New synchrotron-based technique to map adhesive infiltration in wood cell walls

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X-ray Fluorescence Microscopy

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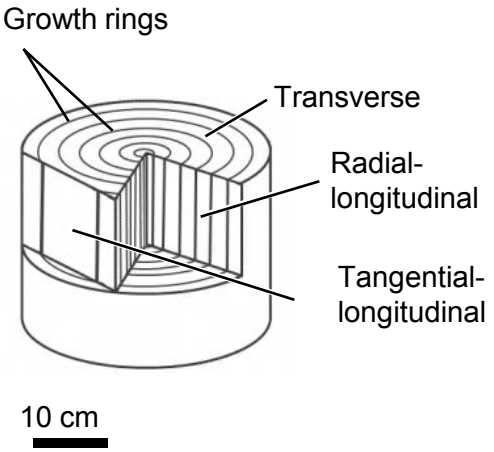
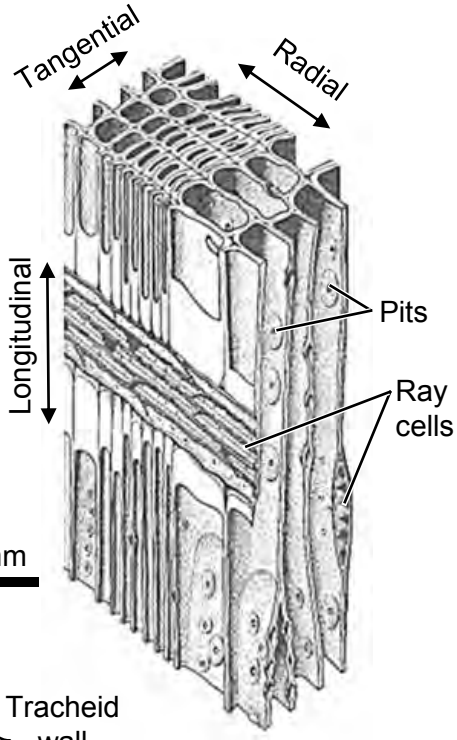
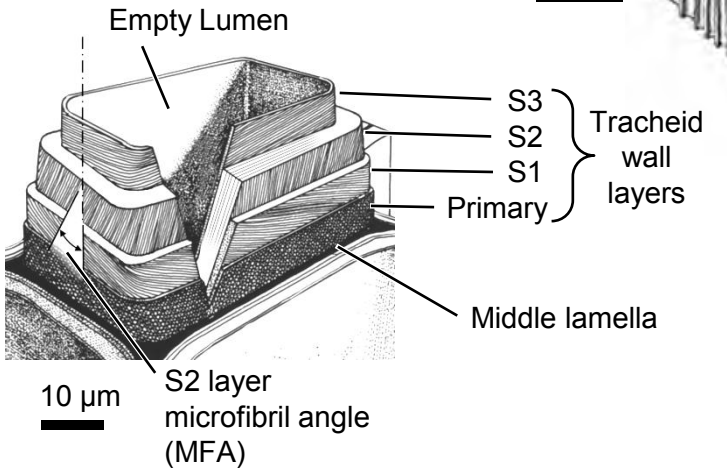
Forest Products Laboratory
United States Forest Service R&D

- Mission: Identify and conduct innovative wood and fiber utilization research that contributes to conservation and productivity of the forest resource, thereby sustaining forests, the economy, and quality of life
- Challenges
  - Job loss in U.S. forest products industry
  - 182 million acres of forest in US (51 million acres in FS) under critical fire risk
- Goals
  - Improve and create new forest products to create more demand
    - Improve moisture durability of wood adhesives

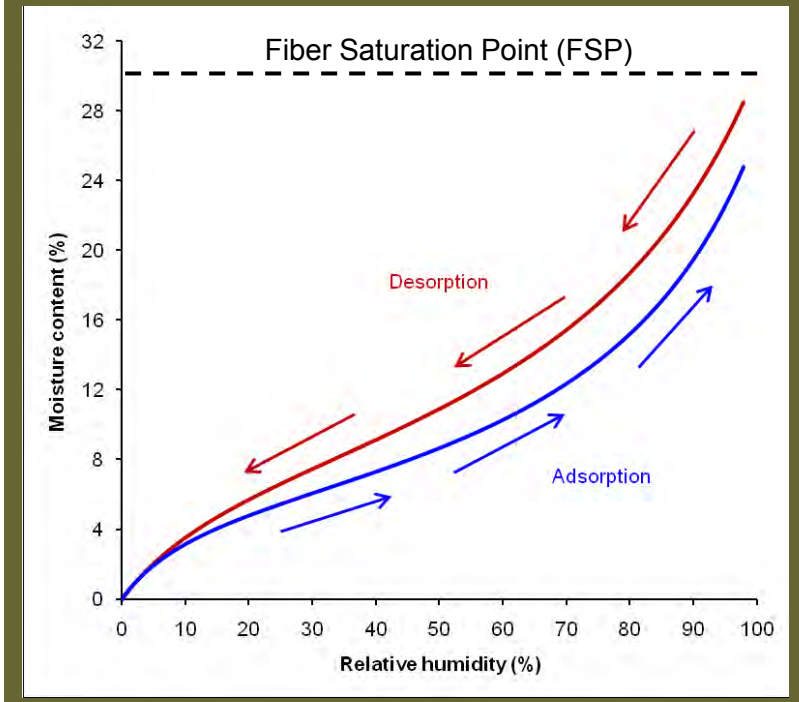
Wood Structure and Moisture





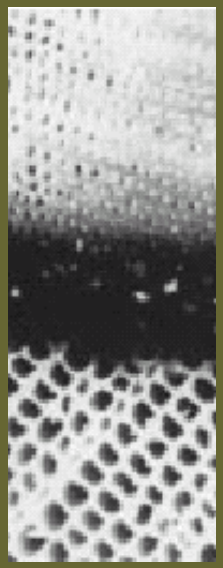


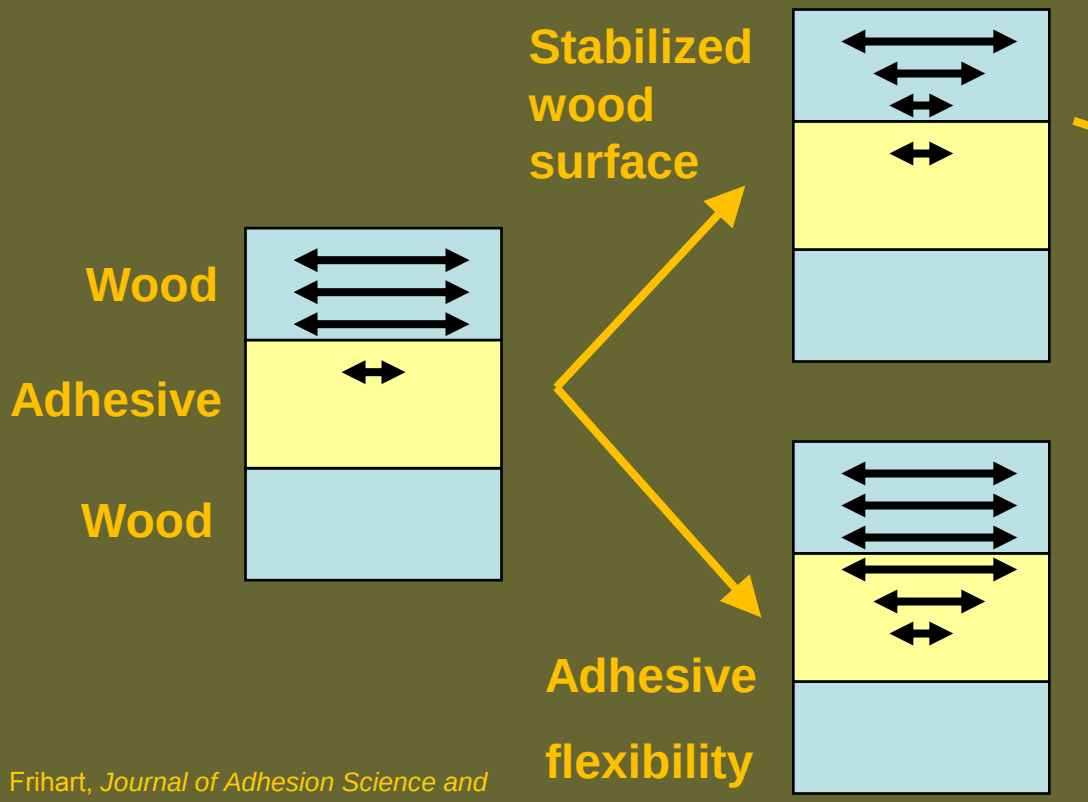
- Moisture can exist in wood as
  - **Bound water** – held within cell wall by intermolecular attractions
  - **Free water** – liquid water in wood cavities



Wood Bonding and Moisture-Induced Swelling

High interfacial strain during moisture-induced swelling can lead to bond failure





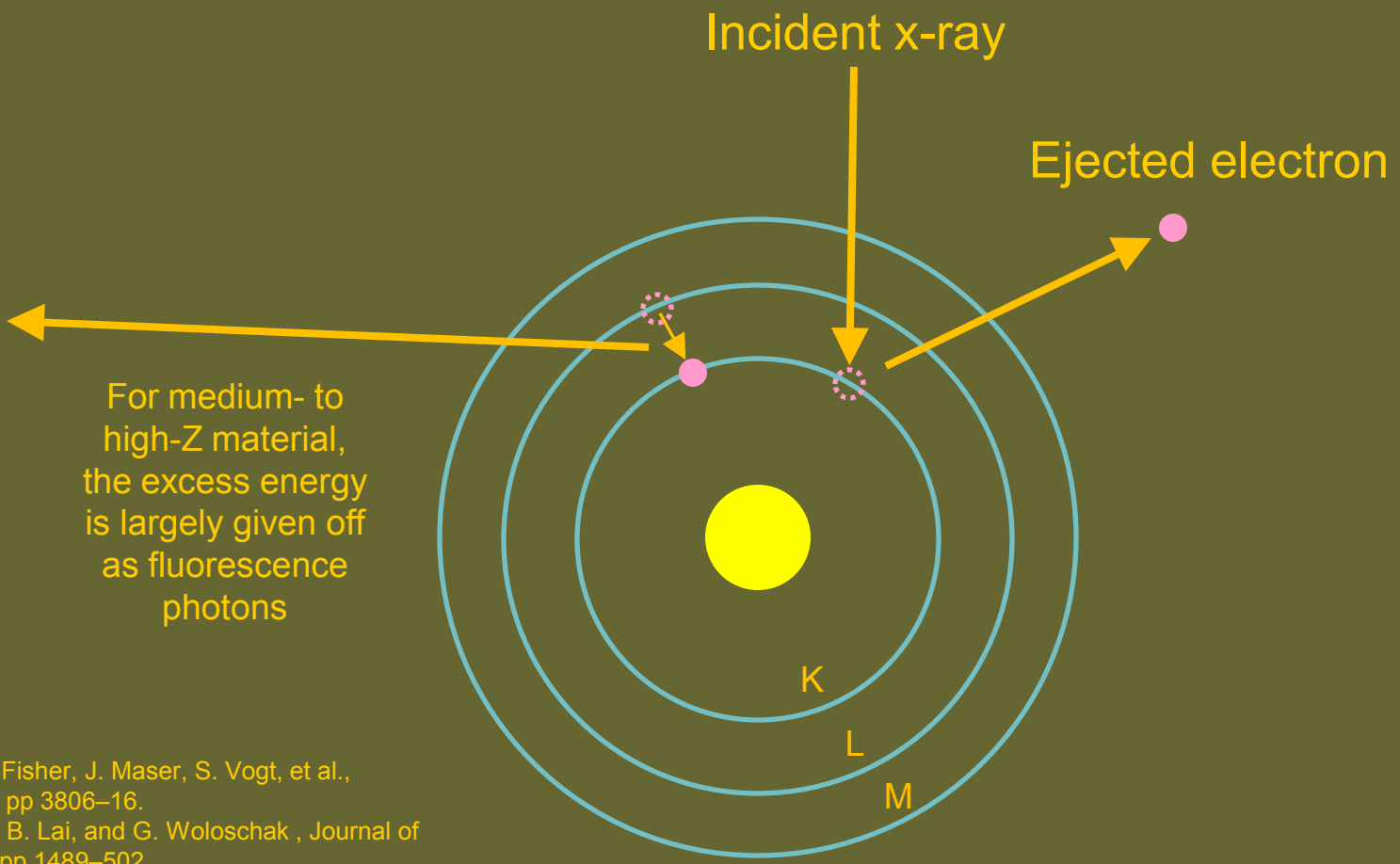
Need methods for cell walls characterization

C.R. Frihart, *Journal of Adhesion Science and Technology*, 2009, 23, pp 611–27.

X-ray Fluorescence Spectroscopy

Energy dispersive detector system

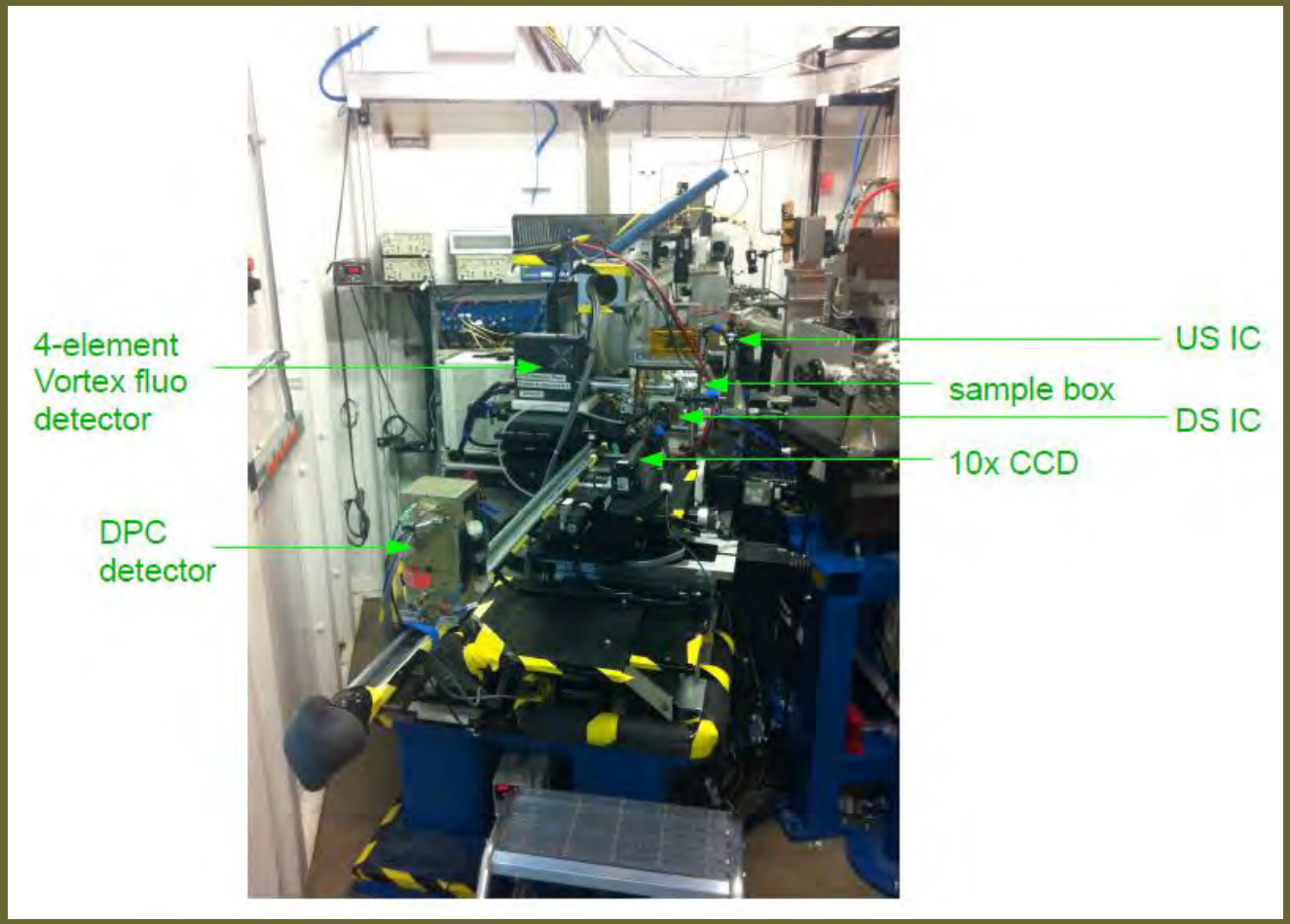
For medium- to high-Z material, the excess energy is largely given off as fluorescence photons



Examples of XFM research:
B.S. Twining, S.B. Baines, N.S. Fisher, J. Maser, S. Vogt, et al., Analytical Chemistry, 2003, 75, pp 3806–16.
T. Paunesku, S. Vogt, J. Maser, B. Lai, and G. Woloschak , Journal of cellular biochemistry, 2006, 99, pp 1489–502.
U.E.A. Fittschen and G. Falkenberg, Spectrochimica Acta Part B: Atomic Spectroscopy, 2011, 66 pp 567–80

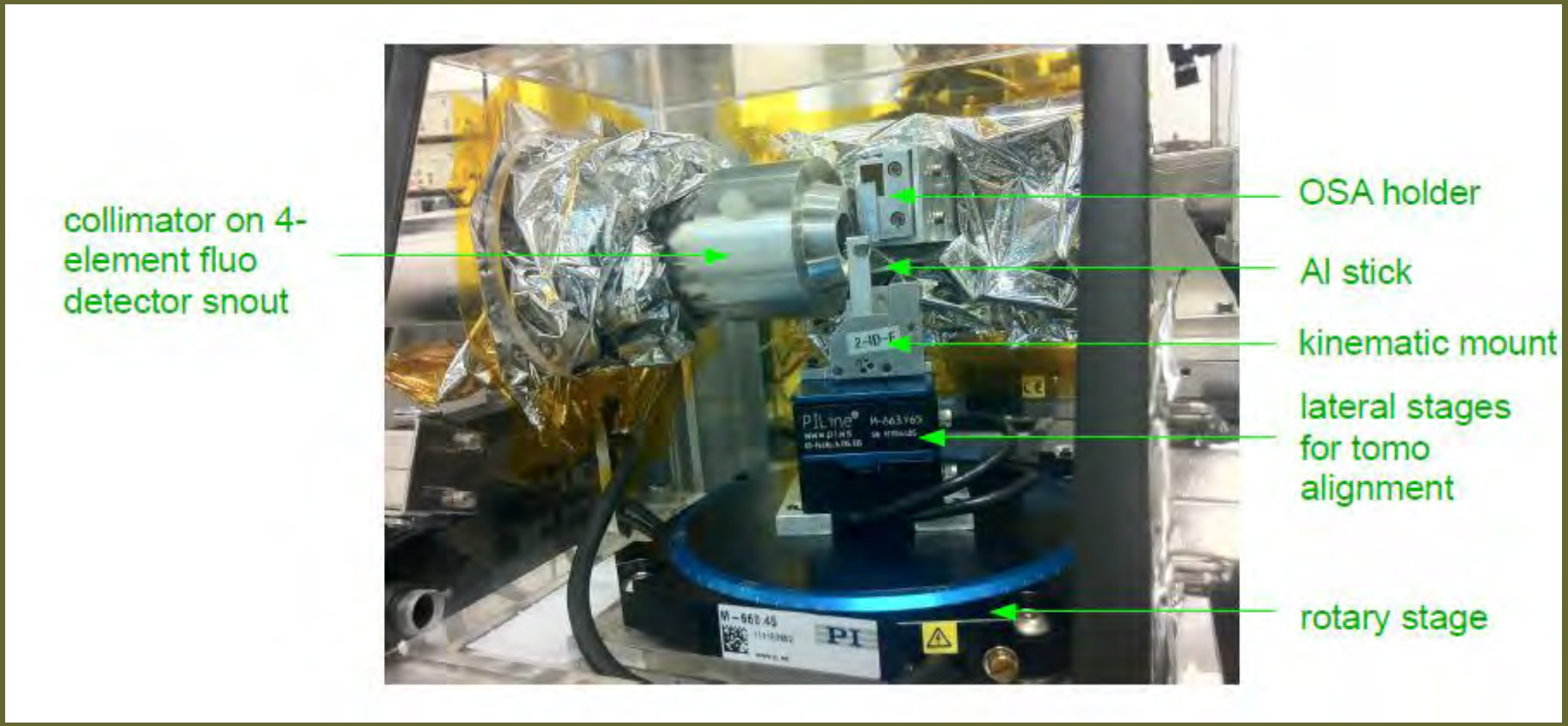
X-ray Fluorescence Microscopy (XFM)

Beamline 2-ID-E at the Advanced Photon Source at Argonne National Laboratory

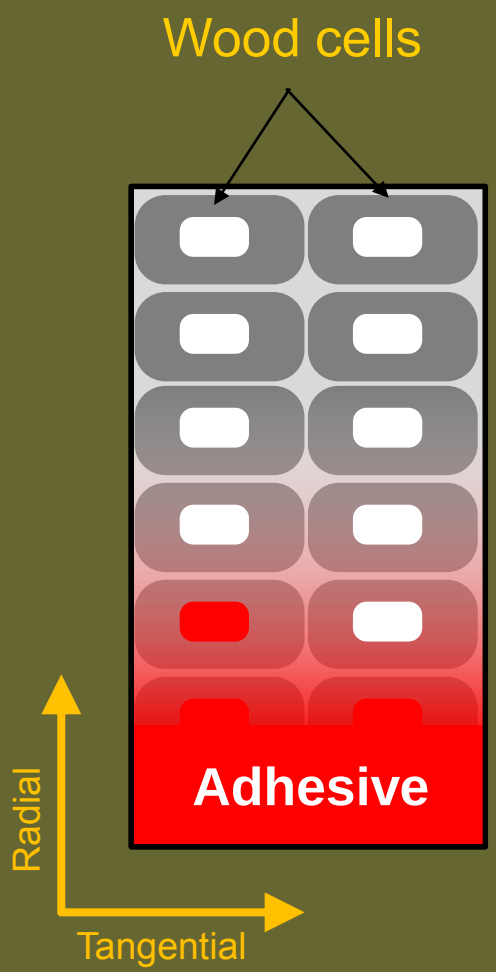


X-ray Fluorescence Microscopy (XFM)

Sample box at beamline 2-ID-E at the Advanced Photon Source at Argonne National Laboratory



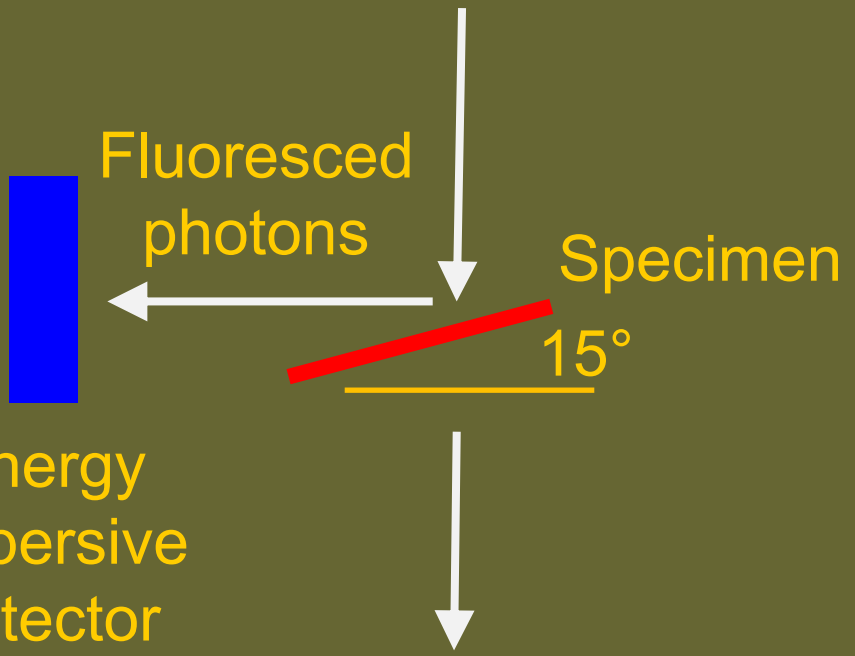
X-ray Fluorescence Microscopy (XFM)



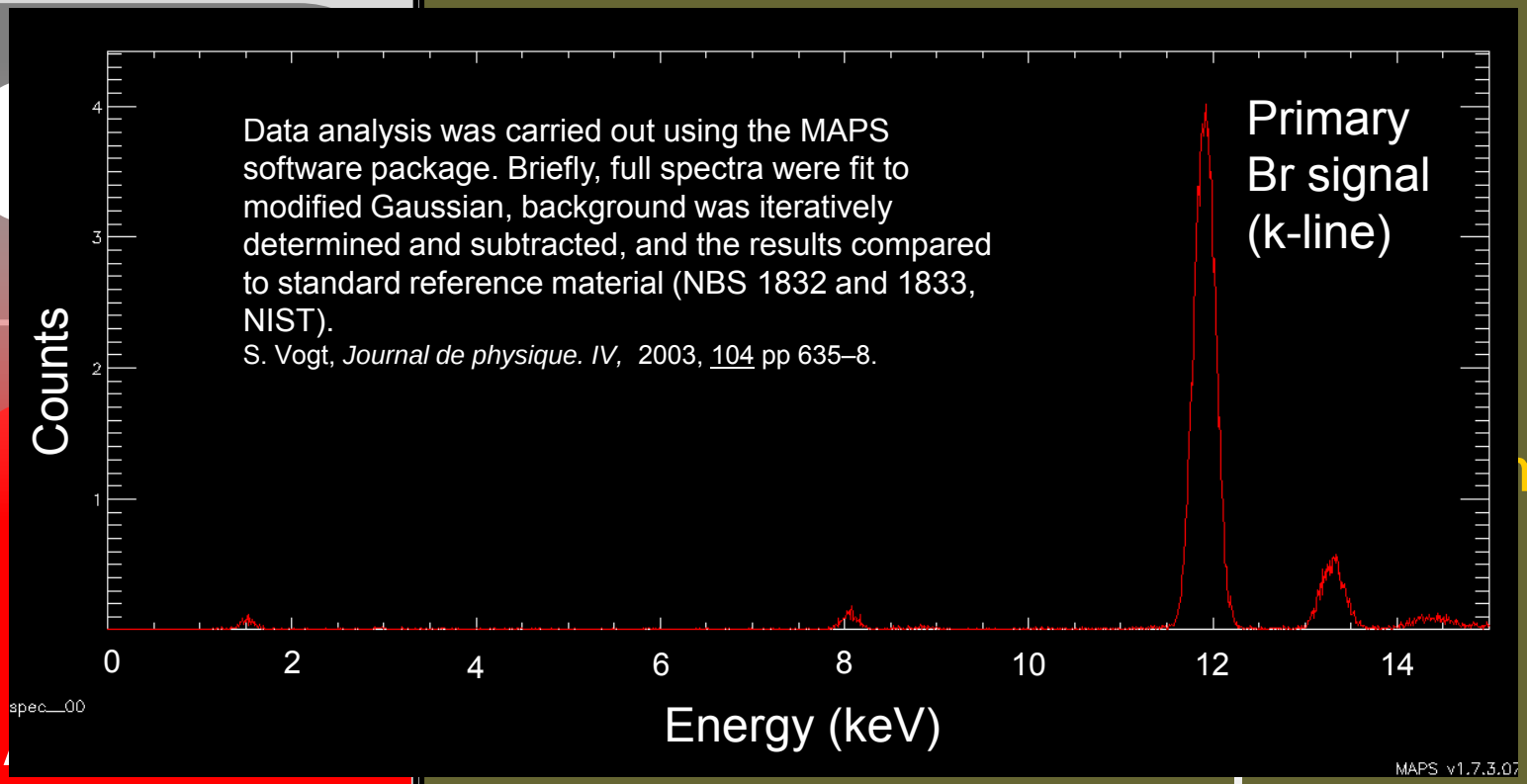
- Bromine-labeled phenol formaldehyde (PF) adhesive
  - 3-bromophenol instead of phenol
  - Aliquots pulled at 5 times during polymerization step
- Pristine tangential-longitudinal surfaces bonded with Br-labeled PF
- Cured in 155°C for 45 min
- 2 µm-thick cross-sections cut with diamond knife, floated in water, and clamped inside foldable TEM grid
- XFM performed at 2-ID-E at the Advanced Photon Source

X-ray Fluorescence Microscopy (XFM)

Top View



X-ray Fluorescence Microscopy (XFM)



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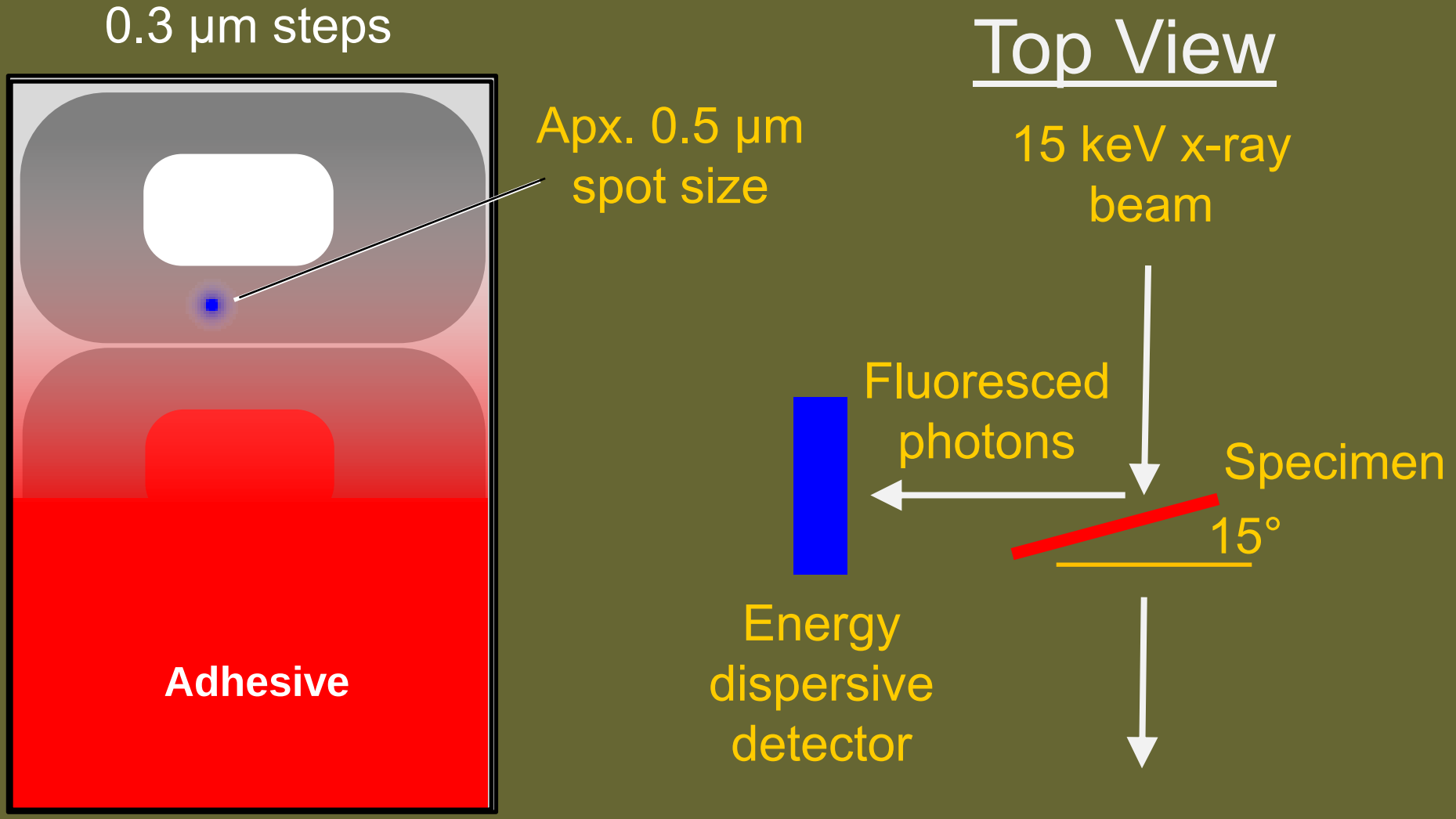
X-ray Fluorescence Microscopy (XFM)



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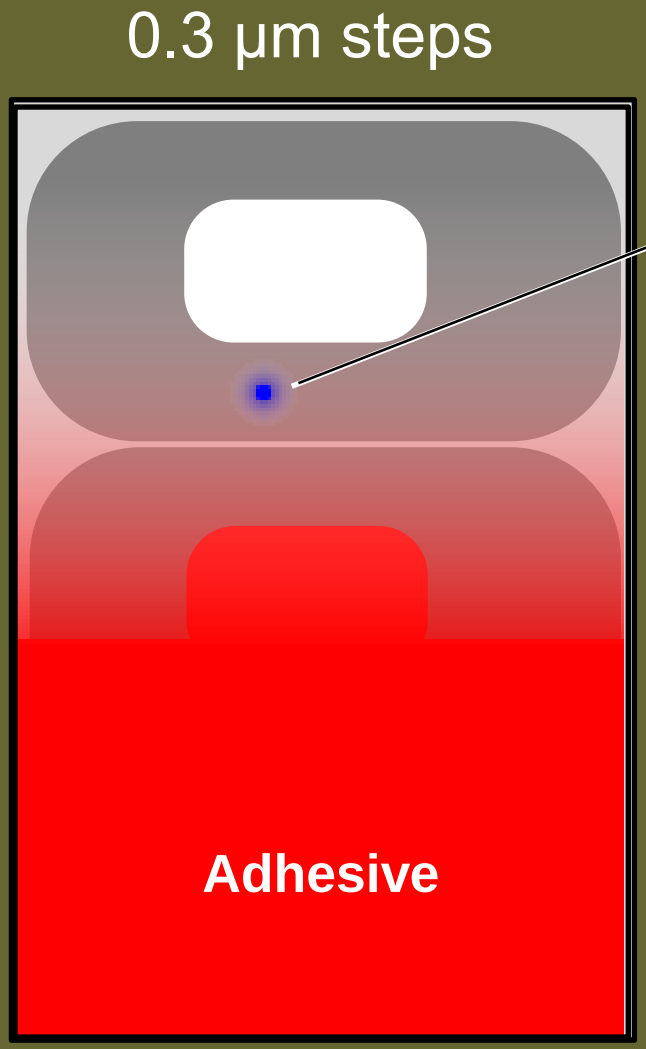
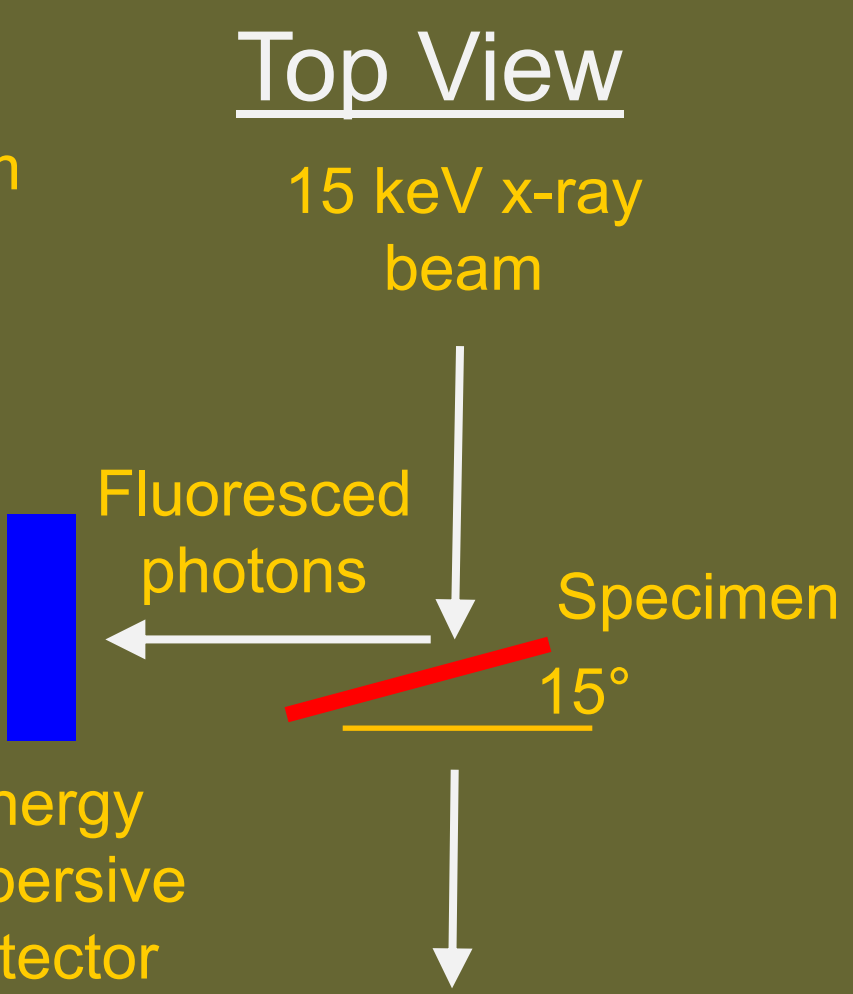
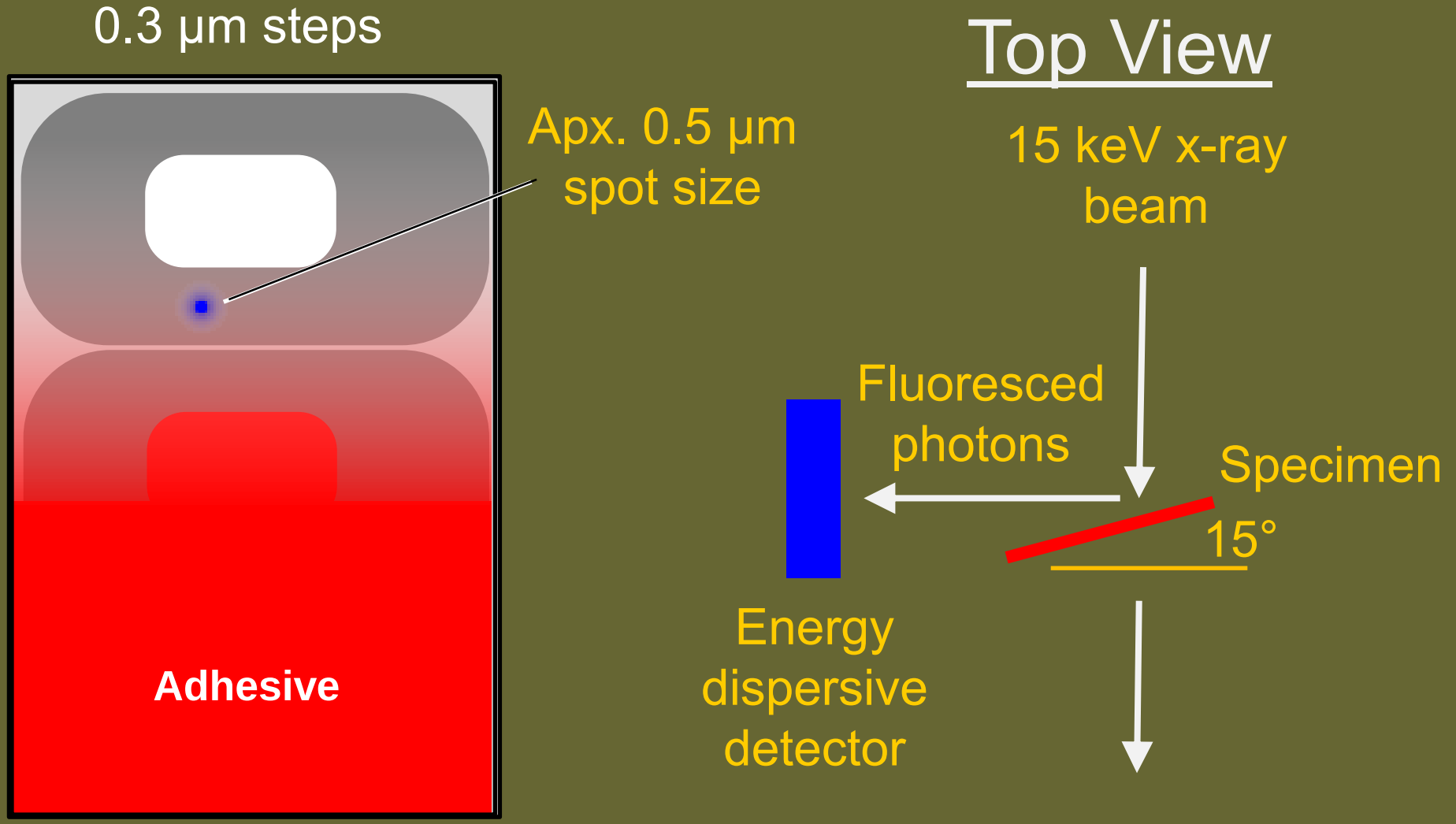




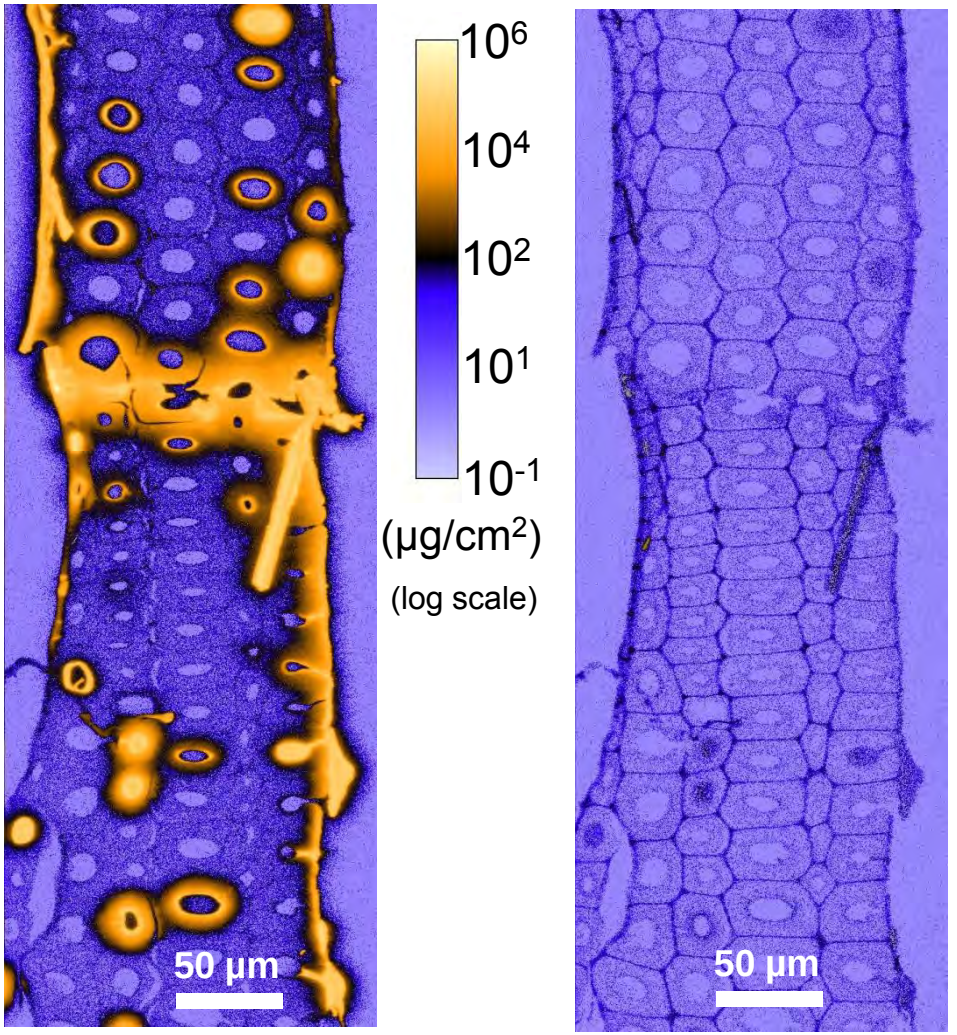
X-ray Fluorescence Microscopy (XFM)



XFM results

Br signal

Zn signal

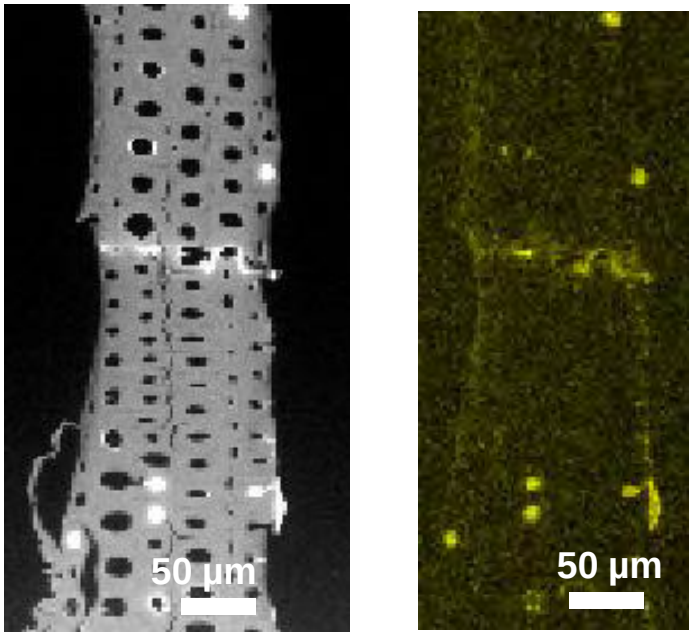


Using TEM-EDXA Saka and Goring (1983) found 400 ppm Zn in CCML, but none in secondary cell walls

SEM EDXA results

Backscattering image

Br EDXA

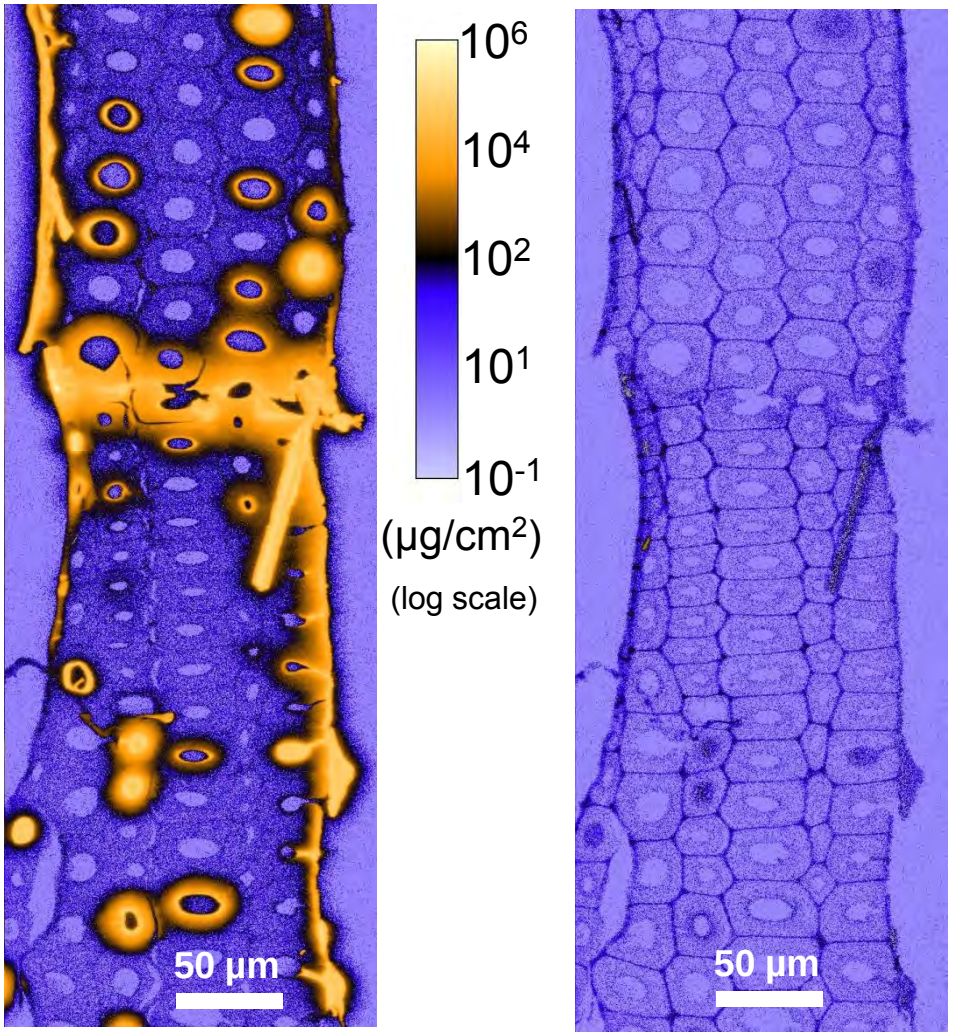


- XFM 2-3 orders of magnitude more sensitive than SEM EDXA
  - No bremsstrahlung background
- Although electrons are easier to focus, x-rays have effectively no side scattering

XFM results

Br signal

Zn signal



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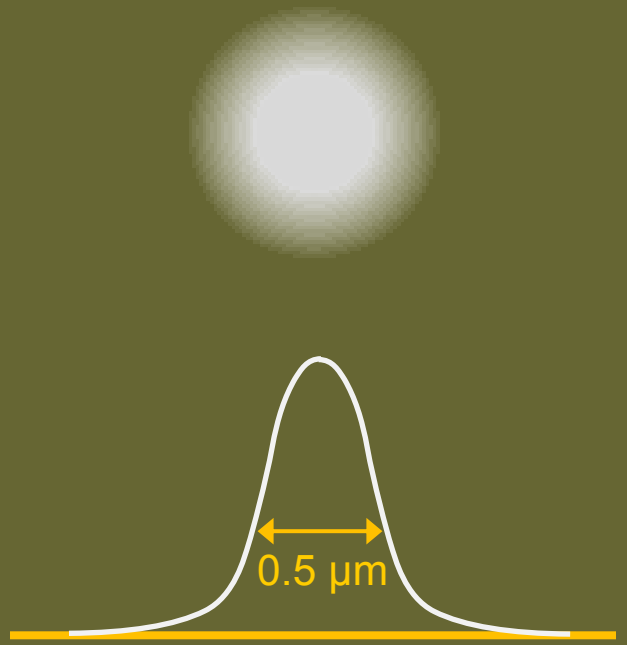
Potential artifacts

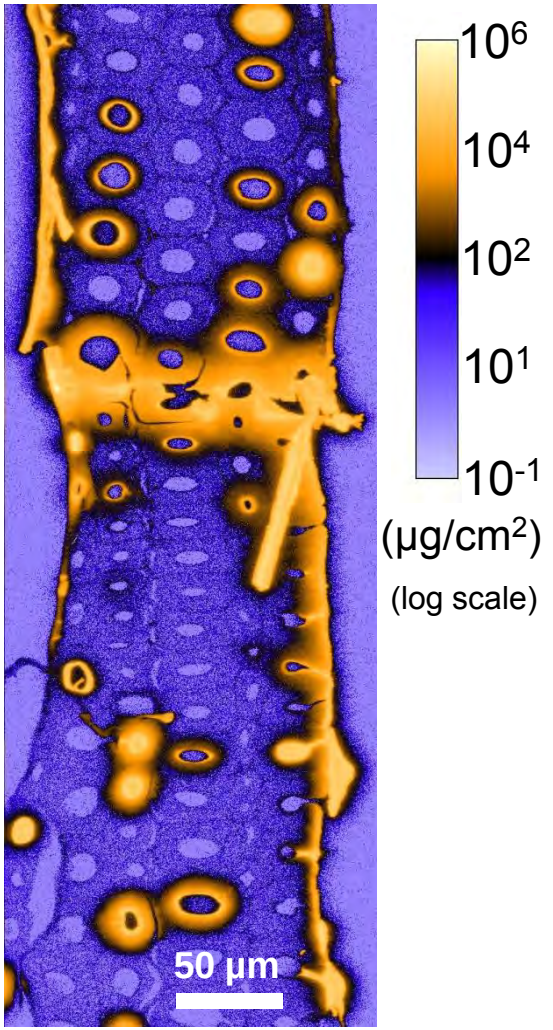
X-ray beam not perfectly focused



Spatial distribution of x-rays

XFM results

Br signal



Potential artifacts

Br separates from Br-PF

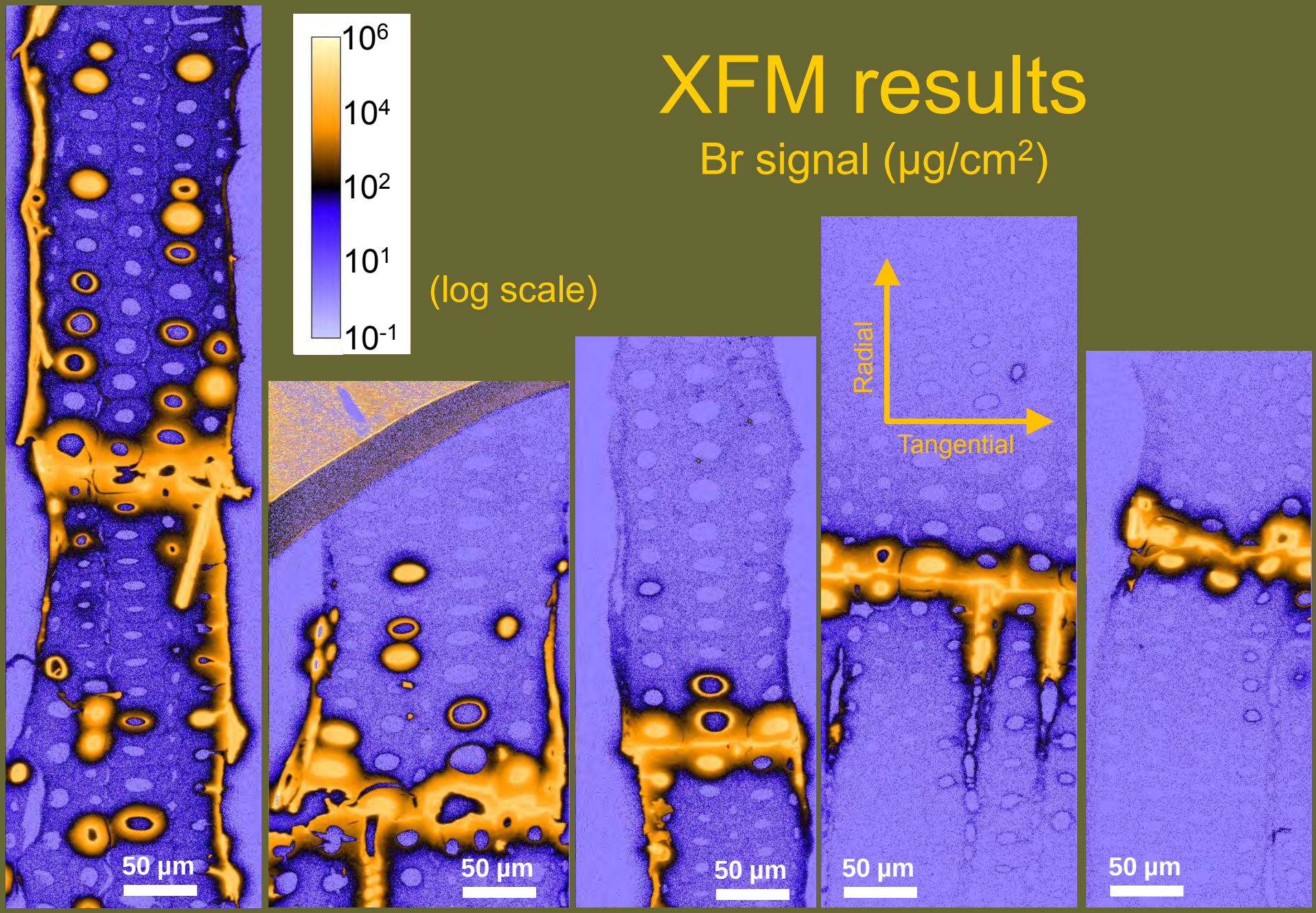
Tested for free Br by:

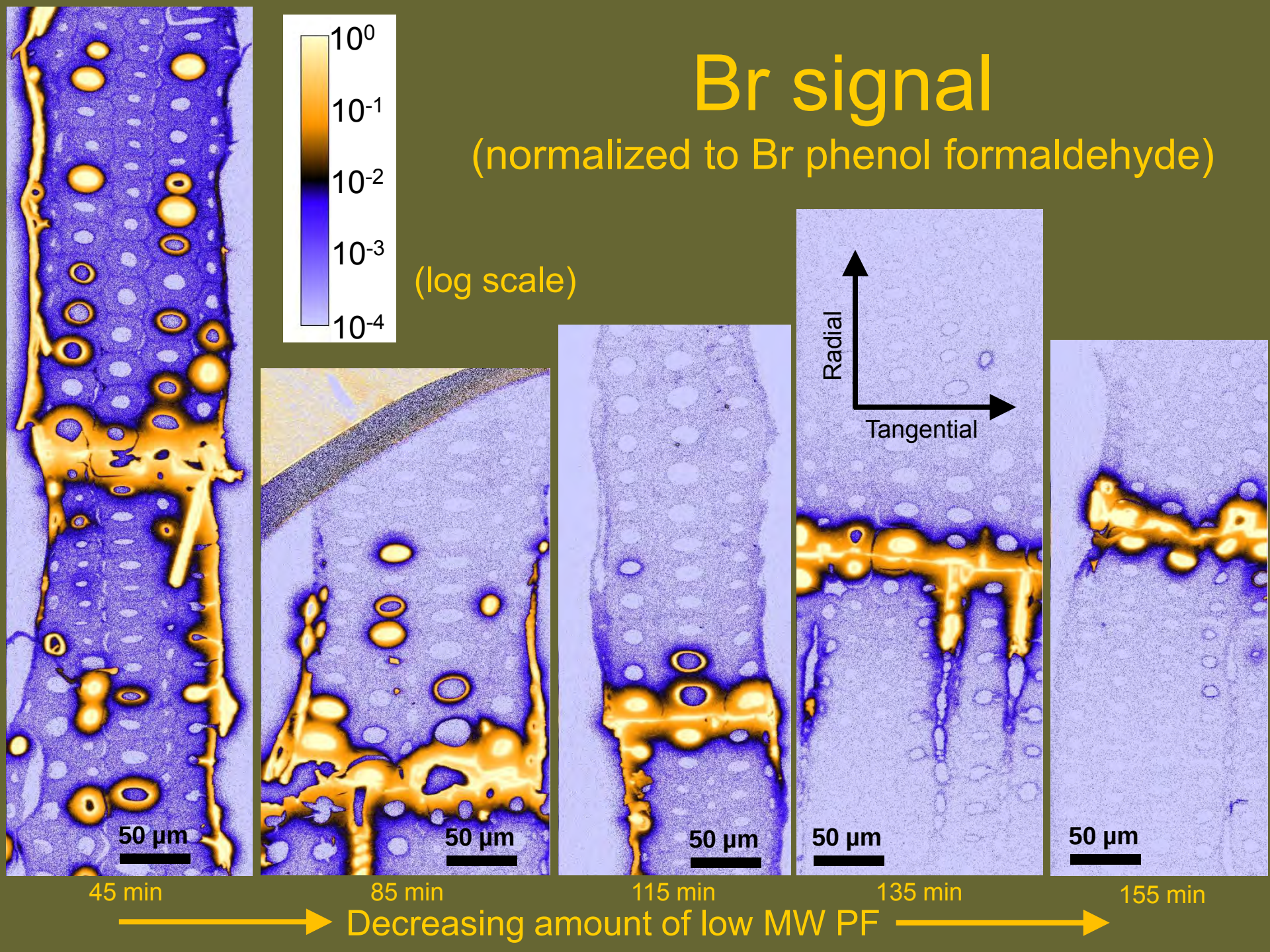
1. Curing adhesive on filter paper
2. Soaking filter paper in water overnight
3. Tested water for Br ions using ion selective electrode and total Br using ICP-MS

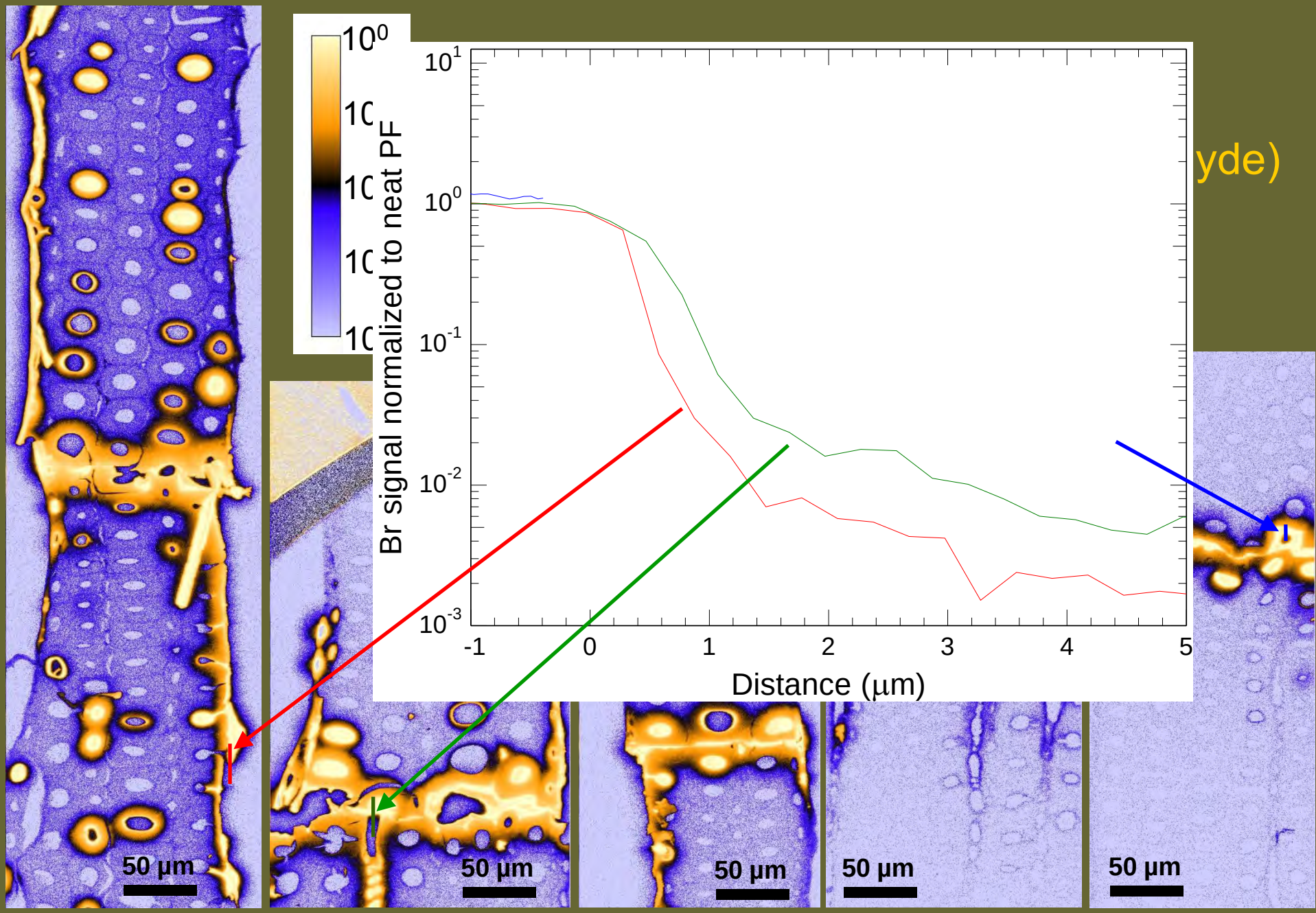
Up to 1% Br atoms fell off Br-PF and became Br ions

XFM results

Br signal (µg/cm^2)




Br signal
(normalized to Br phenol formaldehyde)
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
(log scale)
Radial
Tangential
50 µm
50 µm
50 µm
50 µm
50 µm
45 min
85 min
115 min
135 min
155 min
Decreasing amount of low MW PF


10^0
10
10
10
10
Br signal normalized to neat PF
10^1
10^0
10^-1
10^-2
10^-3
-1
0
1
2
3
4
5
Distance (μm)
yde)
50 μm
50 μm
50 μm
50 μm
50 μm
45 min
85 min
115 min
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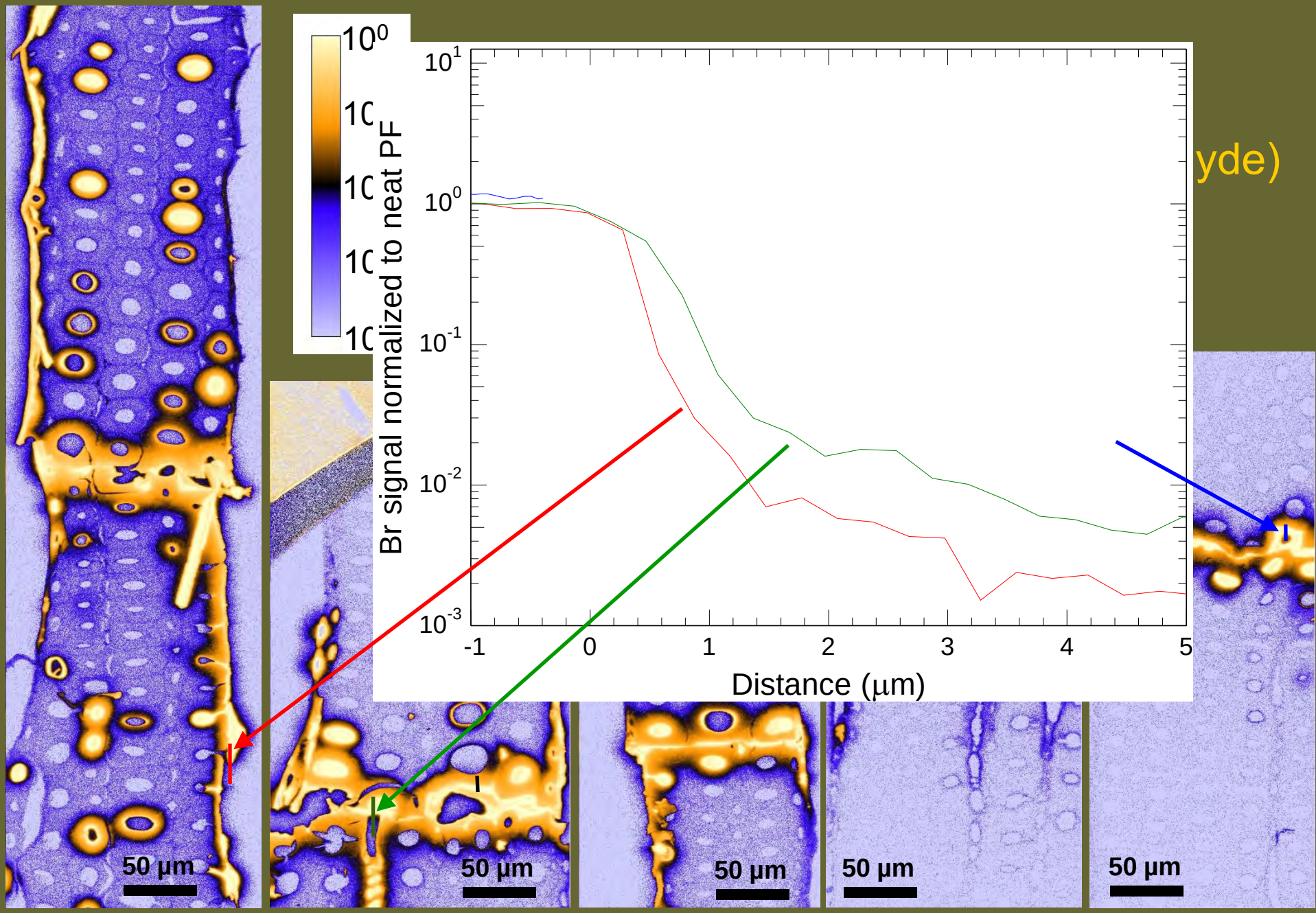
155 min
Decreasing amount of low MW PF


10^0
10
10
10
10
Br signal normalized to neat PF
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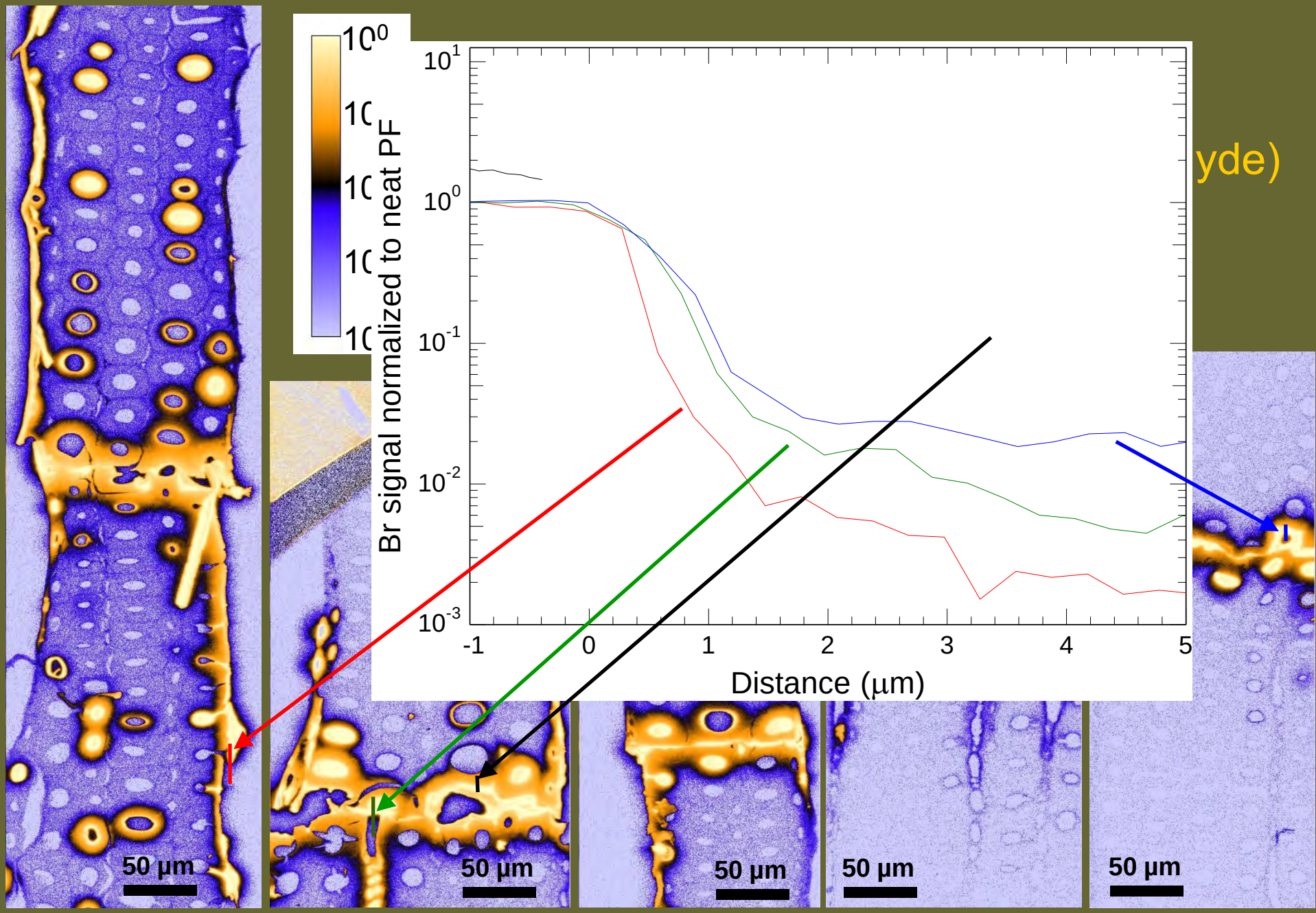
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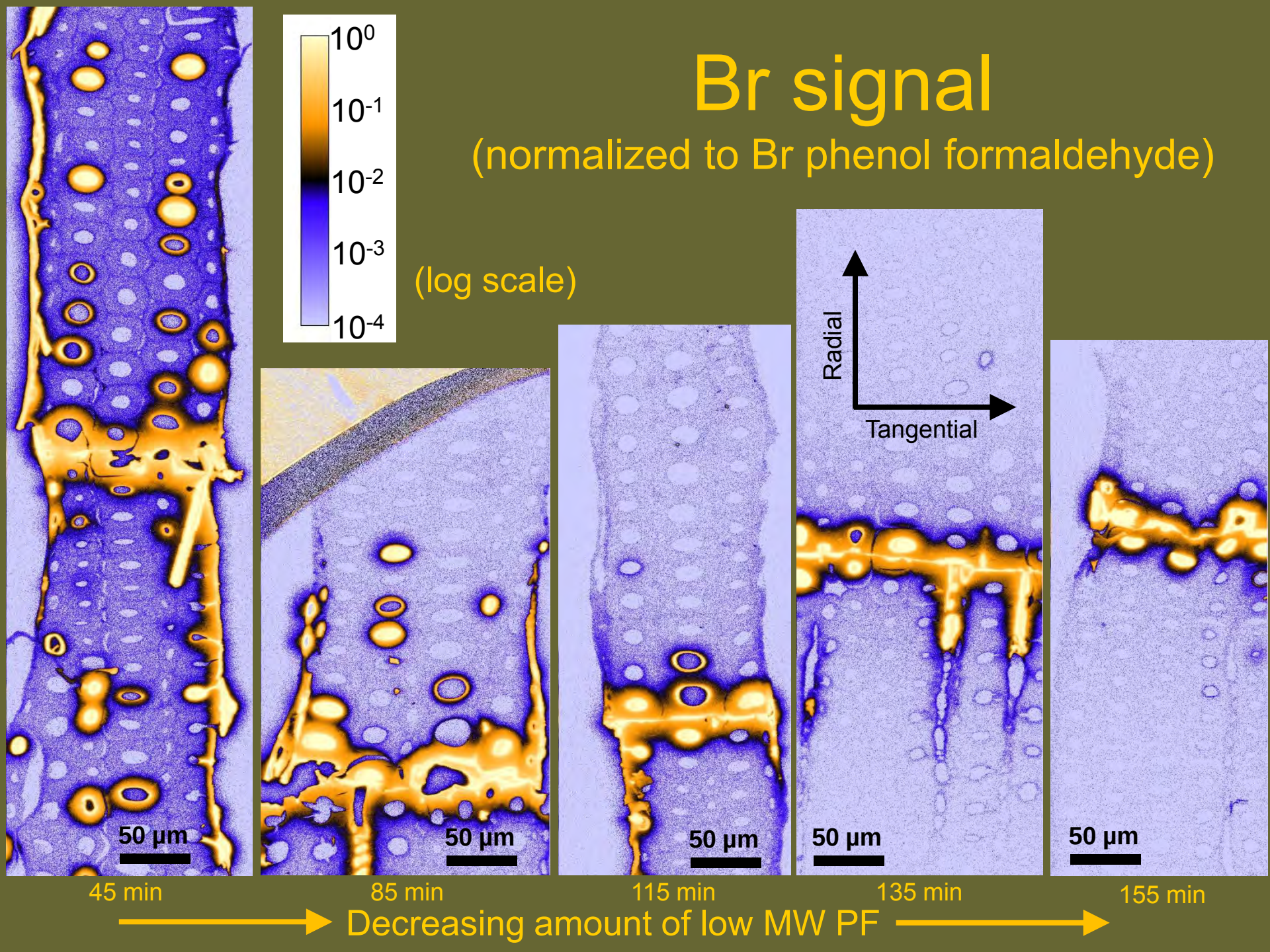
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10^{0}
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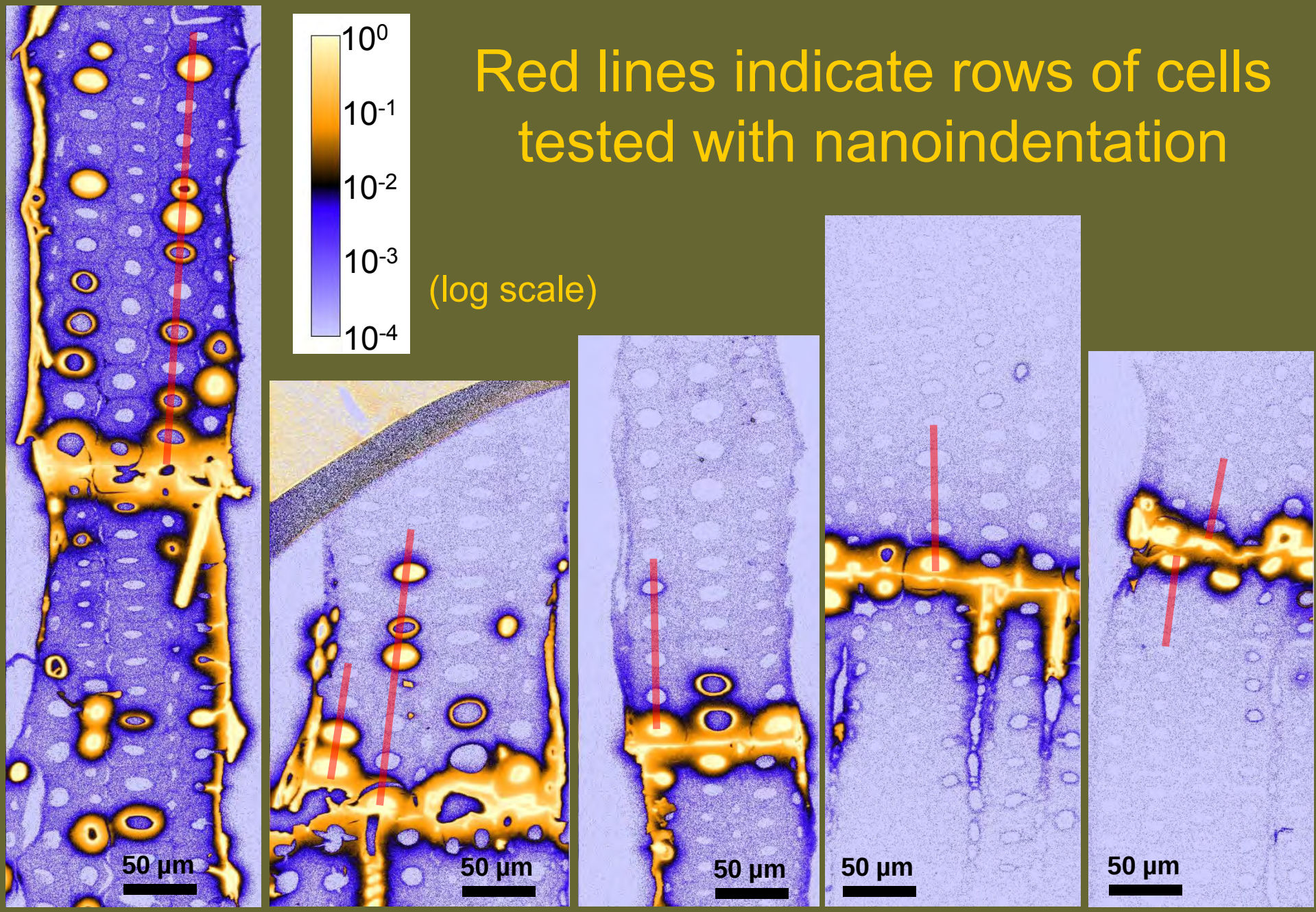
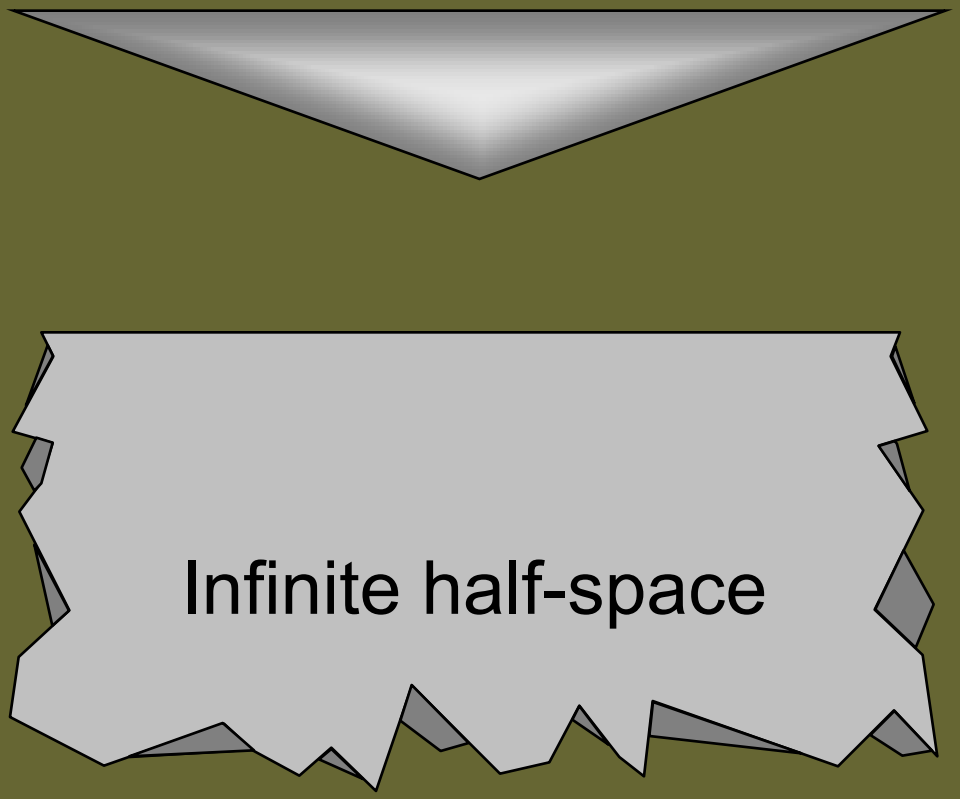
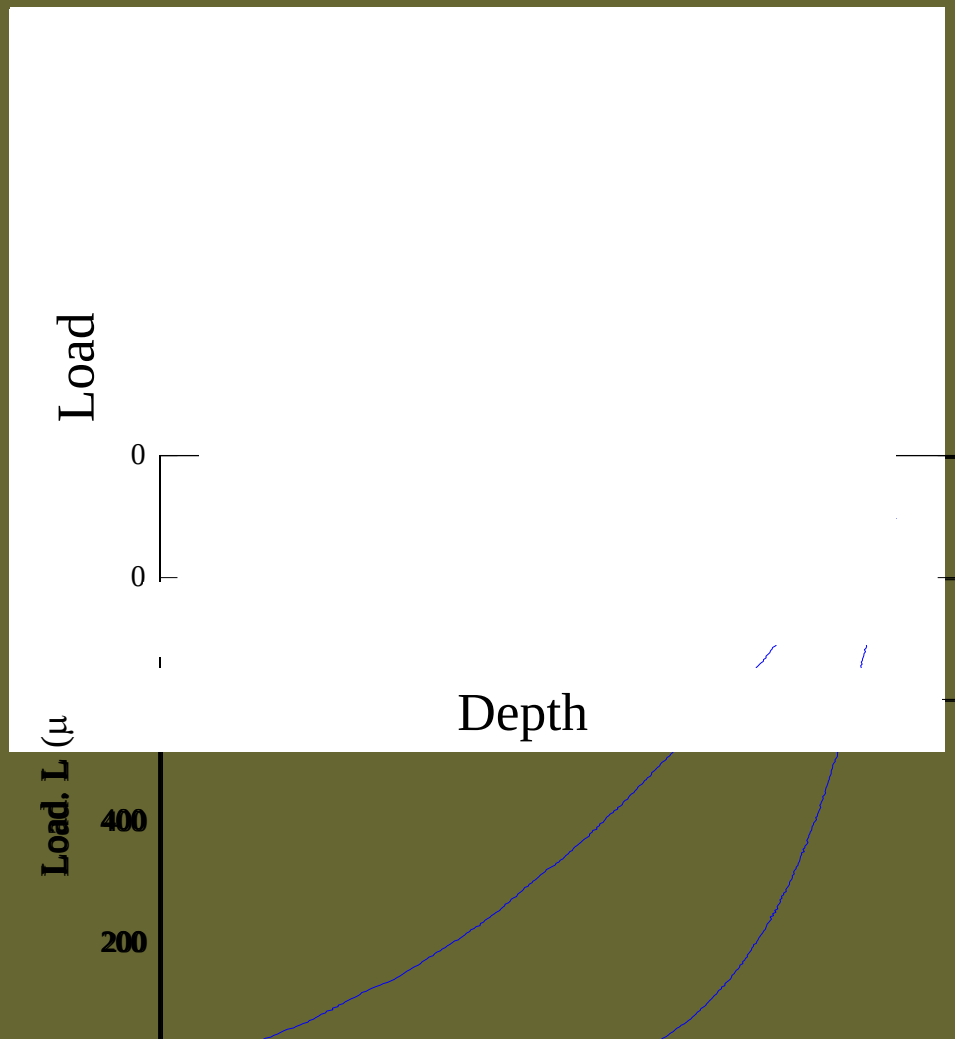
(log scale)
Radial
Tangential
50 µm
50 µm
50 µm
50 µm
50 µm
45 min
85 min
115 min
135 min
155 min
Decreasing amount of low MW PF

Red lines indicate rows of cells tested with nanoindentation



Nanoindentation Experiment





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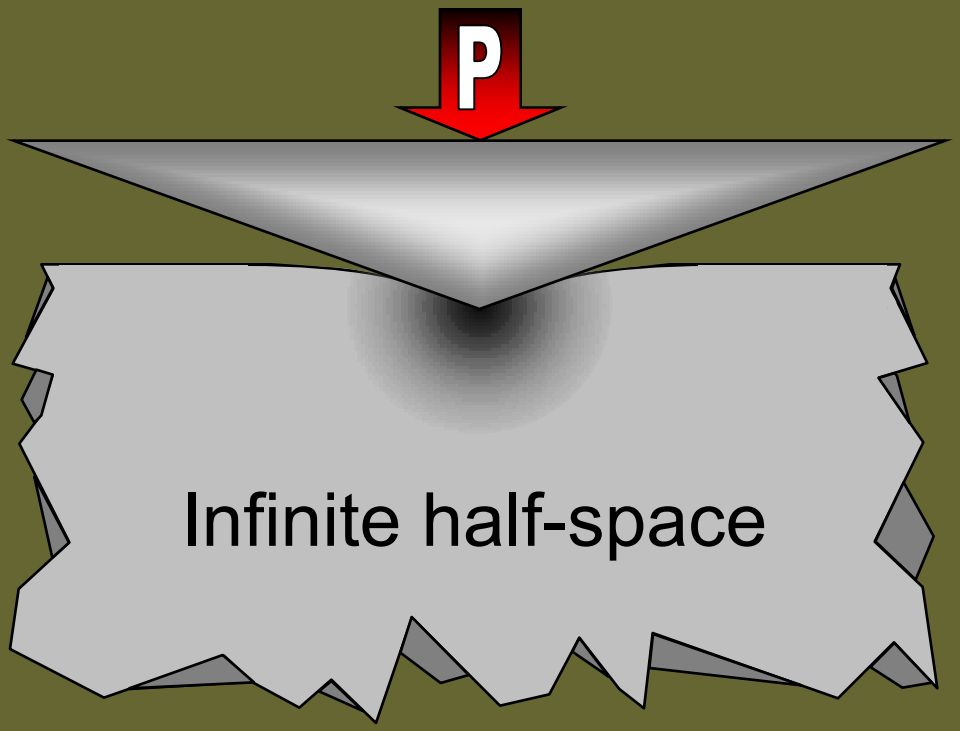

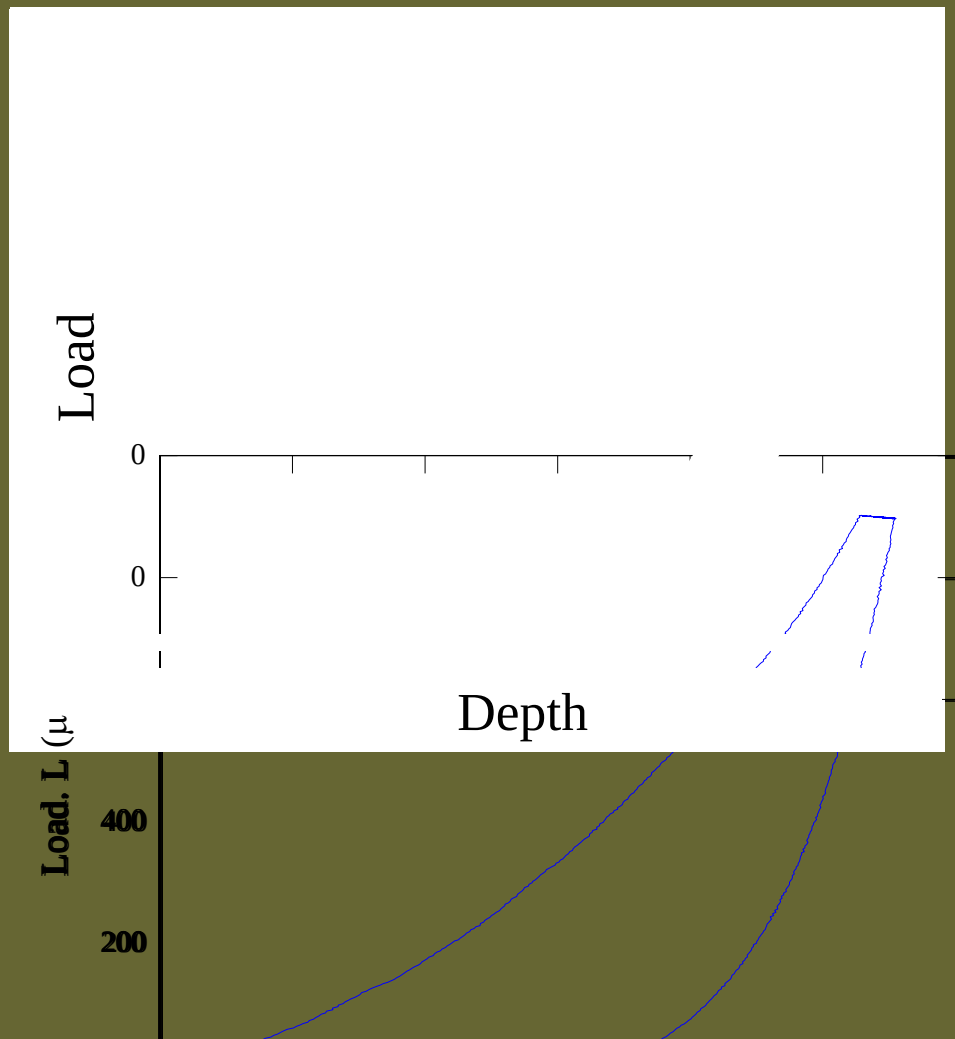

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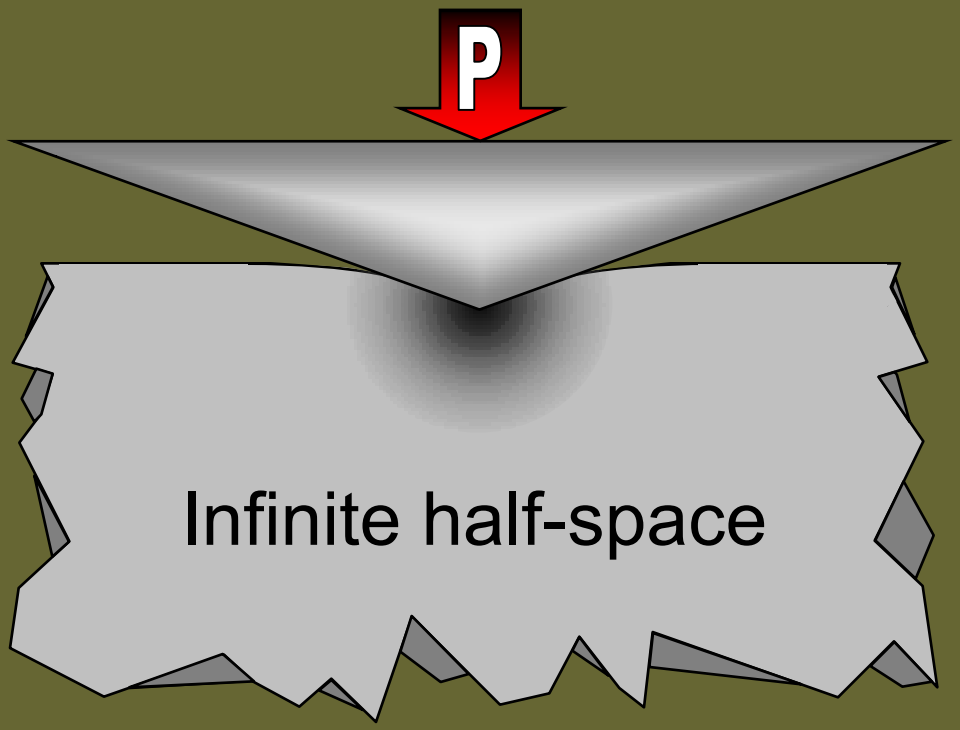

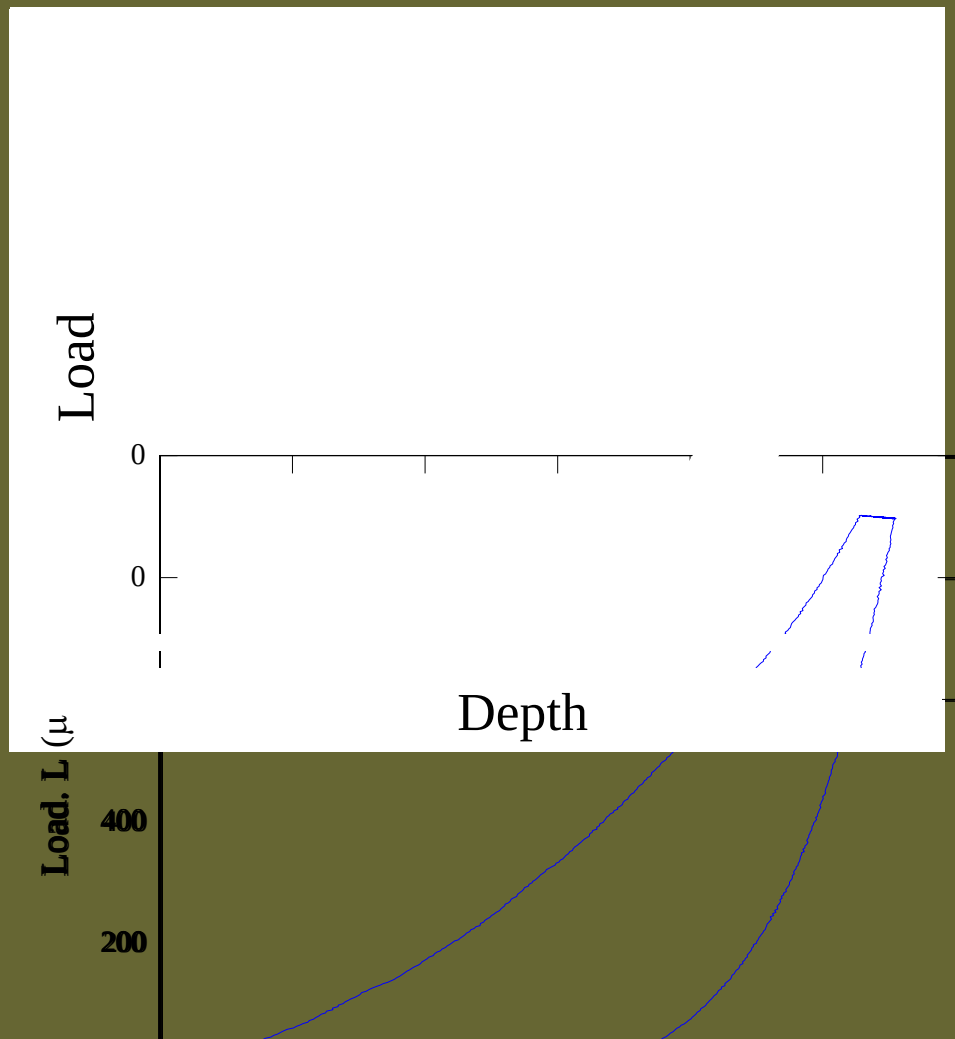

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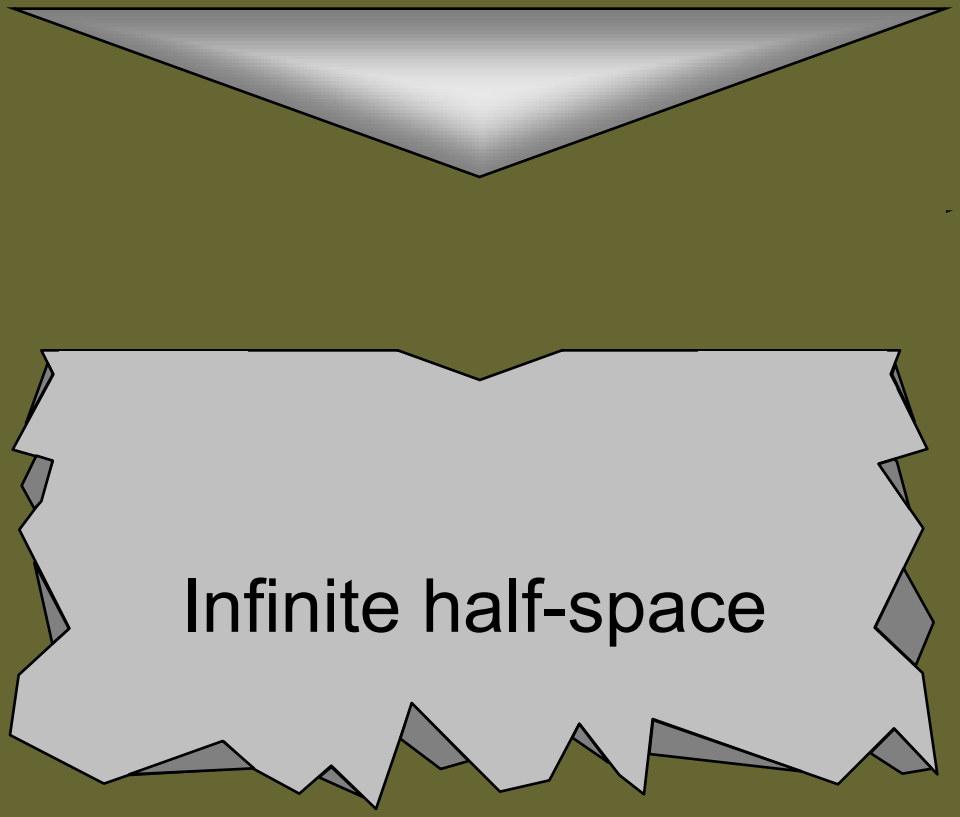

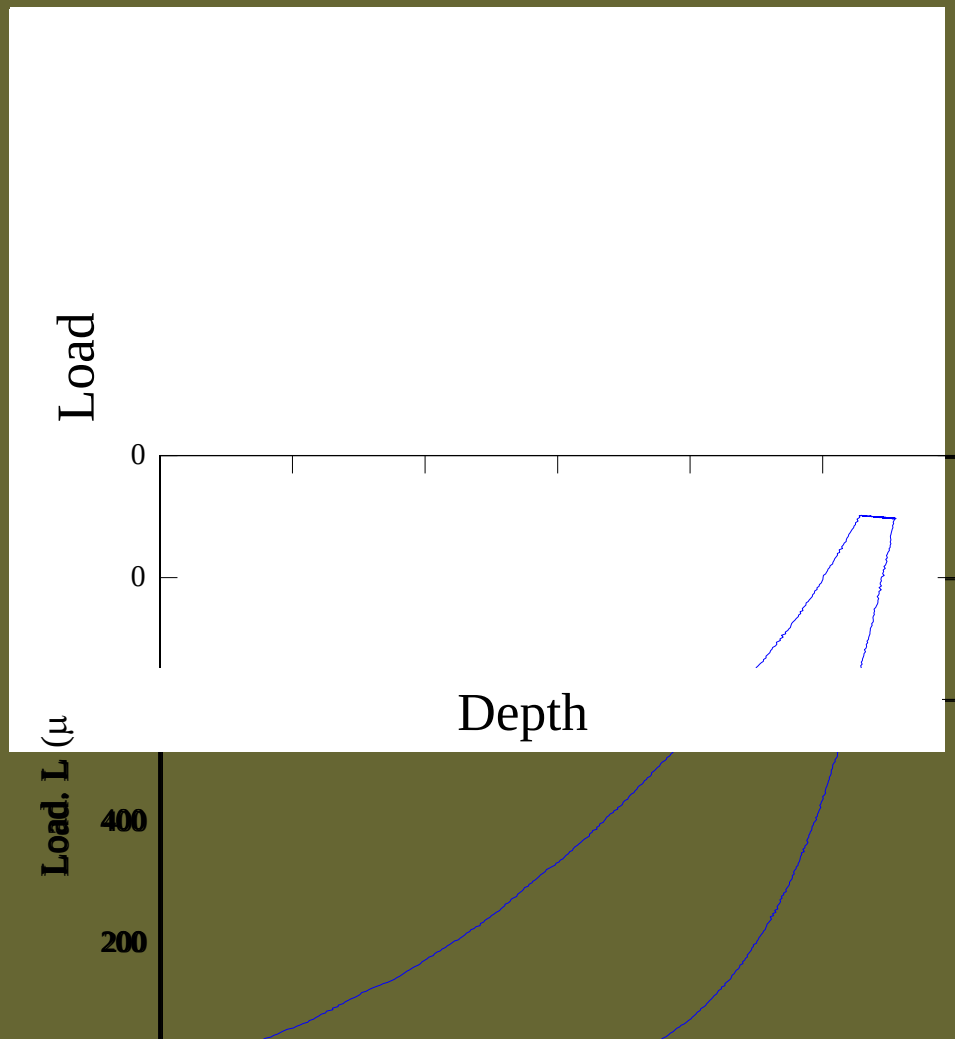

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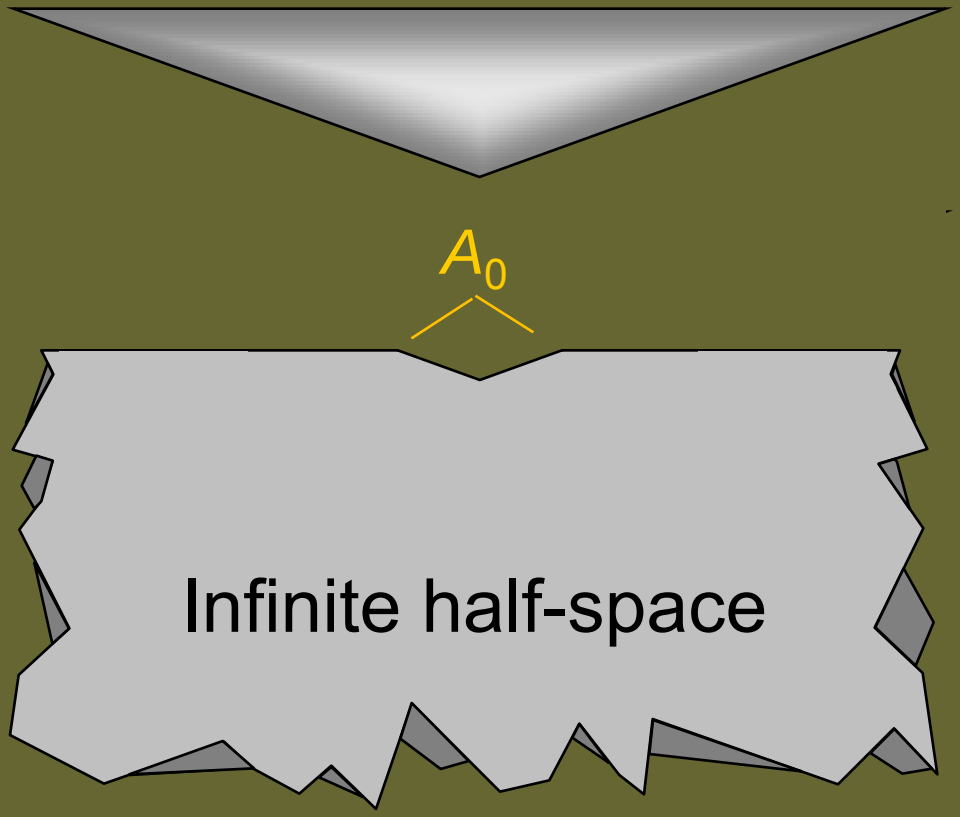
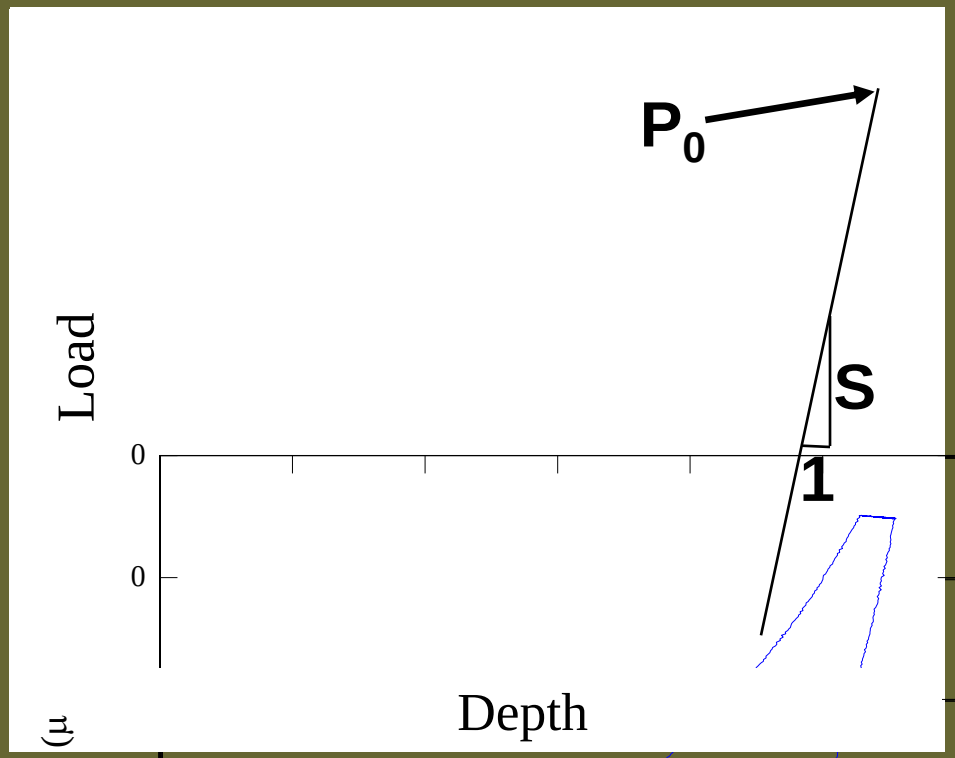




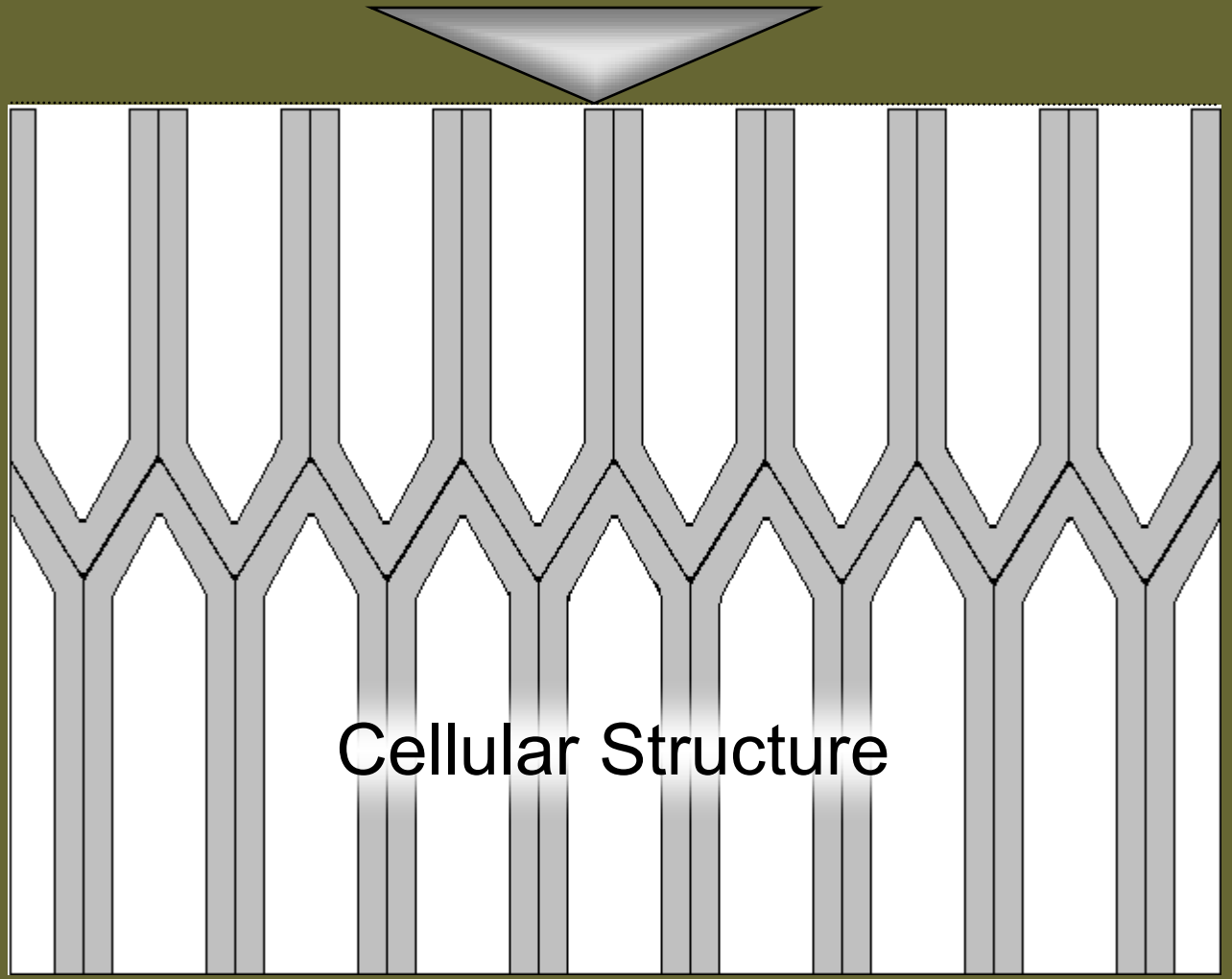
Assess hardness and elastic modulus

$$H = \frac{P_0}{A_0}$$

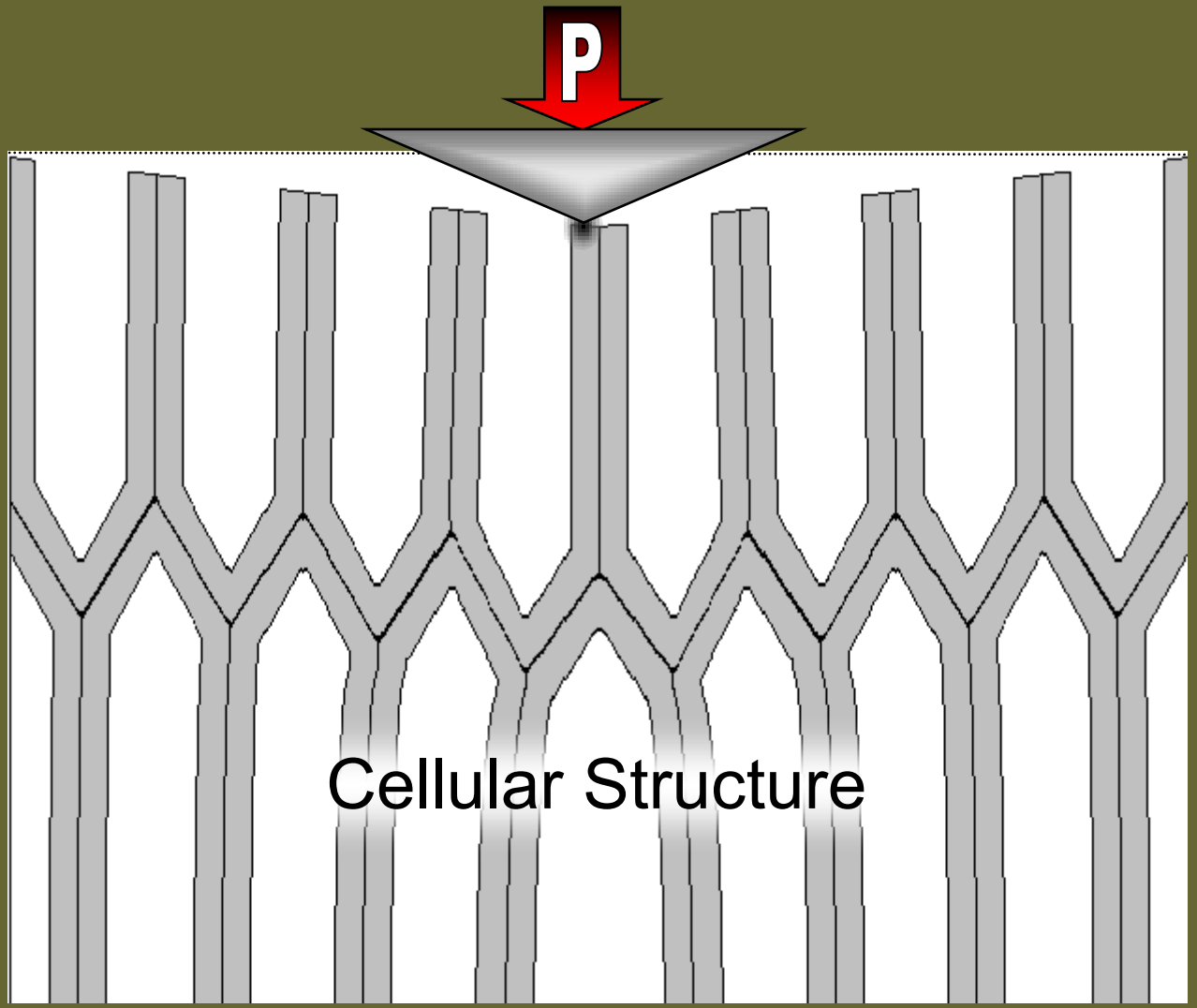
$$E_{eff} = \frac{S}{\sqrt{A_0}}$$

$$\frac{1}{E_{eff}} = \frac{1}{\beta}\left(\frac{1-\nu_s^2}{E_s} + \frac{1-\nu_d^2}{E_d}\right)$$

Nanoindentation of Wood



Nanoindentation of Wood



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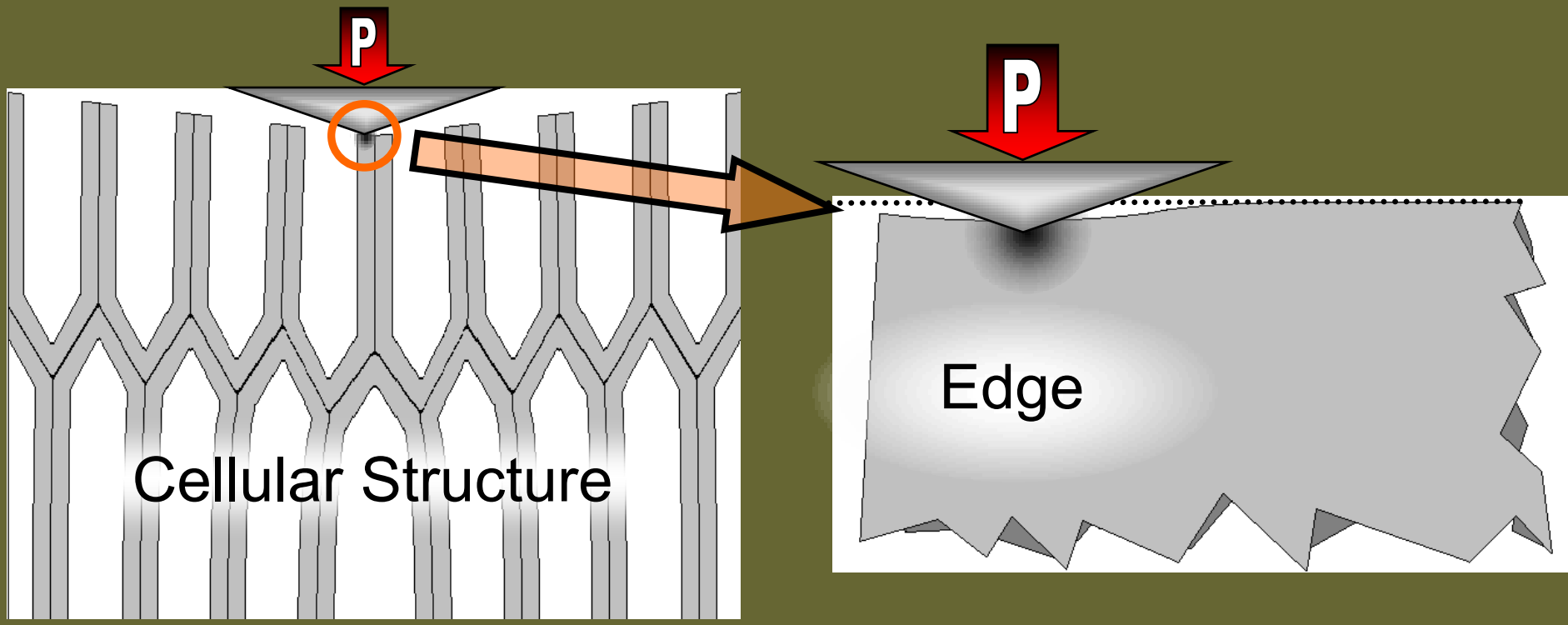


Use structural compliance method to experimentally account for specimen-scale flexing and edge effects

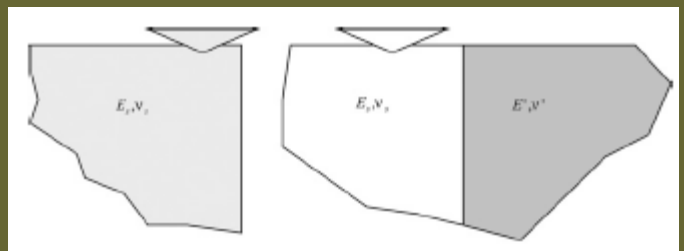
Structural compliance method

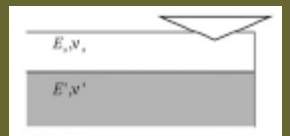
- Effects of specimen-scale flexing and edges can be accounted for by including a structural compliance, C_s, in the analysis
- C_s behaves similar to a machine compliance, C_m
  - Independent of load
- C_s and C_m can be measured using a modified SYS correlation
  - Stone et al. (1991) *J. Vac. Sci. Technol. A* **9**(4) pp. 2543-2547

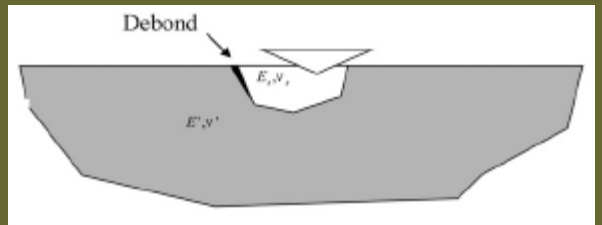
$$C_t\sqrt{P} = (C_m + C_s)\sqrt{P} + \frac{\sqrt{H}}{E_{eff}}$$

Plot $C_t\sqrt{P}$ vs. $\sqrt{P}$

- Full details:
  - Jakes et al. (2008) *J. Mater. Res.* **23**(4) pp. 1113.
  - Jakes et al. (2009) *J. Mater. Res.* **24**(3) pp. 1016.
  - Jakes and Stone. (2010) *Phil. Mag.* **91**(7-9) pp. 1387

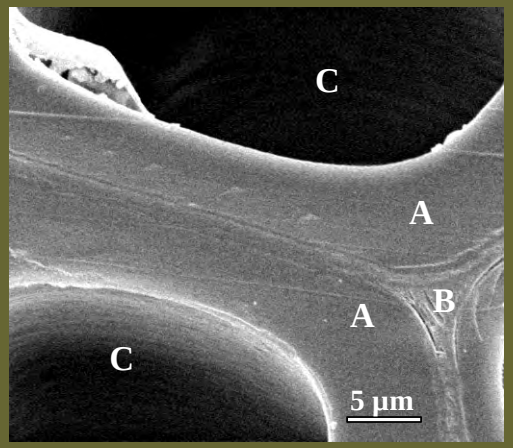




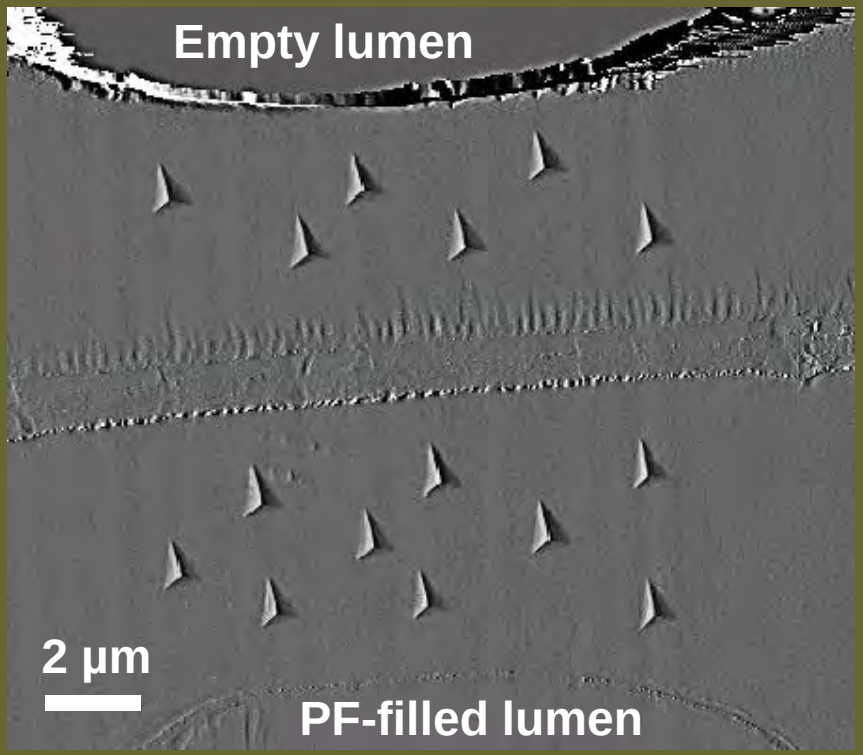


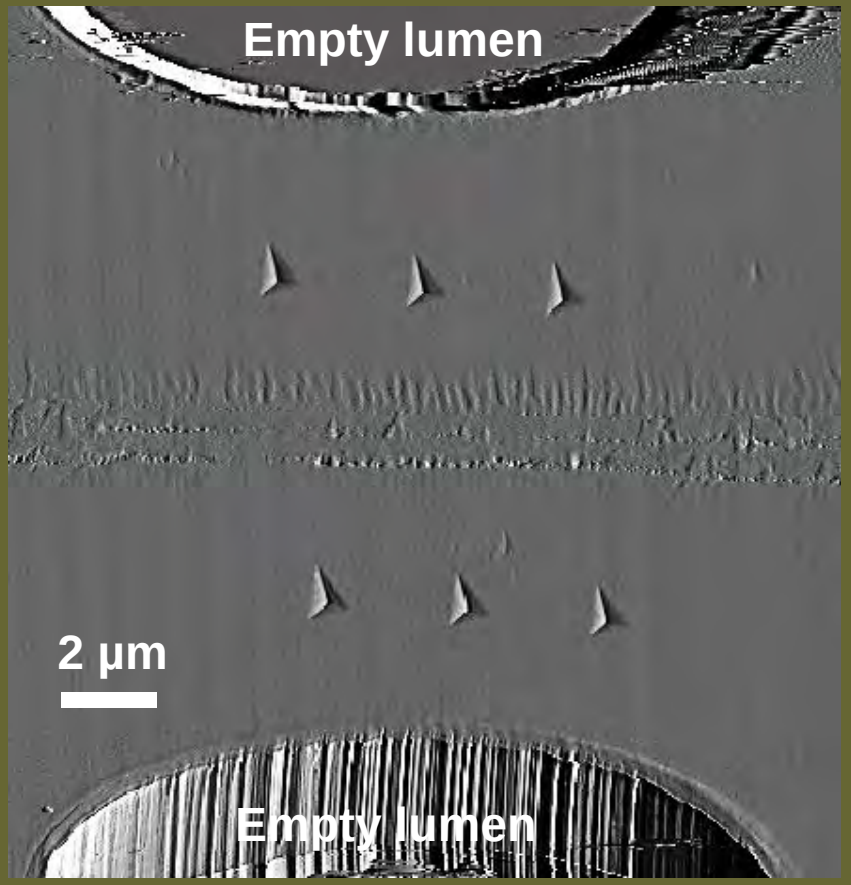
Nanoindentation Procedure for Wood

- Nanoindentation surface prepared on surface remaining after 2 µm-thick XFM section removed
- Nanoindentation
  - Hysitron TriboIndenter equipped with a Berkovich tip
  - Relative humidity (RH) controlled with RH generator
    - RH = 78% and dry air (<1%)
  - Room Temperature
    - 20-23°C
  - Multiload indents
  - Structural compliance method utilized

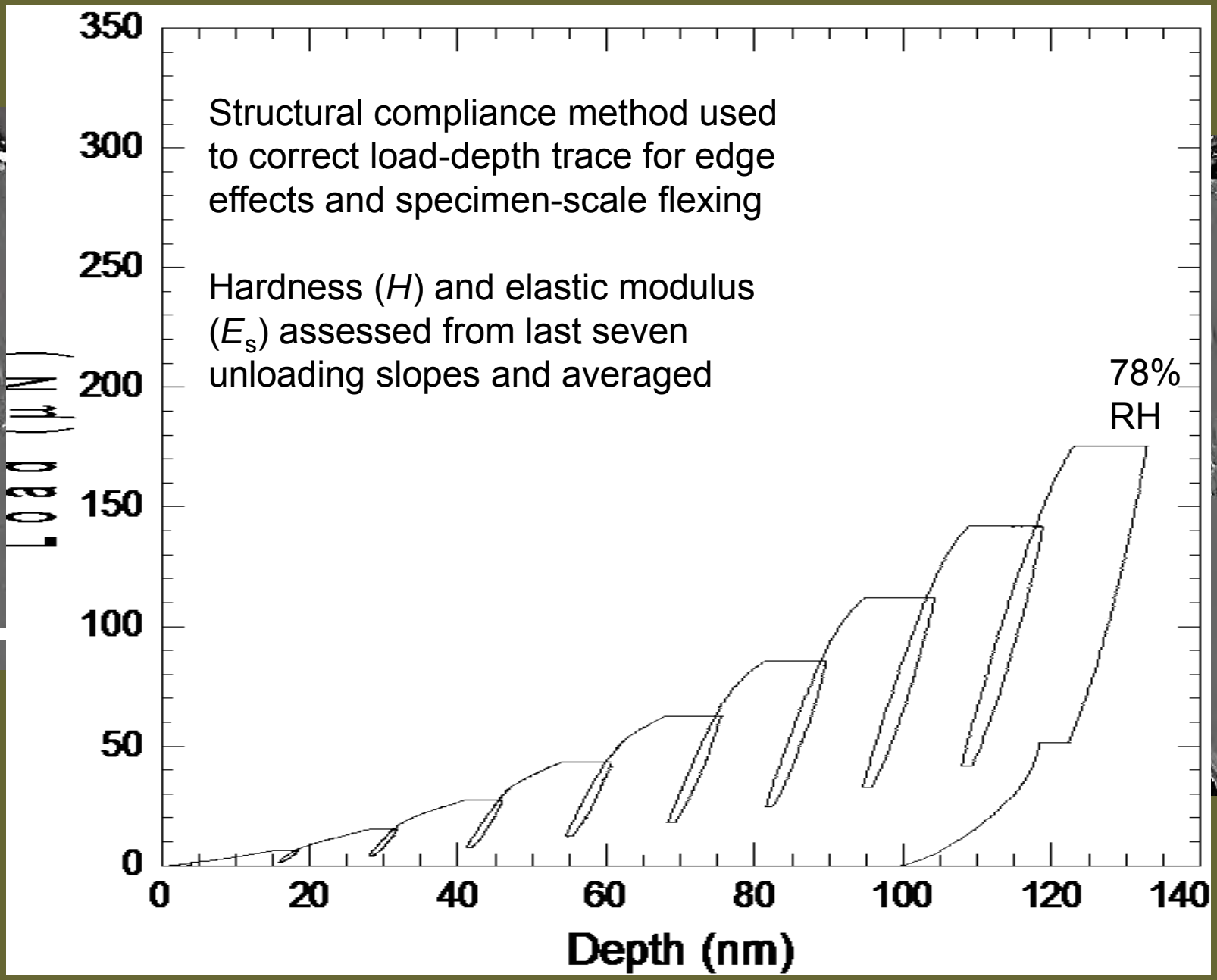


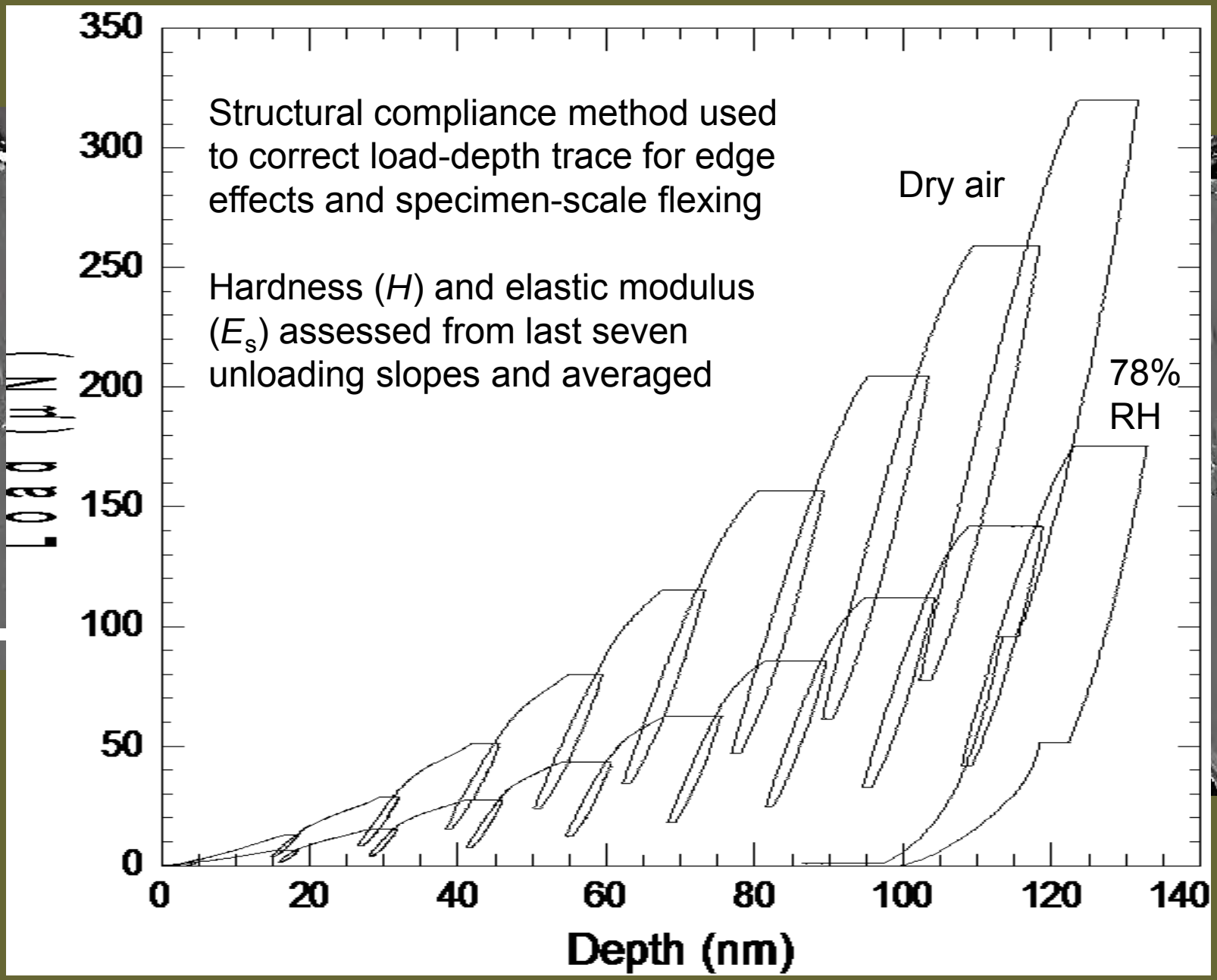
A: S2 cell wall laminae (S2CWL)
B: Compound corner middle lamella (CCML)
C: Empty lumina

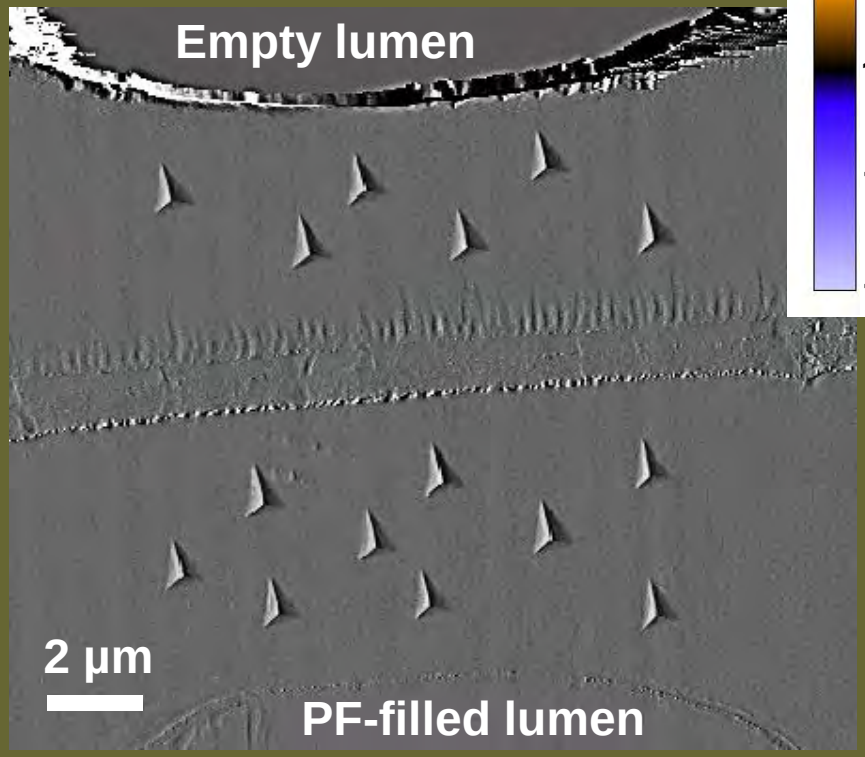


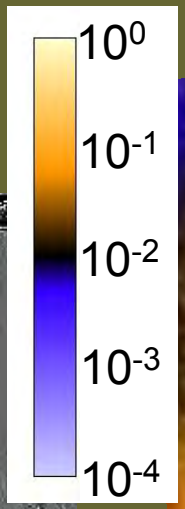


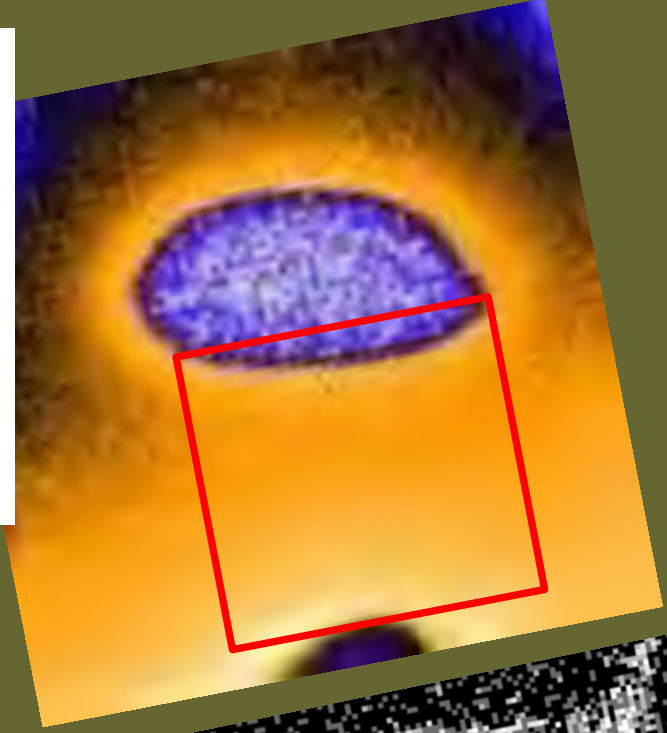
Atomic force microscopy (AFM) images of residual indents


Structural compliance method used to correct load-depth trace for edge effects and specimen-scale flexing
Hardness (H) and elastic modulus (E_s) assessed from last seven unloading slopes and averaged
78% RH
Load (μN)
Depth (nm)
0
50
100
150
200
250
300
350
0
20
40
60
80
100
120
140

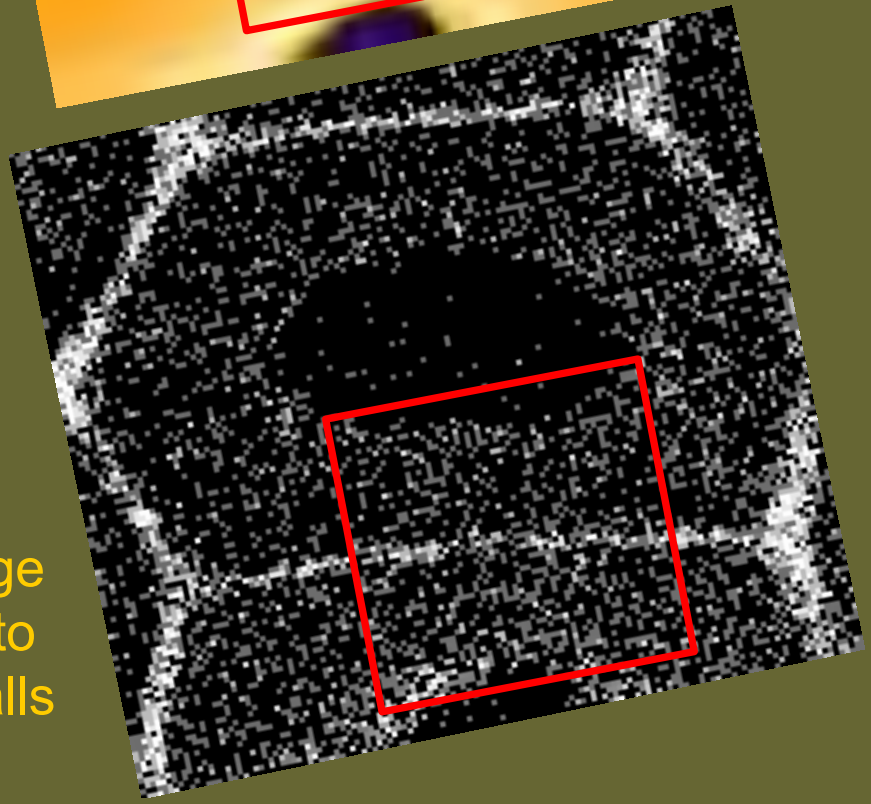

Structural compliance method used to correct load-depth trace for edge effects and specimen-scale flexing
Hardness (H) and elastic modulus (E_s) assessed from last seven unloading slopes and averaged
Dry air
78% RH
Load (μN)
Depth (nm)
0
50
100
150
200
250
300
350
0
20
40
60
80
100
120
140



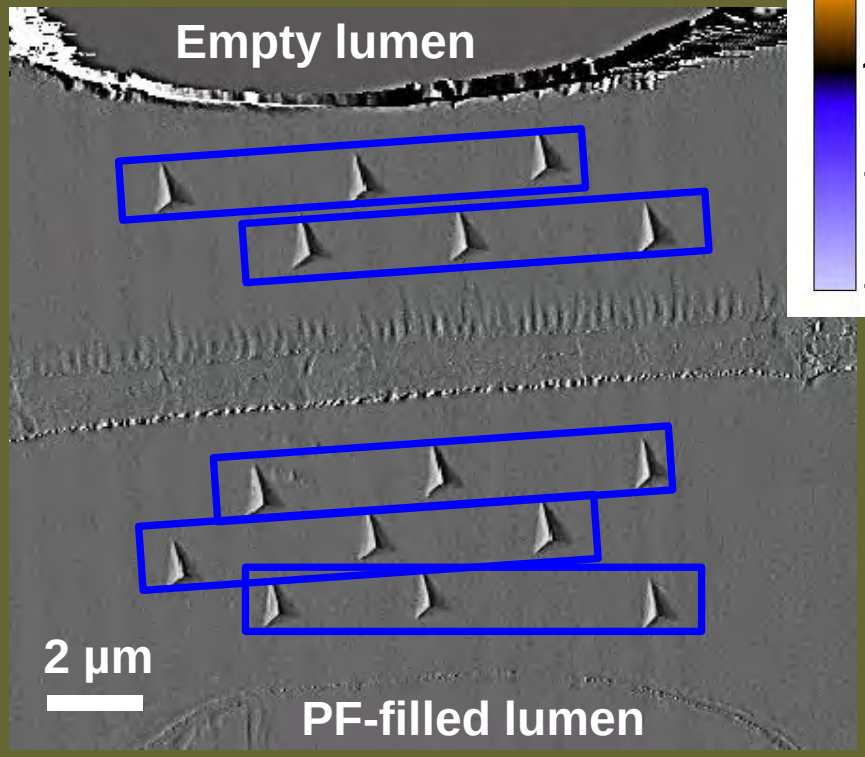


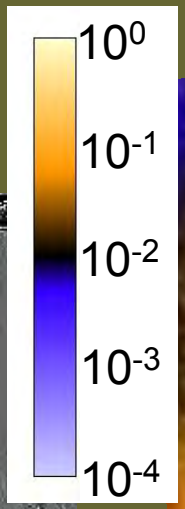


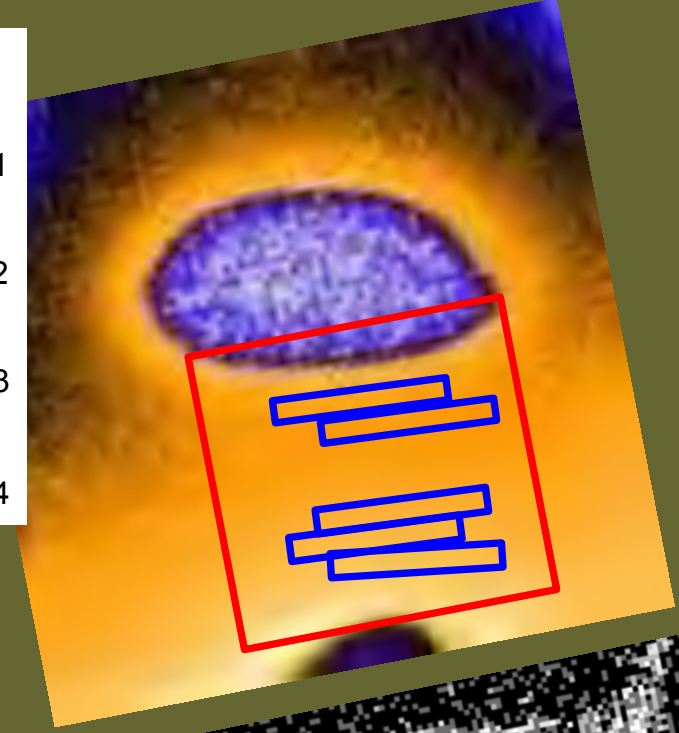
Br XFM image (log scale)



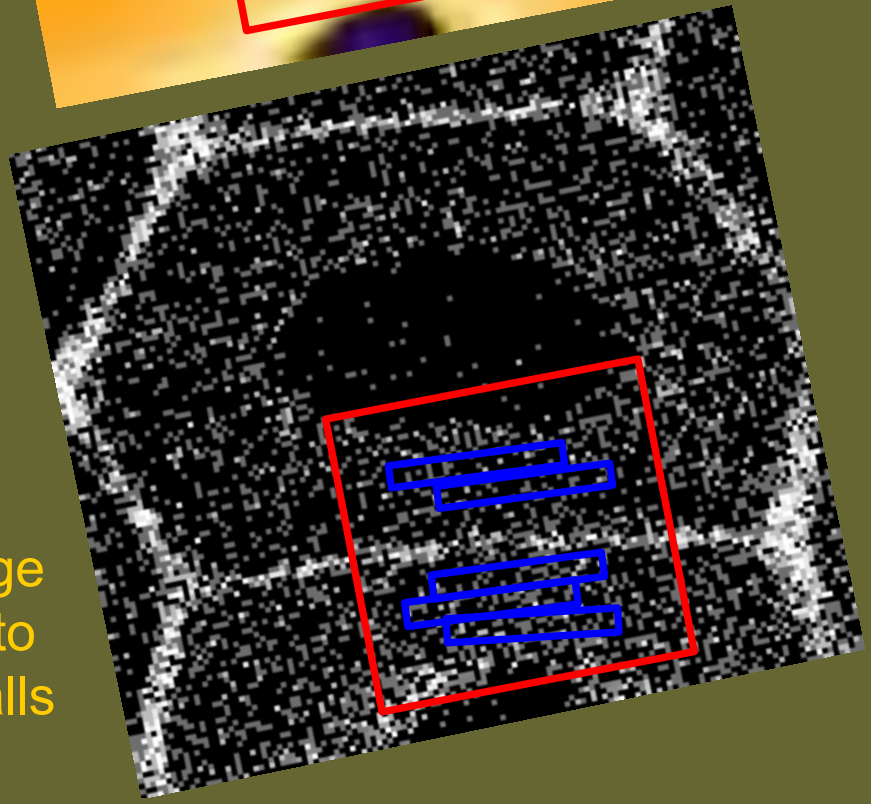
Zn XFM image used as aid to locate cell walls







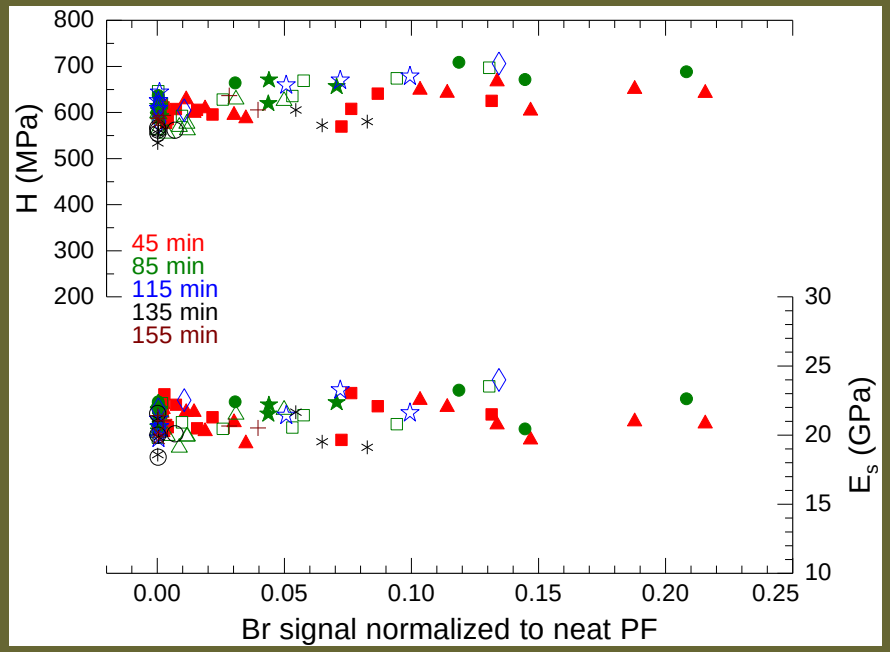
Br XFM image (log scale)



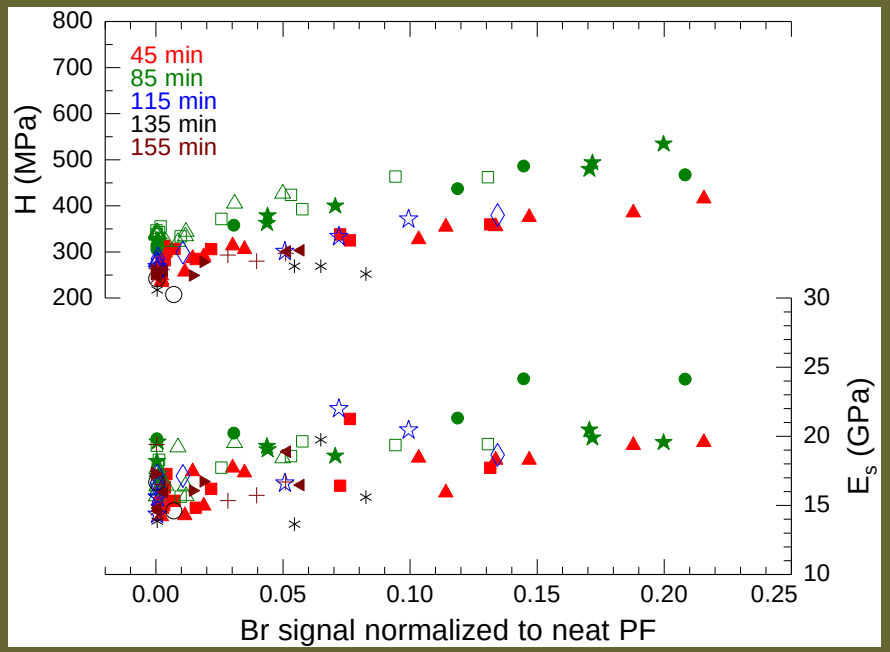
Define ROI's with multiple indents equidistant from lumen edge

Zn XFM image used as aid to locate cell walls

Dry air



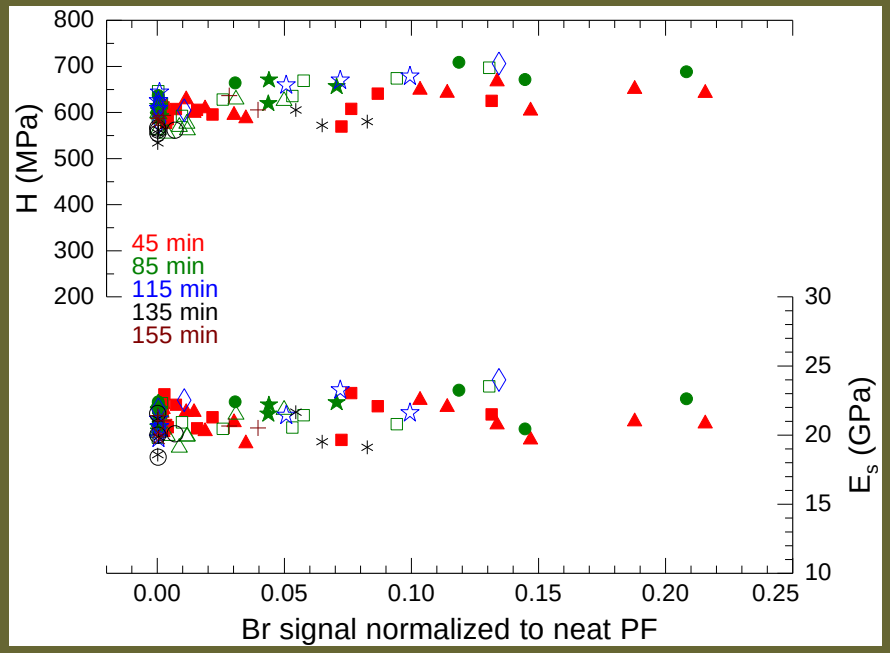
78% RH



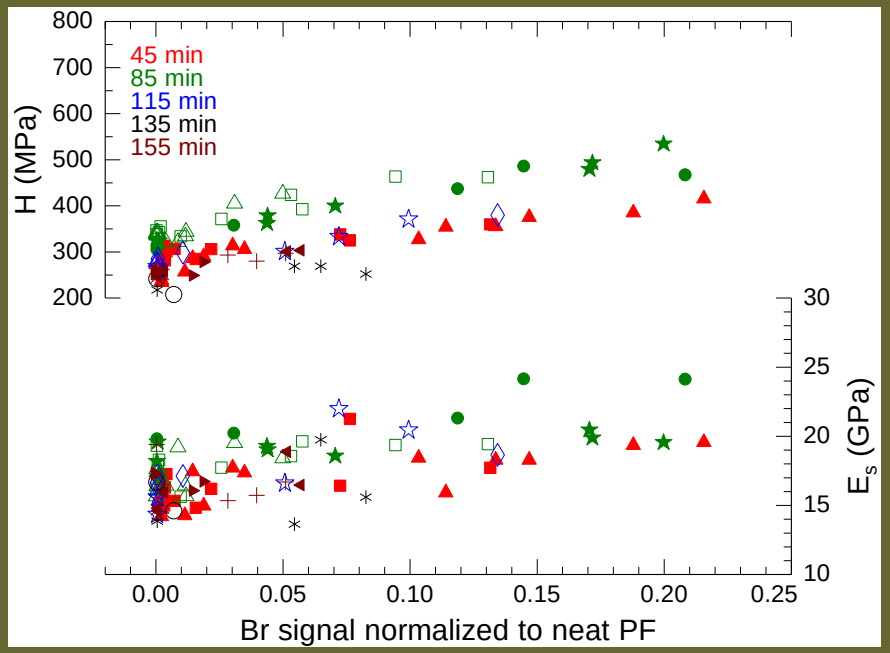
Each symbol type represents a different series

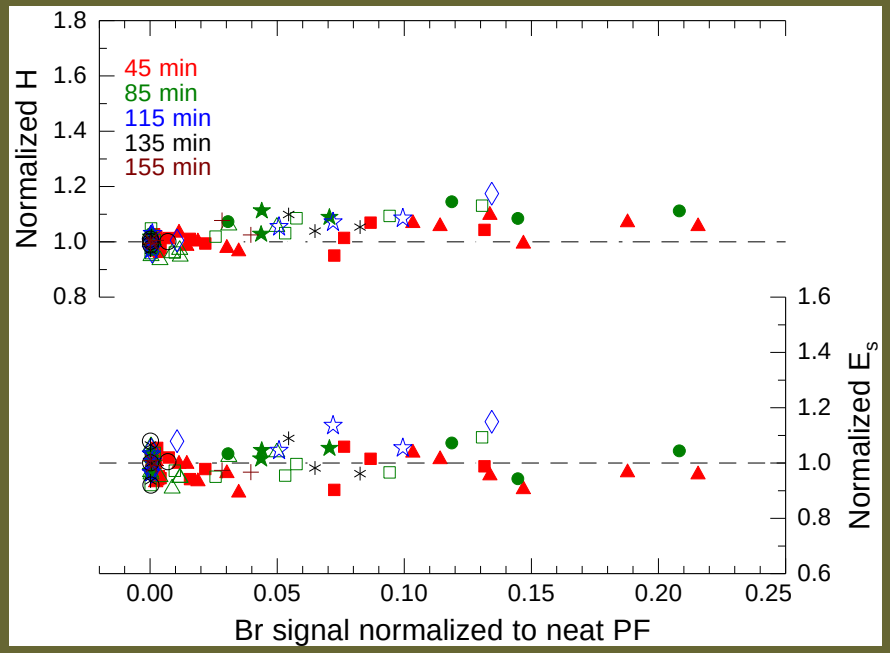
Each data point represents average properties within ROI

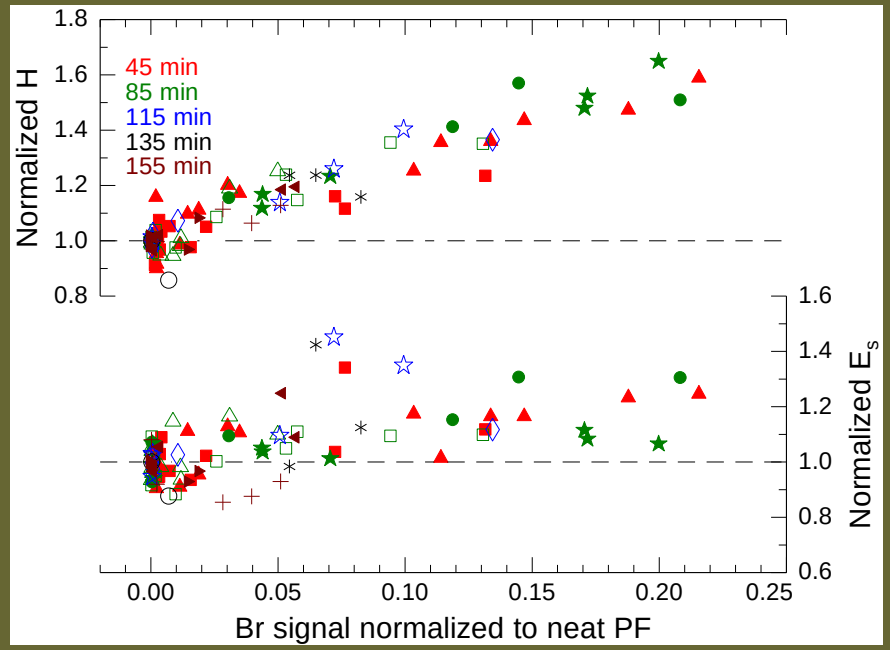
Dry air


H (MPa)
E_s (GPa)
45 min
85 min
115 min
135 min
155 min
Br signal normalized to neat PF

78% RH


H (MPa)
E_s (GPa)
45 min
85 min
115 min
135 min
155 min
Br signal normalized to neat PF


Normalized H
Normalized E_s
45 min
85 min
115 min
135 min
155 min
Br signal normalized to neat PF

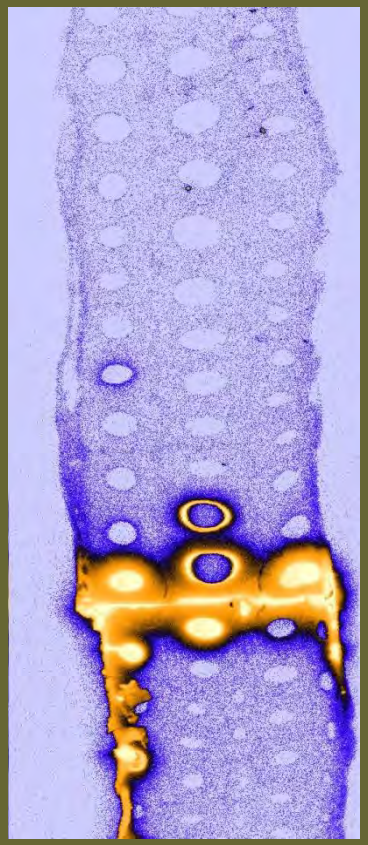

Normalized H
Normalized E_s
45 min
85 min
115 min
135 min
155 min
Br signal normalized to neat PF

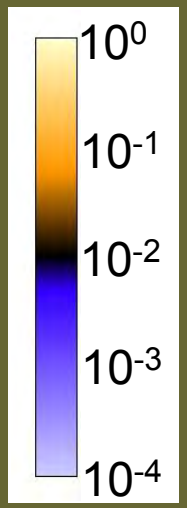
Conclusions

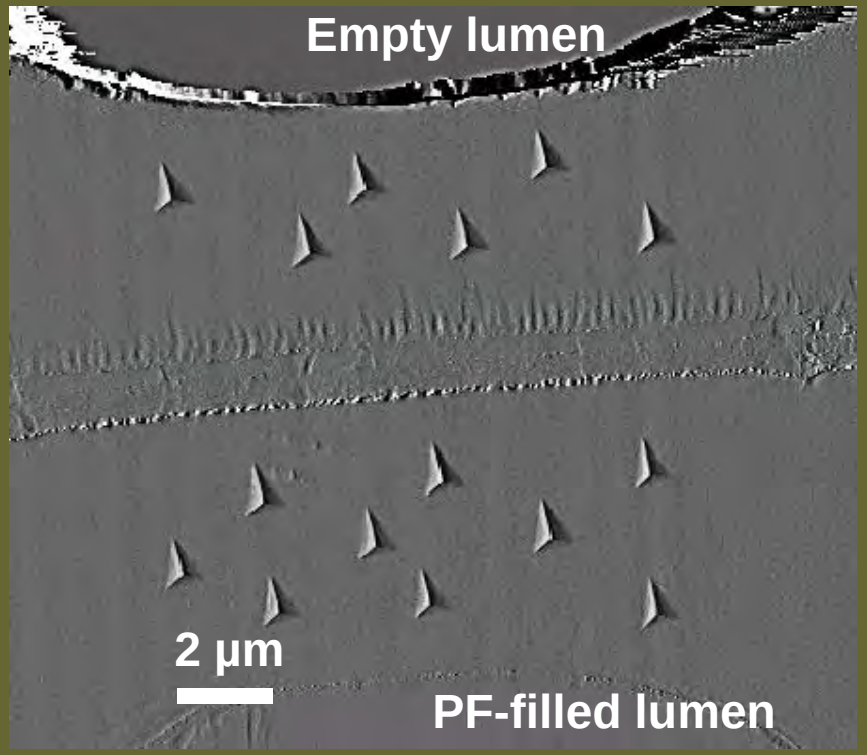
- Synchrotron-based XFM has sensitivity and spatial resolution to map out Br-labeled PF infiltrated into wood cell walls
- Higher MW PF (longer cook times) infiltrate less into cell walls near bondline
- Hardness and elastic modulus directly proportional to PF infiltration
- PF infiltration decreases moisture-induced softening of wood cell walls

Jakes, J.E., S.-C. Gleber, S. Vogt, C.G. Hunt, D. Yelle, W. Grigsby, C. Frihart. 2013. New syncrotron-based technique to map adhesive infiltration in wood cell walls. In the Proceedings of 36th Annual Meeting of the Adhesion Society held in Daytona Beach, FL, USA on March 3-6, 2013. Available online at http://adhesionsociety.org/program2013/

Questions?







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- Federal Highway Administration for funding