

SEM characterization of cell walls in glow discharge plasma-modified wood

*Journées du GN-MEBA et 18ème Colloque de la Société Française des Microscopies
UFR Sciences et Techniques, Université de Rouen
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Rouen*

Arash JAMALI

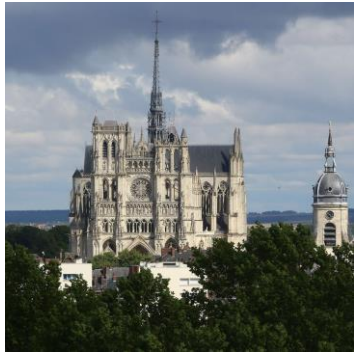
Plateforme de microscopie électronique (PME)

Université de Picardie Jules Verne

Amiens, France

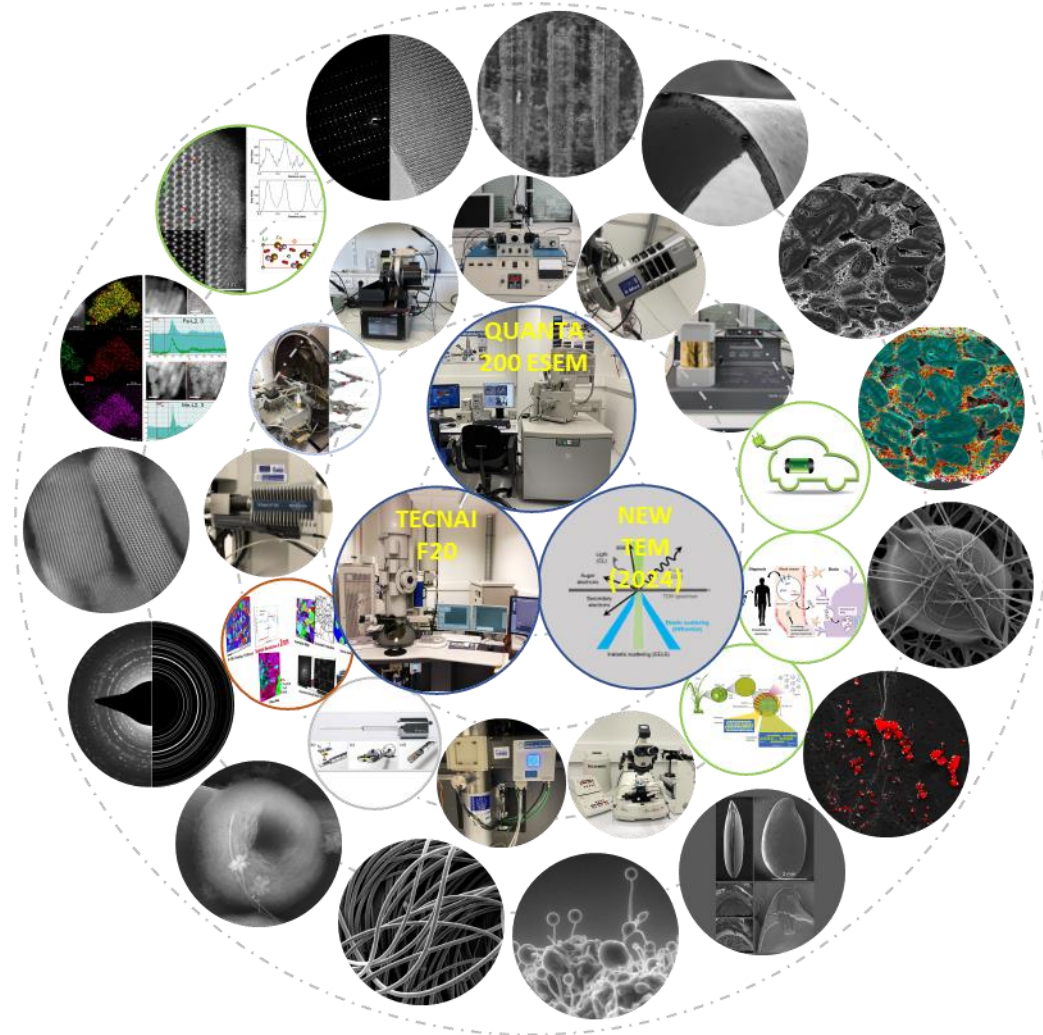
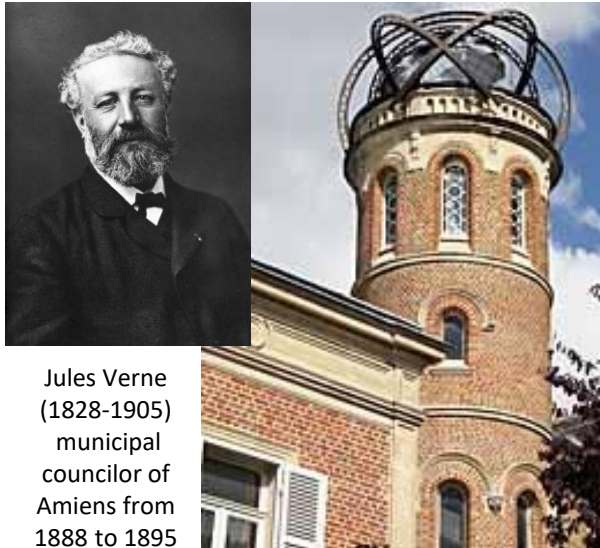
arash.jamali@u-picardie.fr

Amiens



Université de Picardie Jules Verne (UPJV)

« Plateforme de Microscopie Electronique »



Wood for Exterior Application

PVC



Wood



Weathered
Wood



People's dream: finished wood looks new for a long time without maintenance

Wood is Good, but...!

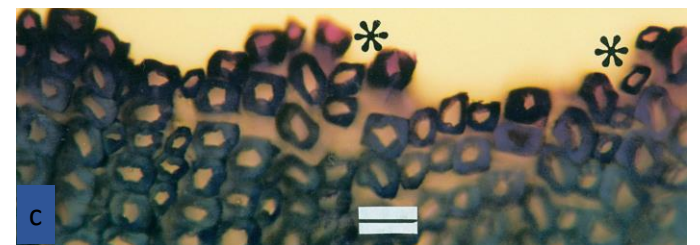
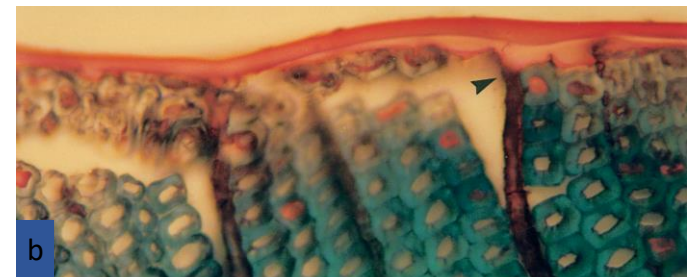
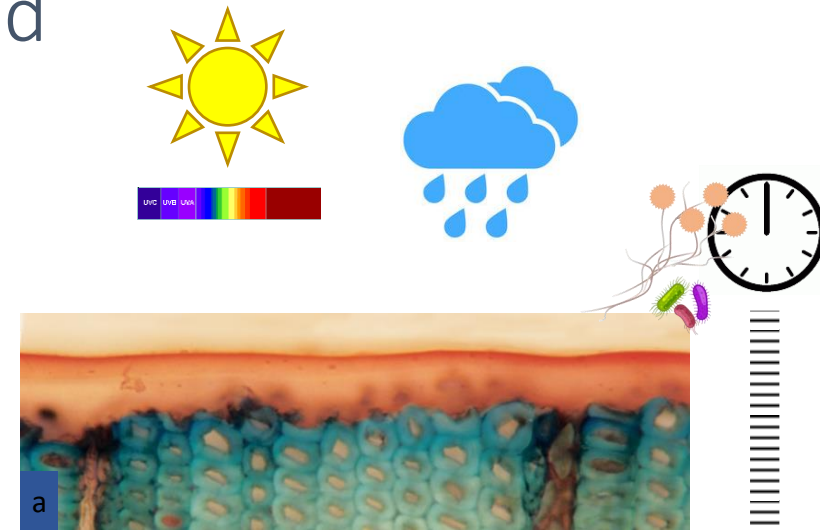
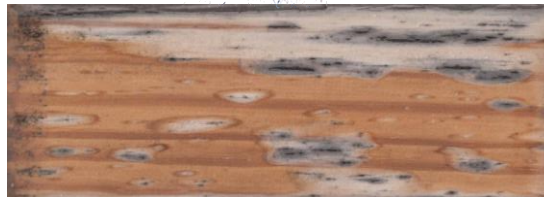
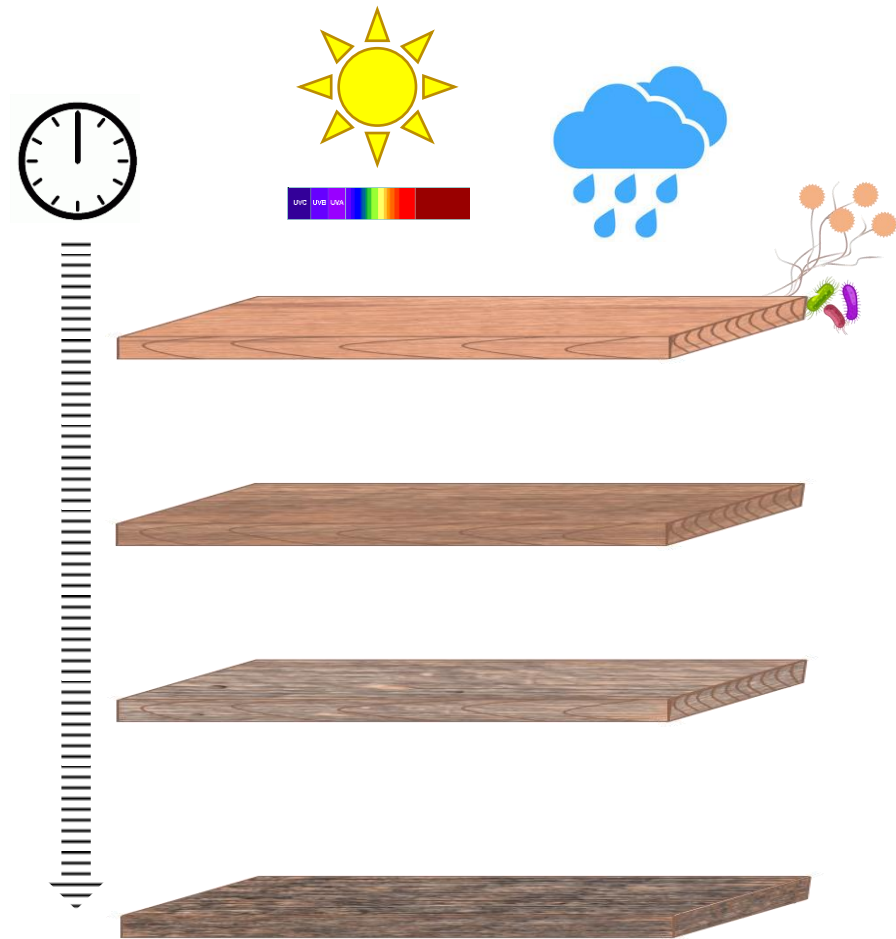
Advantage

- Renewability and Recyclability
- Positive eco-balance: oxygen production and carbon storage
- Low energy consumption and Co₂ emission during production and processing (30 x lower than steel)
- Good mechanical properties (high strength-to-weight ratio) and workability
- Thermal insulation
- Good tactile warmth
- Renewed interest for advanced material

Inconvenience

- Biological degradation (fungi, bacteria, insects etc)
- Natural variation in properties
- Natural mechanical defects (knots, cracks)
- Nuisance dust during processing
- Anisotropy (a double-edged property)
- Outdoor weathering and loss of aesthetic appeal

Surface Weathering of Wood



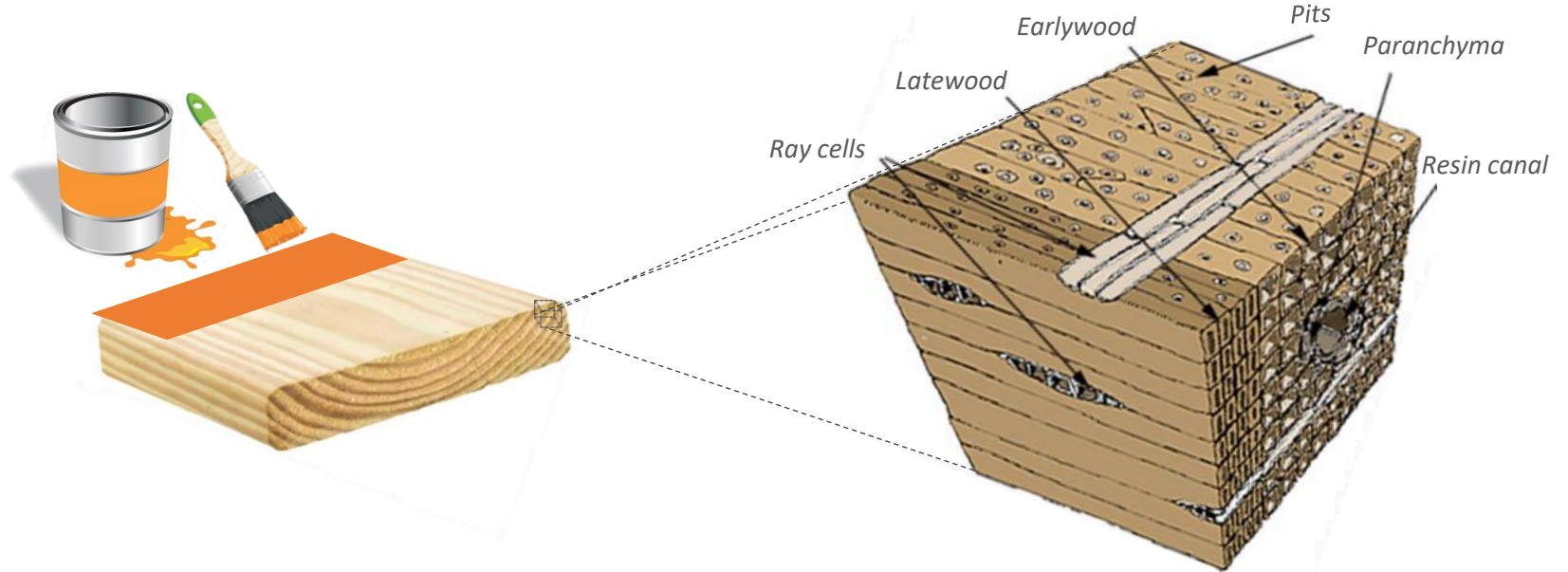
(image: Singh and Dawson 2003)

Wood Surface Quality and Coating's Performance



Sawmilling and Machining

- Silvicultural management
- Log pretreatment
- Saw blades and cutting process
- Temperature control
- Storing techniques



Coating's formulation

- Water-borne/solvent-borne
- Clear coatings
- UV Absorbers
- UV halts
- Primer

Wood surface Modification

- Mechanical: Sanding, planing, perforation, lasers etc
- Chemical functionalization, use of Bonding reagents, etc
- Biological: Bioincising, Enzymatic activation
- High energy: Gamma and UV radiation
- **Plasma treatments**

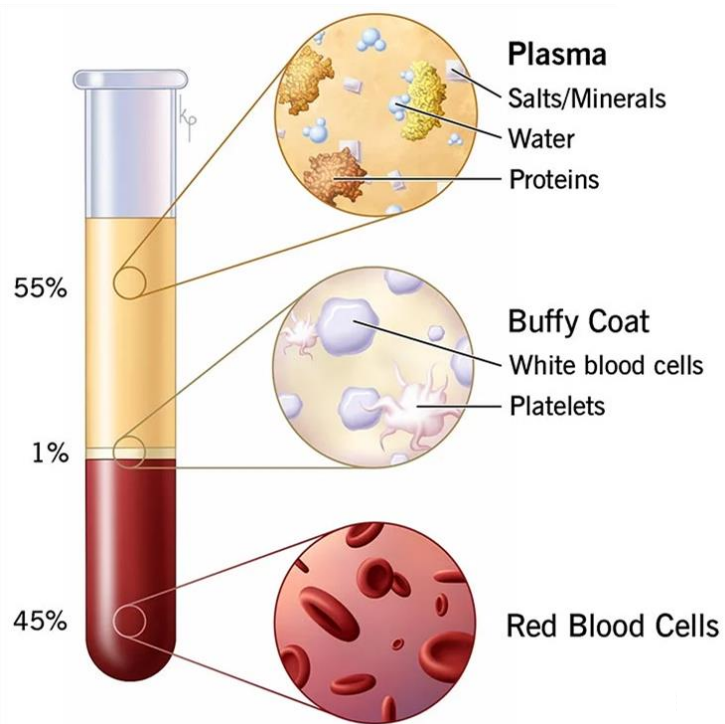
Outline

- Plasma
- “Conventional SEM” for characterisation of plasma-treated wood
- Practical applications of plasma treatment of wood
- Preferential etching of wood cell walls by plasma etching
- (“Environmental SEM” for *in situ* characterisation of plasma-treated seeds and plantlets)
- Wood: past, now and tomorrow

The Fourth State of Matter

“Plasma” comes from the **Greek** word which means “**moldable substance**” or “**jelly**”

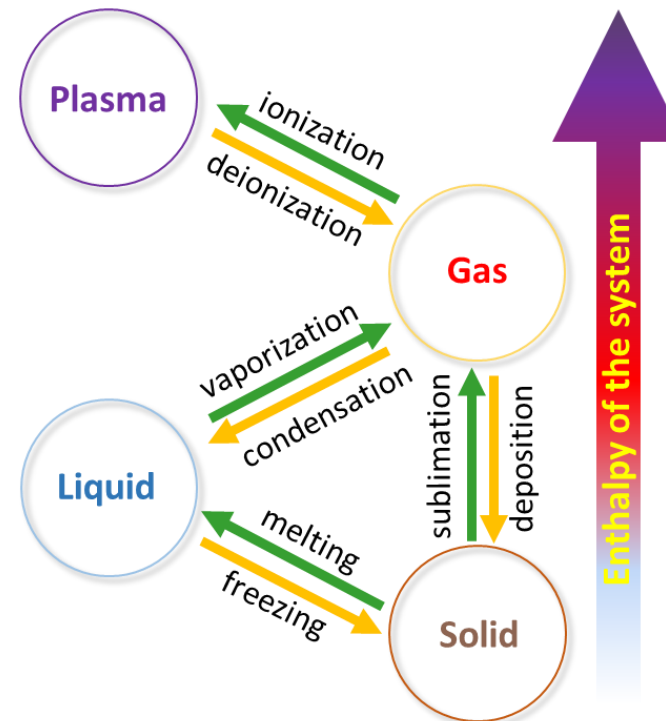
Biology



1839

Named by the Czech medical scientist, Johannes Purkinje (1787-1869)

Physics



1927

Named by the American chemist, Irving Langmuir (1881-1957) (Nobel Prize 1932)

Ways of Classifying Plasma

Degree of ionization

Density

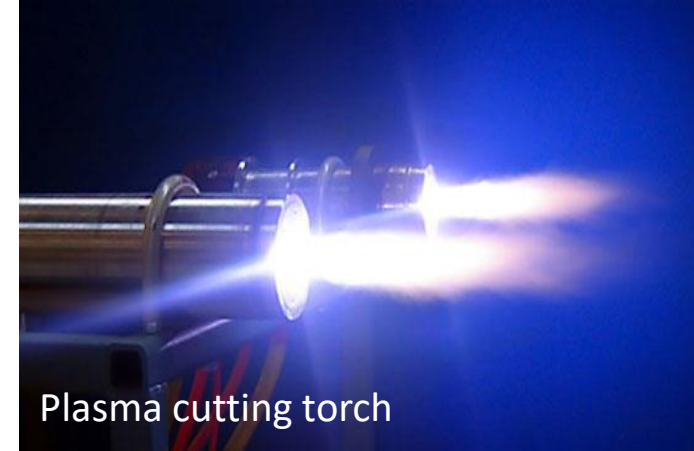
Temperature

Hot (thermal) plasma

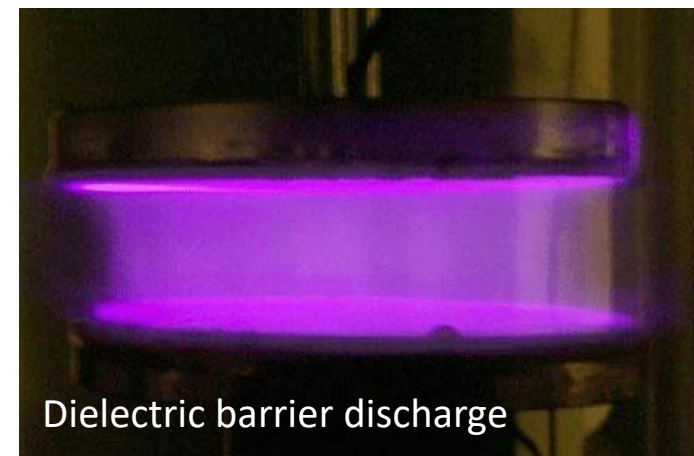
Natural



Man-made

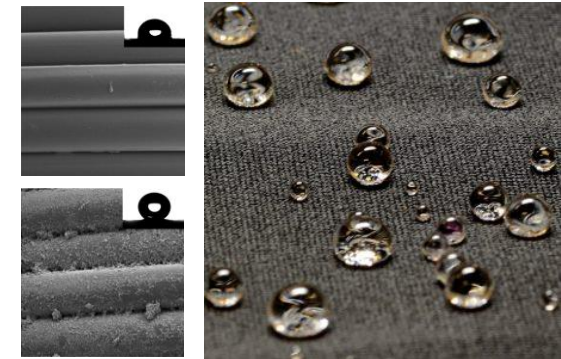
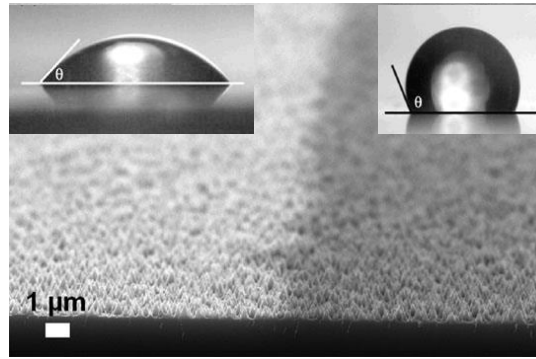
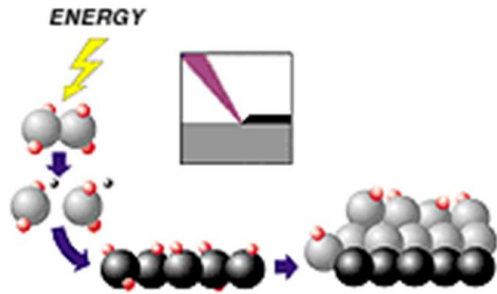


Cold (non-Thermal) plasma



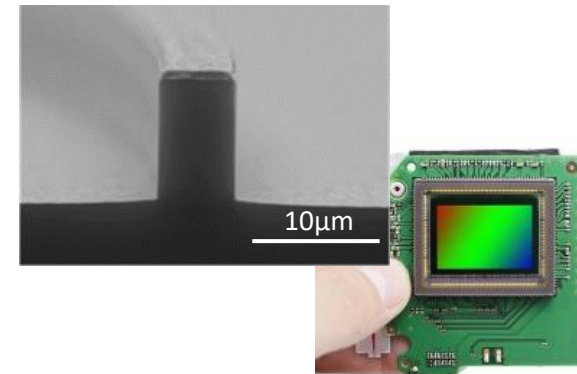
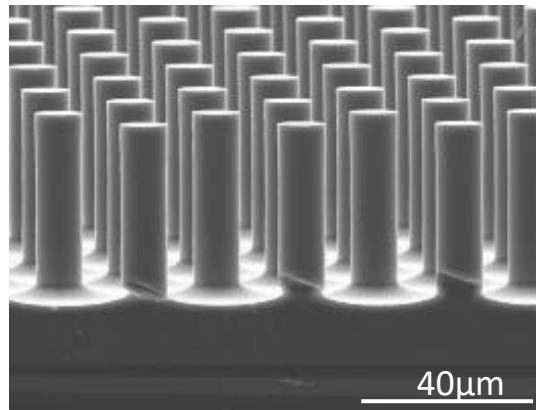
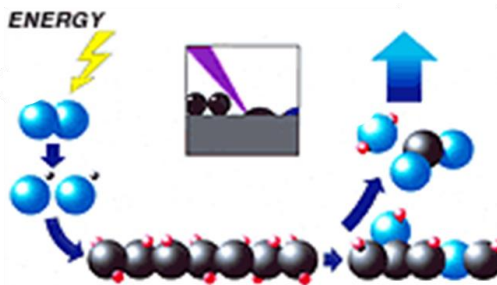
Cold Plasma Surface Modification

Coating



Low-pressure plasma-coating for durable water and oil repellant high-end functional textiles

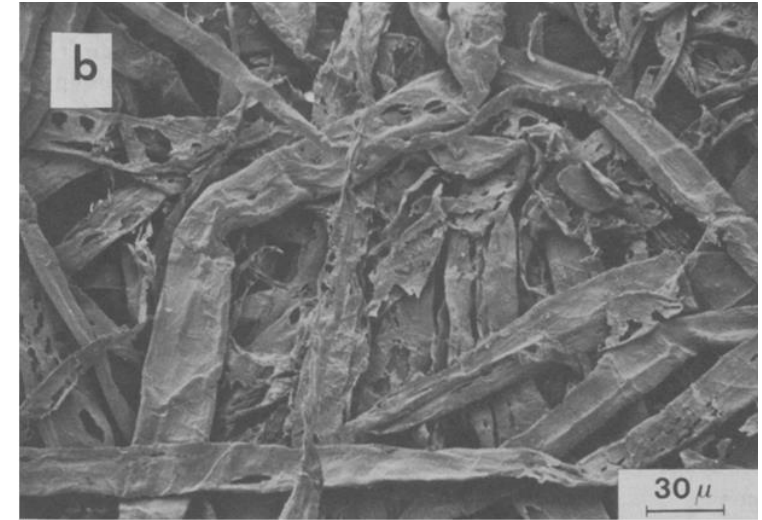
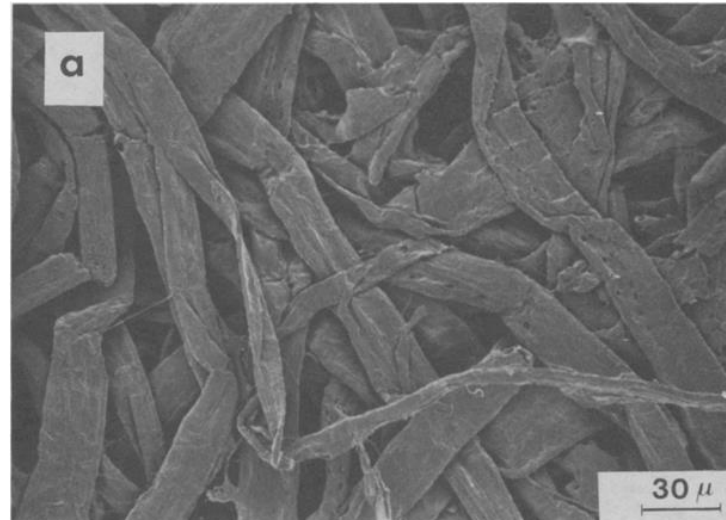
Etching/Functionalization



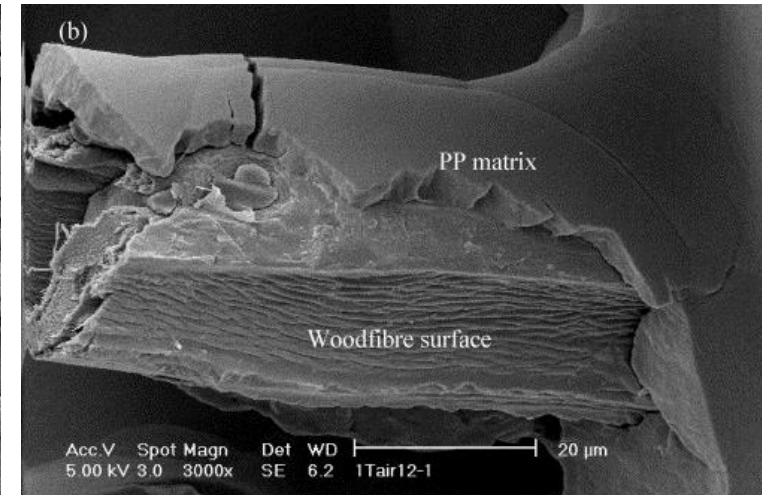
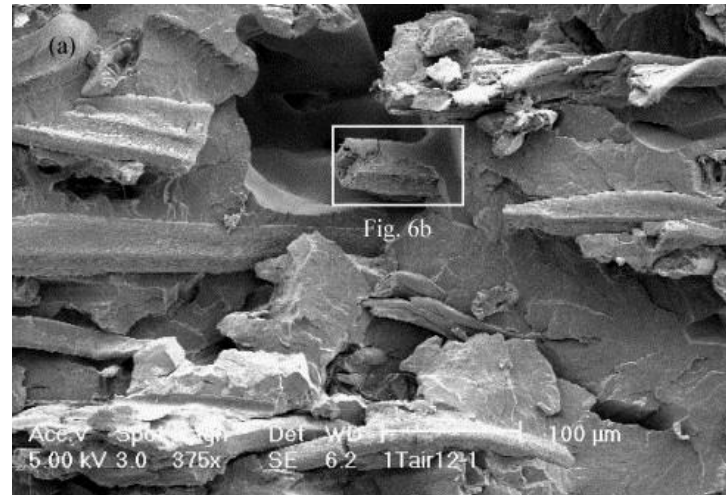
Free-standing silicon cylinders formed by plasma etching of a silicon wafer (left), and a plasma etched waveguide used in CMOS technology (right) (Fitzgerald 2011)

Plasma Treatment of Lignocellulosics

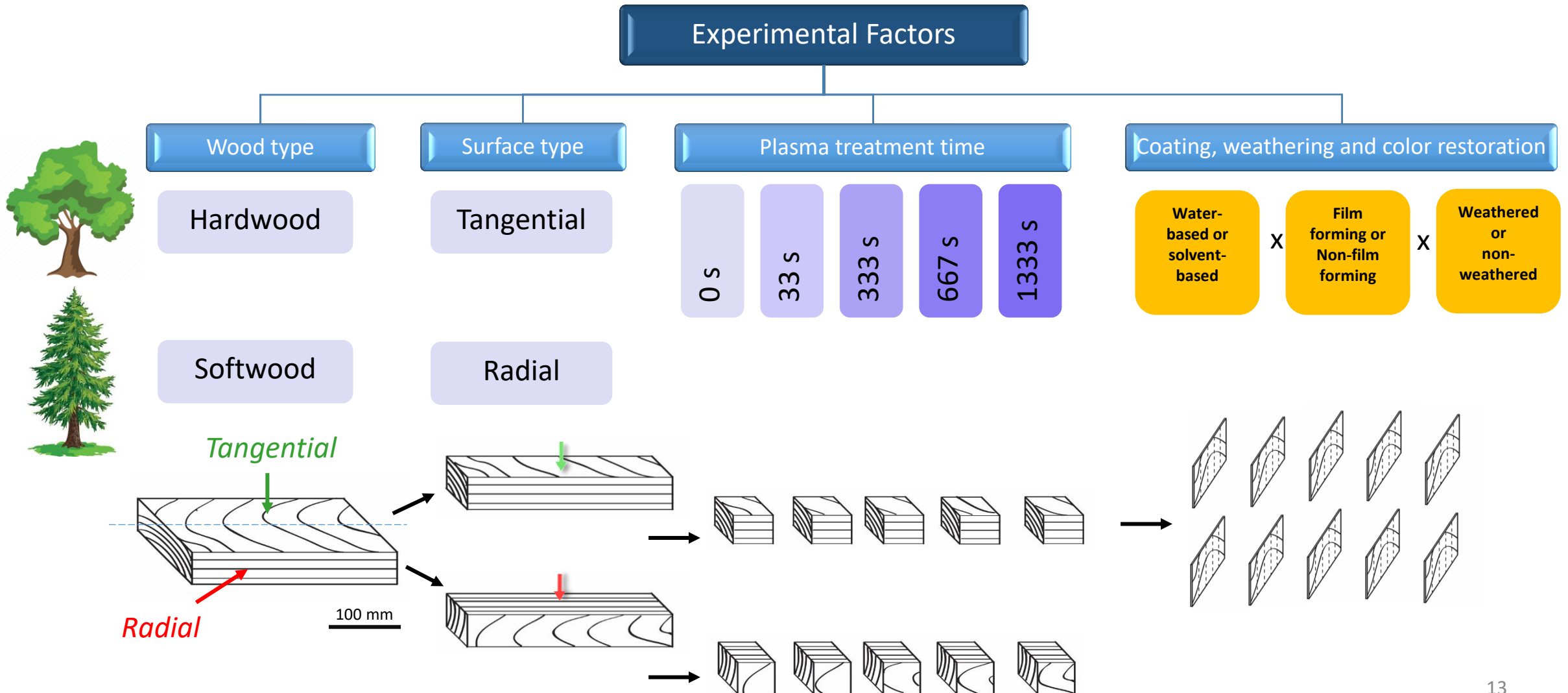
Plasma etching of Kraft paper:
Before (a) and after etching
for 20 minutes(b)
(Sapieha et al. 1988)



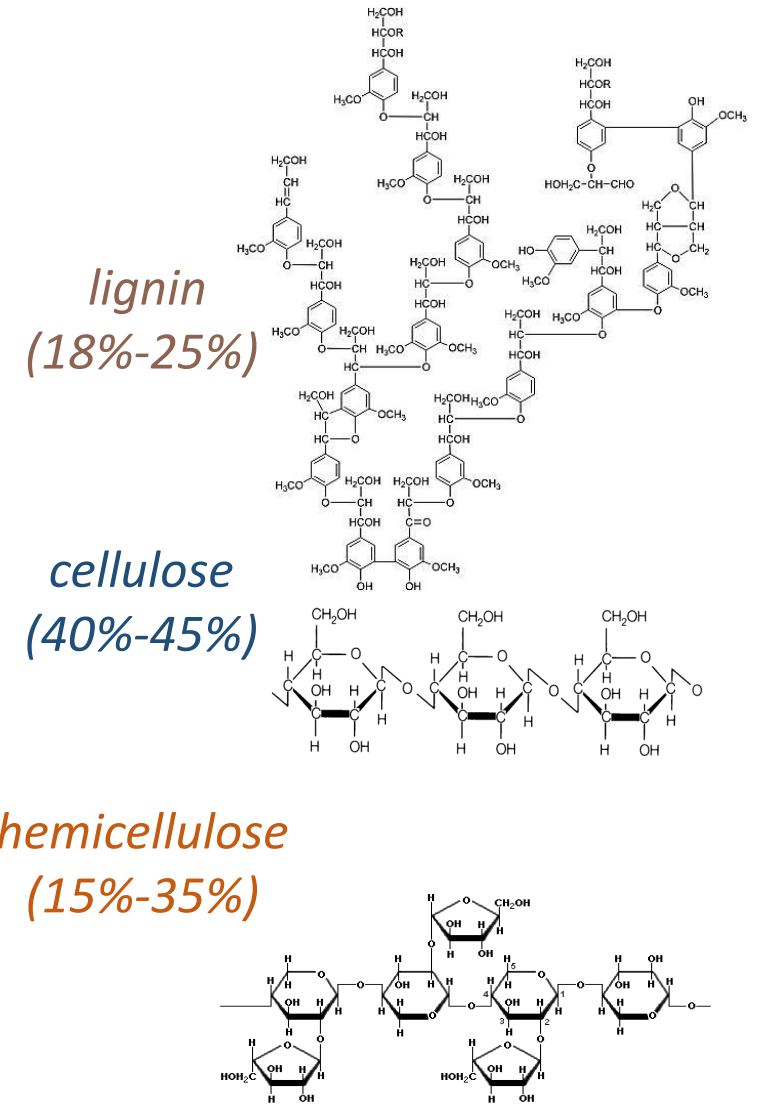
Wood-fibre-polypropylene
composites:
Fracture surface of 30s air-
plasma treated fibers
(Yuan et al. 2004)



Studying Plasma Treatment of Solid Wood



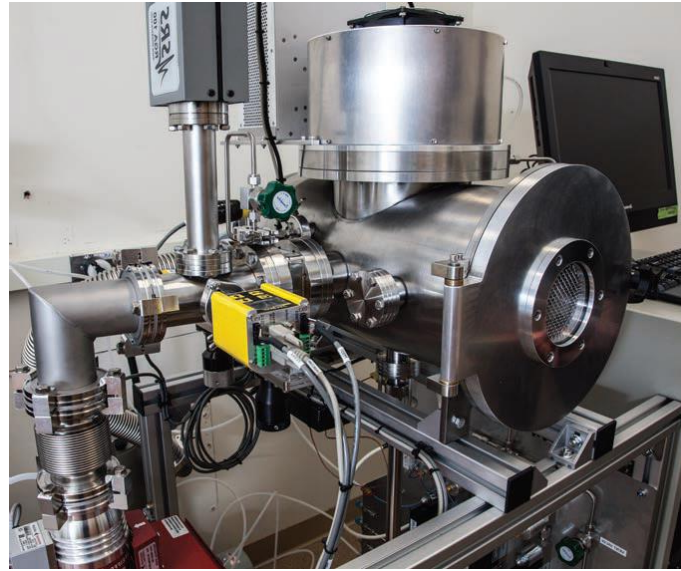
Structure of Wood (softwood)



Source: Modified and extended after Harrington, M. 1996.

Plasma Treatment

- Gas type: H₂O vapor
- Radio frequency of 125 kHz
- RF power: 150 W
- Chamber pressure: 150 mtorr
- Energy applied: treatment time



*Plasma reactor in Wood Surface Science lab (Evans' lab),
UBC, Vancouver, Canada*

Methods

Microscopy

Microtomy

ultraviolet (UV) laser ablation

Hitachi S-4700 FE-SEM

FEI Quanta 200 FEG ESEM

Chromatic confocal profilometry

Carl Zeiss light microscope

Chemical analyses

Structural carbohydrate analysis using HPLC, GC-LC/MS

Acid-insoluble (Klason) and acid-soluble lignin

Fourier Transform Infrared Spectroscopy (FTIR)

X-ray Photoelectron Spectroscopy (XPS)

Surface performance

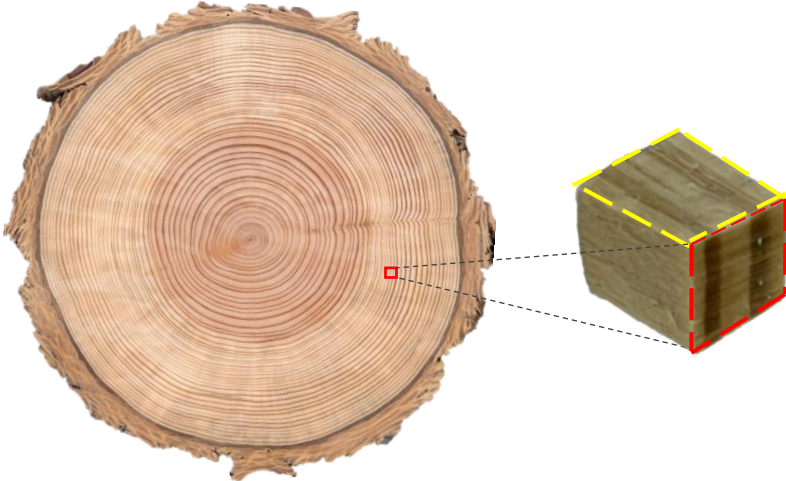
Natural and artificial Weathering

Contact Angle and permeability

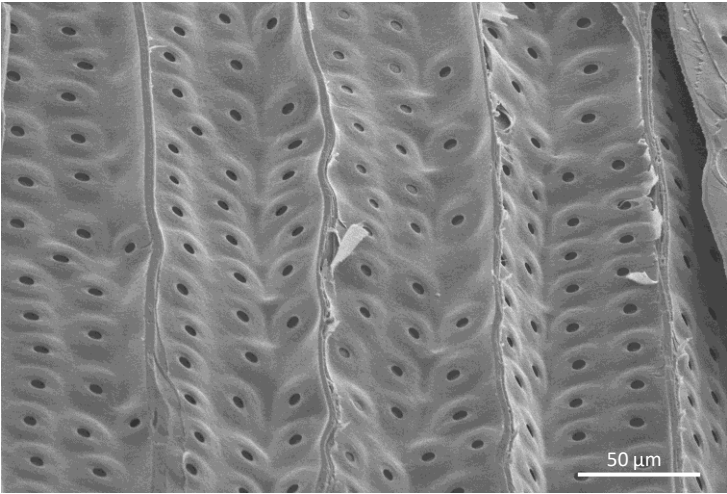
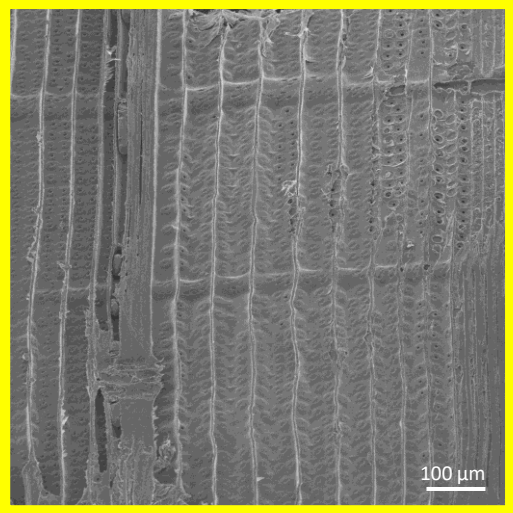
Evaluation of Coating Performance and Adhesion

Etching of cellulose and lignin pellets

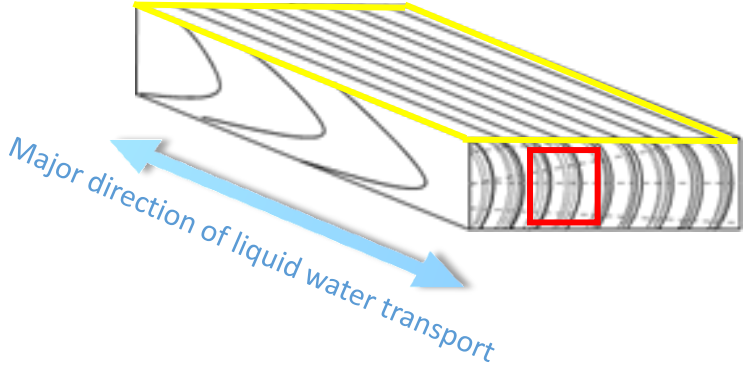
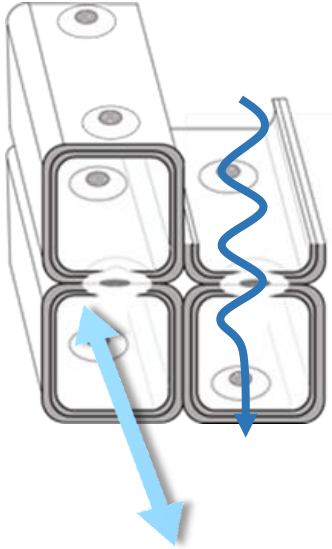
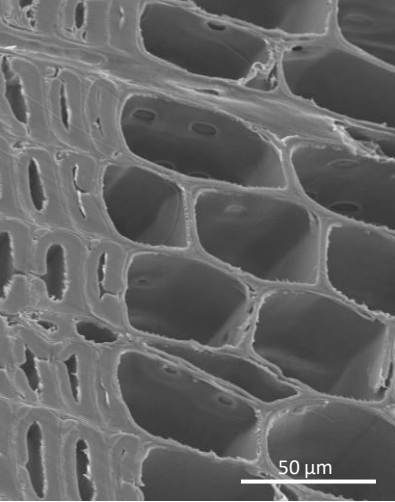
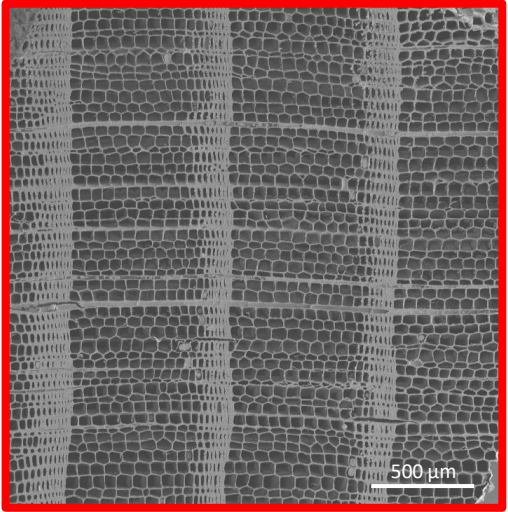
Perforation and Liquid Transfer in Wood



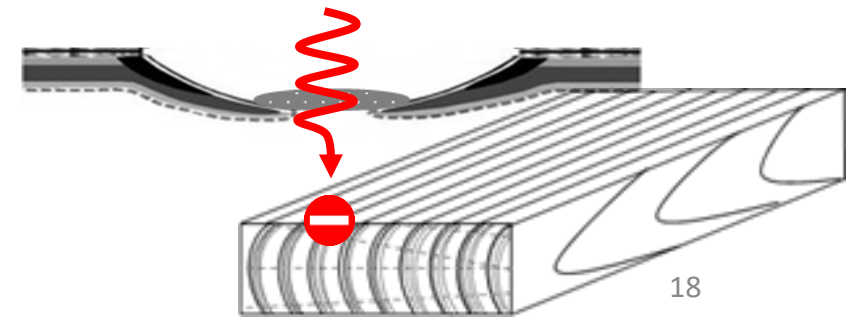
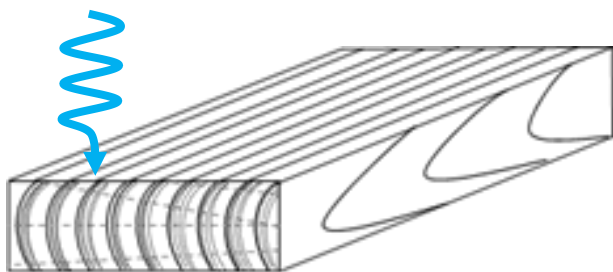
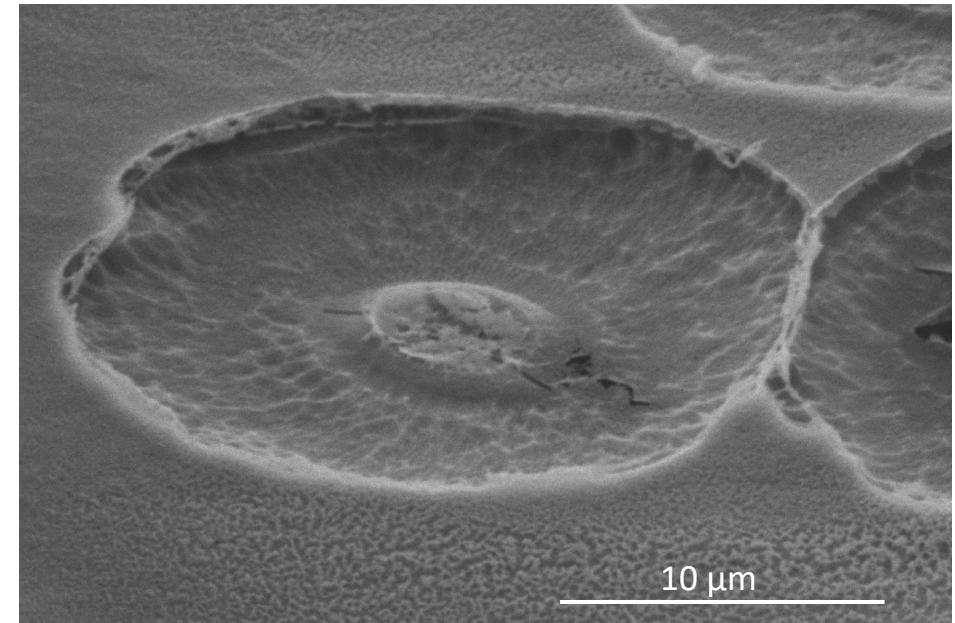
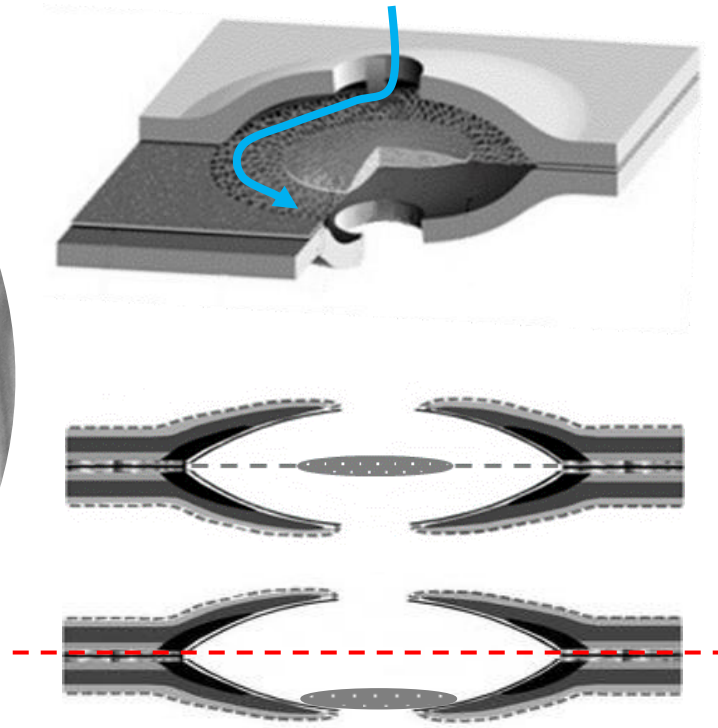
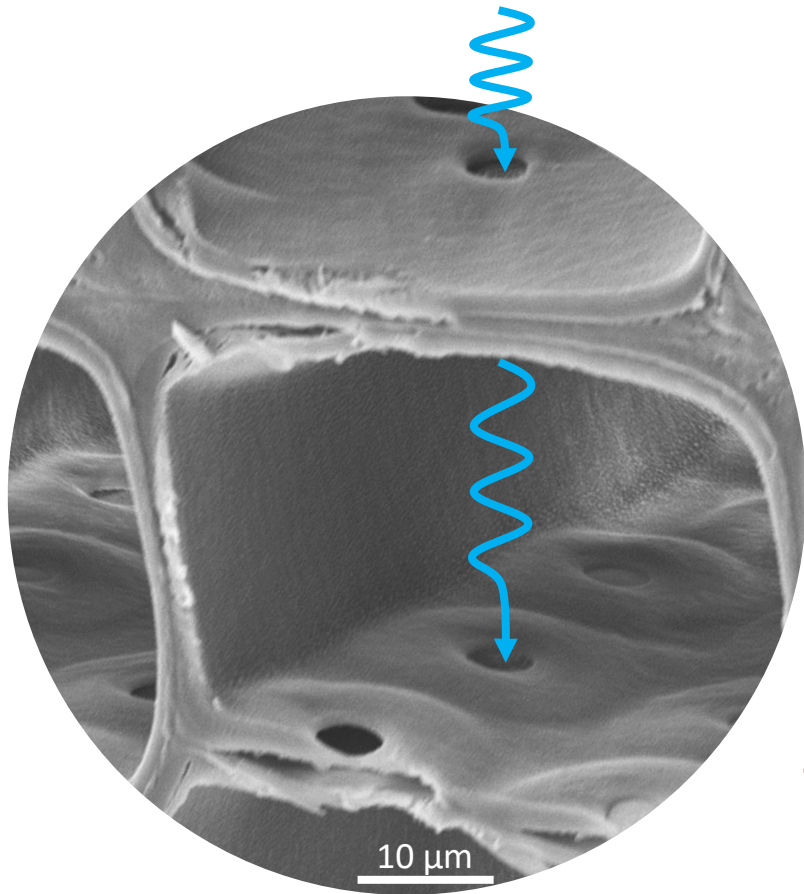
Radial surface



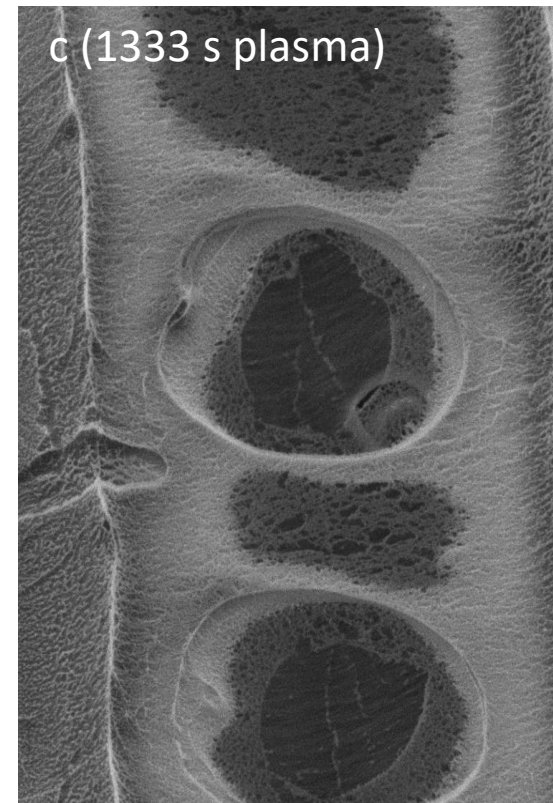
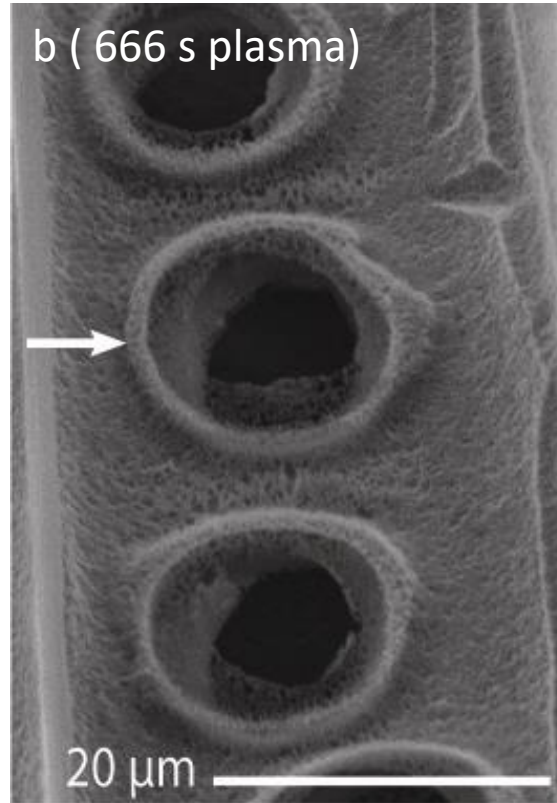
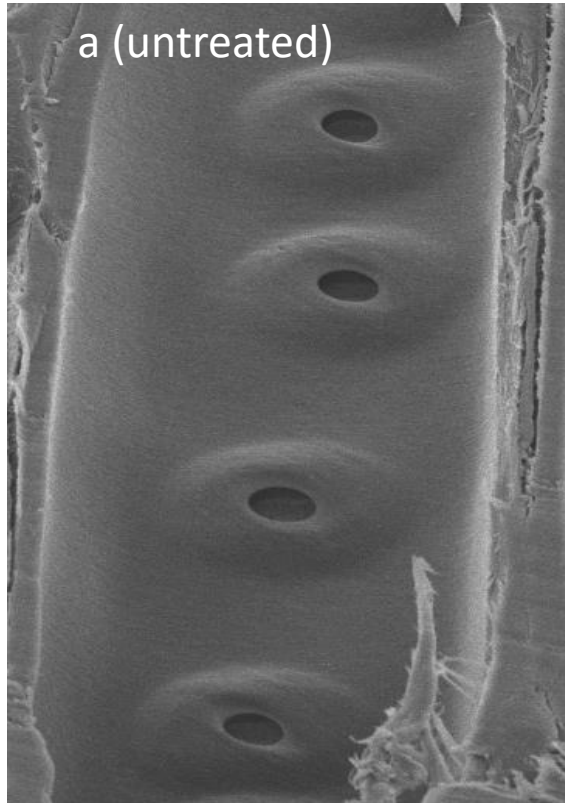
Transverse surface



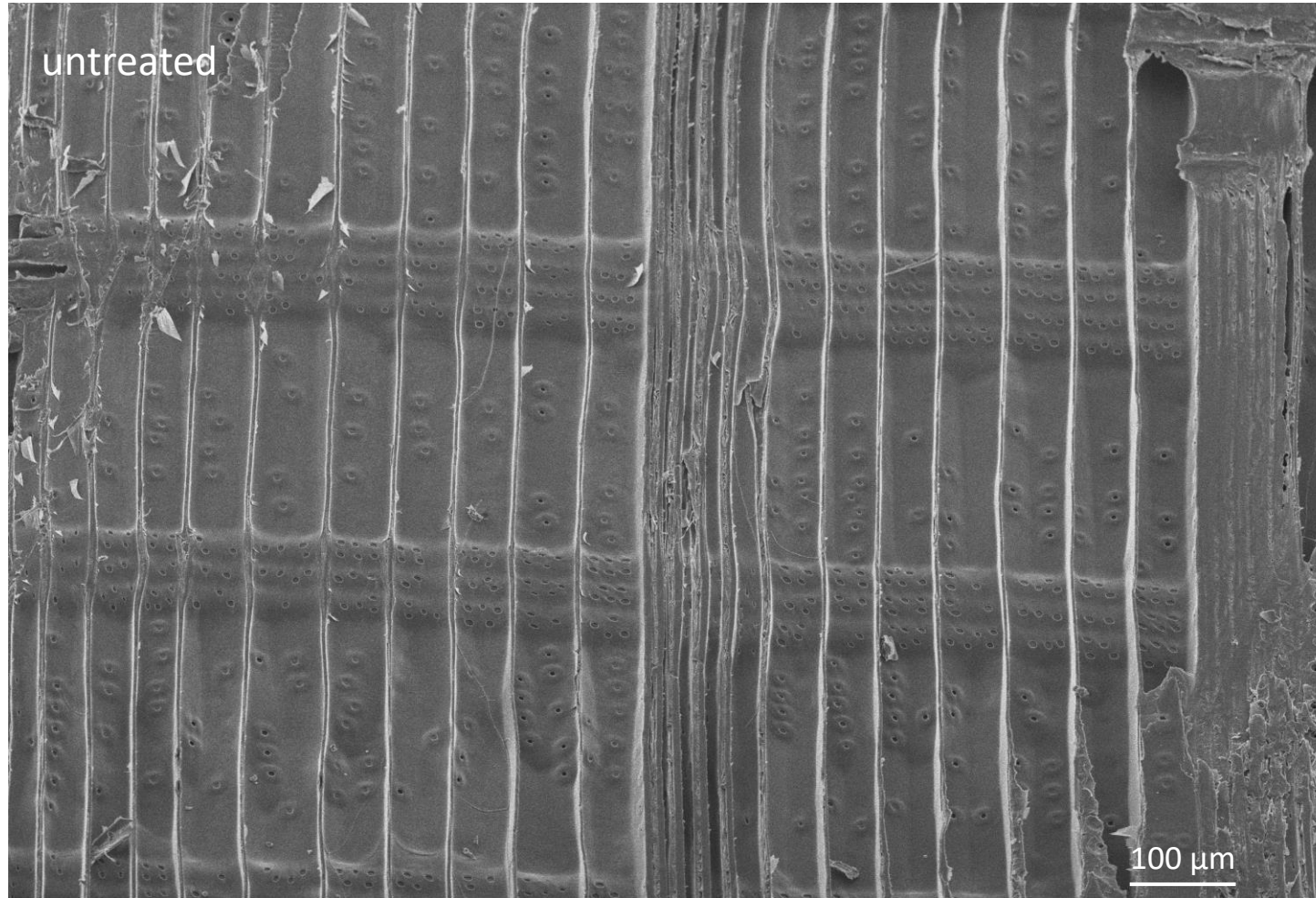
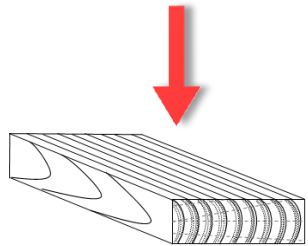
Bordered Pits and Liquid transfer in Softwoods



Plasma Etching of Bordered Pits

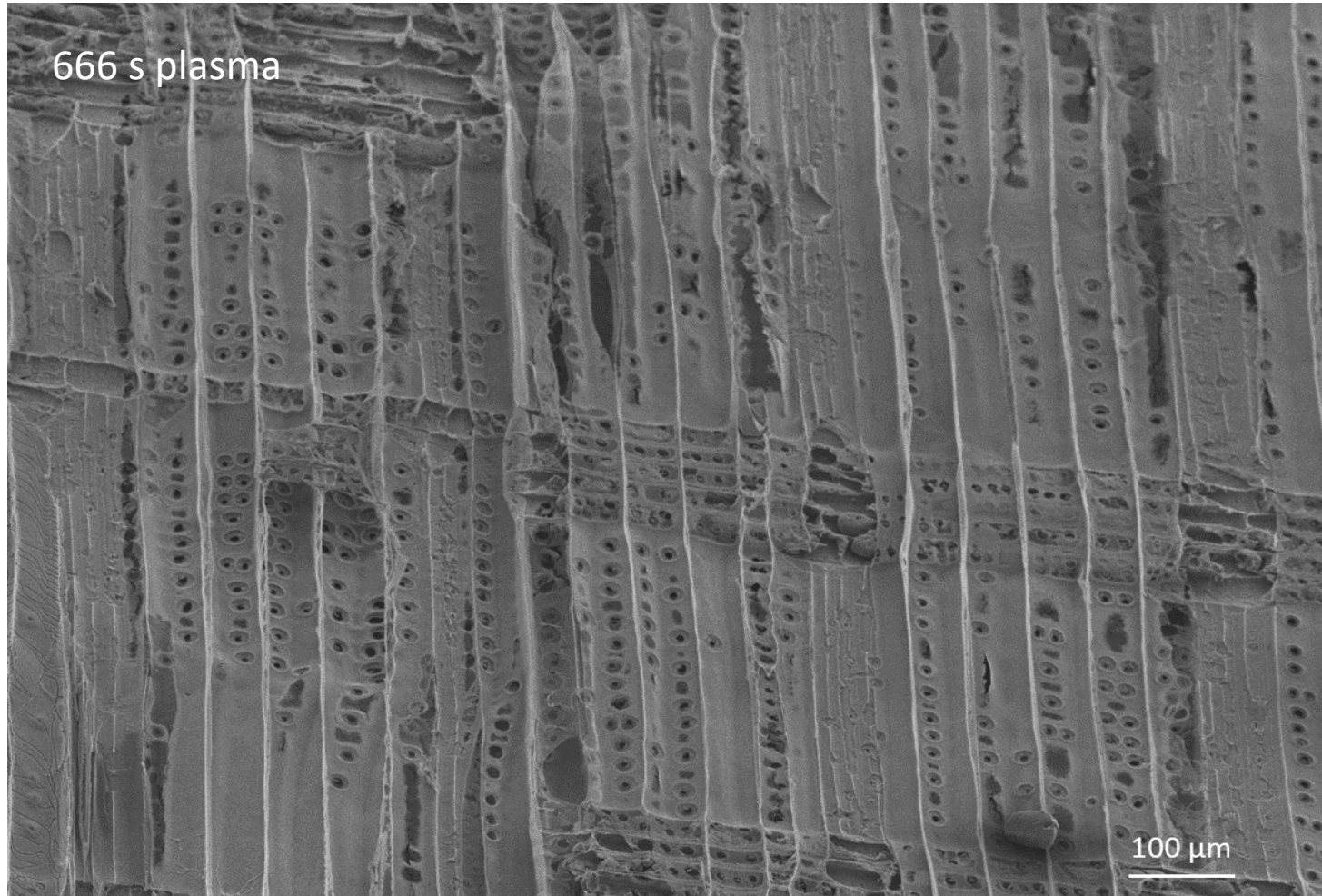
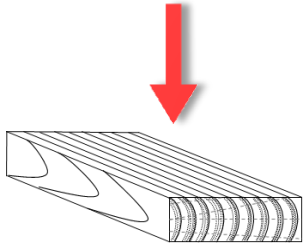


Effect of Plasma on Surface Morphology of Wood



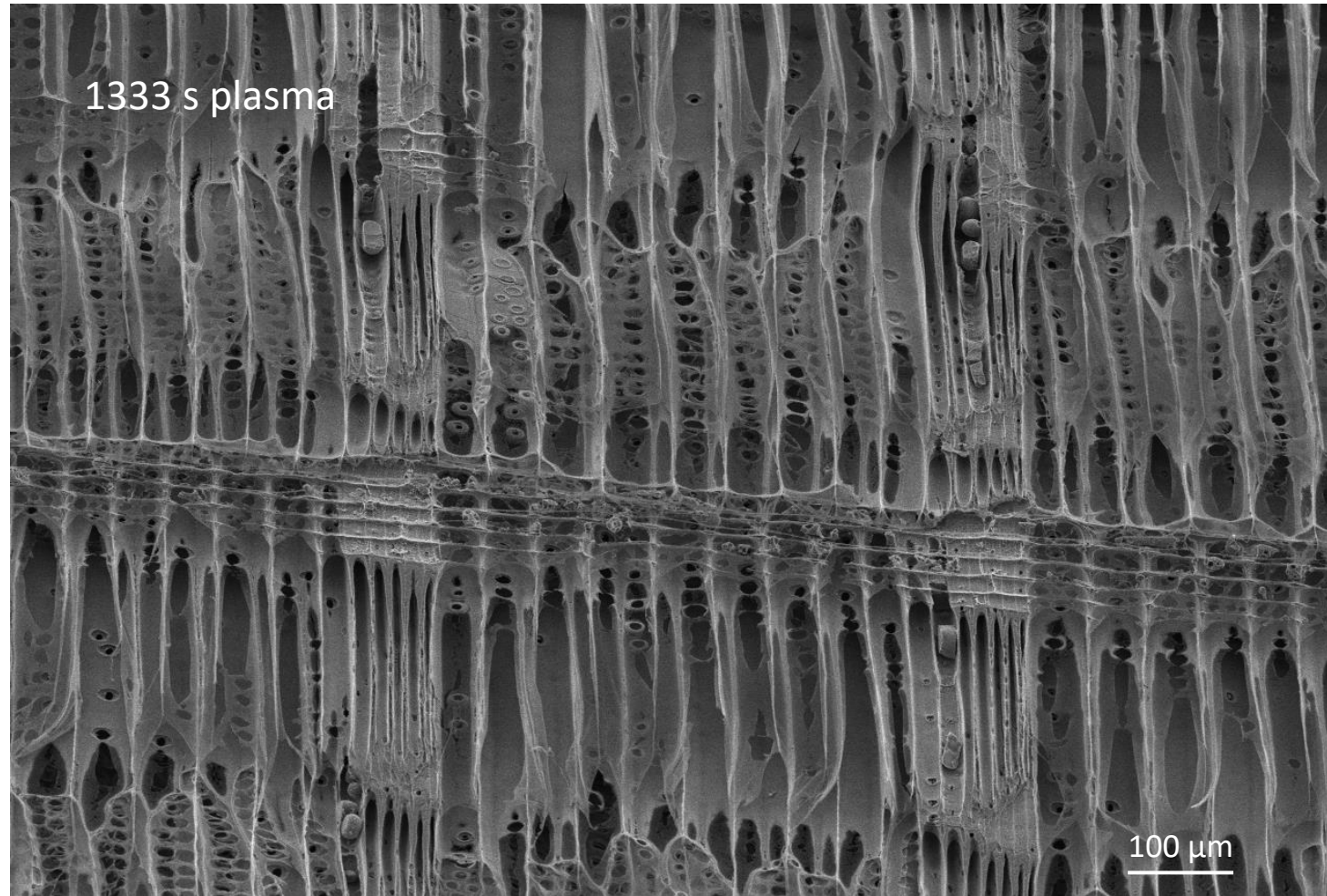
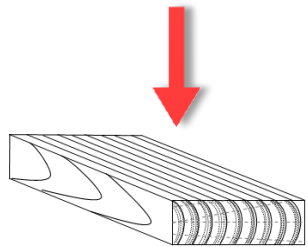
Radial longitudinal surfaces of redwood

Effect of Plasma on Surface Morphology of Wood



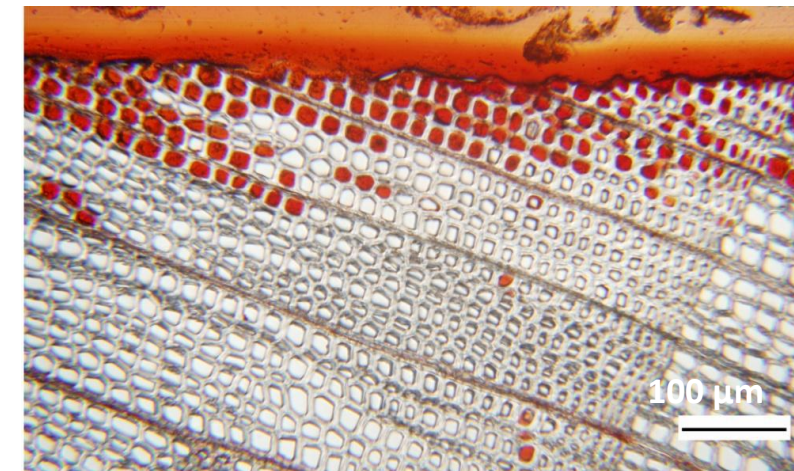
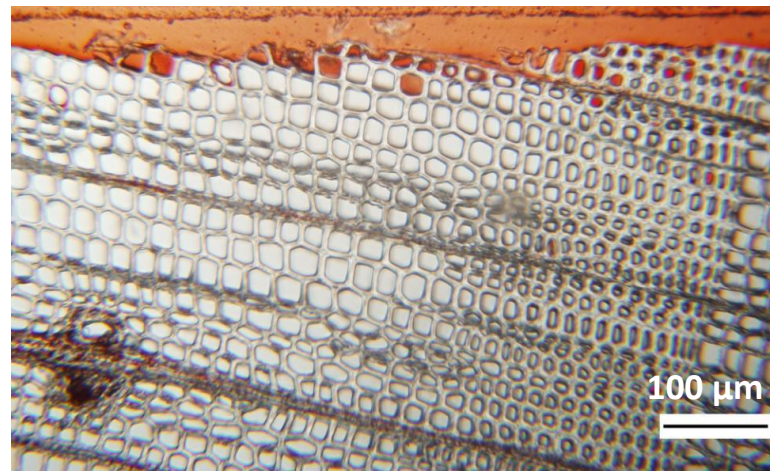
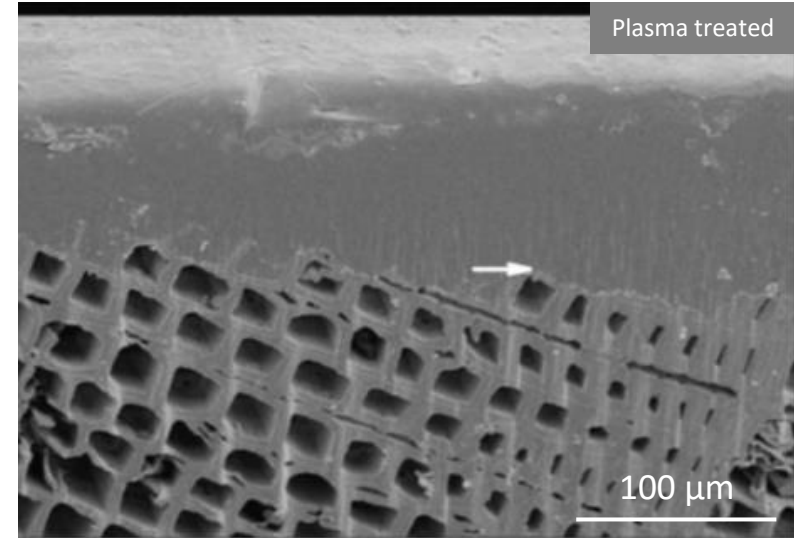
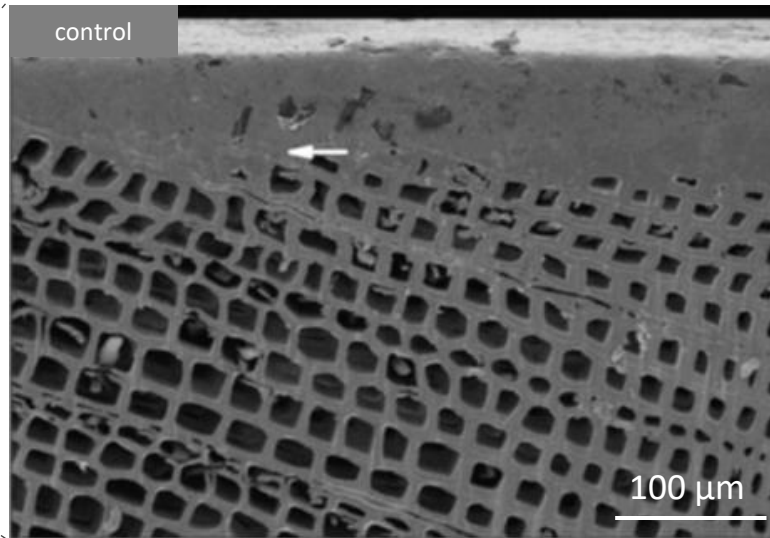
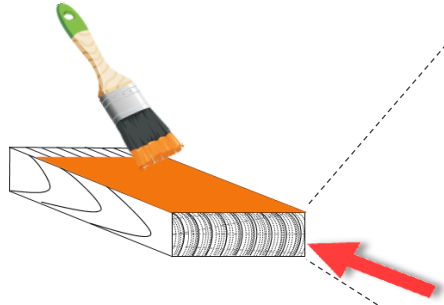
Radial longitudinal surfaces of redwood

Effect of Plasma on Surface Morphology of Wood



Radial longitudinal surfaces of redwood

Coatings on plasma treated wood



Artificial Weathering Performance of Coating



QUV accelerated-weathering tester
(weatherometer)

untreated

Plasma treated

2000 h.



2500 h.



3000 h.



15 mm

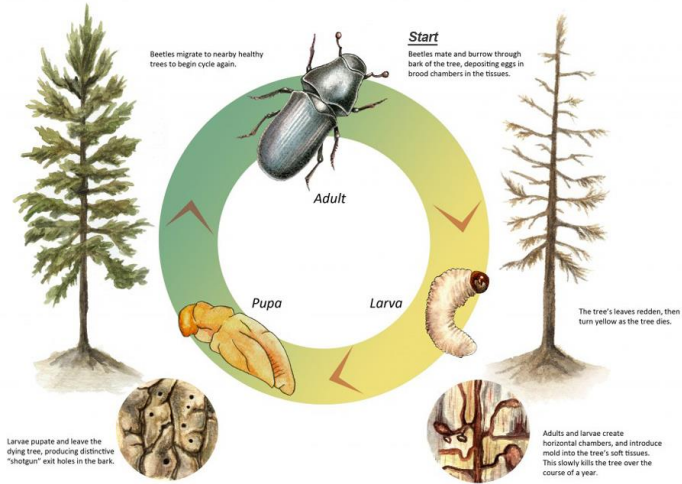
Step	Function	Temp. (C°)	Duration (h)	Remark
1	Condensation	45°C	24	
2	Subcycle step 3+4		144	
3	UV	60°C	2.5	UVA-340 nm
4	Spray			6-7 Litres/min UV light off
5	Go to step 1			

Total (1 cycle) = 168h (1 week)

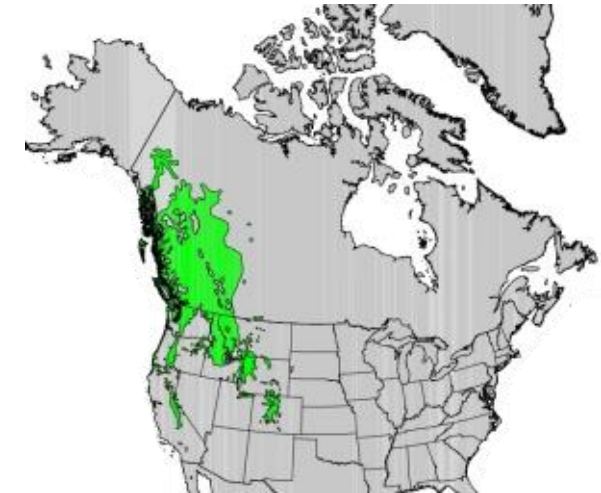
Hasse et al. 2019,, Coatings, 9 (1)

Mountain Pine Beetle and Infested Wood

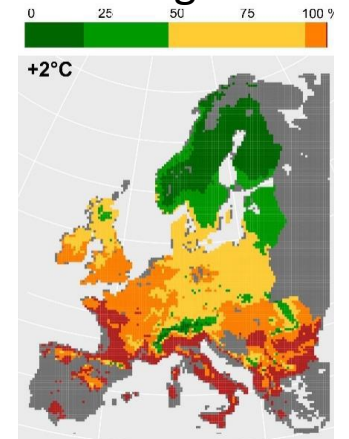
Life Cycle of Mountain Pine Beetle, *Dendroctonus ponderosae*



Western North America



Sub-Atlantic region of Europe

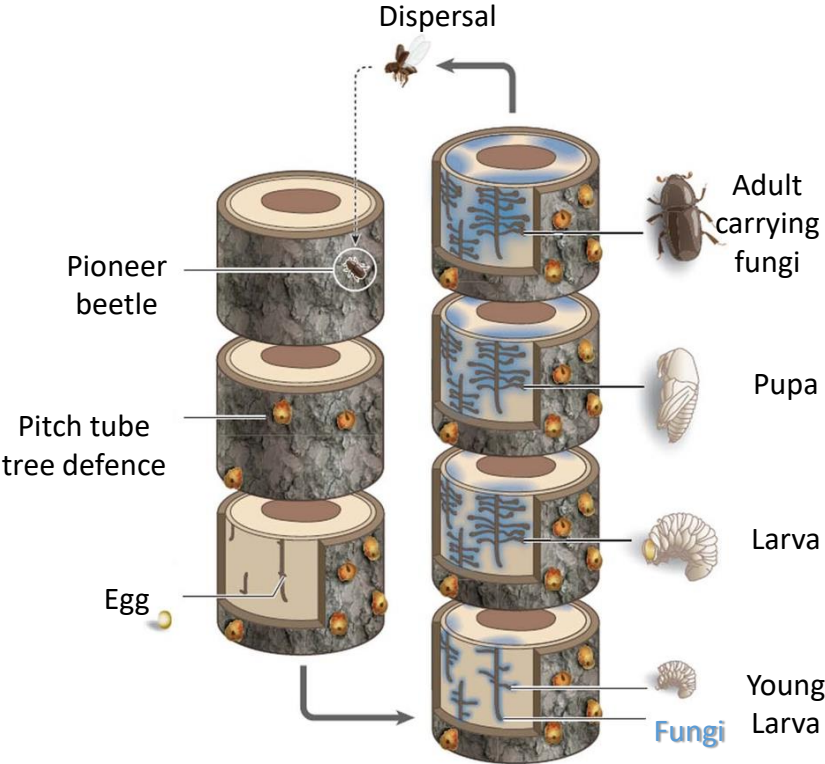


An outbreak of the mountain pine beetle and its microbial associates has affected more than 160,000 km² of pine forest in western North America

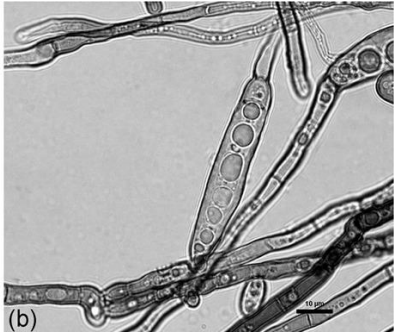
Sean Twiddy, 2010, <https://climatesight.org>



Blue-stained Pine



A Lodgepole pine trunk and the produced lumbers showing the stained wood



Grosmannia clavigera

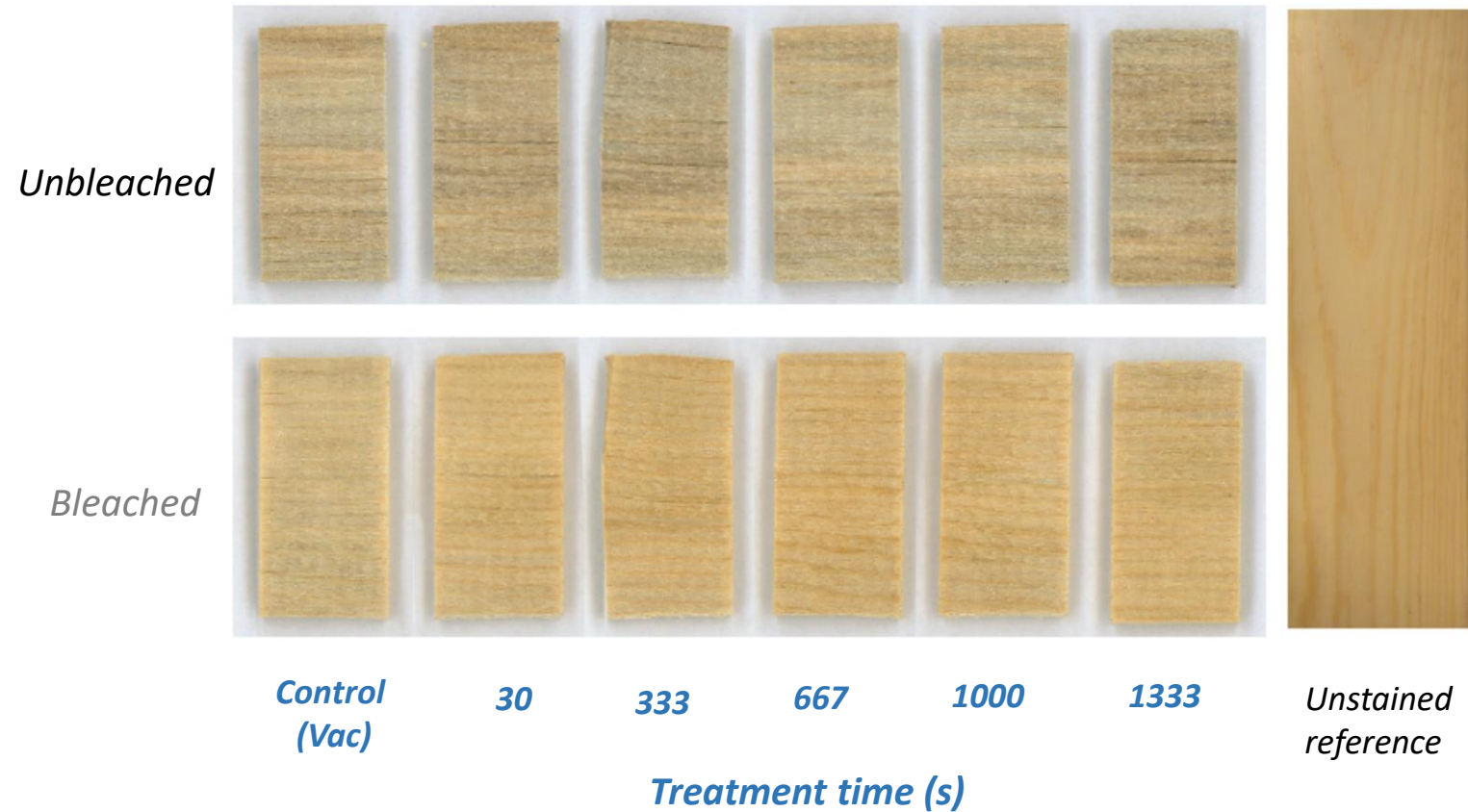
Bleaching to Restore the Color of Blue-stained Pine

Bleach spraying of wood surfaces



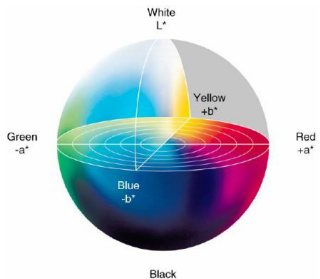
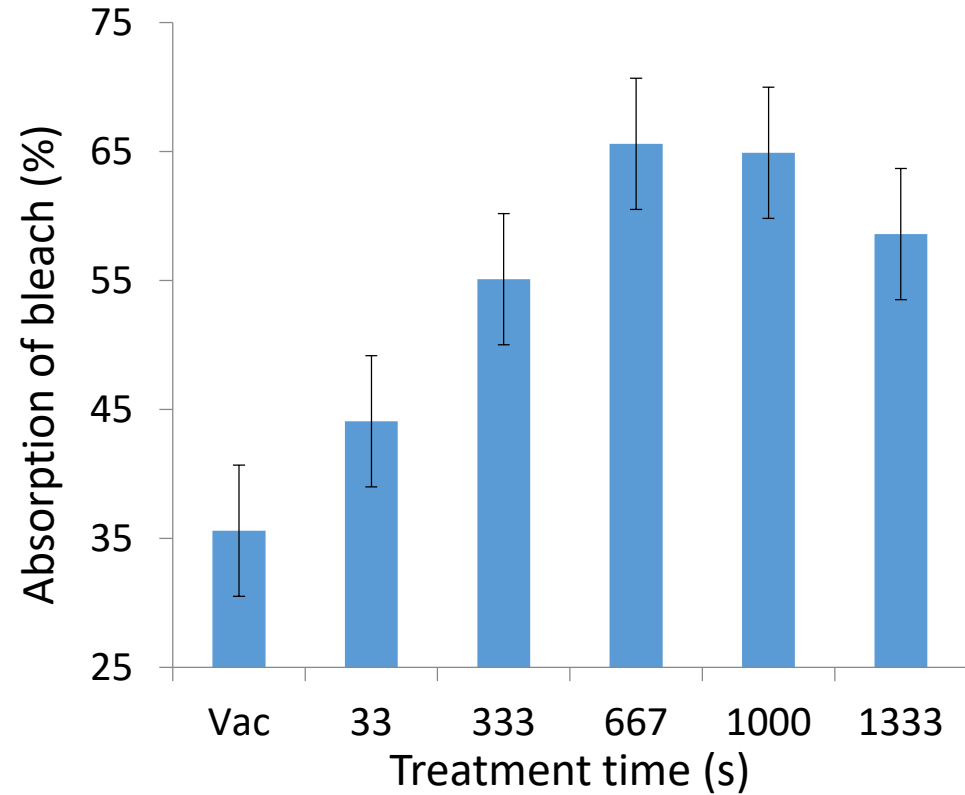
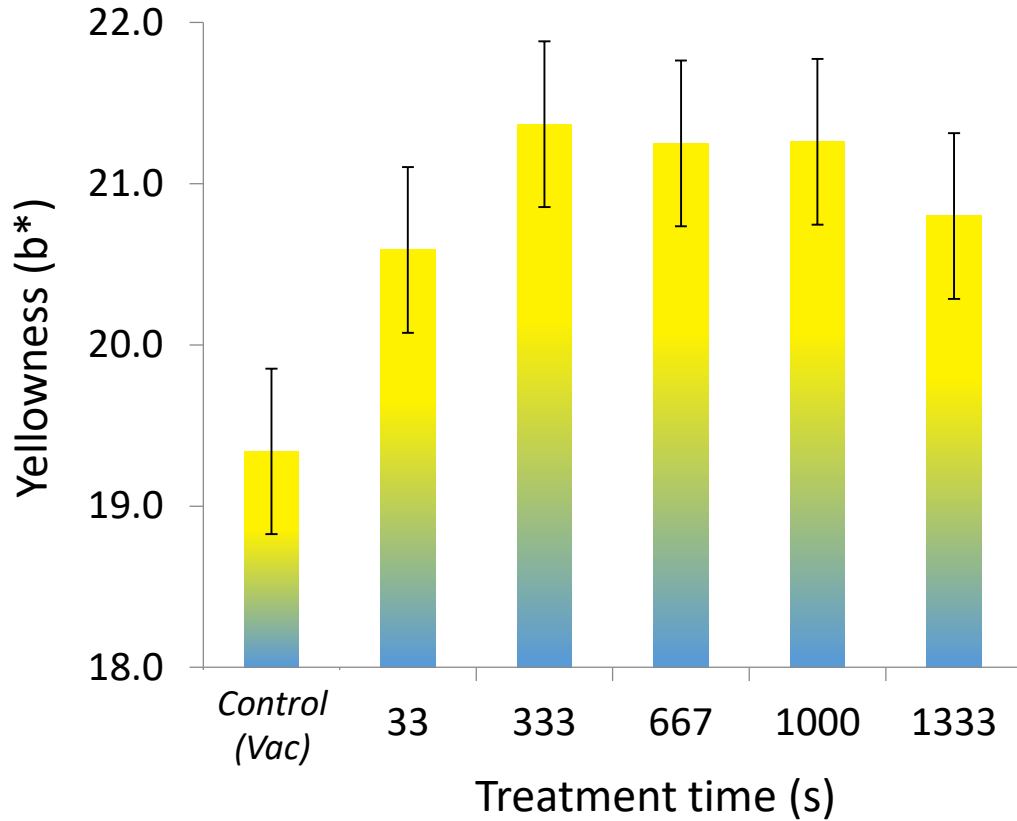
<http://www.rmfp.com/blue-stain>

Effect of Plasma on the Color of Blue-stained Pine



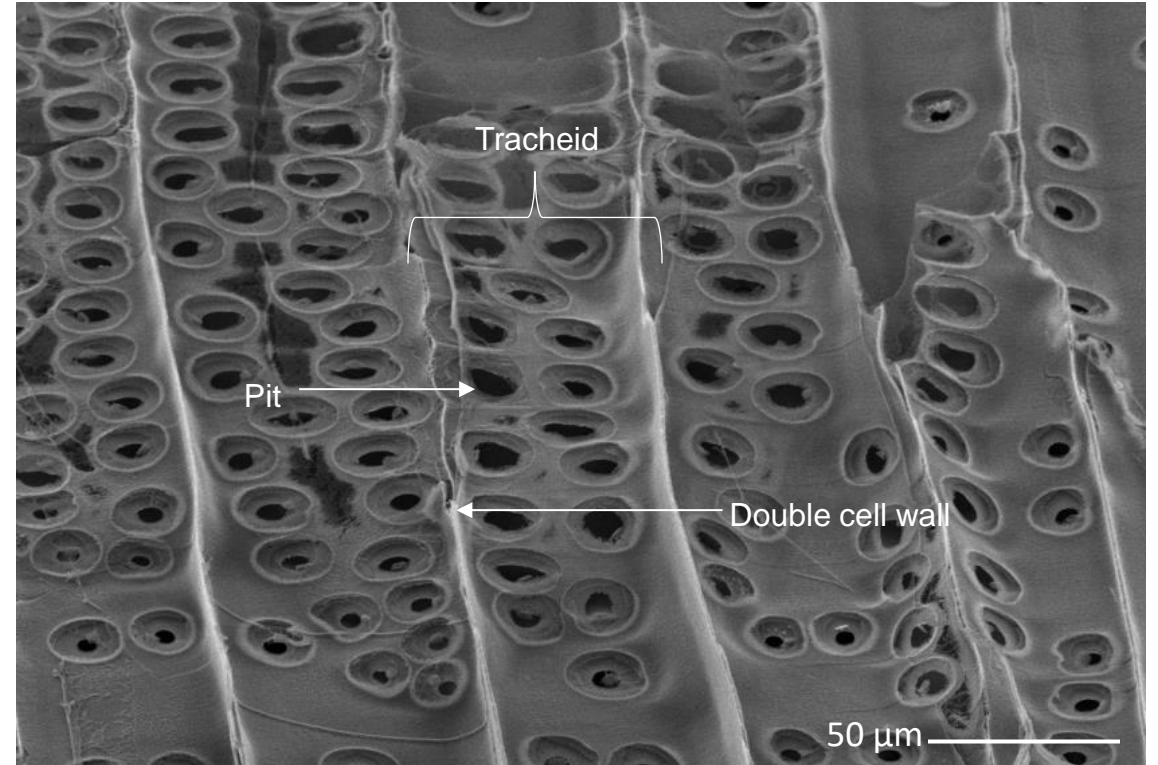
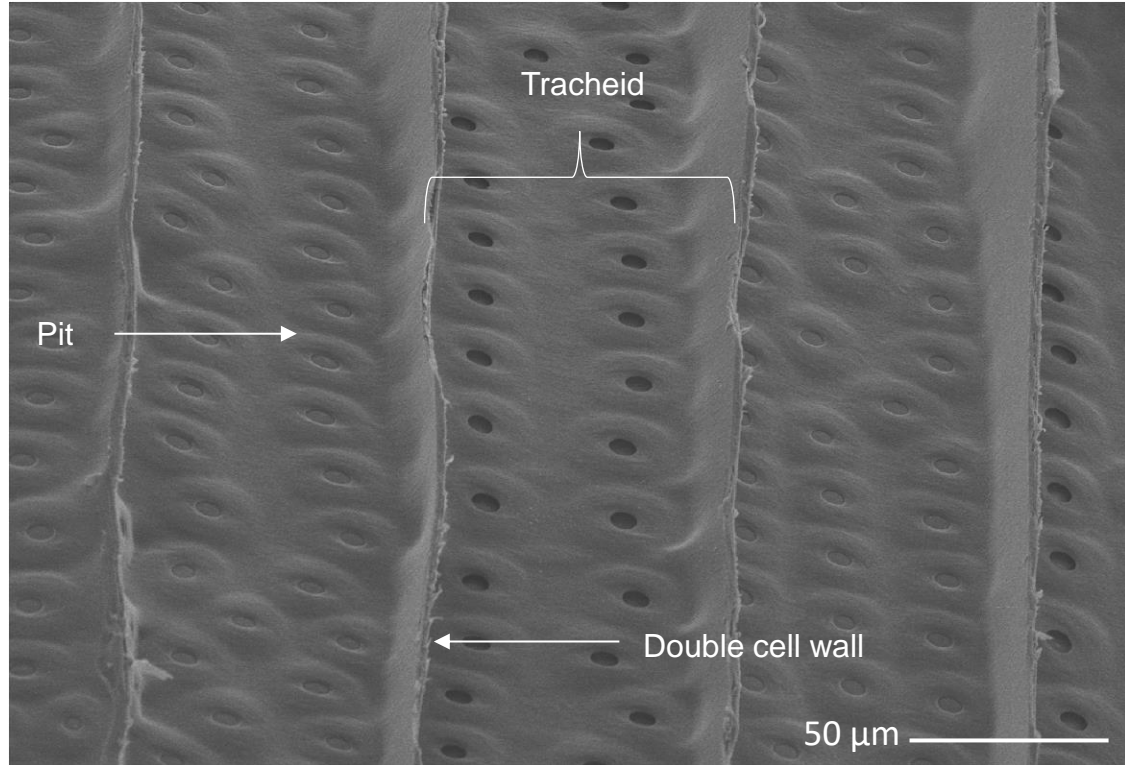
Changes in the appearance of blue-stained lodgepole pine sapwood specimens (upper row) exposed to plasma for different periods of time (left to right) and bleached by sodium hypochlorite (12 % w/v), and a sample of unstained lodgepole pine sapwood (right of the image)

Wood's Color Change and Permeability to Bleach



This system uses three parameters to express the color of materials:
L*(lightness on a scale of 0 [black] to 100 [white]),
a* (+60 [red] to -60 [green])
b* (+60 [yellow] to -60 [blue]).

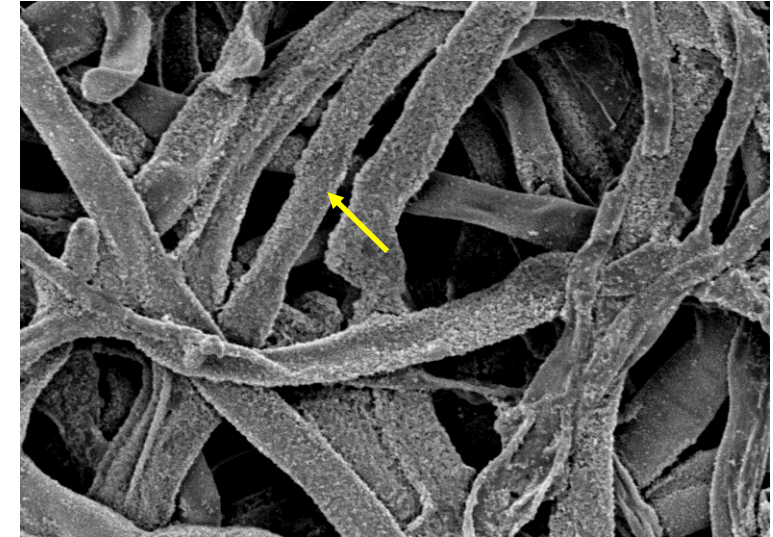
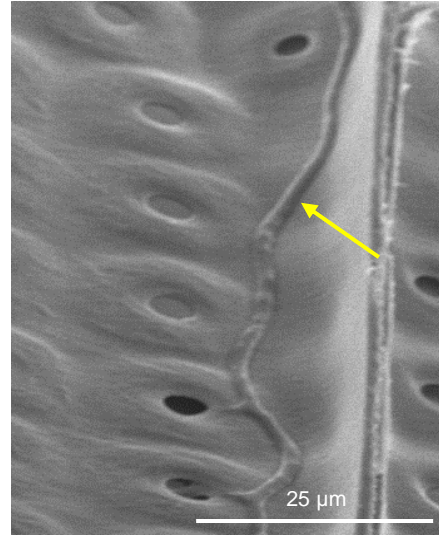
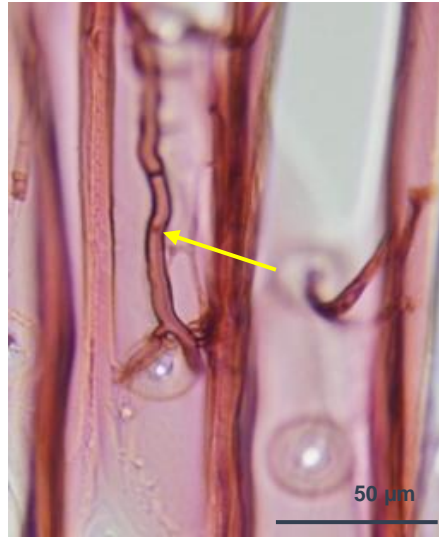
Increased Surface Porosity



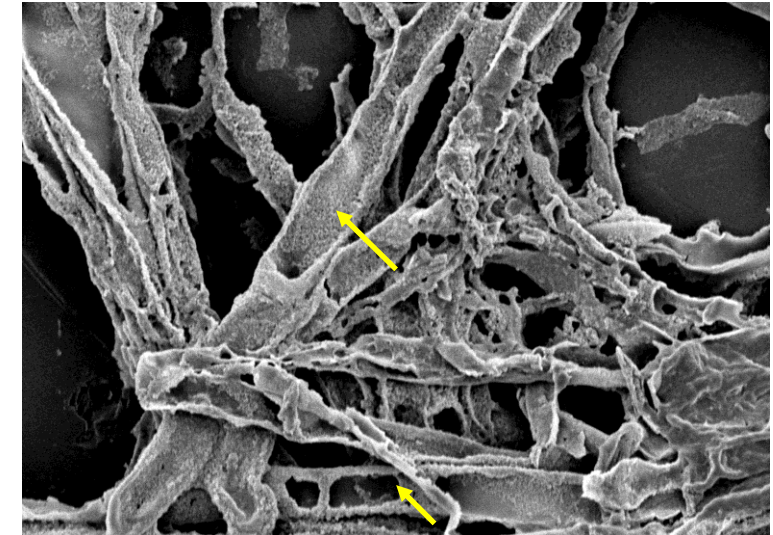
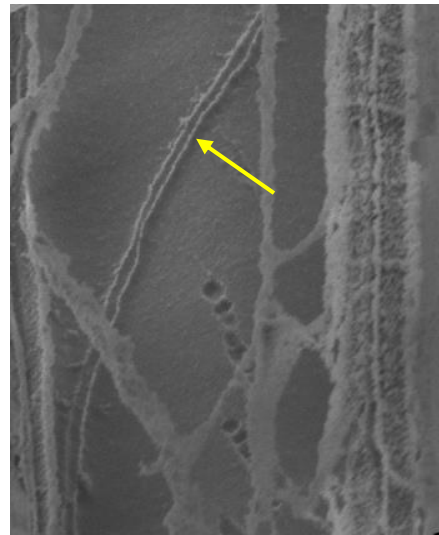
Untreated and plasma treated wood for 667 s

Plasma Etching of Fungal Hyphae

Untreated



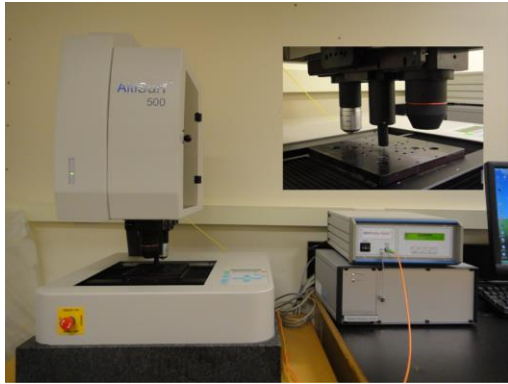
Plasma-treated
(333 s)



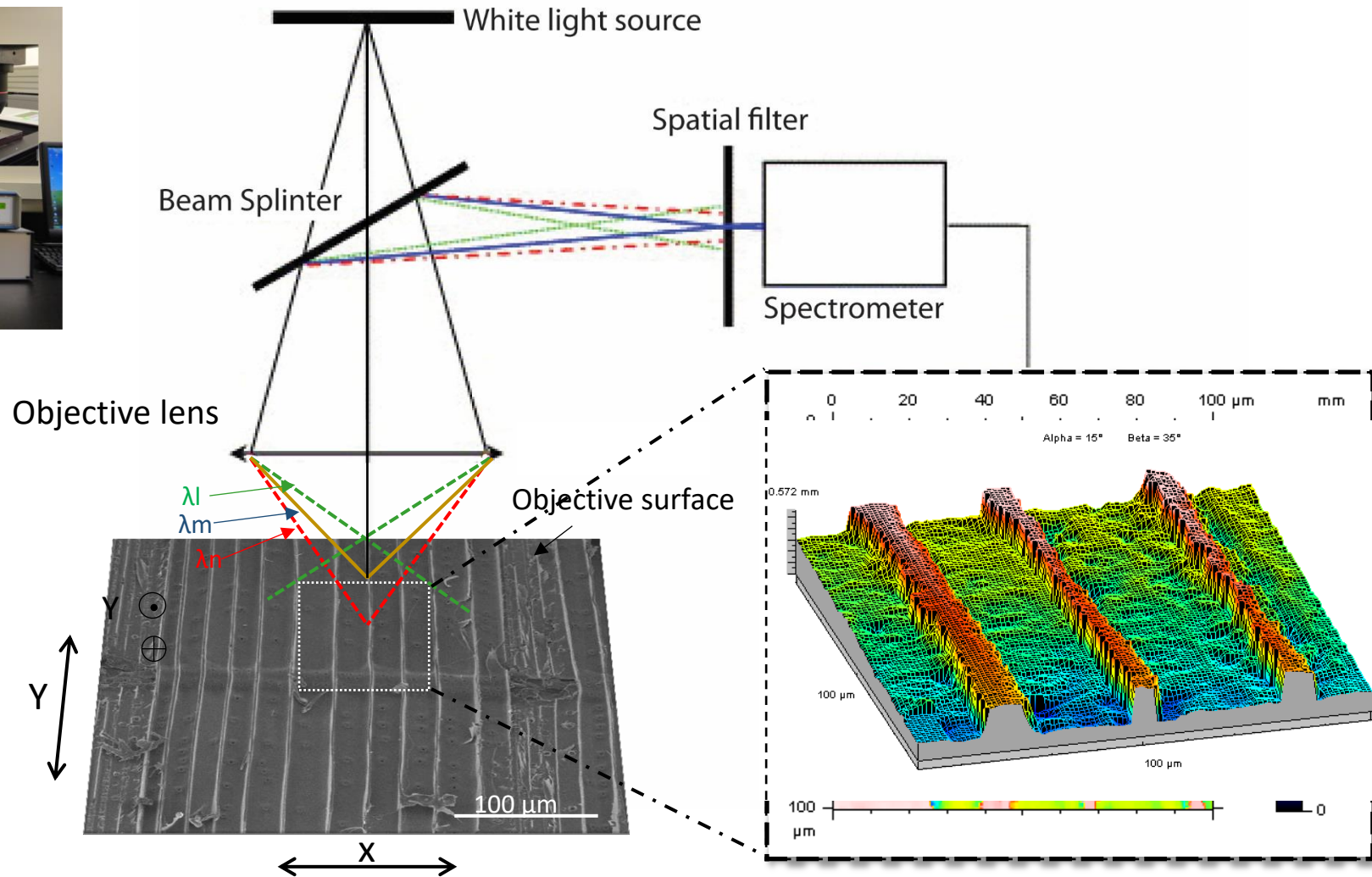
Light microscopy and SEM images of hyphae in wood

*Isolated hyphae of *G. clavigera**

Quantification of Wood's Cell Wall Etching

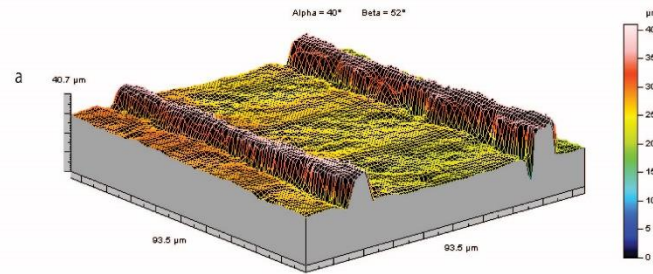


Confocal Profilometer

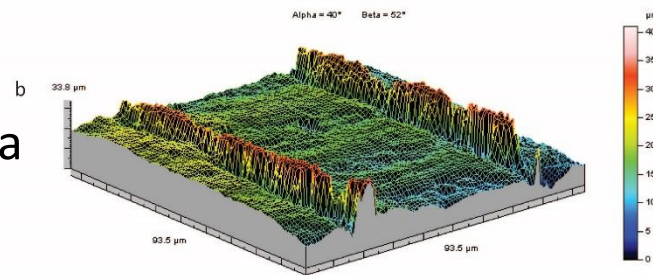


Quantification of Wood's Cell Wall Etching

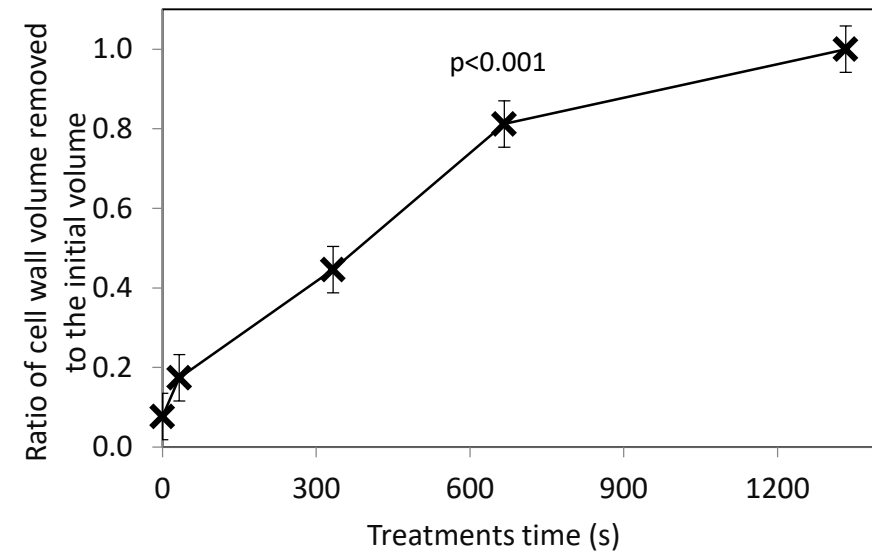
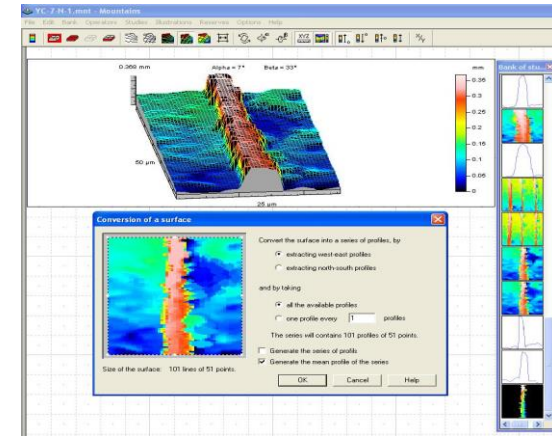
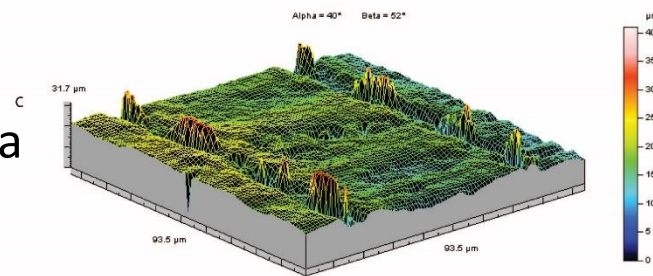
Untreated



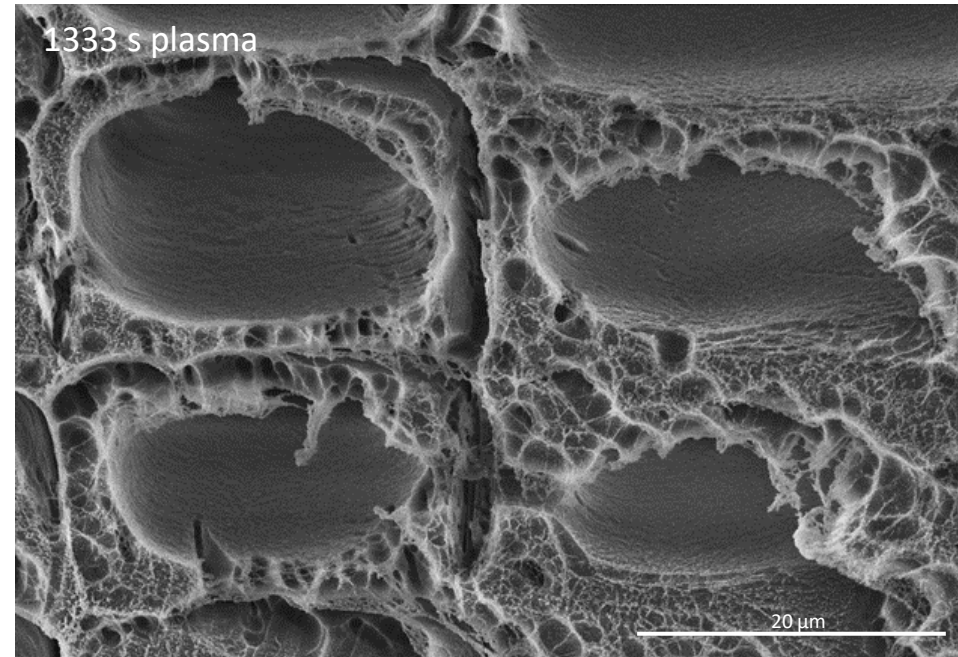
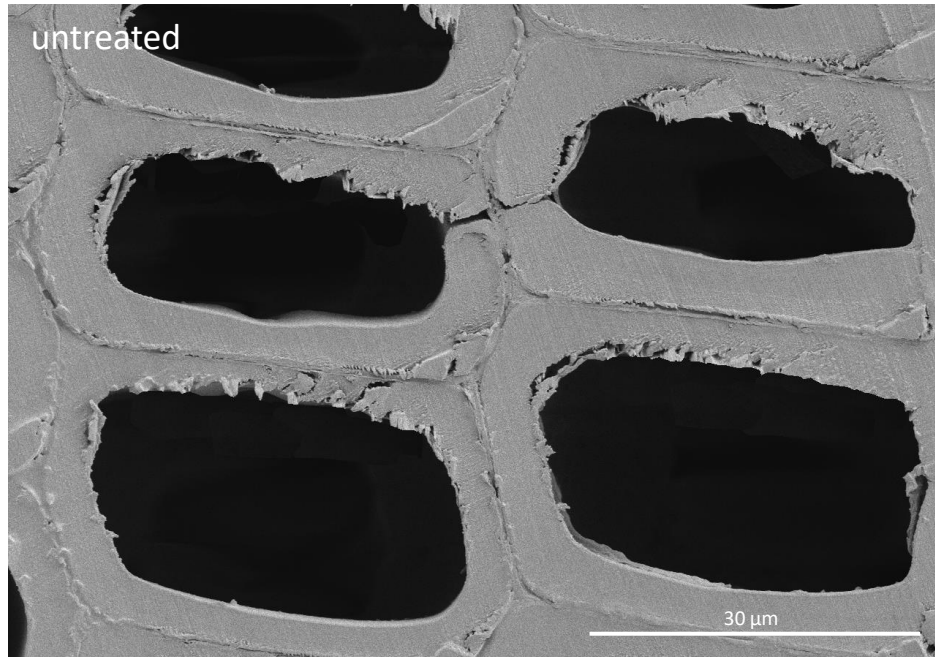
333 s plasma



667 s plasma



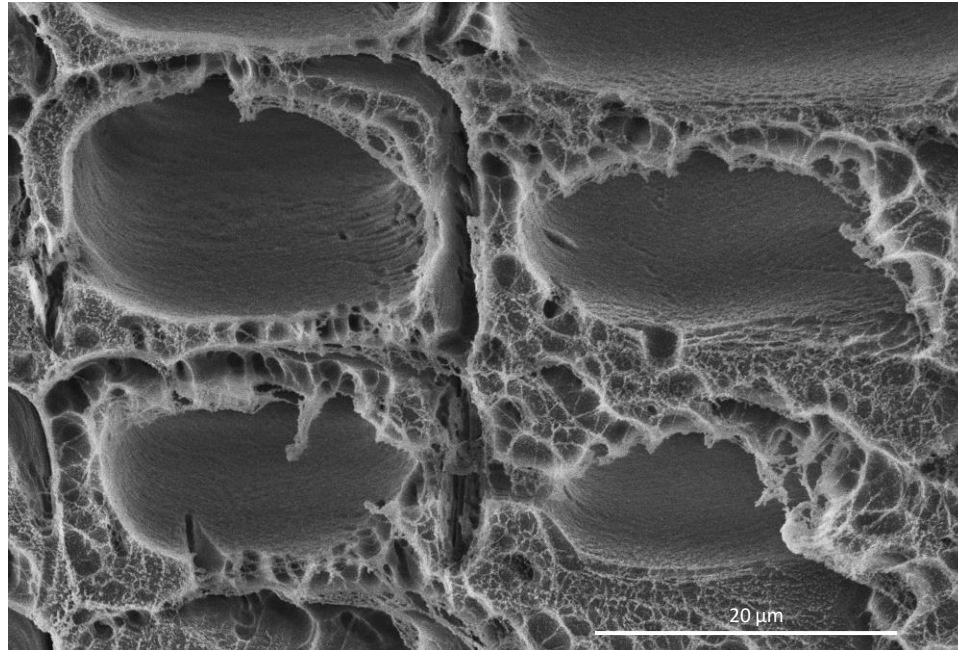
Differential Plasma Etching of Cell Wall Material



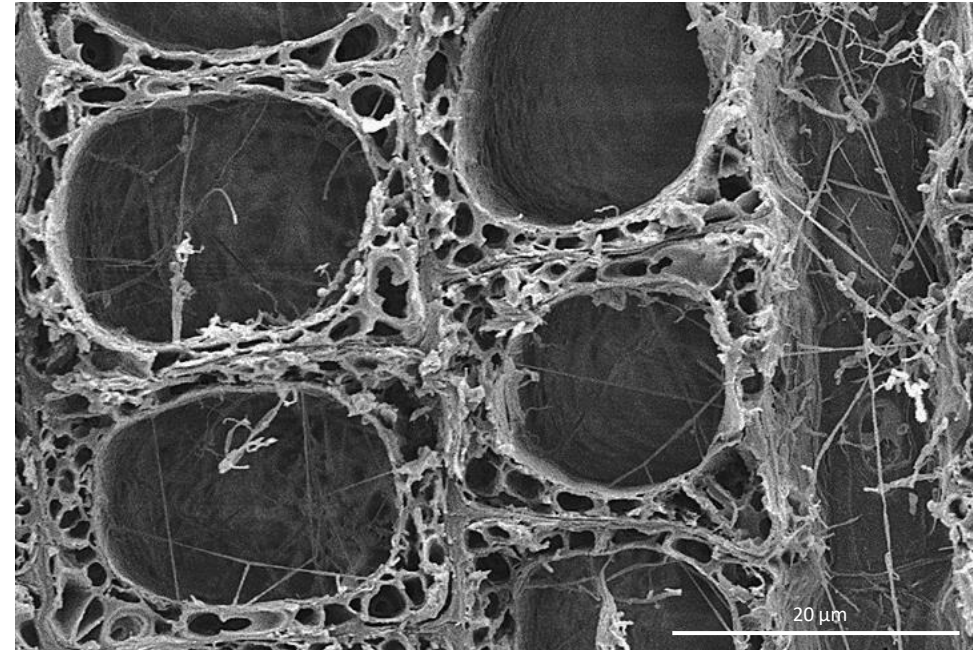
Transverse surfaces of latewood tracheids in redwood

Preferential Etching of Cell Wall Material

Plasma Treated wood



Soft-rot decayed wood

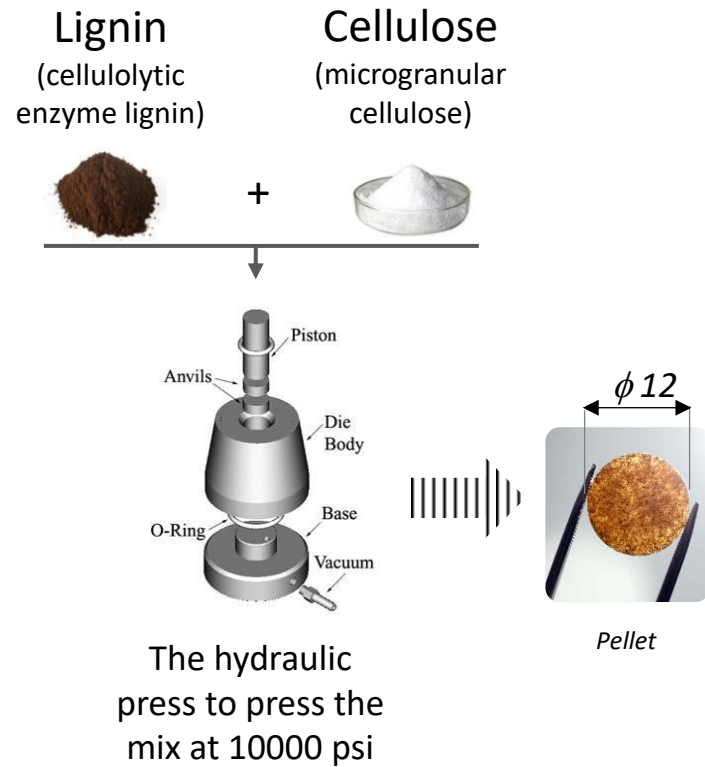


Transverse surface of redwood cell walls

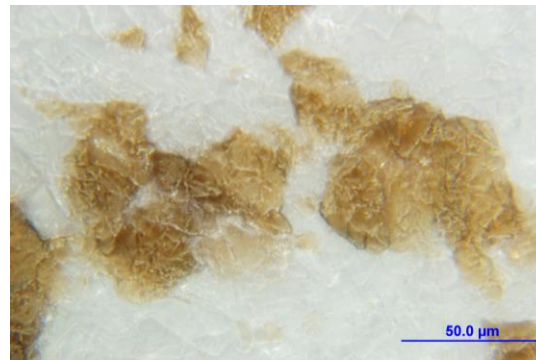
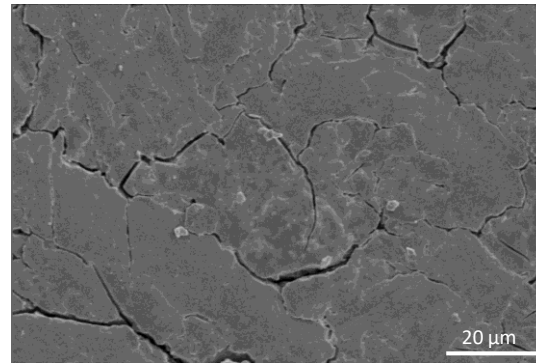


Degradation of cell-wall carbohydrates and cavity formation by brown-rot and soft-rot in wood

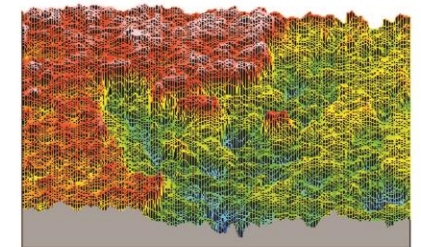
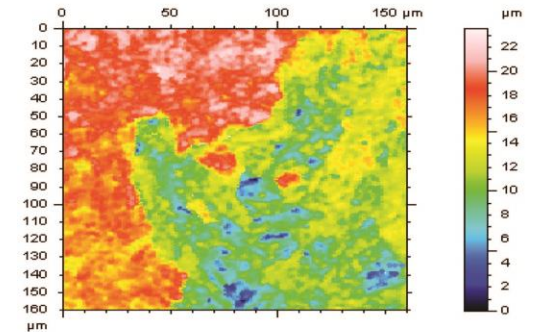
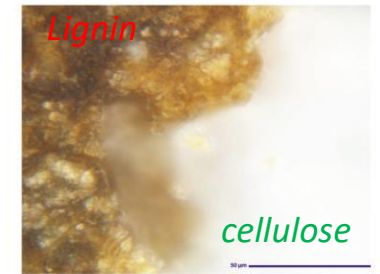
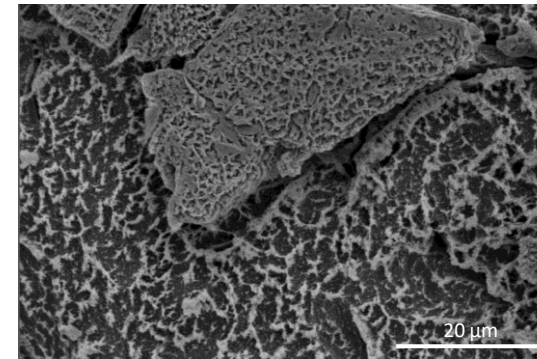
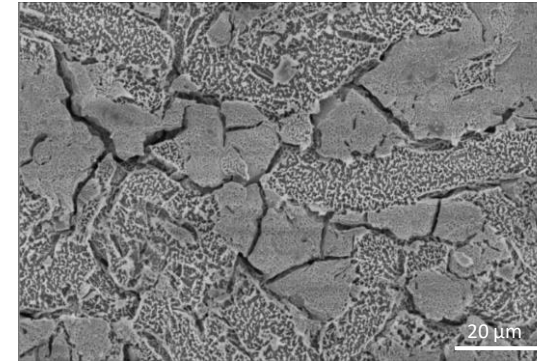
Differential Etching of Cellulose/Lignin Pellets



untreated

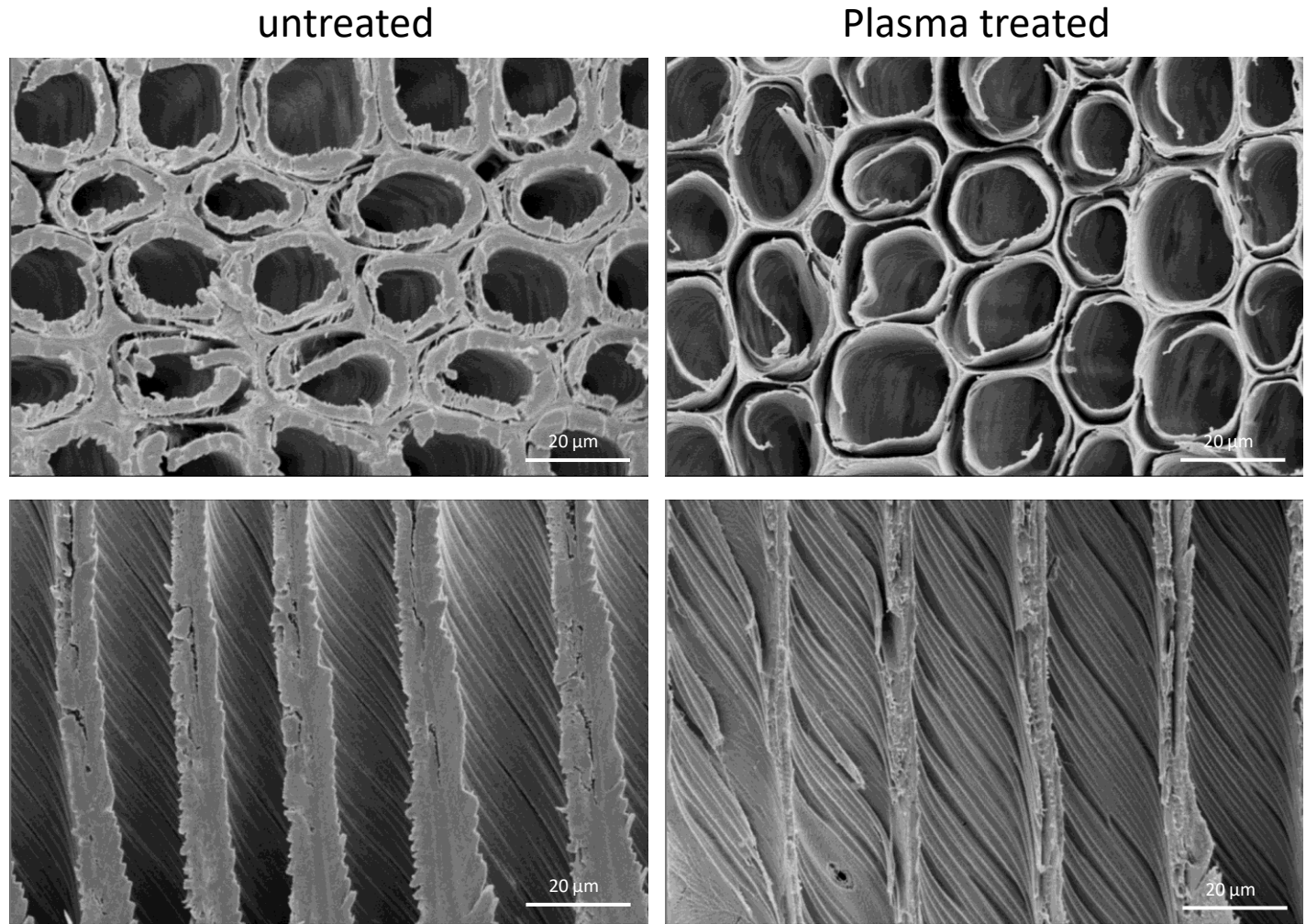
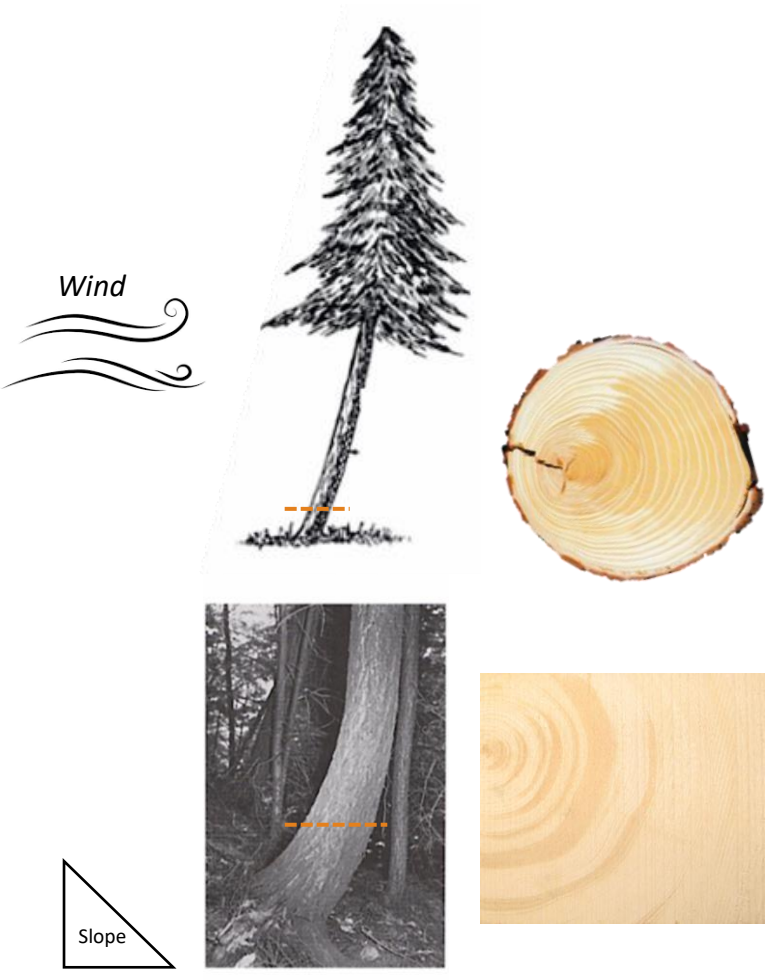


Plasma treated



SEM and reflected light microscopy images with Topographical maps of pellets revealing micro-roughening of the surface by differential plasma etching (1333s) of cellulose and lignin

Resistance of Lignin to Plasma Etching



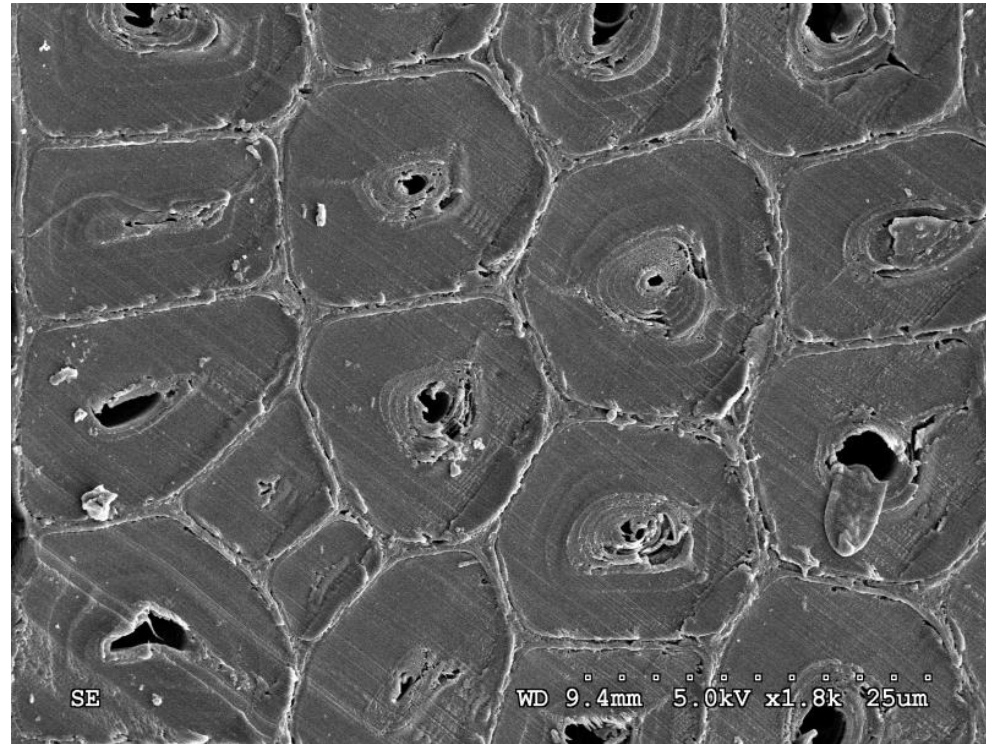
Transverse and radial surfaces of compression wood tracheids in the earlywood of yellow cedar

Resistance of Lignin to Plasma Etching

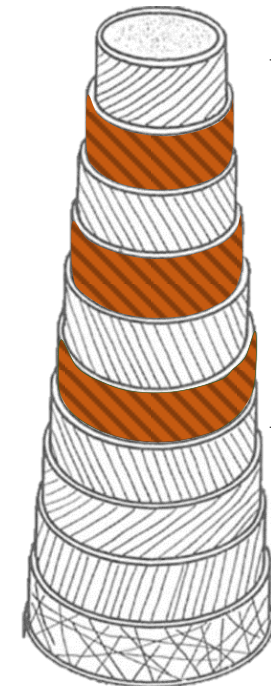


Homalium

Homalium foetidum (Roxb.) Benth.

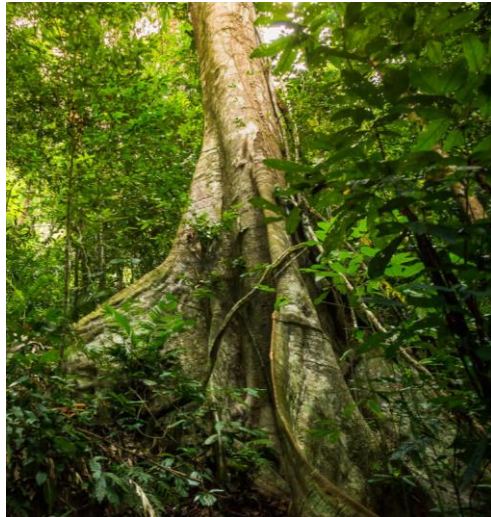


SEM images of the transverse surfaces of late wood fibers and differential etching of multi-lamellar S2 layer



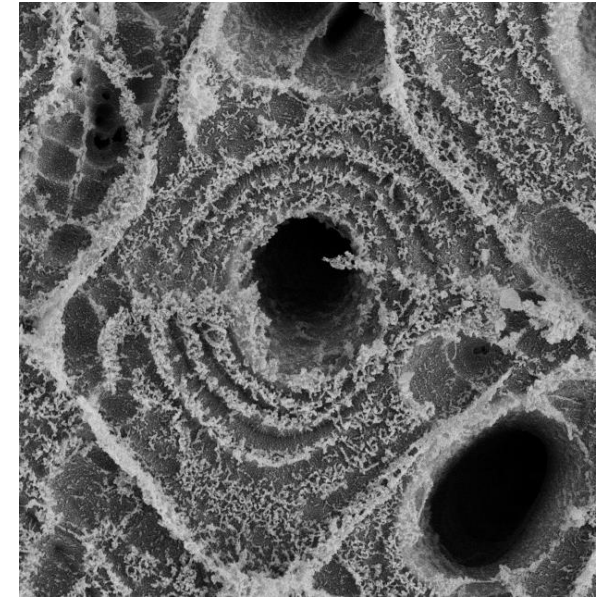
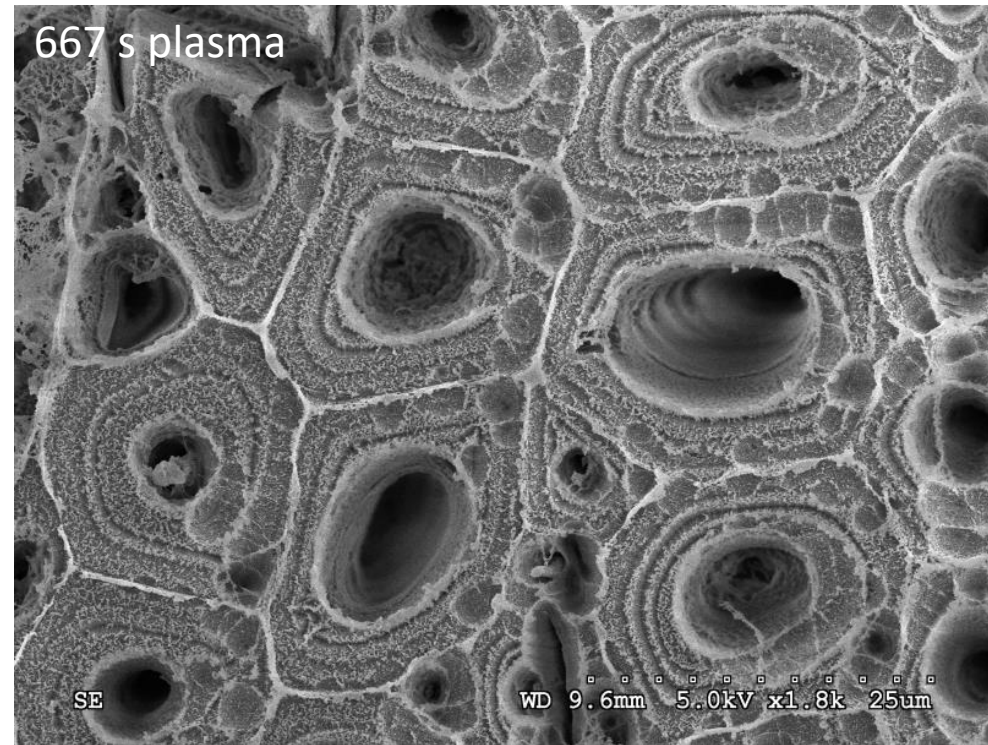
S2
multi-lamellar wall:
consisting of highly lignified thin lamellae

Resistance of Lignin to Plasma Etching



Homalium

Homalium foetidun (Roxb.) Benth.

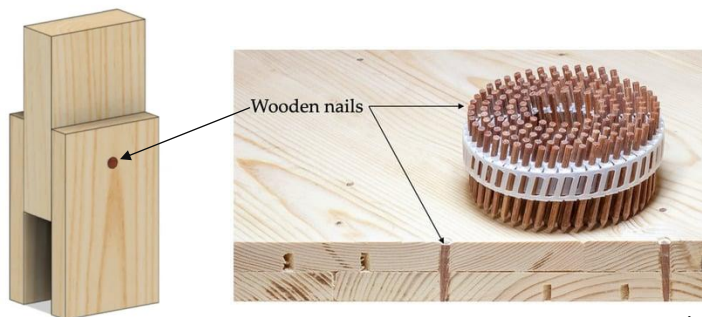
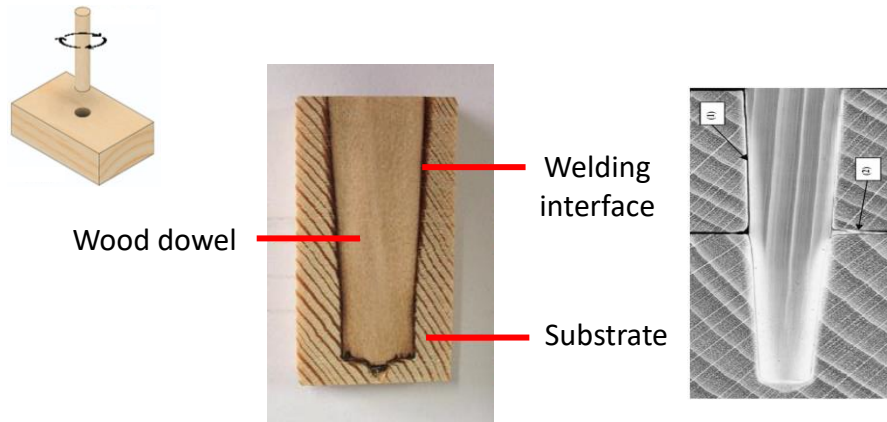


SEM images of the transverse surfaces of late wood fibers and differential etching of multi-lamellar S2 layer

Potential Applications of Preferential Plasma Etching

WOOD INDUSTRY

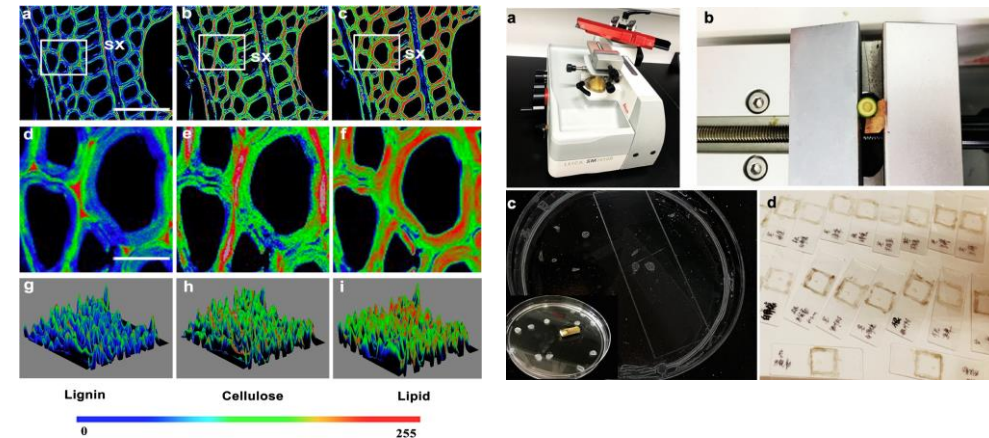
- *welding and self-bonding of wood particles and veneers*



Han et al. (2023), *Forests*, 14(2)

BIOTECHNOLOGY

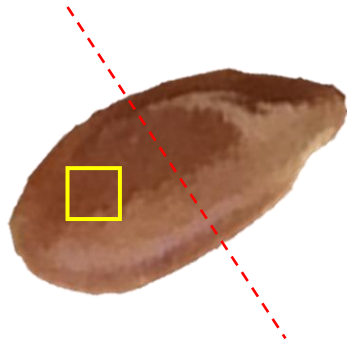
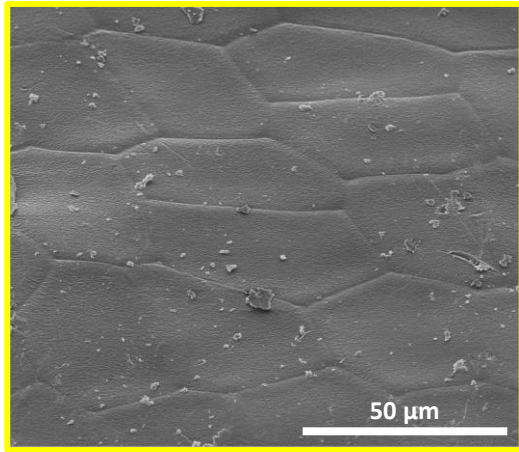
- *Characterization of the cell wall ultrastructure in transformants*
- *Screening of mutants:*
 - *Increased/decreased lignin deposition*
 - *Ectopic lignification*
 - *Altered lignification pattern within cell walls*



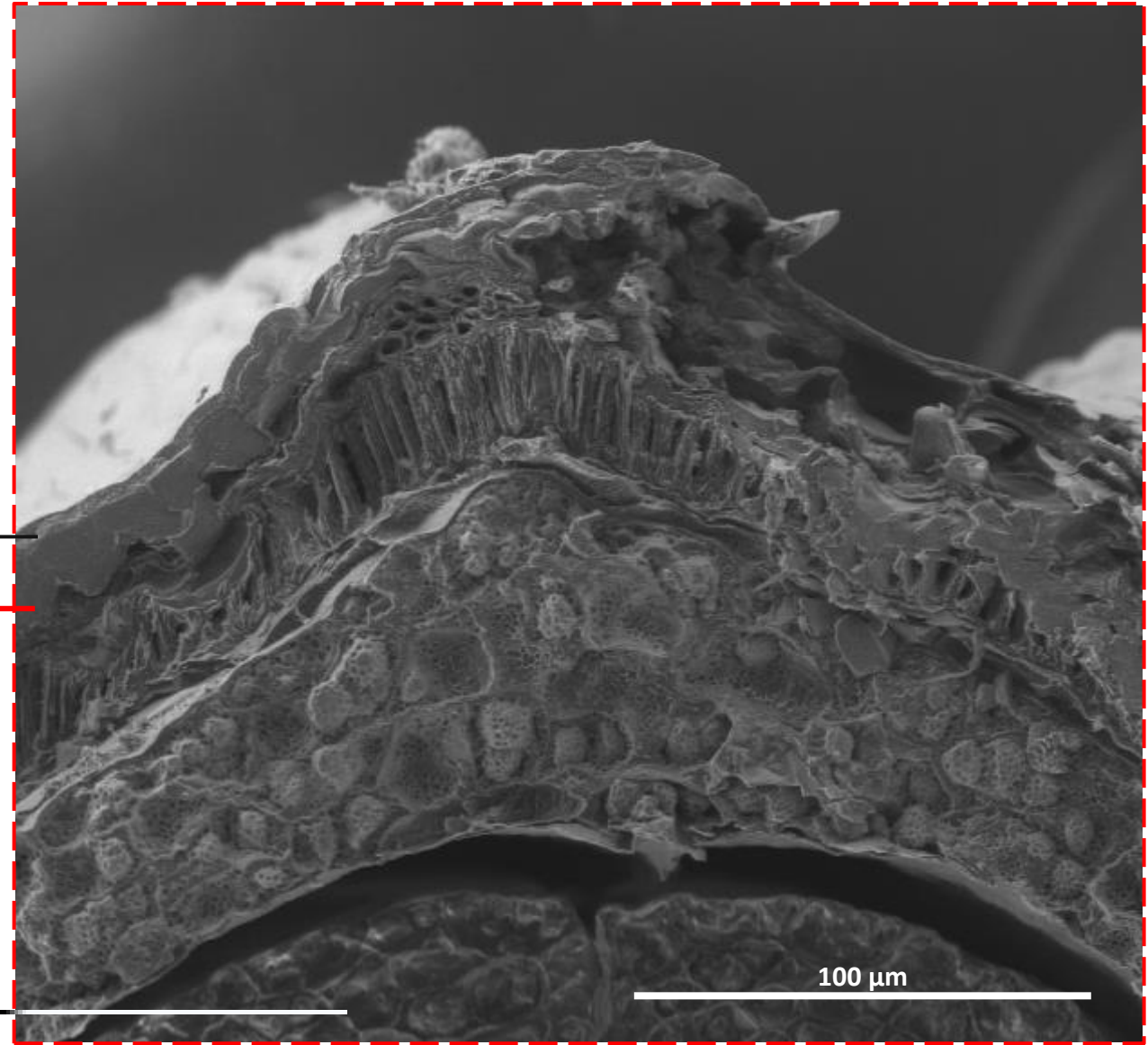
Xu et al. (2021), *Plant Methods Forests*, 17(29)

Cells in Flax Seed Coat

Surface



Transverse section



cuticle

Epidermal cells containing mucilage

Parenchyme

Sclerite layer

Membraniform layer

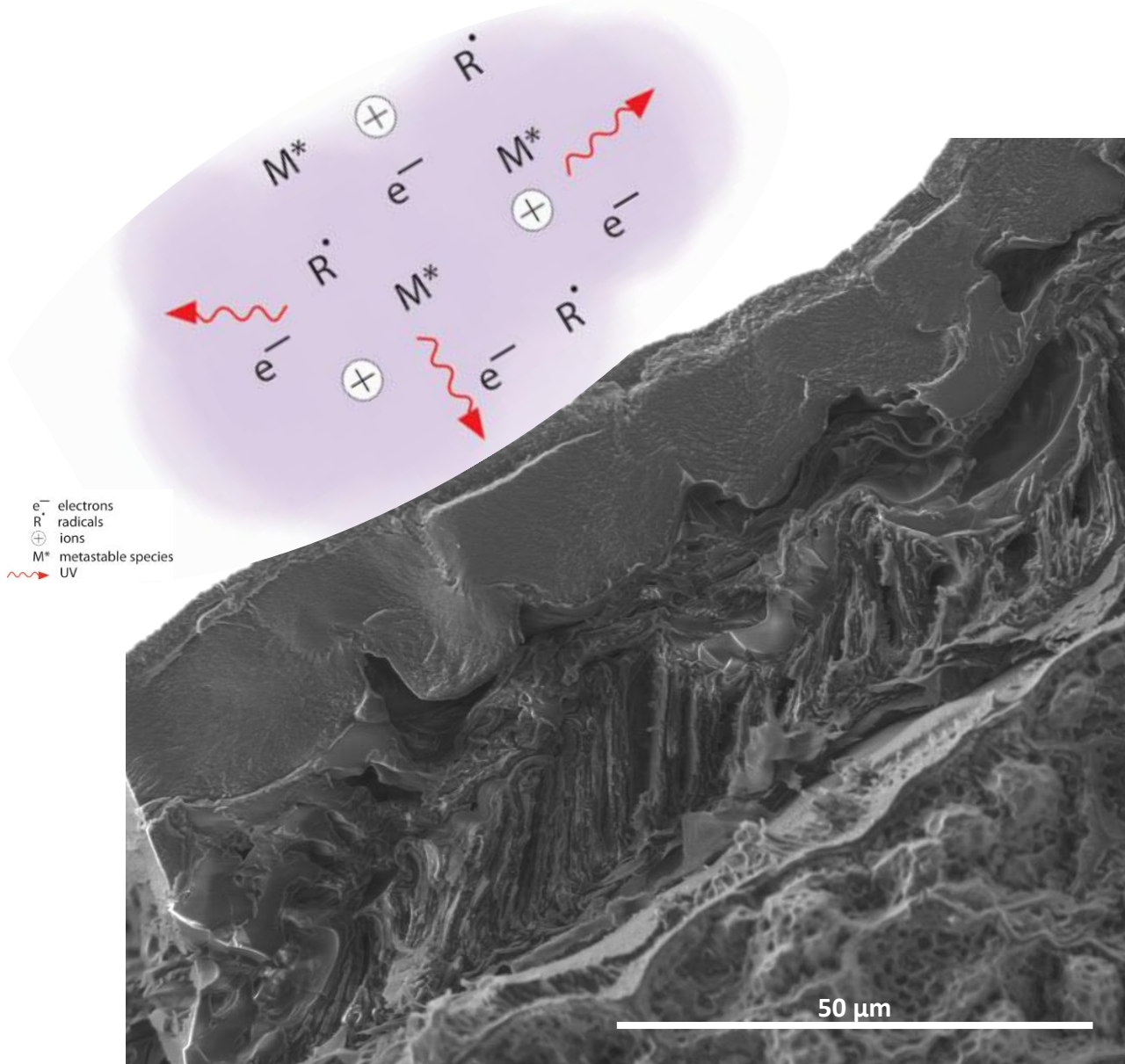
Brown layer

Endosperm

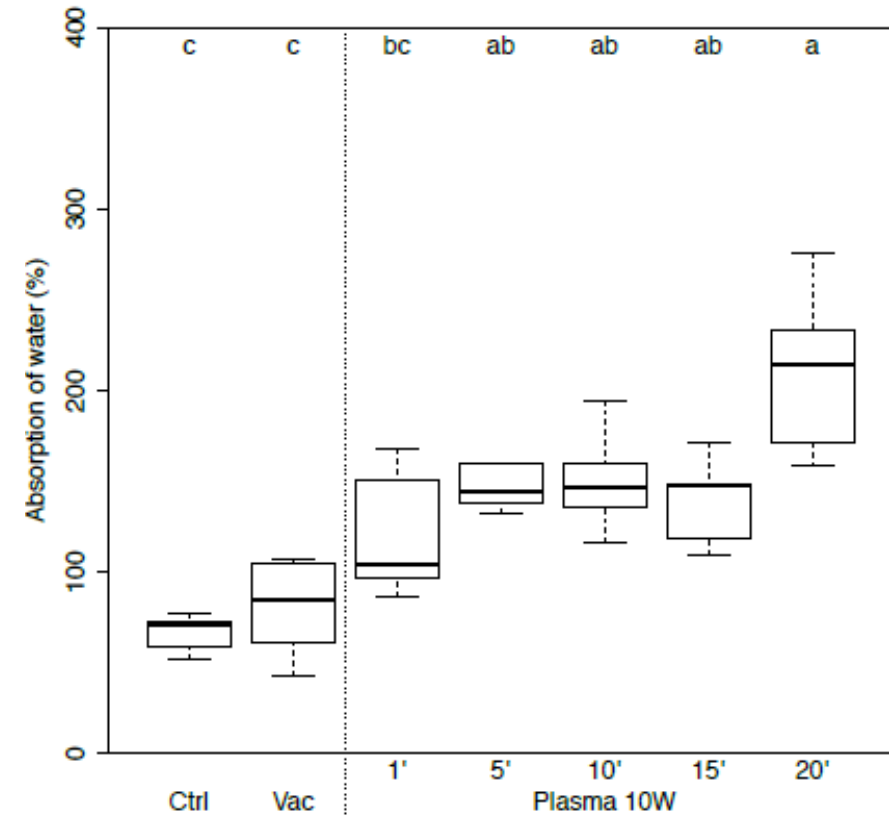
Cotyledons

Cross-section of a flaxseed (Image: LV / 1torr / 5kV)

Plasma Treatment and Water Absorption of Seeds

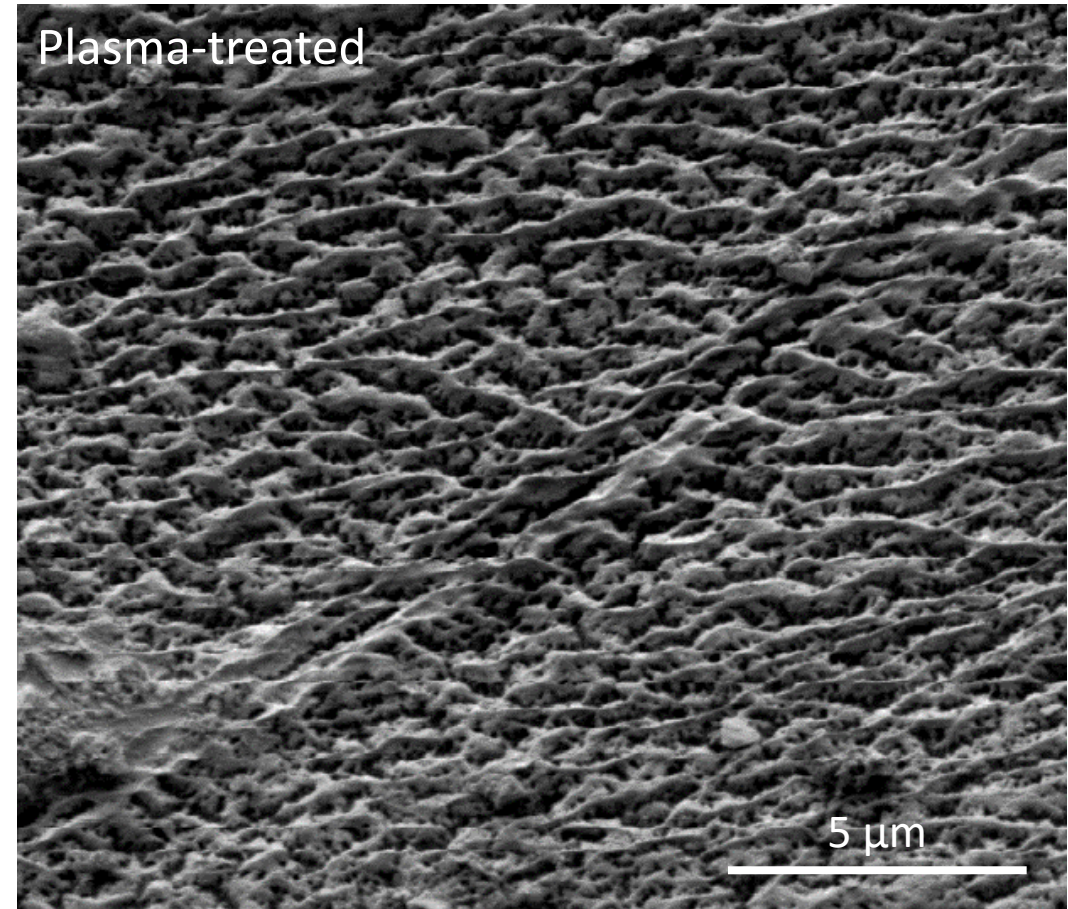
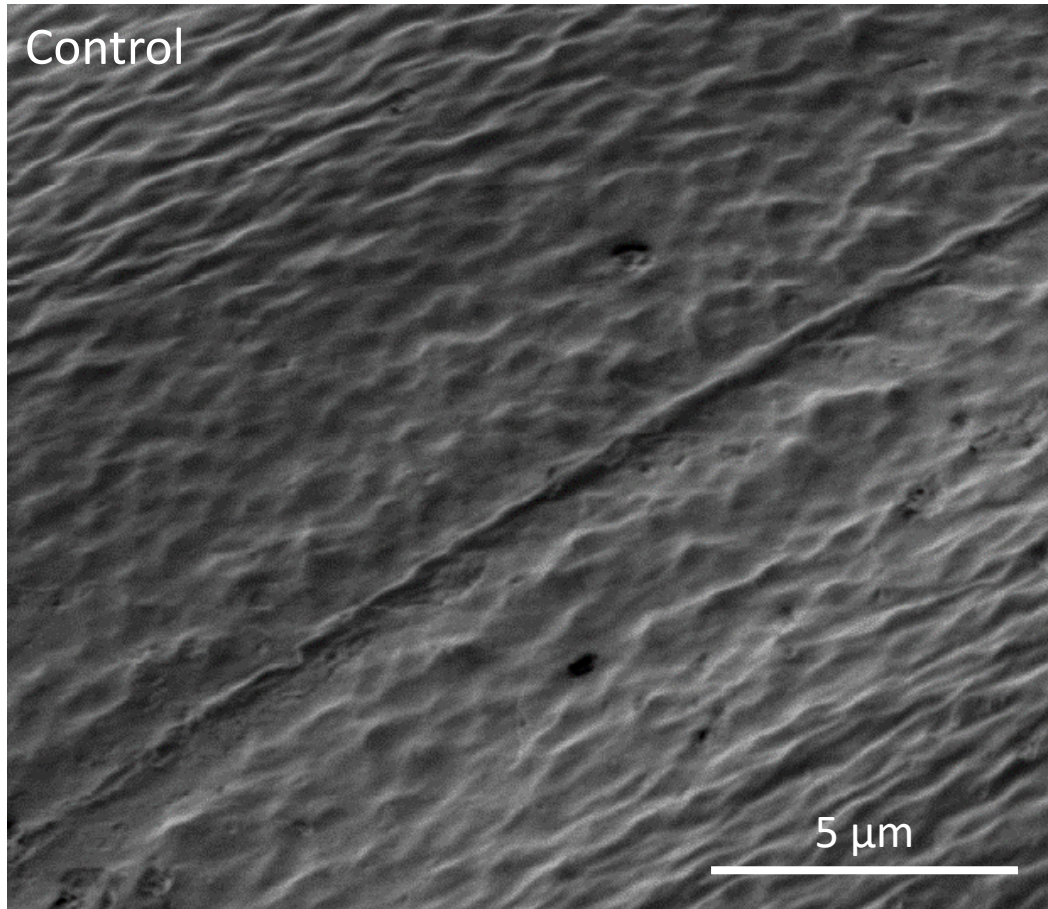


Cross-section view of a flaxseed



Absorption of water by seeds after 15 minutes of imbibition

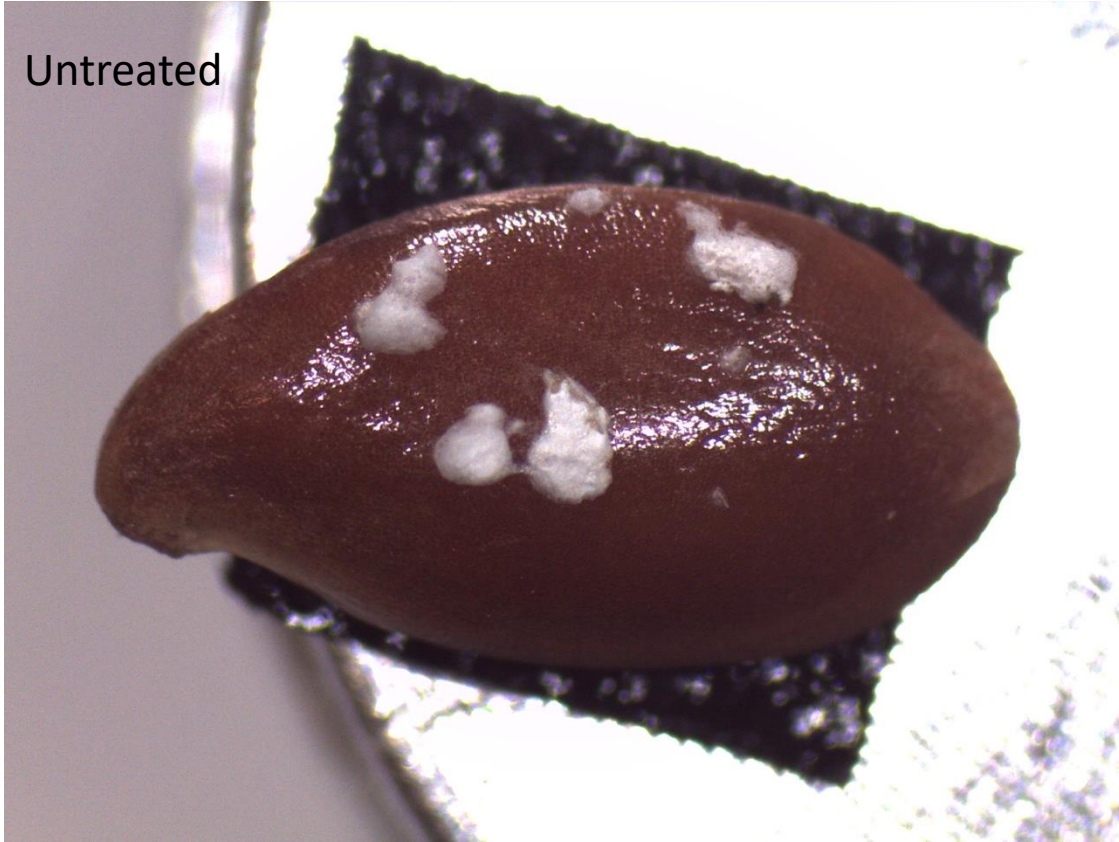
Effect of Plasma Treatment on Flaxseed Surfaces



Surface of flaxseed: mucilage secretory cells and the junction between their outer cell walls (*image: Hi.Vac. / 2kV*)

Hydration of Flaxseeds

Untreated



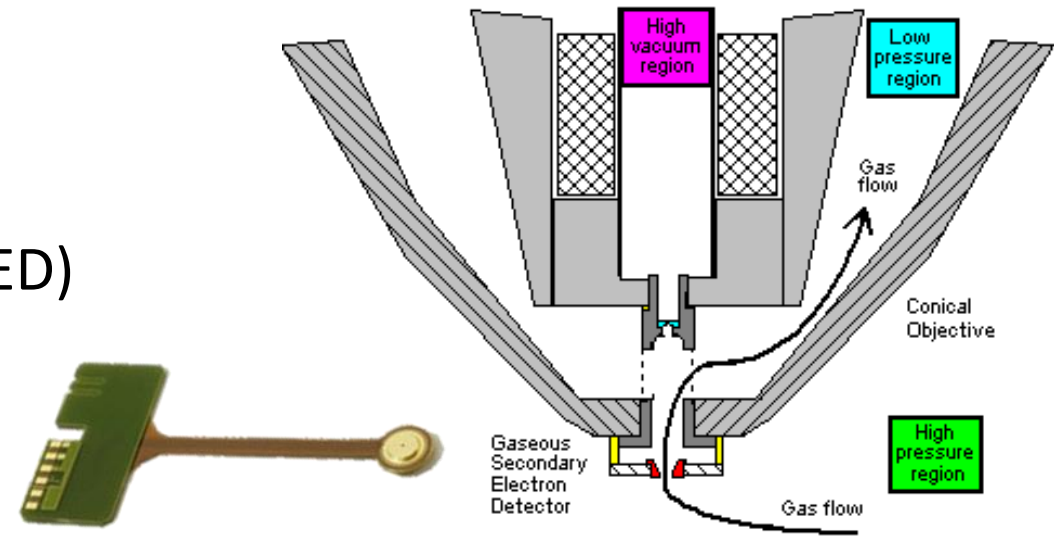
Plasma treated (10W 20 min.)



Flax seed surfaces after deposition of water (20 μ L) and observation in Low Vac. mode

Quanta 200 FEG

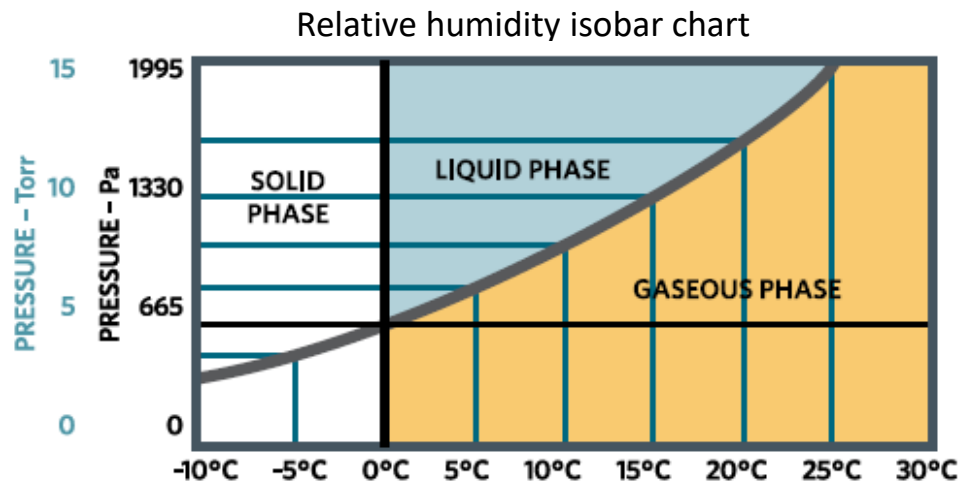
- Gaseous Secondary Electron Detector (GSED)
- High specimen chamber pressure
<20 Torr (2700 Pa) for H₂O
- Controlled relative humidity
Variation in temperature/pressure



(FEI Company/Thermo Fisher Scientific)

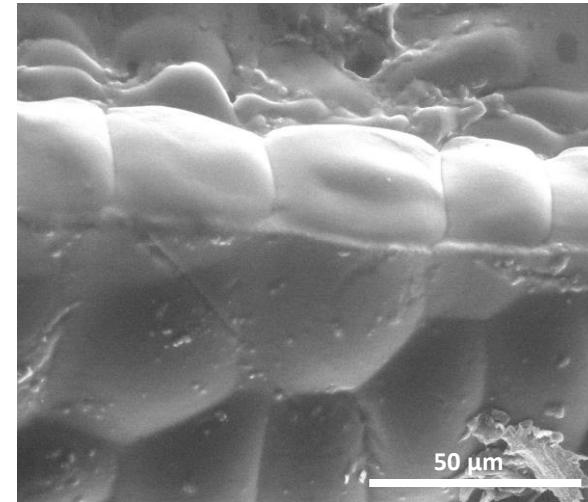
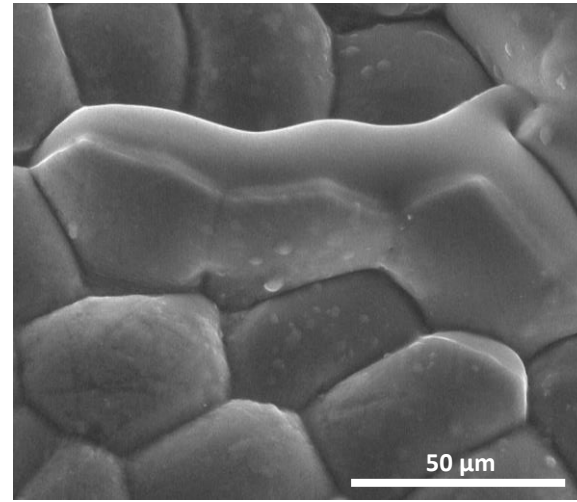
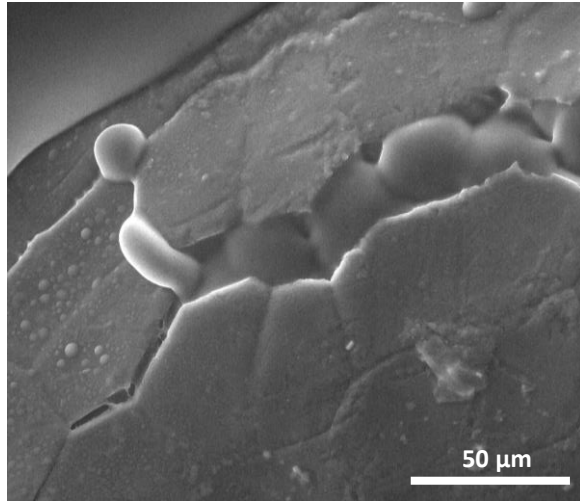


Thermo-electric Peltier Module

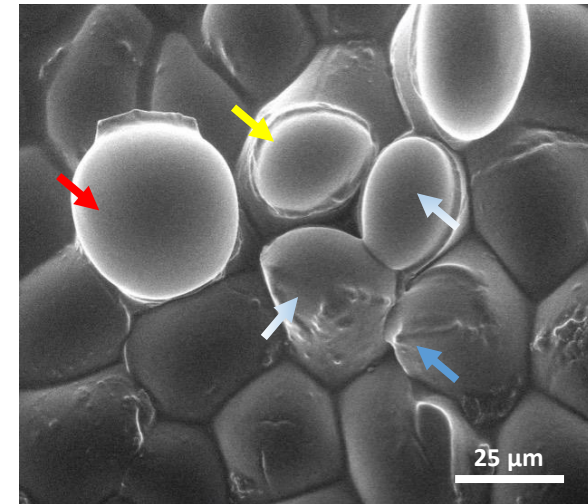
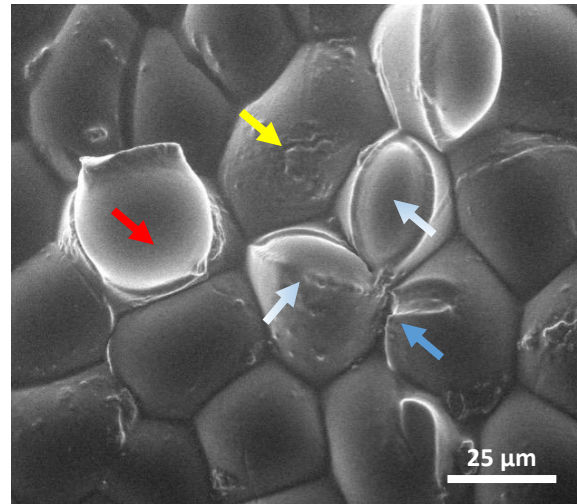
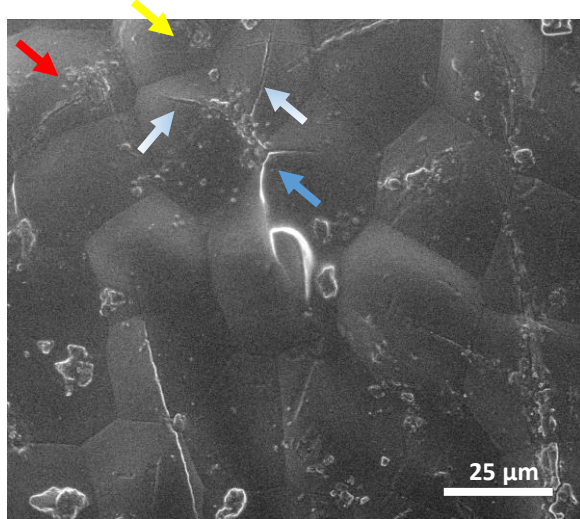


In Situ Hydration of Flaxseeds in “ESEM”

Untreated
(Hard epidermal walls)



Plasma treated
(Soft epidermal walls)



Rupture of the cell walls of the seed coat of a flaxseed and release of the mucilage by varying the relative humidity from 75% to 90%.

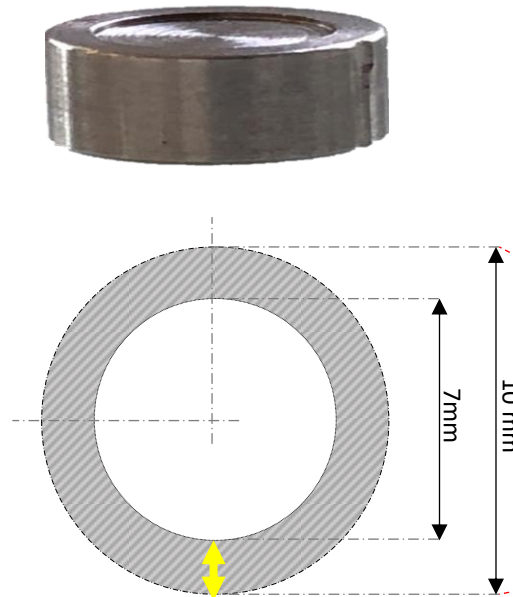
Standard Cooling Stage (Peltier/Seebeck) of the ESEM



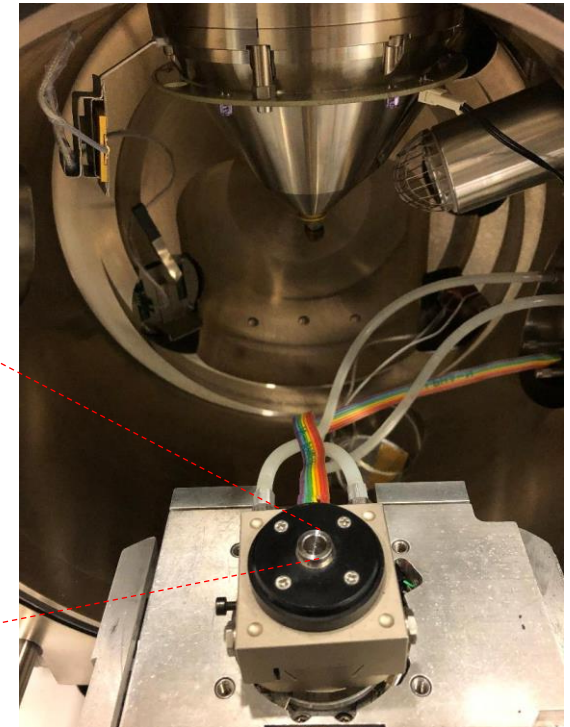
4-days-old
flax plantlets



a flaxseed



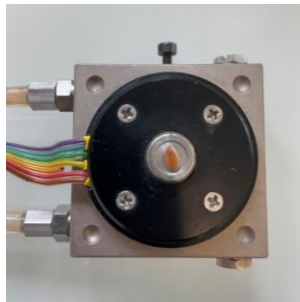
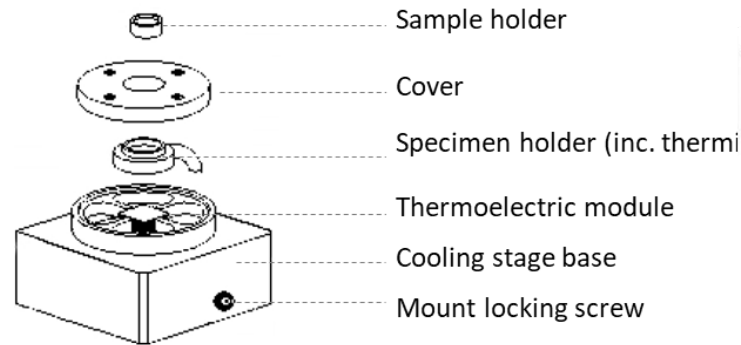
Cooling stage Specimen Stubs



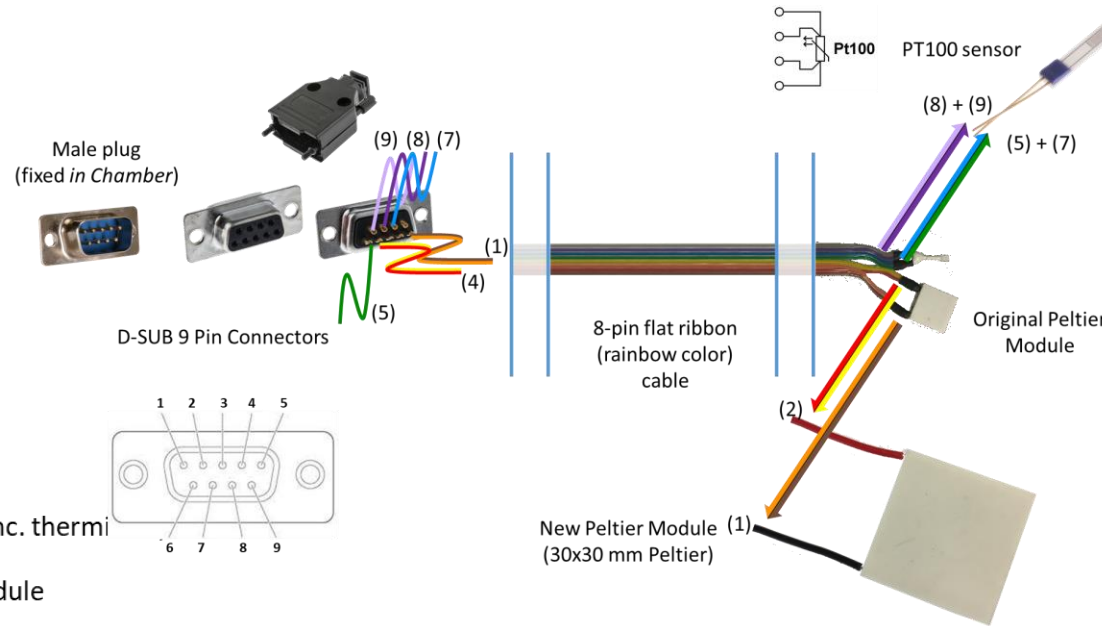
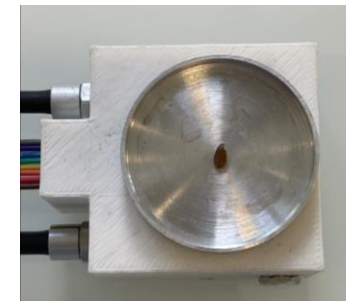
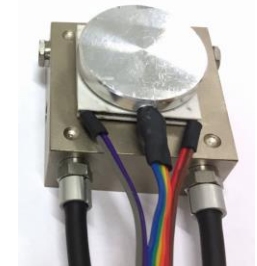
Standard cooling stage
module of the ESEM

Modification of the Standard Cooling Stage (Peltier/Seebeck)

0.8 cm²
stub surface



5 cm²
stub surface



Specification	Peltier device	
	Standard (FEI)	New
Tension	3,6V	15.4 V
Theoretical optimum current (Amp)	1,5A	3 A
delta T max (max.)	55 °C	65 °C
Length	10 mm	30 mm
Width	10 mm	30 mm
Height	1,5 mm	3.6 mm

“Bio-Chamber”



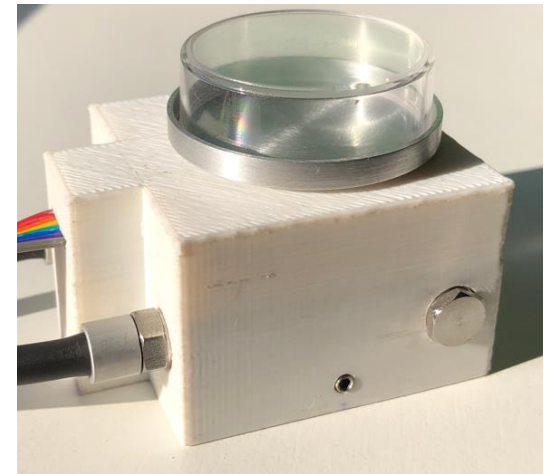
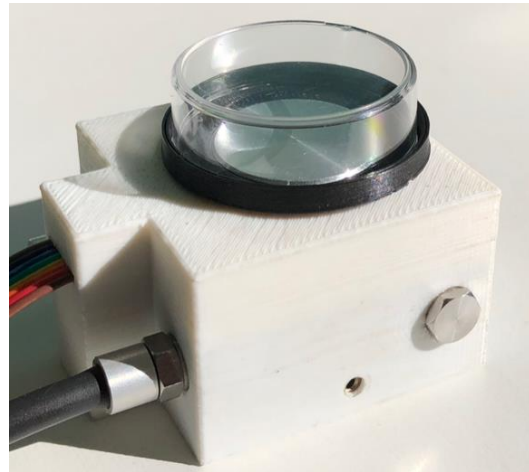
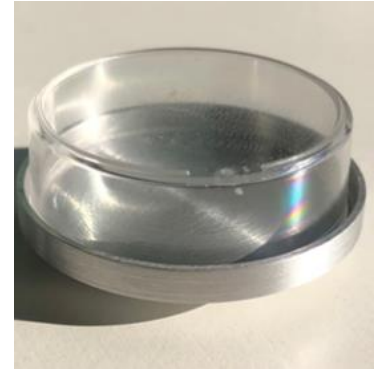
0.8 cm²



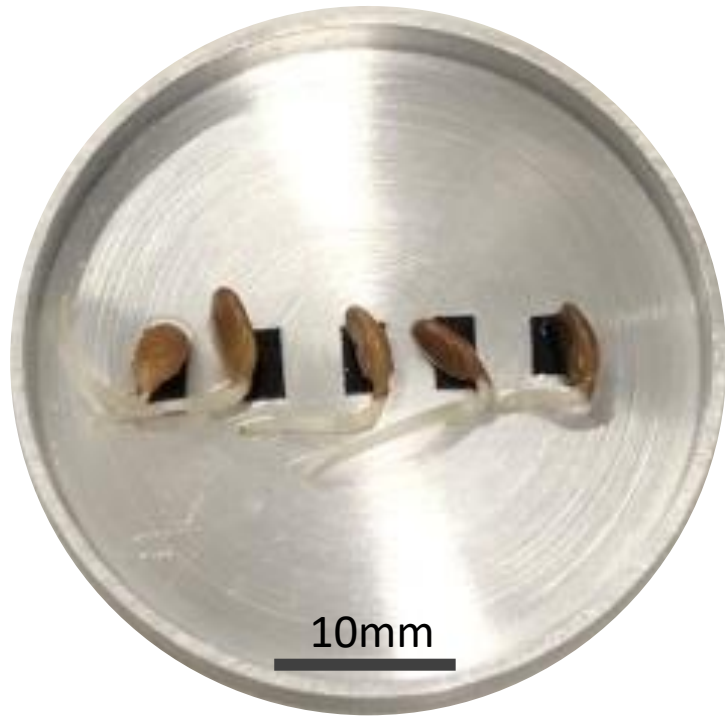
5 cm²



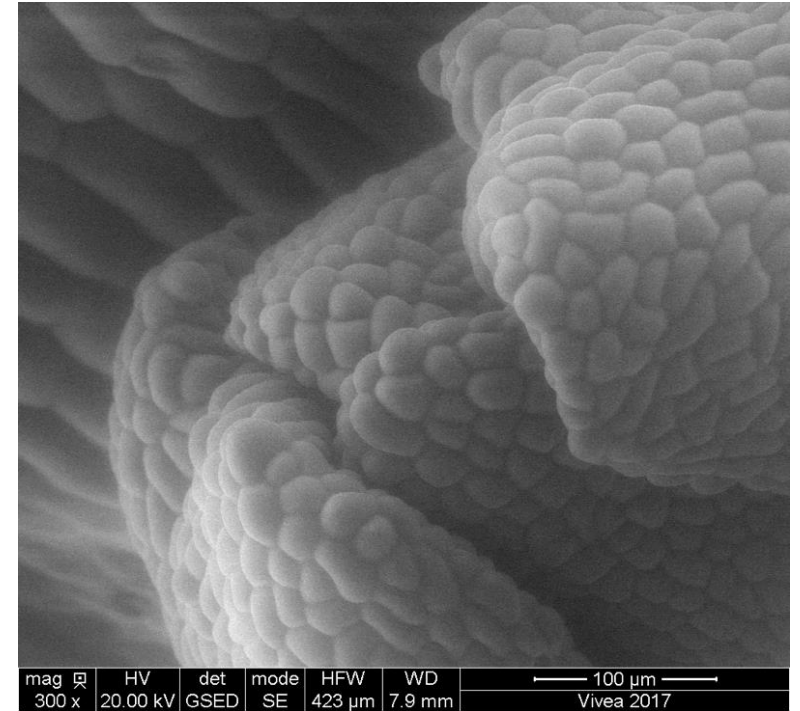
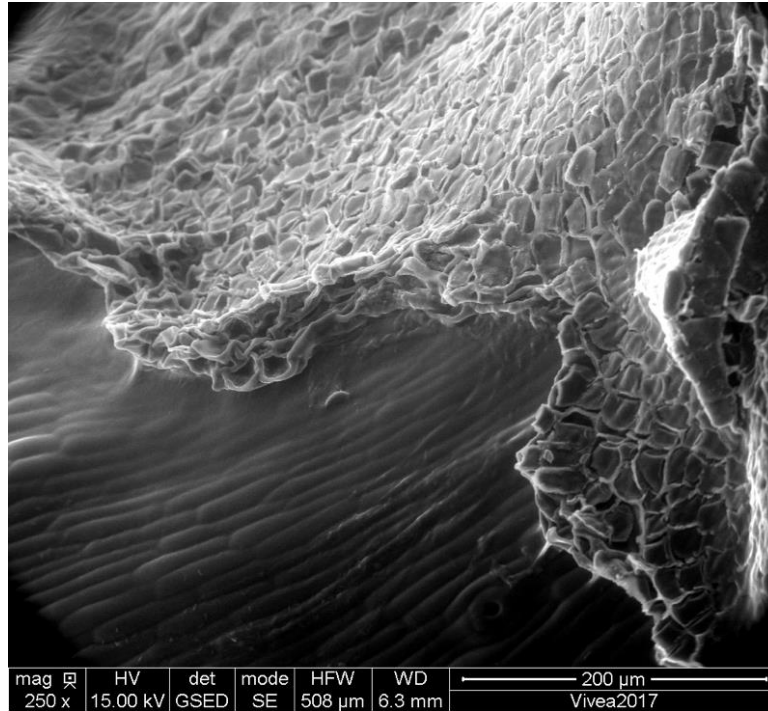
10 cm²



Seed Germination and Observation in “Bio-Chamber”



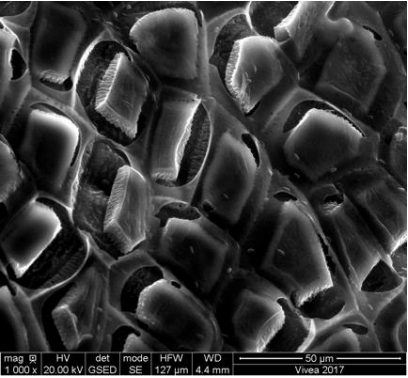
Day 2



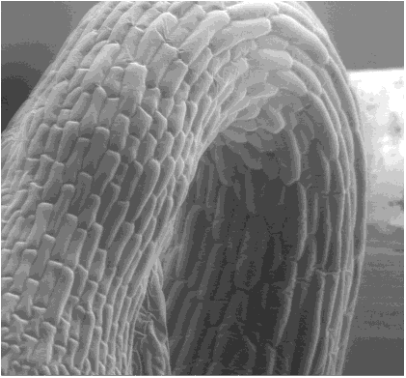
Observation of flaxseeds 2 days after germination in the « bio-chamber »
(image: 85% HR : 7T/8°C et 6 torr/6°C)

ESEM Observation of Seedling Growth

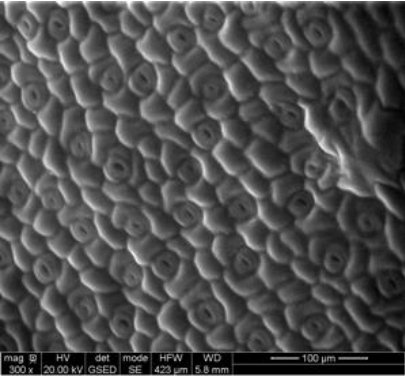
D5



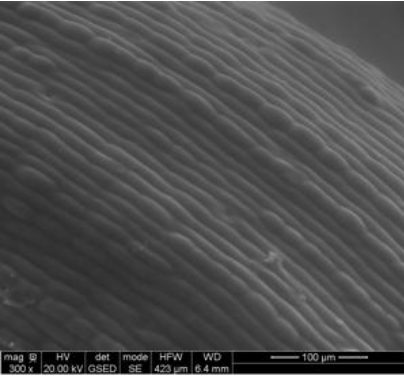
D6



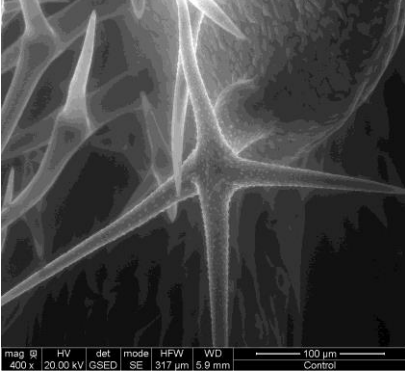
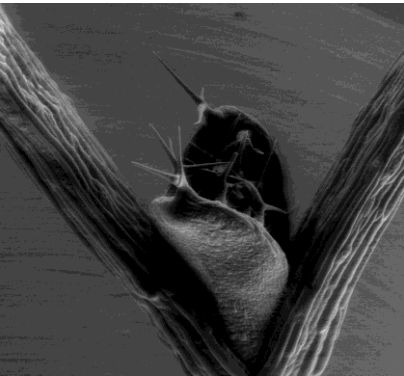
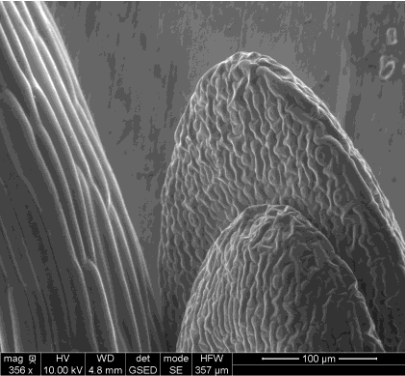
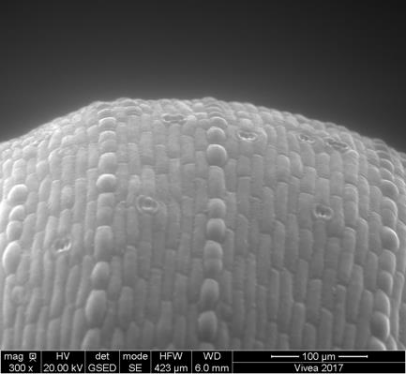
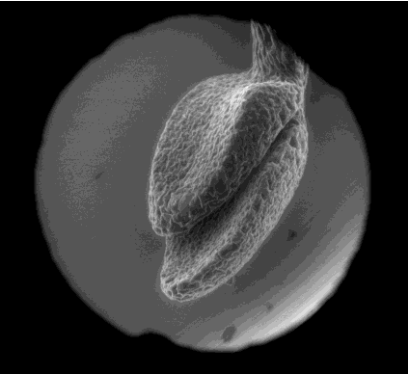
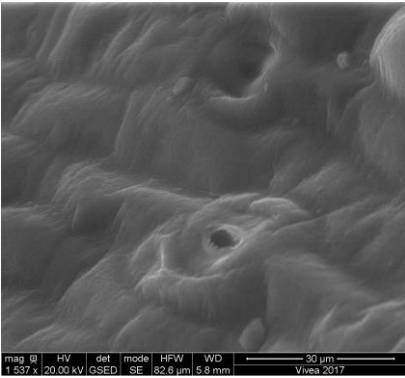
D7



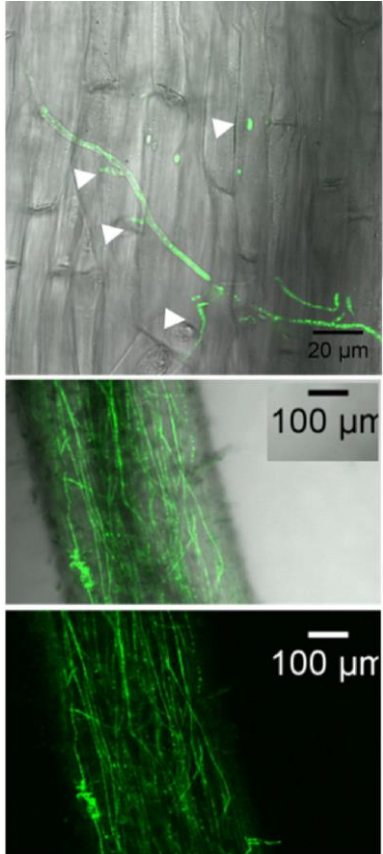
D8



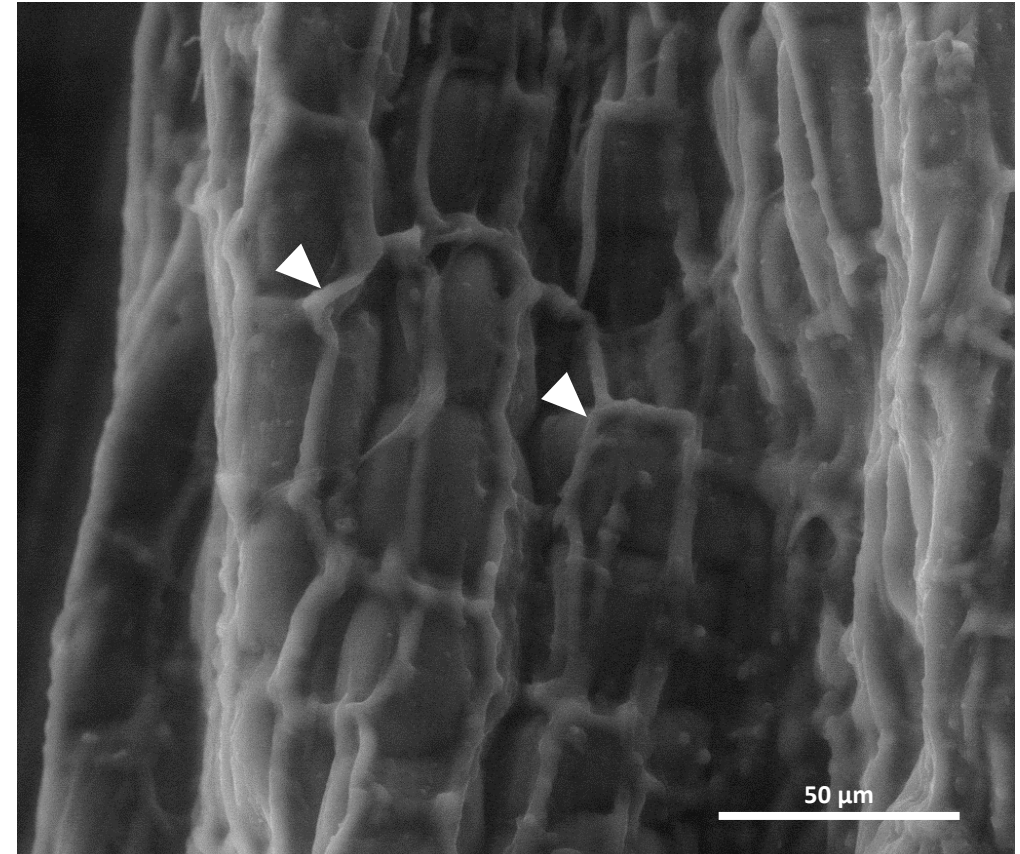
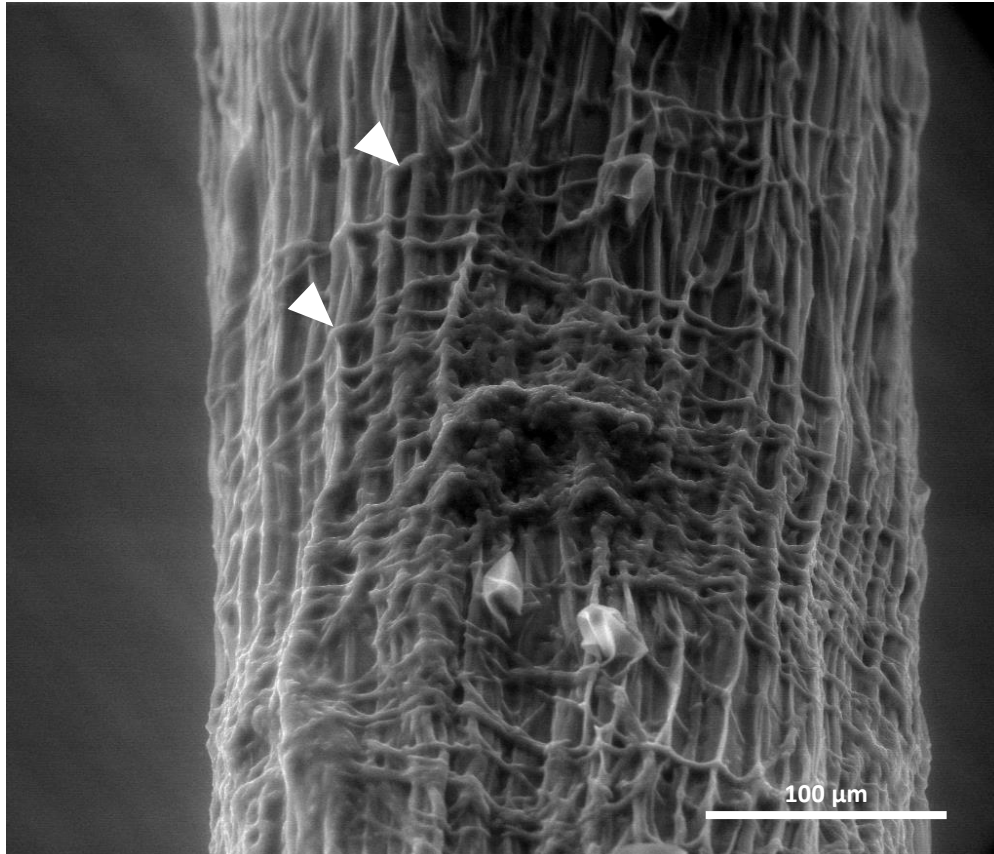
D9



Plant-Pathogen Interaction on the Surface

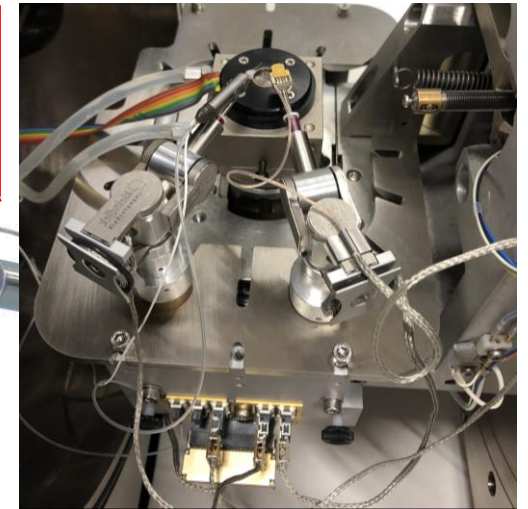
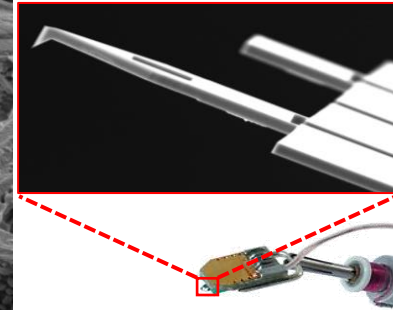
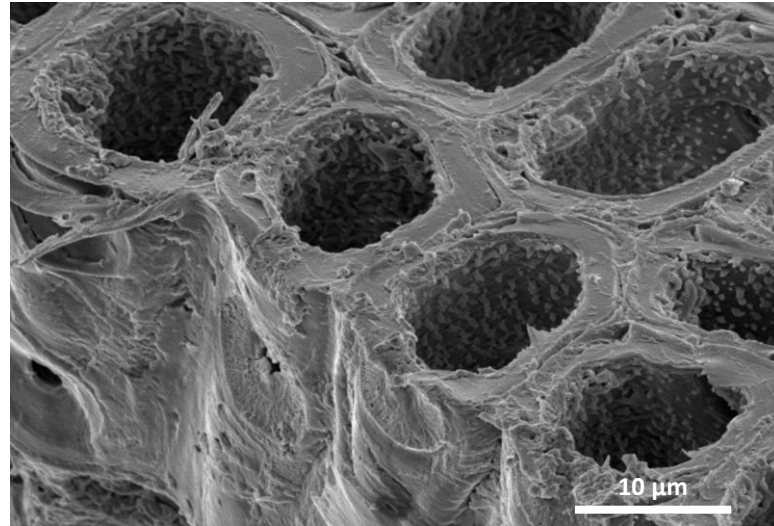
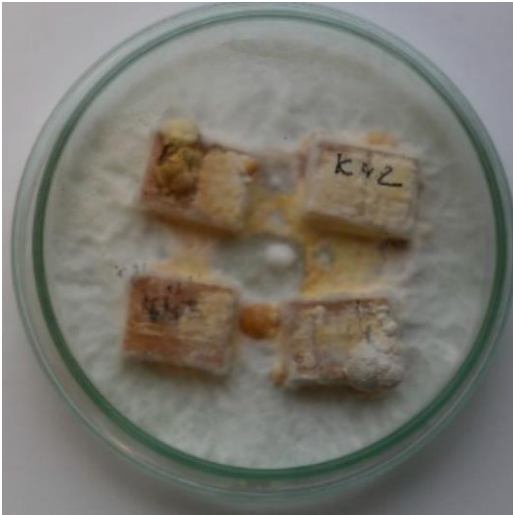


Brightfield /fluorescent images (Blum et al. 2018)

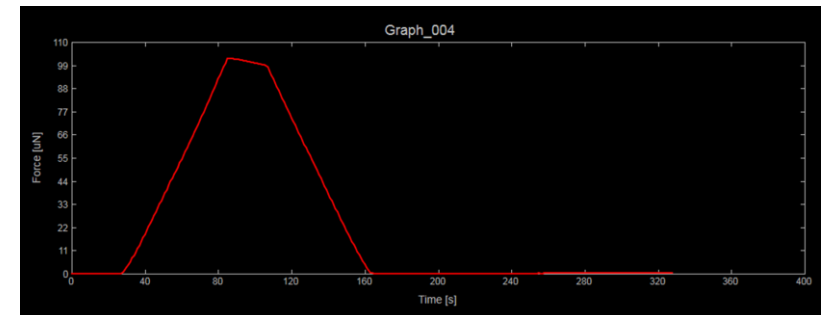
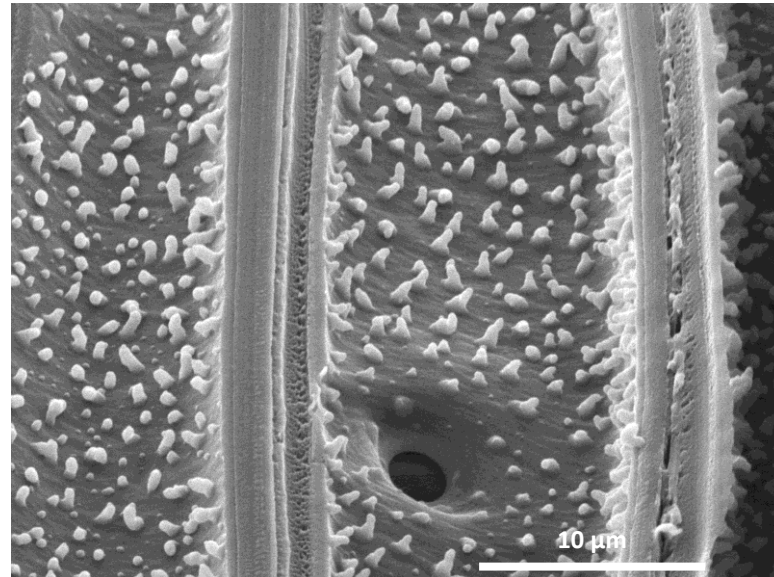
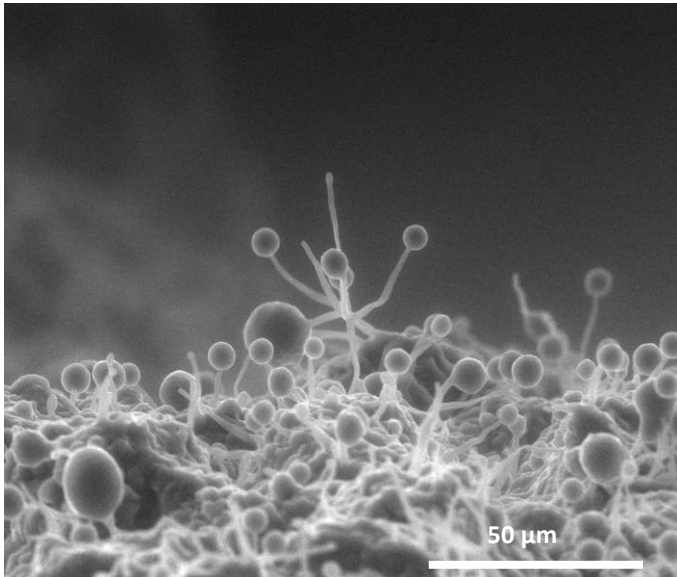


Immersion of flax plantlets in the inoculum of fungous *V. dahliae*:
Coverage of rhizodermal cells with fungal sheath 2hours after contact
(images:85% RH : 9 torr/18°C)

In situ Testing of Wood Decay



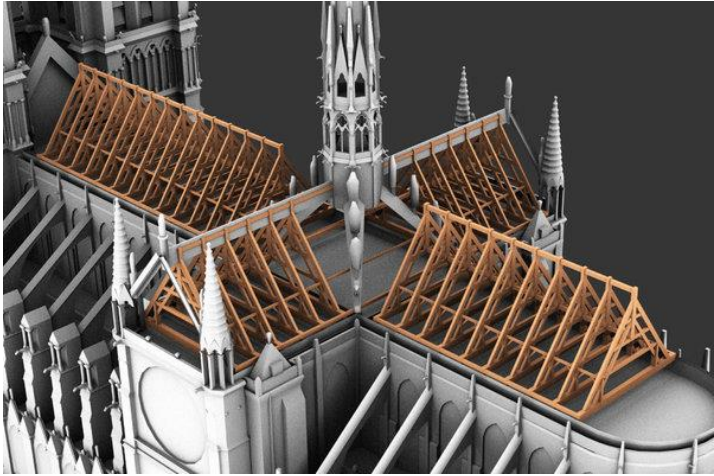
MM3A-EM: MIS-EM and FMS-EM
KleinDiek Nanotechnik



Fungal degradation of Wood in the culture medium and the ESEM images of mycelium of *Verticillium dahlia* (left), *Actinostrobos tracheids* (right)

Wood is Carrying on

Construction/restoration

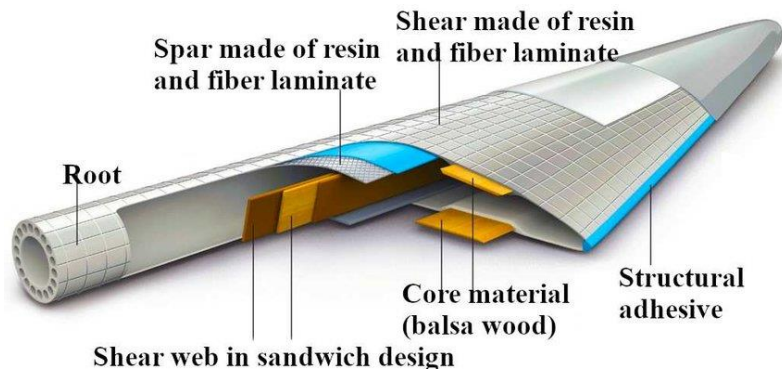


Wood is Carrying on

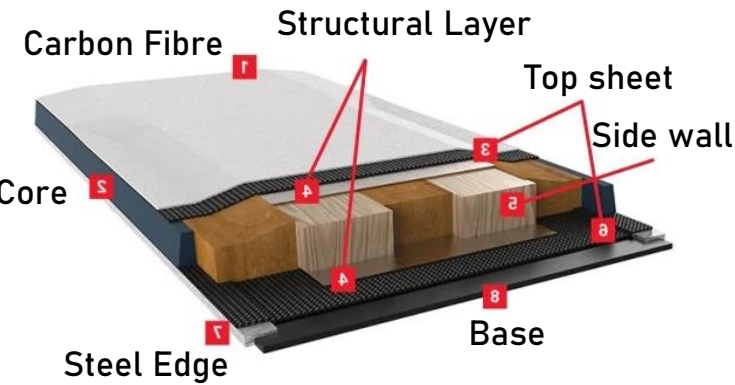
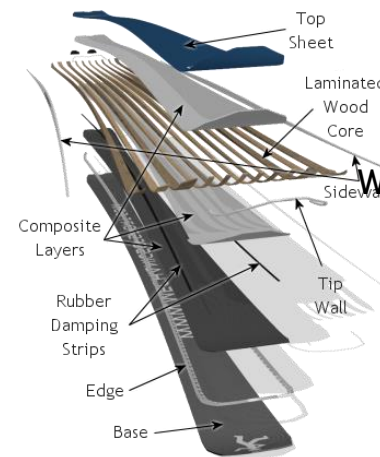
high-performance structural material



France's national team member (<https://olympics.com>)



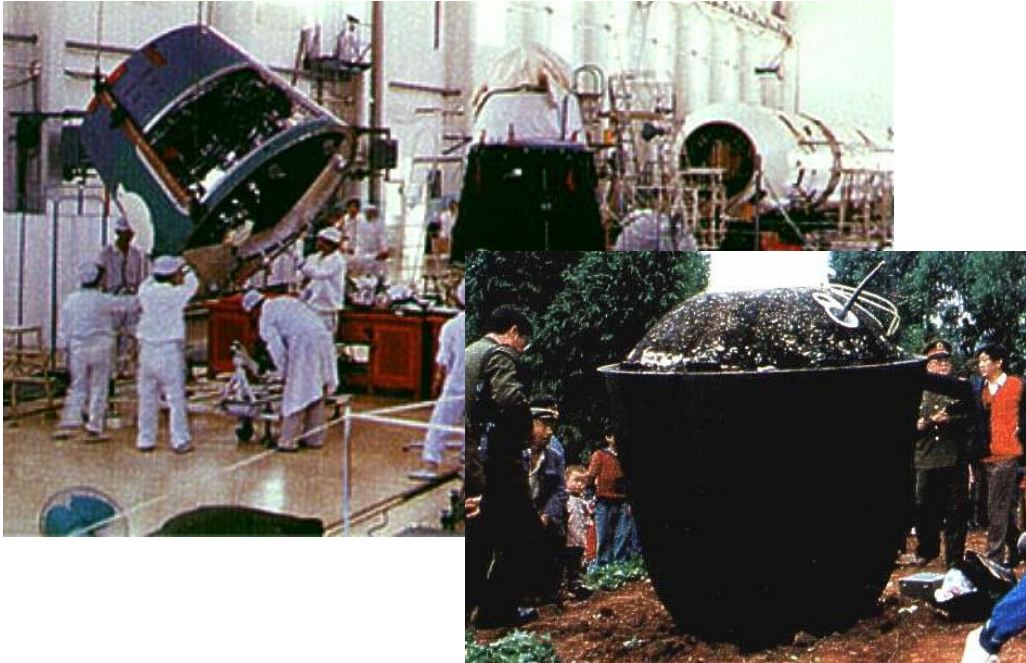
Oliveria et al. 2020



Wood is Carrying on

Wood in Space

1976:



*Chinese recoverable spacecraft
(FSW-02)*

2021:

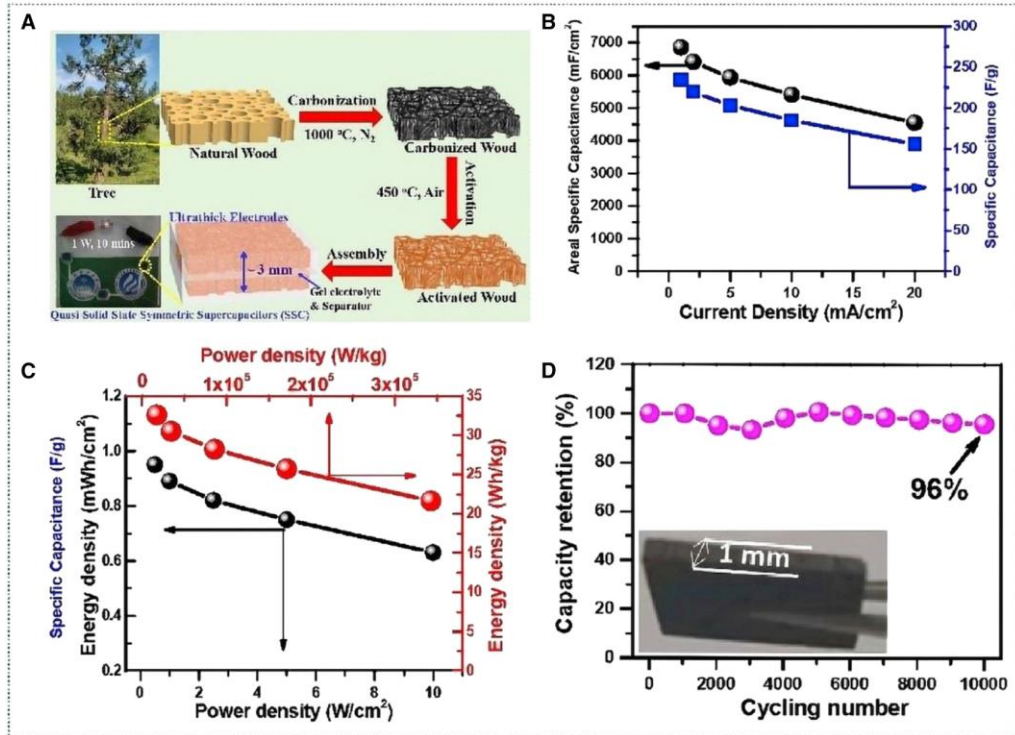


*Finnish WISA Woodsat
Supported by European space agency (ESA)*

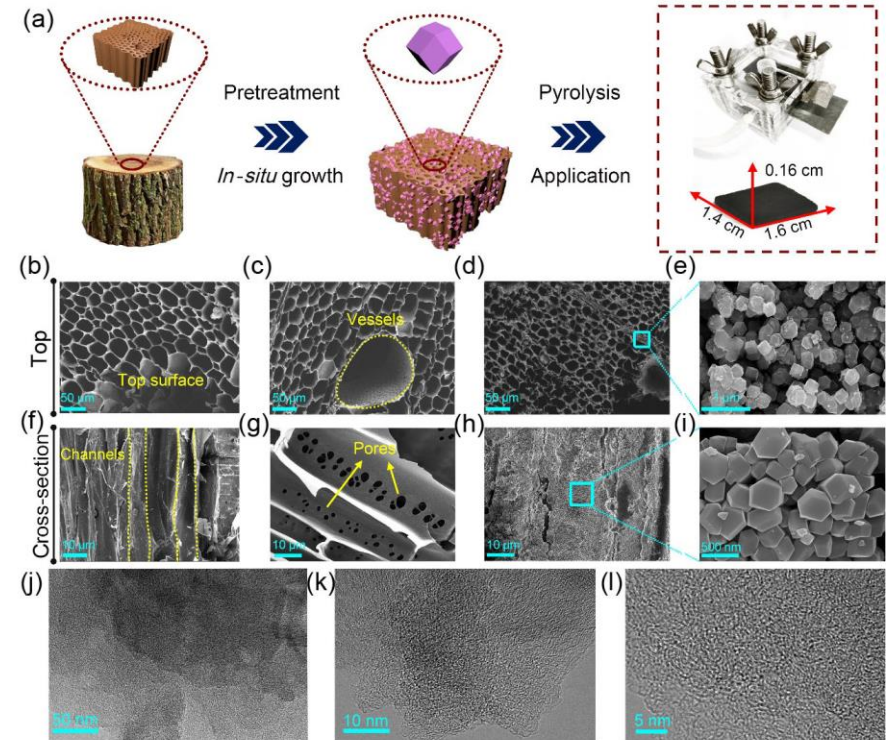
United Press International (UPI), 2021

Wood is Carrying on

Wood for application in Electrochemical Energy Storage Devices



Construction of a quasi-solid-state symmetric supercapacitor (SSC) based on activated wood carbon (AWC) monoliths as freestanding ultrathick electrodes. Shan et al. 2021, *Physical science*, 2(12),



Wood-derived integrated air electrode, Zhou et al. 2022, *NanoResearch*, 15(2)

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Associated publications:

Roulard, R., Trentin, M., Lefebvre, V., Fournet, F., Hocq, L., Pelloux, J., Husson, E., Pineau, C., Dupont, L., Jamali, A. (2022). In situ ESEM using 3-D printed and adapted accessories to observe living plantlets and their interaction with enzyme and fungus. *Micron*. 153. 103185.

Jamali, A. and Evans, P.D. (2022). Chemical and morphological modification of softwood and hardwood surfaces by an oxygen glow discharge plasma. *Journal of Wood Chemistry and Technology*, 42(5): 381-394.

Dauwe, R., Roulard, R., Ramos, M., Thiombiano, B., Mesnard, F., Gontier, E., Jamali, A. (2021). Etching of the seed cuticle by cold plasma shortens imbibitional leakage in *Linum usitatissimum* L. *Industrial Crops and Products*, 167. 113536.

Jamali, A., Evans, P.D. (2020). Plasma treatment reduced the discoloration of an acrylic coating on hot-oil modified wood exposed to natural weathering. *Coatings*, 10(3), 248.

T H A N K Y O U