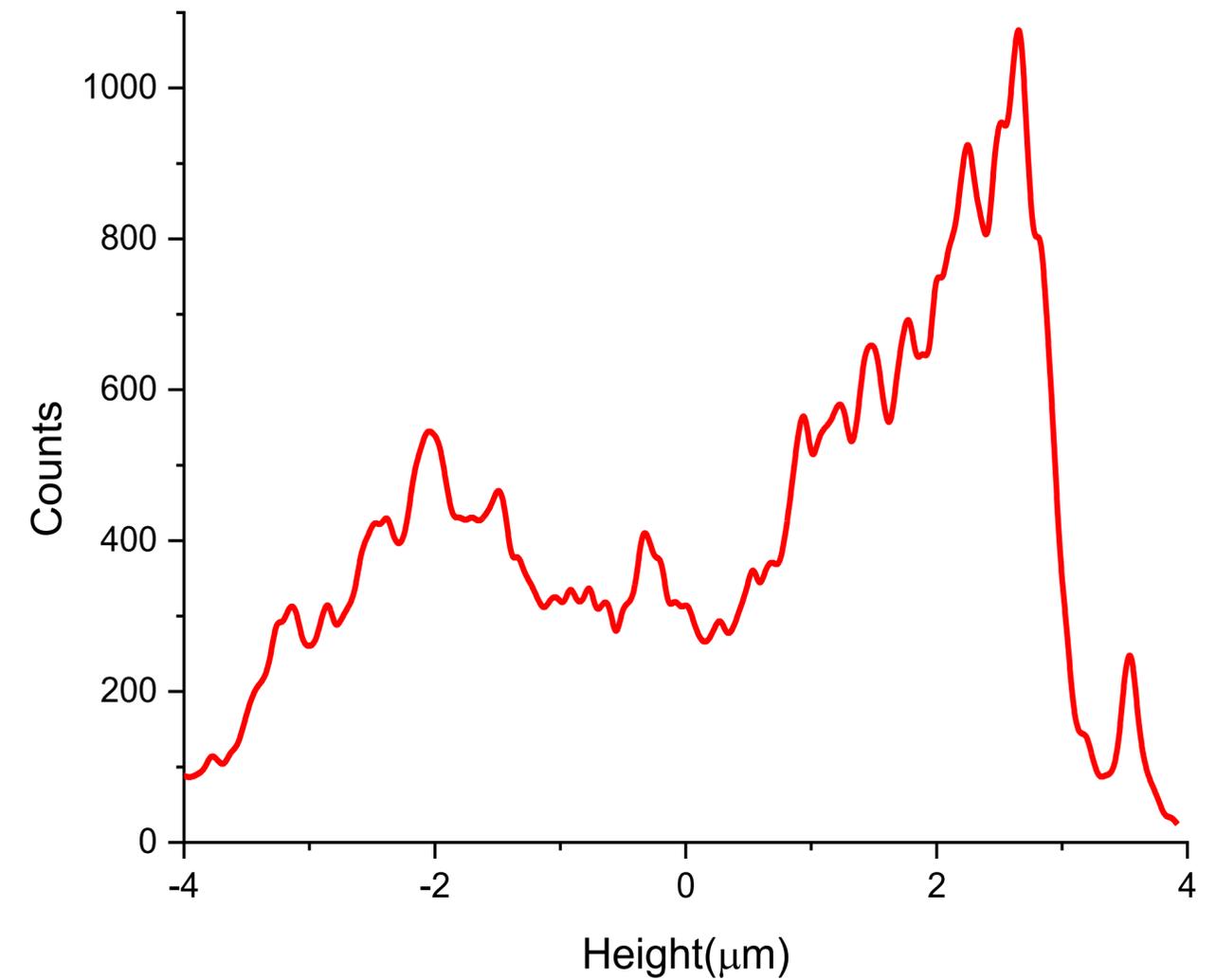
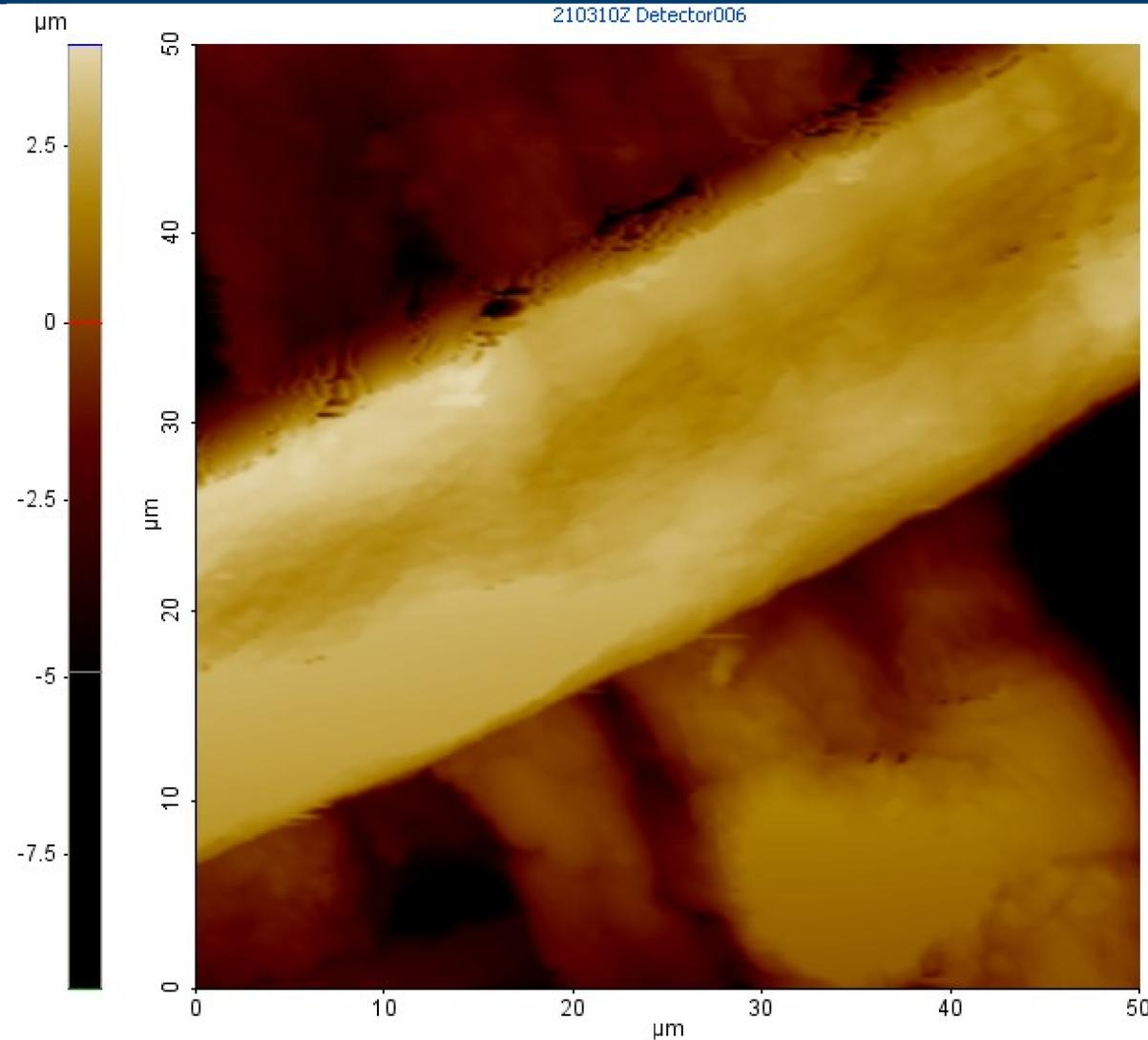
The microscope utilizes 5X, 10X, 50X, 100X magnifying objectives. The laser power can be attenuated by neutral density filters to avoid damaging of paper. The paper samples were fixed to the surface of sample holder.

No- printed book areas from $50\ \mu\text{m} \times 50\ \mu\text{m}$ up to $800\ \mu\text{m} \times 800\ \mu\text{m}$ were scanned with step size ranging from 1 to $10\ \mu\text{m}$ in X and Y.

The corresponding Raman/luminescence maps were obtained contrasting point to point the changes of spectral parameters.



AFM



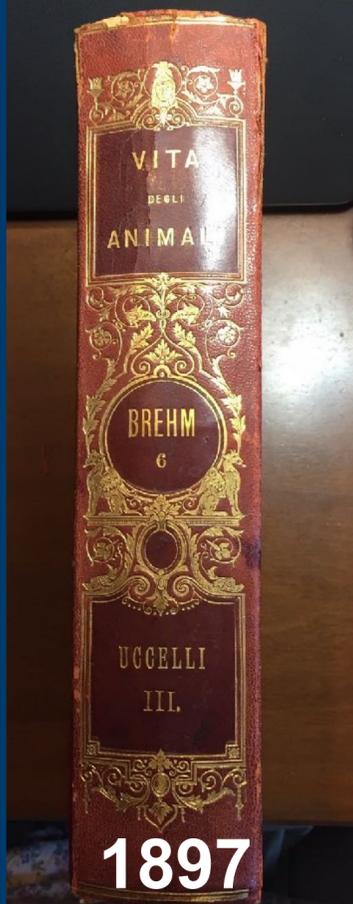
- For each examined area it is possible to build the height histogram.
- The surface roughness can be defined as the standard deviation of the surface height respect to the mean value.

MATERIALS

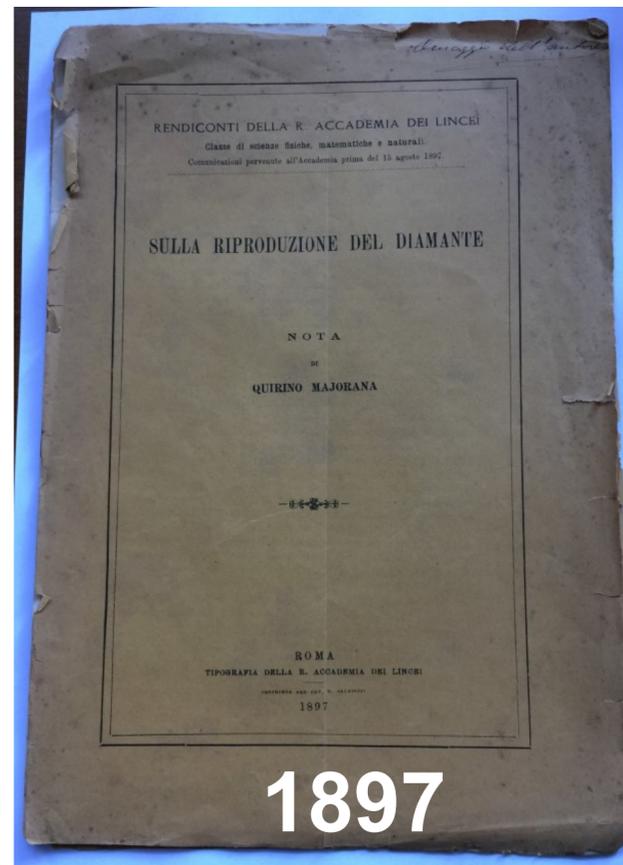
We studied several paper samples selected from non – printed areas of books coming from library private heritage.

The paper age was certified from the publication date and spans over three centuries (XIX, XX, XXI).

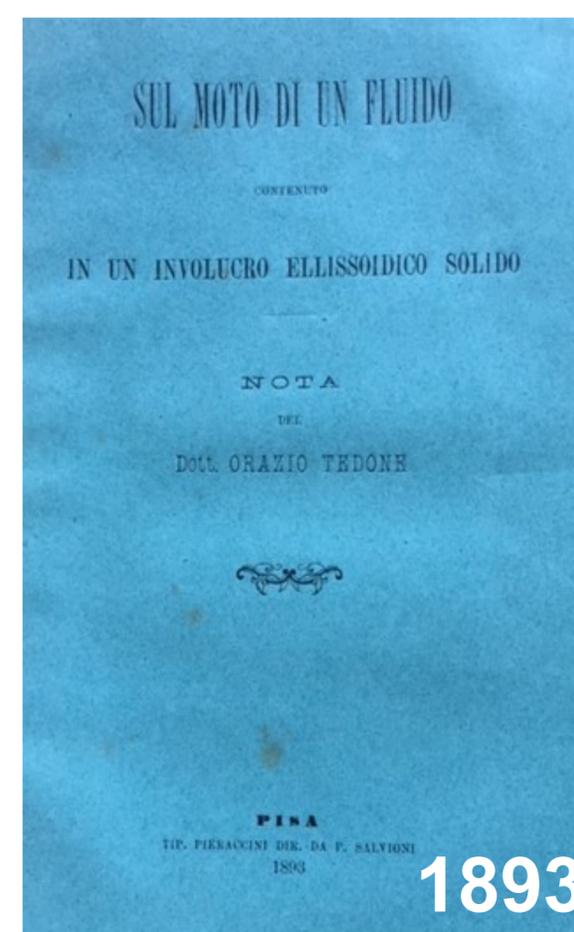
As modern paper samples we used also laser printer paper and Fabriano paper.



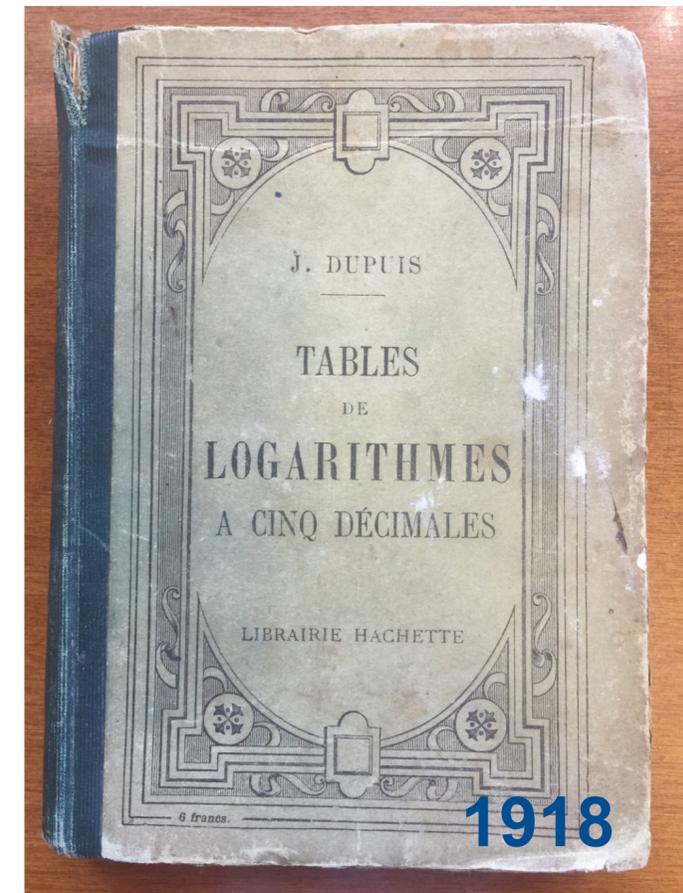
1897



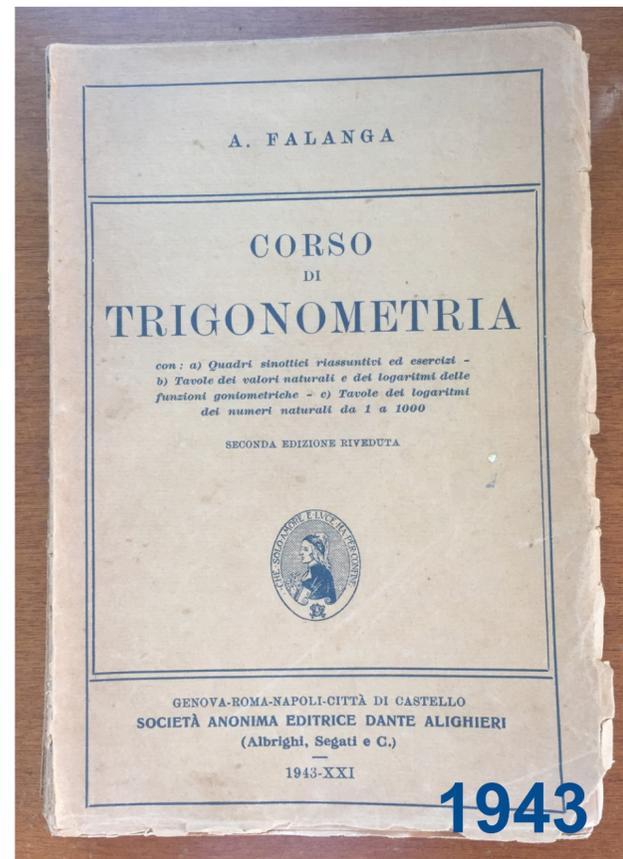
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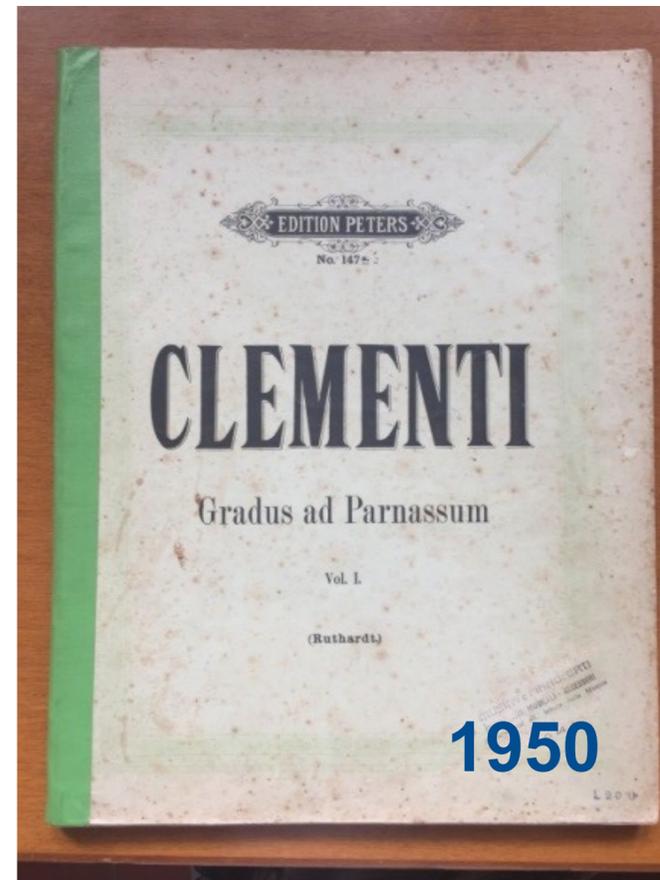
1893



1918



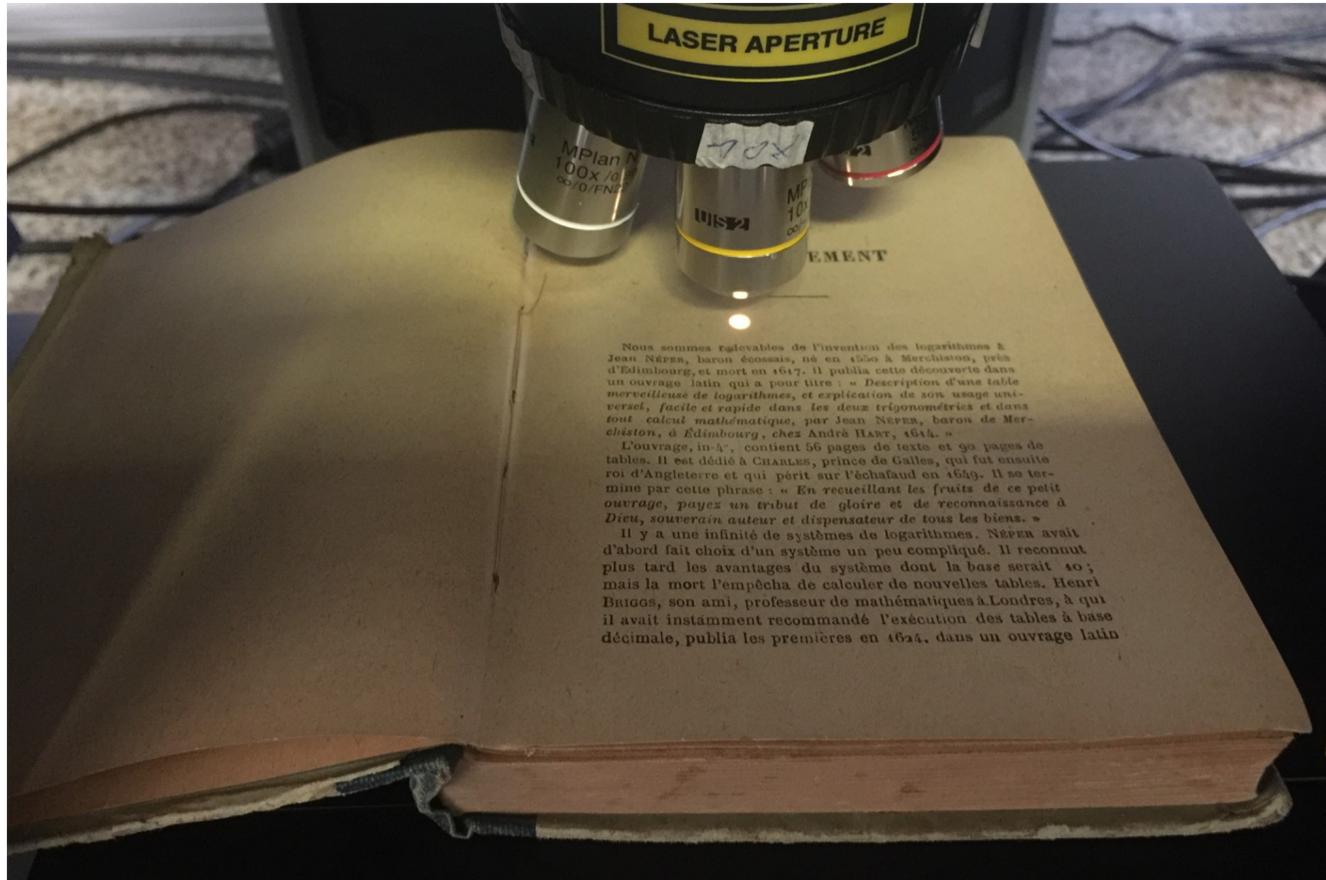
1943



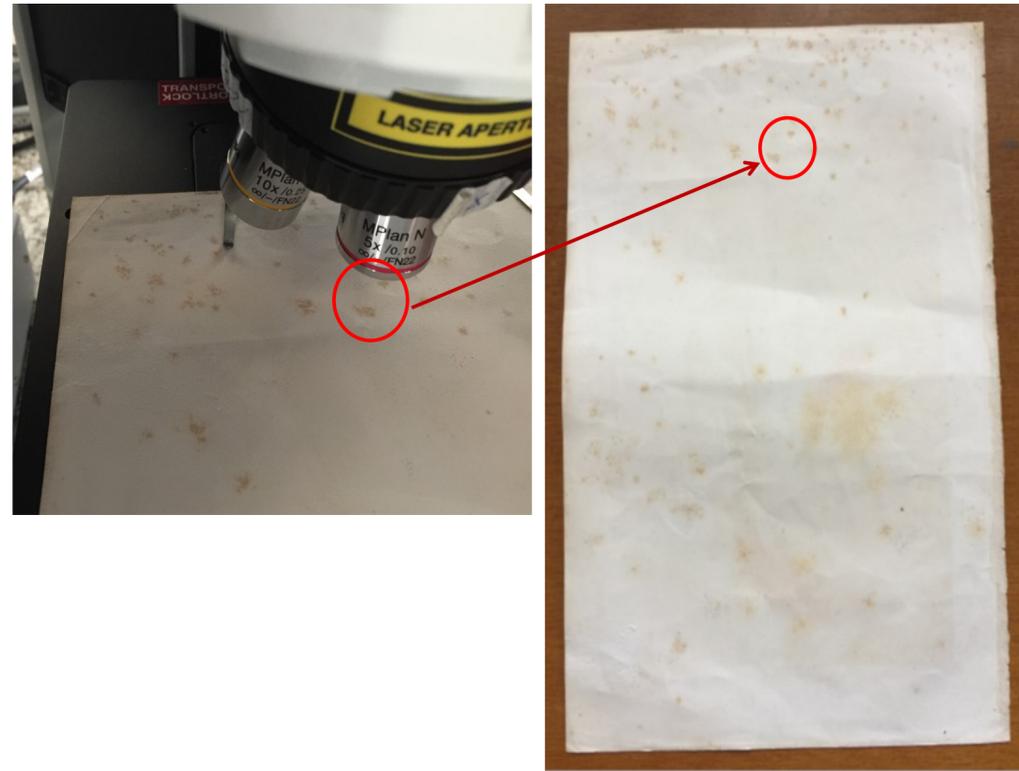
1950



1973



1

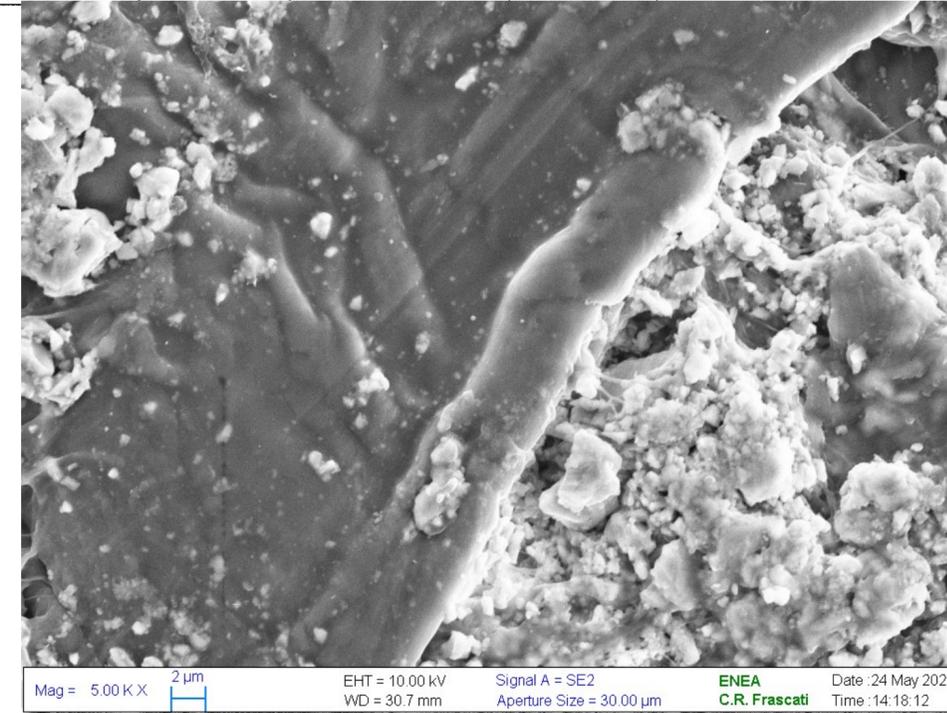
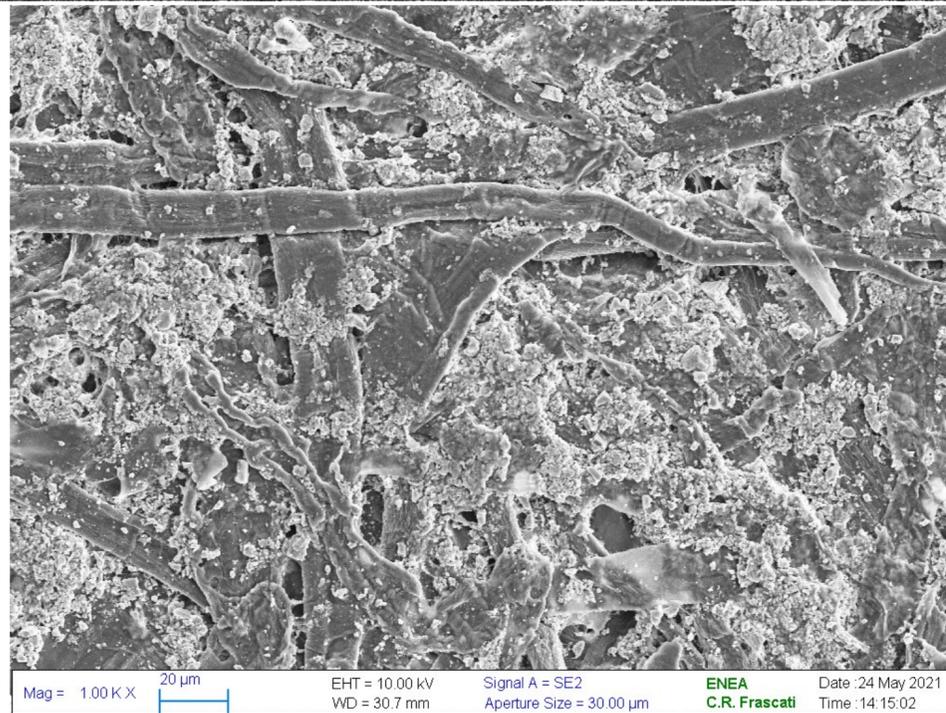
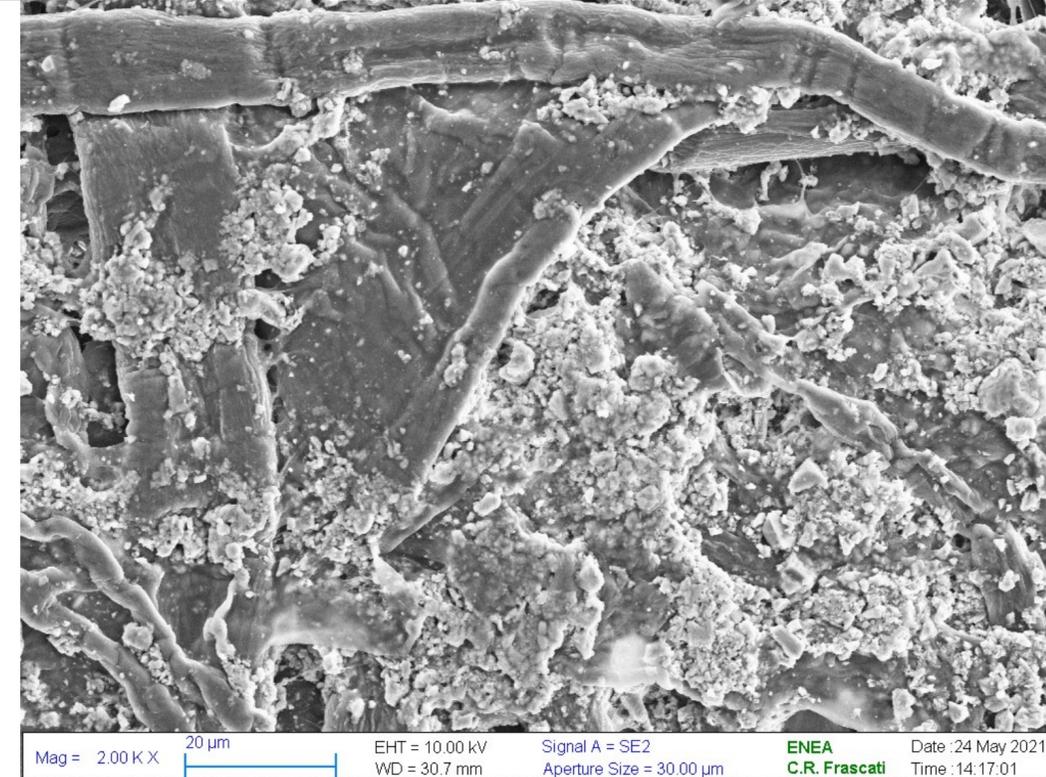
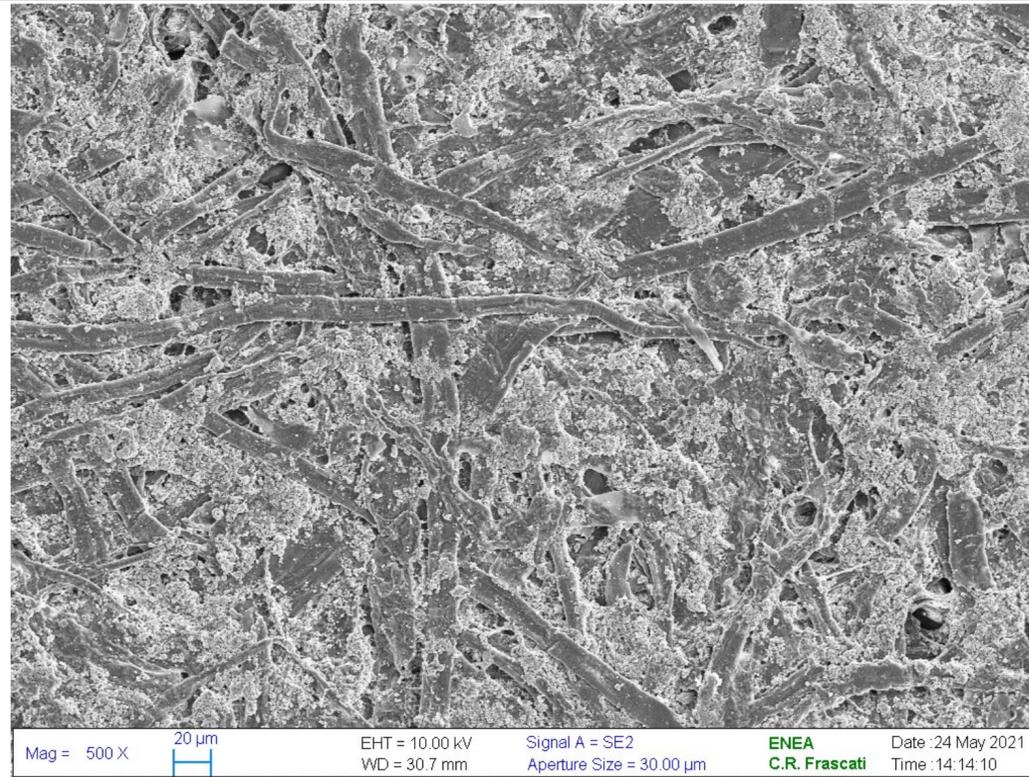


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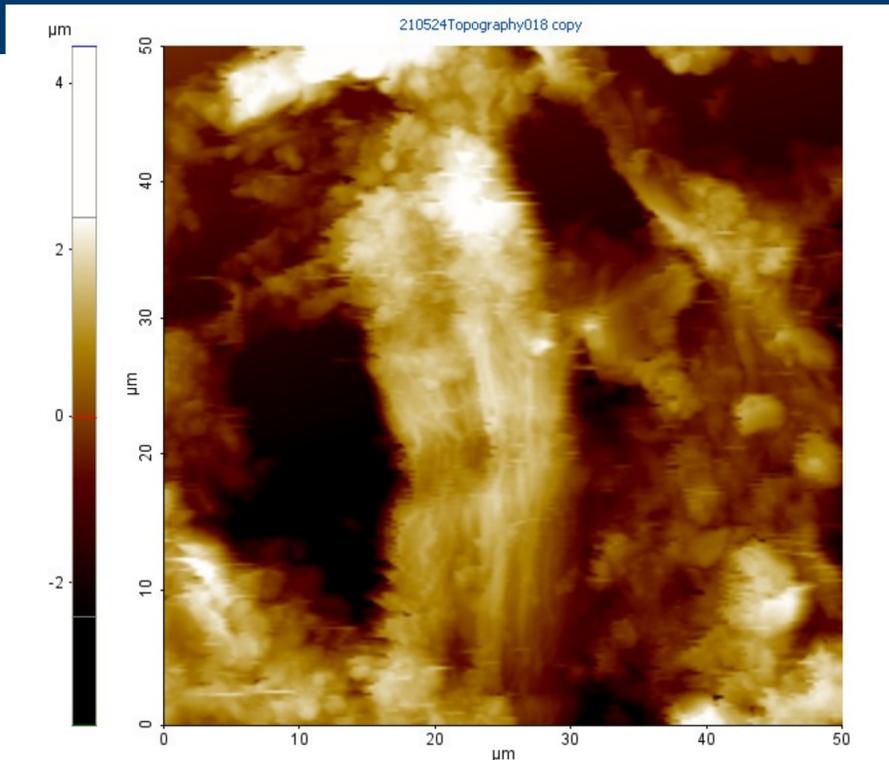


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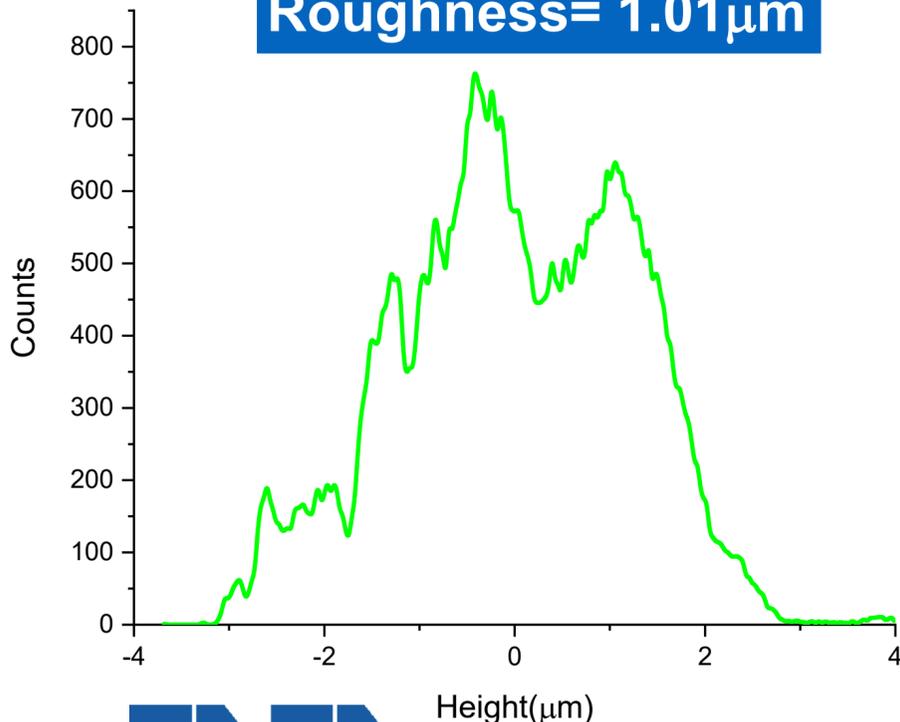
HR-SEM analysis of modern paper (2020)



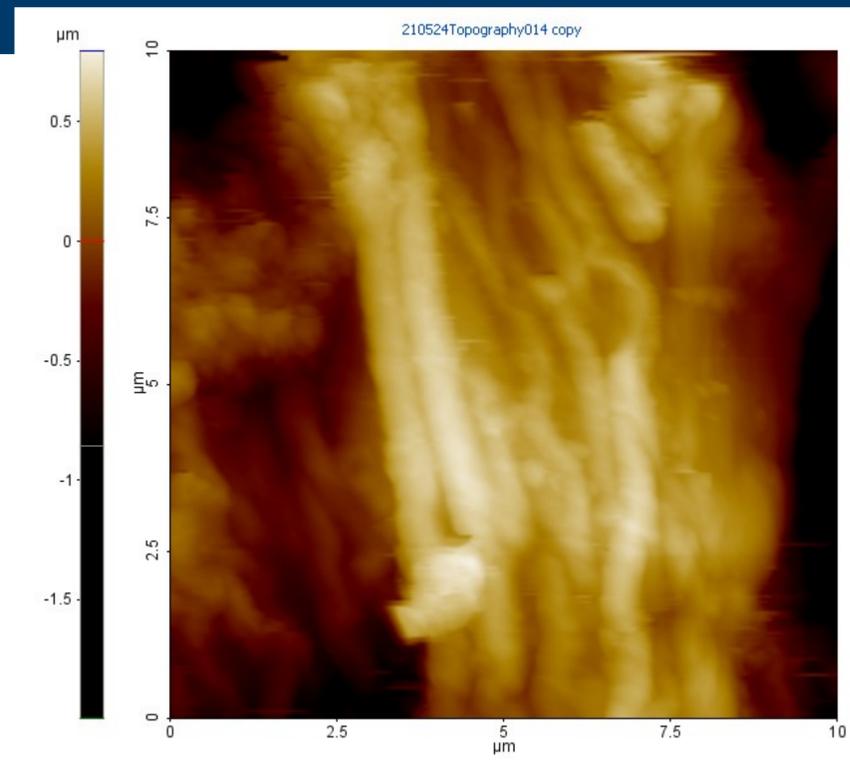
AFM analysis of modern paper (2020)



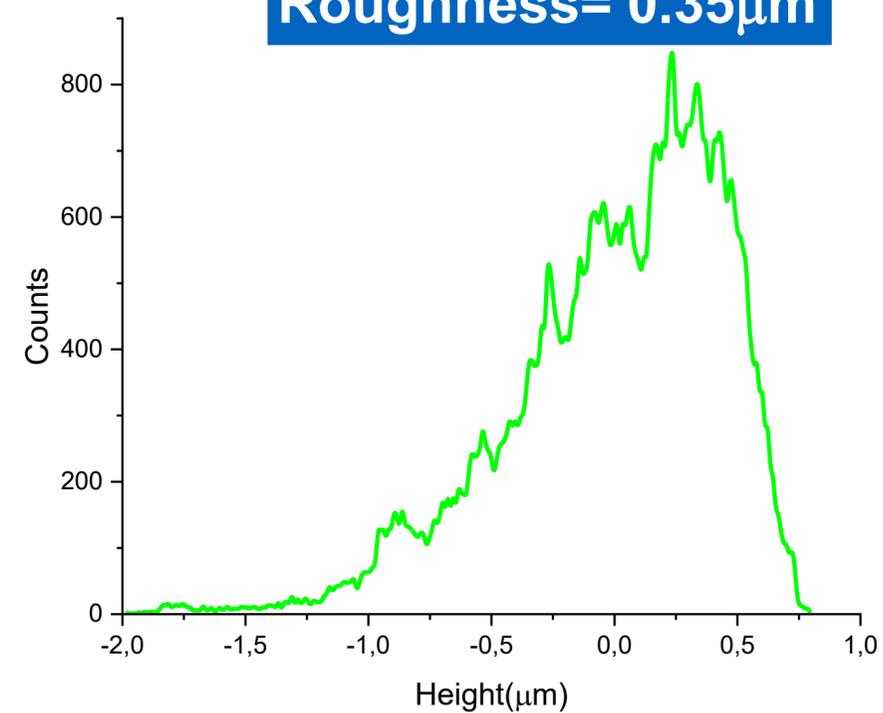
Roughness= 1.01 μm



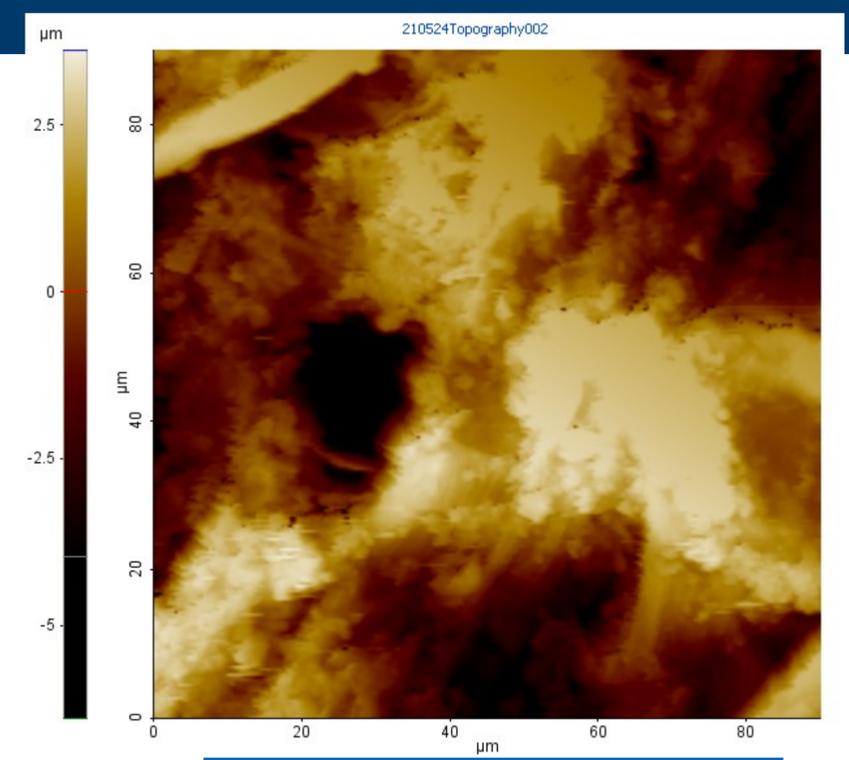
Area: 50 μm x 50 μm



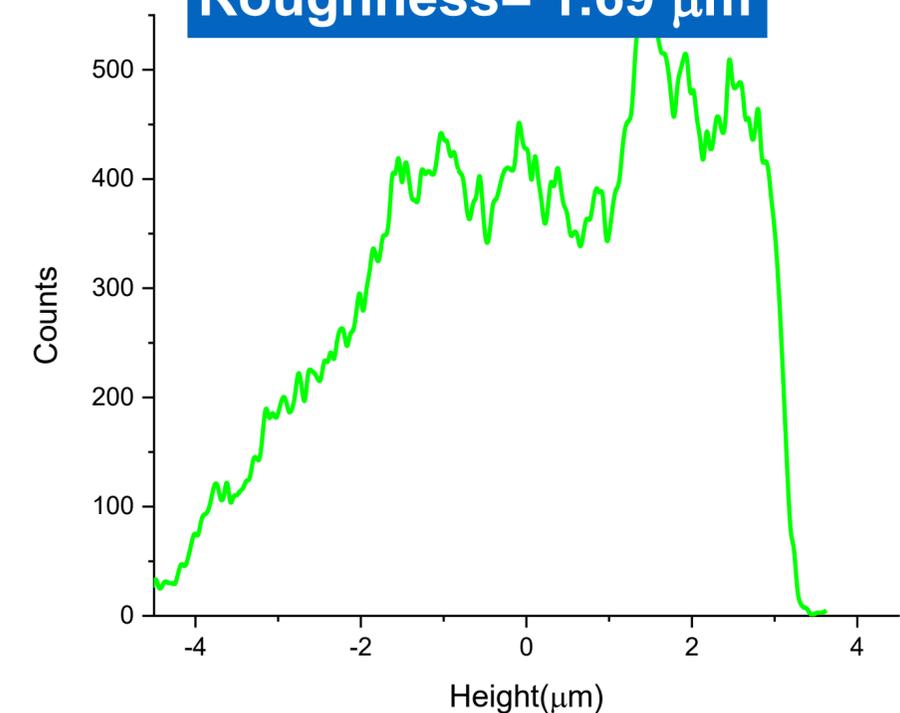
Roughness= 0.35 μm



Area: 10 μm x 10 μm

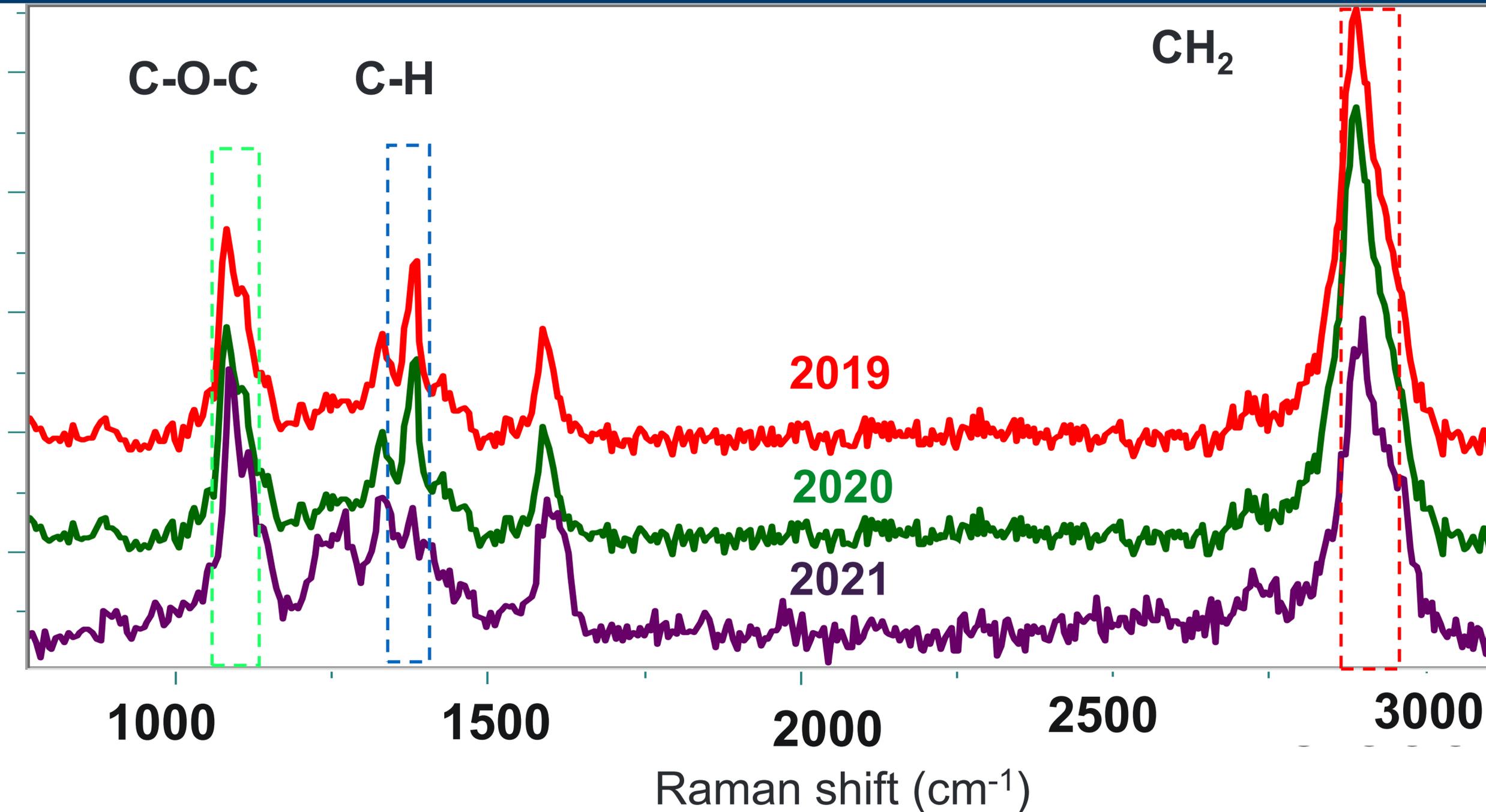


Roughness= 1.69 μm



Area: 80 μm x 80 μm

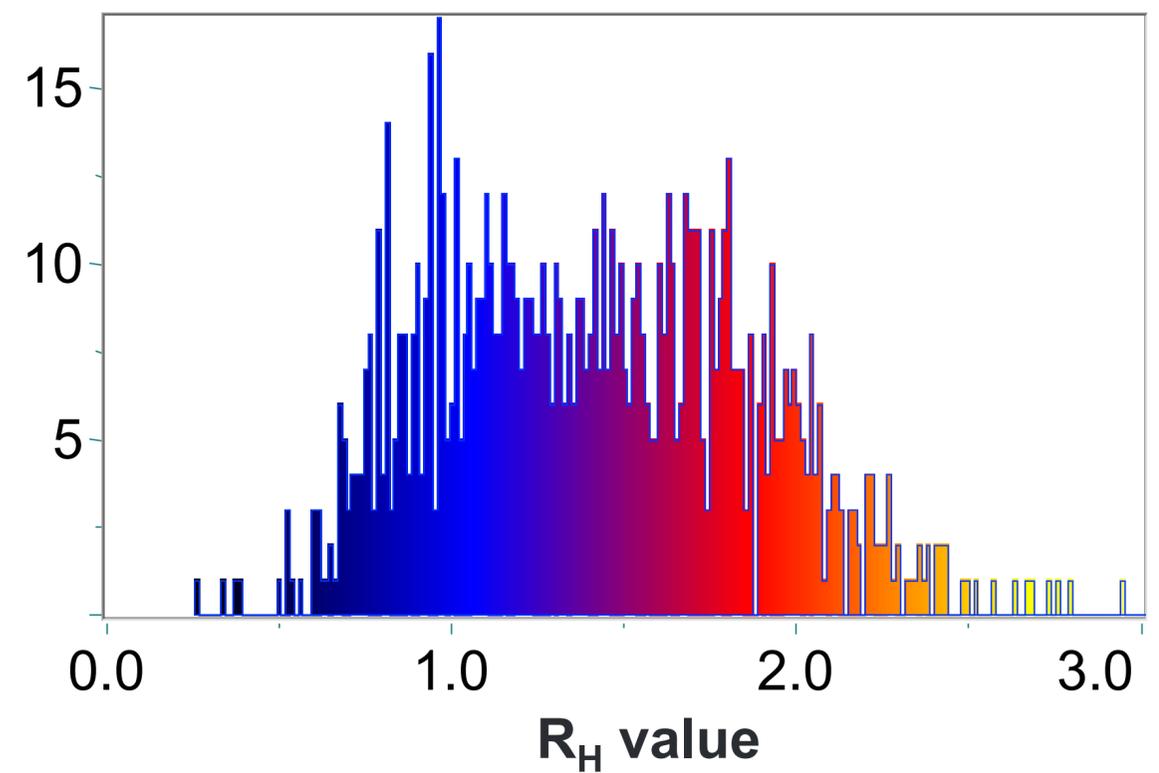
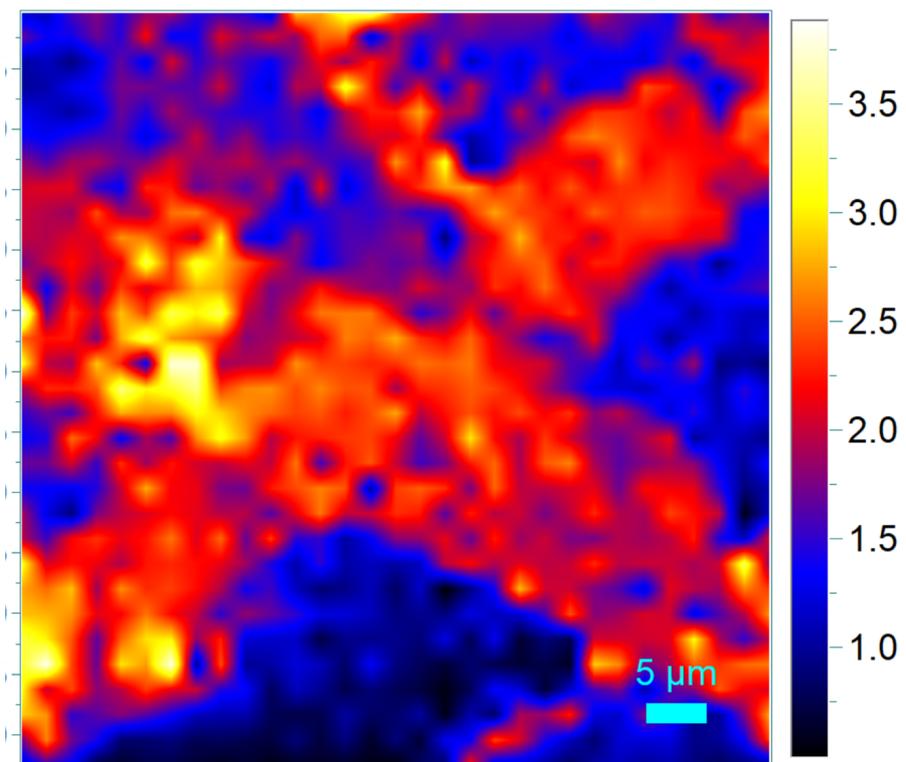
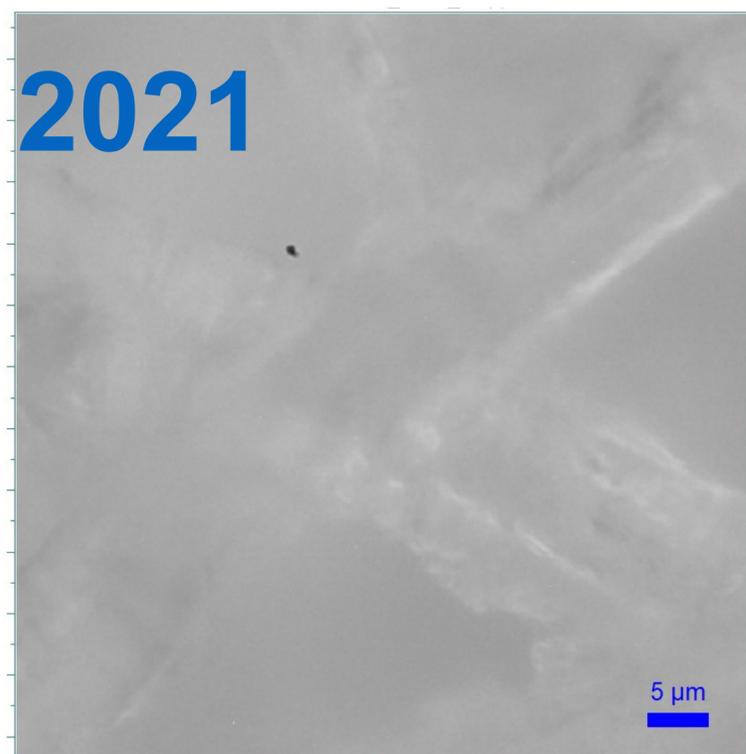
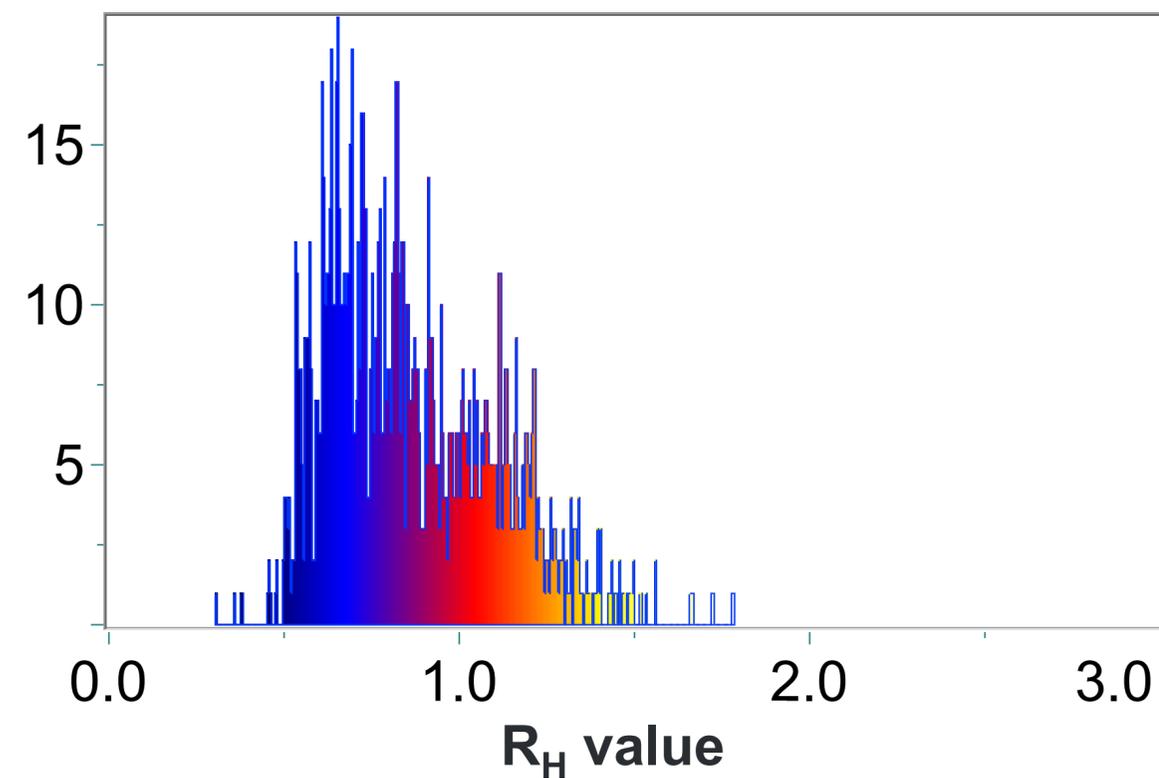
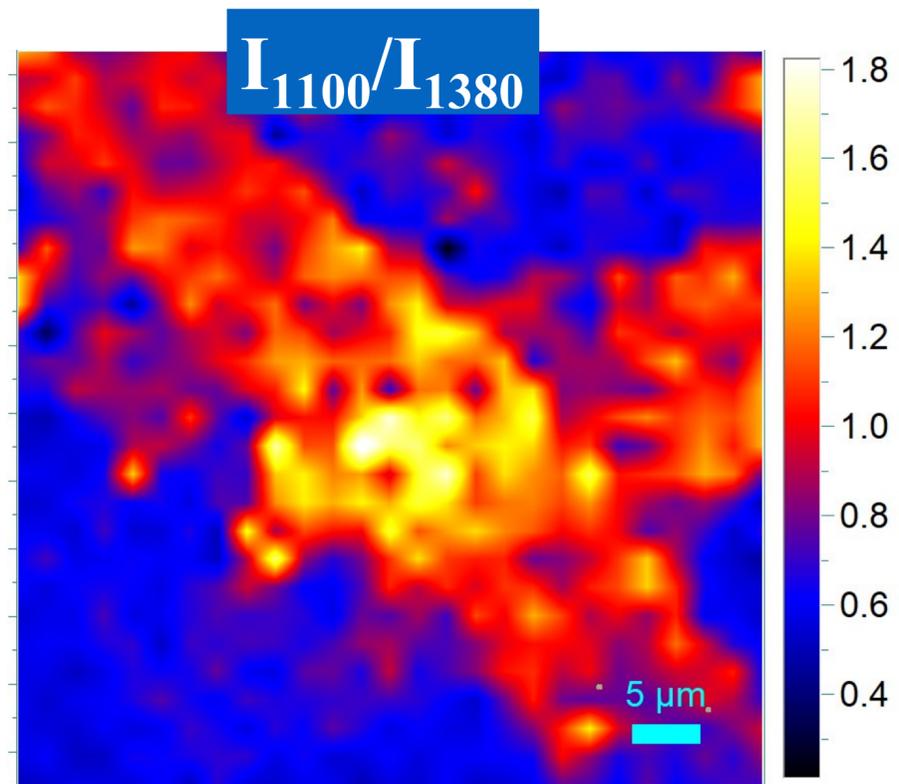
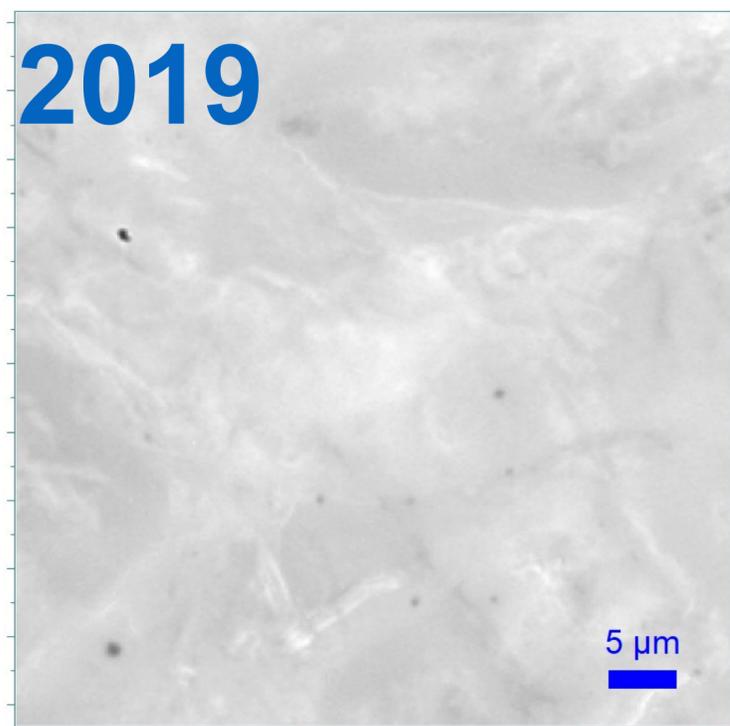
MODERN PAPER (XXI): Raman spectra



$$R_H = I_{1100}/I_{1380}$$

The scission of glucosidic linkages is reflected in a decrease of 1100 cm^{-1} band, differently the internal vibrations of C-H group are expected to be weakly sensitive to a change of cellulose fiber length.

Raman mapping of R_H marker (60 μm x 60 μm , 2 μm grid step size, 900 spectra)



MODERN PAPER (XXI): luminescence spectra

R_H

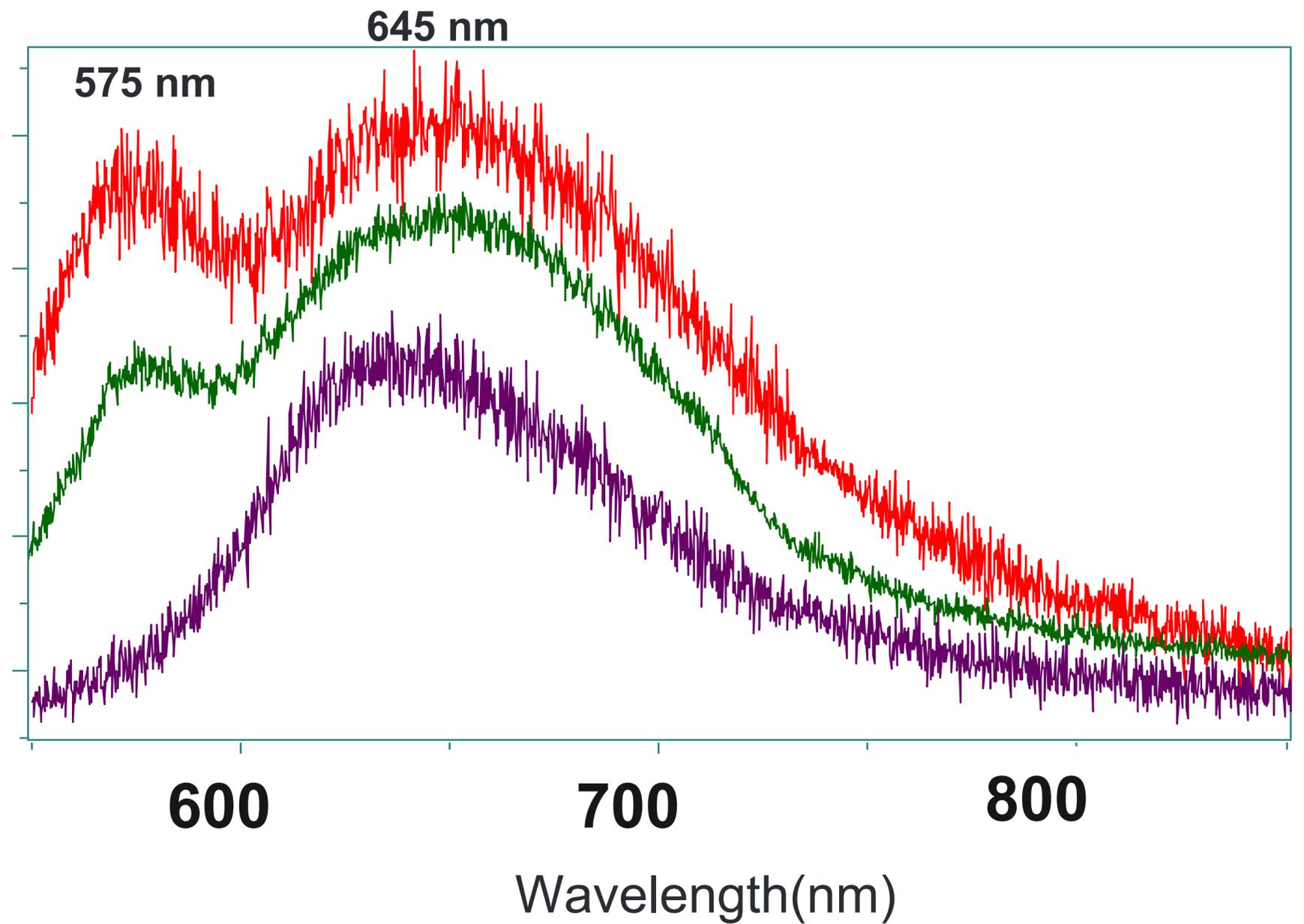


I_{575}/I_{645}

2019

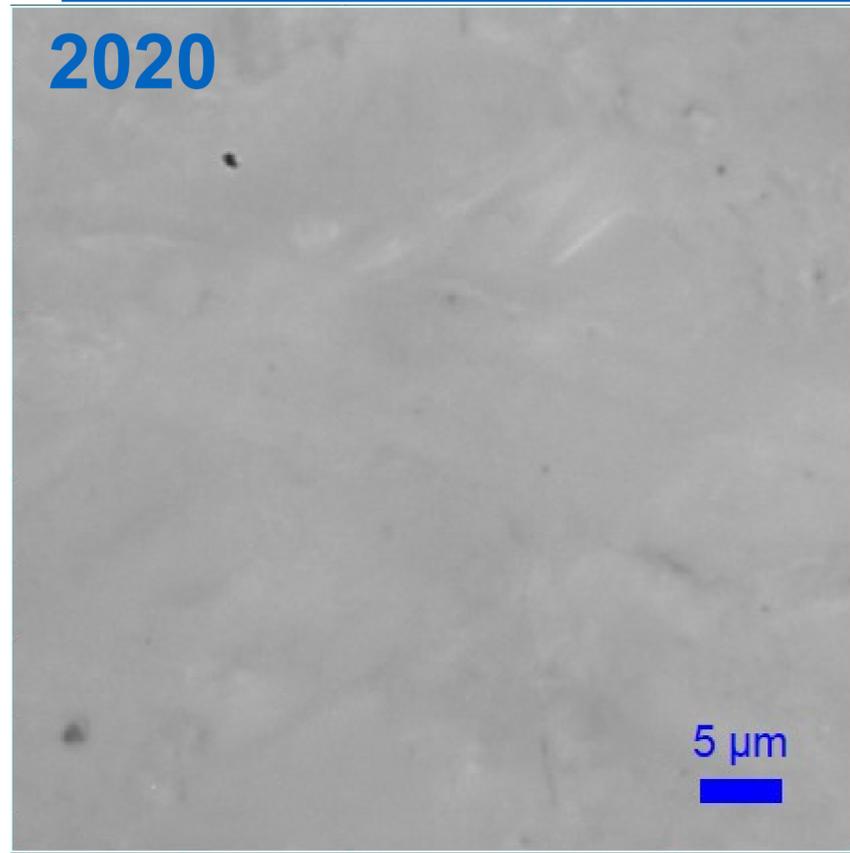
2020

2021

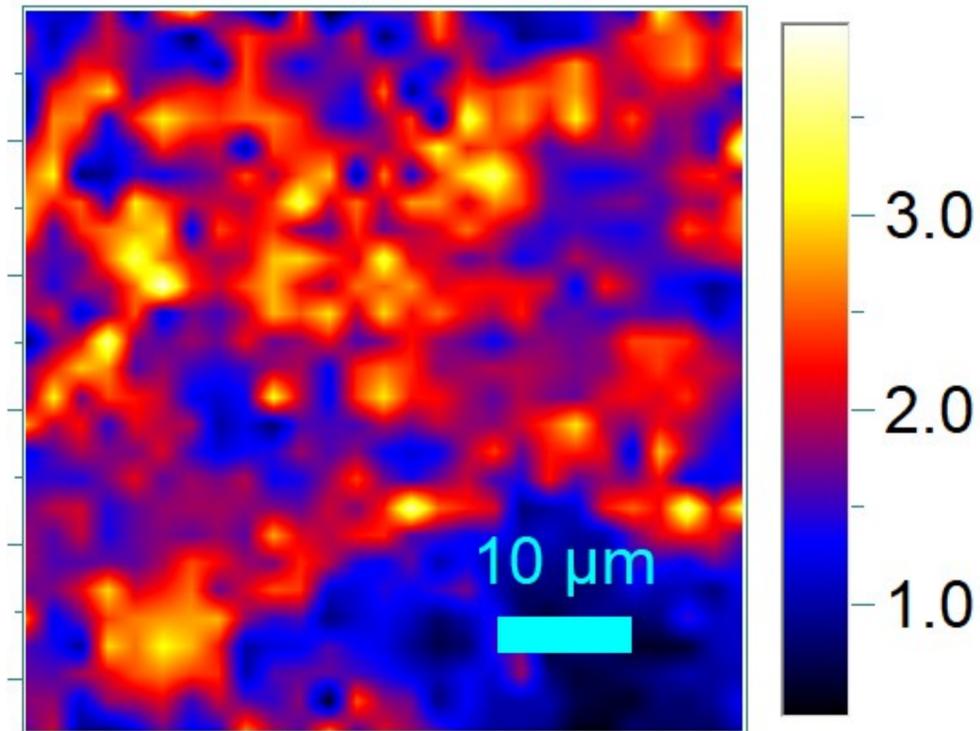


Raman mapping of R_H and I_{575}/I_{645} marker (50 μm x 50 μm , 2 μm grid step size, 625 spectra)

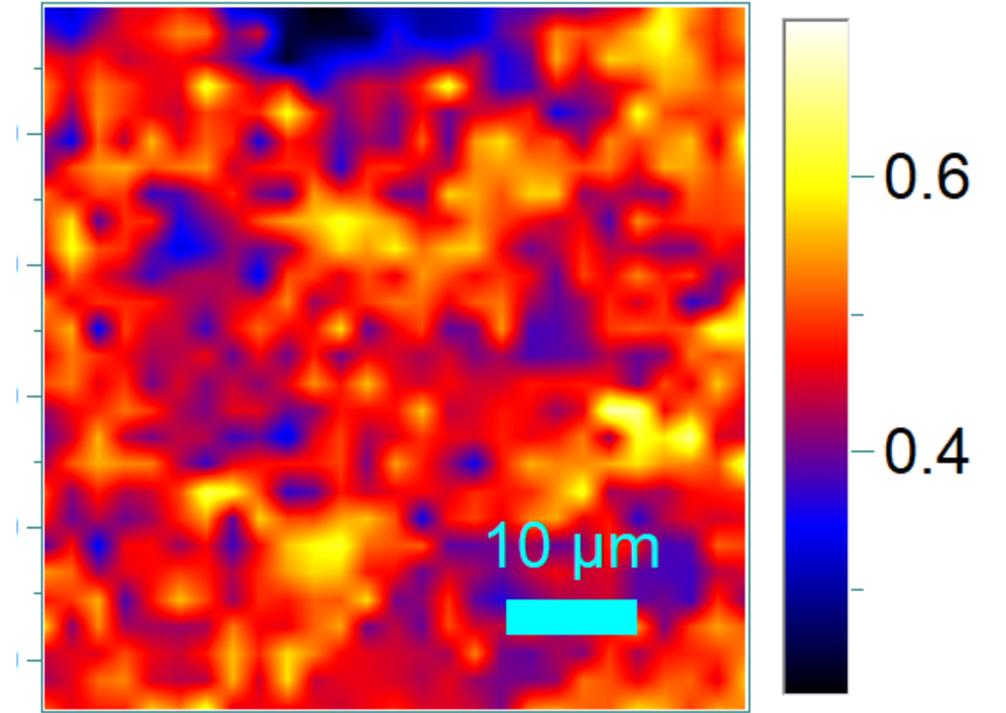
2020



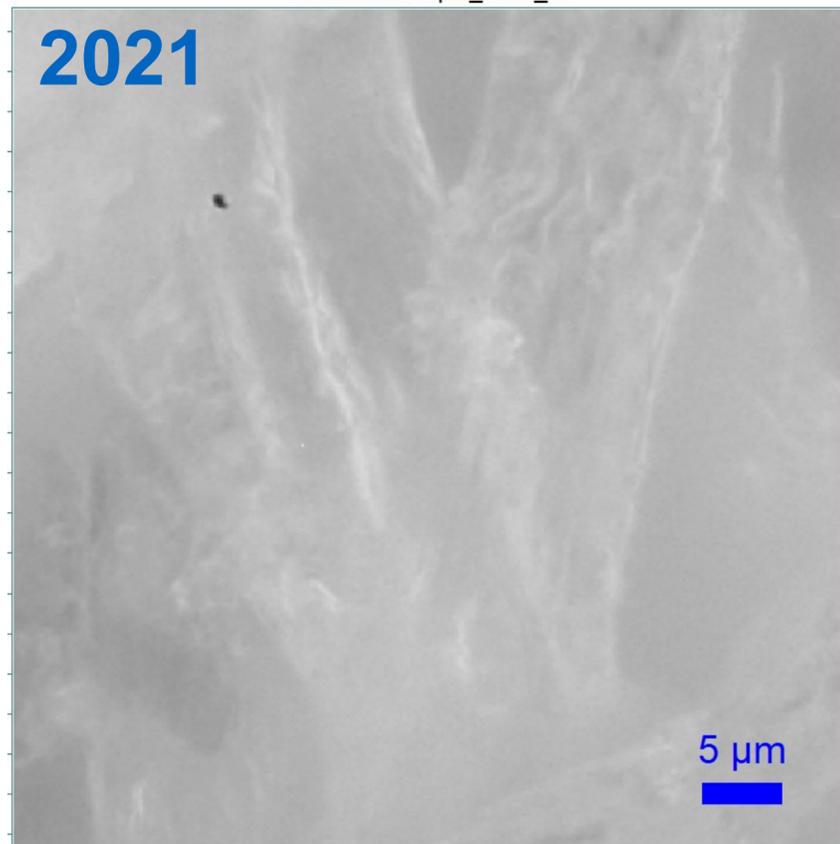
R_H



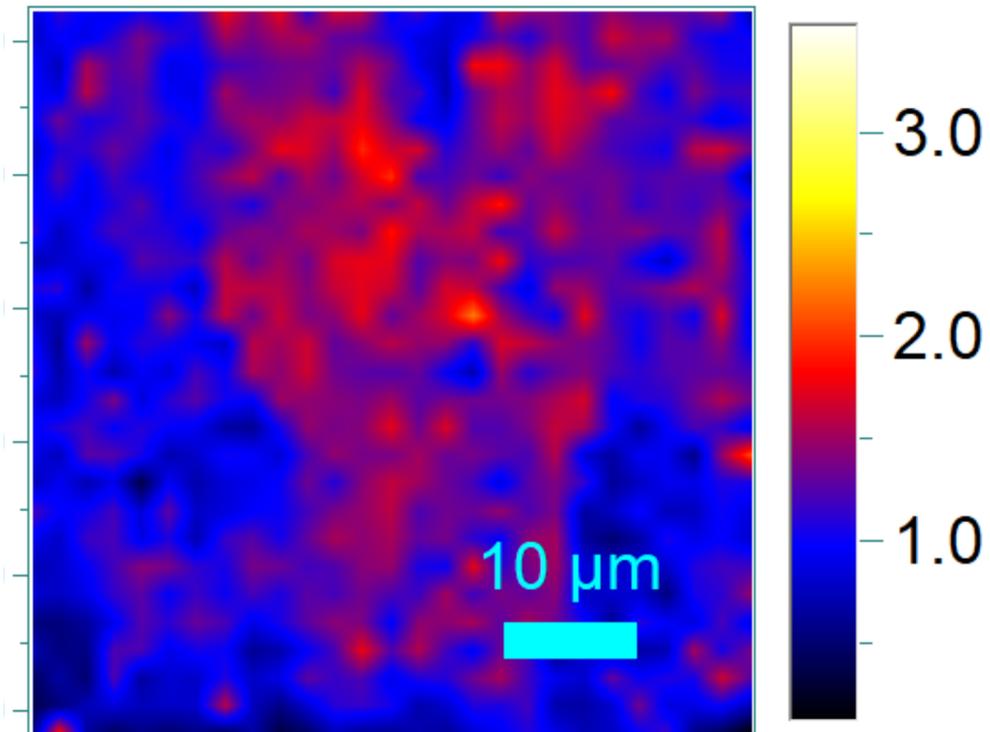
I_{575}/I_{645}



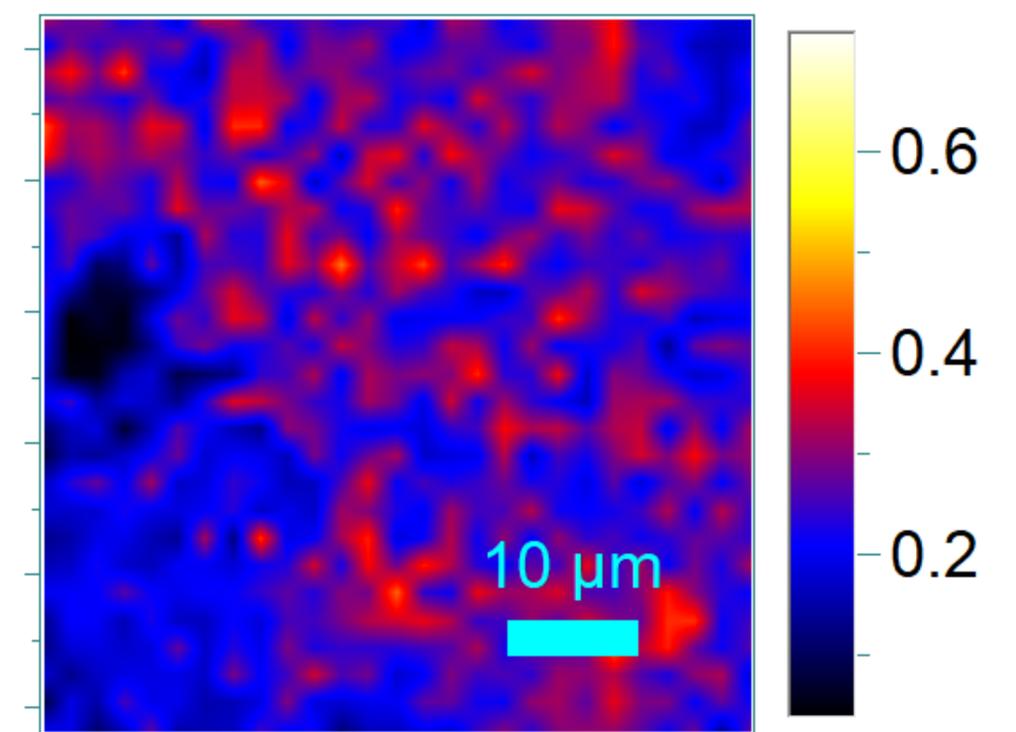
2021



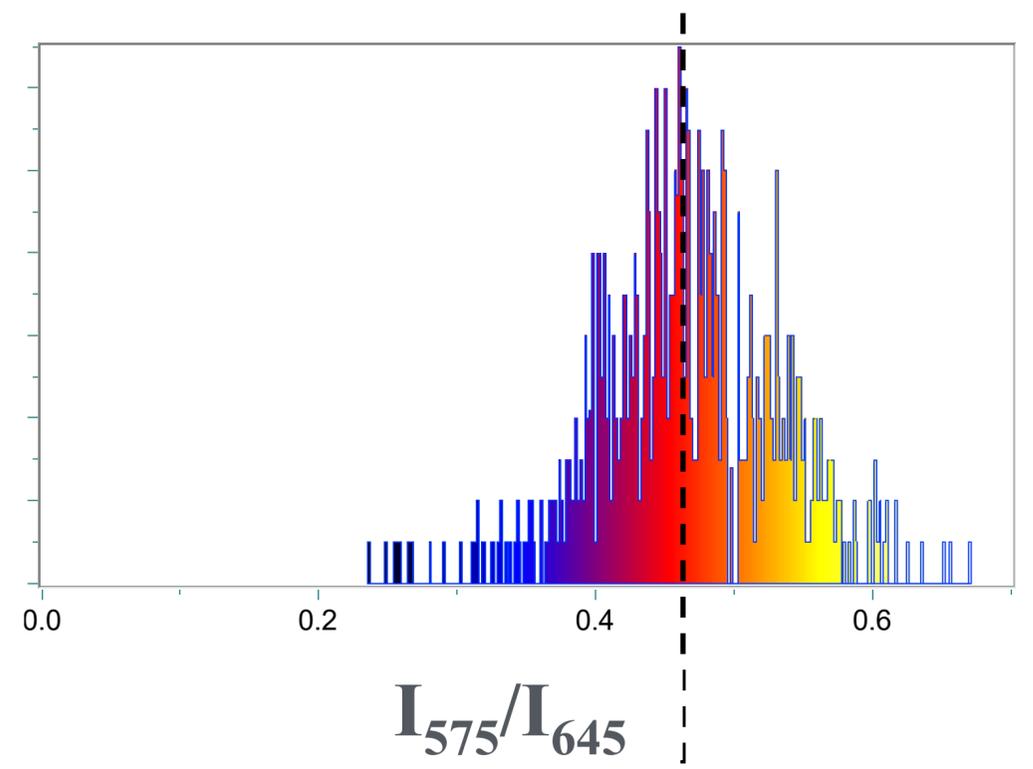
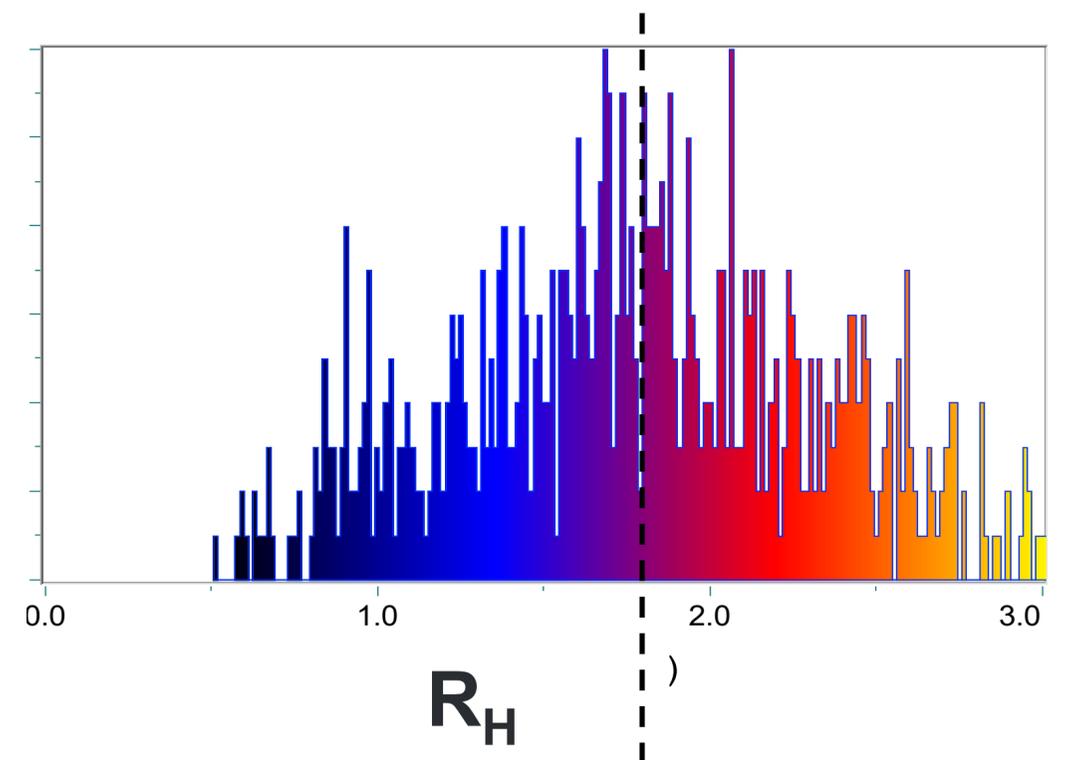
R_H



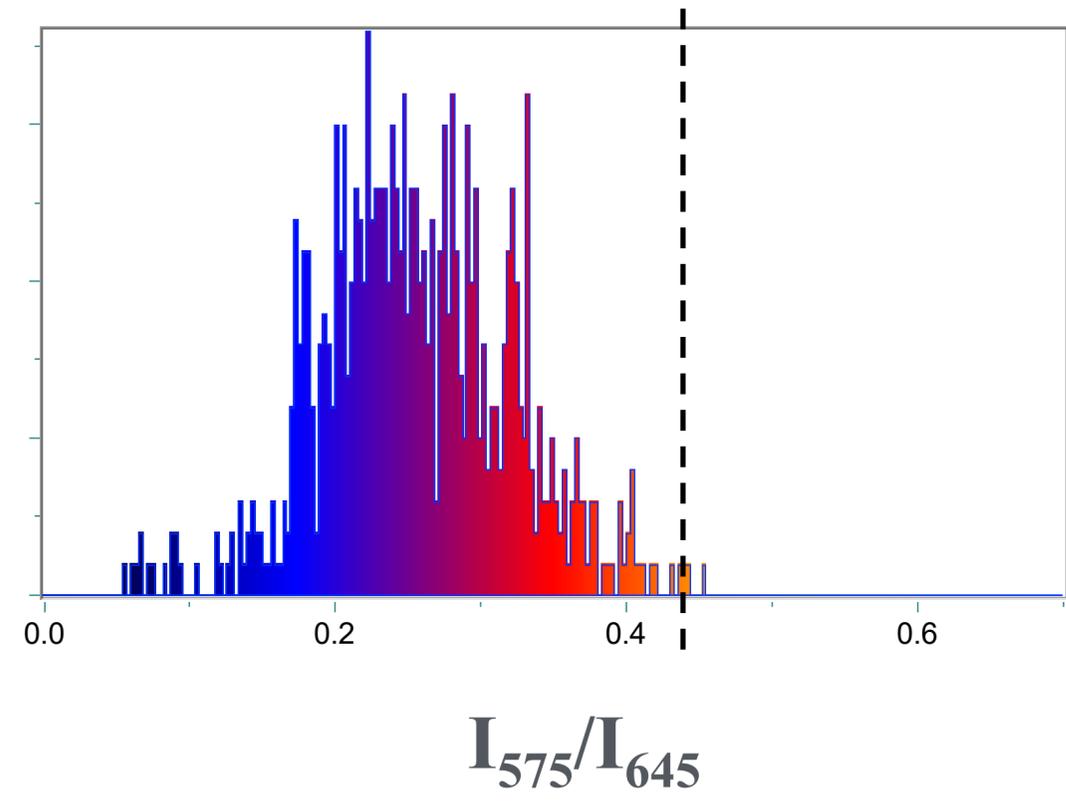
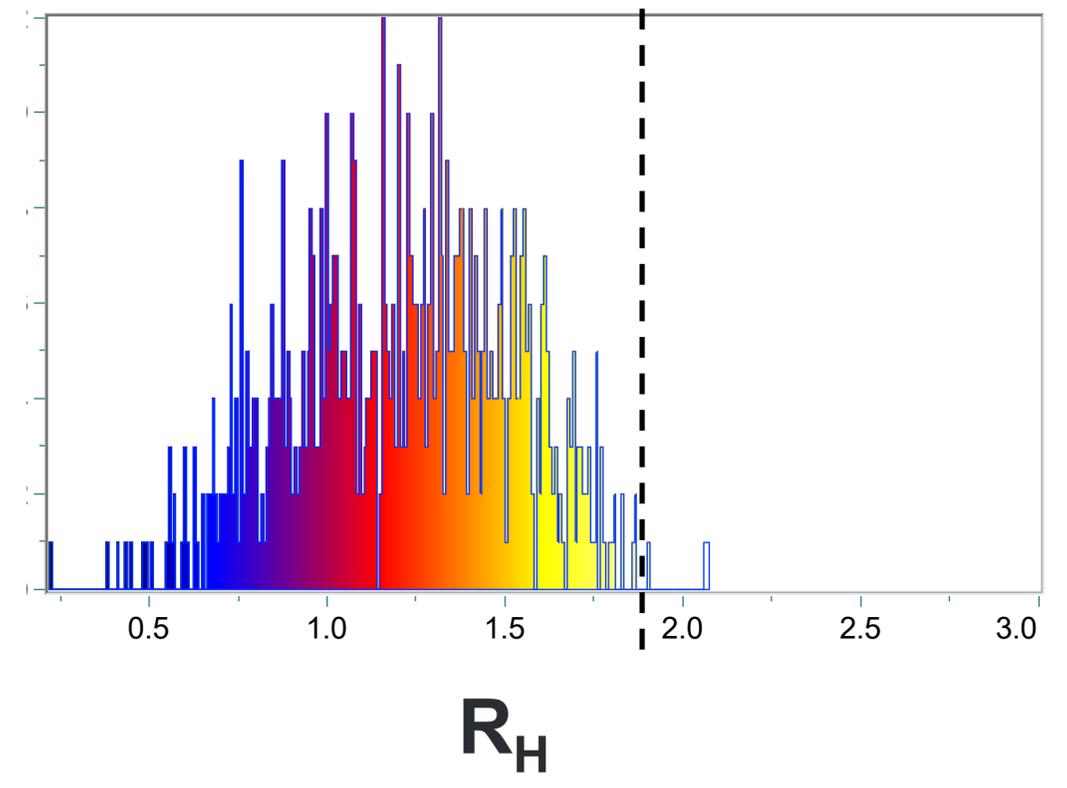
I_{575}/I_{645}



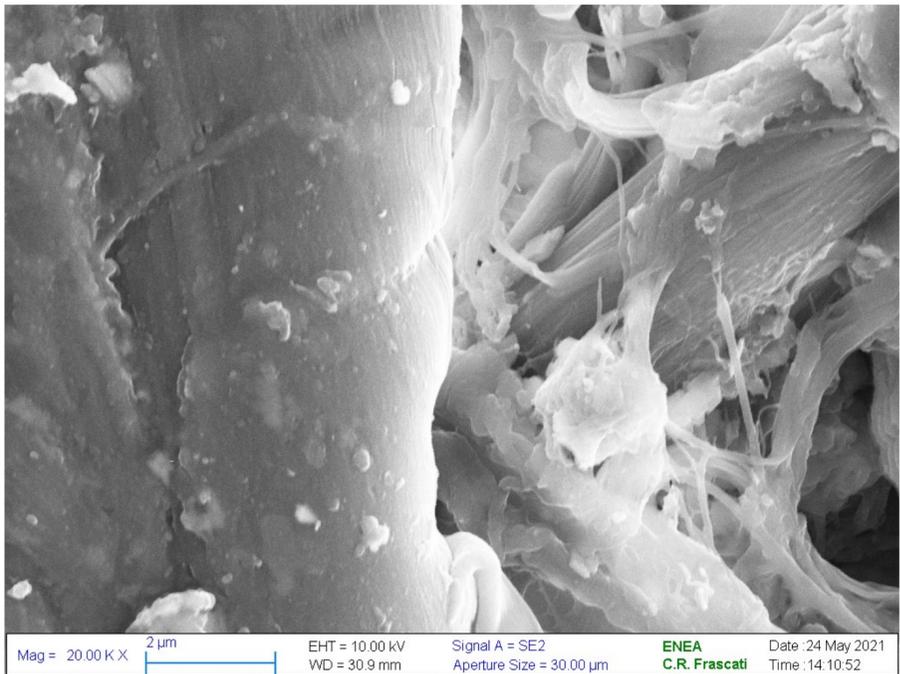
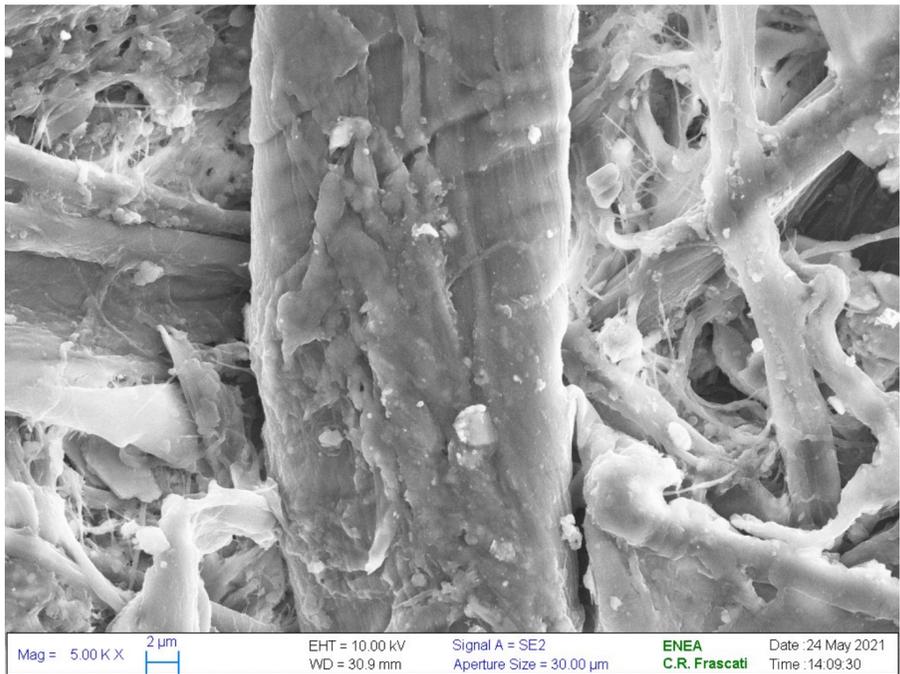
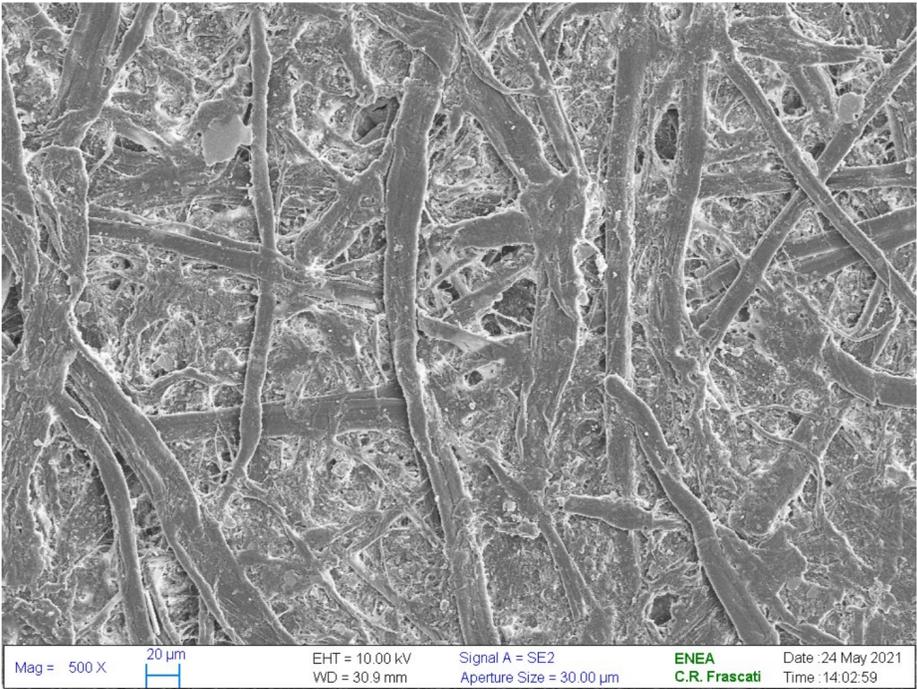
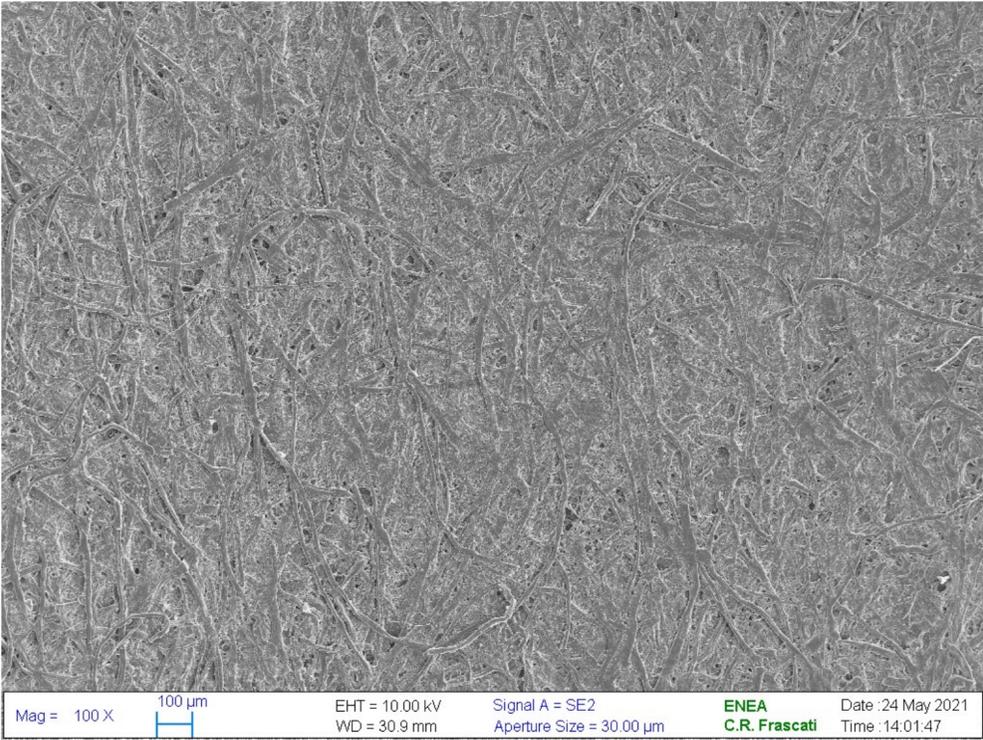
2020



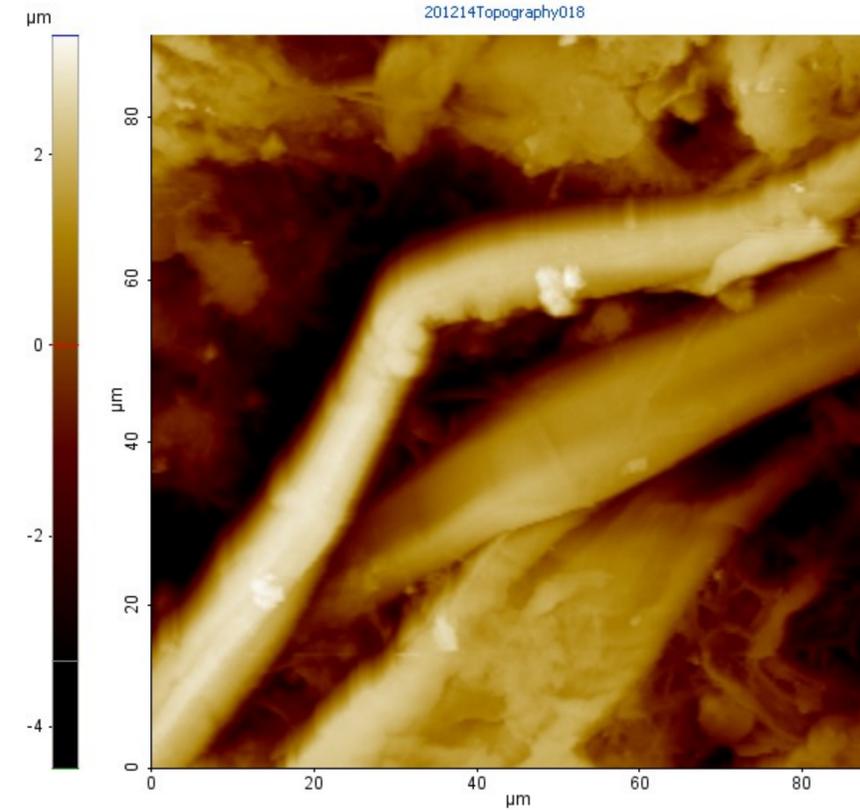
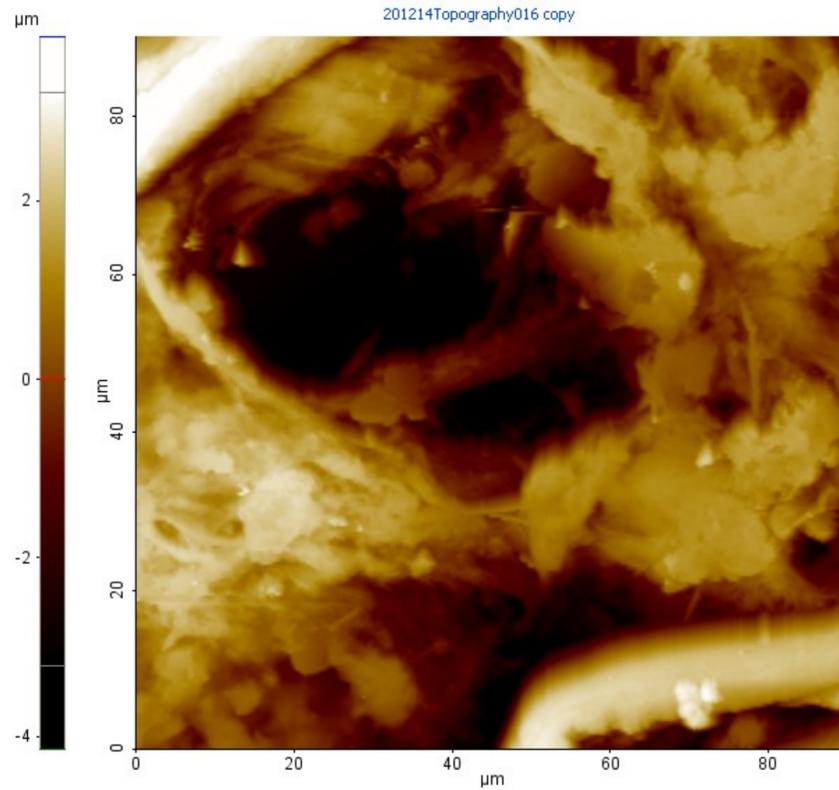
2021



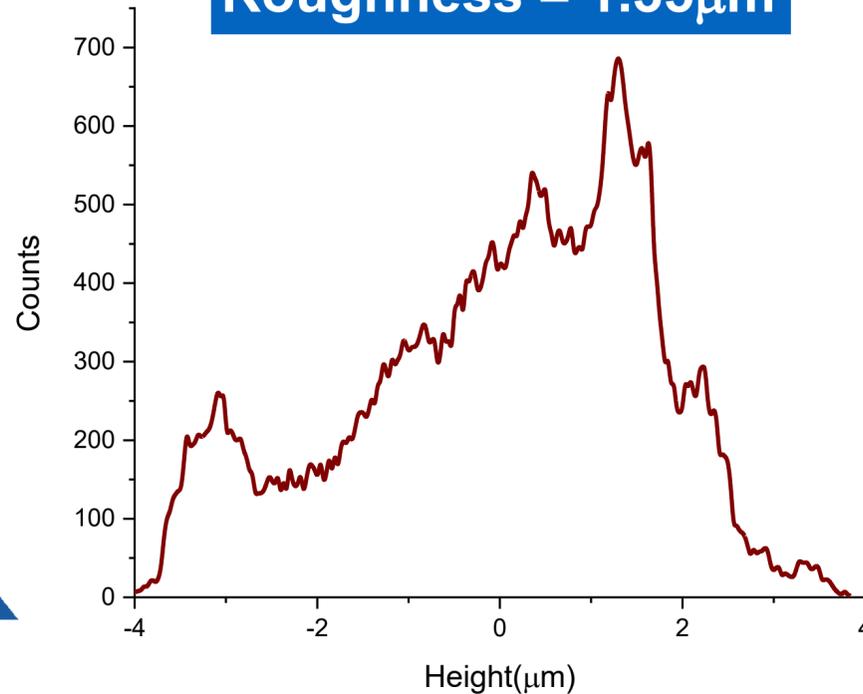
HR-SEM analysis of ancient paper (1893)



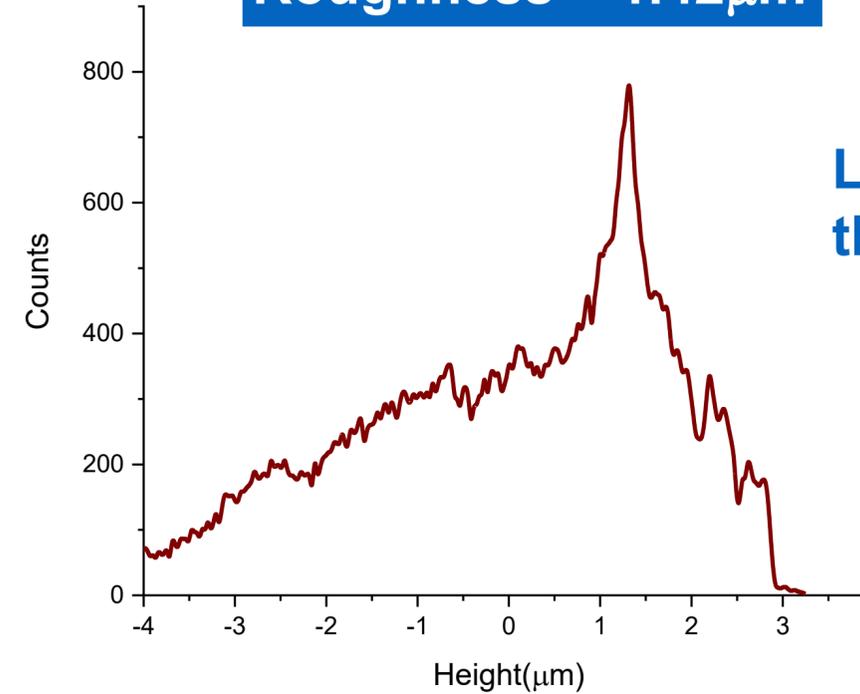
AFM analysis of ancient paper (1893)



Roughness = $1.35\mu\text{m}$



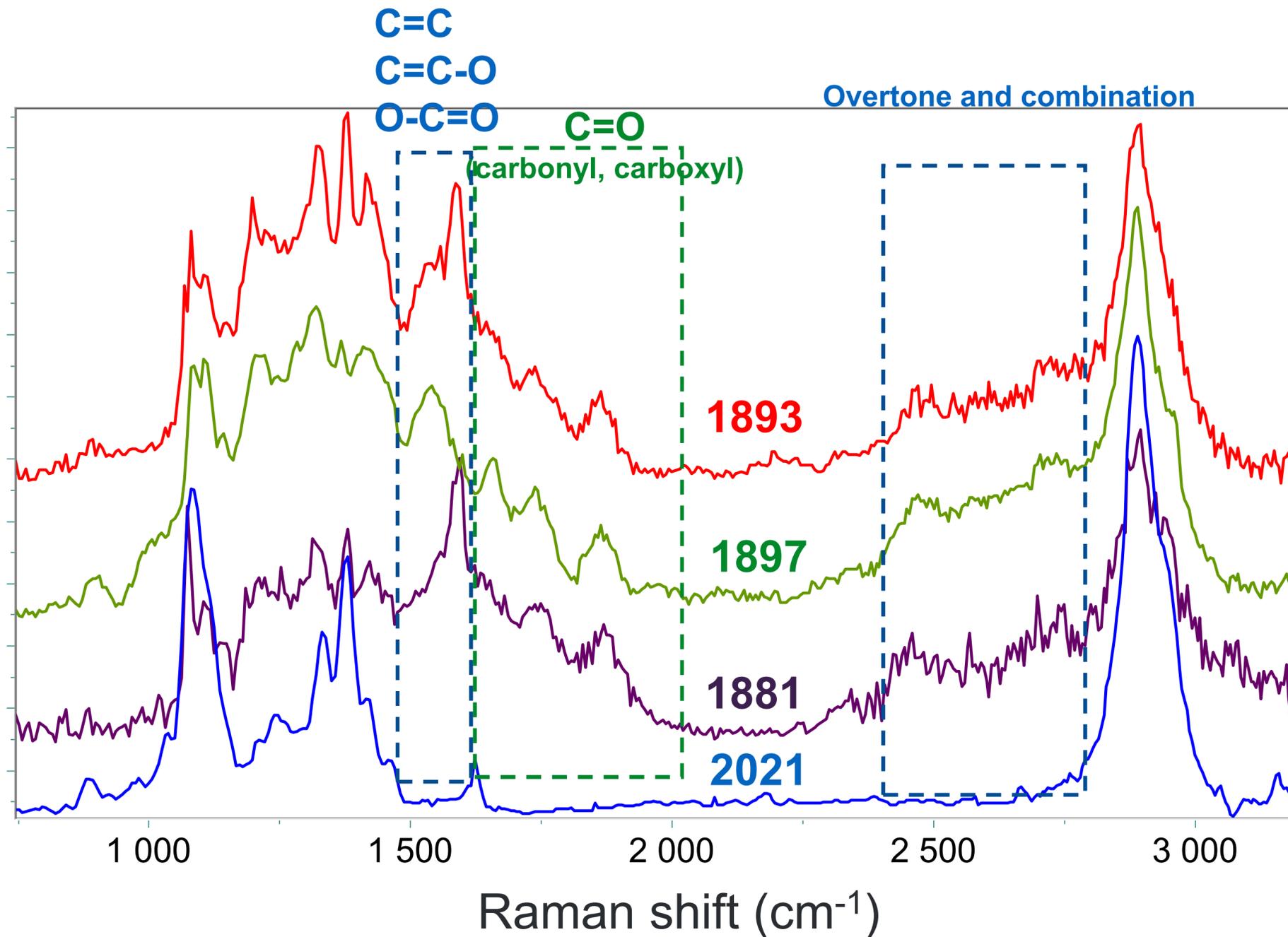
Roughness = $1.42\mu\text{m}$



Local roughness larger than that of modern paper ($1\mu\text{m}$).

Area: $80\mu\text{m} \times 80\mu\text{m}$

ANCIENT PAPER (XIX): Raman spectra

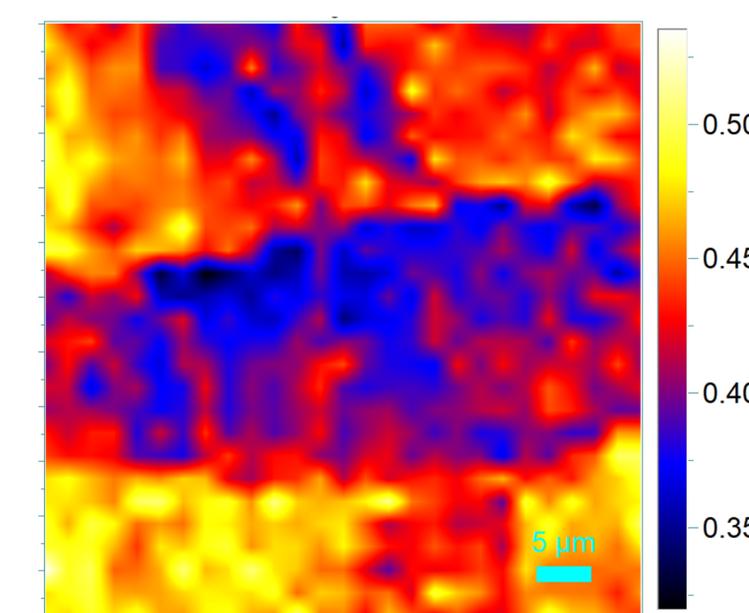
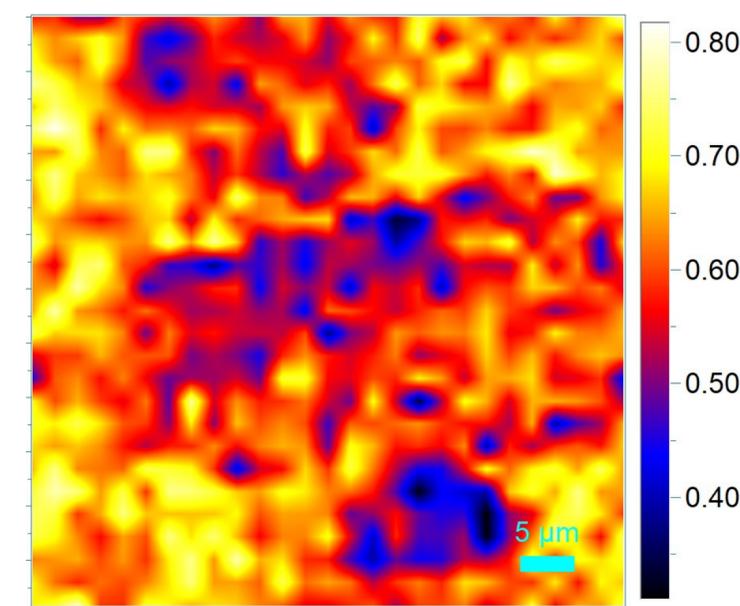
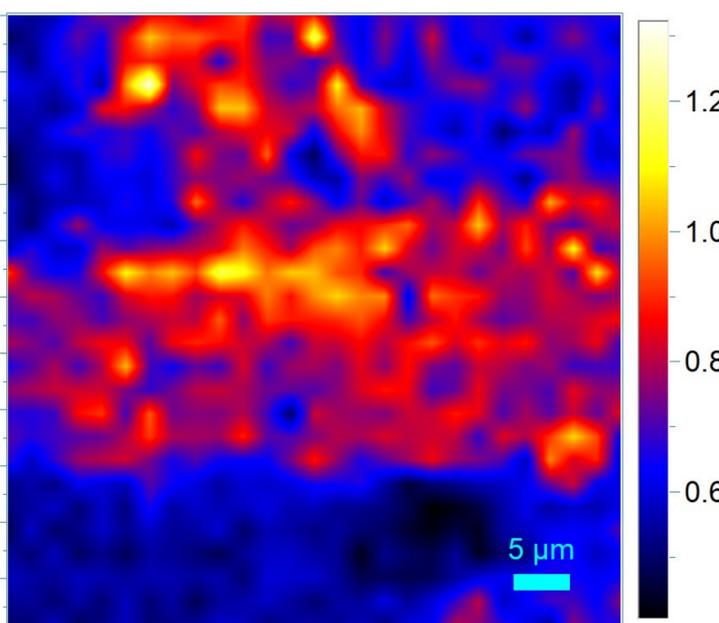
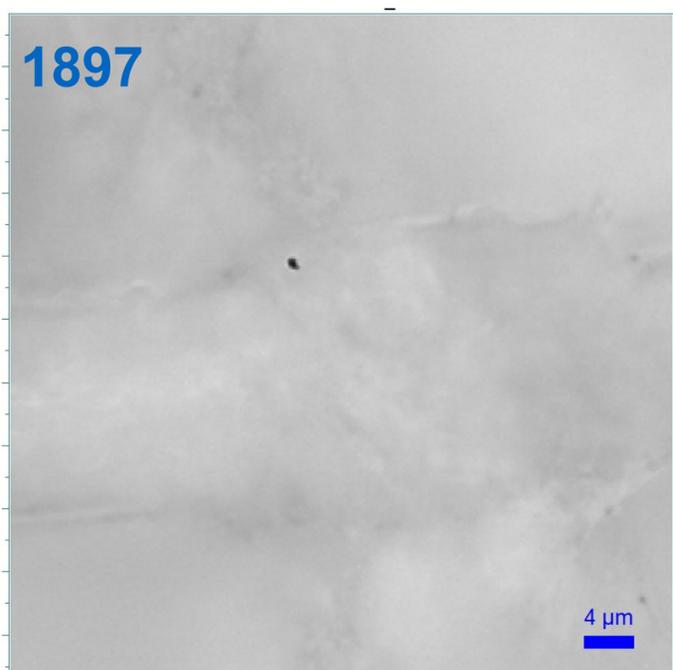
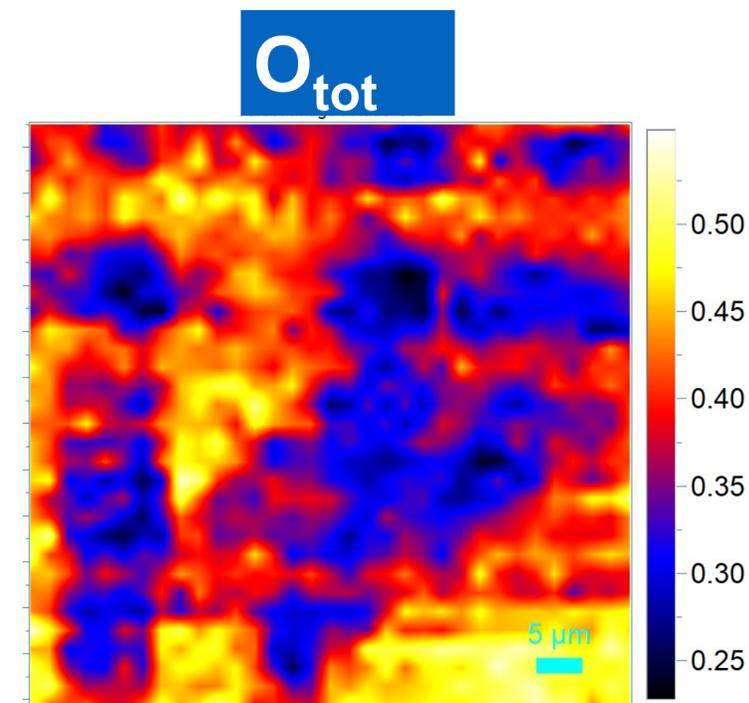
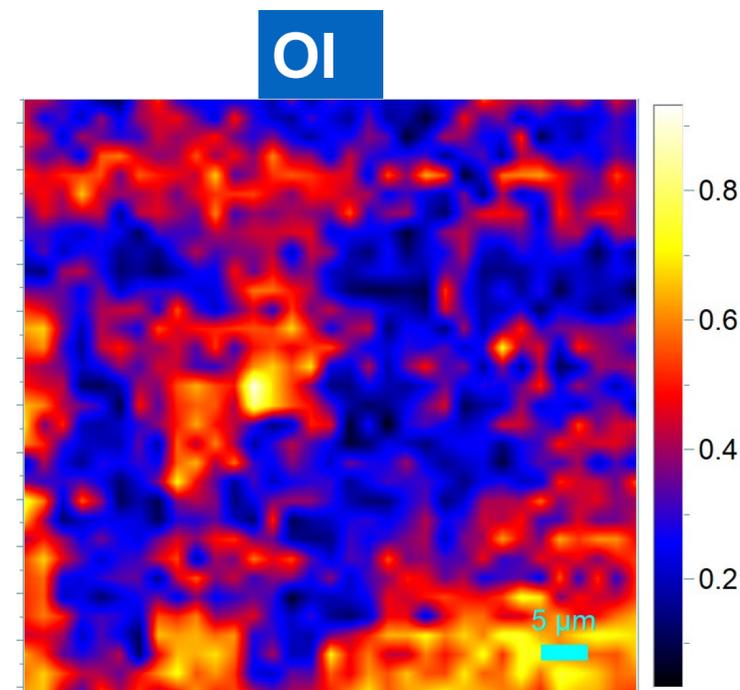
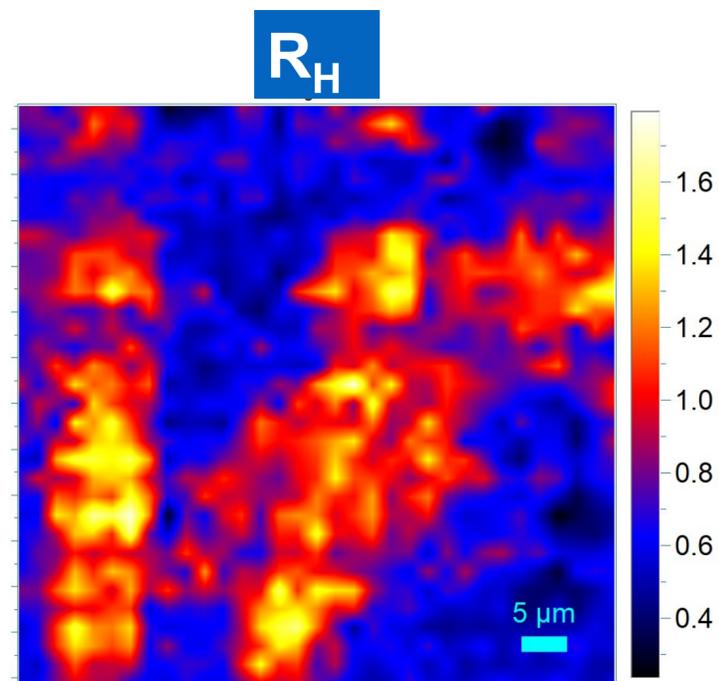
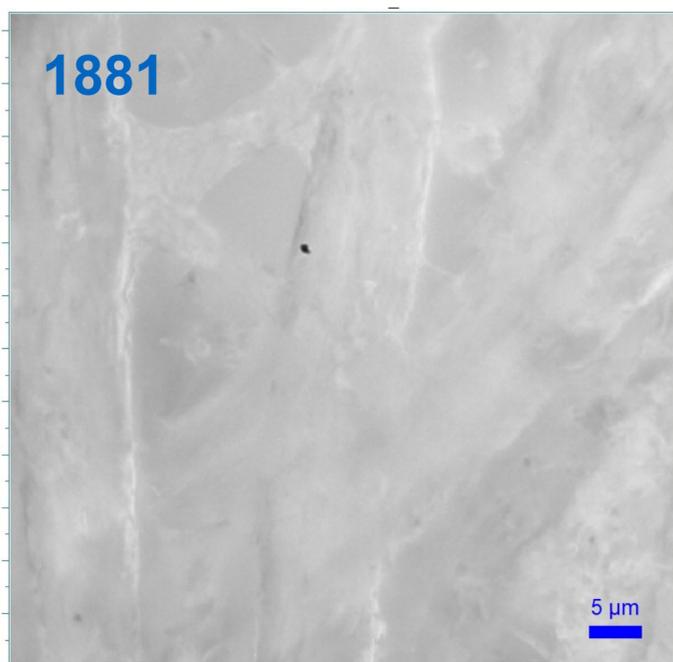


$$\text{OI} = A_{1640-1850} / A_{1500-1600}$$

$$\text{O}_{\text{tot}} = A_{1500-2800} / A_{700-3000}$$

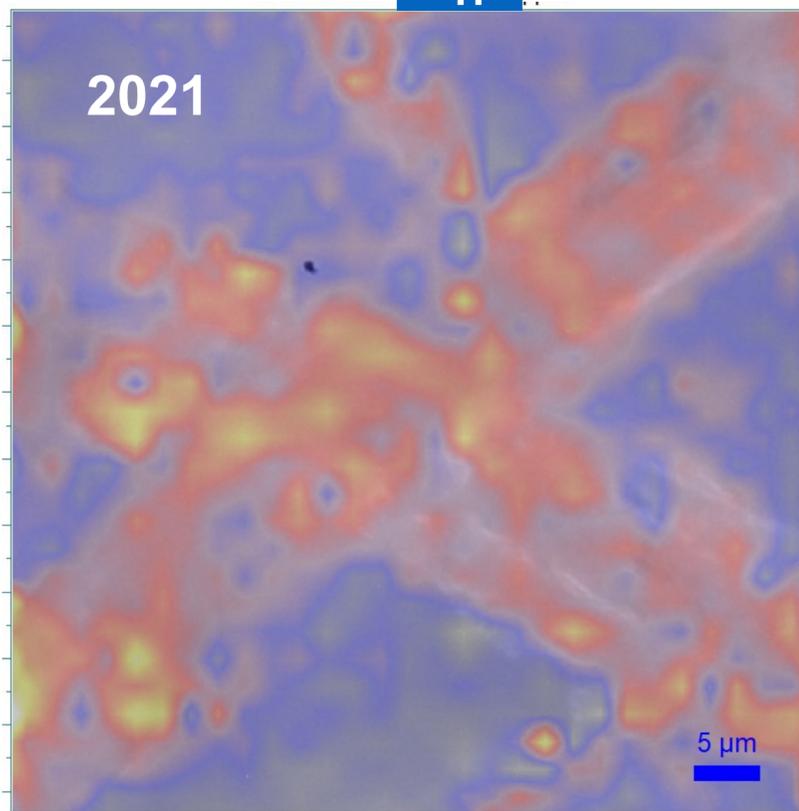
- In ancient paper new peaks appear that are attributed to functional groups deriving from oxidation.
- The structure of main cellulose peaks can be lost

Raman mapping of R_H , OI and O_{tot} markers (60 μm x 60 μm , 2 μm grid step size, 900 spectra)
PAPER OF XIX century

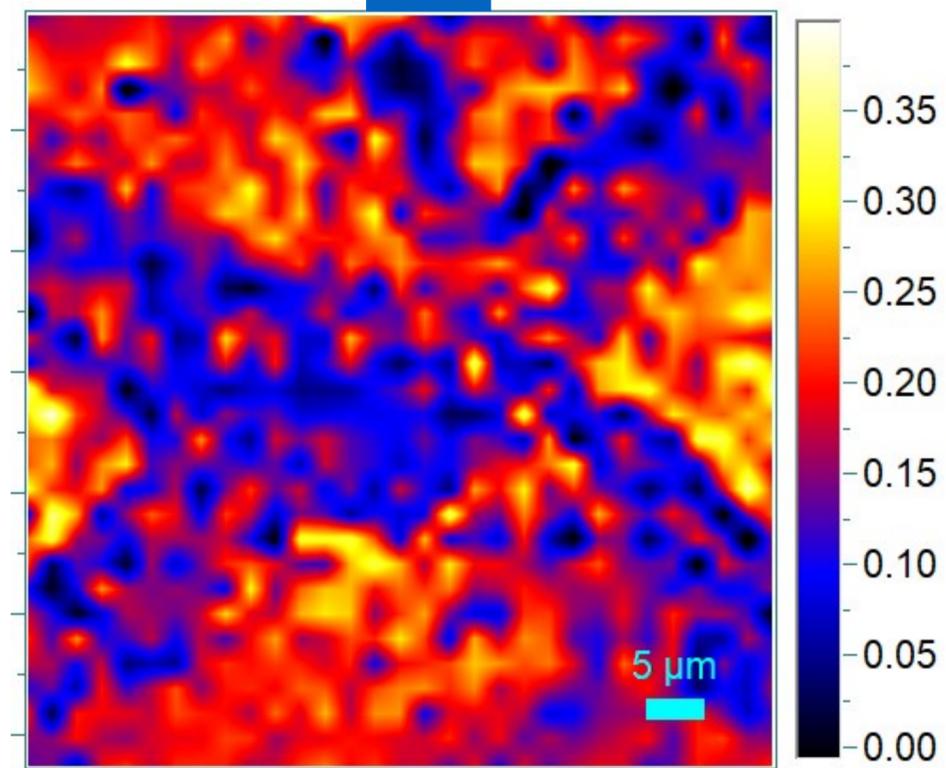


Raman mapping of R_H , OI and O_{tot} markers (60 μm x 60 μm , 2 μm grid step size, 900 spectra)
PAPER OF XXI century

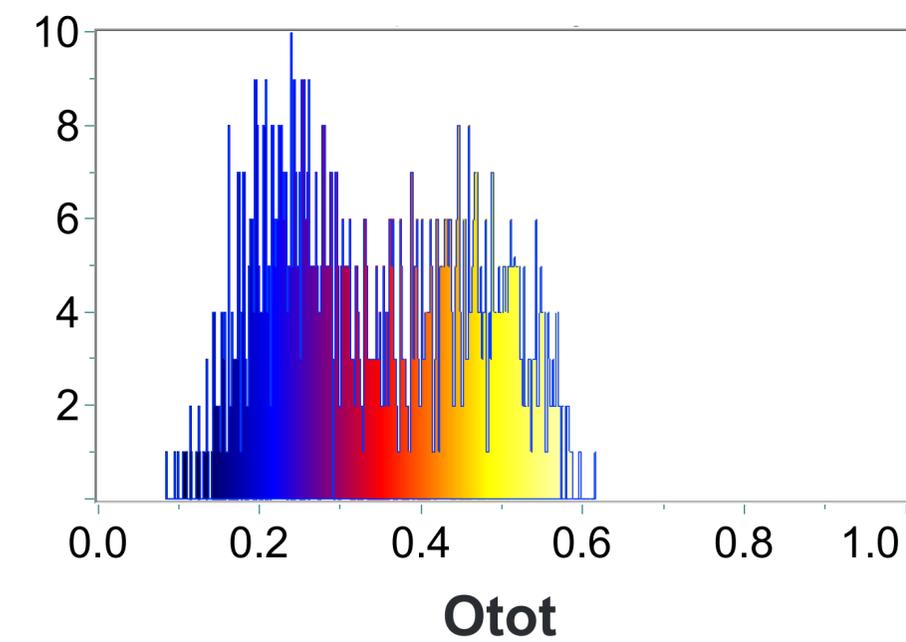
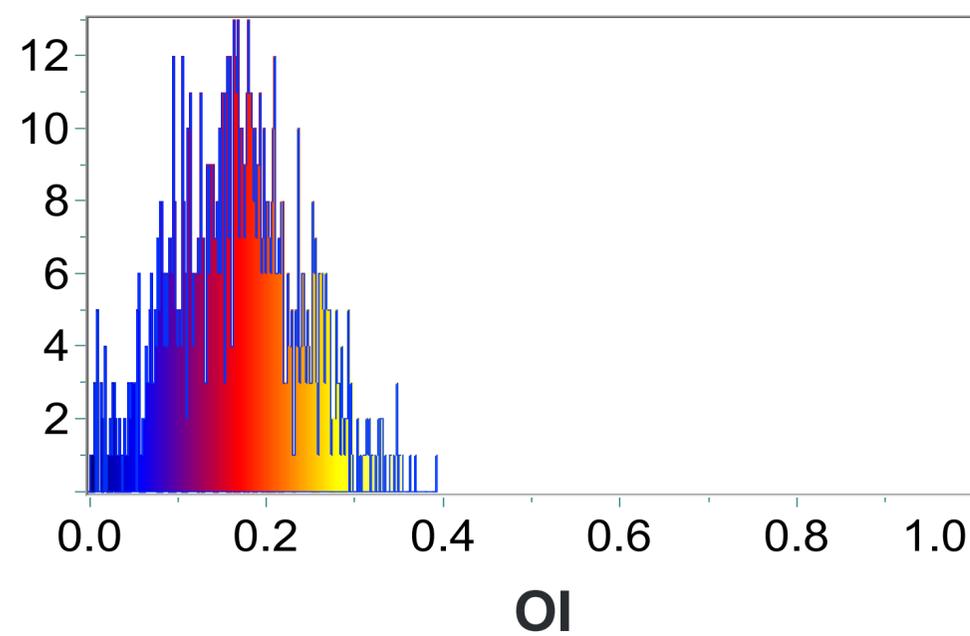
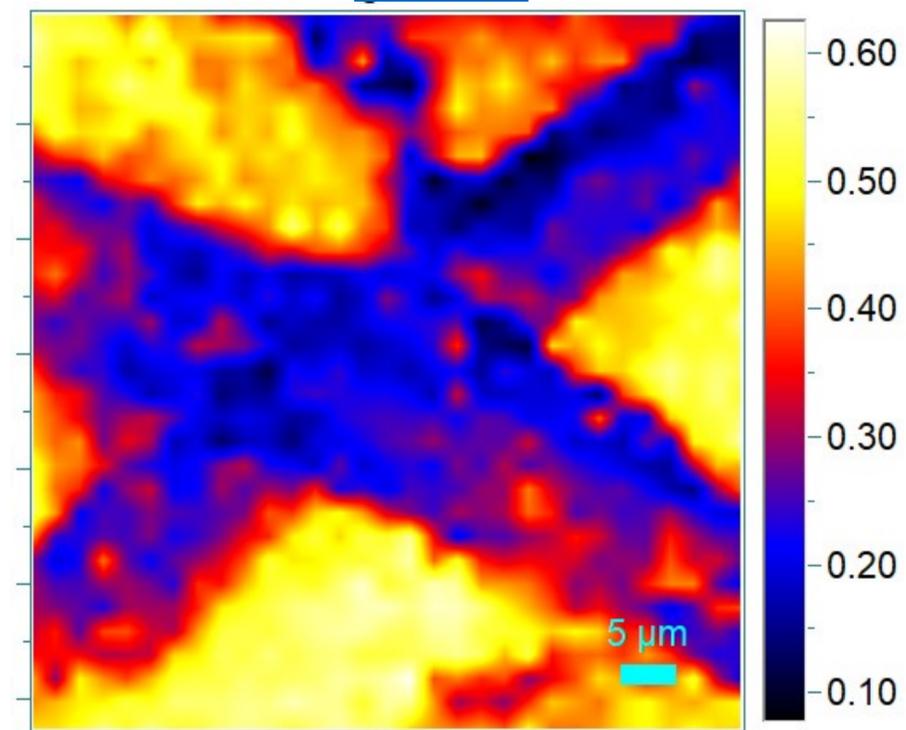
R_H

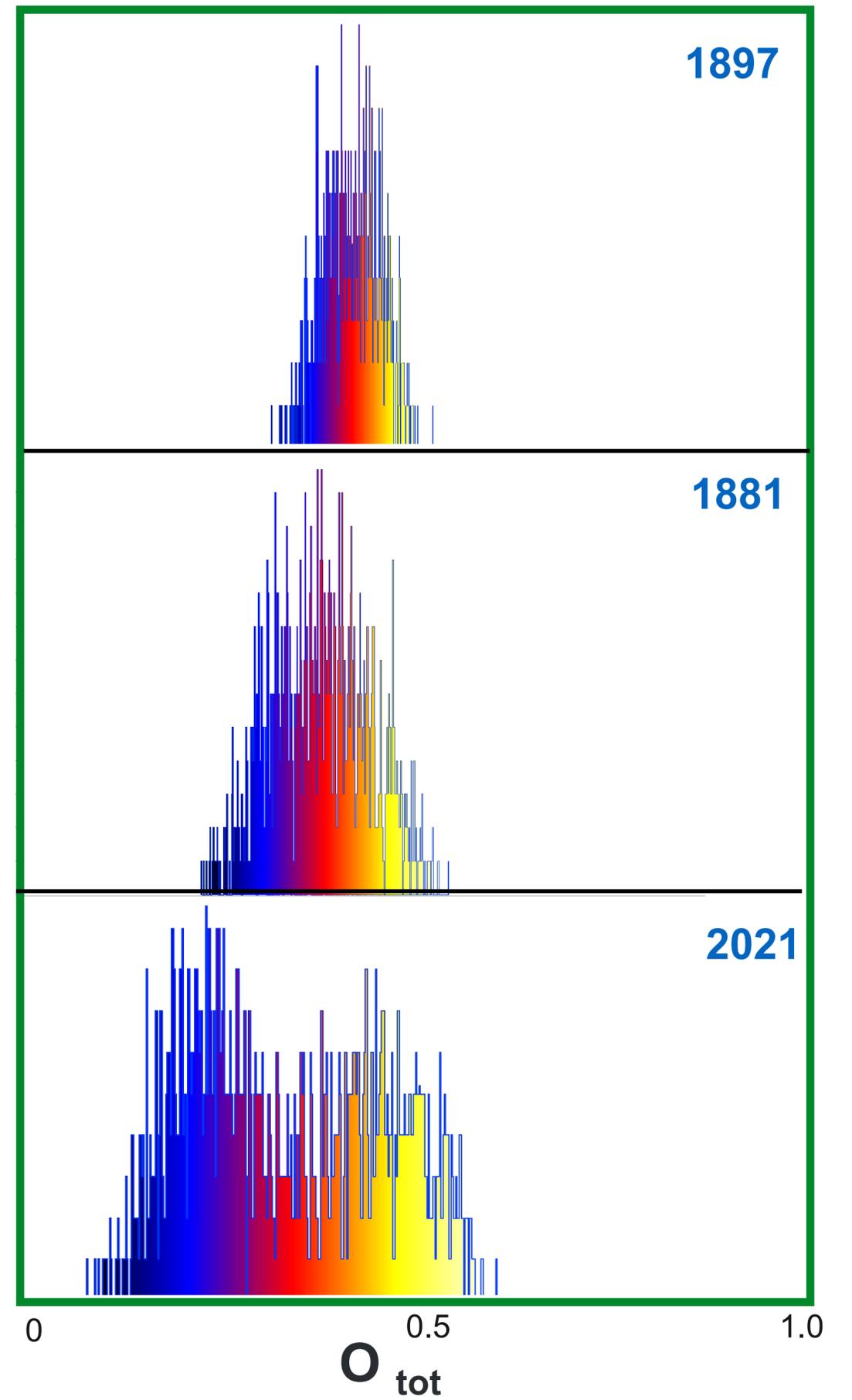
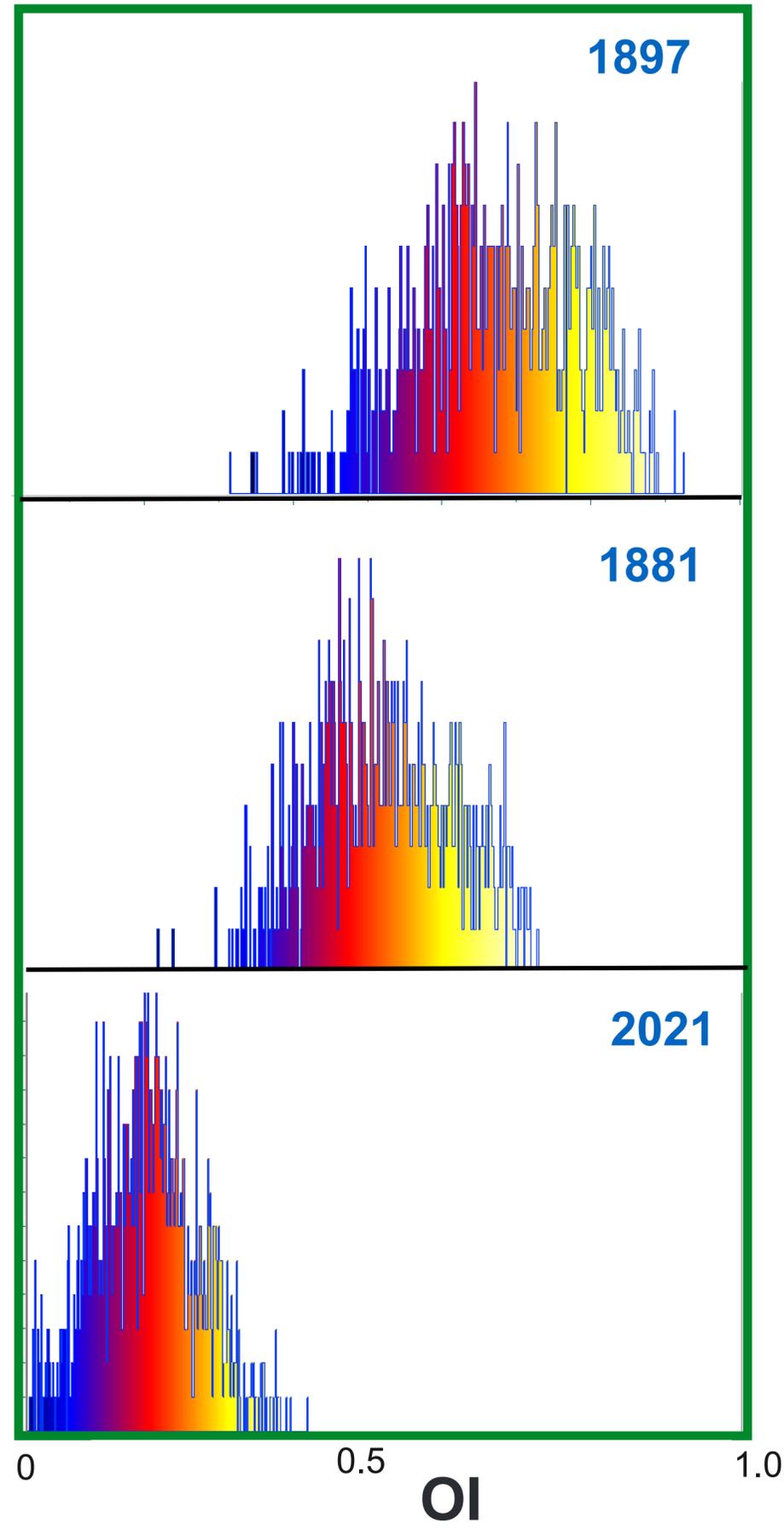
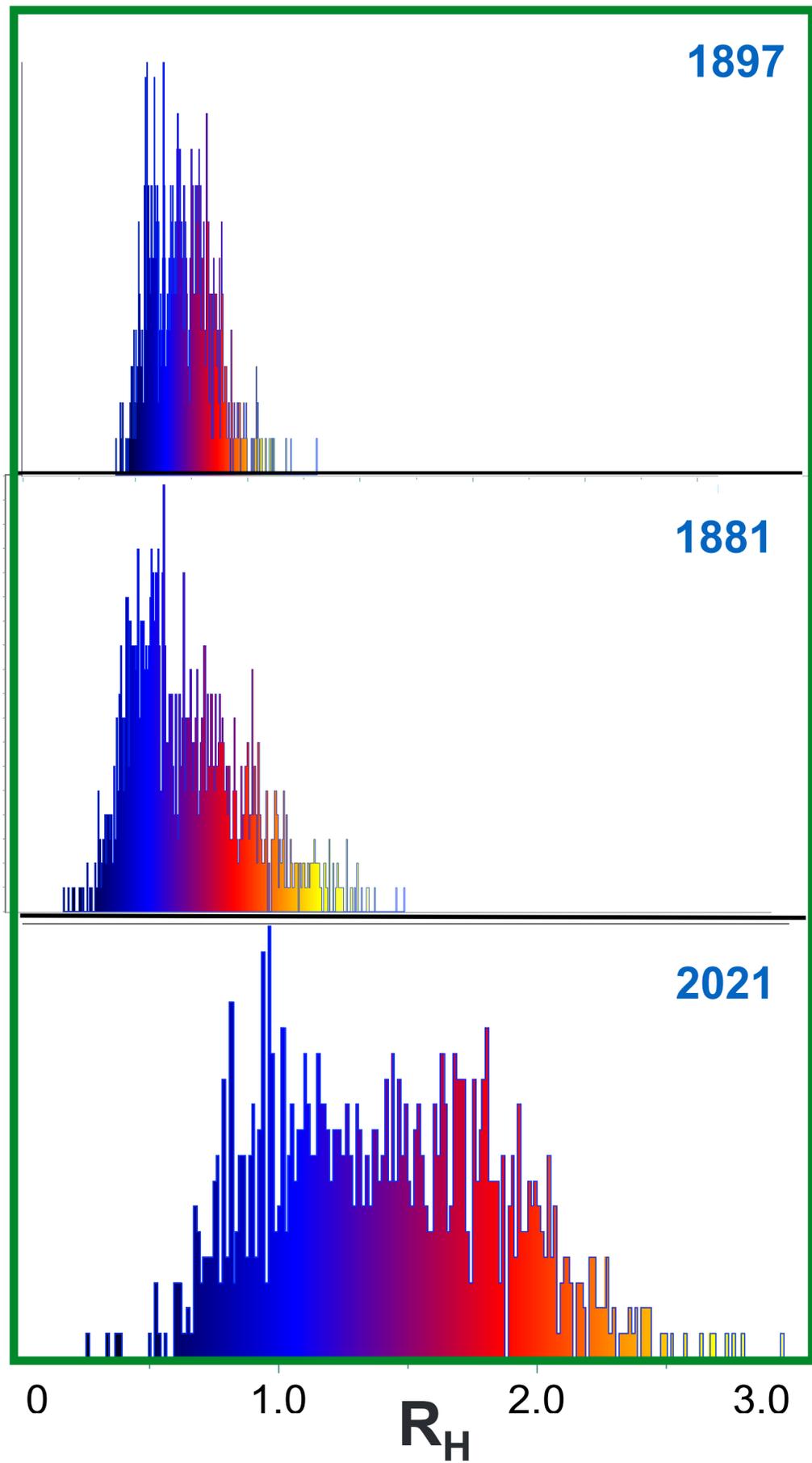


OI

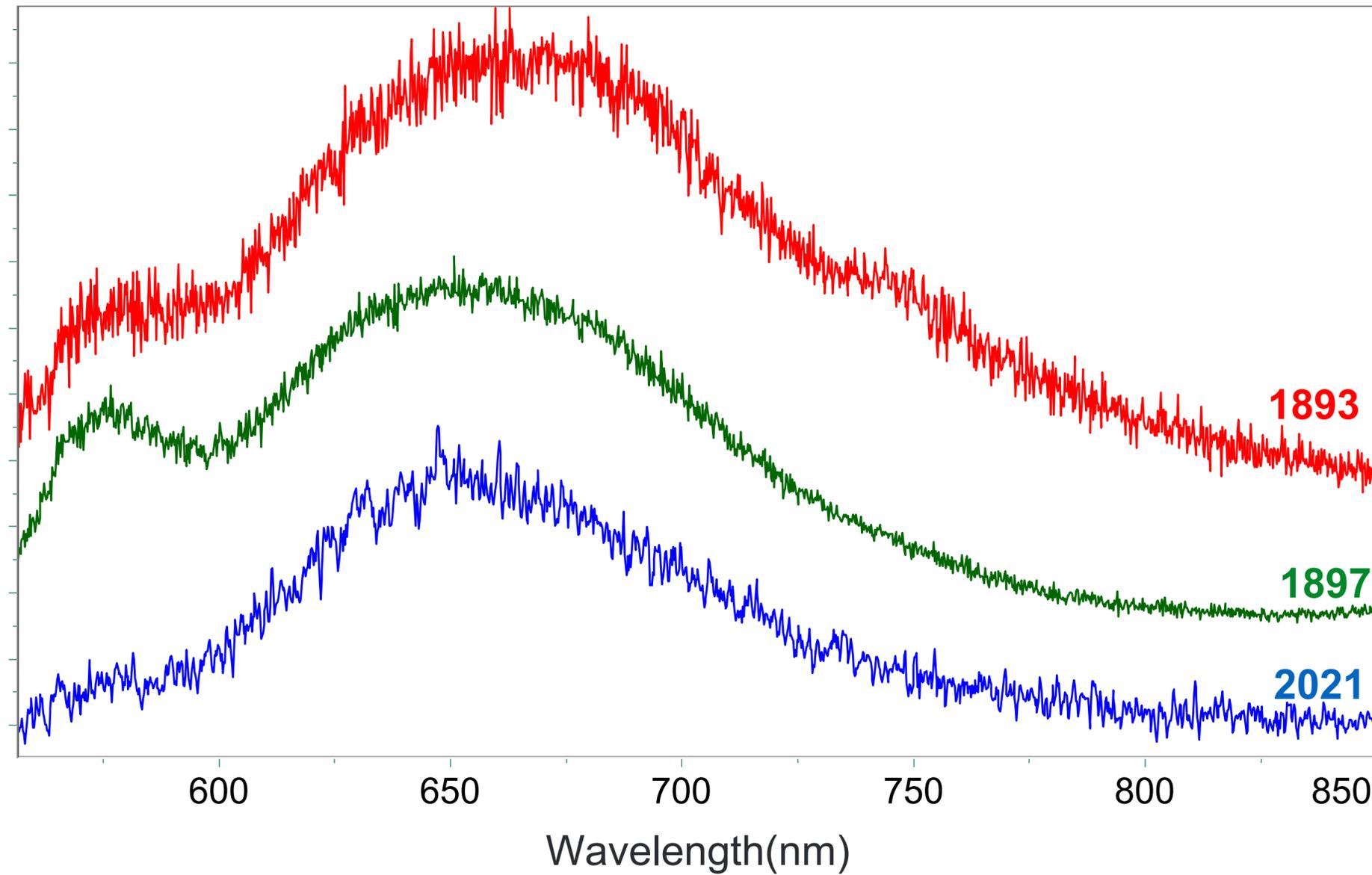


O_{tot}



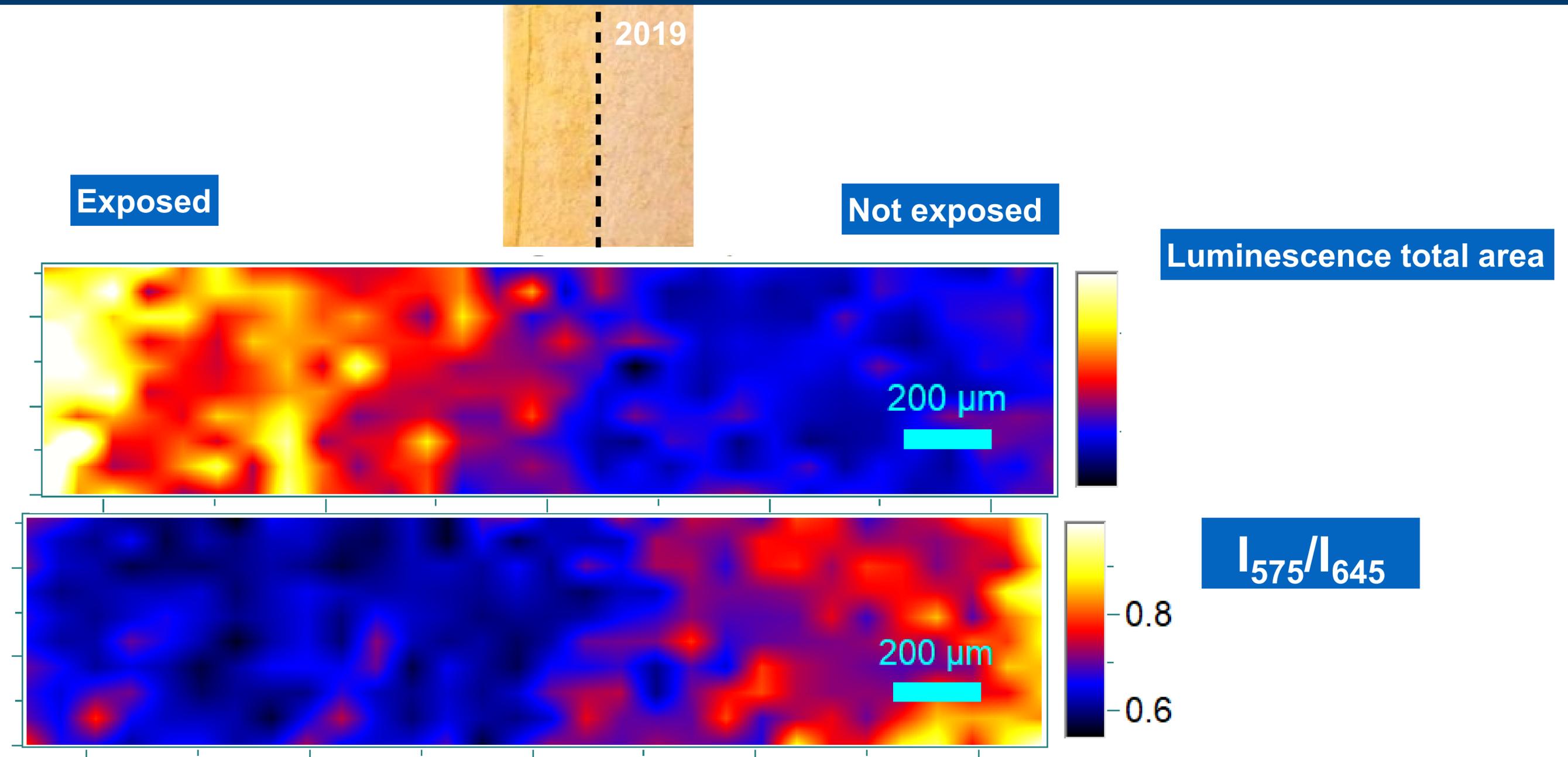


ANCIENT PAPER (XIX): luminescence spectra



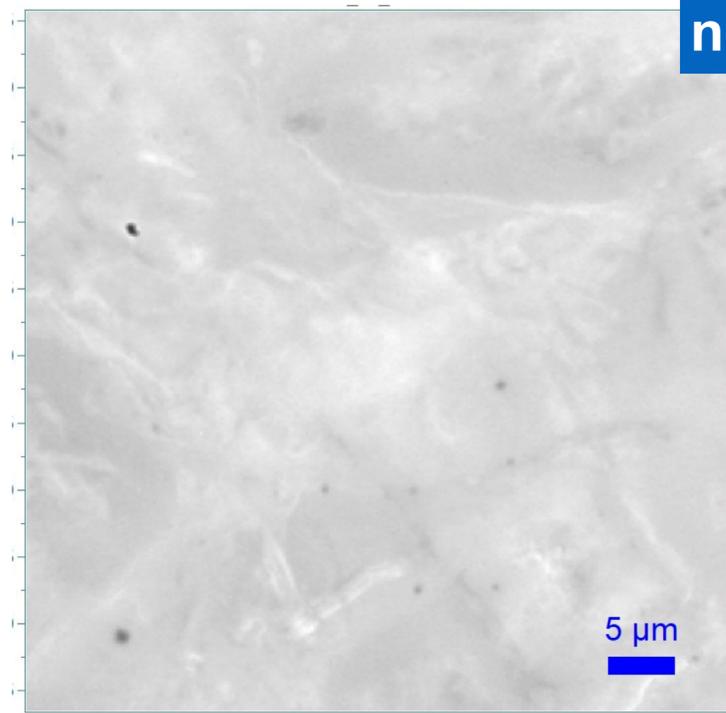
- No clear behaviour of luminescence shape with ageing
- Increase of luminescence intensity with paper age

Luminescence mapping (2198 μm x 379 μm , \sim 70 μm x 50 μm step size, 300 spectra)
PAPER OF XXI century

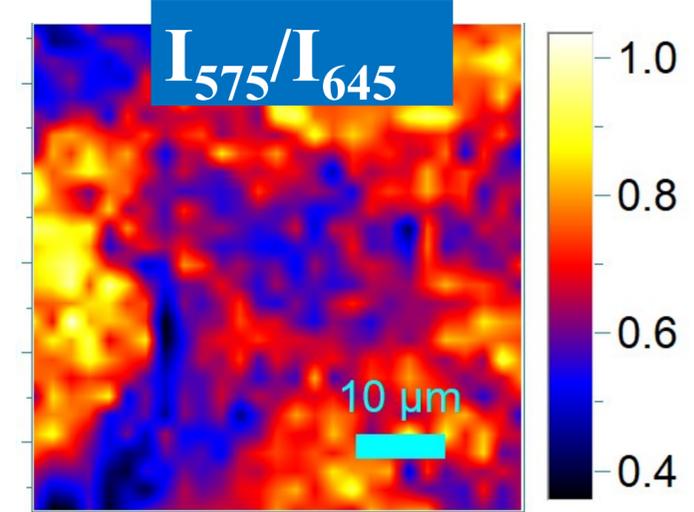
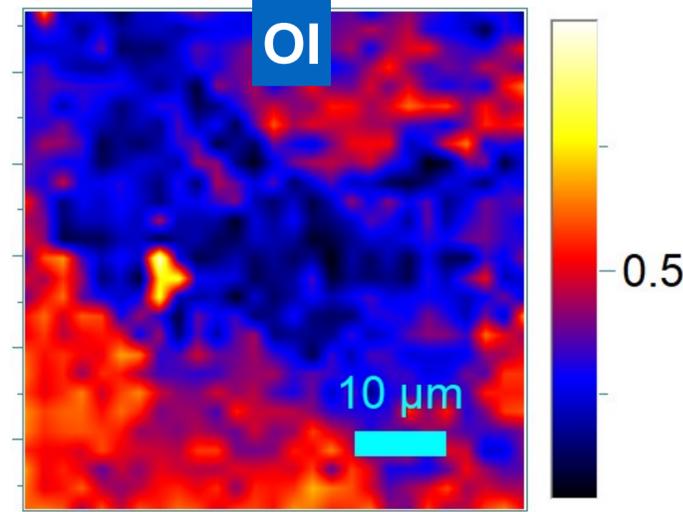
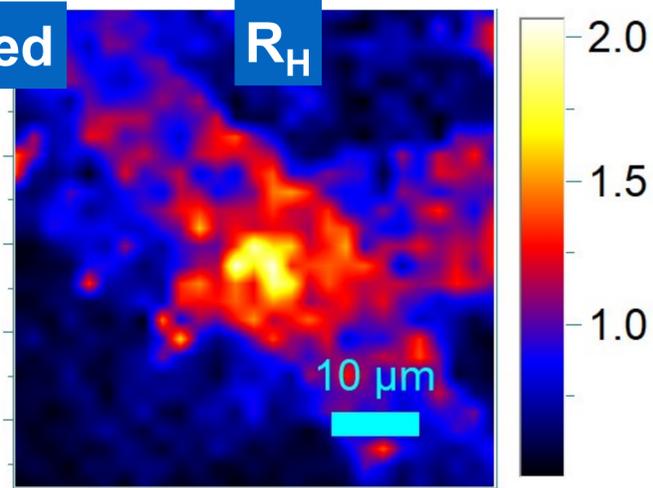


Exposition to ambient light for 9 months:

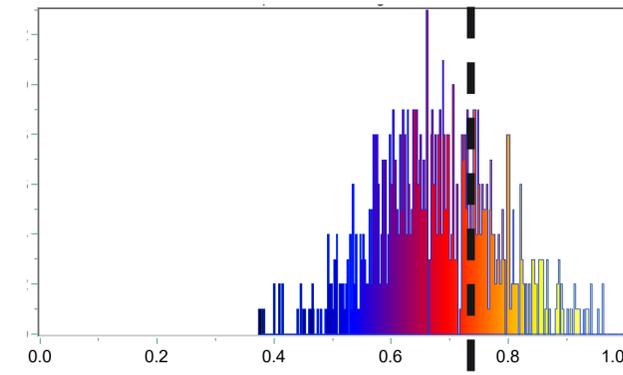
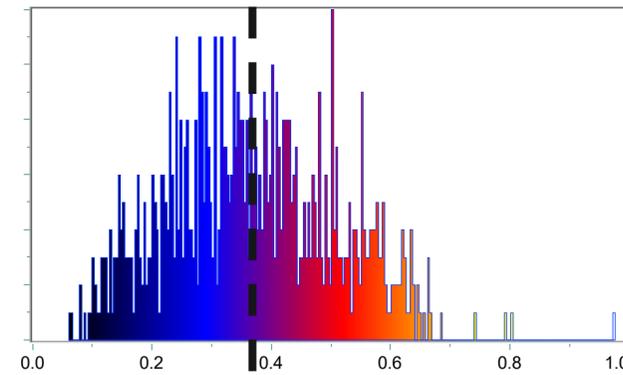
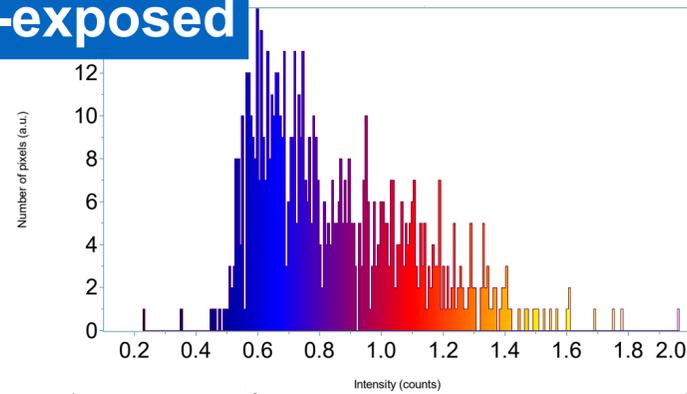
- Decrease of 575 nm peak intensity
- Increase of luminescence total area
- No peak shift observed



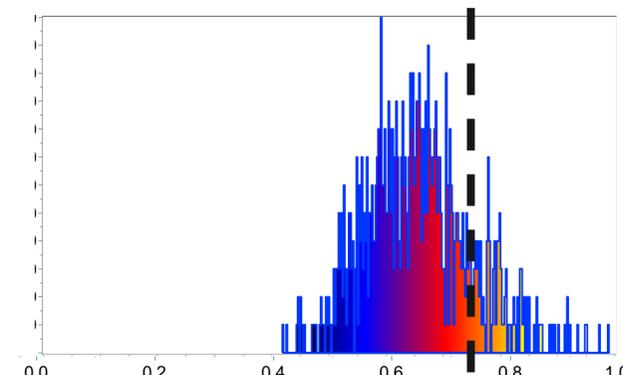
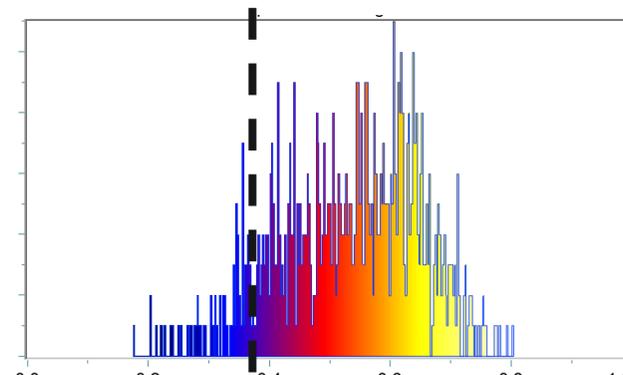
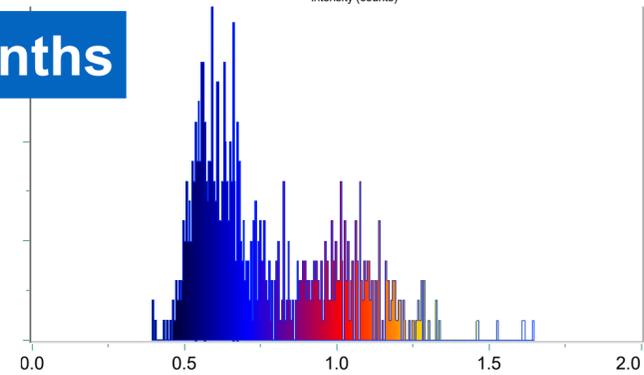
not-exposed



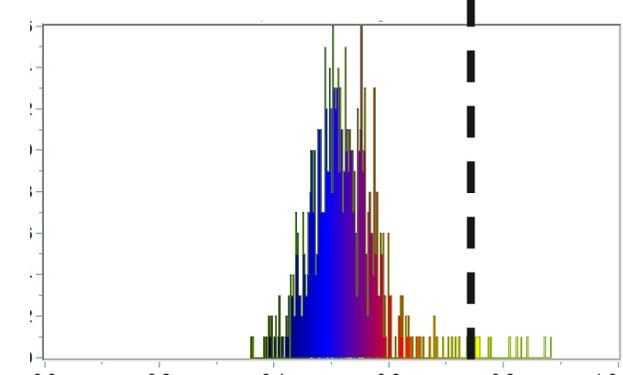
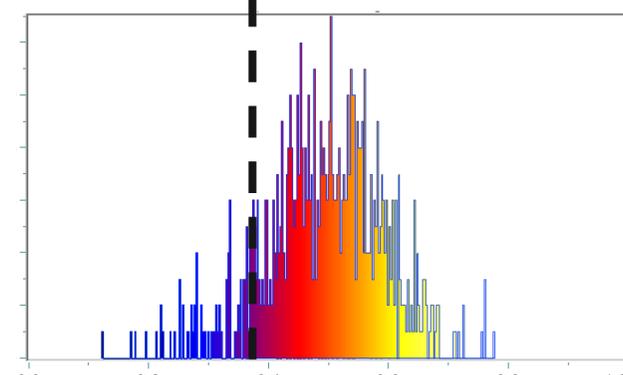
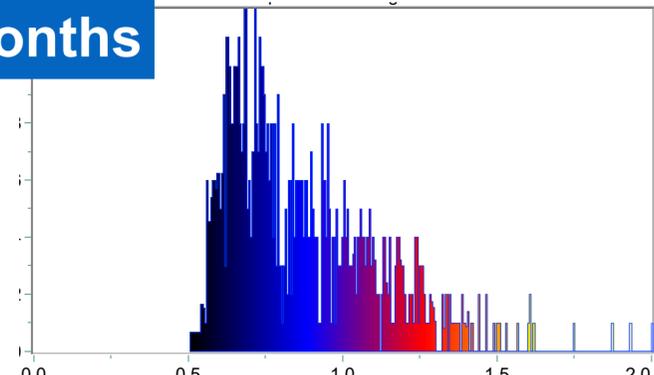
not-exposed



9 months



22 months

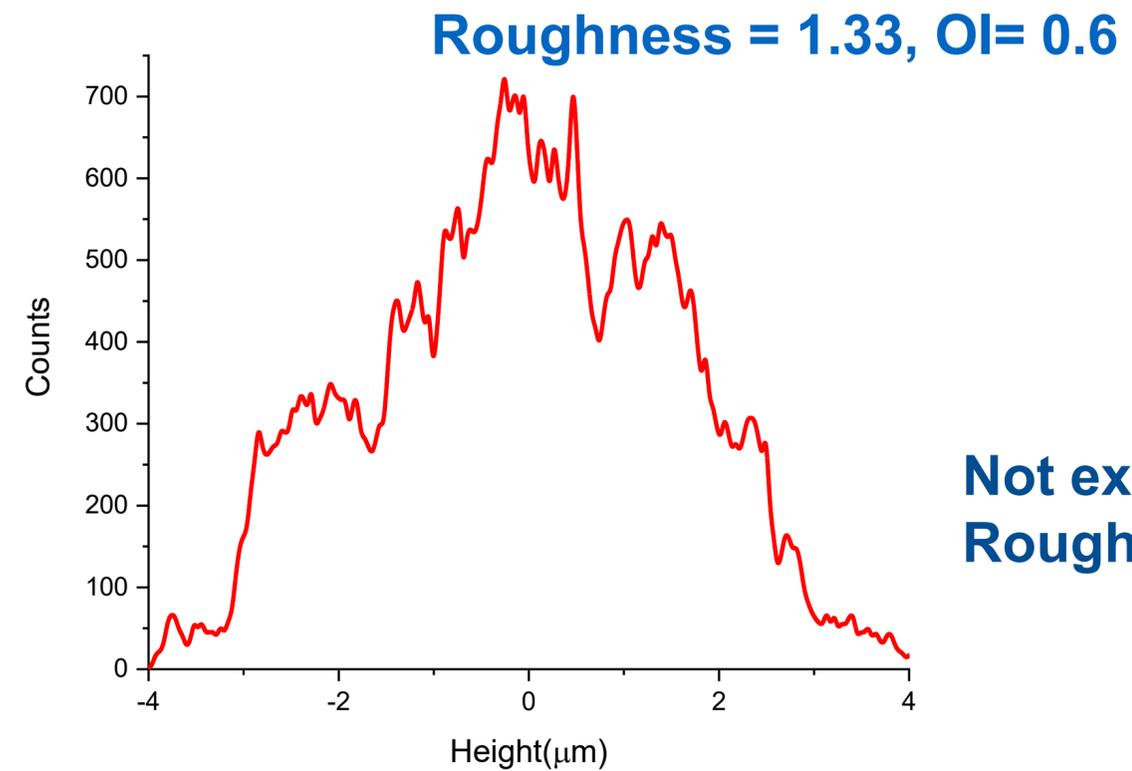
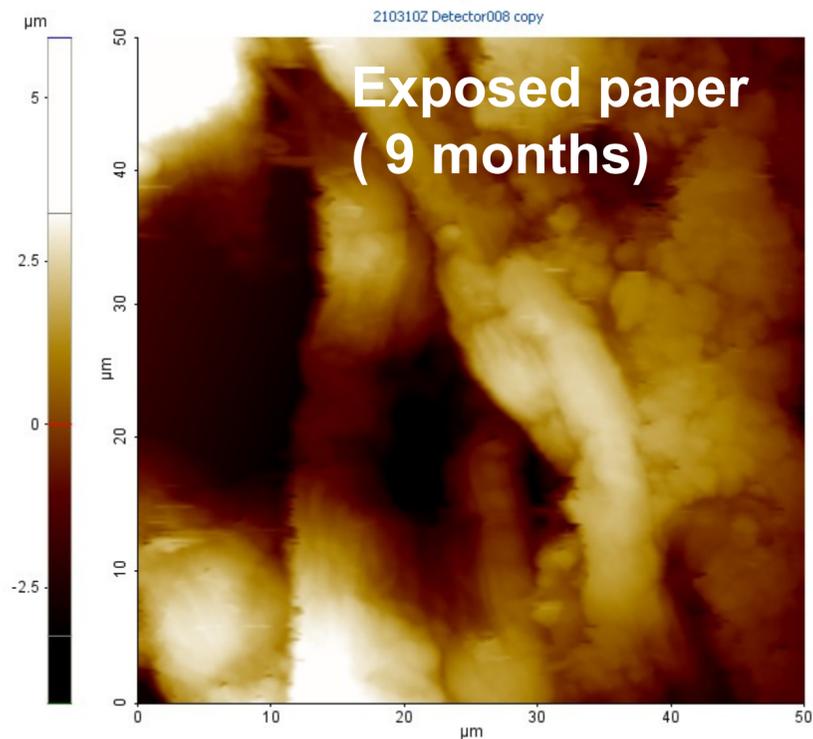
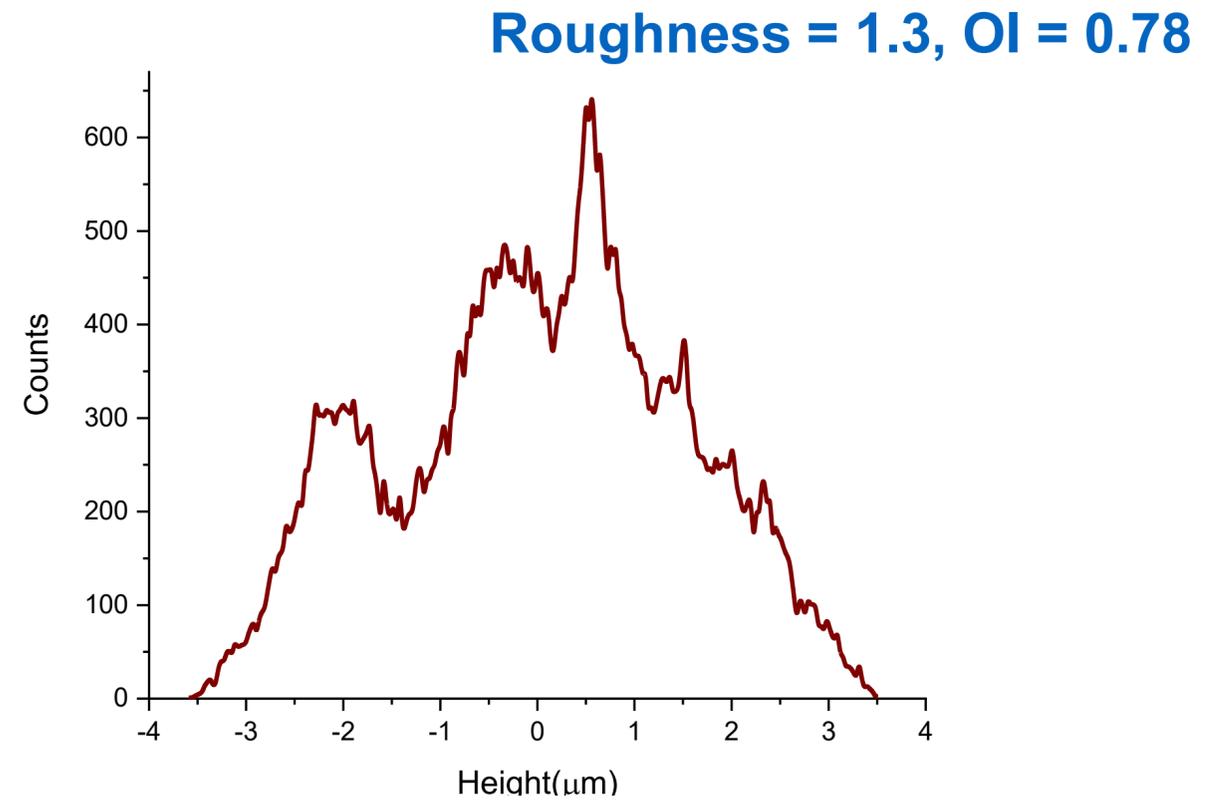
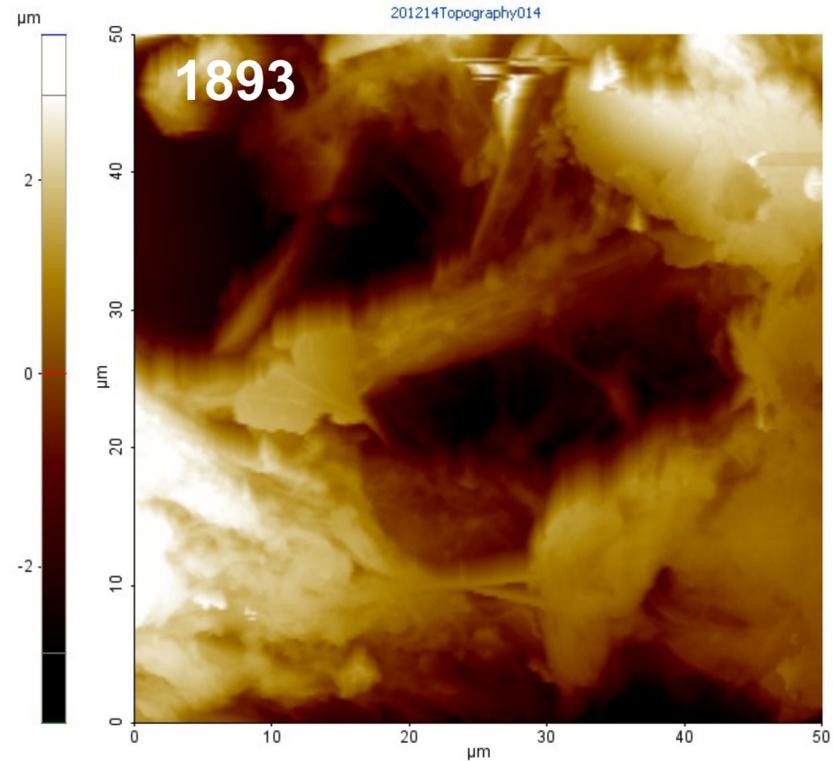


R_H

OI

I_{575}/I_{645}

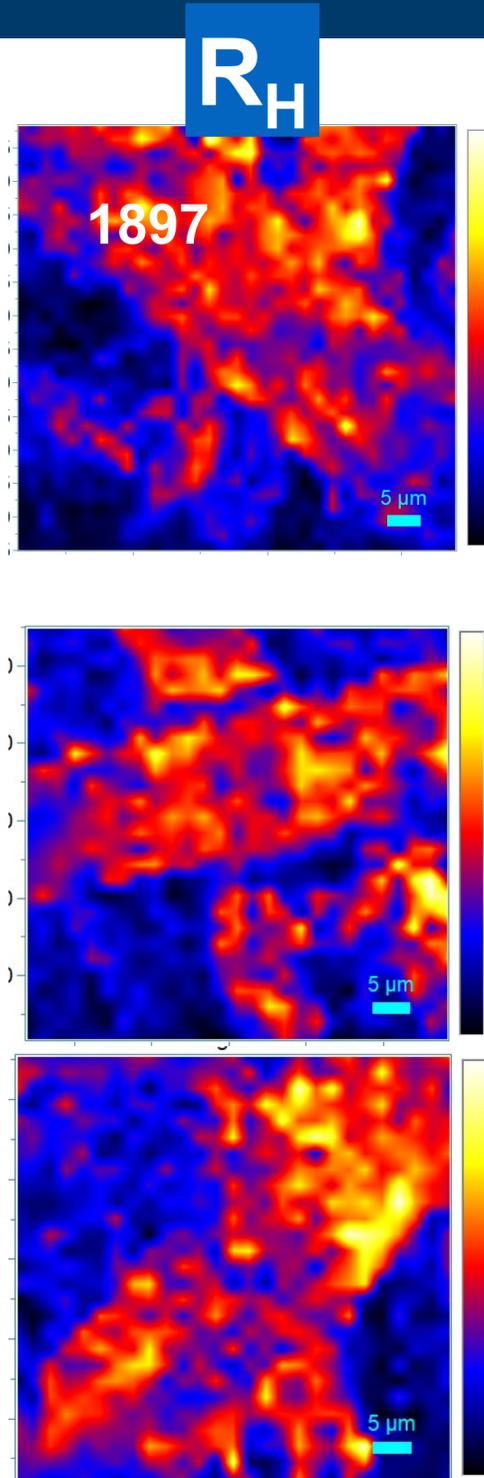
Comparison between roughness of exposed paper and of ancient paper (50 μm x 50 μm)



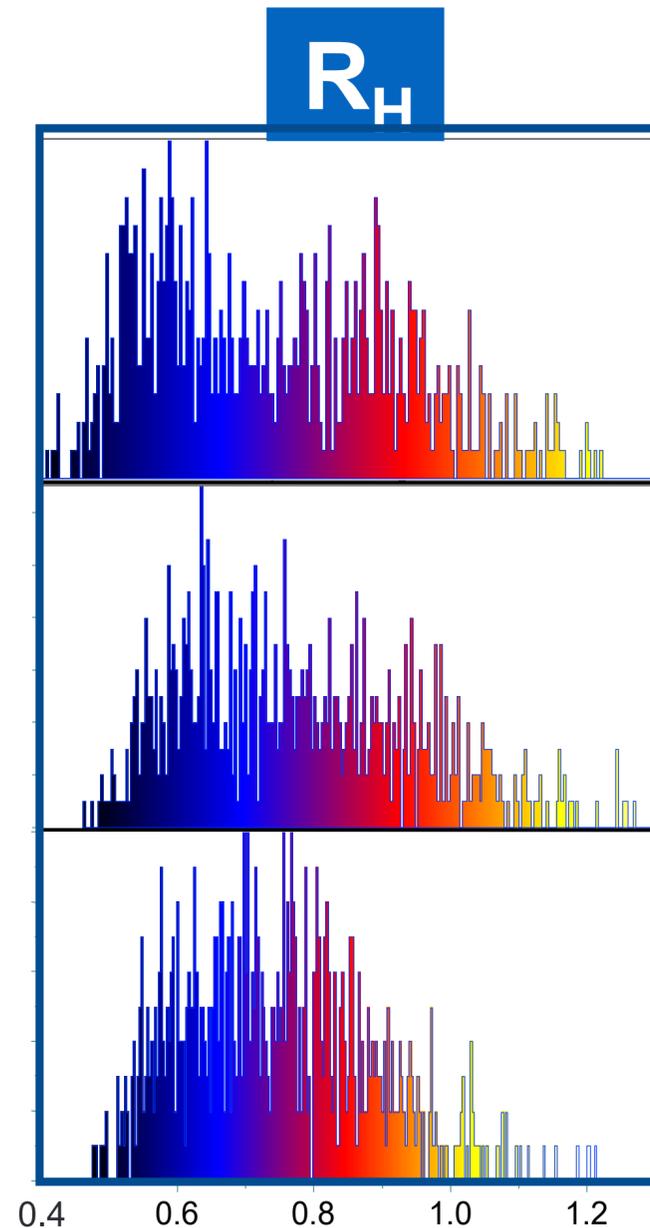
Not exposed:
Roughness <1 μm , OI=0.38

Area: 50 μm x 50 μm

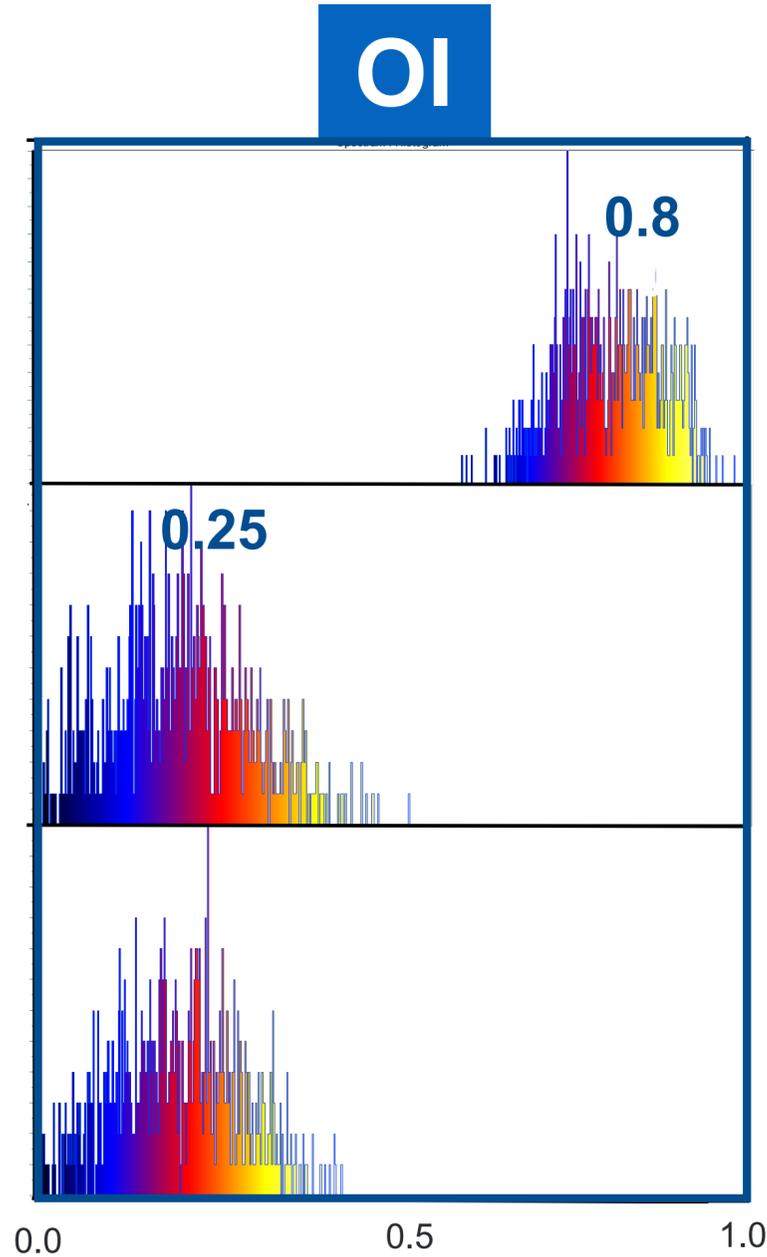
Hydrogel cleaning treatment of XIX century paper (1897)



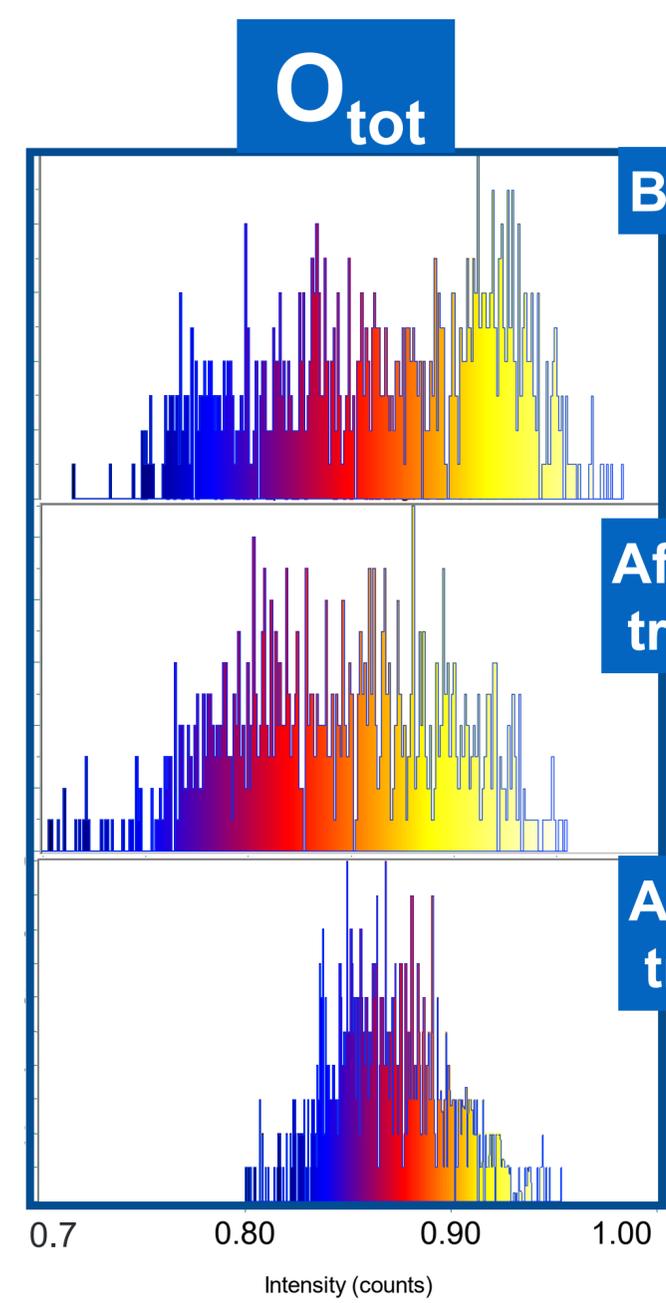
R_H



R_H



OI



O_{tot}

Before treatment

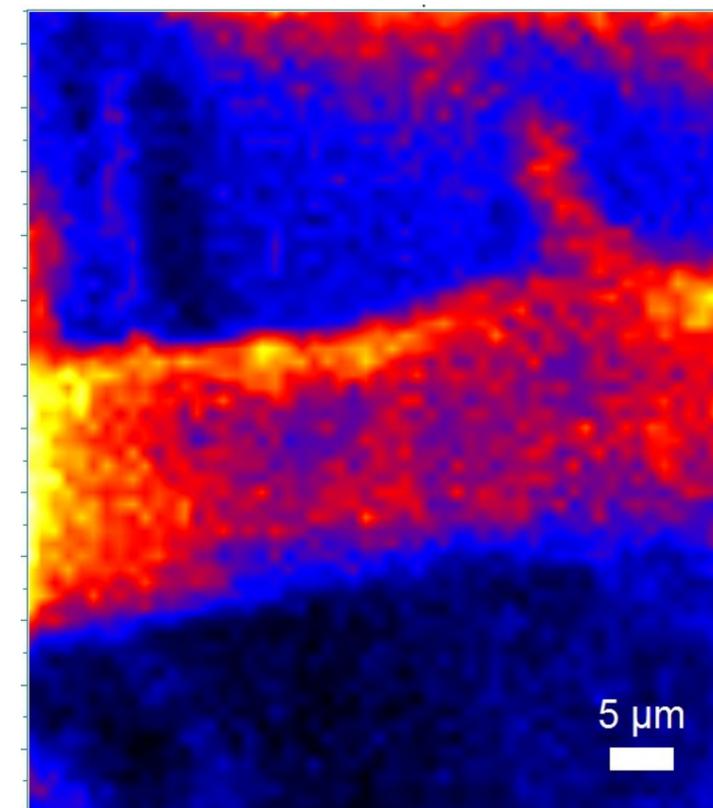
After 40 minutes of treatment

After 90 minutes of treatment

- Progressive decrease of oxidation markers
- Same value of R_H and I_{575}/I_{645} ratio
- Progressive decrease of luminescence intensity

Conclusions

- The ageing paper study can take advantages from using non-destructive spectroscopic technique.
- From Raman spectra, we defined different markers, that can follow hydrolisis and oxidation processes.
- The Raman and luminescence mapping is multiscale and can describe the degradation pattern from fiber to the page.
- This method can be used as tool to evaluate the paper cleaning treatment.



Thanks for your attention
Mail your comments to sabina.botti@enea.it

