UNIVERSITÀ
DEGLI STUDI
DI PALERMO

Water confined in cellulose fibers

Relevance to Cultural Heritage

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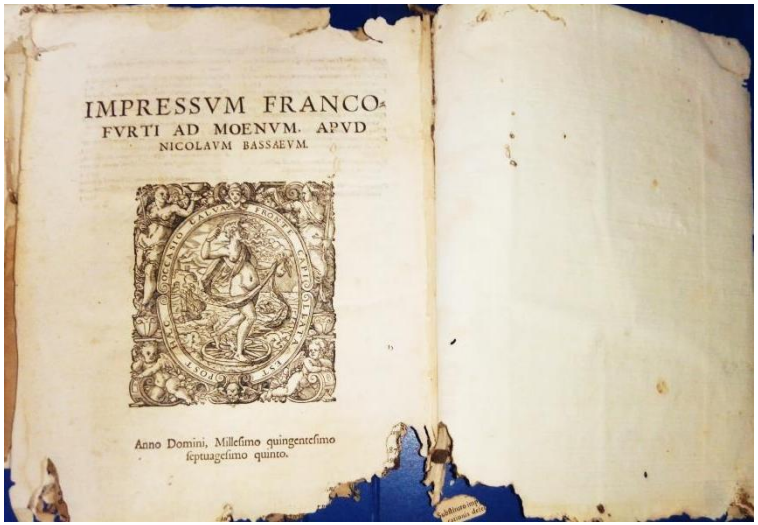
THANKS TO:

Dr. Margarita Fomina – for performing most of the experiments

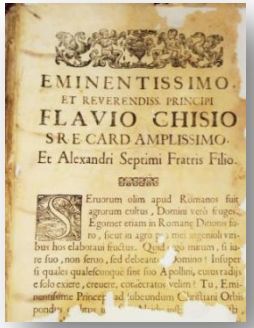
Project TECLA (Responsible: Prof. Bruno Pignataro) - for funding

Samples

Book printed in 1575, Frankfurt

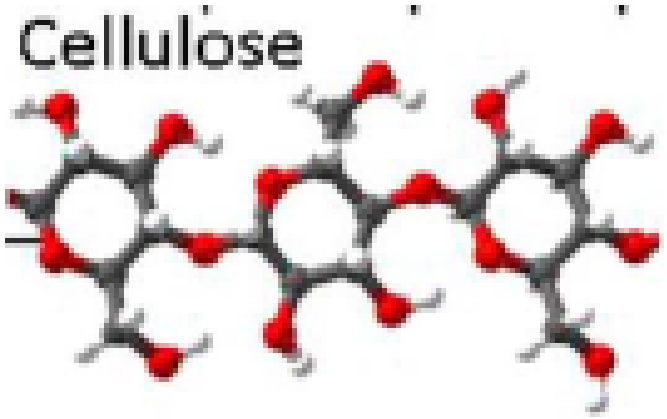


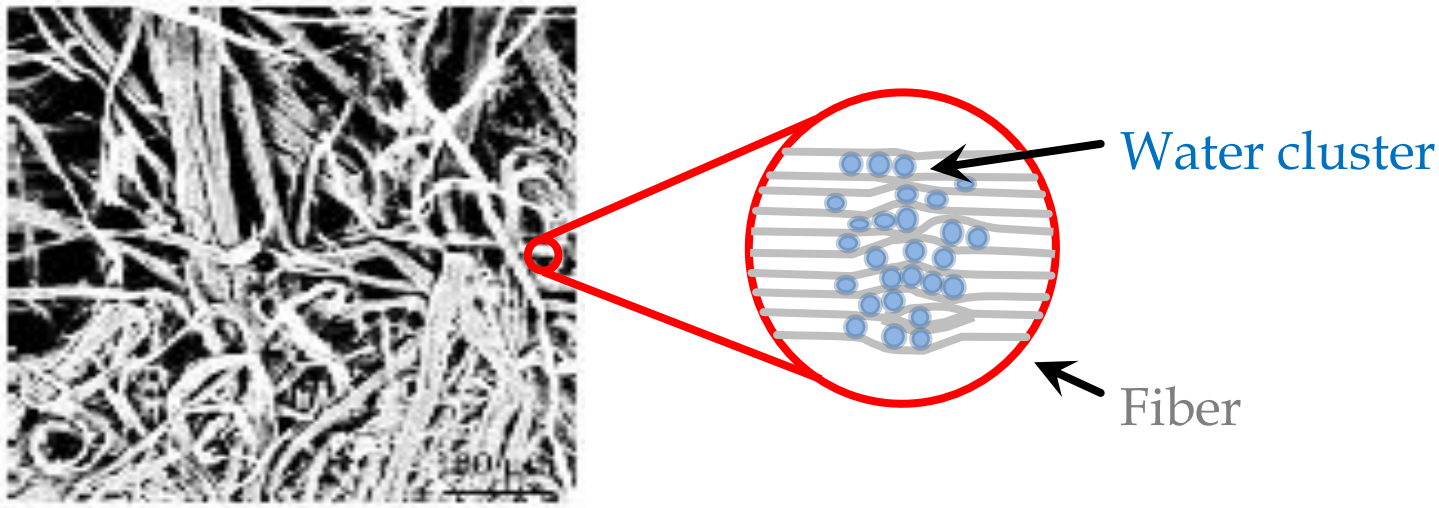
Modern paper

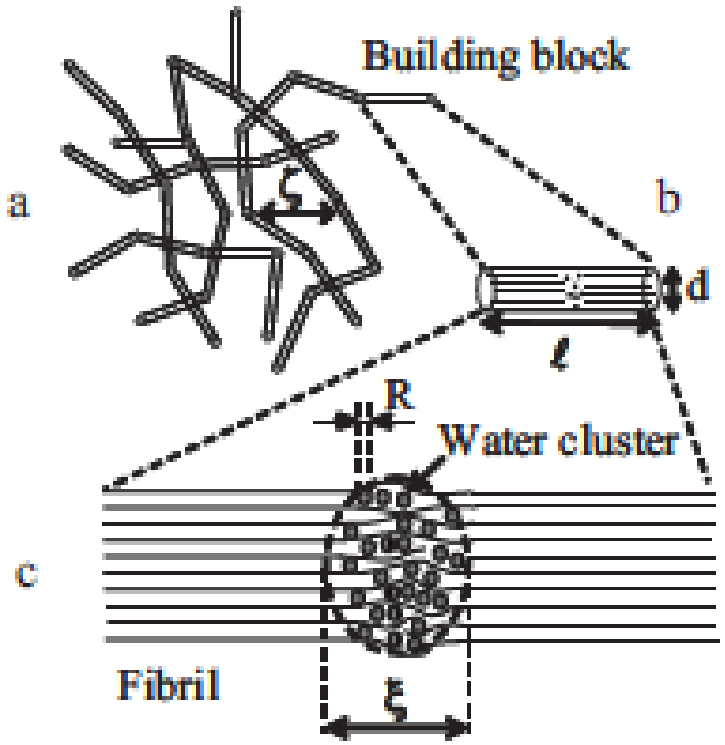


Cellulose fibers:

- random network
- inhomogeneous







From De Spirito et al., Phys. Rev. E 77, 041801, 2008

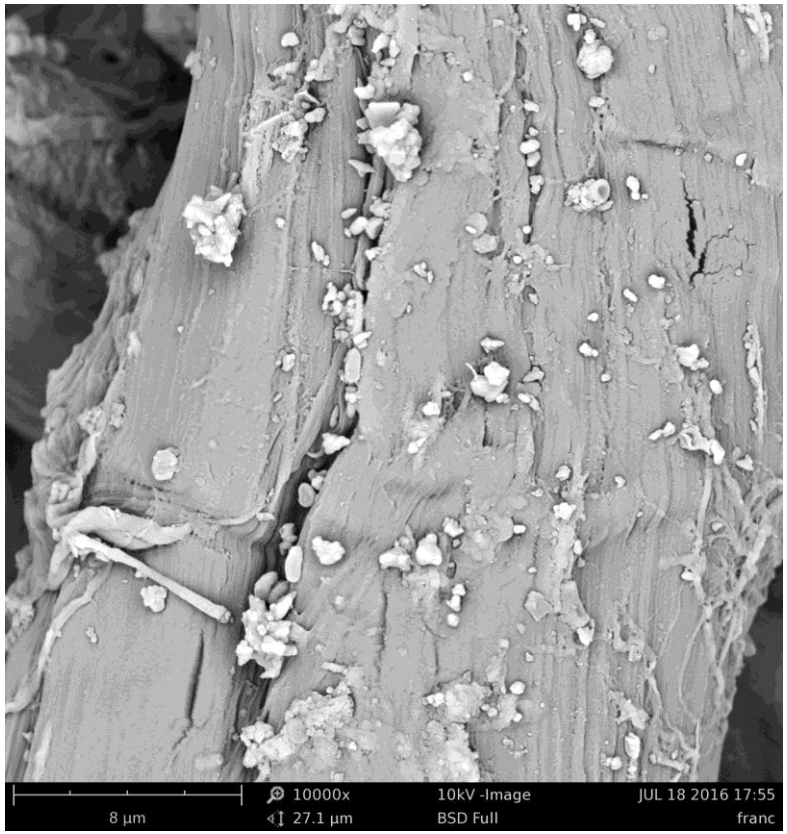
Mean cluster radius (SANS) ~ 1.5 nm (modern paper)
~ 2.0 nm (historical paper)

SEM images
80 µm

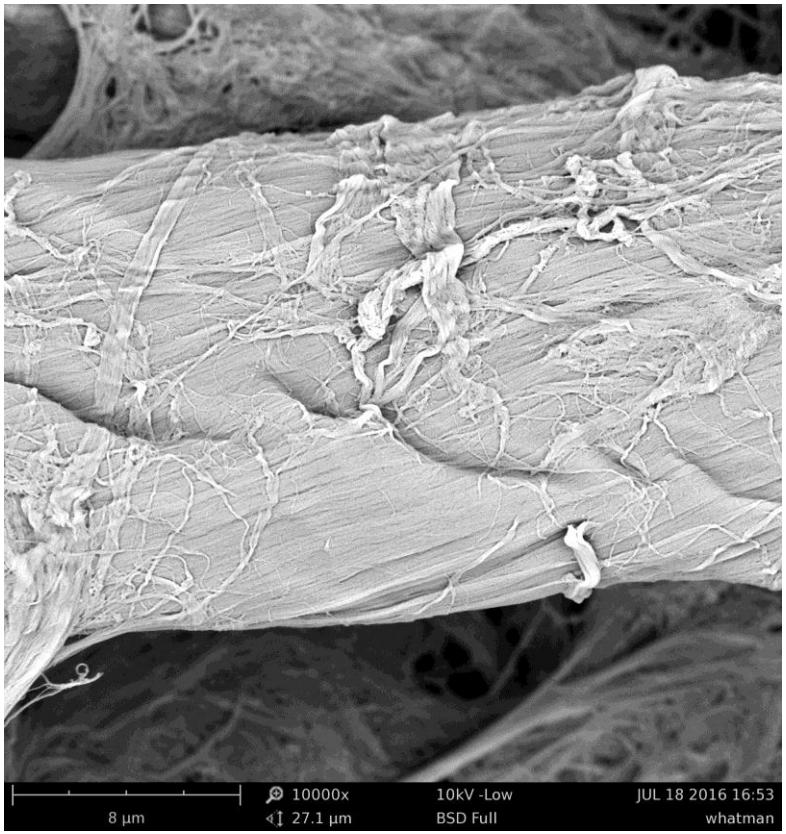
Frankfurt 1575

Whatman №1

SEM images
8 µm



Frankfurt 1575



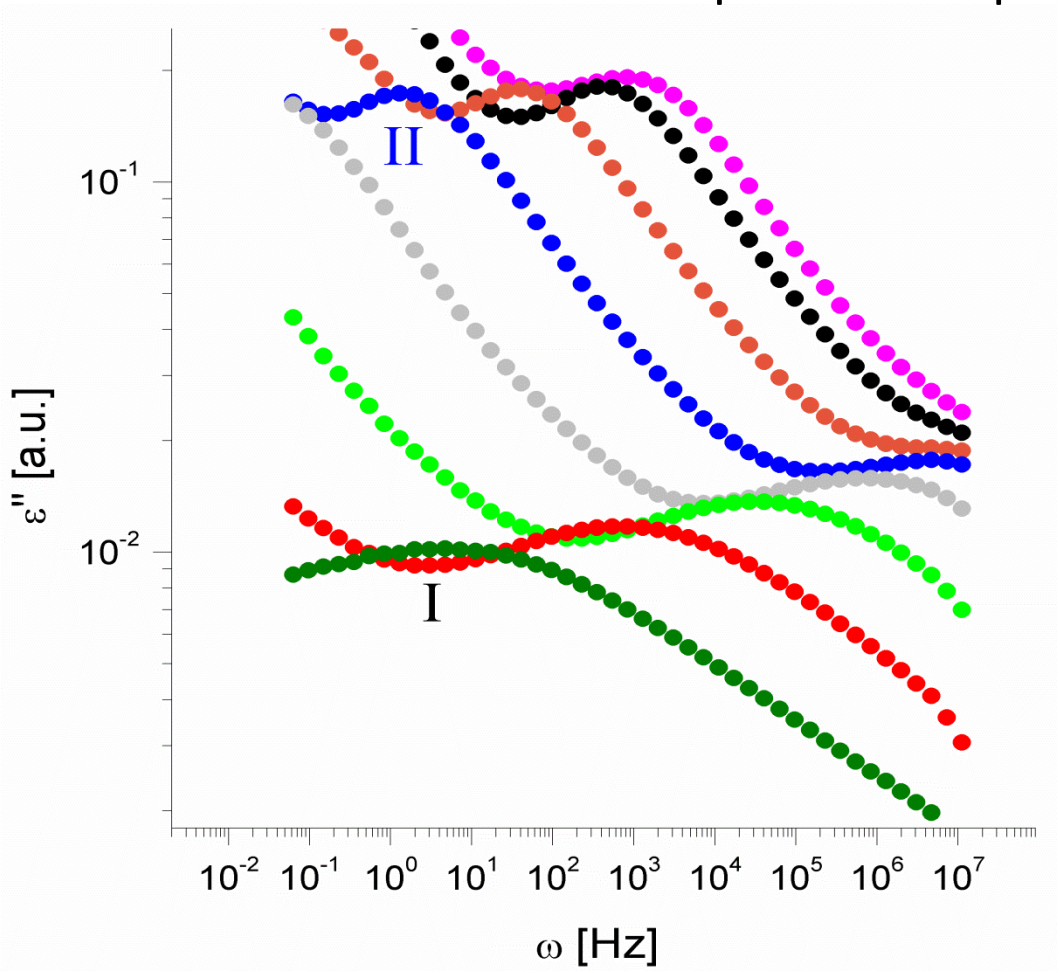
Whatman №1

Dielectric spectroscopy studies

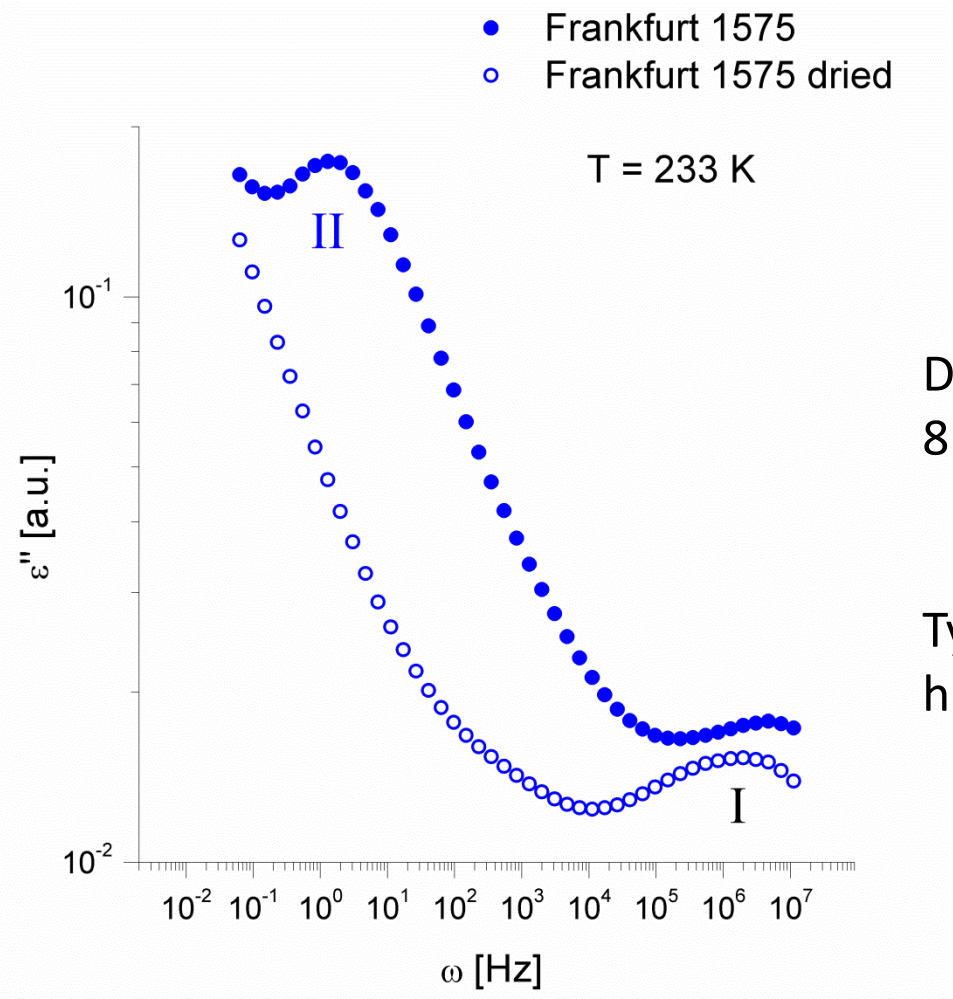
Water relaxations in cellulose matrix revealed by Dielectric Spectroscopy

XVI cent. paper

Temperature dependence



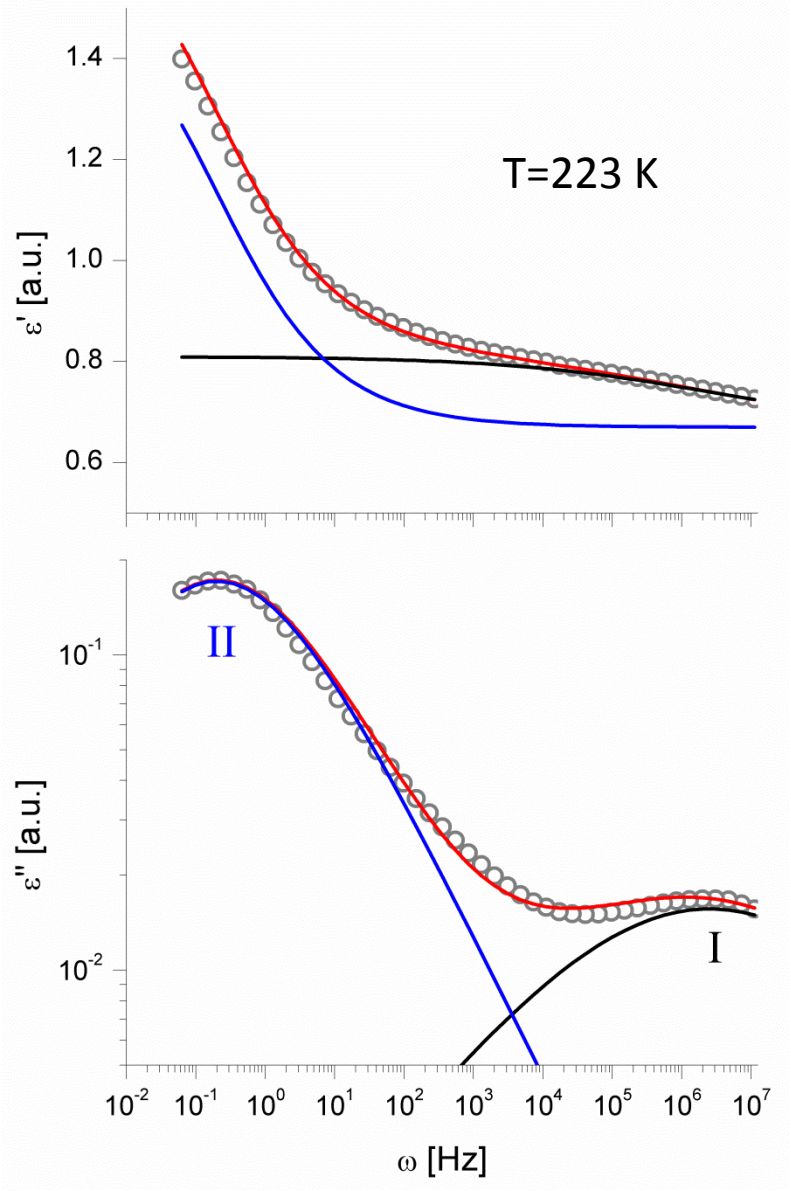
293 K
273 K
253 K
233 K
213 K
193 K
173 K
153 K



DRYING:
8 hours at 60 °C under vacuum

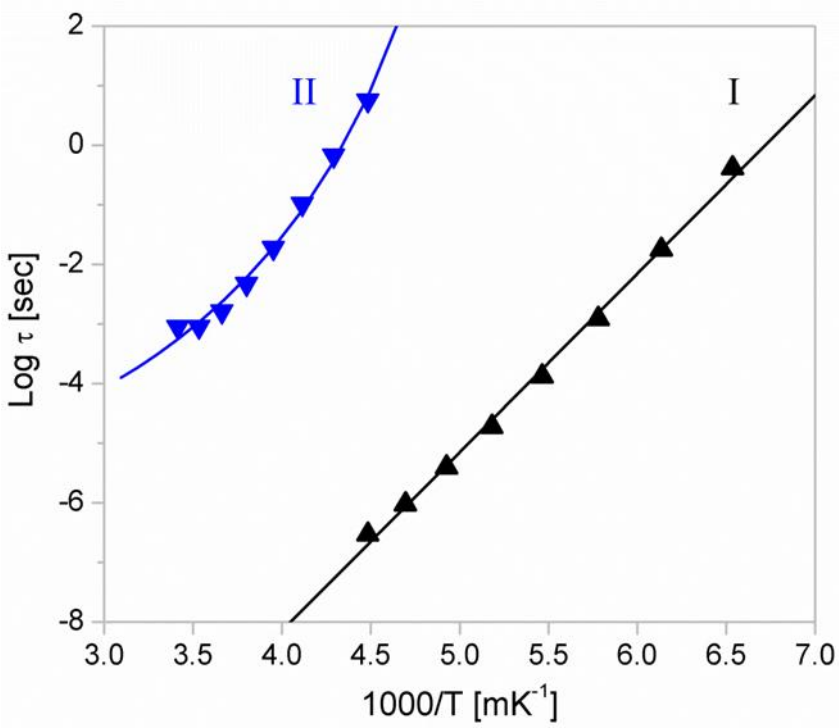
Typical hydration:
h = 0.075 ± 0.025 gr H_20 / gr paper

Fit by Cole-Cole function



$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum \frac{\Delta\varepsilon_i}{1 + (j\omega\tau_i)^{\beta_i}}$$

i = 1,2

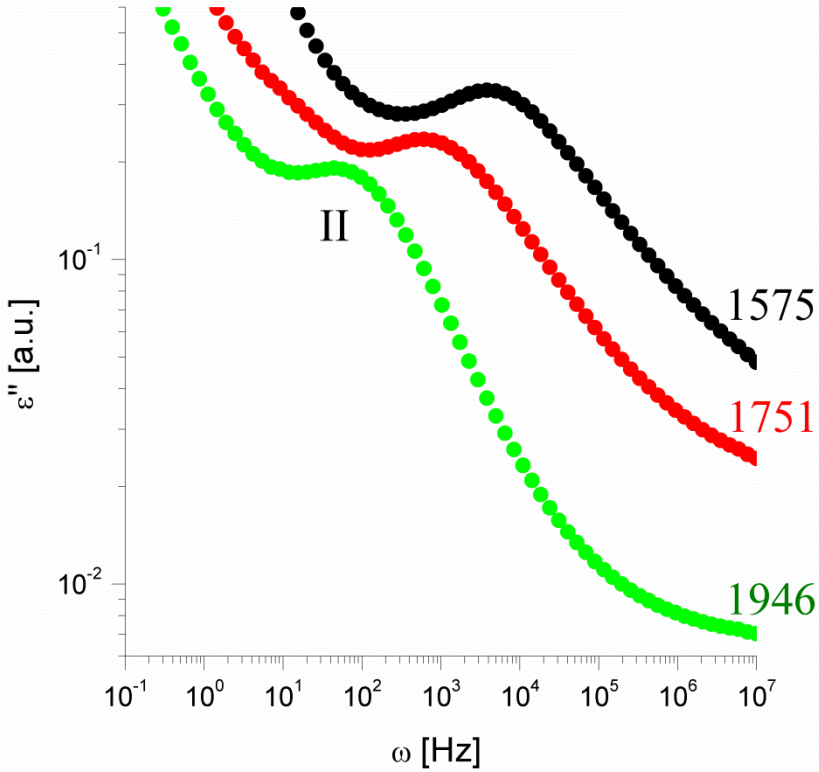


Process I: Arrhenius temperature dependence ; $\log \tau = \log \tau_0 + \Delta H/RT$; $\Delta H \sim 57$ kJ/mol

Process II : VFT temperature dependence; $\log \tau = \log \tau_0 + B/(T-T_0)$; $T_0 \sim 165$ K ; $T_{100} \sim 215$K

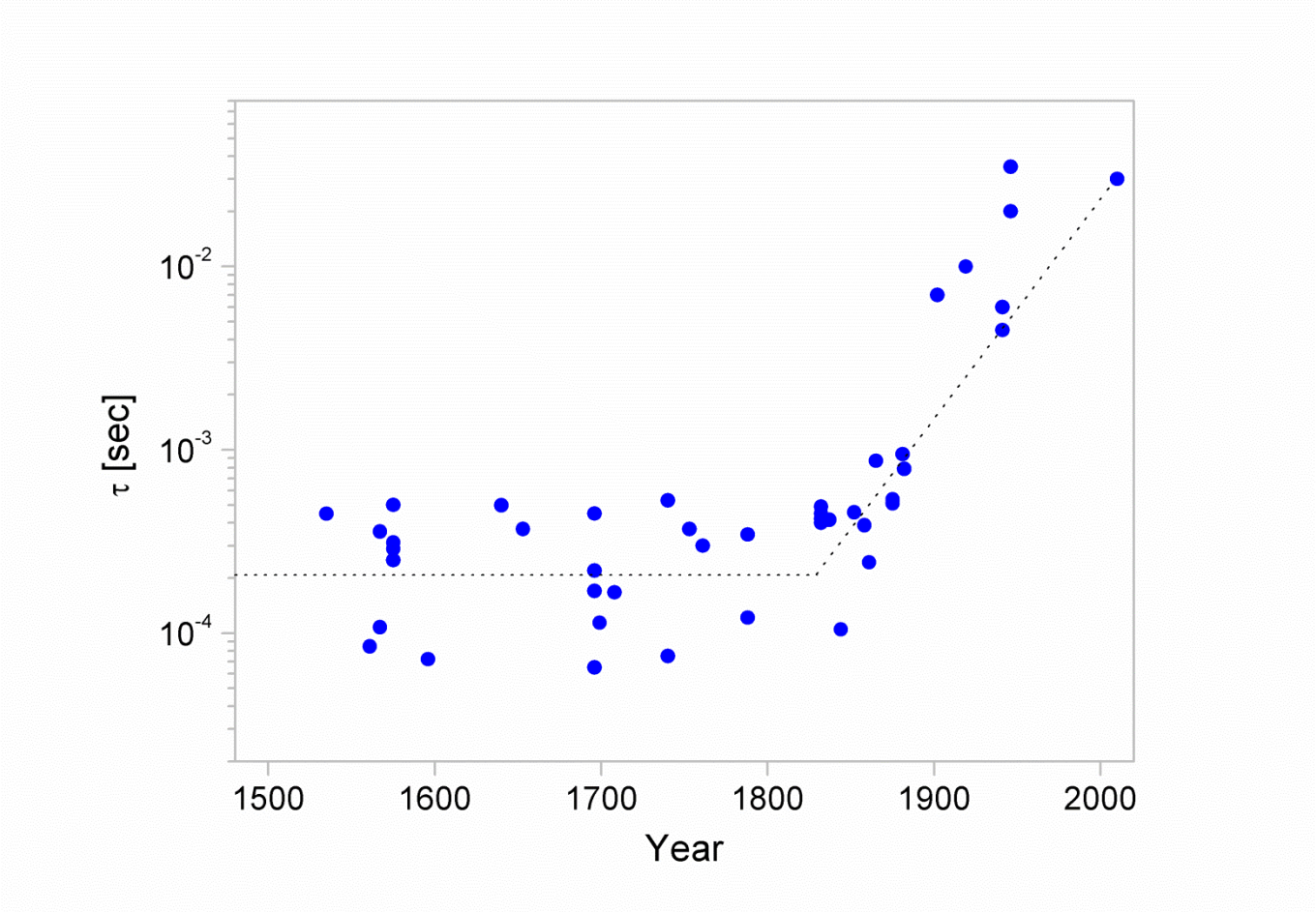
Paper from books printed in various centuries

Room Temperature

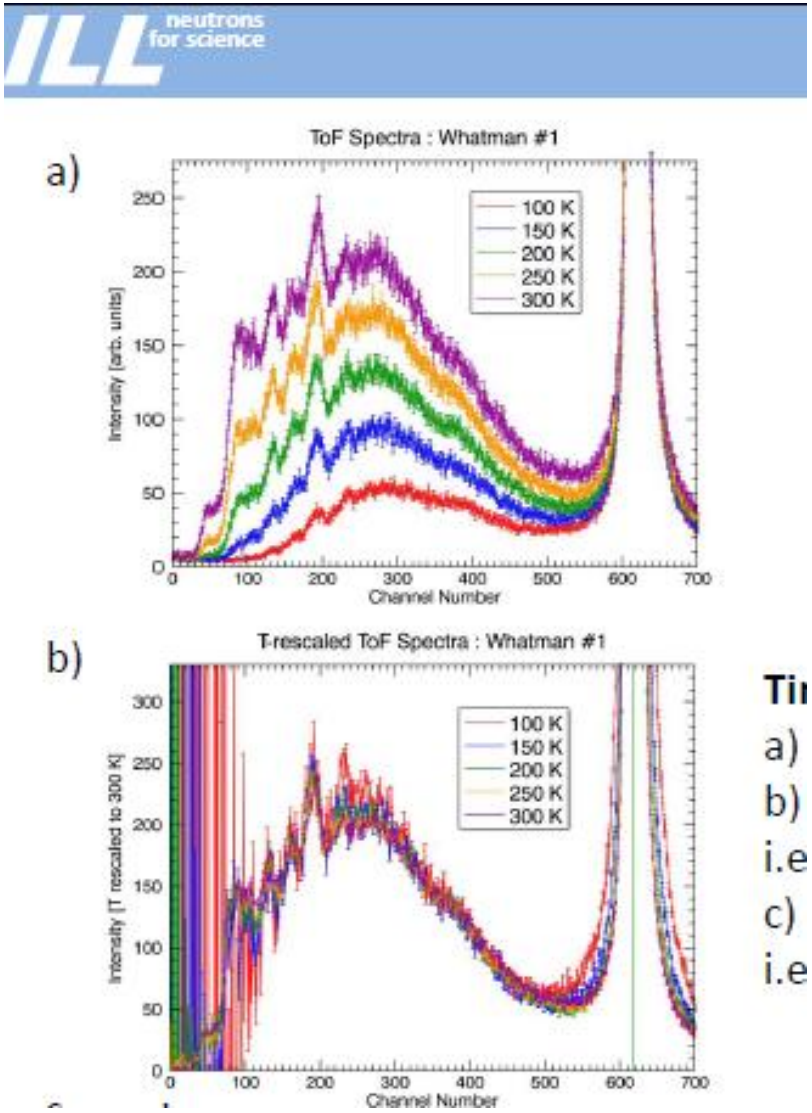


In ancient books water resonance shifts towards higher frequencies
Water becomes more mobile!

Paper from books printed in various centuries
Room temperature



Ageing induces increased water mobility : the first 150÷200 years are crucial

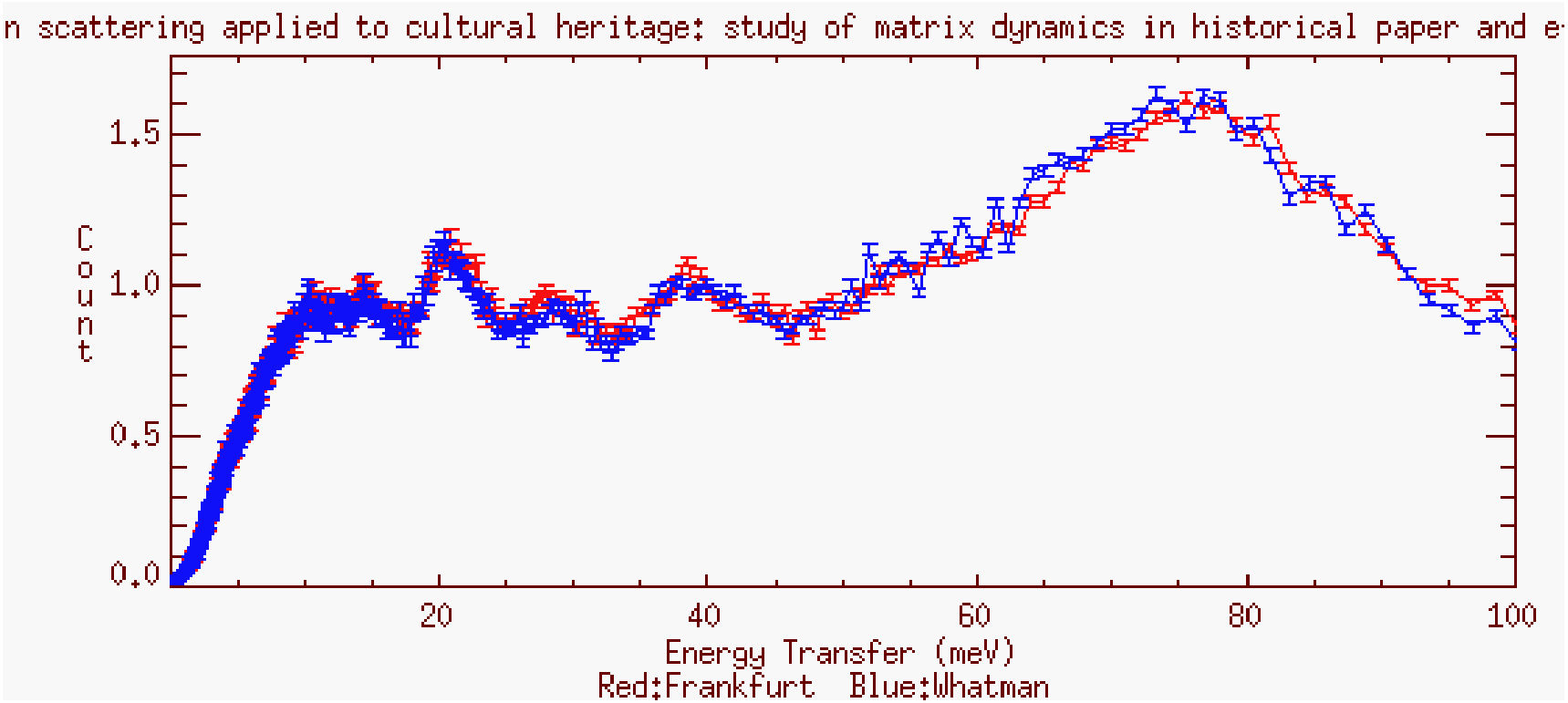


Ti
a)
b)
i.e
c)
i.e

Typical TOF spectra taken at IN6

a) Various temperatures

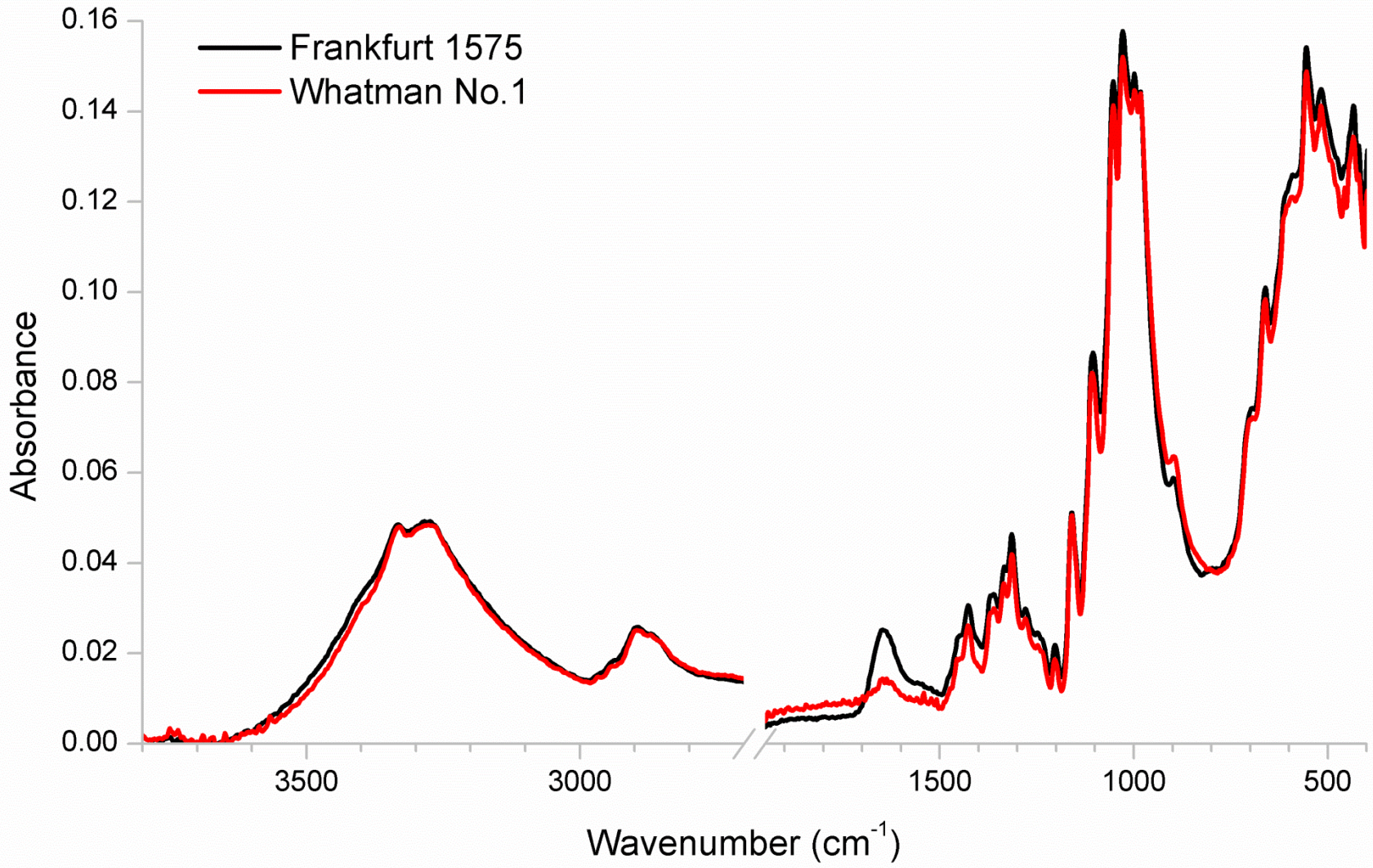
b) Bose-Einstein rescaling

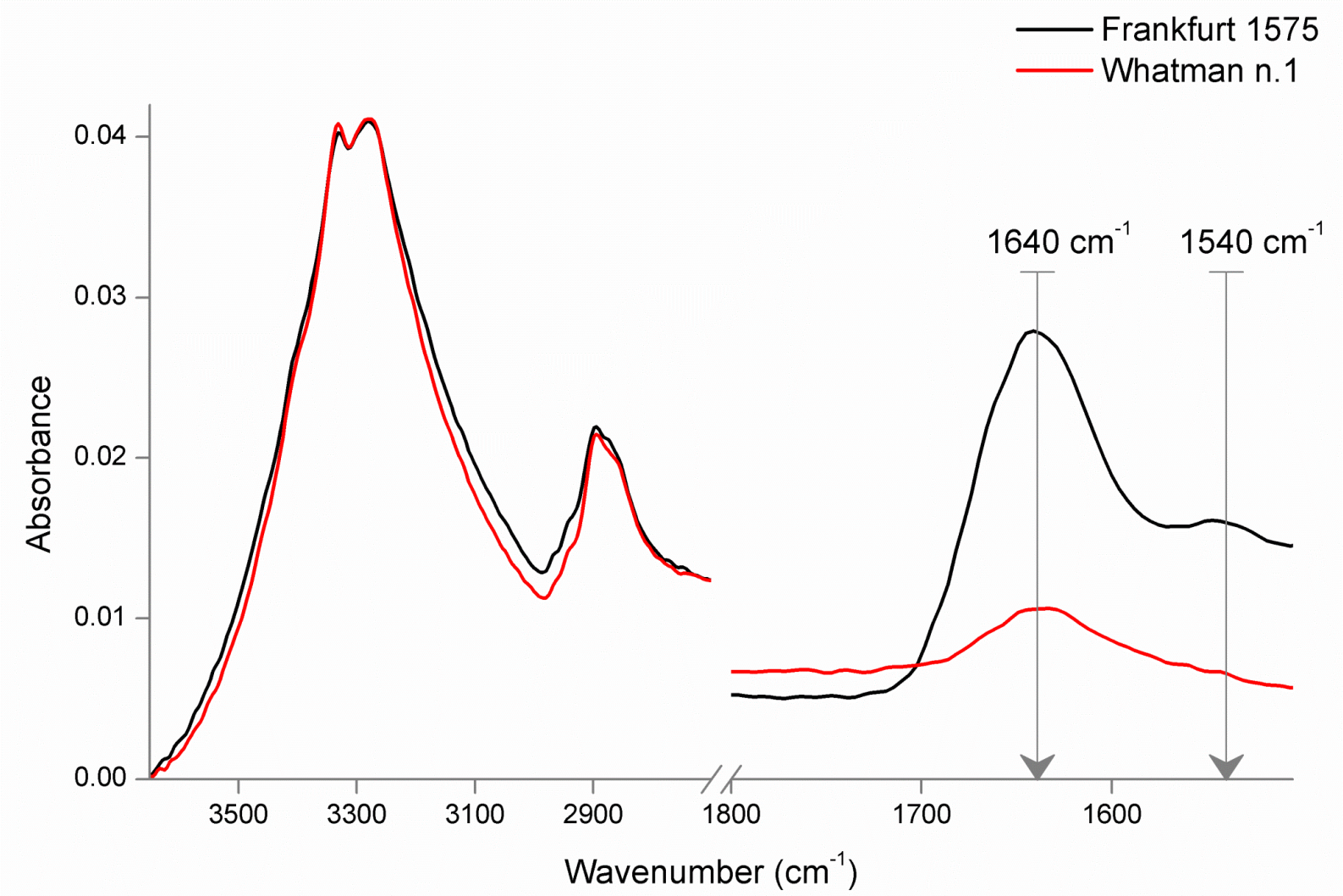


The vibrational dynamics of the cellulose matrix in moderne and historical paper is the same.

The effect detected by dielectric spectroscopy involves rotational dynamics and has to be attributed to water

ATR - FTIR


Frankfurt 1575
Whatman No.1
Absorbance
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3500
3000
1500
1000
500
Wavenumber (cm-1)

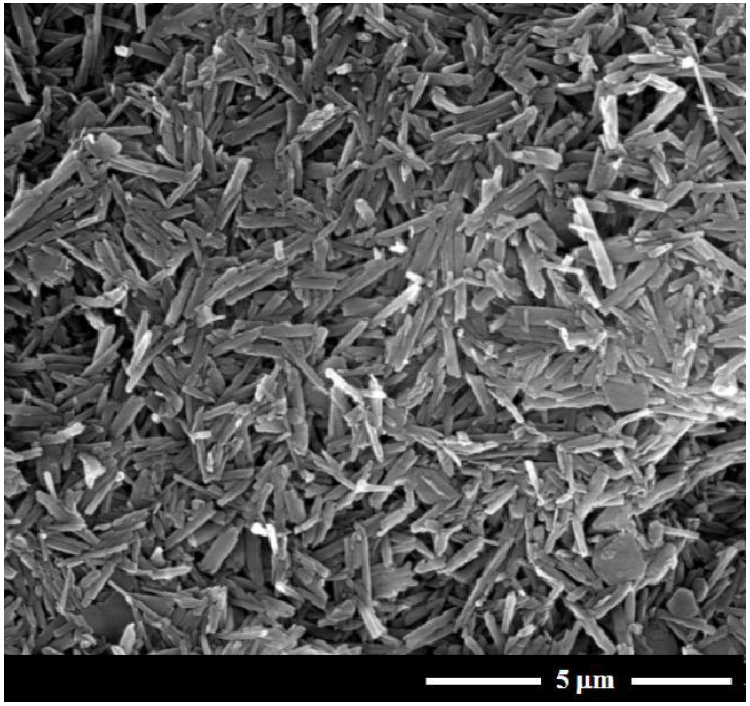


In ancient paper the bands at 1640 amd 1540 cm^{-1} are remarkably more intense : effect of «sizing».

CAN WE PROTECT HISTORICAL PAPER AGAINST DEGRADATION?

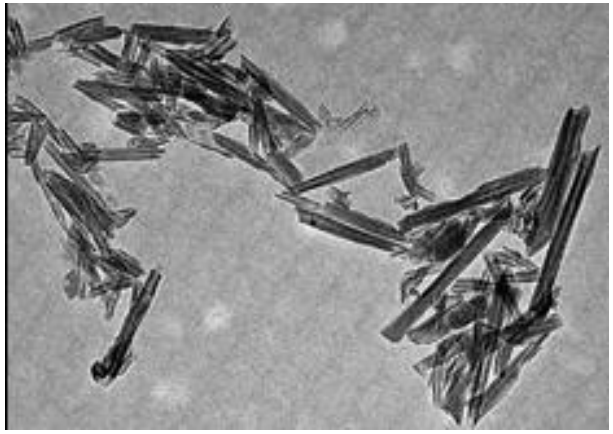
Treatment with Halloysite nanotubes

(in collaboration with G. Lazzara and S. Milioto)



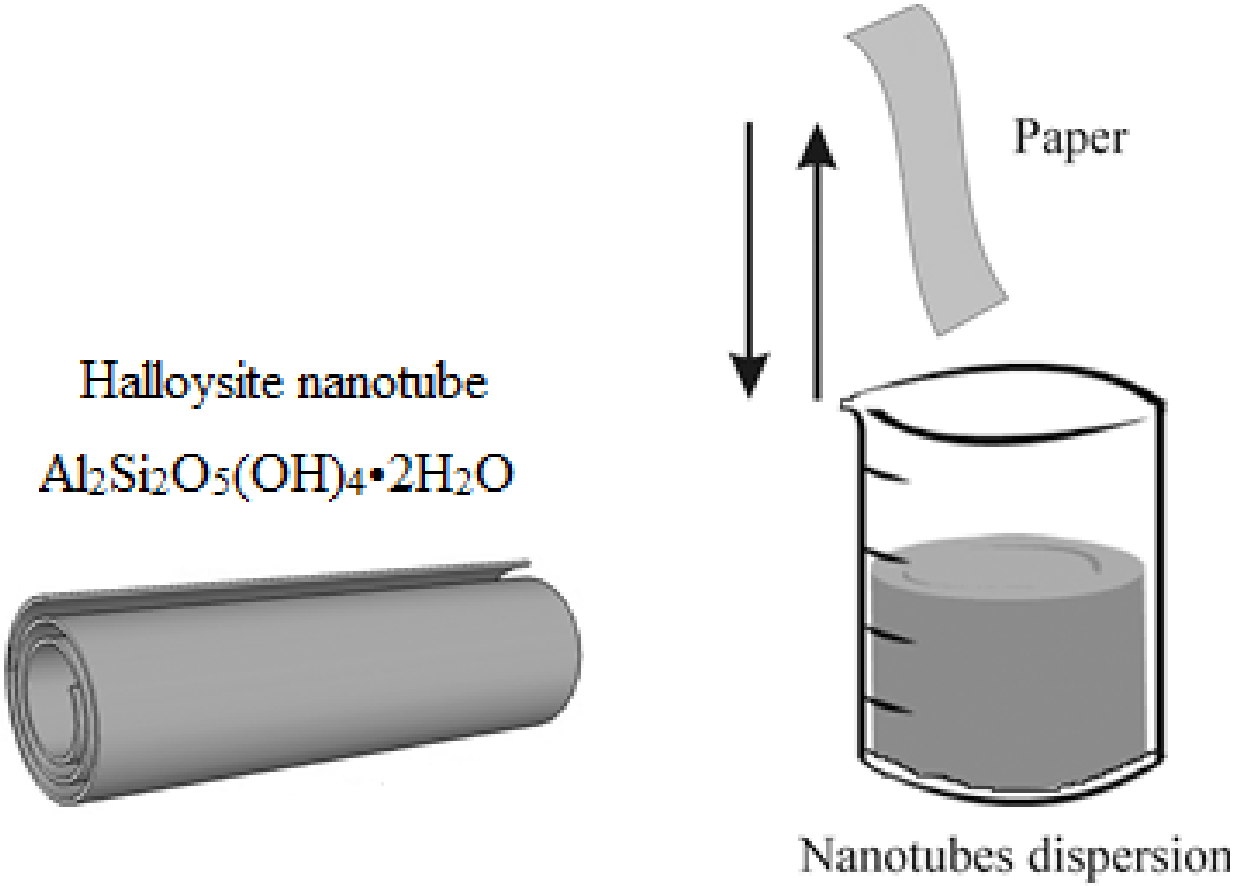
SEM micrograph for Halloysite nanotubes (HNT)

$Al_2Si_2O_5(OH)_4 \bullet 2H_2O$

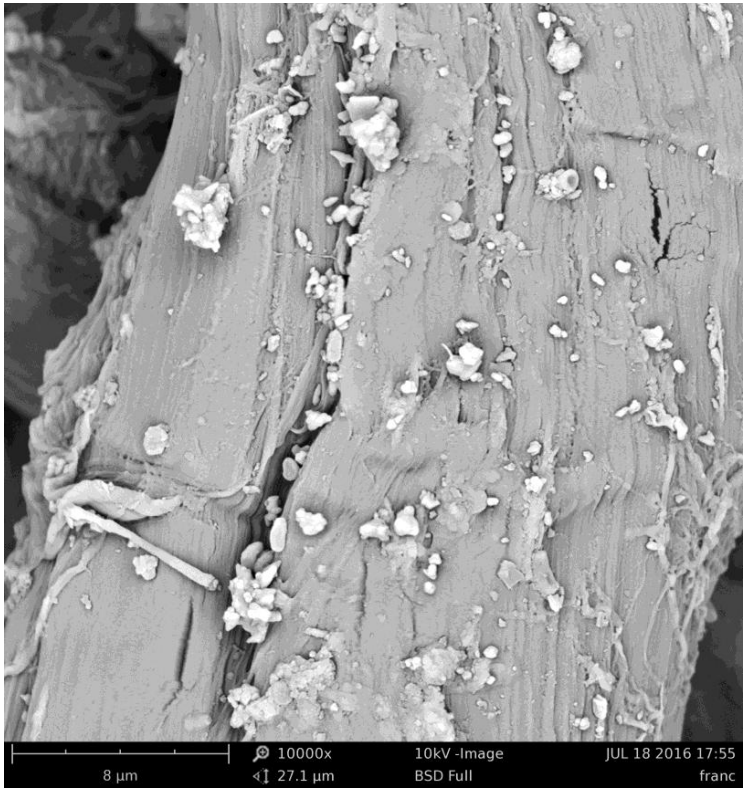


TEM Image of 50 nm diameter HNT

Schematic representation of HNT and paper treatment:



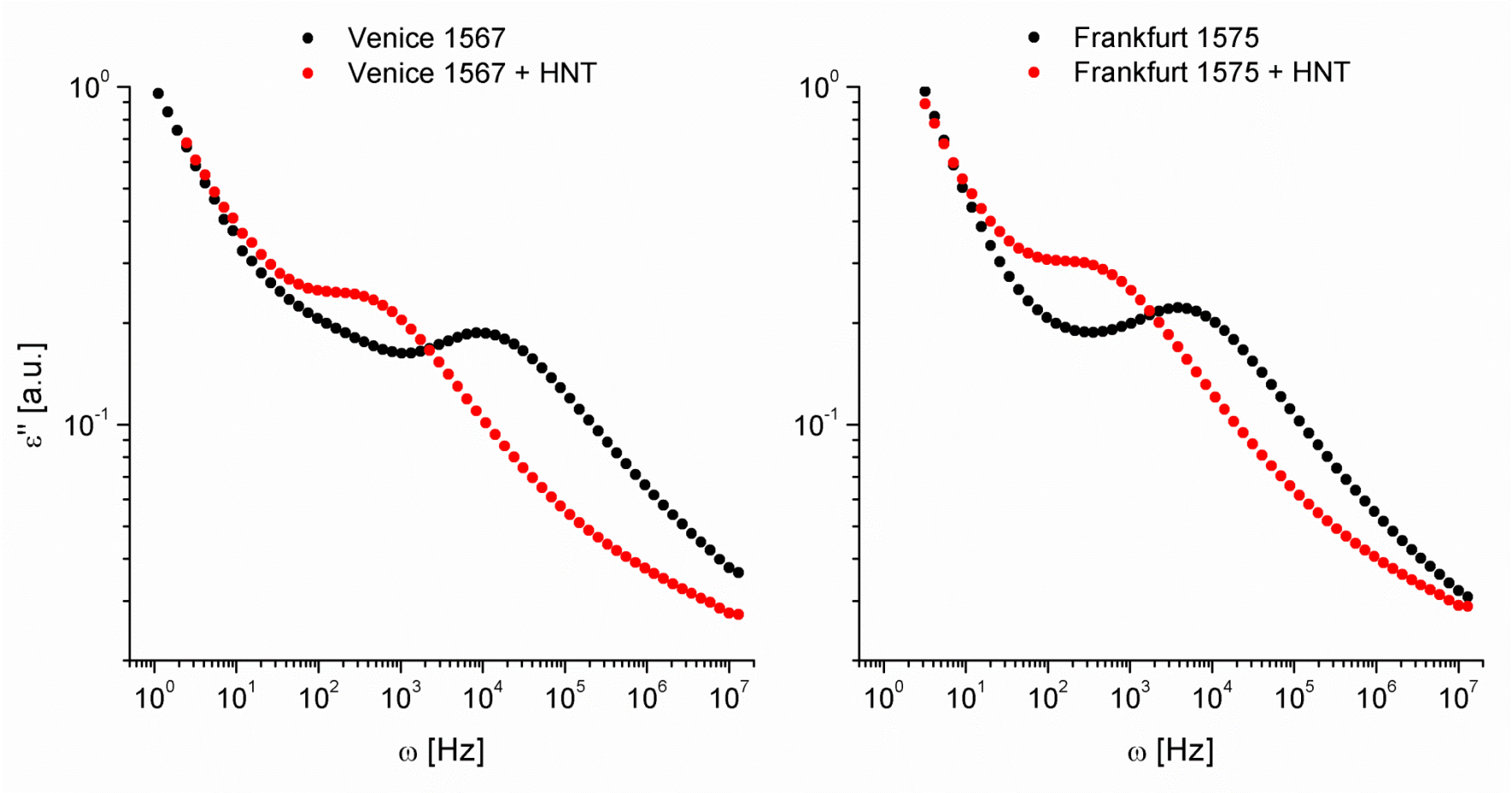
SEM images 8 µm

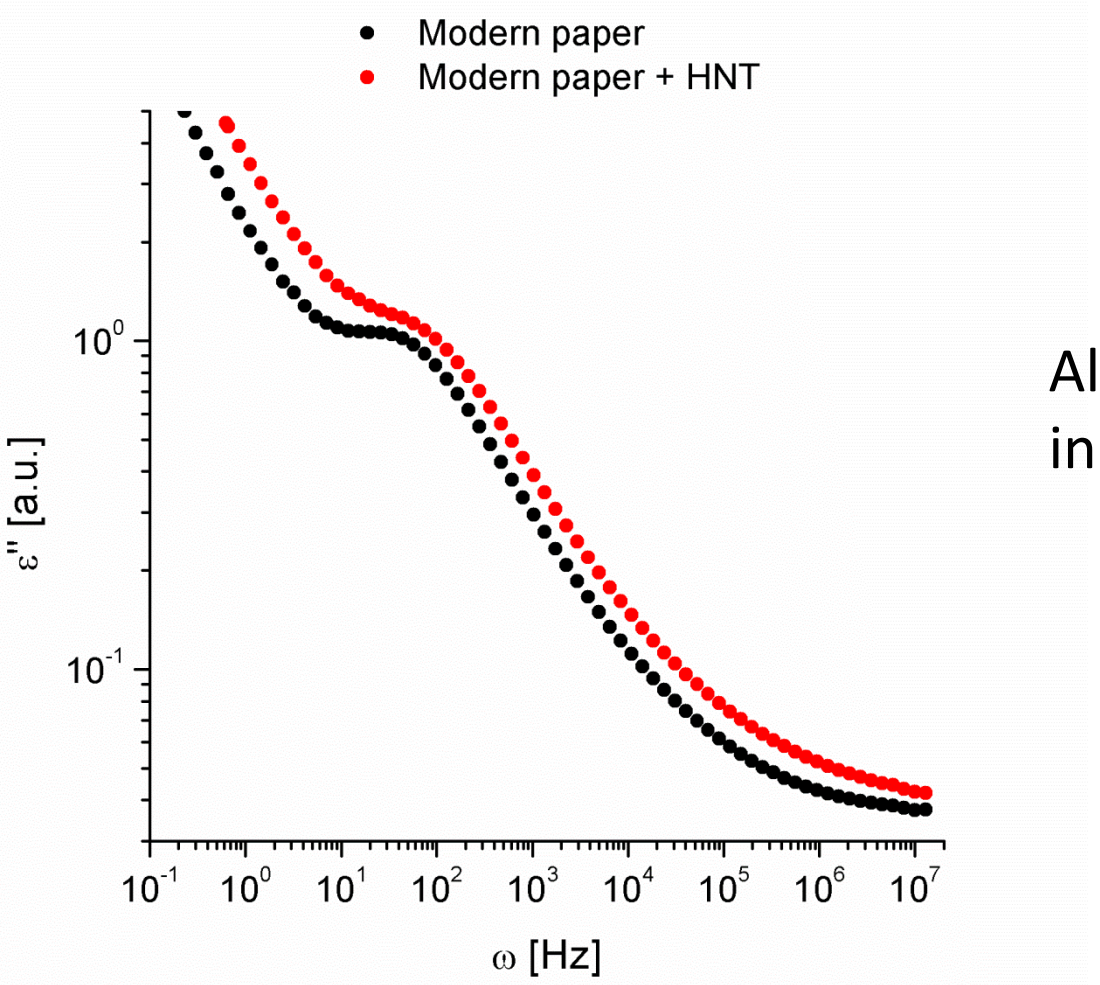


Frankfurt 1575

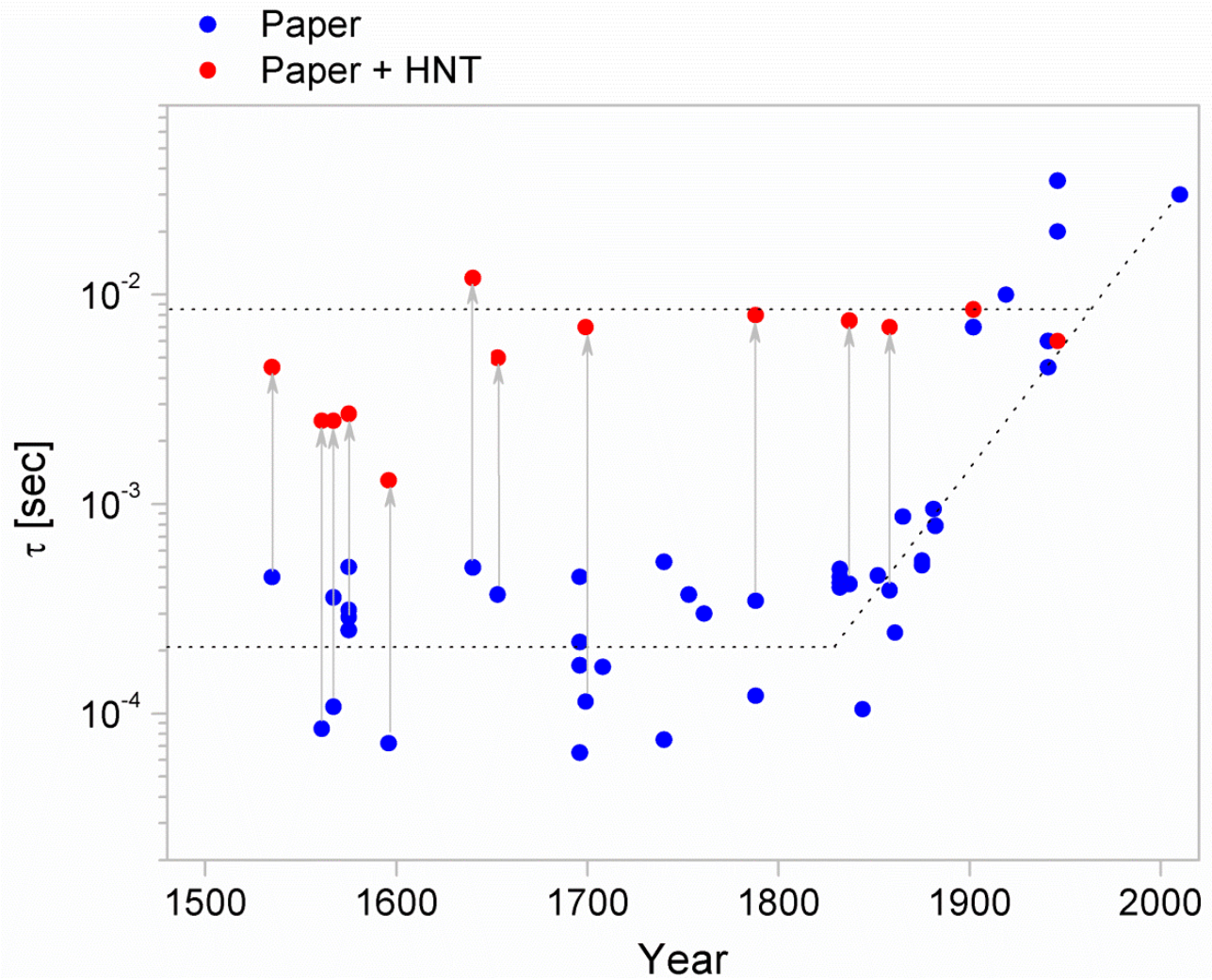
Frankfurt 1575 – HNT treated

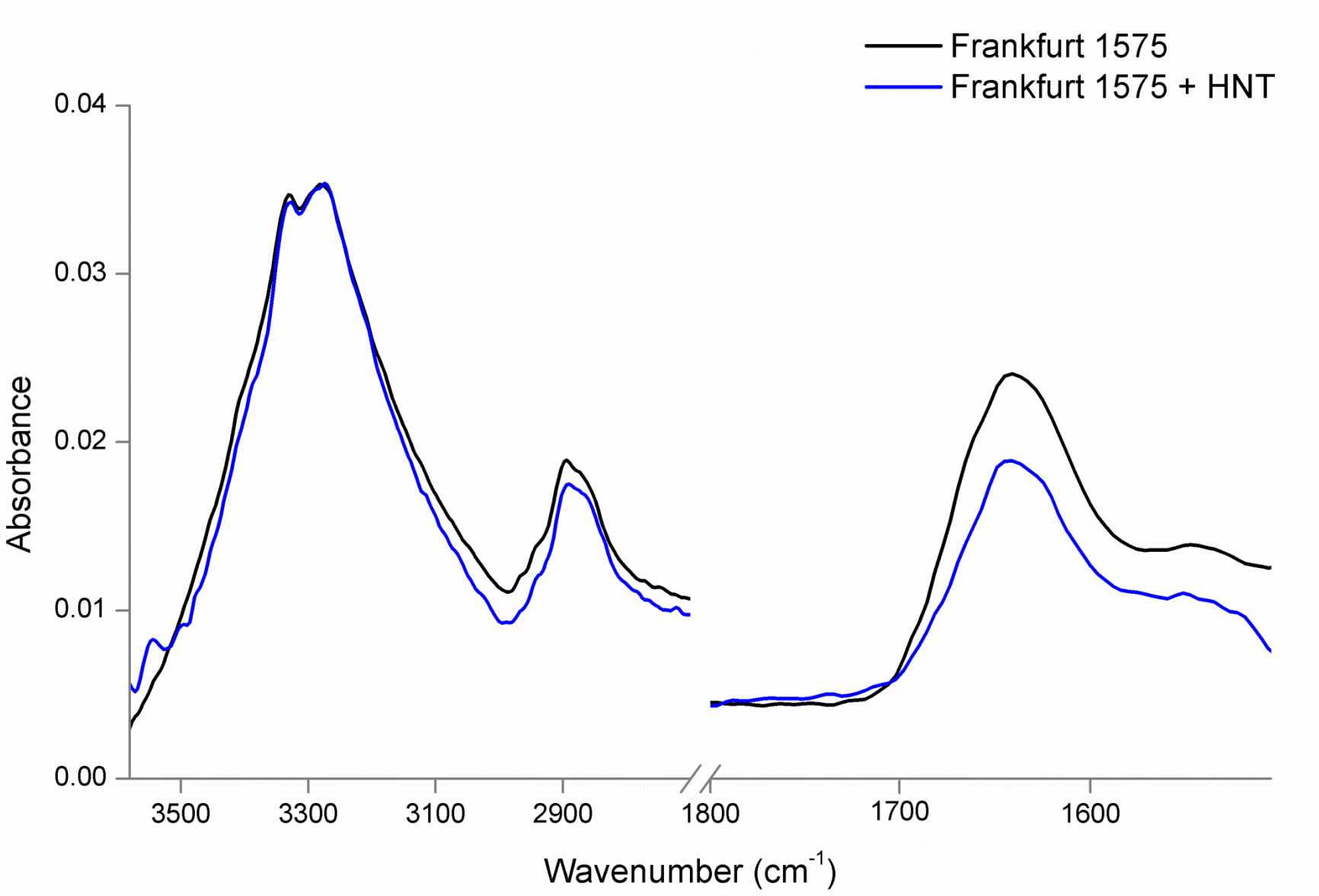
Treatment with HNT affects the dielectric spectra of historical paper





Almost no effect is seen in modern paper


Paper
Paper + HNT
τ [sec]
10-2
10-3
10-4
1500
1600
1700
1800
1900
2000
Year


Frankfurt 1575
Frankfurt 1575 + HNT
0.04
0.03
0.02
0.01
0.00
Absorbance
3500
3300
3100
2900
1800
1700
1600
Wavenumber (cm-1)

CONCLUSIONS

Dielectric spectroscopy can be used to monitor paper ageing

Paper ageing causes (is caused by) increased rotational mobility of water inside the pores of the cellulose matrix

Treatment with Halloysite nanotubes is effective in reducing water rotational mobility and may be an effective tool for ancient paper preservation