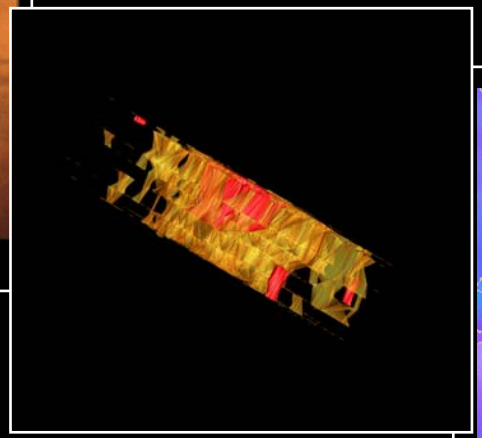
Lecture given by
Prof. Dierk Raabe (d.raabe@mpie.de)
at University Cambridge
12. May 2006

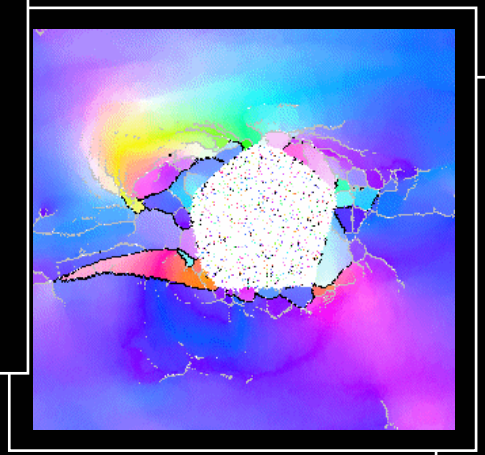
shortened version for the
edoc System of Max Planck Society
without movies

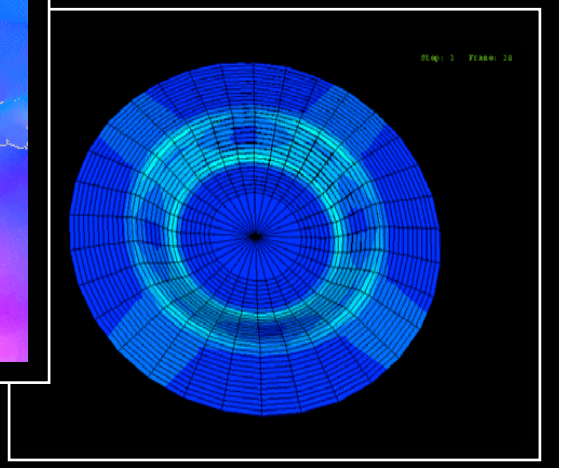
Crystal Mechanics and Fresh Lobster

Dierk Raabe

Roters, Ma: crystal mechanics
Sachs, Romano, Al-Sawalmih, Fabritius: chitin-composites
Zaefferer, Bastos: 3D Microscopy
Neugebauer, Petrov, Limperakis: ab initio and MD







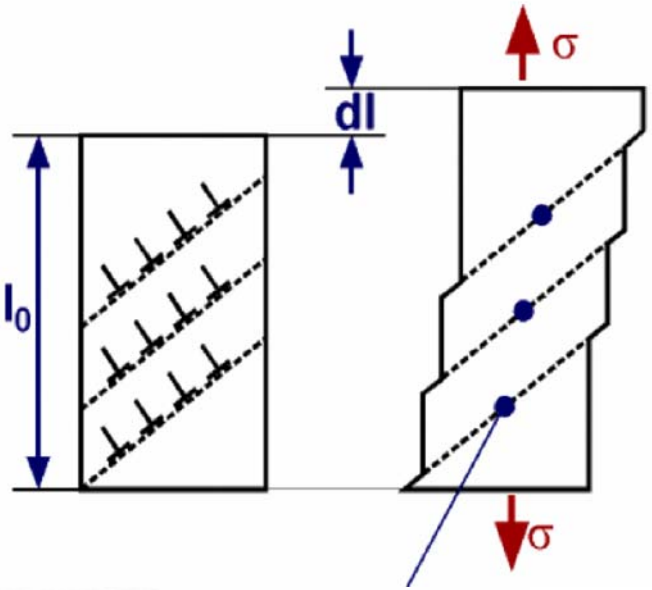
Overview

Mechanics of few crystals (CP-FEM)

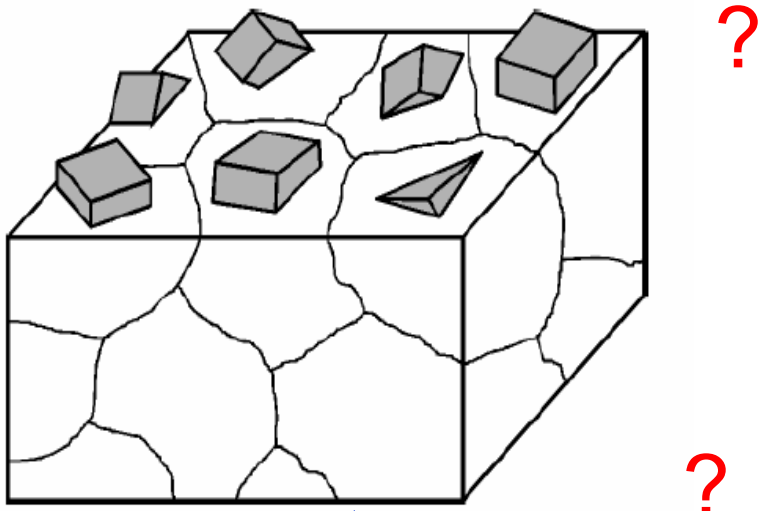
Mechanics of many crystals (TF-CP-FEM)

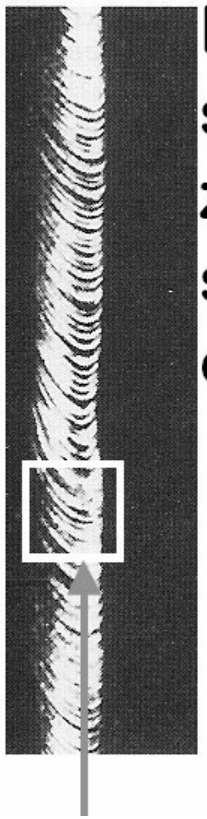
3D electron microscopy

Chitin-composites



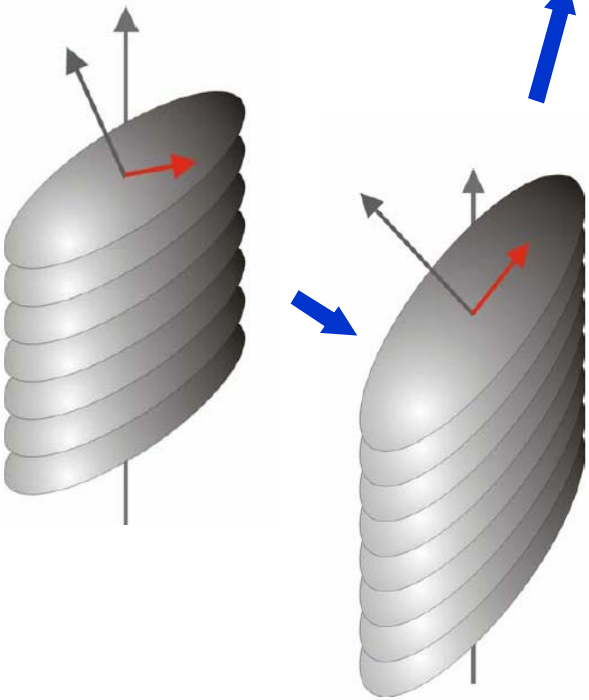
strain is the symmetric part of plasticity

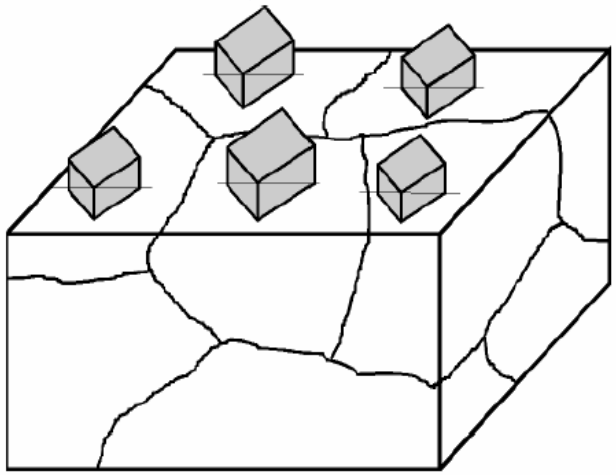




Plastically stretched zinc single crystal.

Adapted from Fig. 7.9, *Callister 6e.* (Fig. 7.9 is from C.F. Elam, *The Distortion of Metal Crystals*, Oxford University Press, London, 1935.)

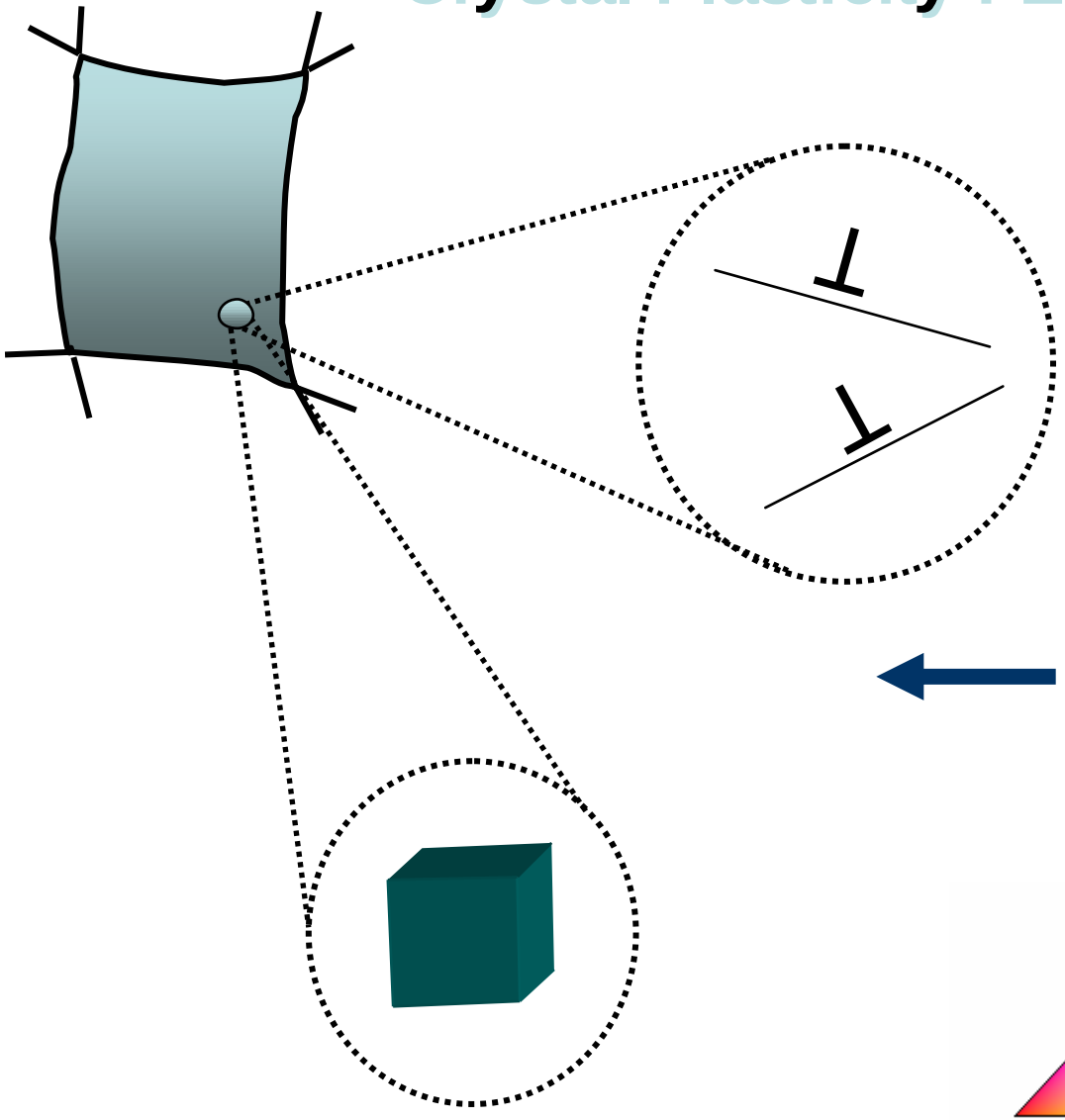


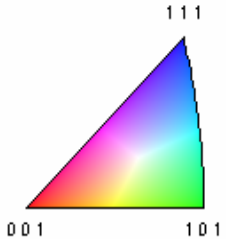


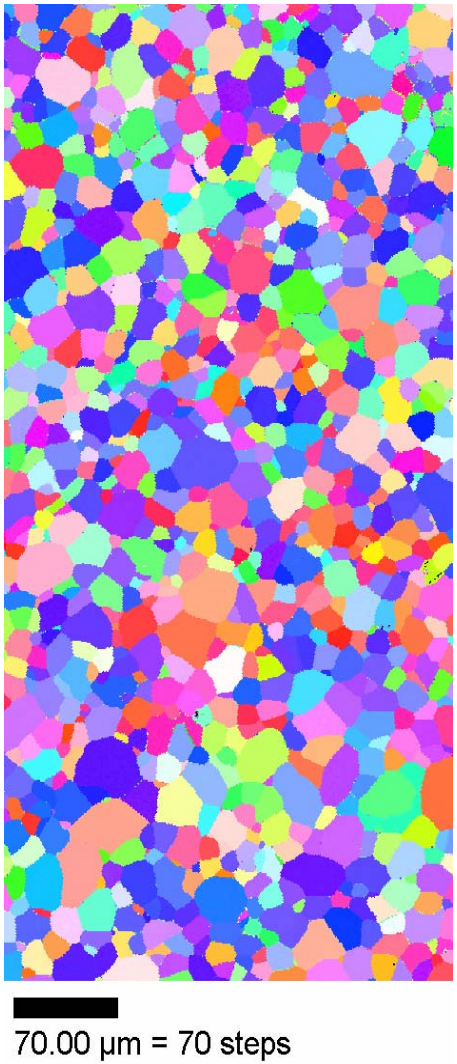
rotation (texture) is the antisymmetric part of plasticity

Crystal Mechanics FEM (General)

Crystal Plasticity FEM (CPFEM) - Family







Crystal Plasticity FEM (include more physics)

Multiplicative Decomposition of the Deformation Gradient

F* : elastic and rotation deformation gradient
F : total deformation gradient
Fp : plastic deformation gradient
Lp : plastic velocity gradient
Le : elastic velocity gradient

flow law

constitutive reduction of DOF:

$$\tilde{\mathbf{L}}_{\mathrm{p}} = \sum_{\alpha=1}^{24} \dot{\gamma}_\alpha \tilde{\mathbf{d}}_\alpha \otimes \tilde{\mathbf{n}}_\alpha$$

$\dot{\gamma}_\alpha(\tau_\alpha, \tau_{c\alpha}, \theta)$ ——— Phenomenological

$\dot{\gamma}_\alpha(\tau_\alpha, \boldsymbol{\rho}, \theta)$ ——— Dislocation density laws

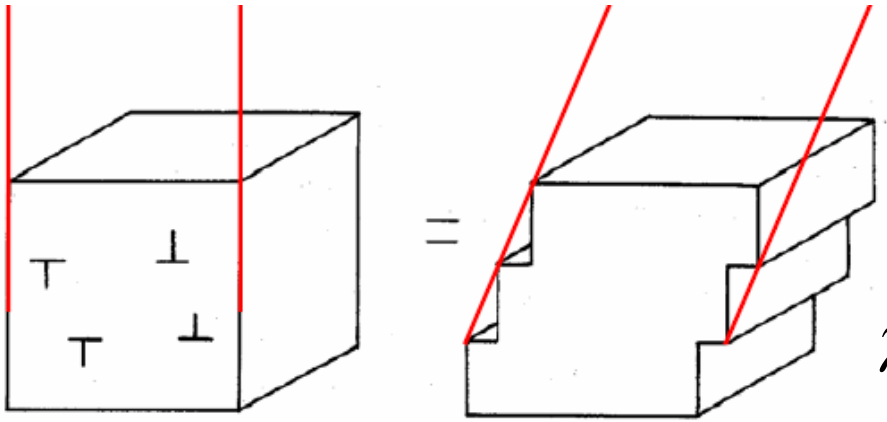
Definitions:

$$\mathbf{L} := \dot{\mathbf{F}}\mathbf{F}^{-1}$$

$$\mathbf{L}_{\mathbf{e}} := \dot{\mathbf{F}}_{\mathrm{e}}\mathbf{F}_{\mathrm{e}}^{-1}$$

$$\tilde{\mathbf{L}}_{\mathrm{p}} := \dot{\mathbf{F}}_{\mathrm{p}}\mathbf{F}_{\mathrm{p}}^{-1}$$

$$\mathbf{L}_{\mathrm{p}} := \mathbf{F}_{\mathrm{e}}\tilde{\mathbf{L}}_{\mathrm{p}}\mathbf{F}_{\mathrm{e}}^{-1}$$



$$\dot{\gamma} = \frac{\mathrm{d}\gamma}{\mathrm{d}t} = n\frac{\mathrm{d}x}{X}\frac{b}{Z}\frac{1}{\mathrm{d}t} = \rho_{\mathrm{m}} b v$$

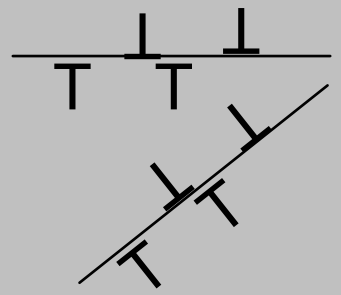
physics-based constitutive laws

1

1. set internal variables

dyadic flow law based on <u>dislocation rate theory</u>

Taylor, Kocks, Mecking, Estrin,....

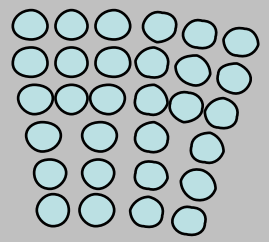


2

2. set internal variables

plastic <u>gradients</u>,
size scale and orientation gradients (implicit)

Nye, Ashby1, Kröner,....

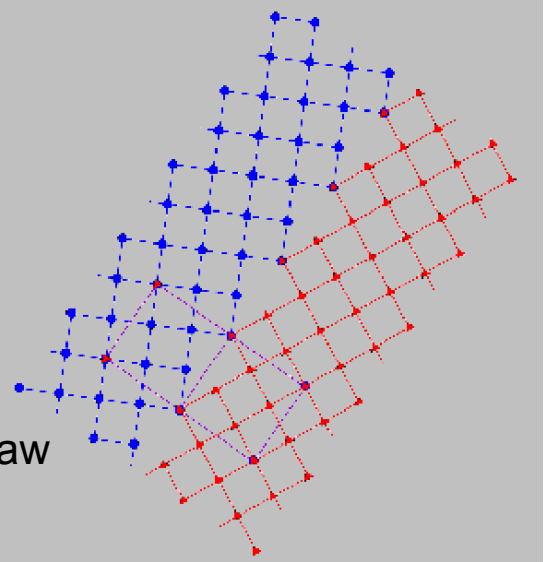


3

3. set internal variables

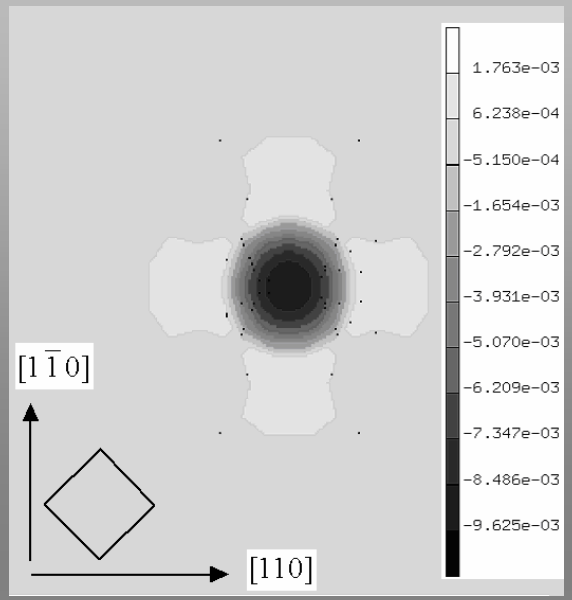
grain <u>boundaries</u>

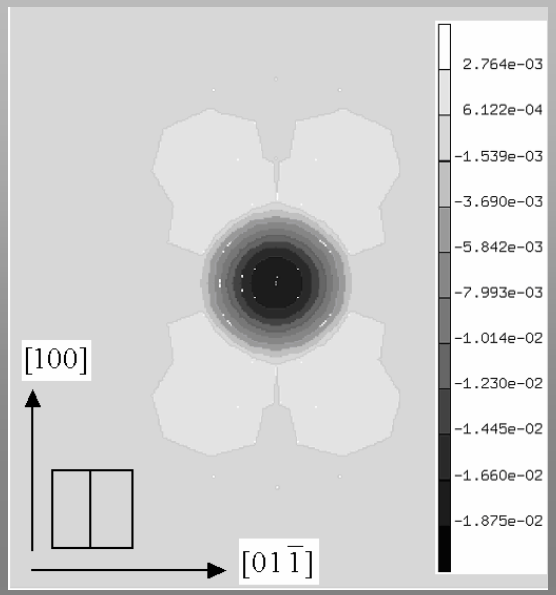
activation concept:
energy of formation upon slip penetration: conervation law

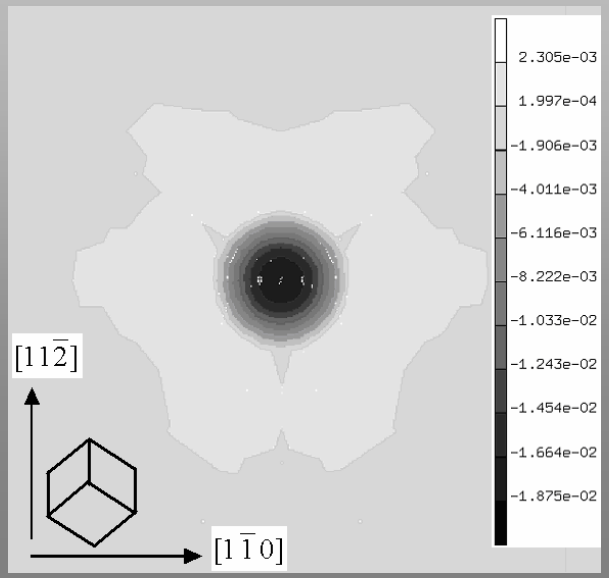


Nanoindentation - 2D

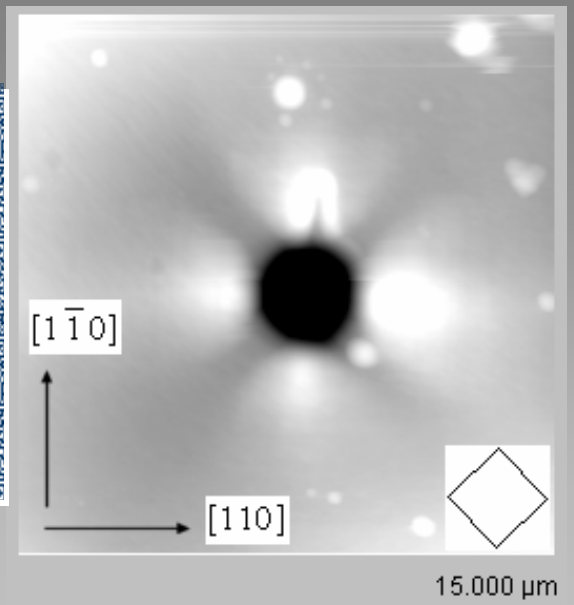
simulation

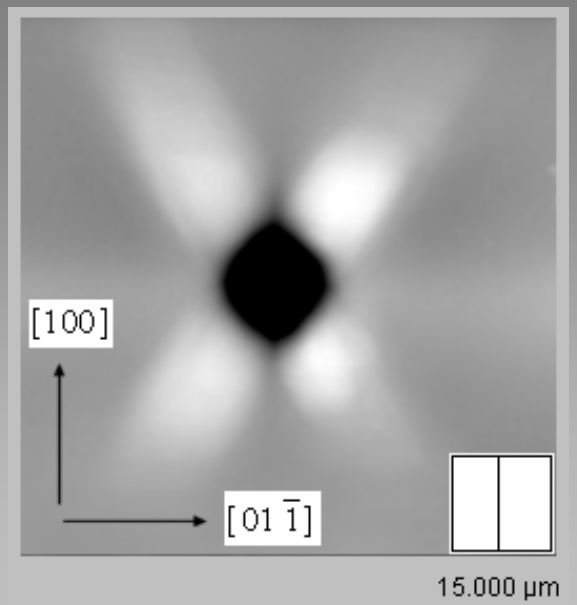


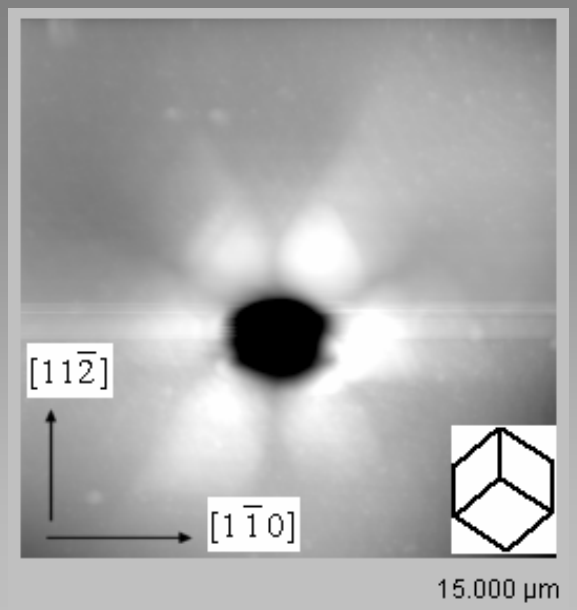




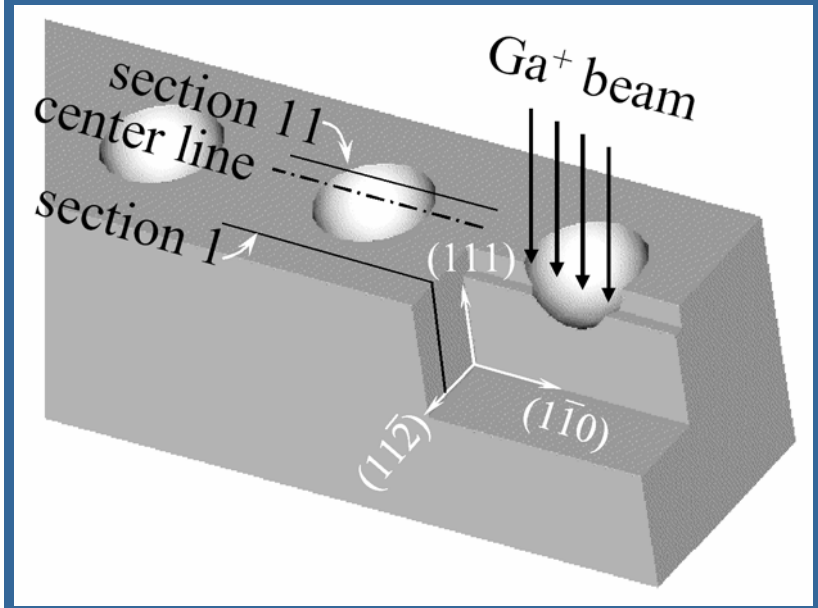
experiment

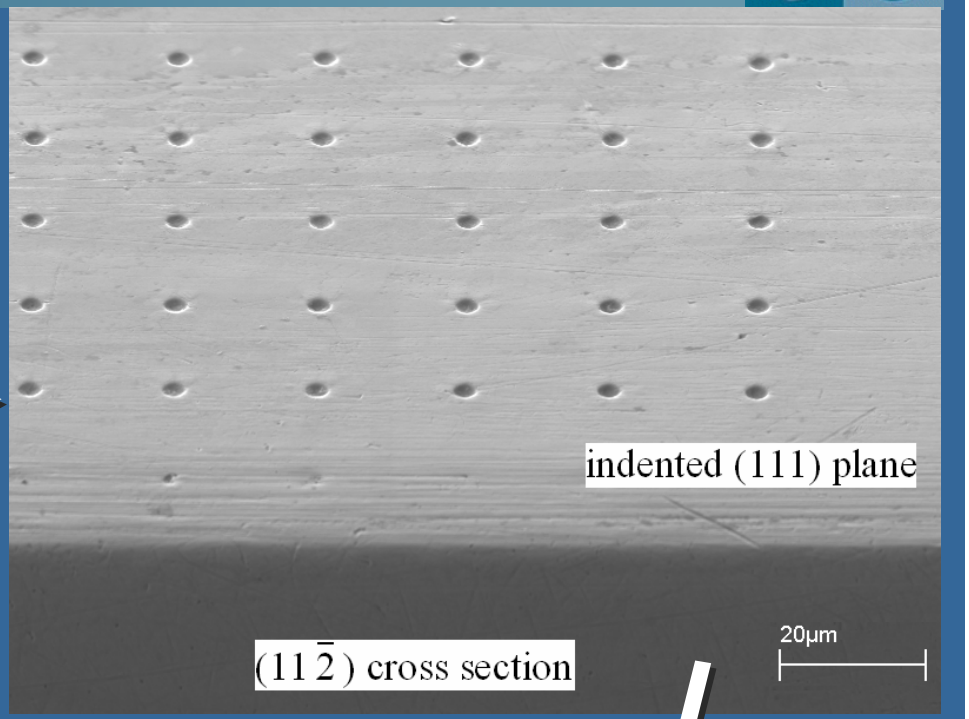


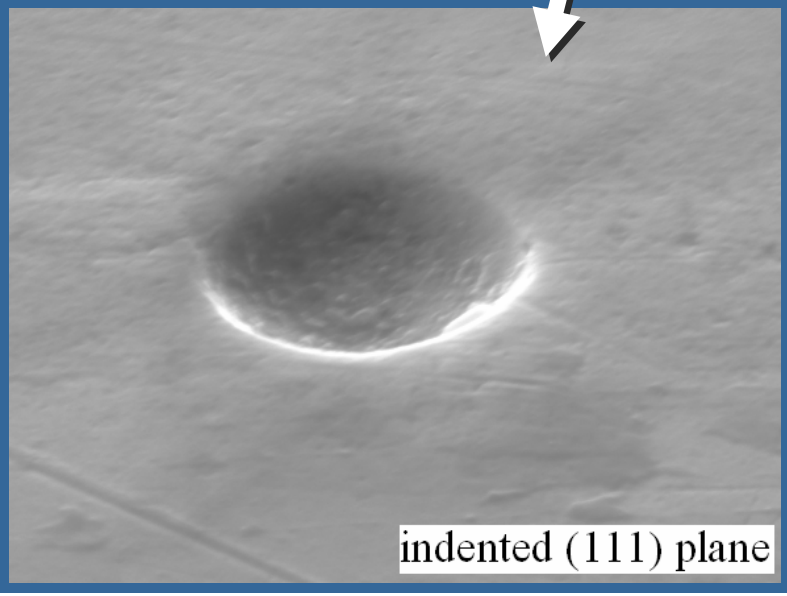


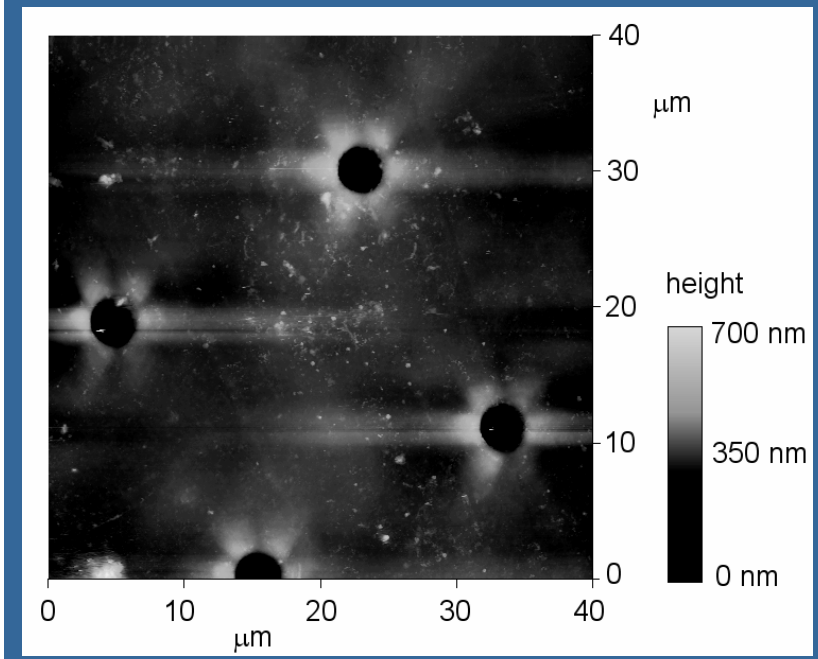


Nanoindentation - 3D

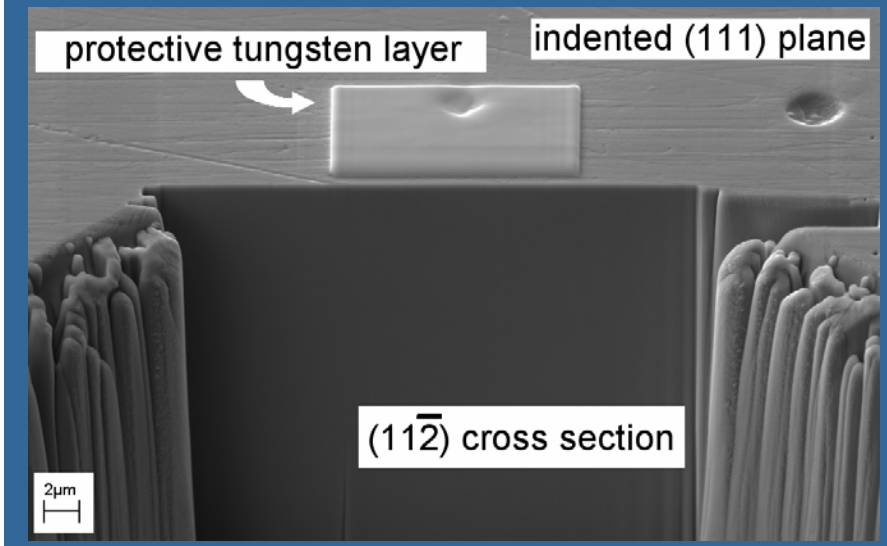


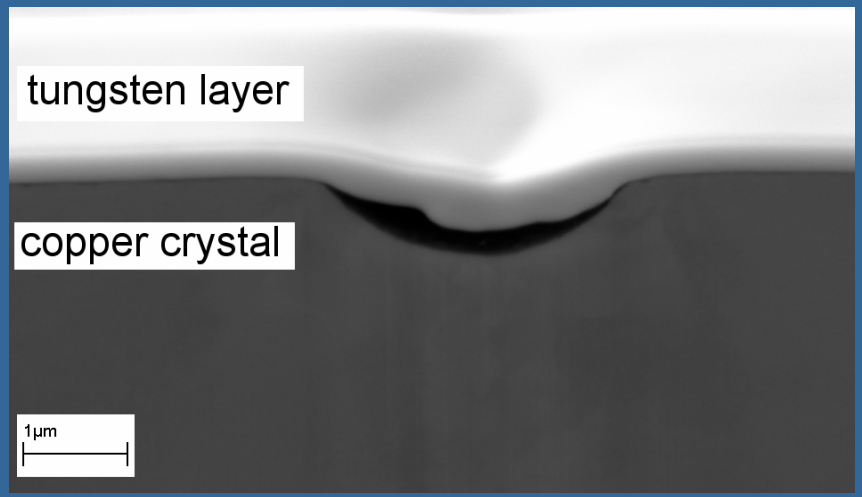




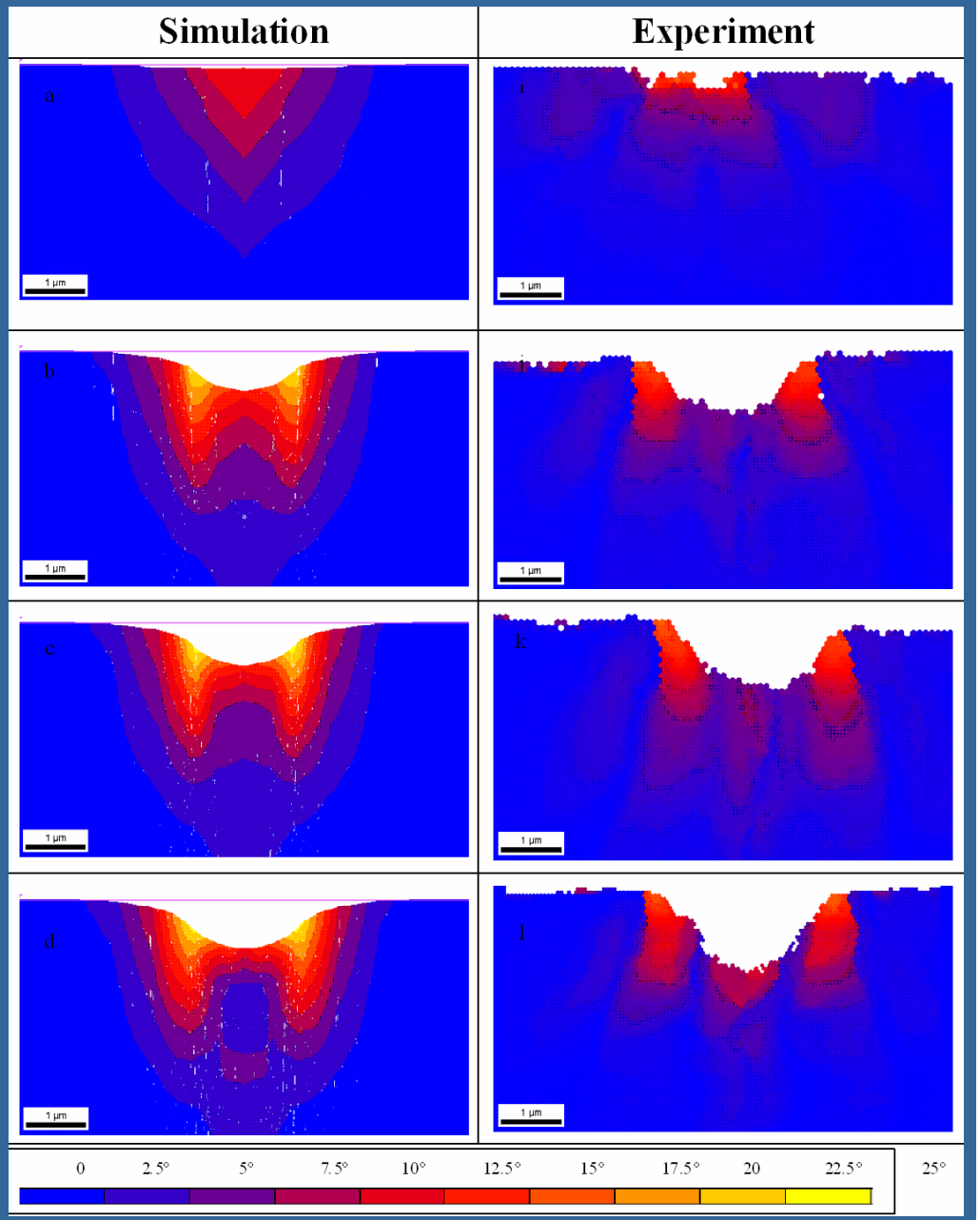


Nanoindentation - 3D

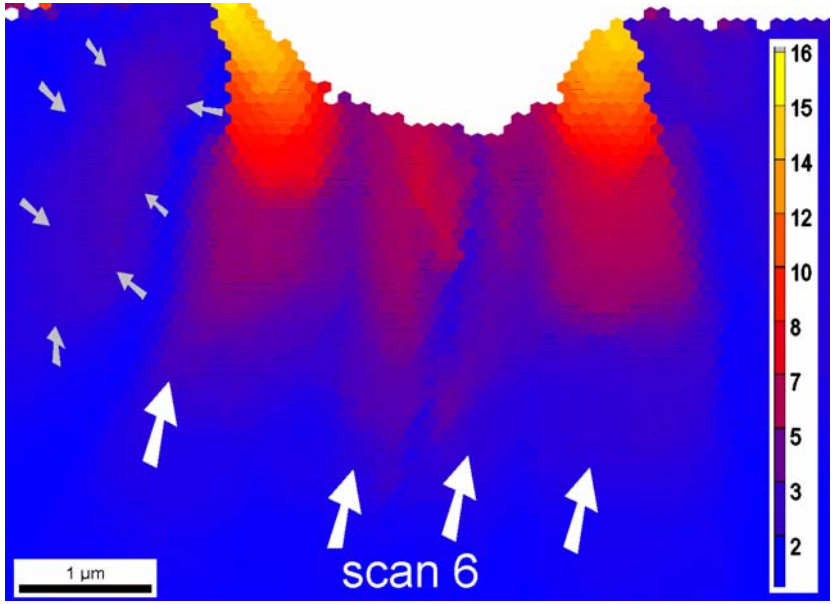


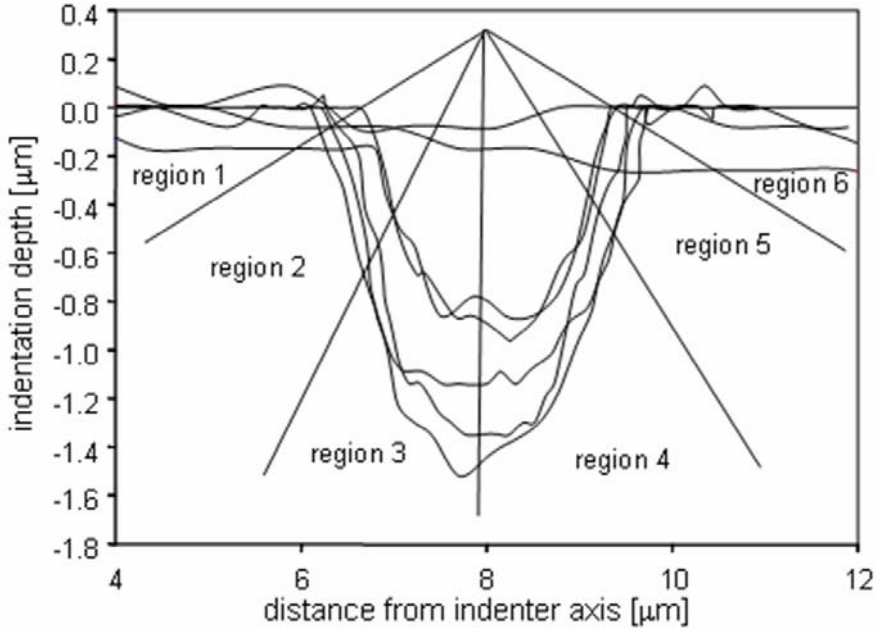


absolute values of orientation change



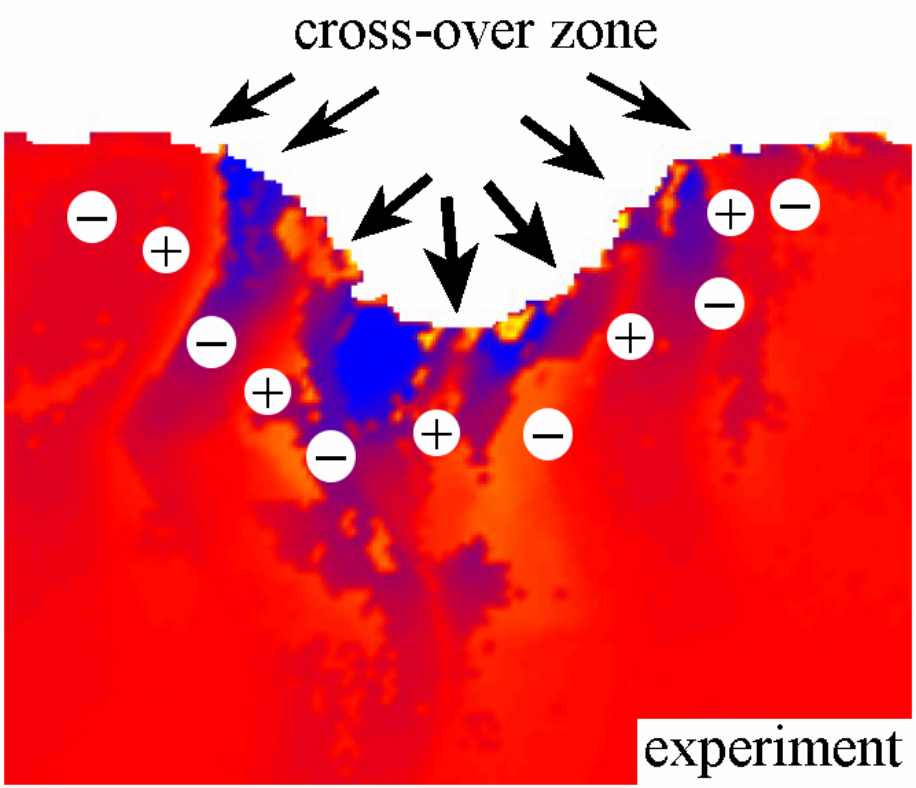
Nanoindentation - 3D



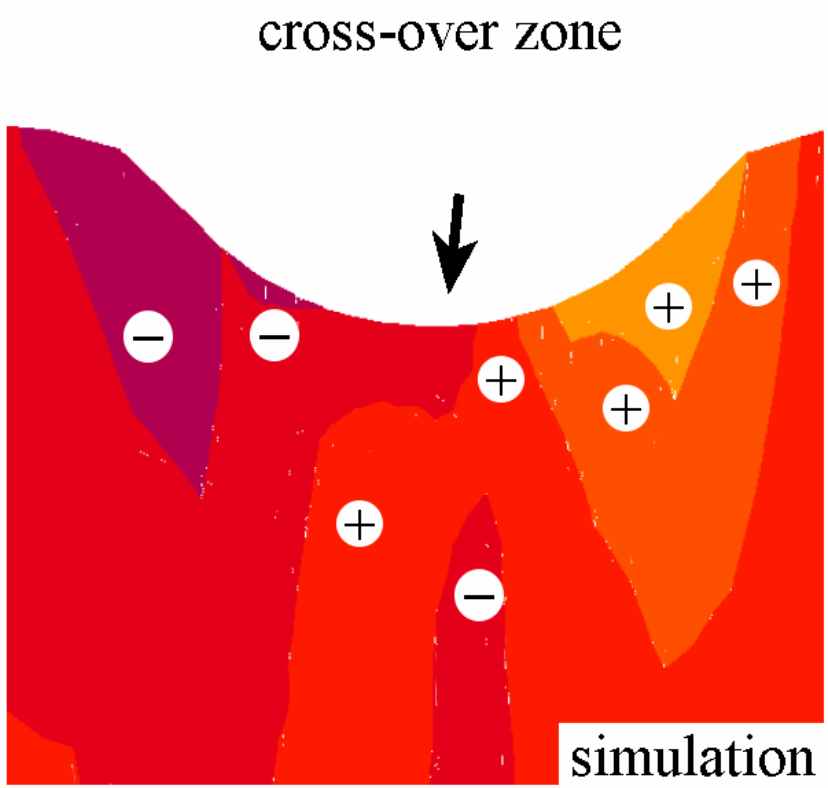


Closer view of the experimentally observed pattern of the absolute values of the deformation-induced crystalline lattice rotations in ° in the vicinity of the indent

Nanoindentation - 3D

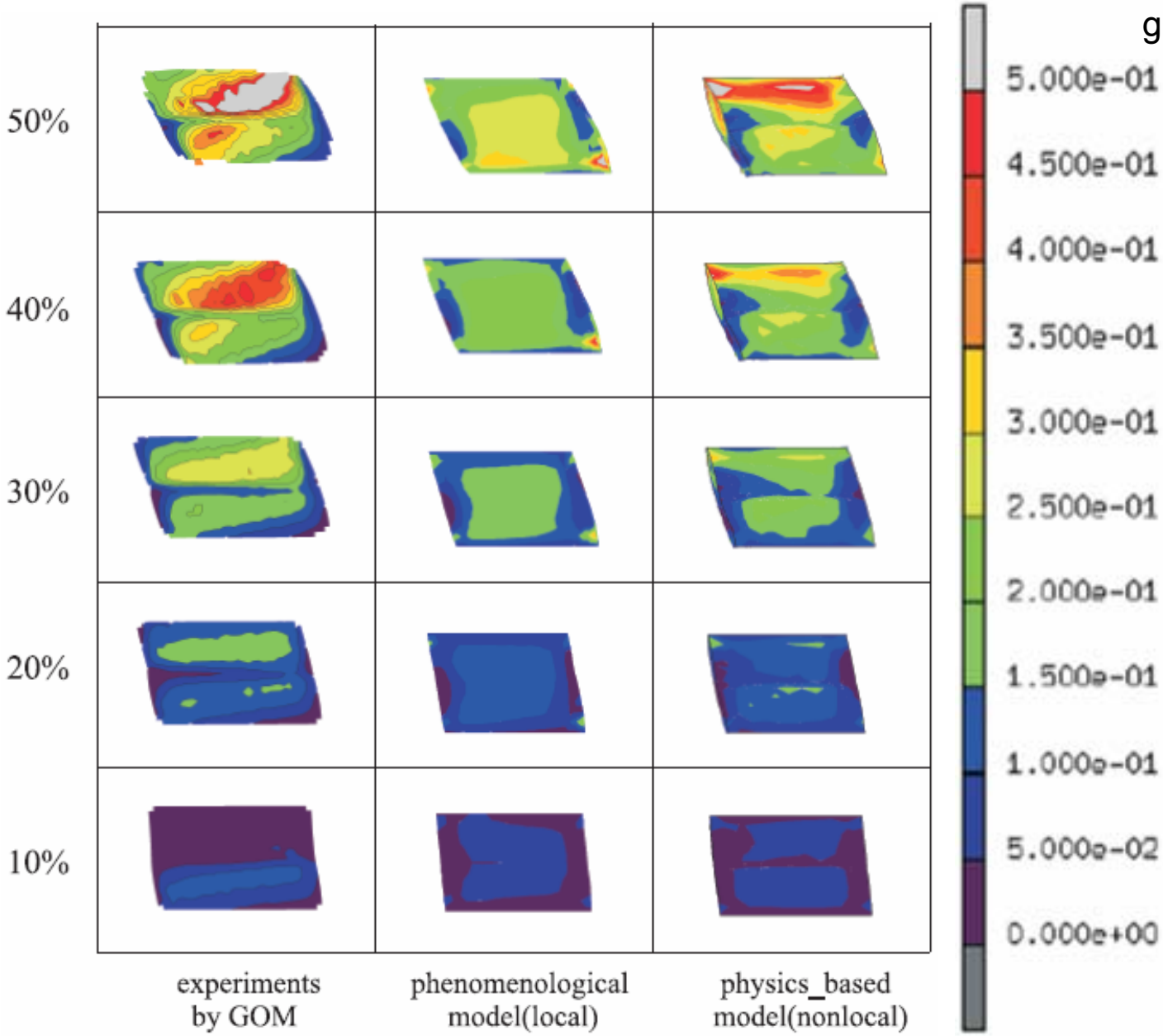


$(11\bar{2})$ plane; scaled: -8° to +8°
rotation axis: $[11\bar{2}]$



$(11\bar{2})$ plane; scaled: -20° to +20°
rotation axis: $[11\bar{2}]$

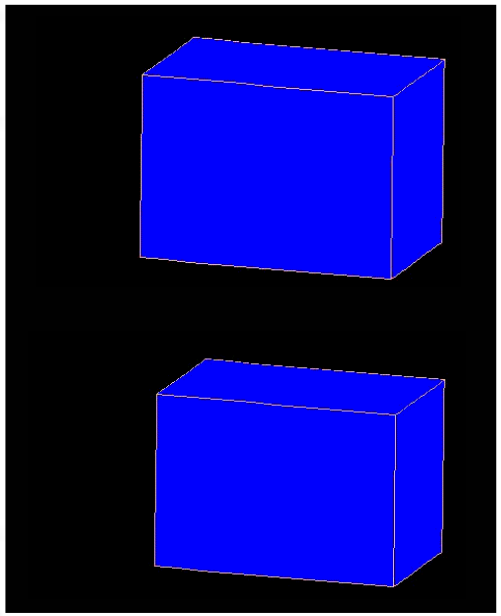
Bicrystals



grain boundary mechanics

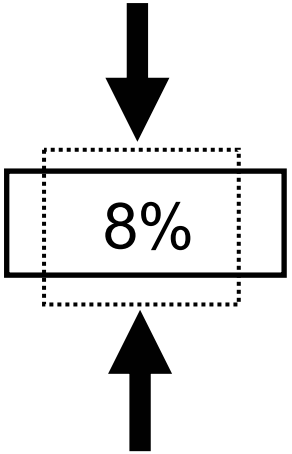
7.4°
v. Mises
Al

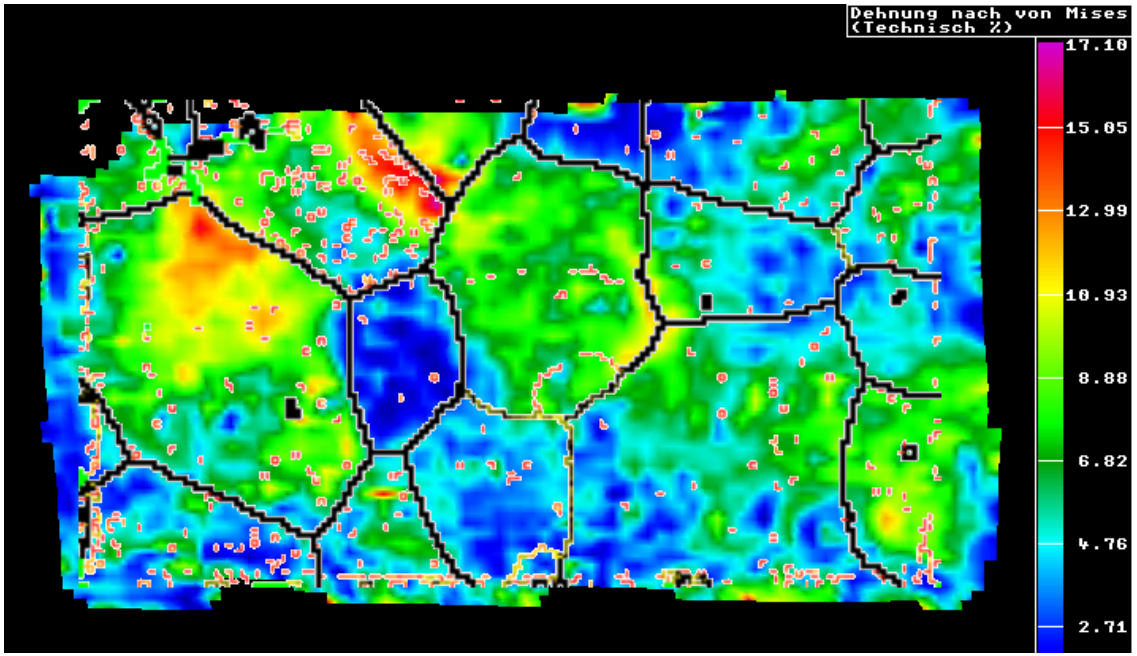
SSD



GND

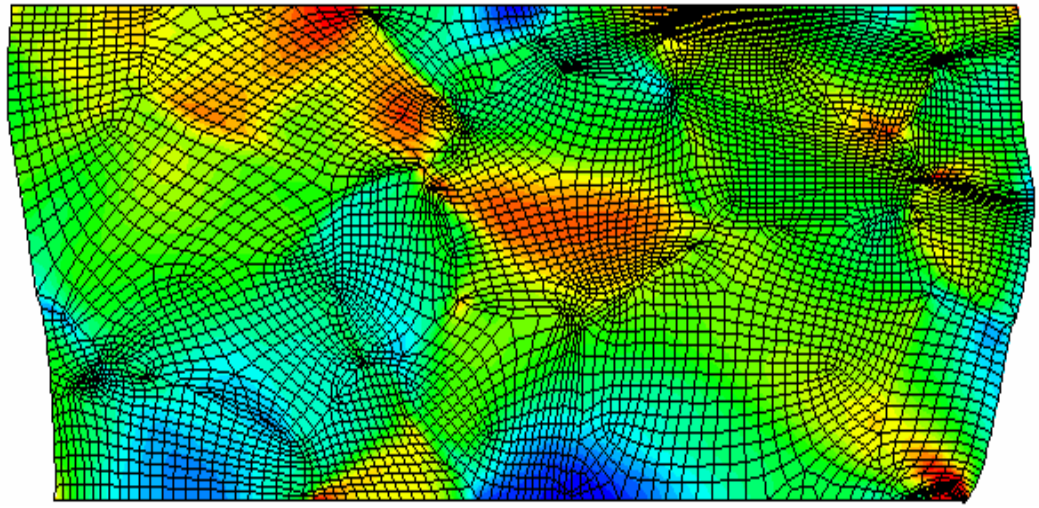
2D Oligocrystals (few grains), Al, plane strain



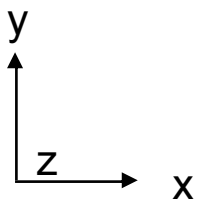


Experiment
(DIC, EBSD)
v Mises strain

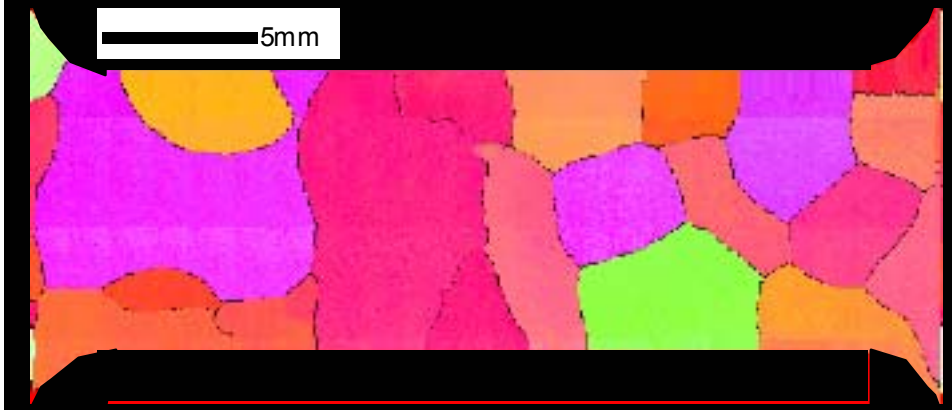
von-Mises strain

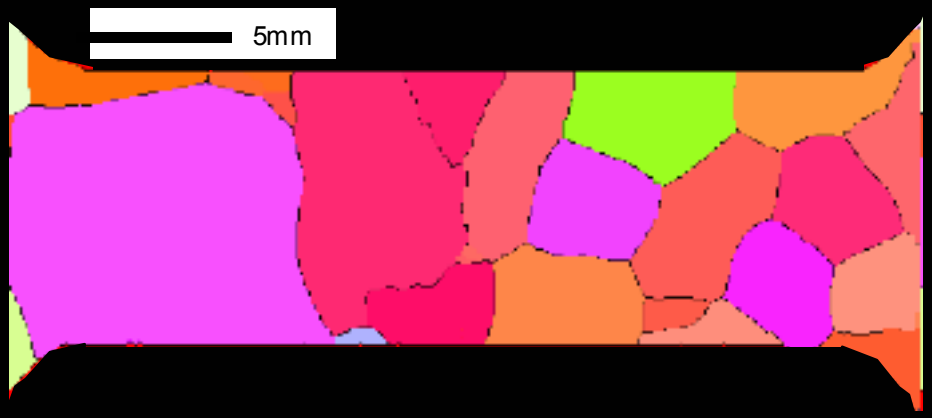


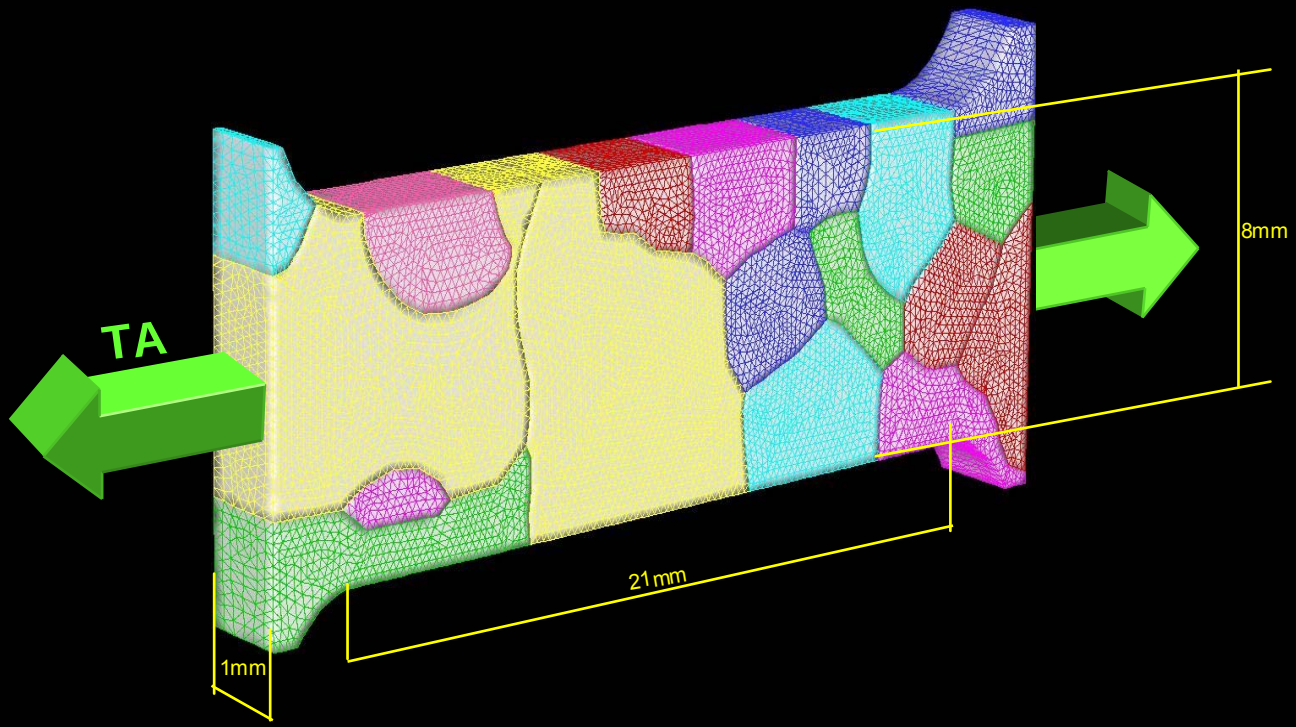
Simulation
(CP-FEM)
v Mises strain



3D Oligocrystals (few grains), Al, 1000 processors





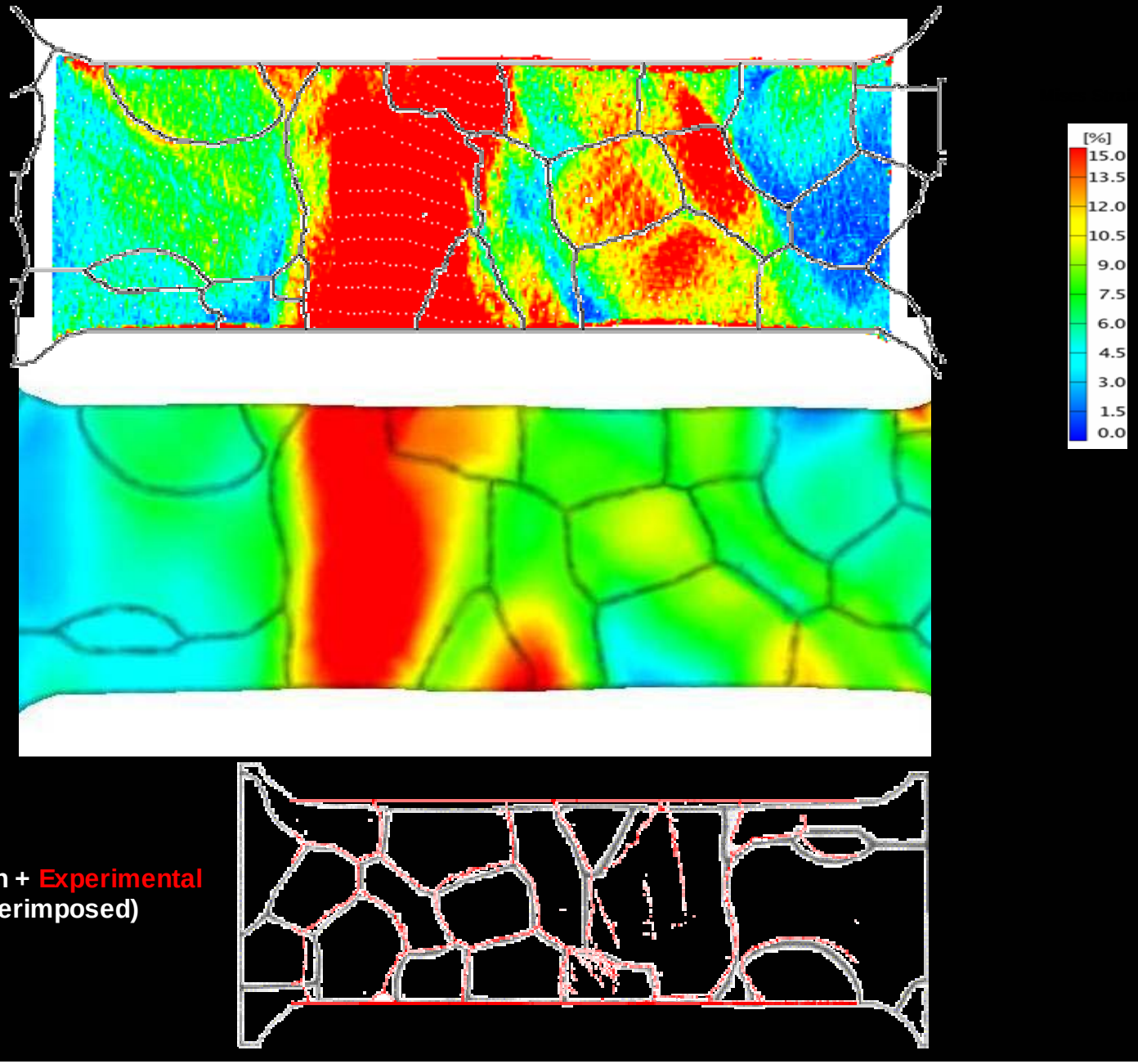


3D Oligocrystals (few grains), Al

Experimental

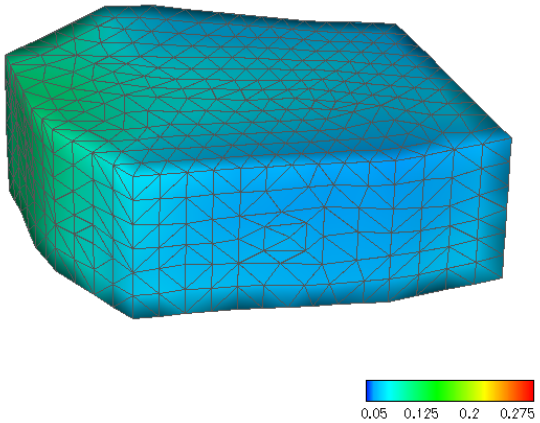
Simulation

Simulation + Experimental
(Superimposed)

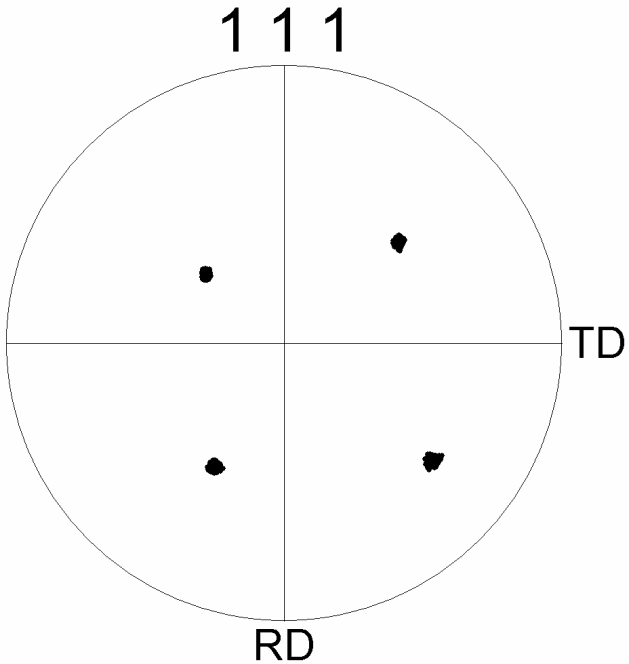


3D Oligocrystals (few grains), Al

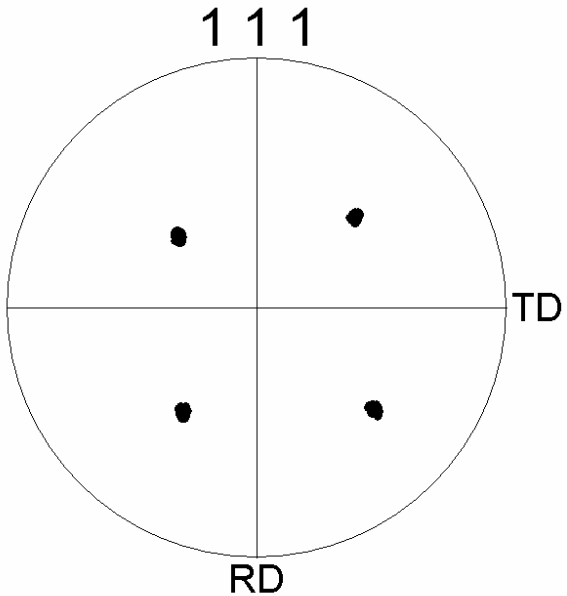
Grain 15



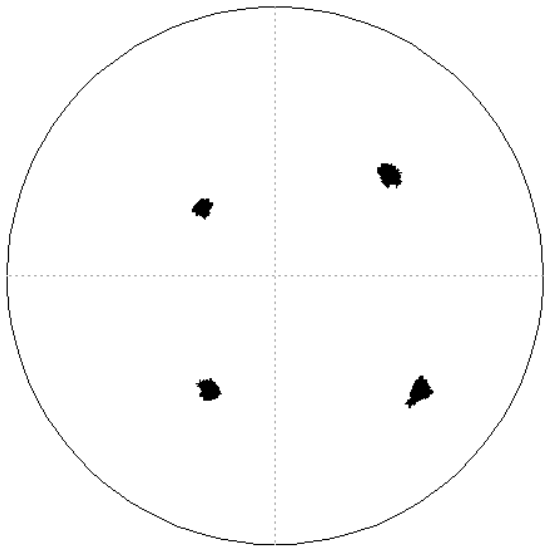
Initial Experimental Polefigure



Deformed Experimental Polefigure



Simulated Polefigure



Overview

Mechanics of few crystals (CP-FEM)

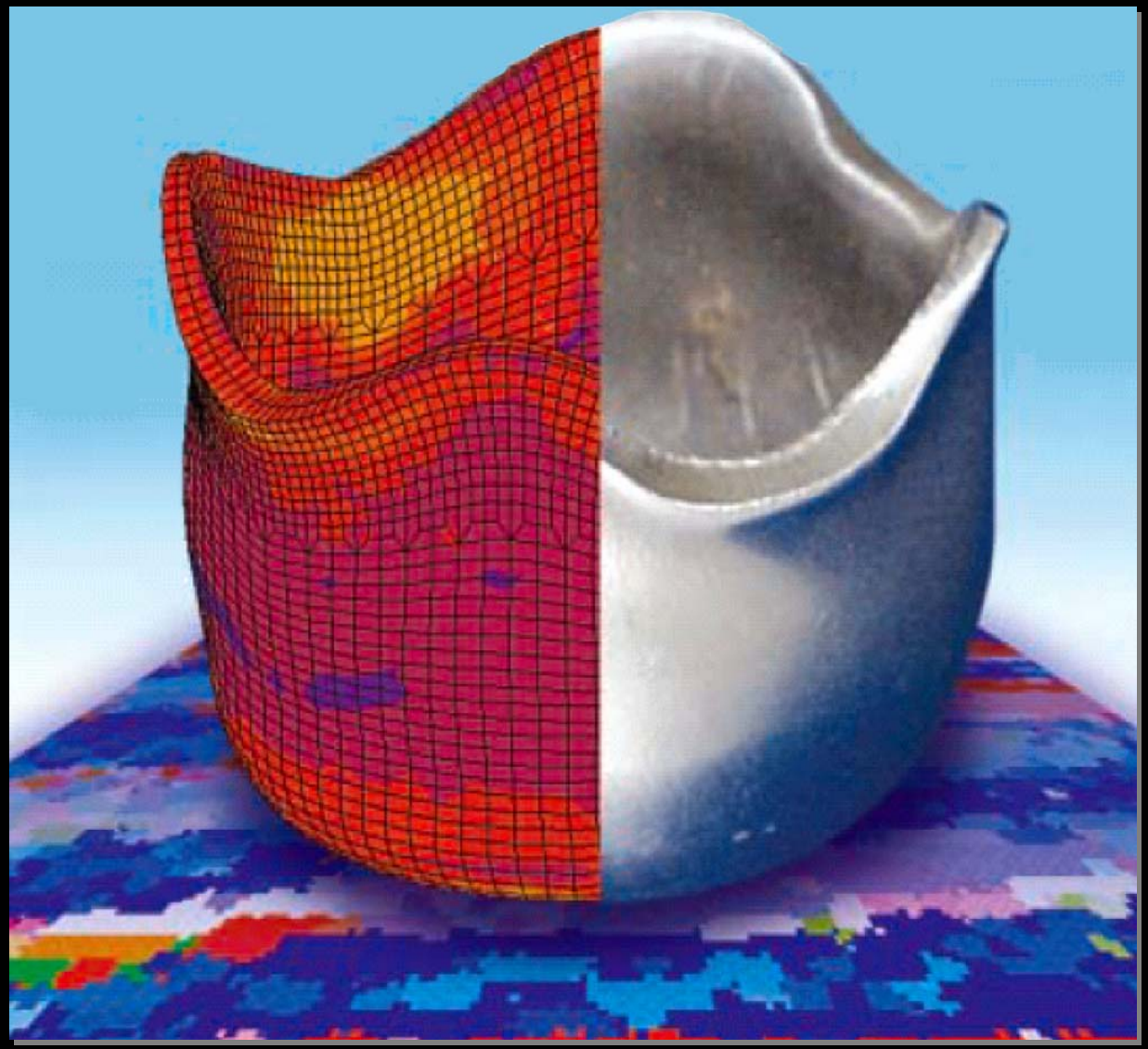
Mechanics of many crystals (TF-CP-FEM)

3D electron microscopy

Chitin-composites

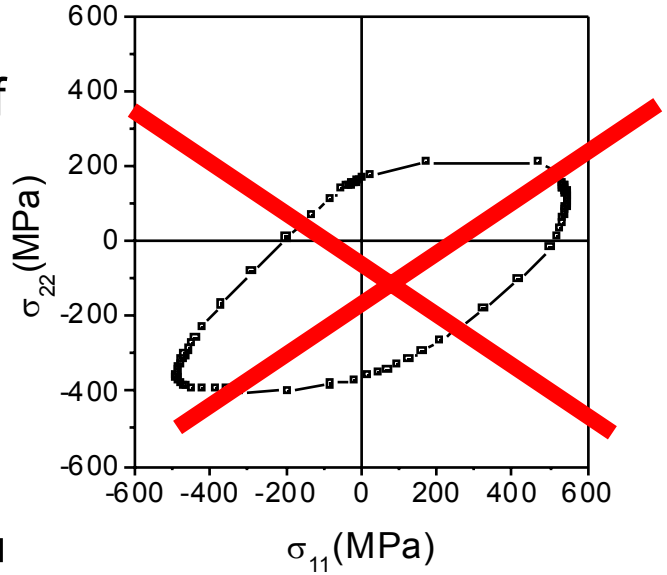
Crystal Mechanics FEM (large scale)

many crystals (10^{10})

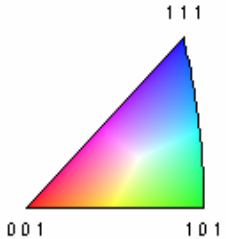


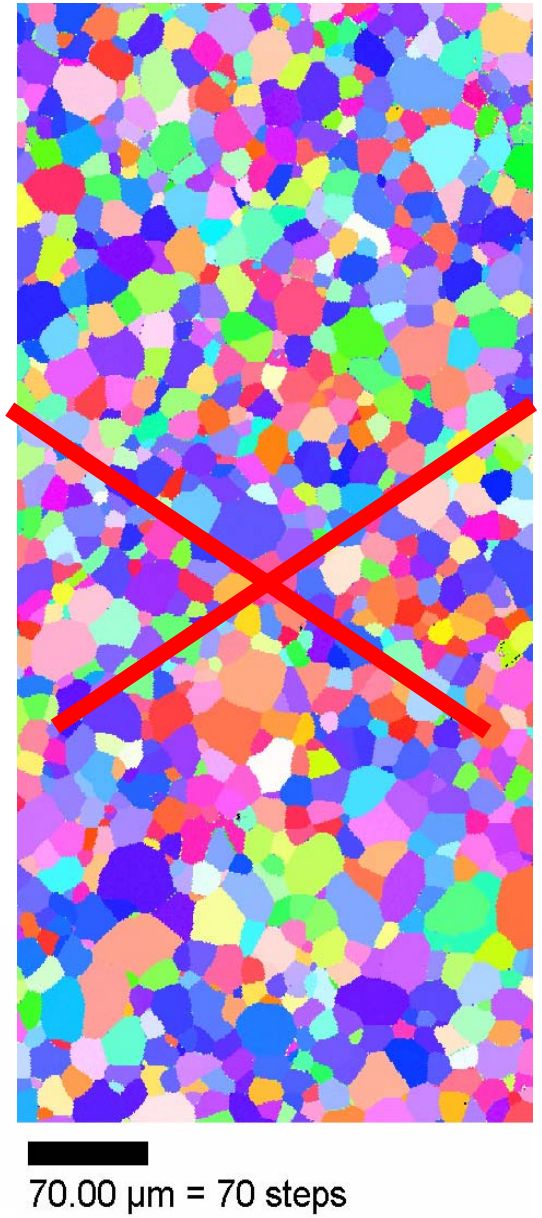
10 billion grains

too empirical
(no update of
anisotropy)

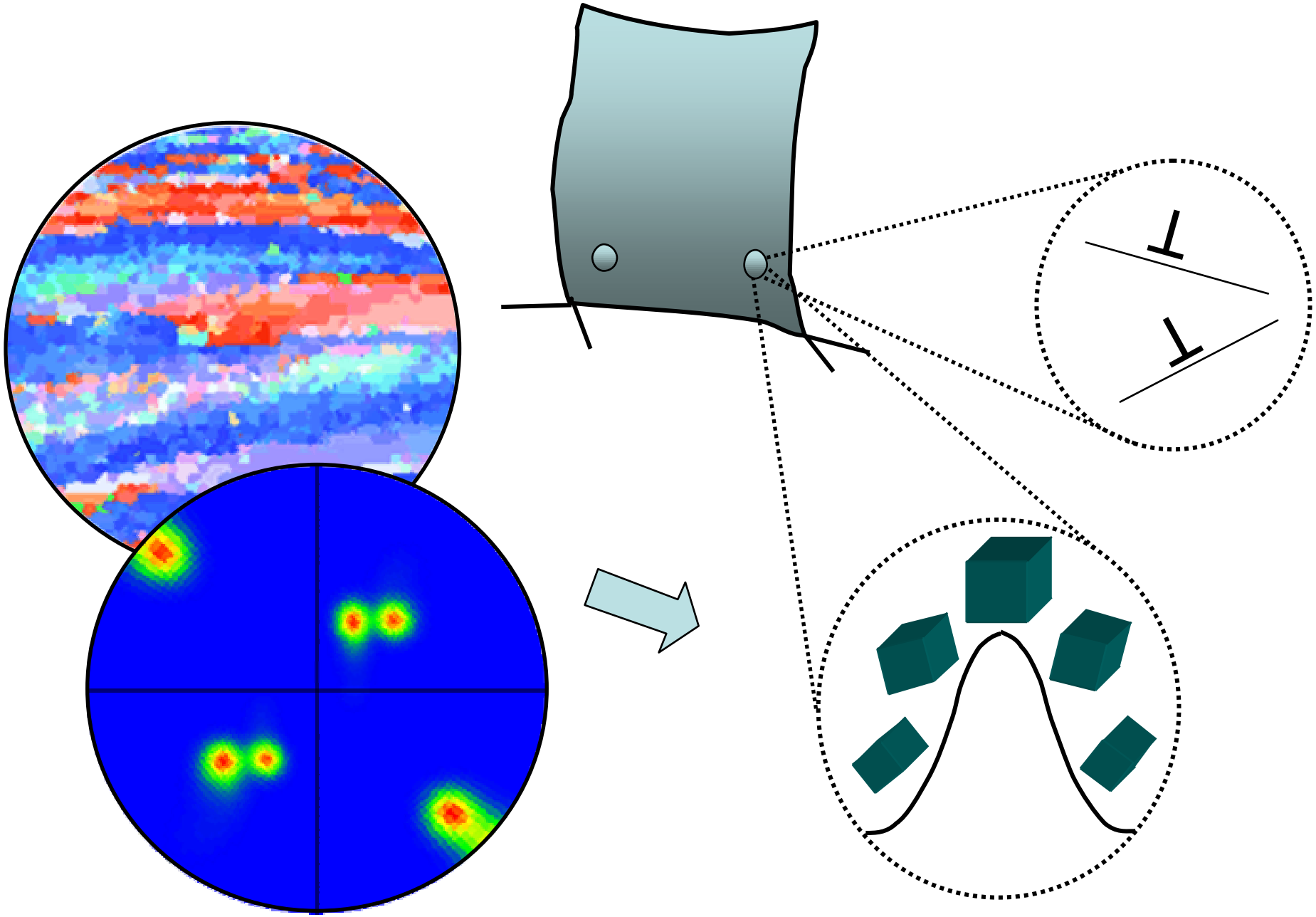


too many
grains

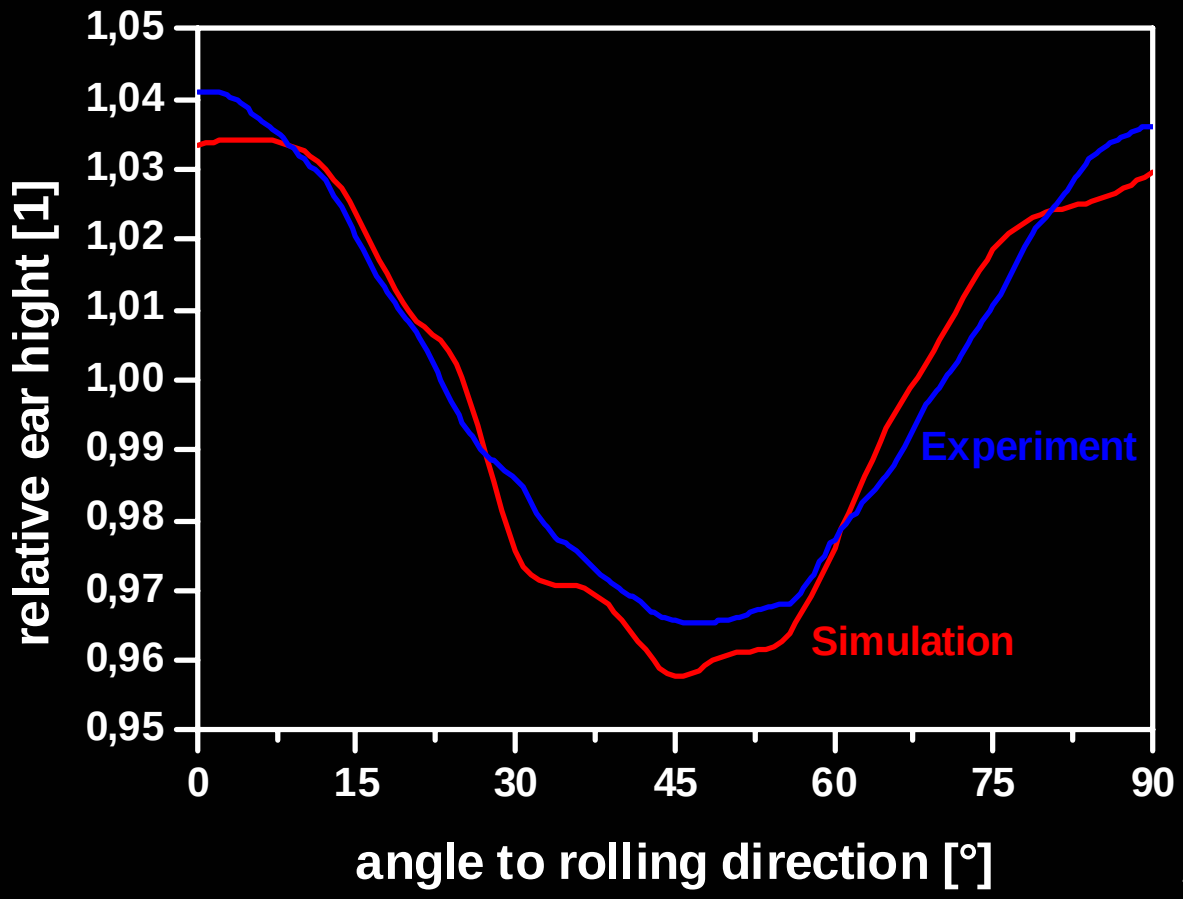


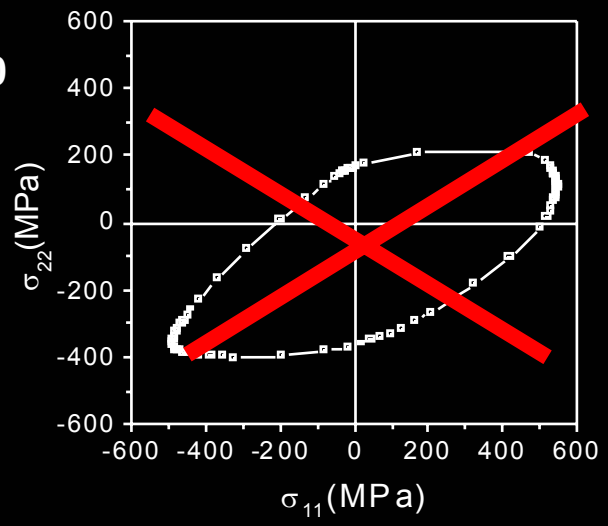


Using spherical functions in FEM



Crystal Plasticity FEM





Overview

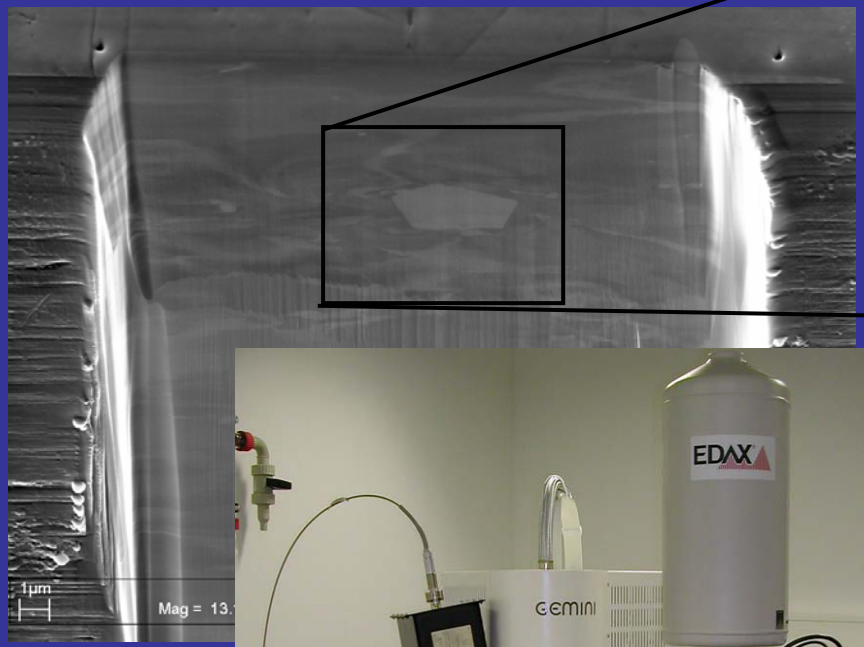
Mechanics of few crystals (CP-FEM)

Mechanics of many crystals (TF-CP-FEM)

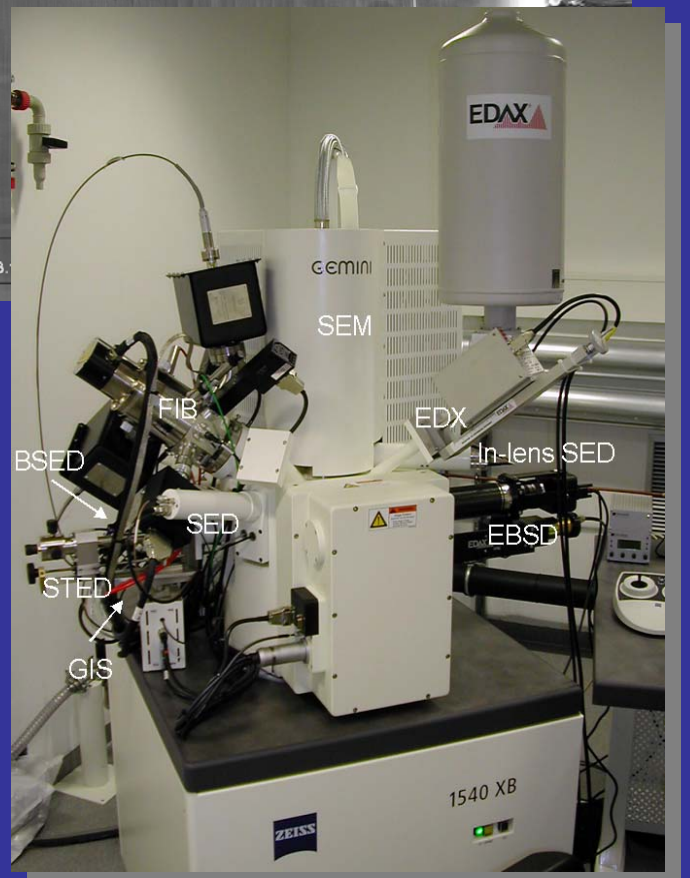
3D electron microscopy

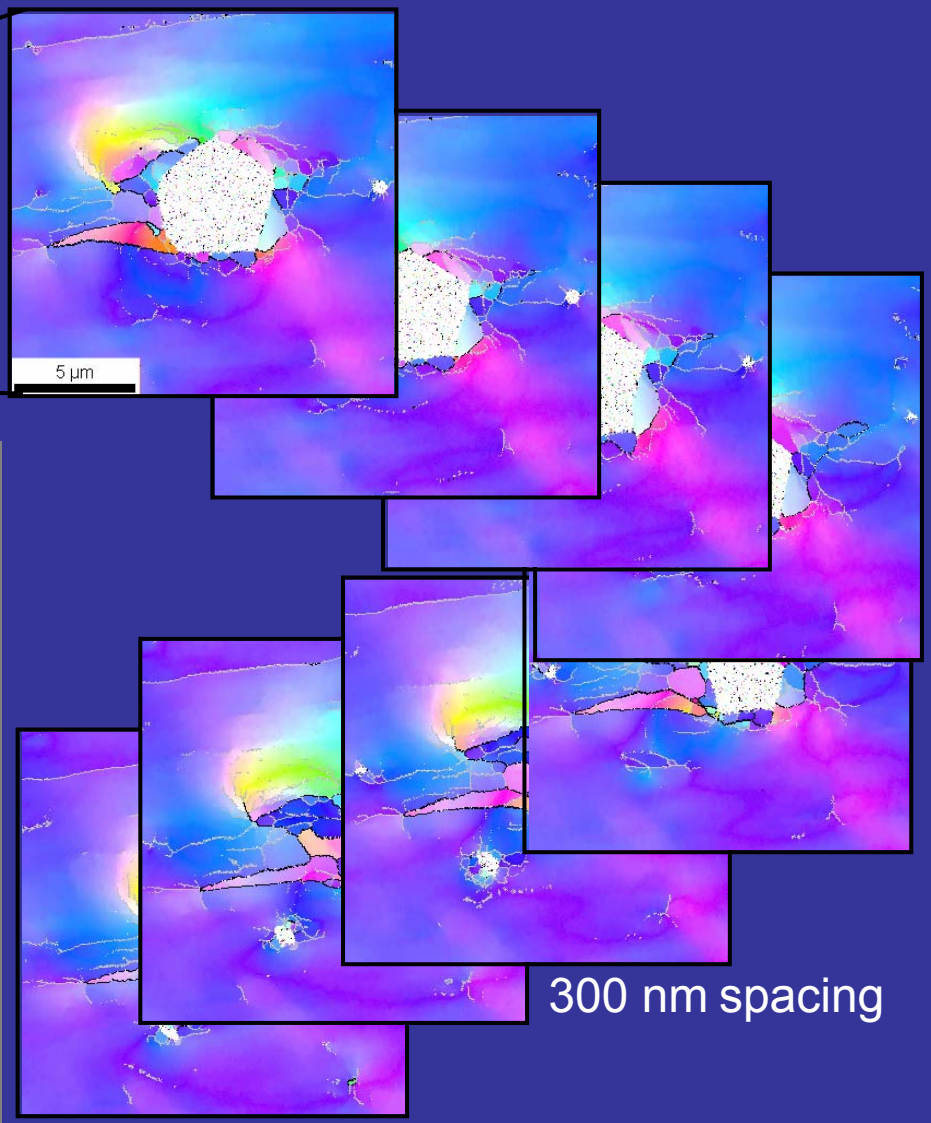
Chitin-composites

3D electron orientation microscopy



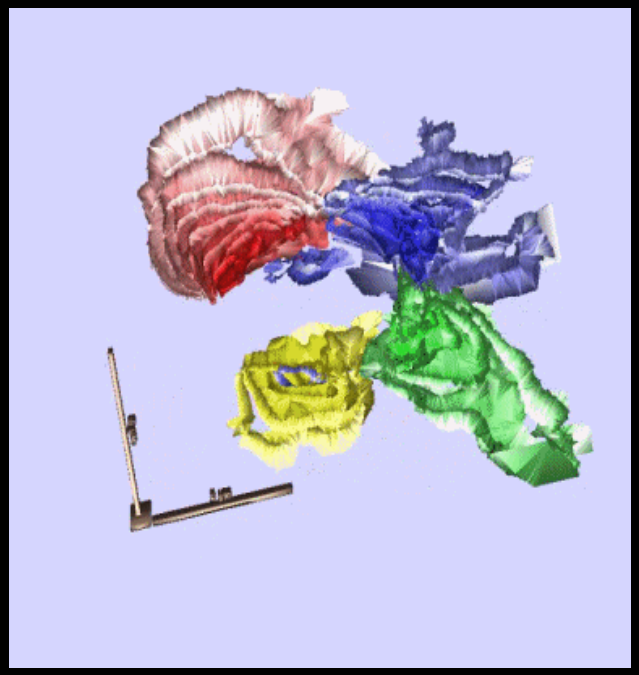
SE-image





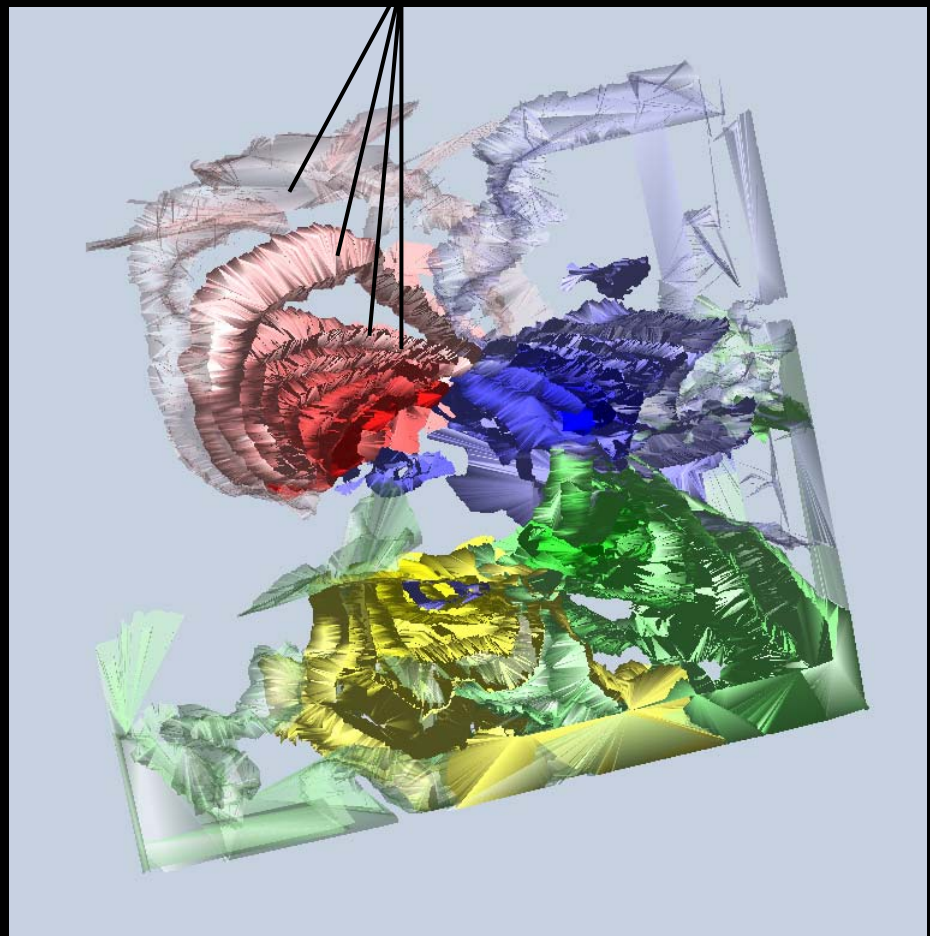
300 nm spacing

3D electron orientation microscopy



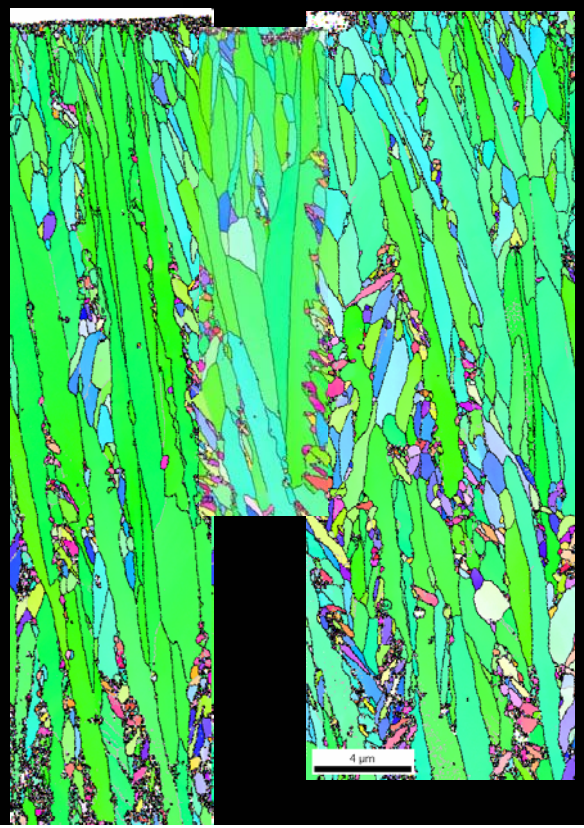
lattice rotations around Laves phase in Fe_3Al

5° misorientation steps from shell to shell



3D : EBSD, EDX, SEM, FIB

3D electron orientation microscopy



Overview

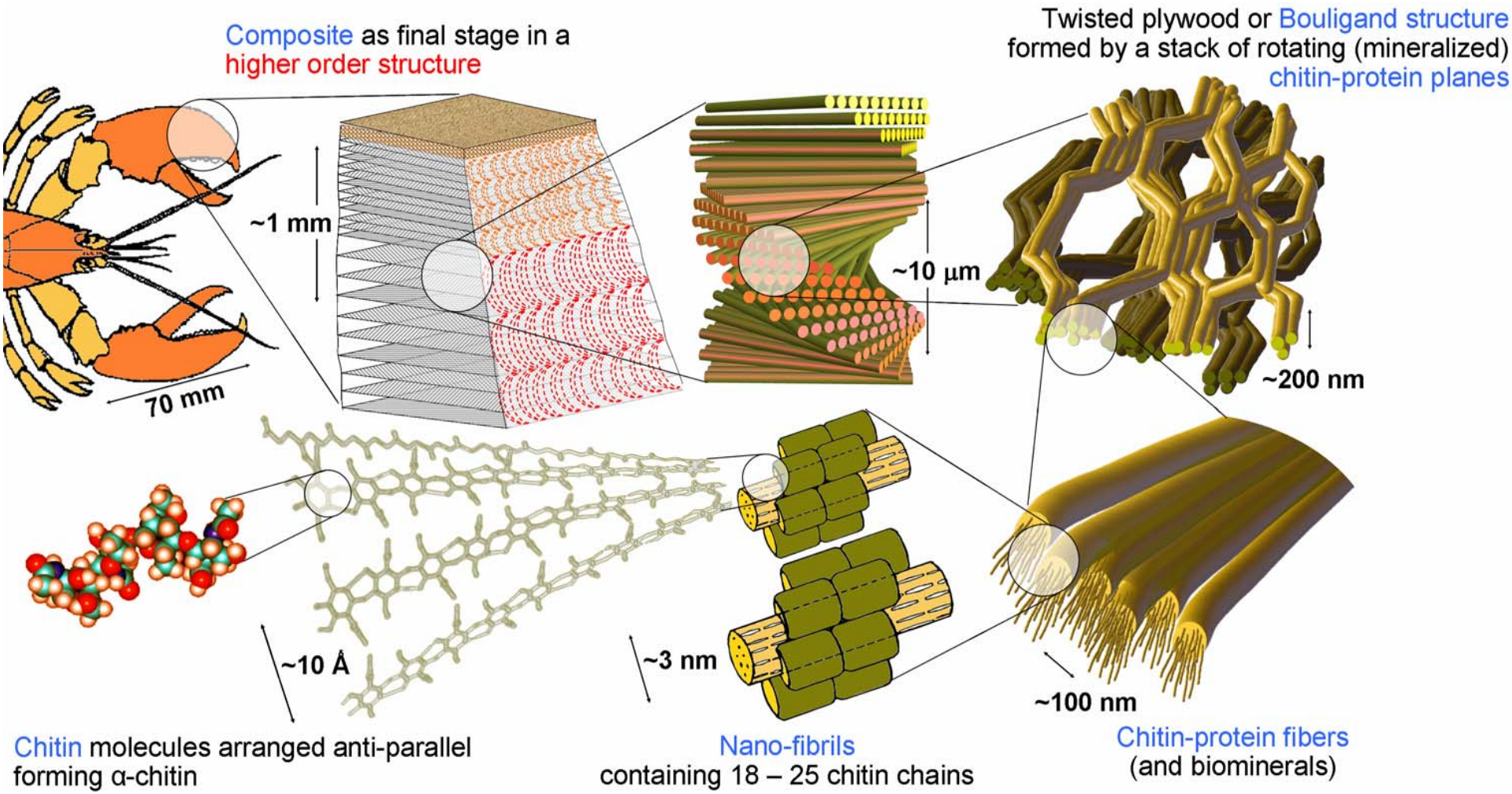
Mechanics of few crystals (CP-FEM)

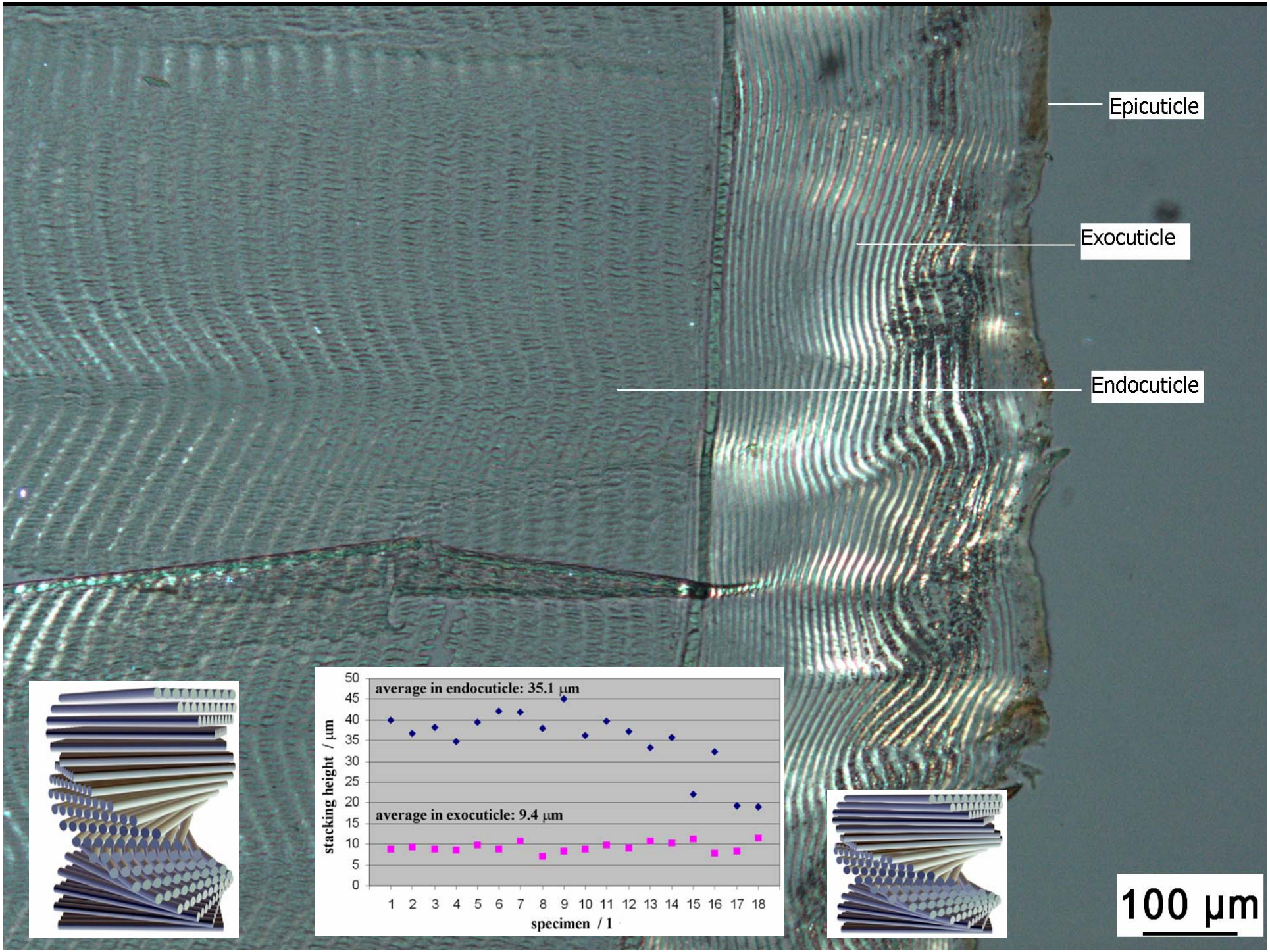
Mechanics of many crystals (TF-CP-FEM)

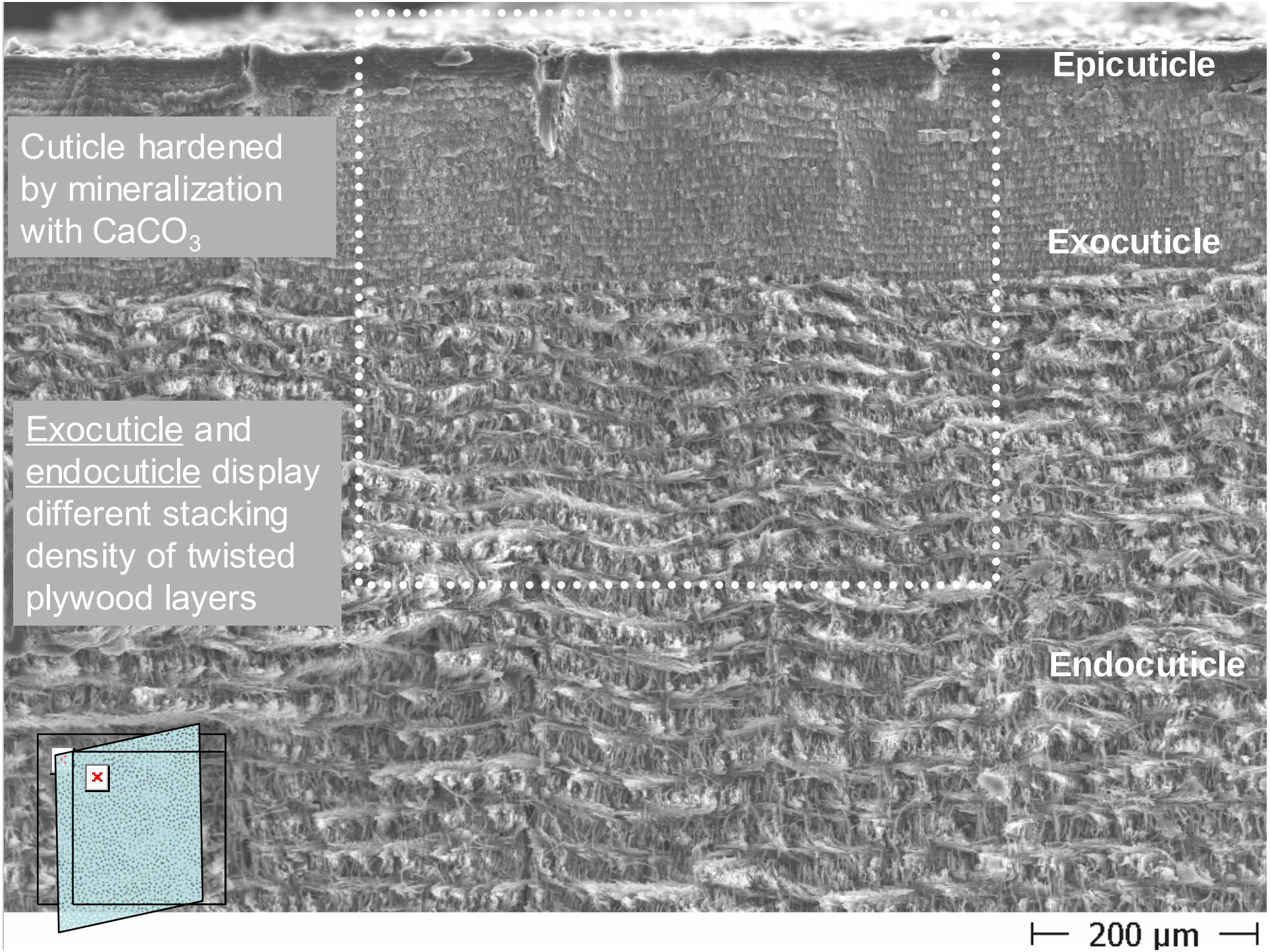
3D electron microscopy

Chitin-composites

Structure Hierarchy (*Homarus americanus*)

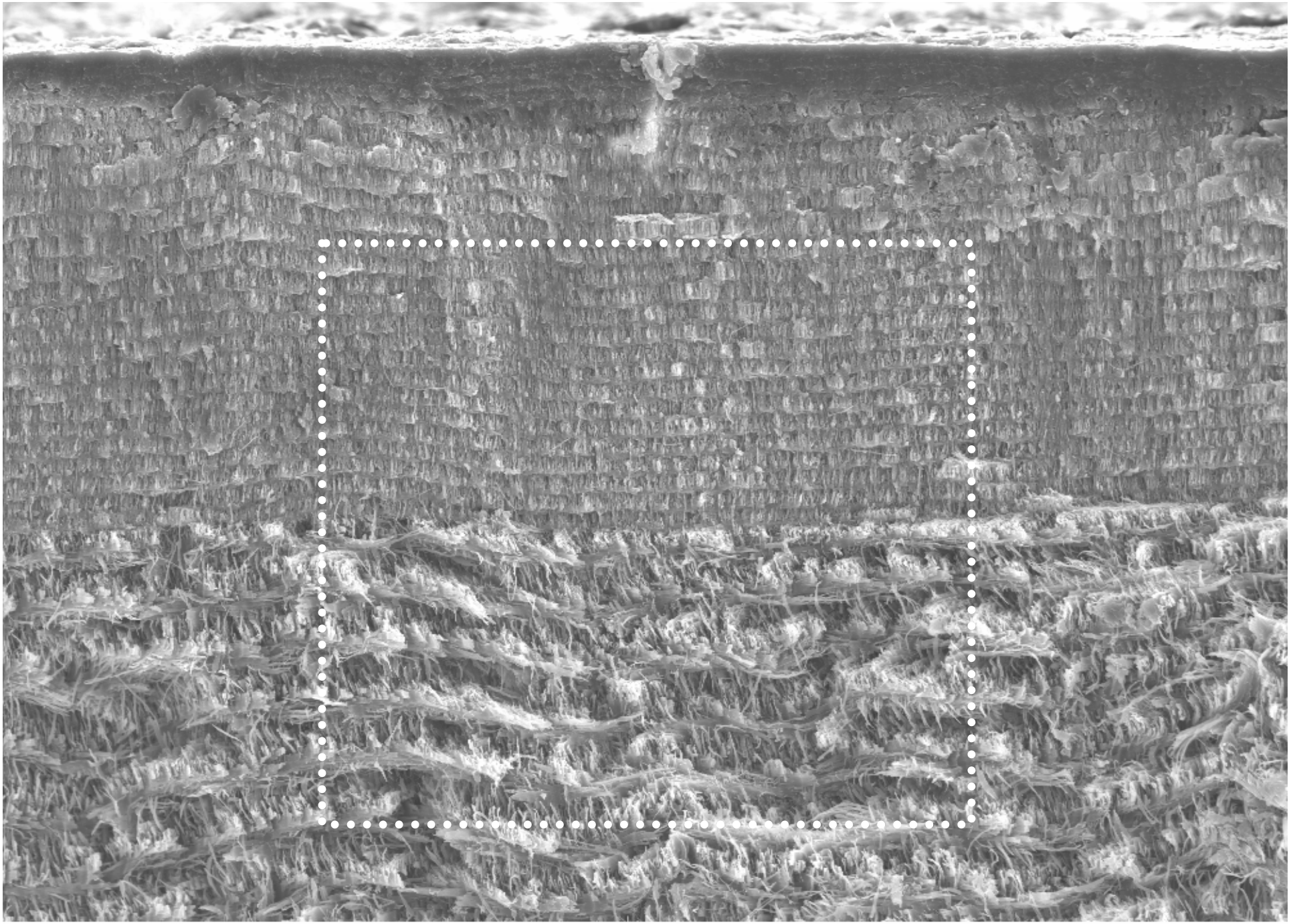


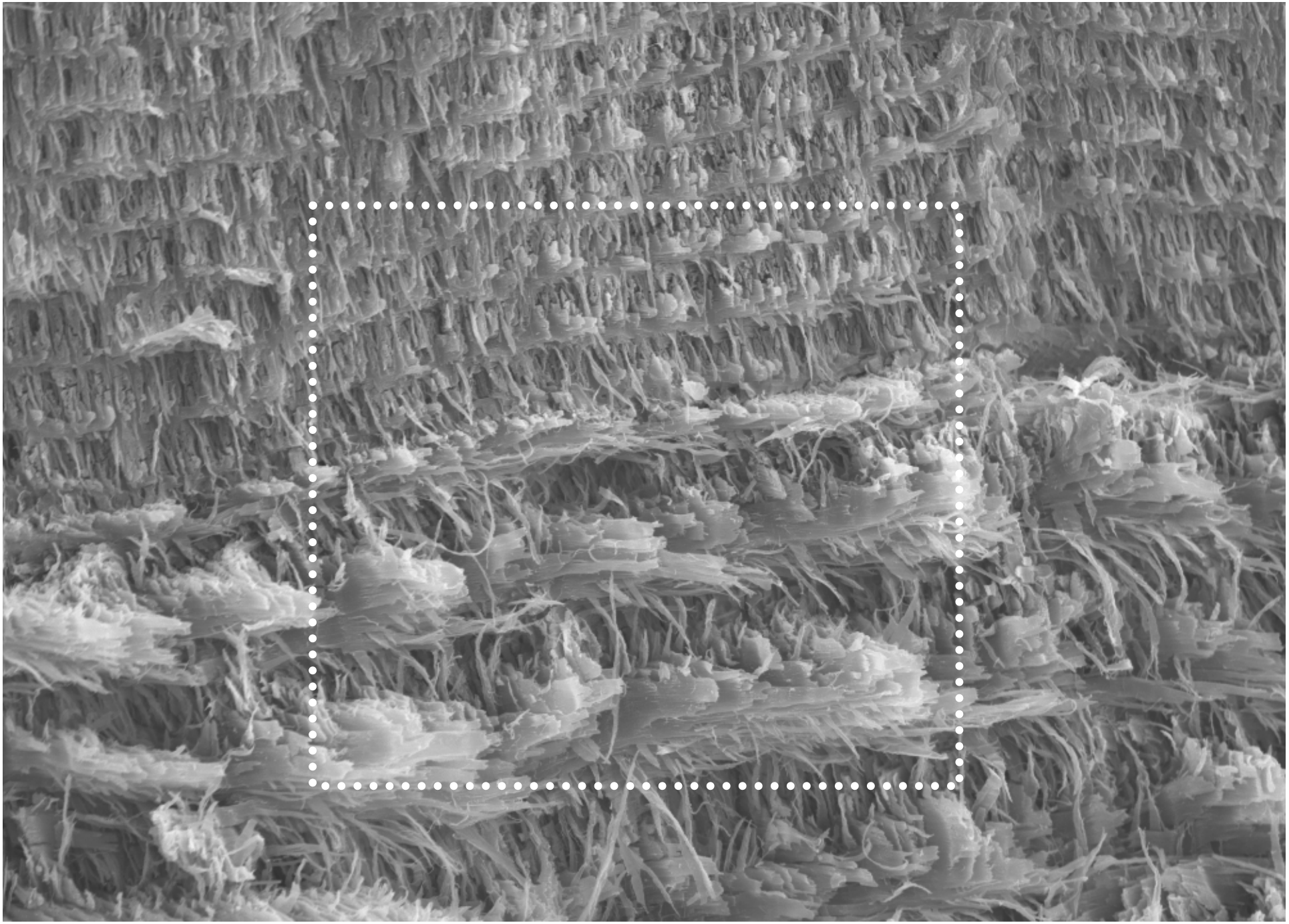

Epicuticle
Exocuticle
Endocuticle
average in endocuticle: 35.1 µm
average in exocuticle: 9.4 µm
stacking height / µm
specimen / 1
0
5
10
15
20
25
30
35
40
45
50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
100 µm

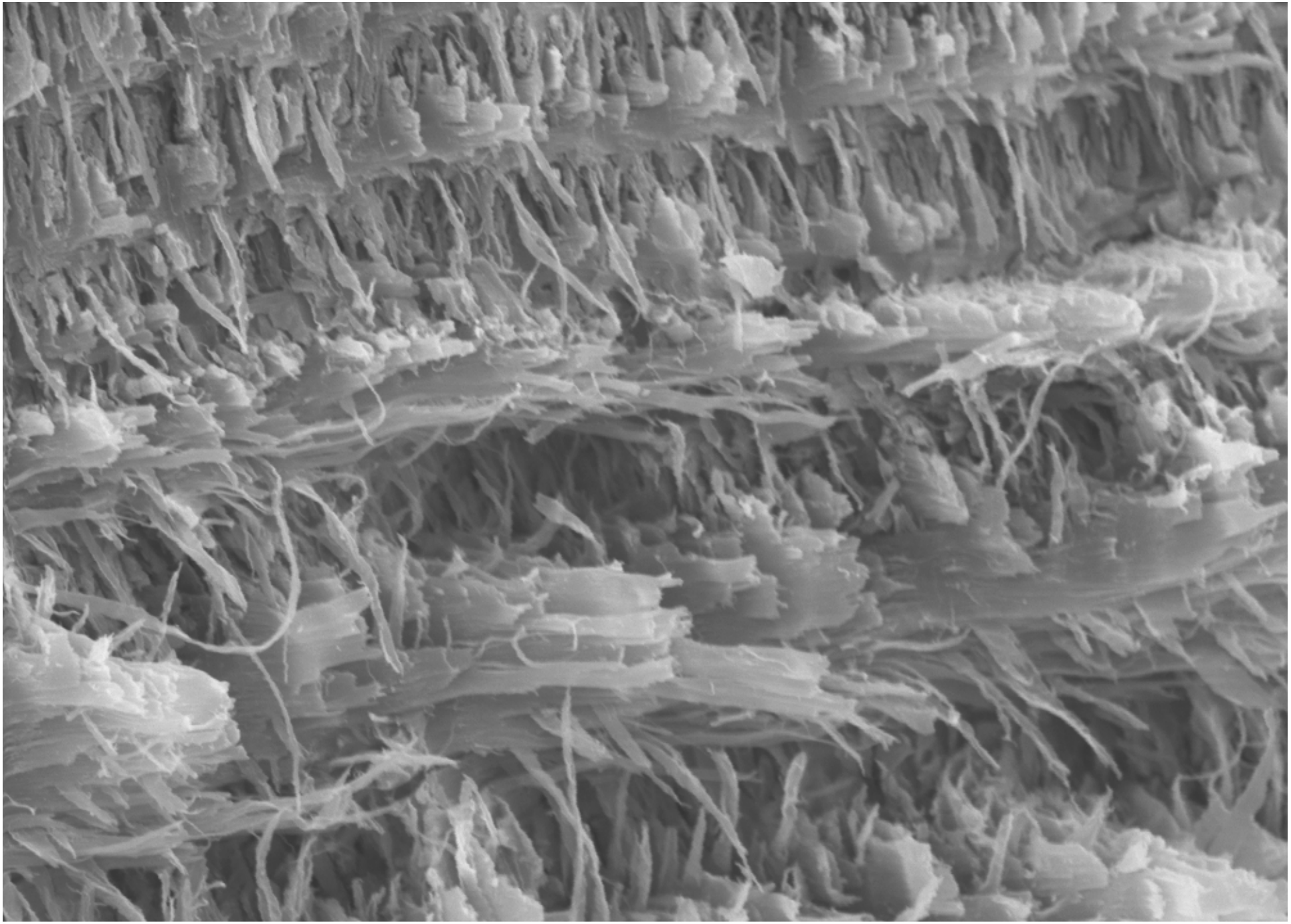


Cuticle hardened by mineralization with $CaCO_3$

Exocuticle and endocuticle display different stacking density of twisted plywood layers

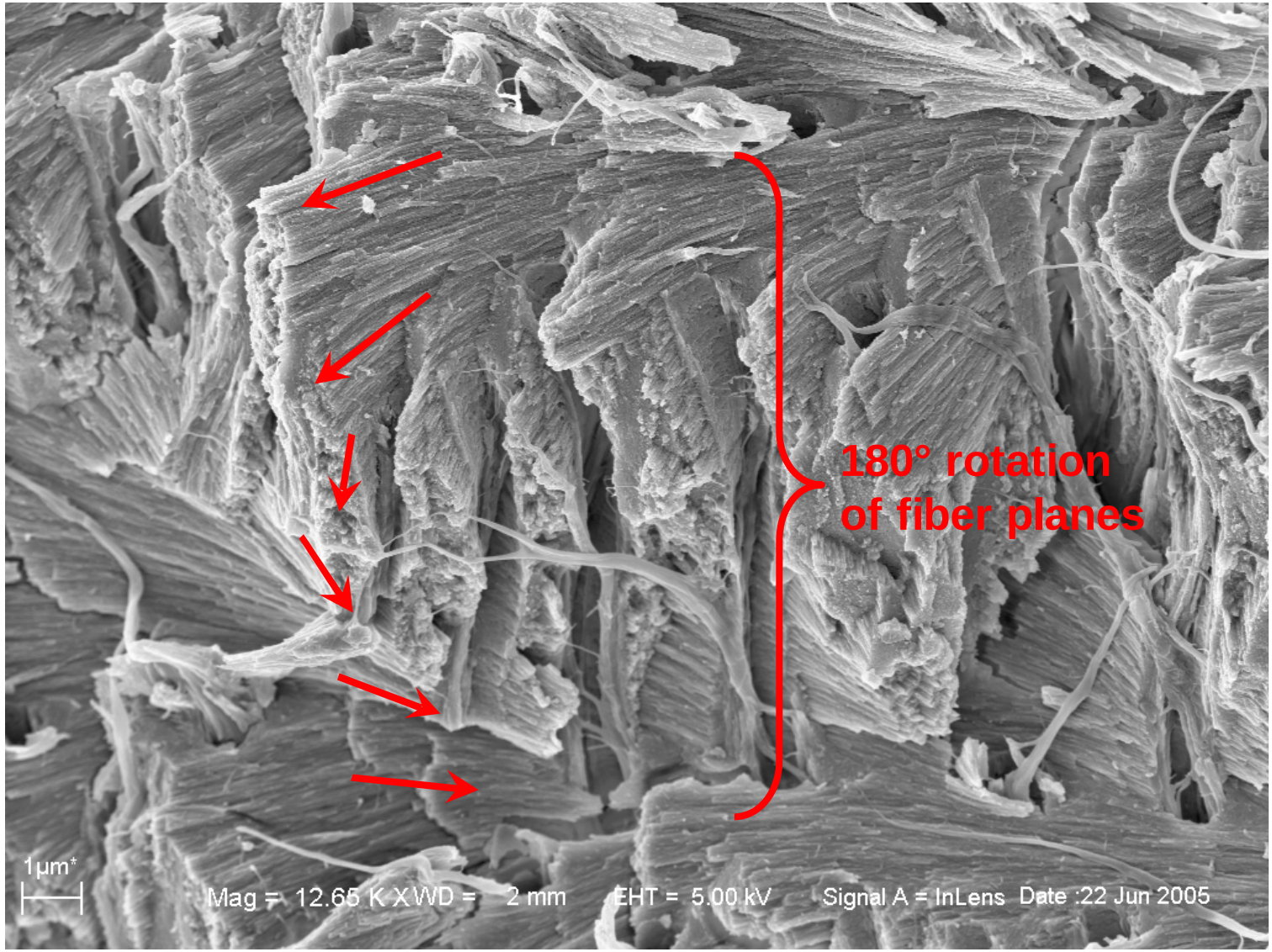

100 µm

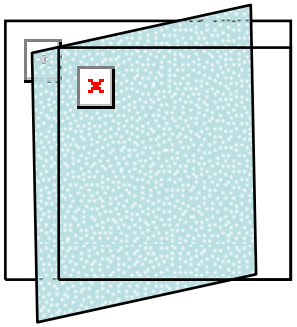

30 µm

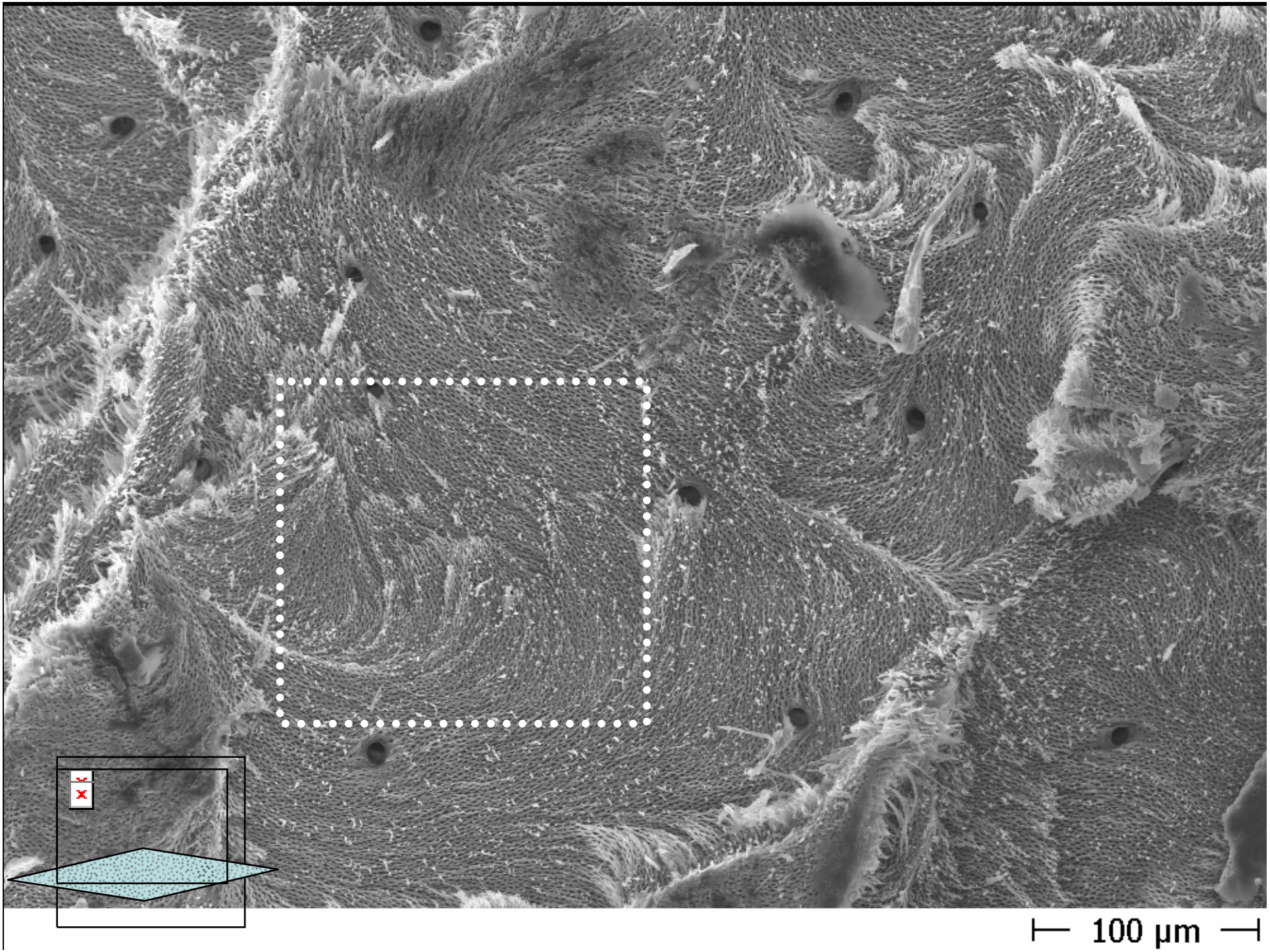


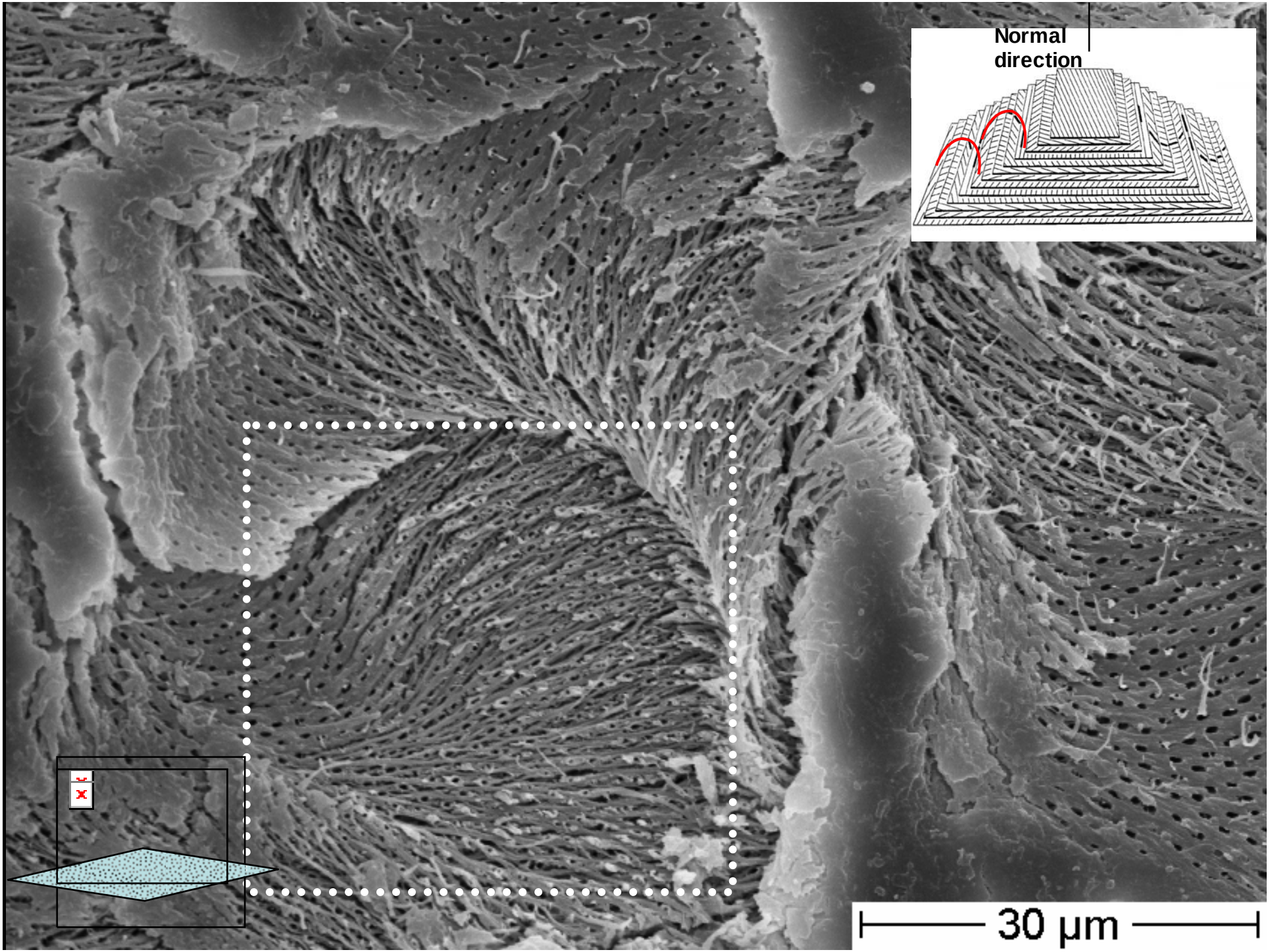
⊢ 10 µm ⊣

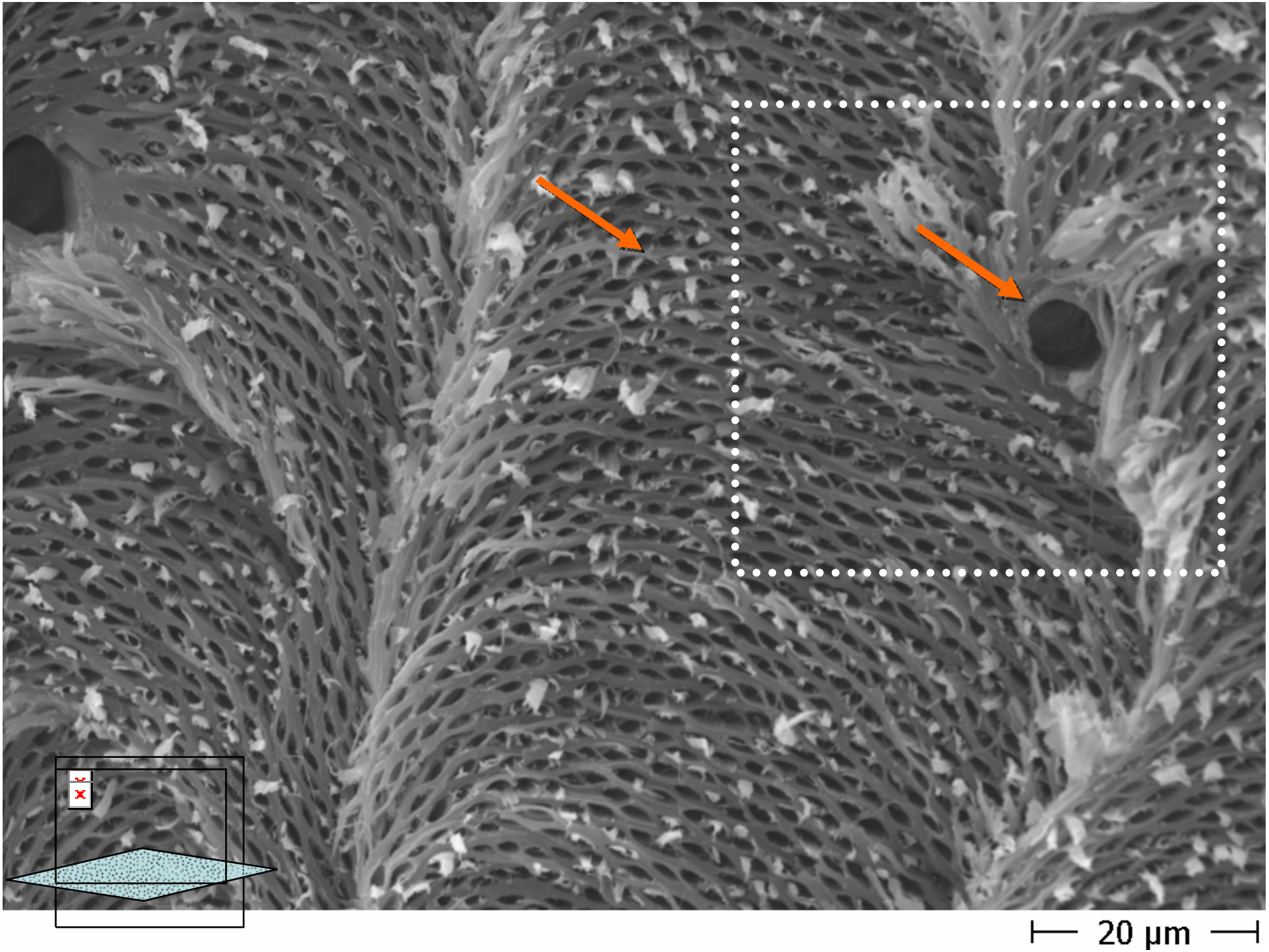
SEM: Lobster endocuticle, untreated



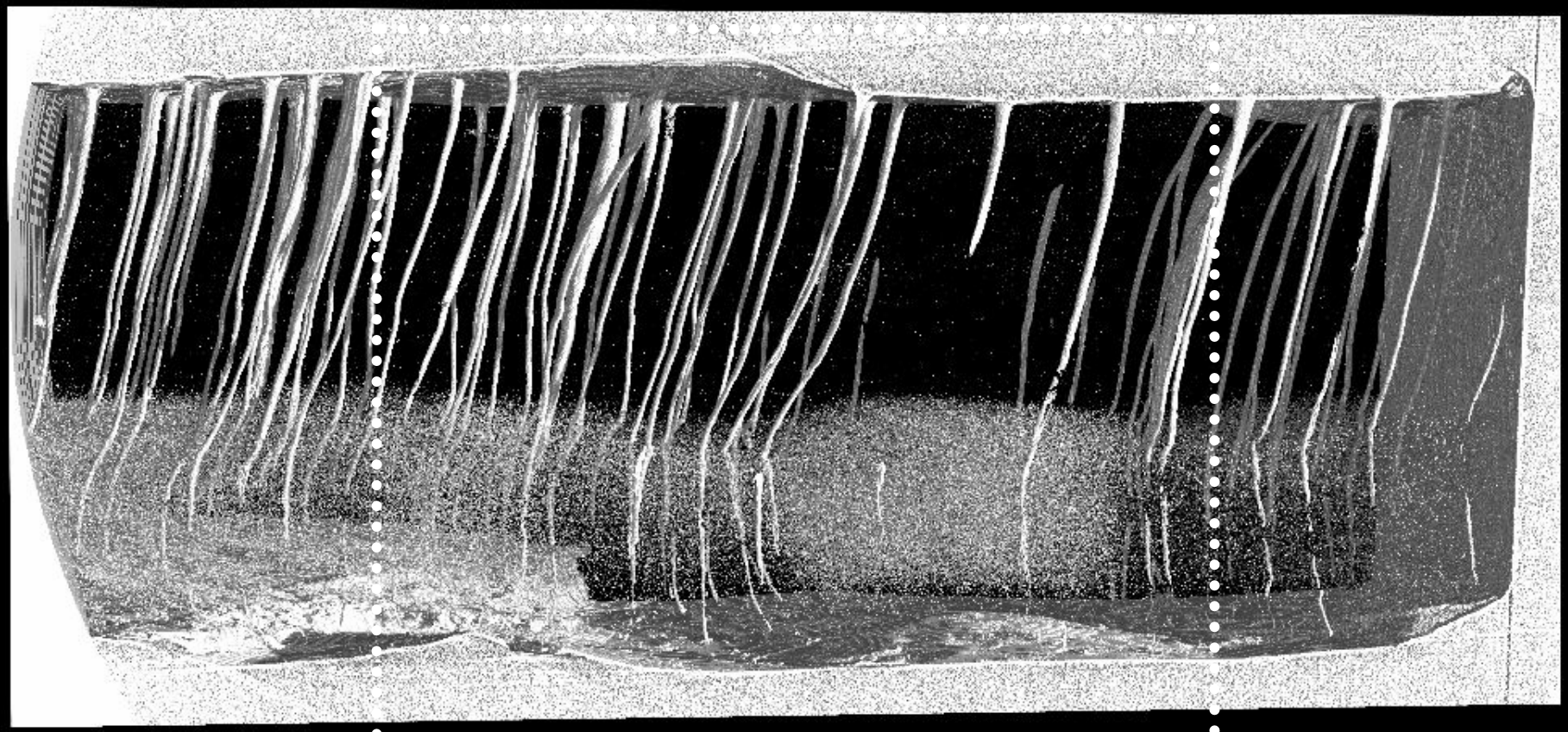



Y
X
100 µm


Normal
direction
30 µm

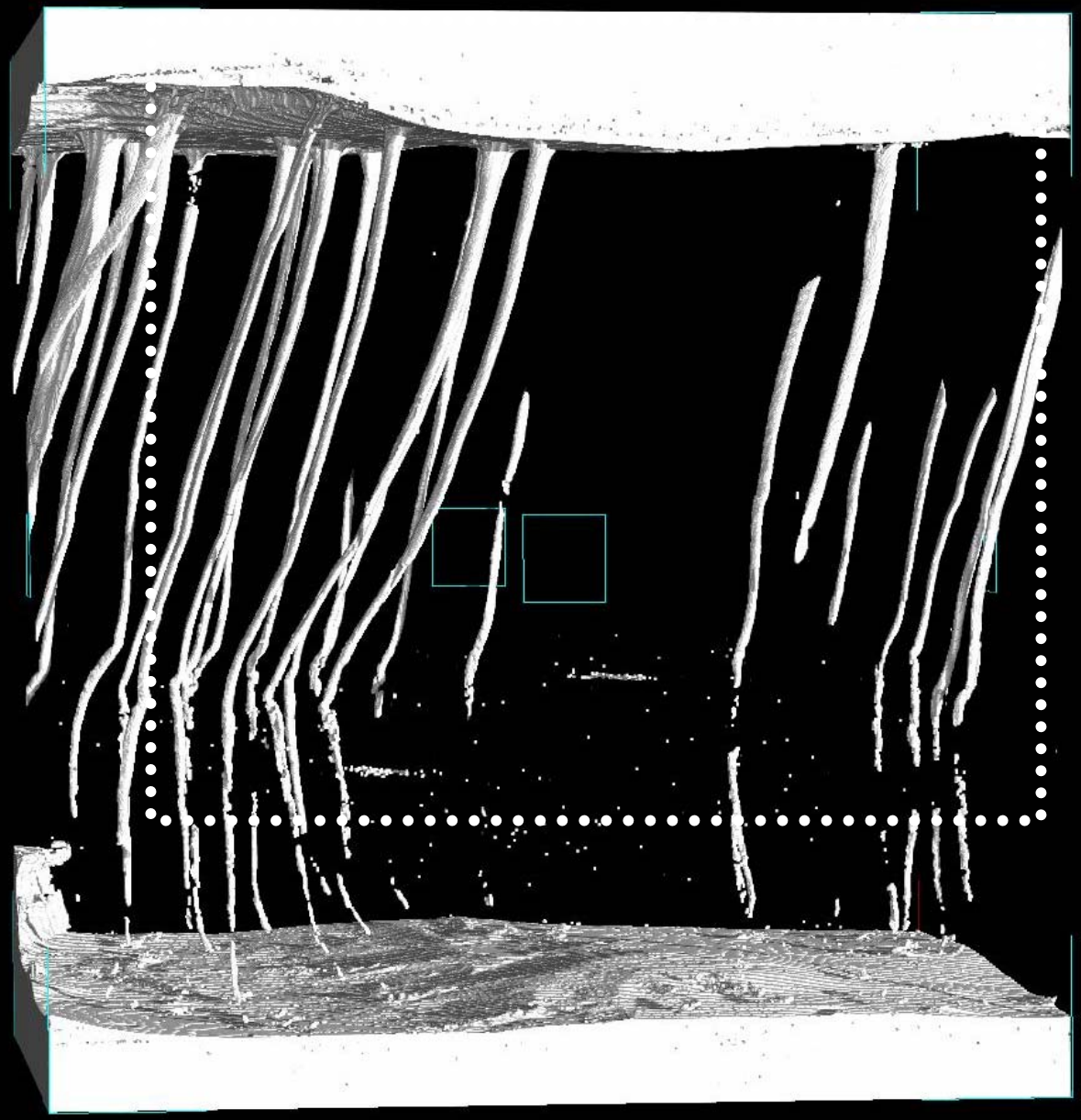

y
x
20 µm

X-ray tomography, cuticle, horseshoe crab

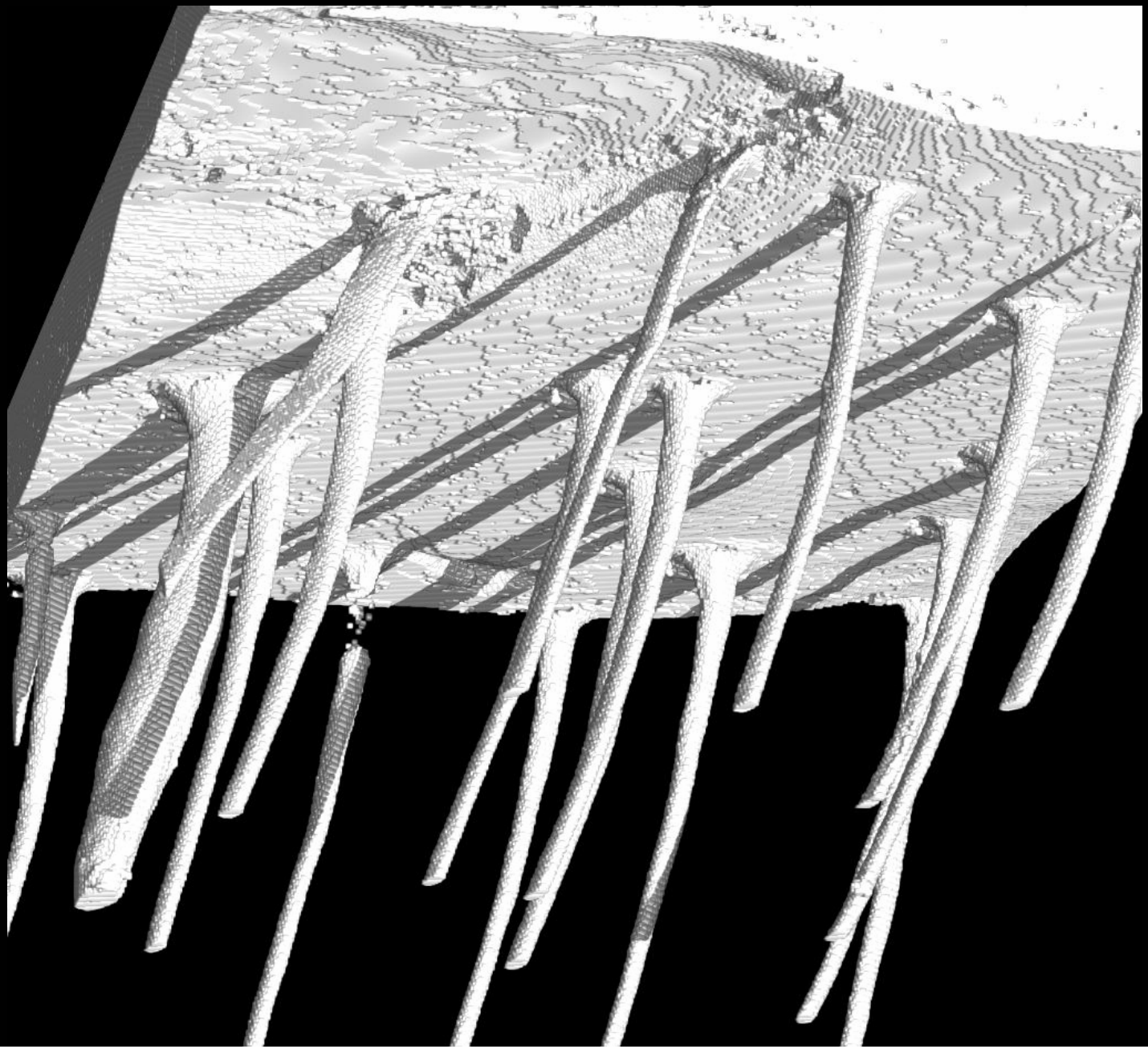


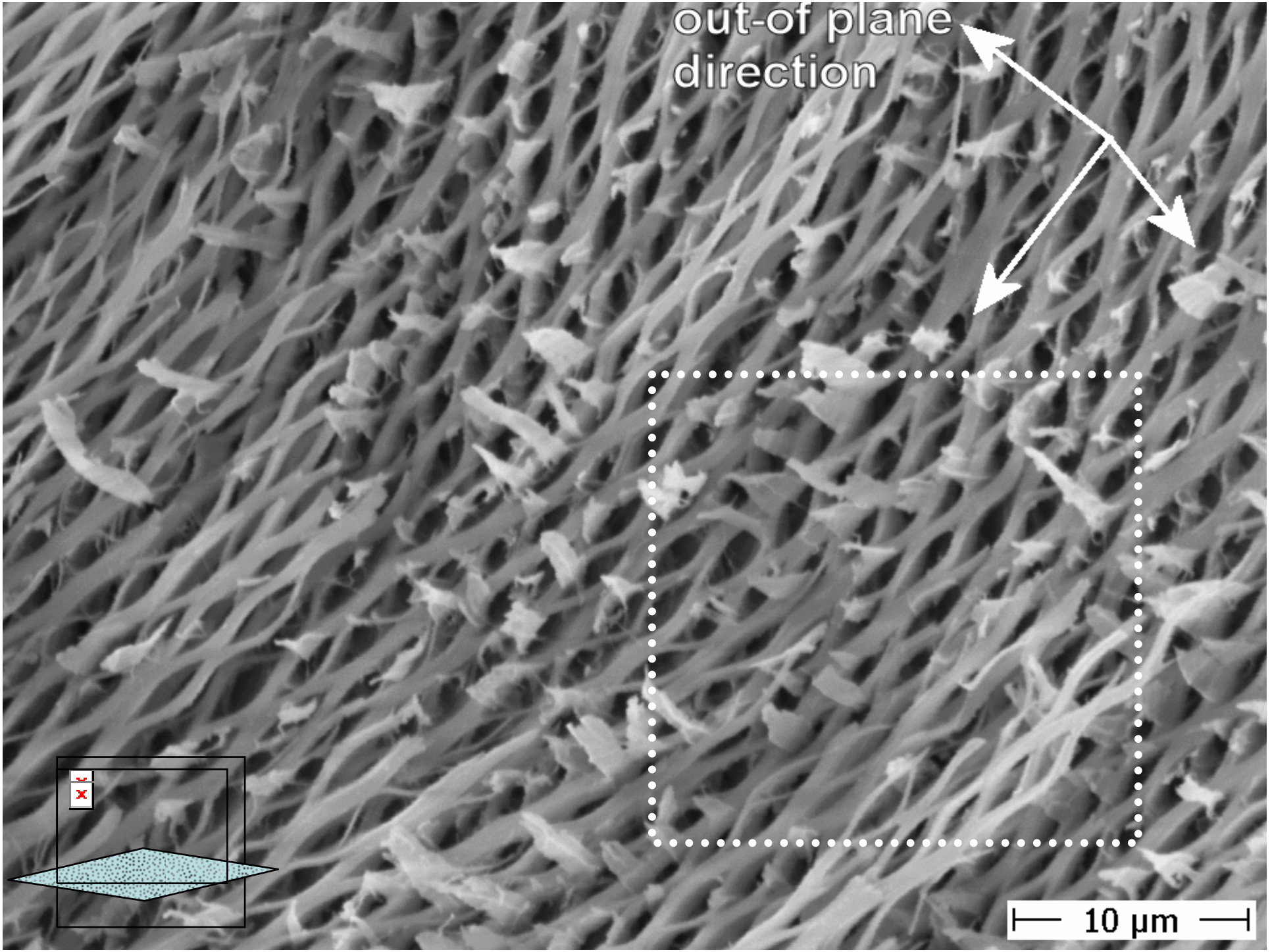
measurements at : HMI Berlin

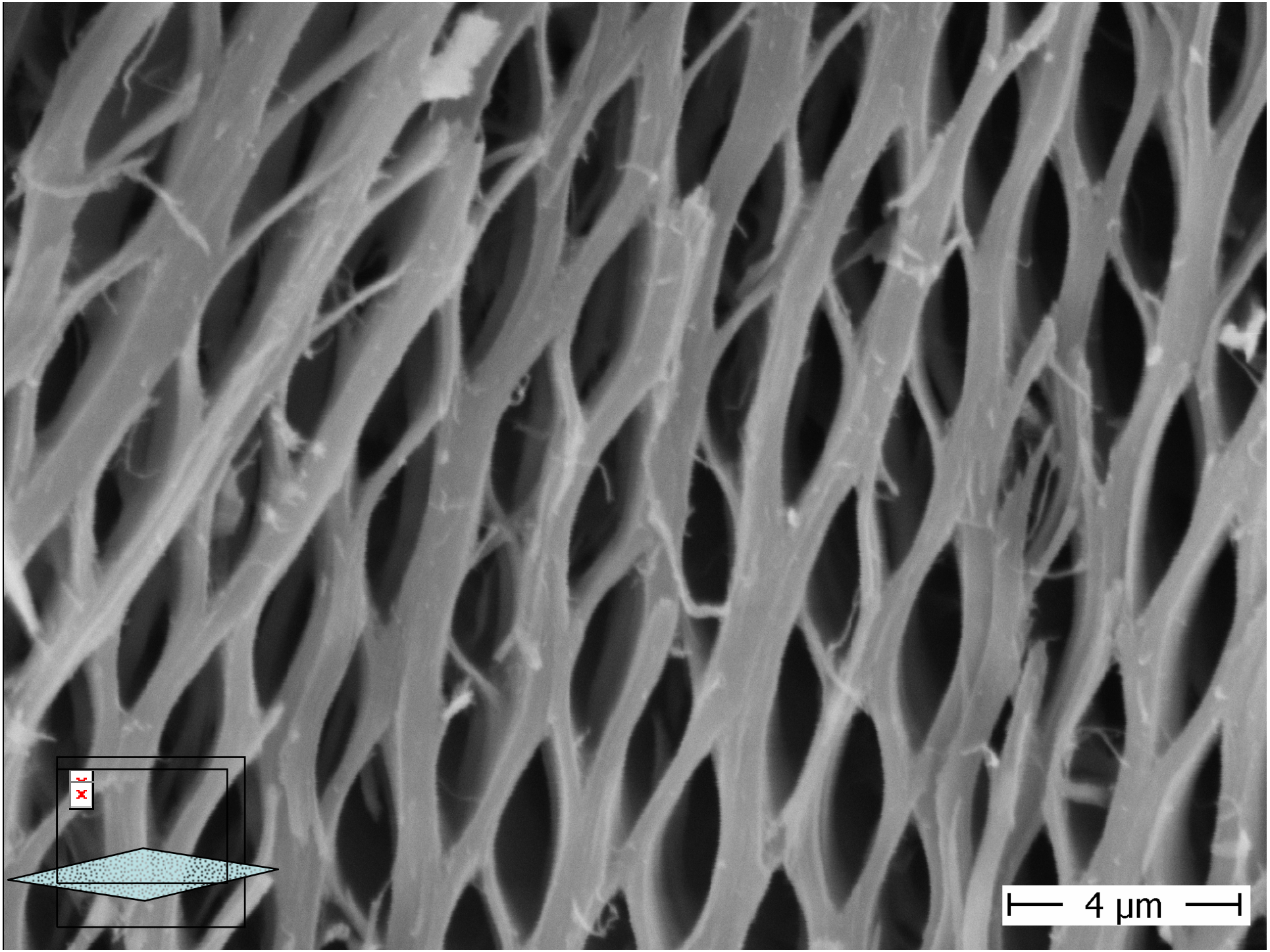
X-ray tomography, cuticle, horseshoe crab

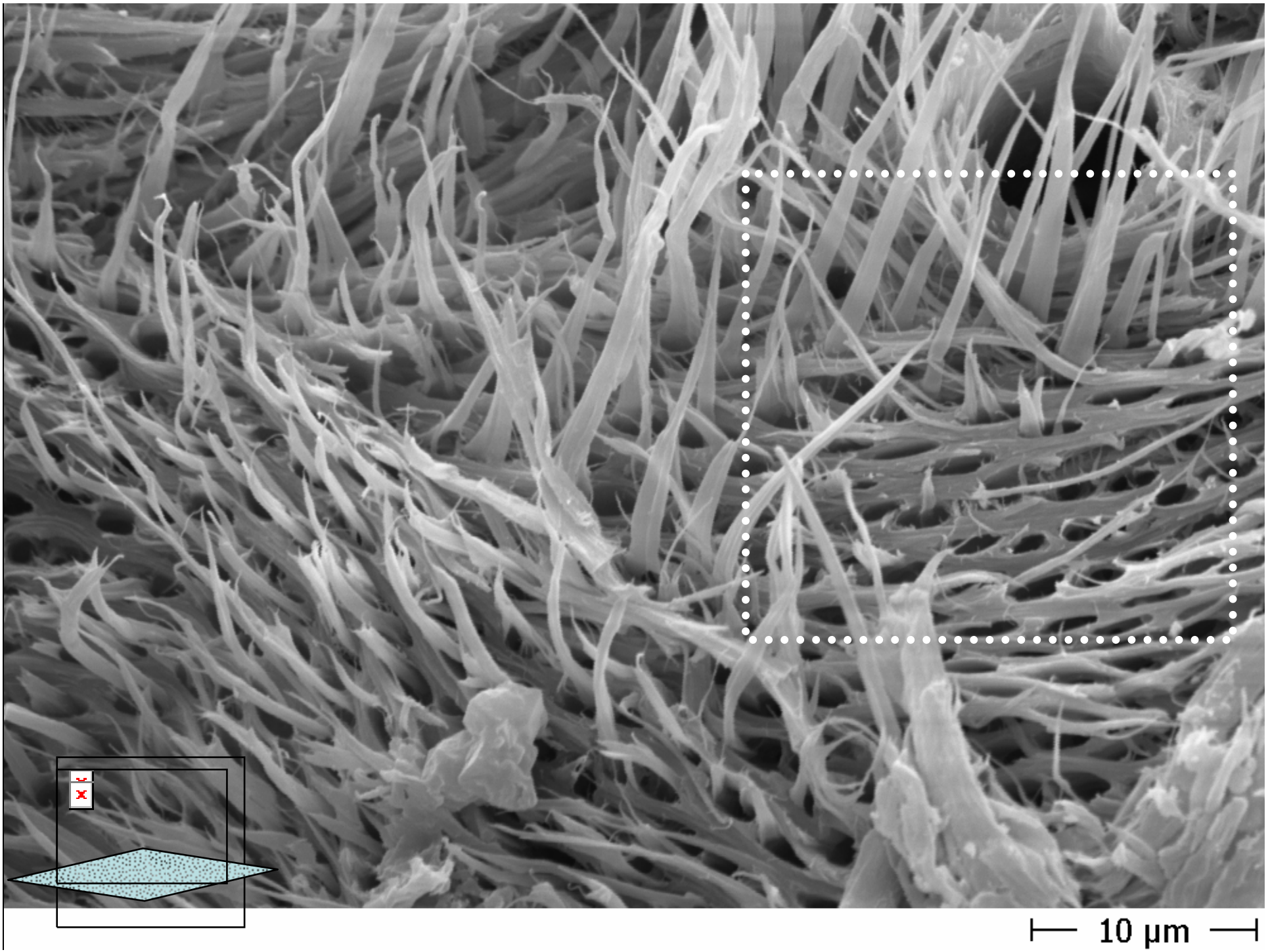


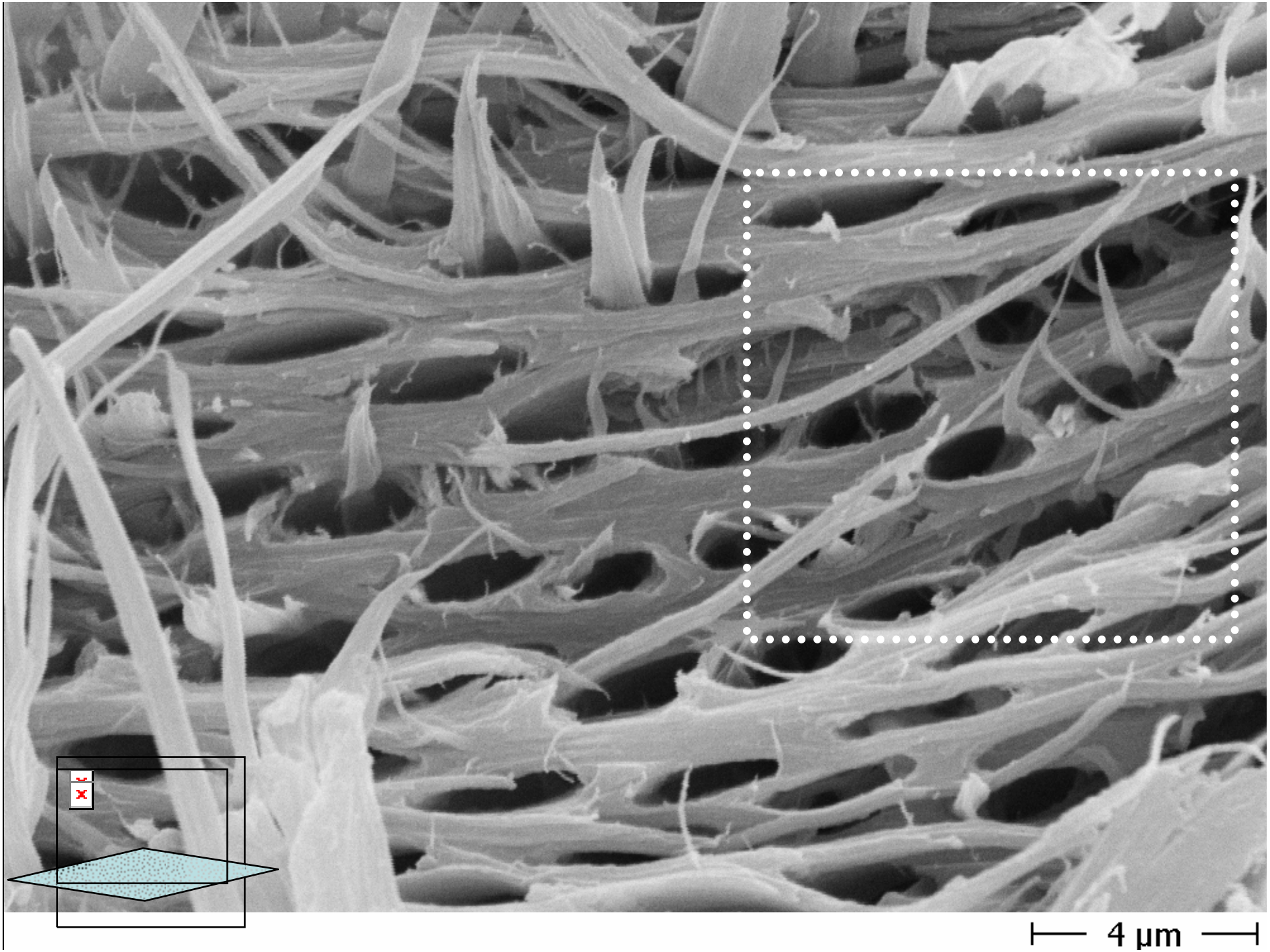
X-ray tomography, cuticle, horseshoe crab

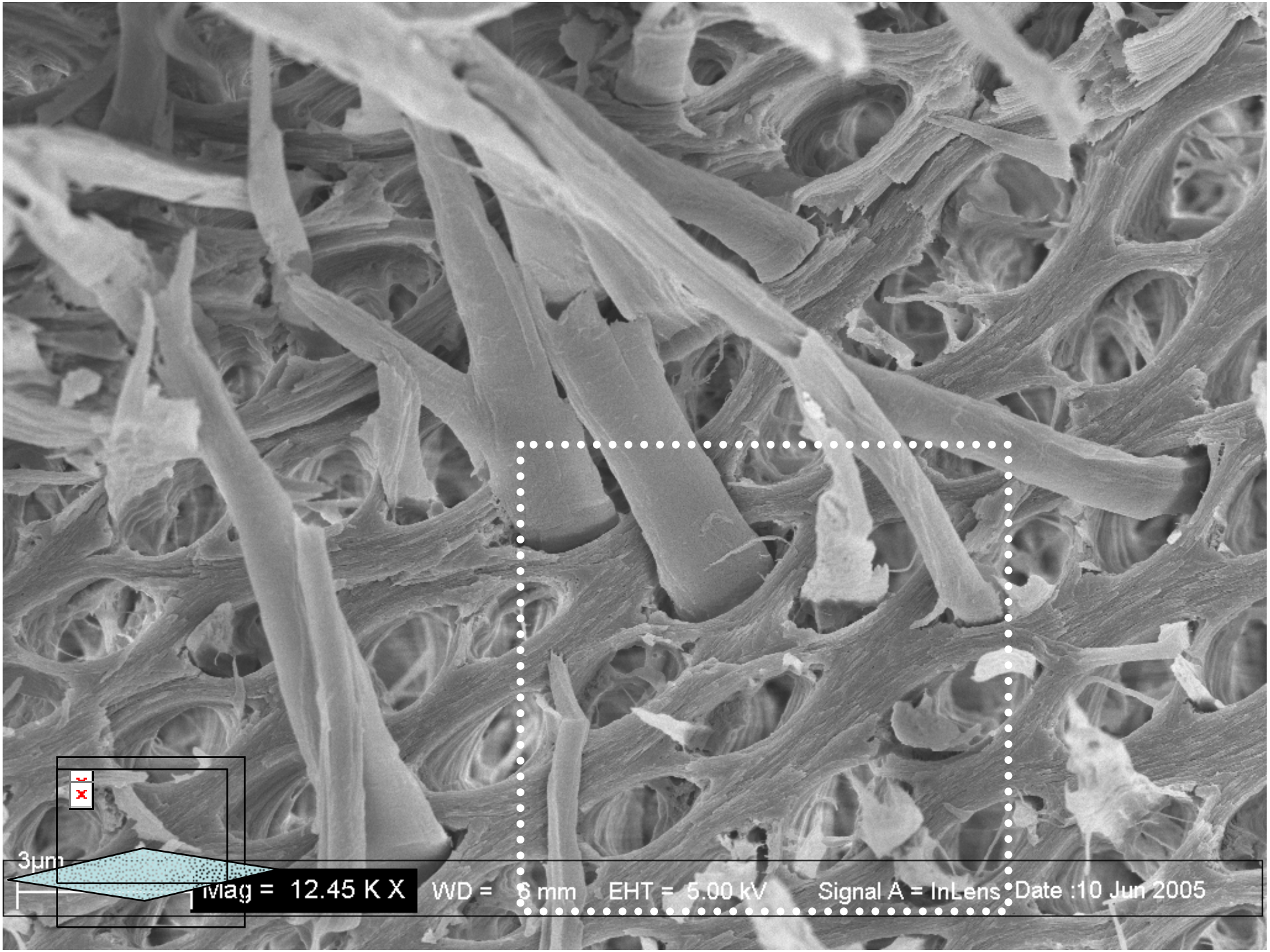


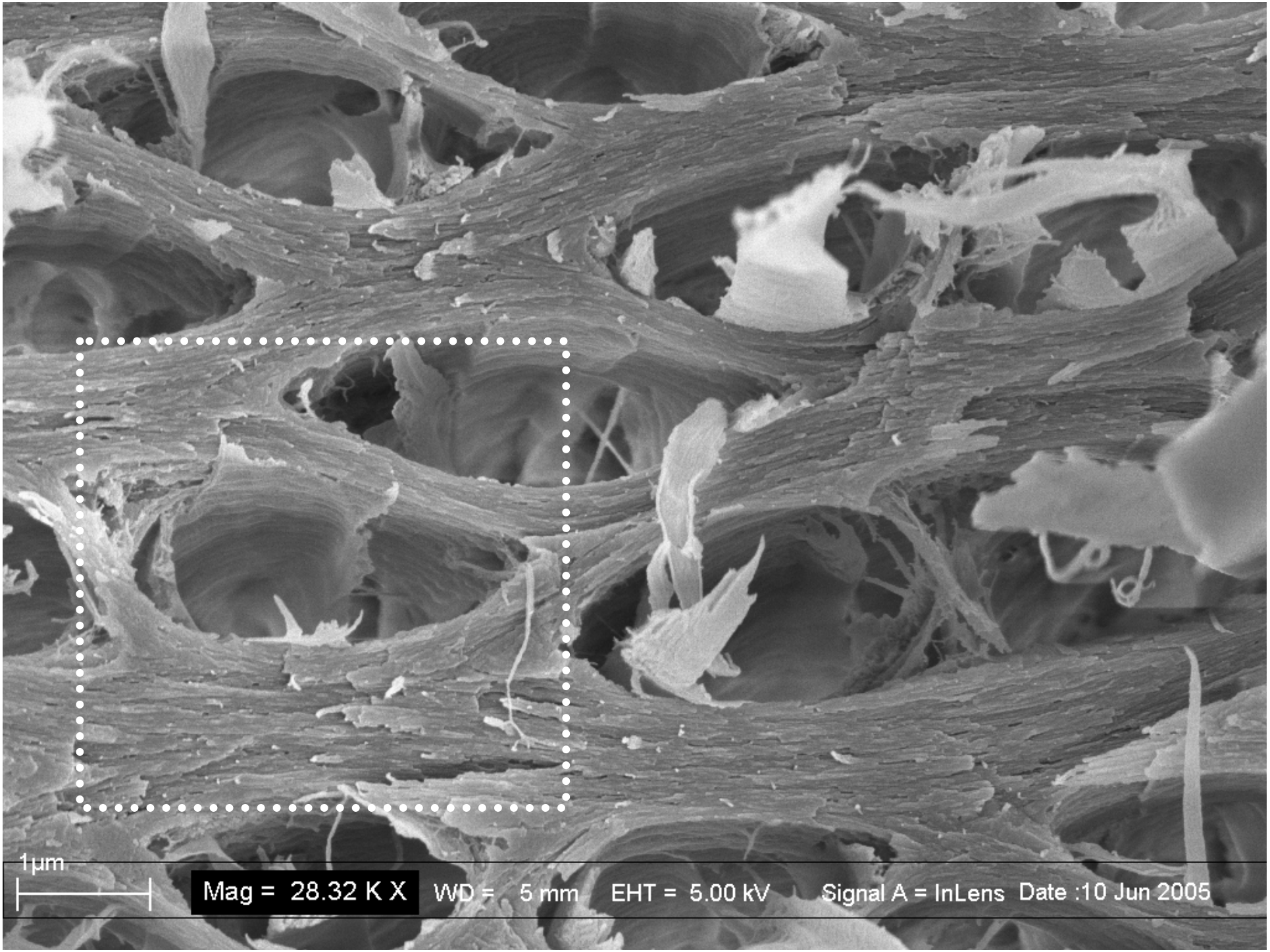

out-of plane
direction
y
x
10 µm

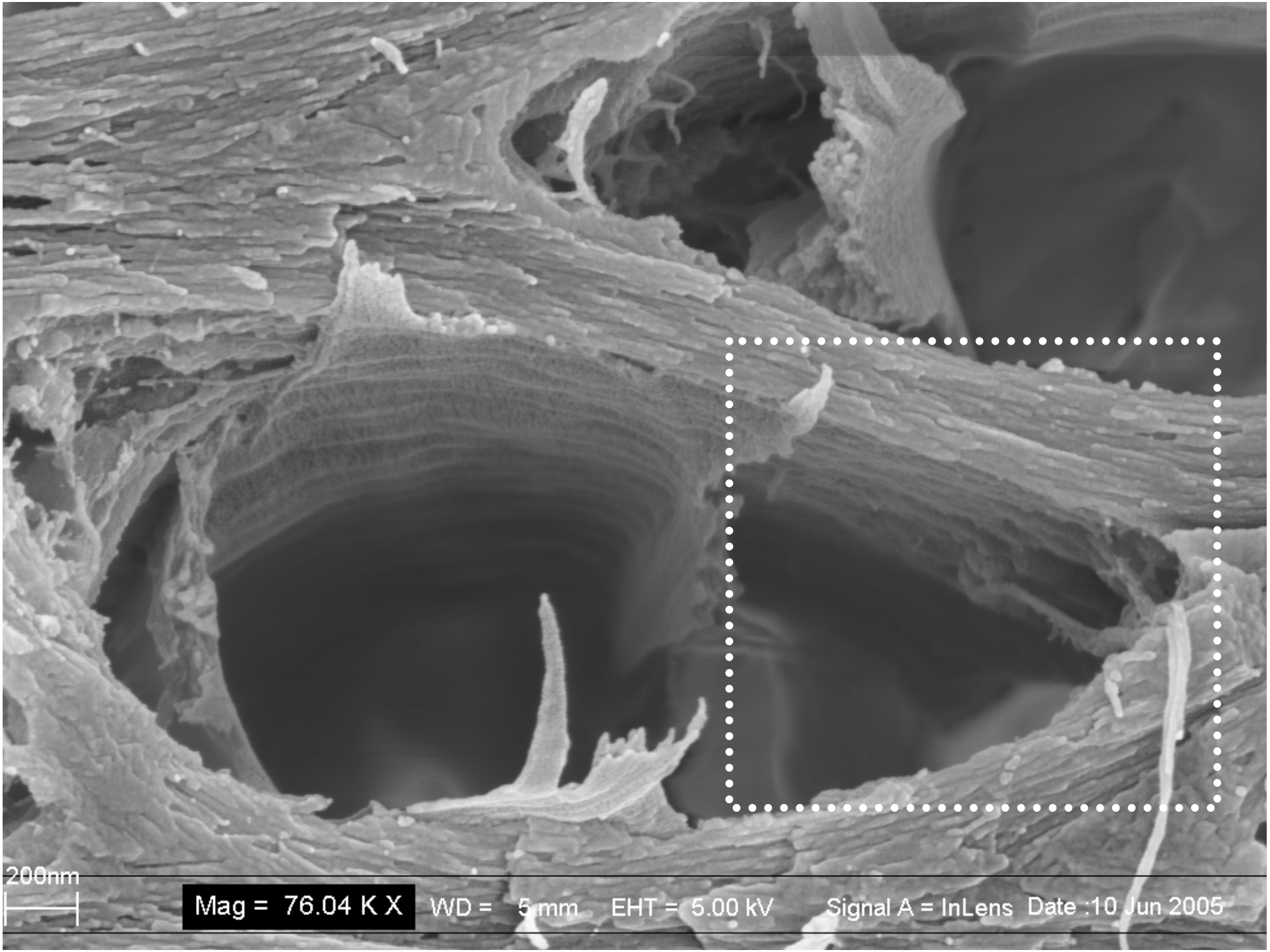

y
x
4 µm


Y
X
10 µm


y
x
4 µm


3µm
Mag = 12.45 K X
WD = 6 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005


1µm
Mag = 28.32 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005

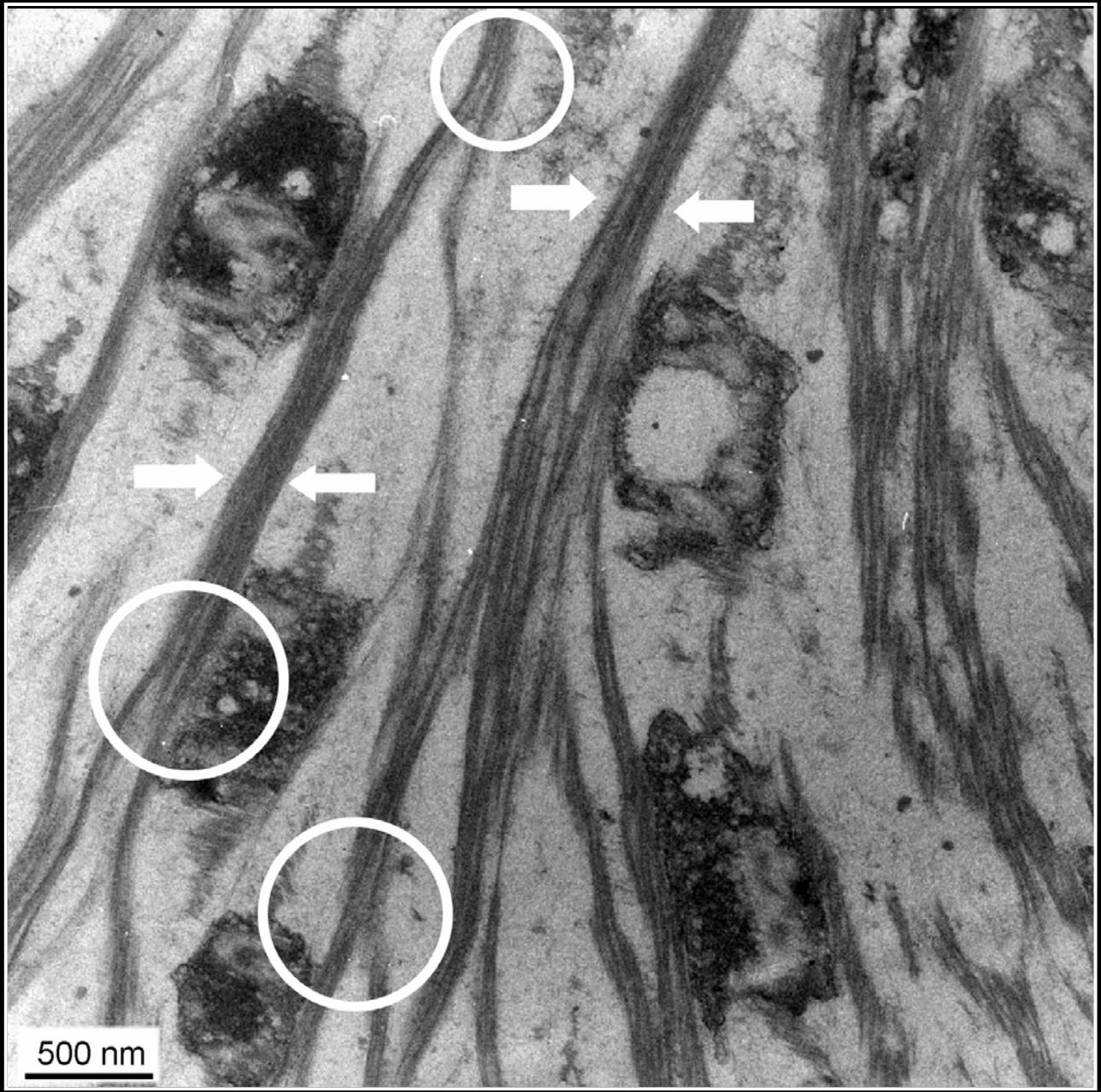

200nm
Mag = 76.04 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005


100nm
Mag = 133.31 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens Date :9 Jun 2005

TEM, lobster

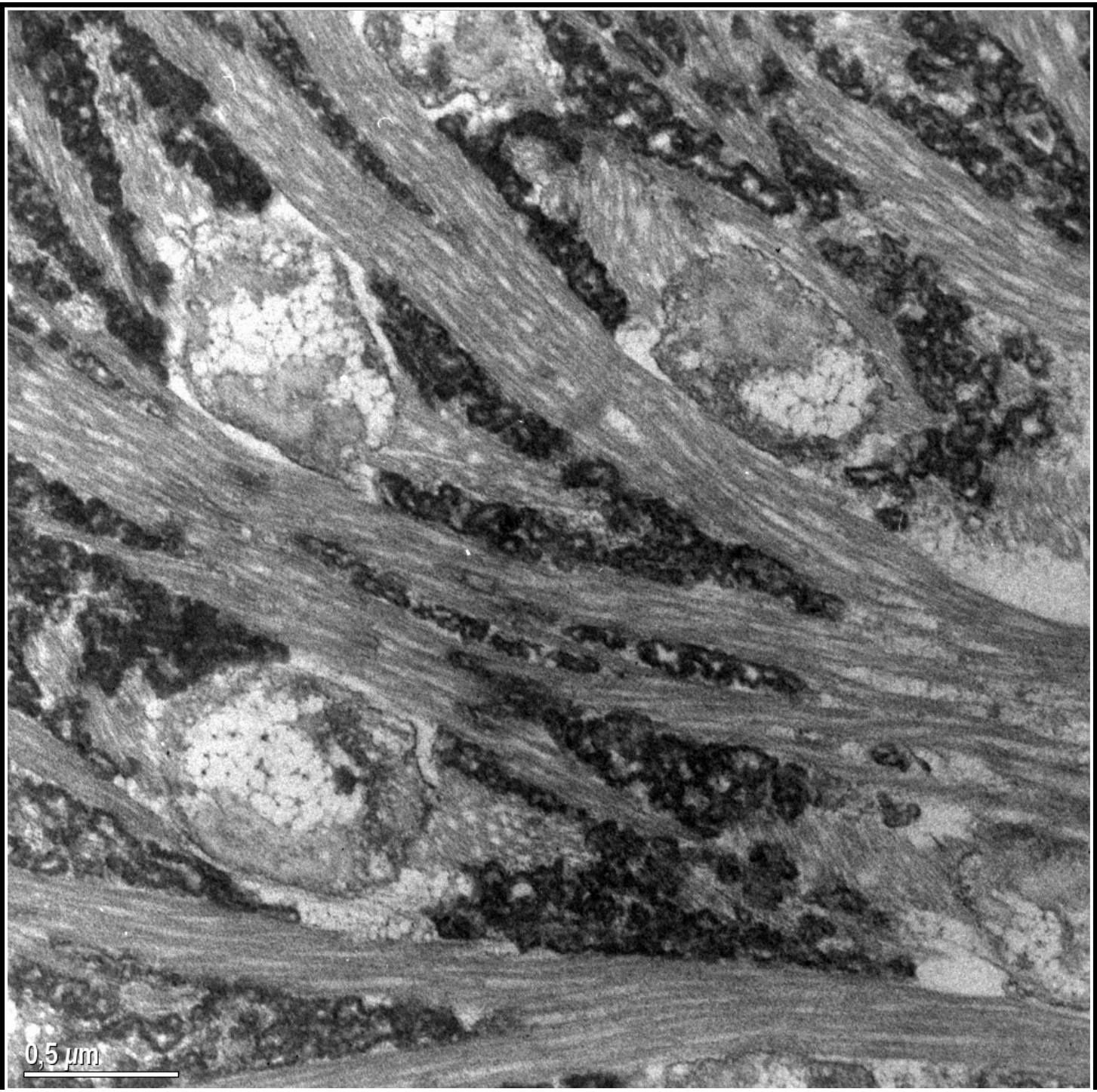
chitin fibril bundles

branching



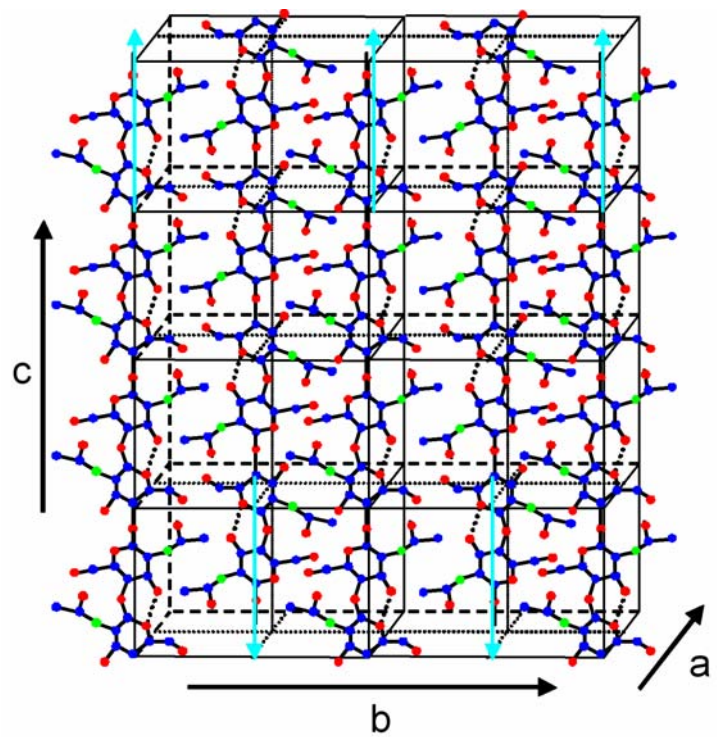
TEM

chitin fibril bundles



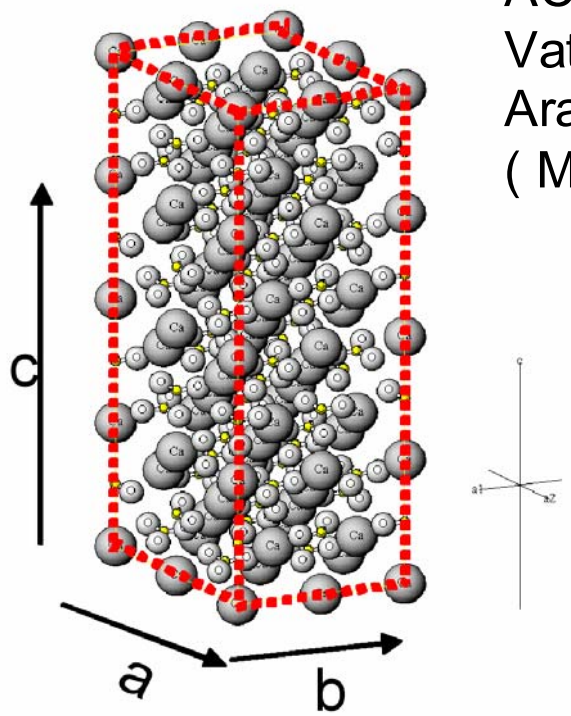
Phases and crystallography in crustaceans

α-Chitin $C_8H_{13}NO_5$



Calcite $CaCO_3$

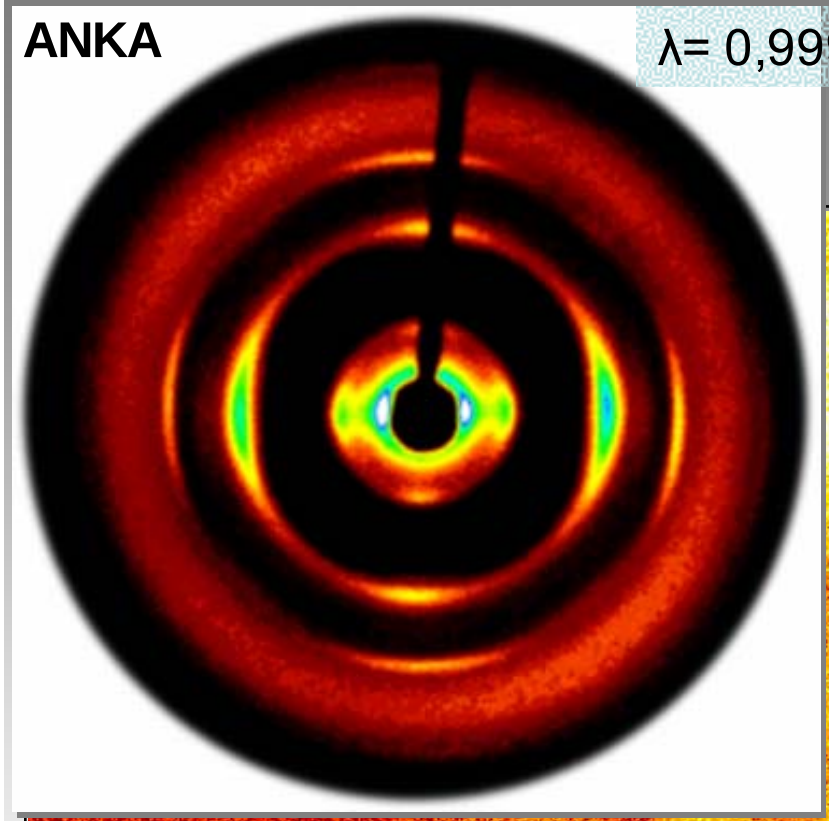
CC (calcite)
ACC
Vaterite
Aragonite
(Mg !)



- Density: 1,41 gm/cm^3
- Lin. absorbtion coef : 3700 μm^{-1} (@14 KeV(~ 1 Å))
- Orthorhombic **a= 4.74 Å, b= 18.86 Å, c= 10.32 Å** (Takai et al, 1992)
- Space group: P222 (# 16 @ITC)
- Point group: 222

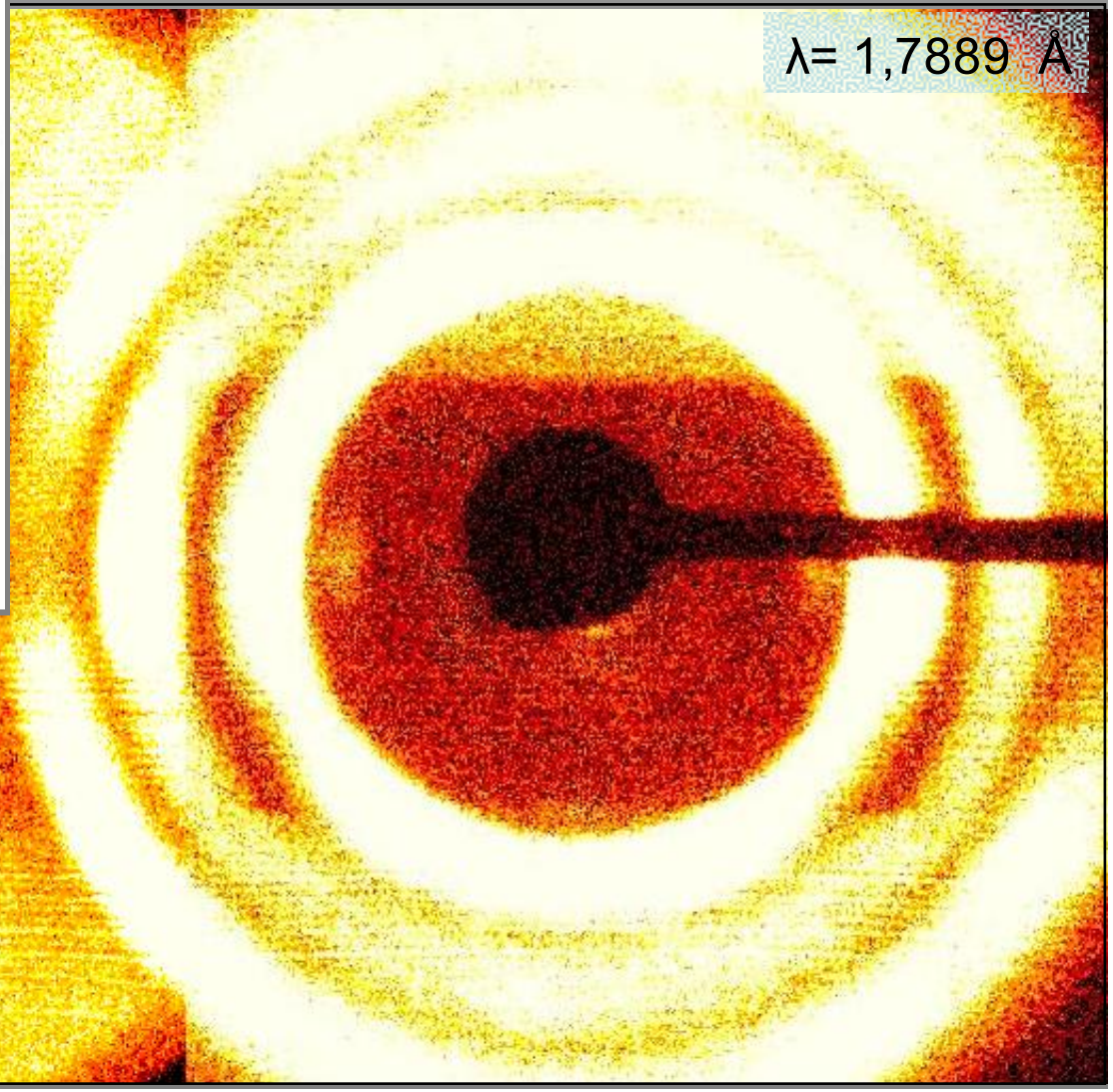
- Density: 2,71 gm/cm^3
- Lin. Absorbtion Coef. : 200 μm^{-1}(@14 KeV(~ 1 Å))
- Hexagonal , **a=b=4,989 Å, c=17.062 Å** (Maslen et al. 1993)
- Space group: R -3 2/c (#167 @ITC)
- Point group: -3 2/m

X-ray wide angle diffraction, lobster

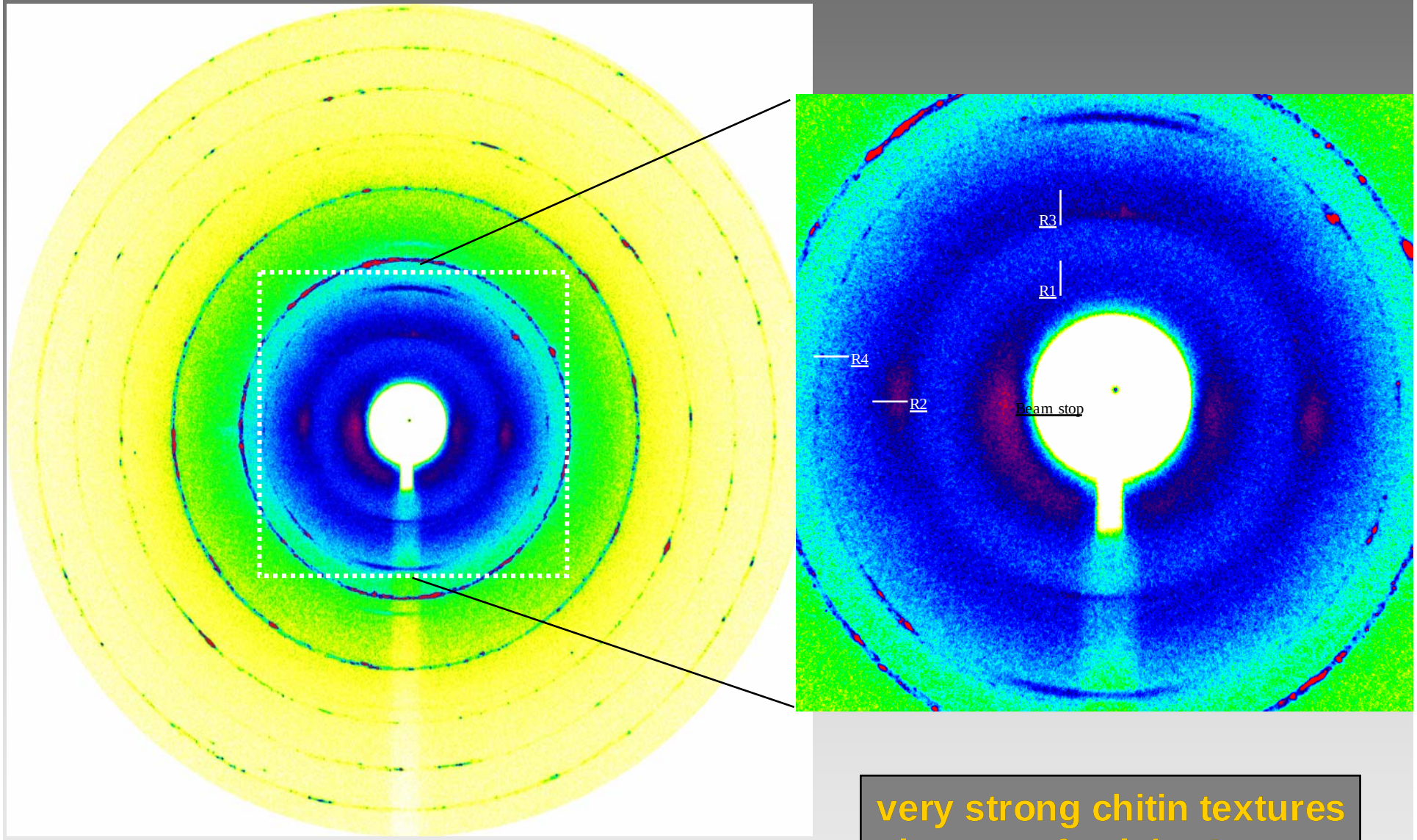


very strong chitin textures

Co-target



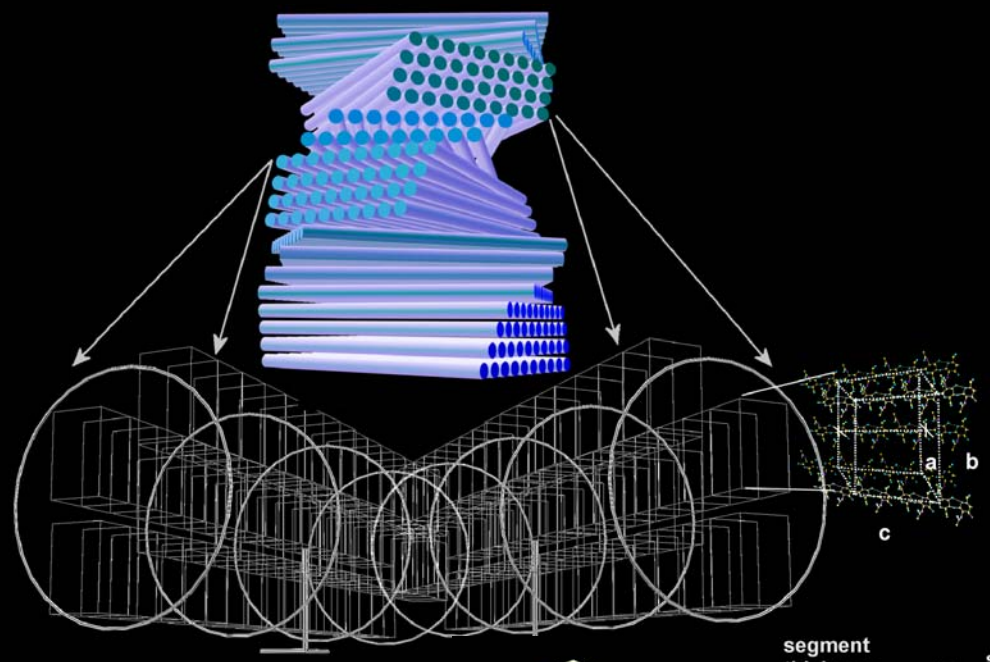
Synchrotron x-ray, wide angle, lobster

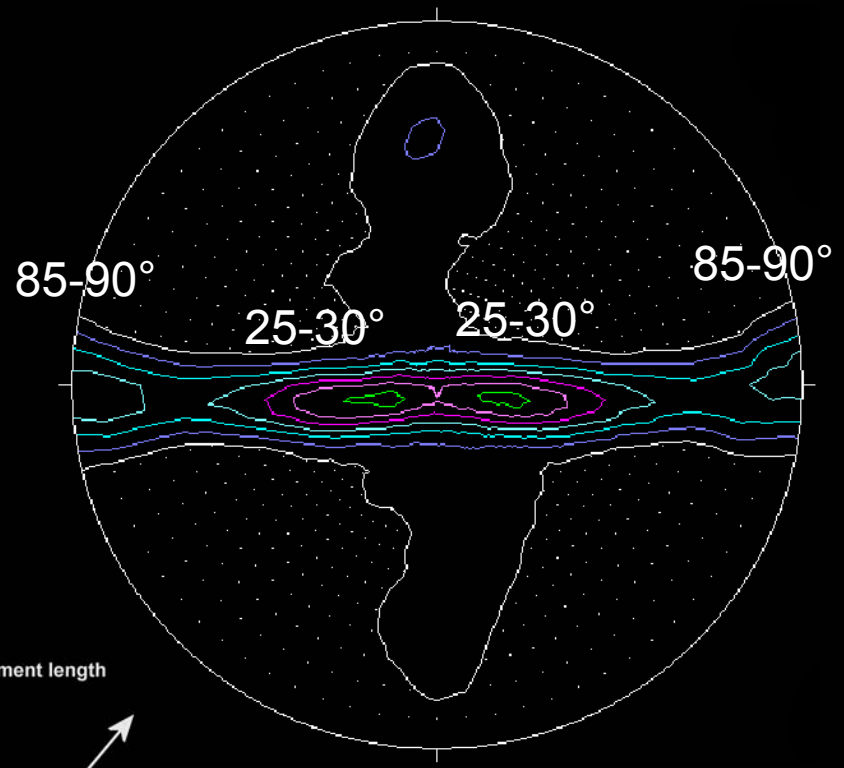


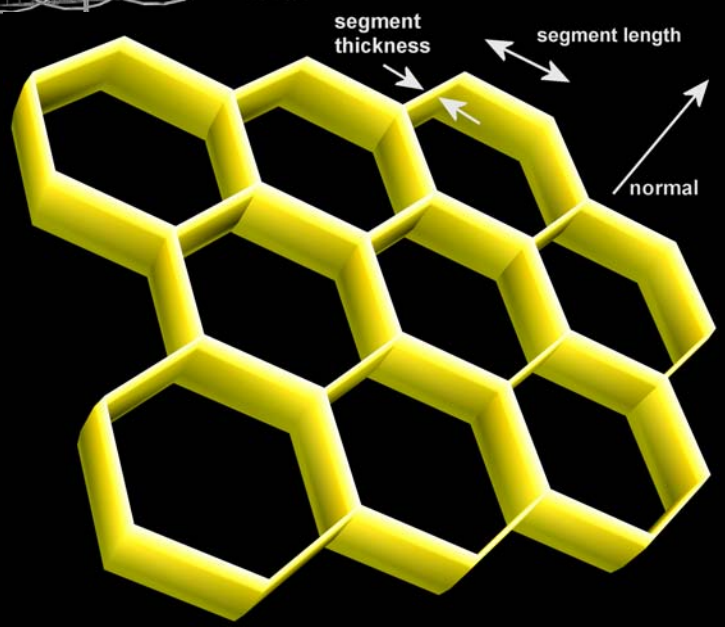
very strong chitin textures
clusters of calcite ?

DESY (BW5), λ=0.196 Å.

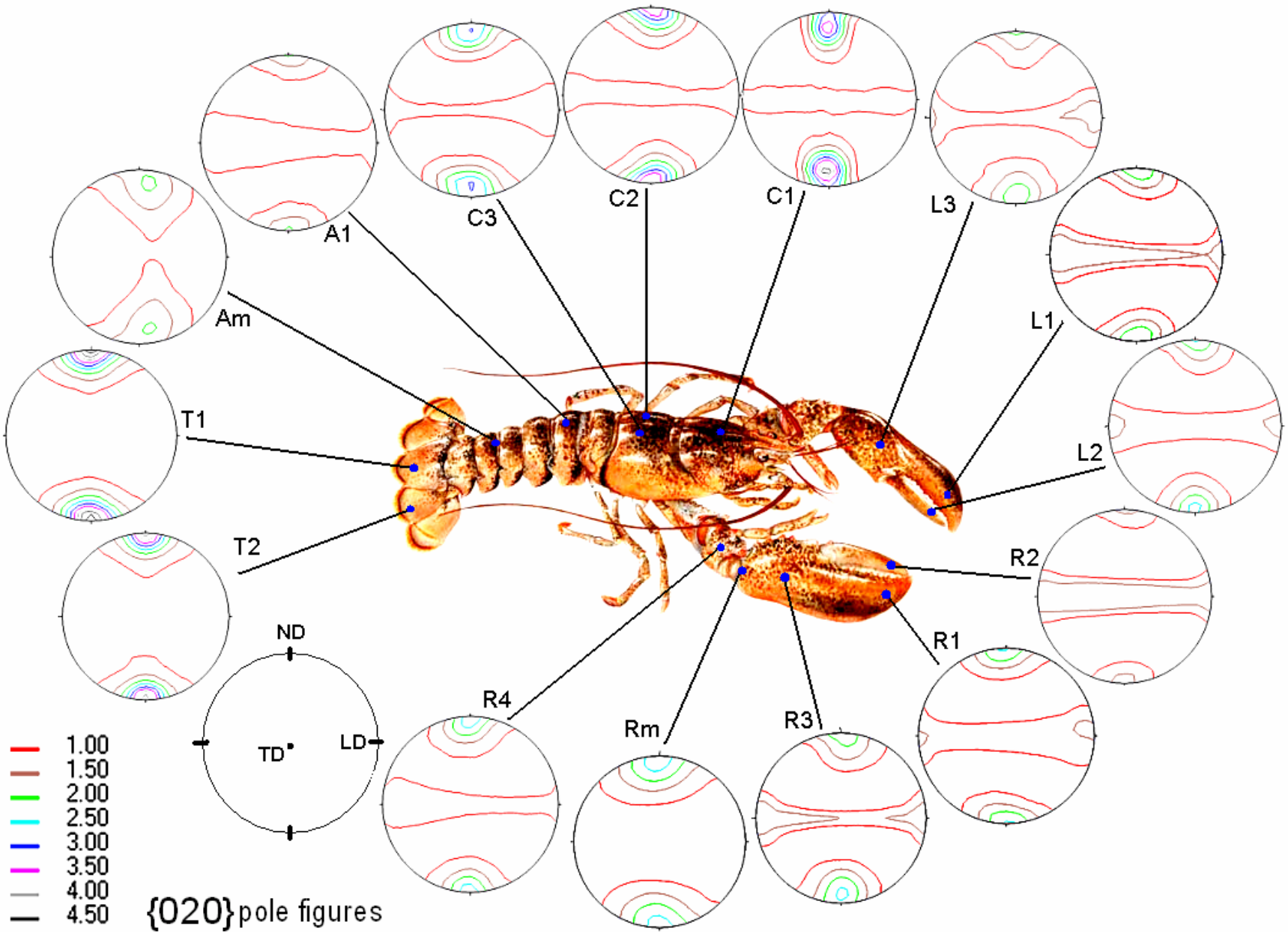
Structure and texture of chitin



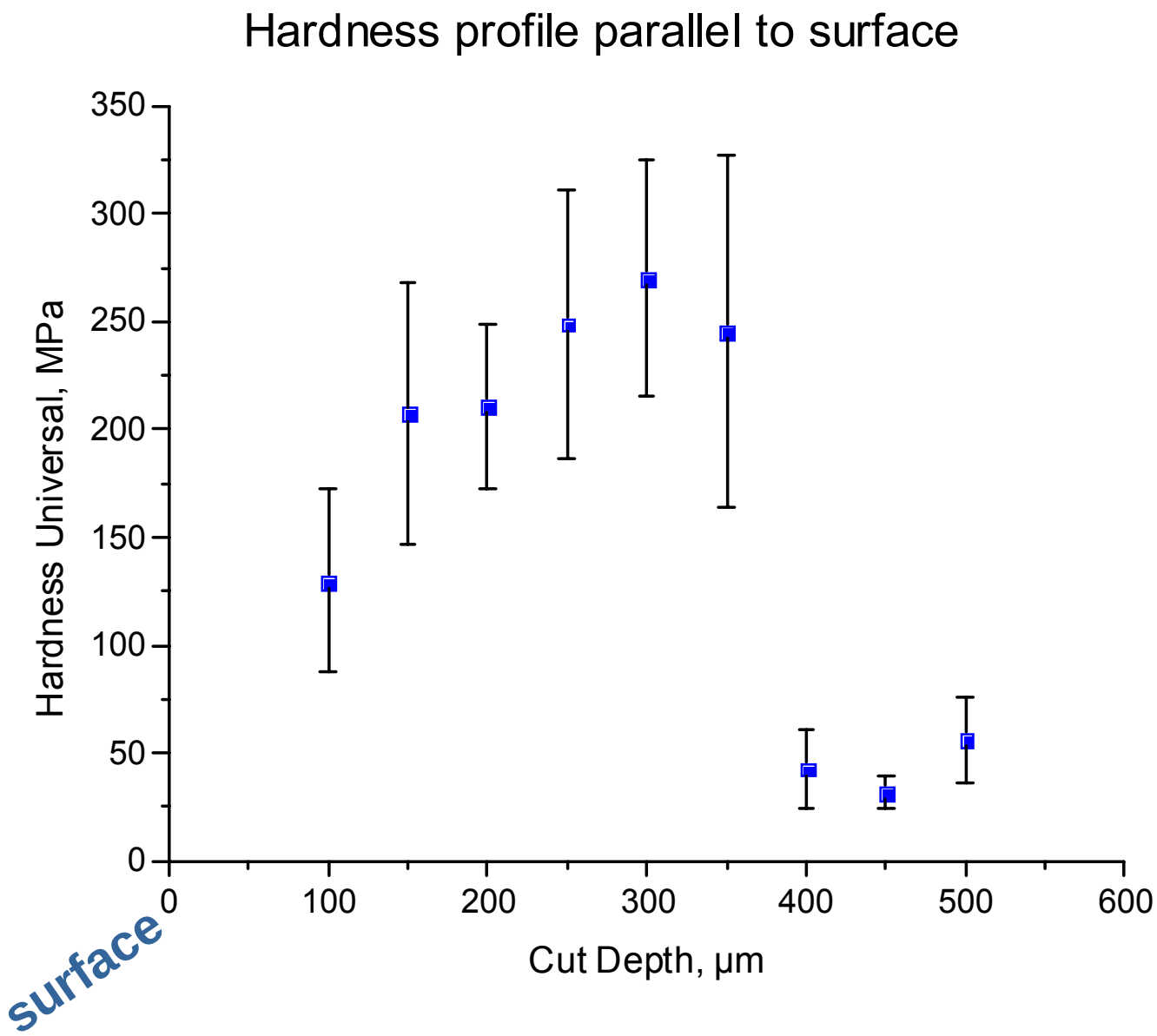




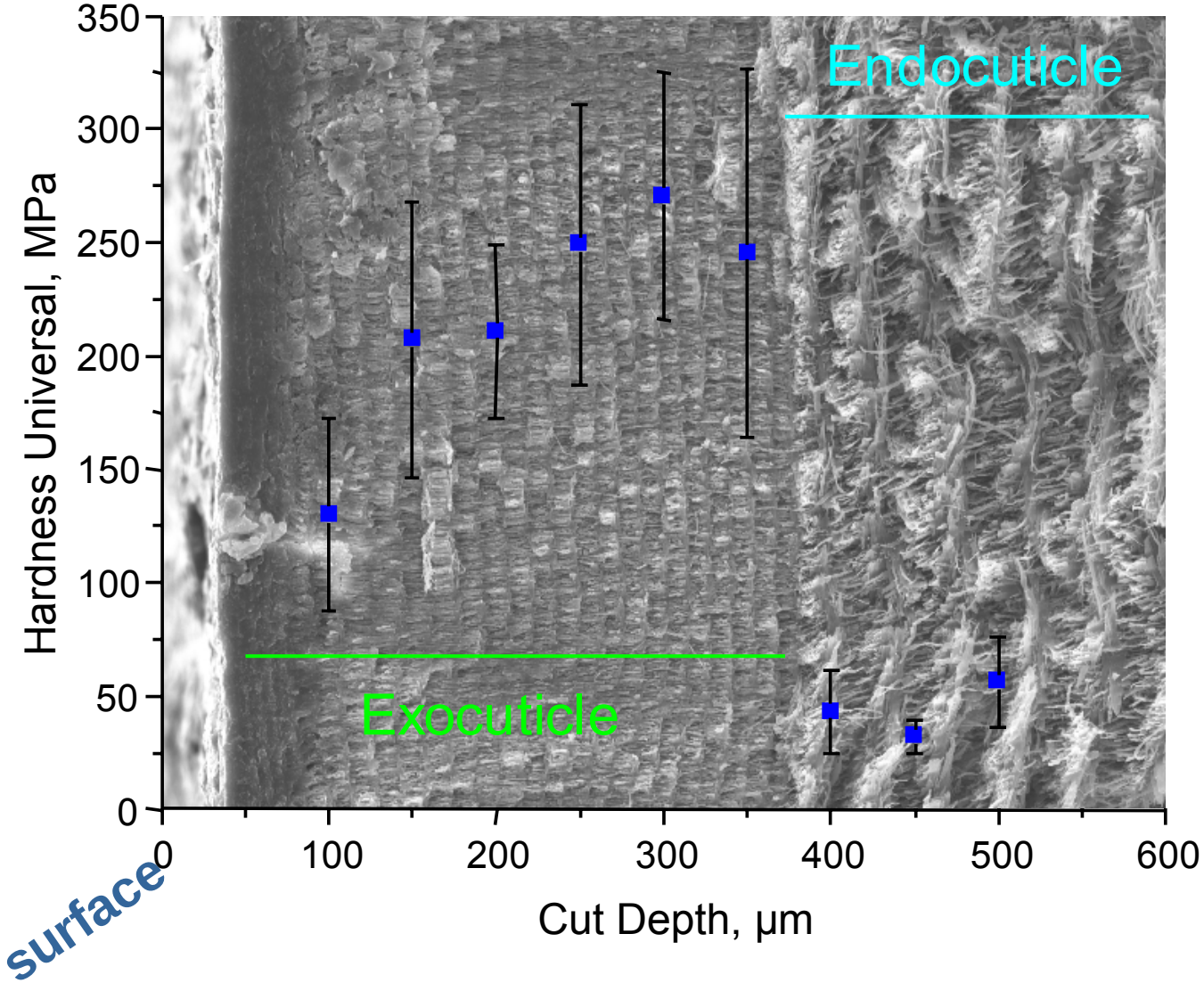
Smart design, local coordinate system



Hardness

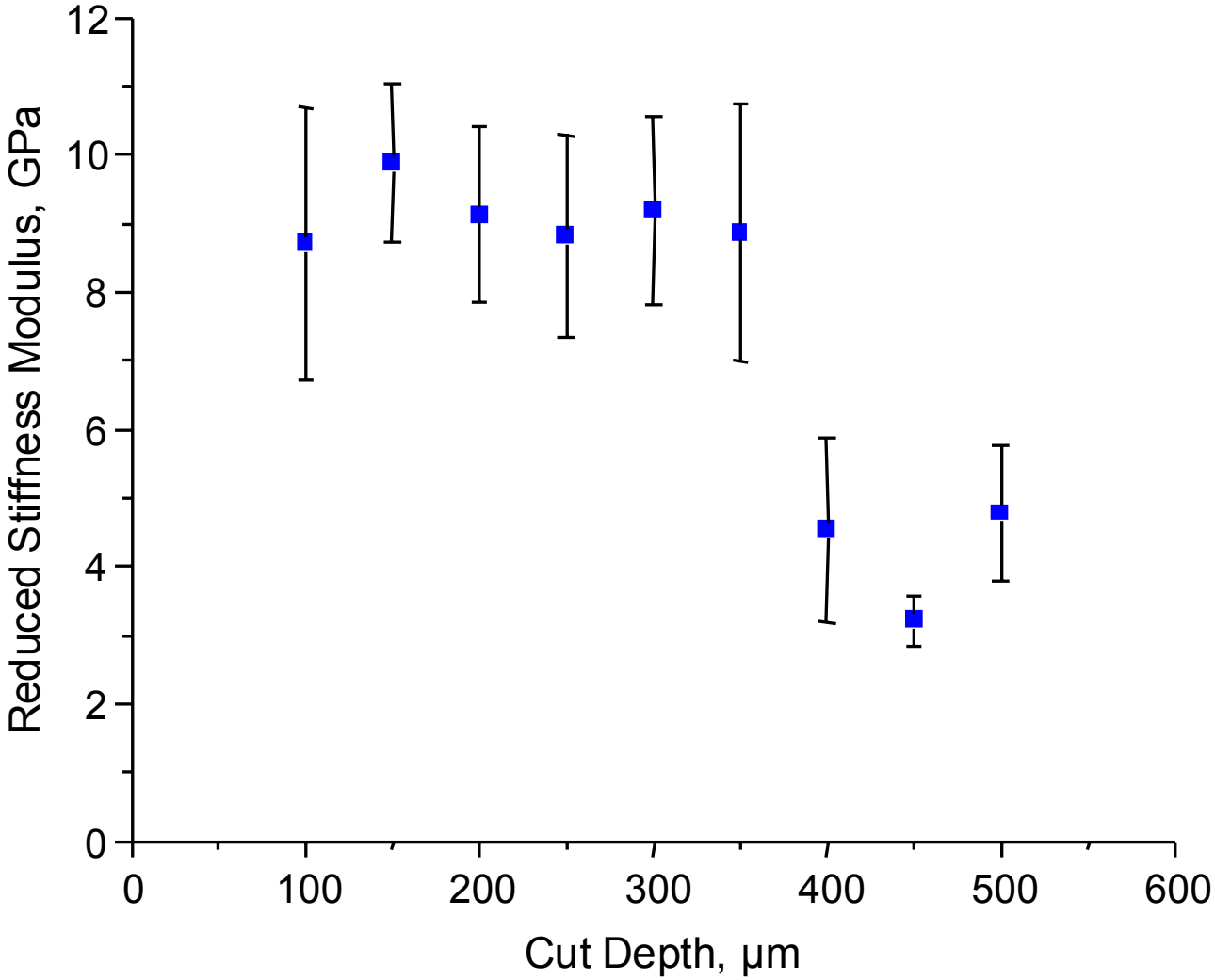

Hardness profile parallel to surface
Hardness Universal, MPa
350
300
250
200
150
100
50
0
0
100
200
300
400
500
600
Cut Depth, µm
surface

Hardness

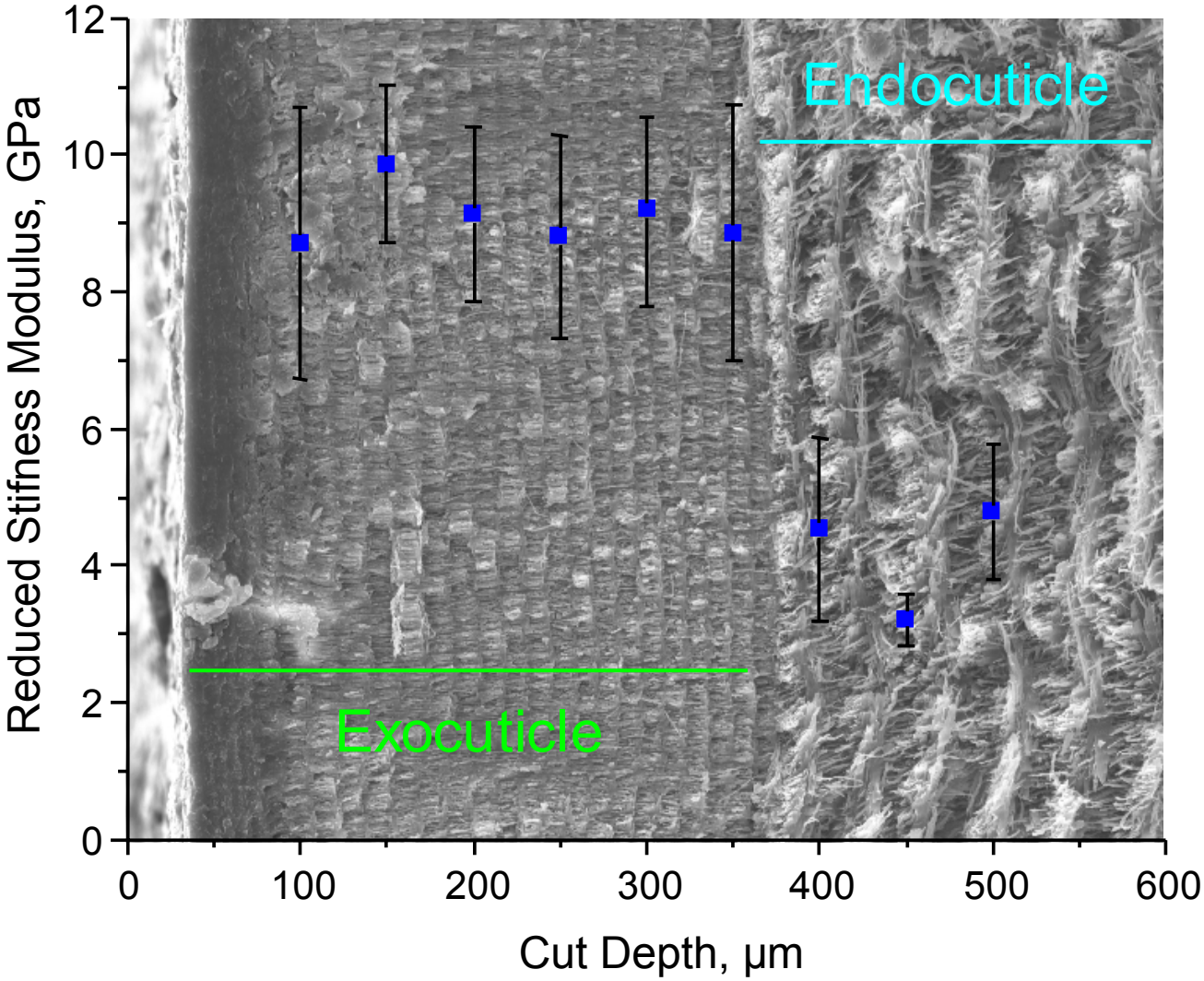

Endocuticle
Exocuticle
Hardness Universal, MPa
350
300
250
200
150
100
50
0
0
100
200
300
400
500
600
Cut Depth, µm
surface

Micro-Indentation - stiffness

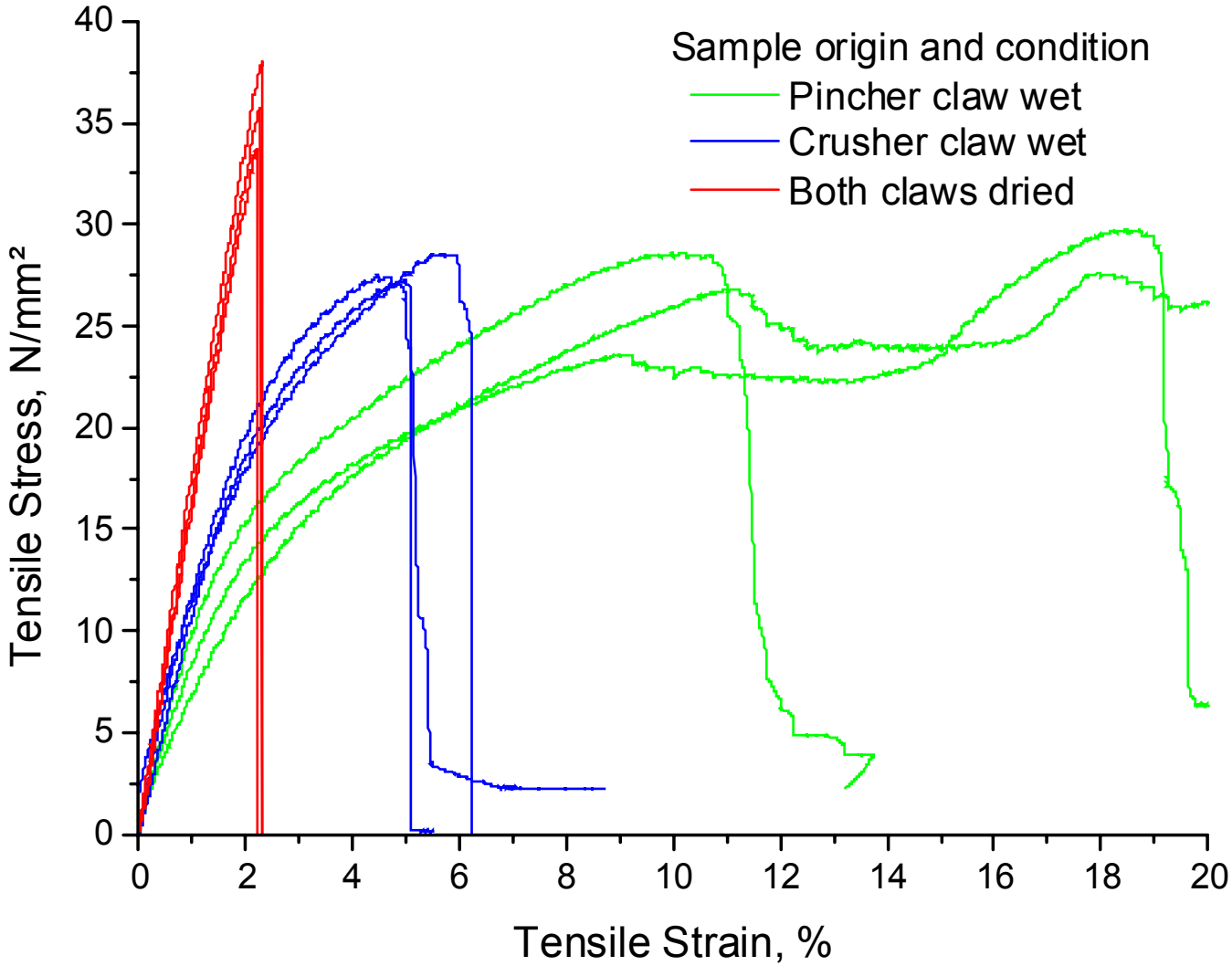
Reduced stiffess profile parallel to surface



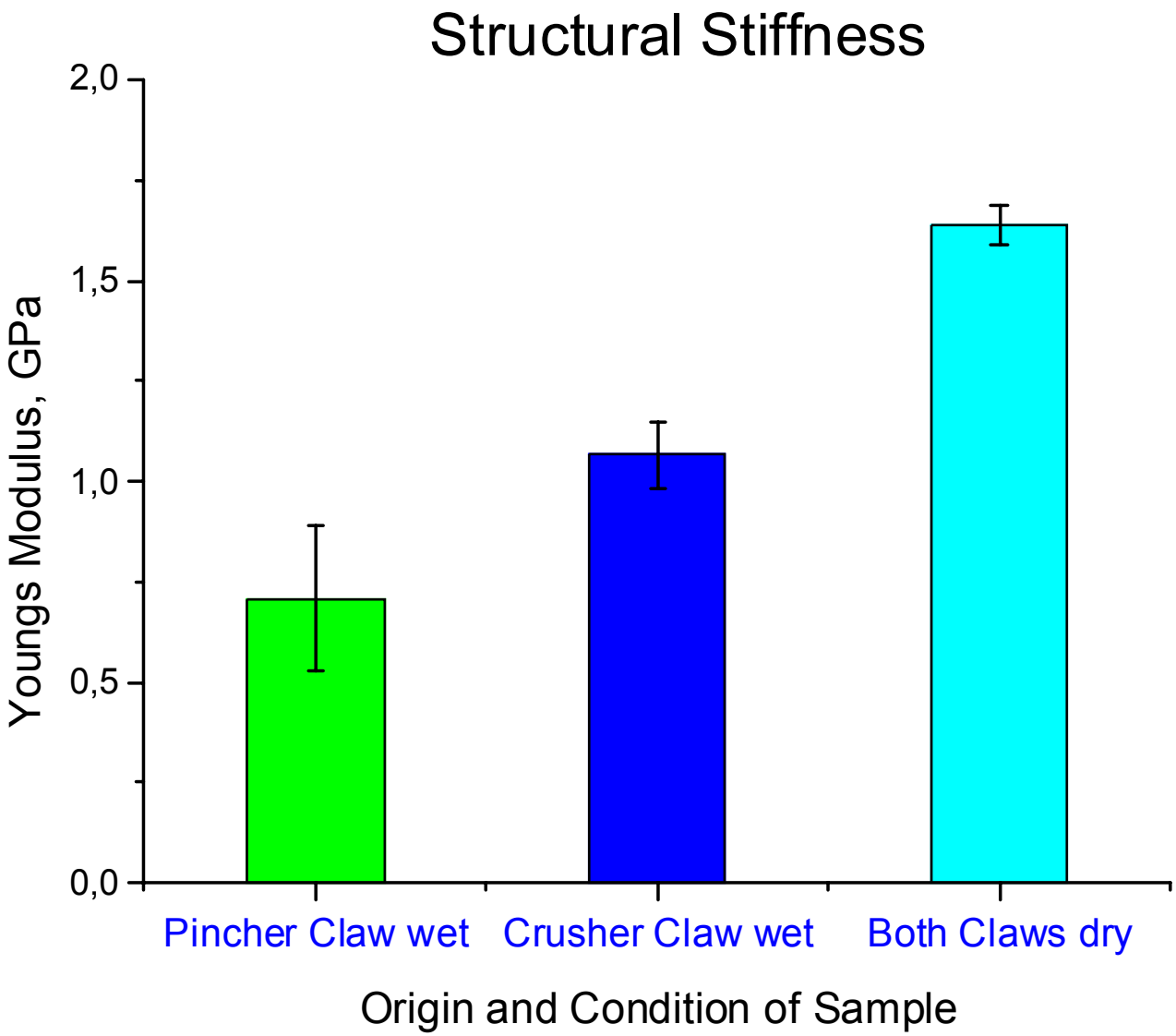
Micro-Indentation - stiffness



Tensile testing



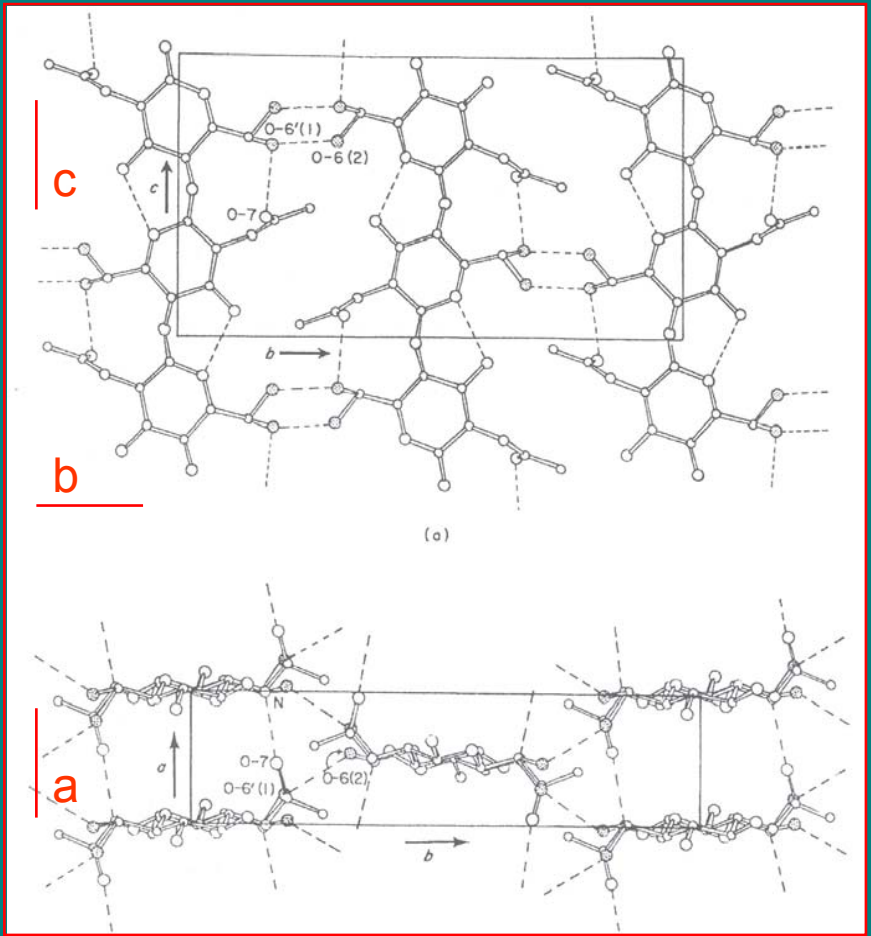
Tensile testing



MD, LDF (Petrov, Limperakis, Neugebauer)

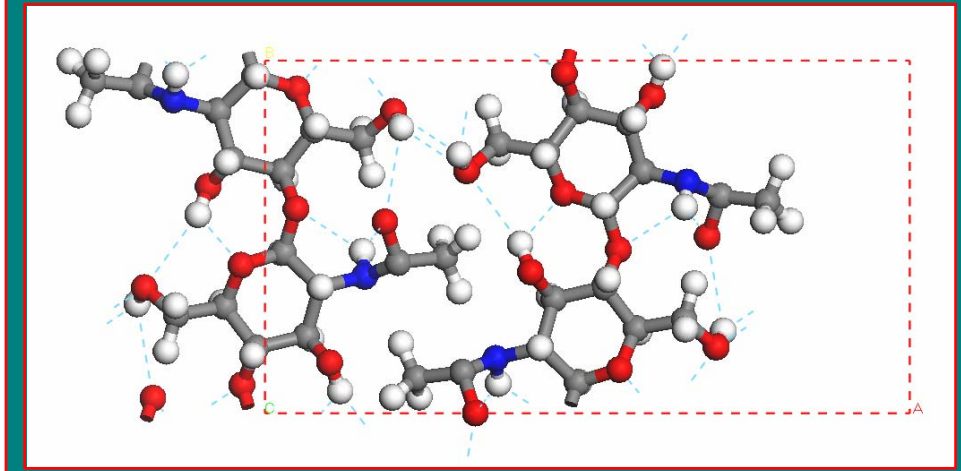
Searching the structure, checking available data

Ref: R. Minke and J. Blackwell, J. Mol. Biol. 120, 167 – 181 (1987).



Atomic geometry for atomic scale calculations?

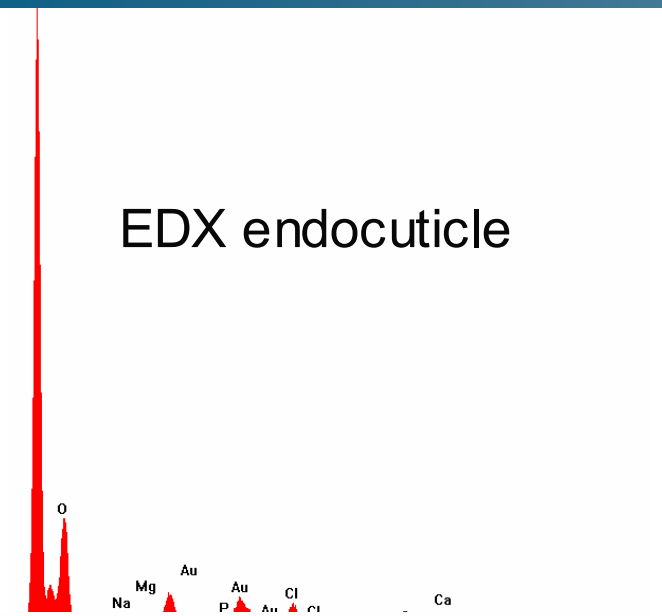
conformational analysis with respect to potential energy and H-bond formation

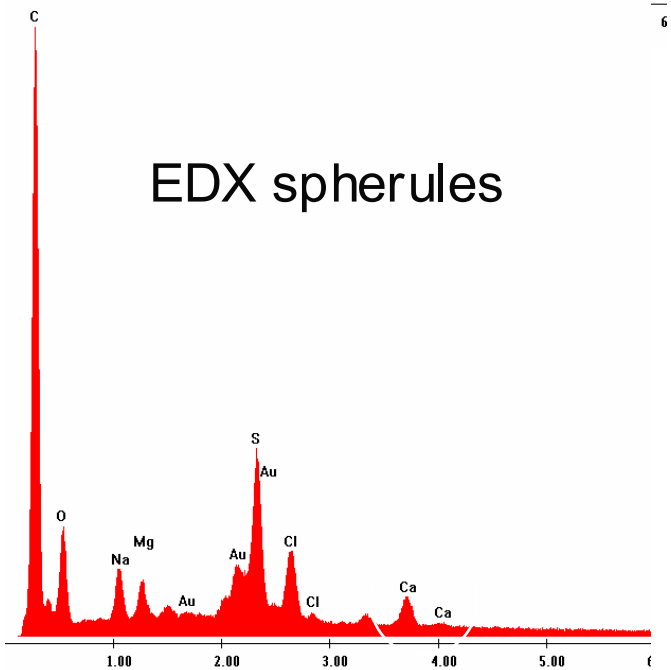


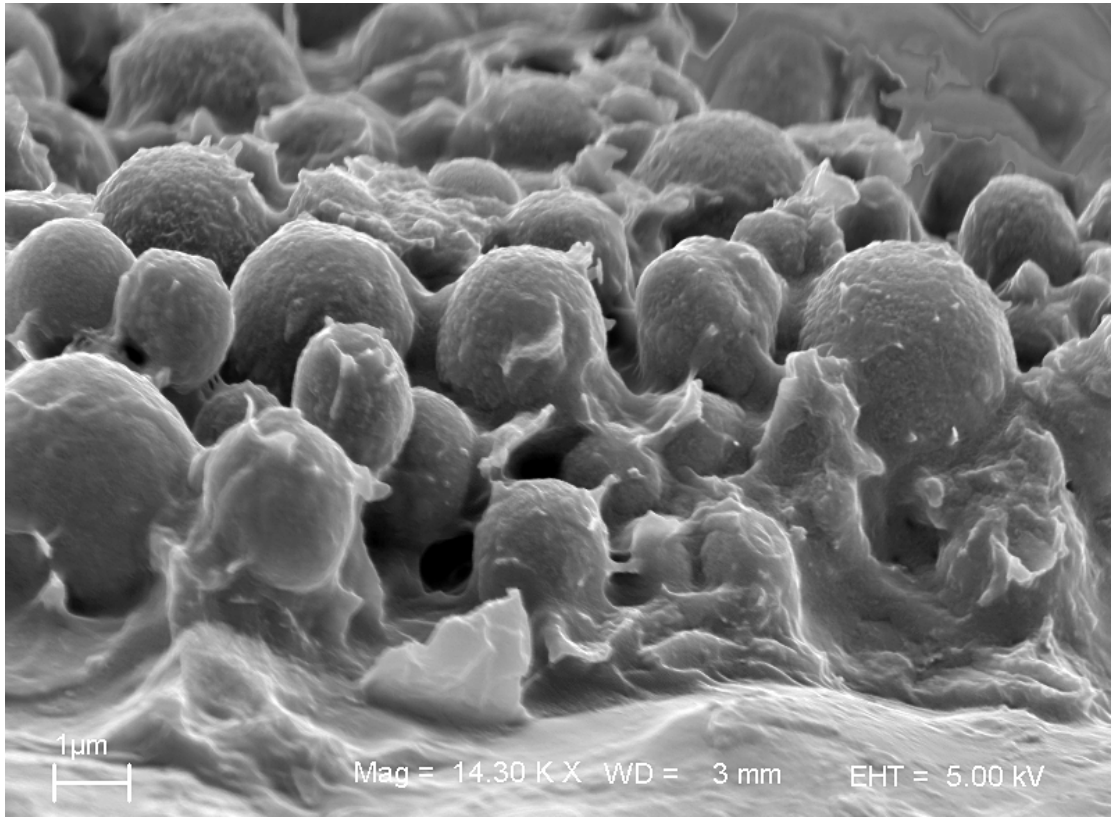
find a stable atomic geometry of the α - chitin

SEM: Horseshoe crab endocuticle, untreated

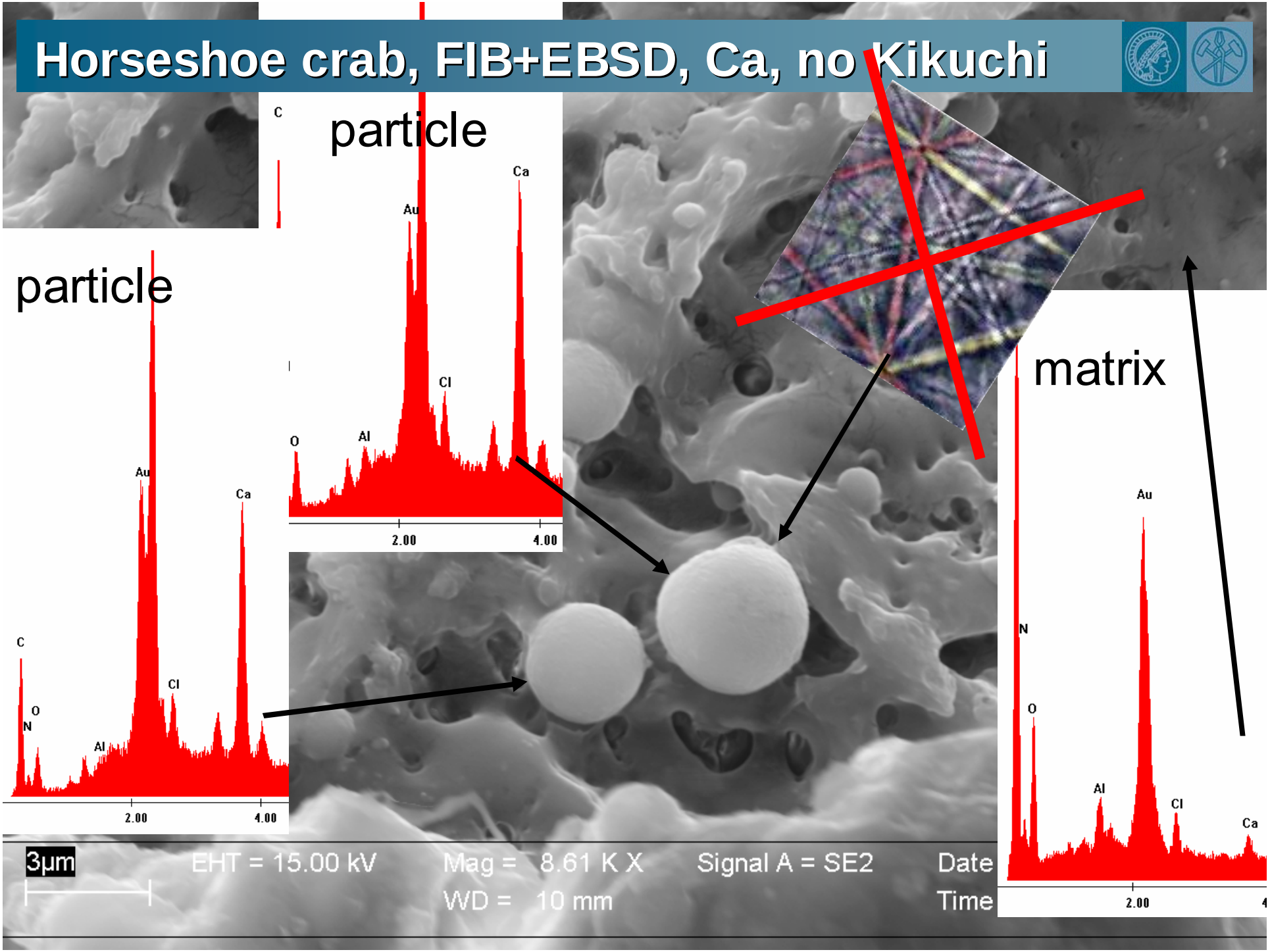
The spherules contain calcium, probably as $CaCO_3$







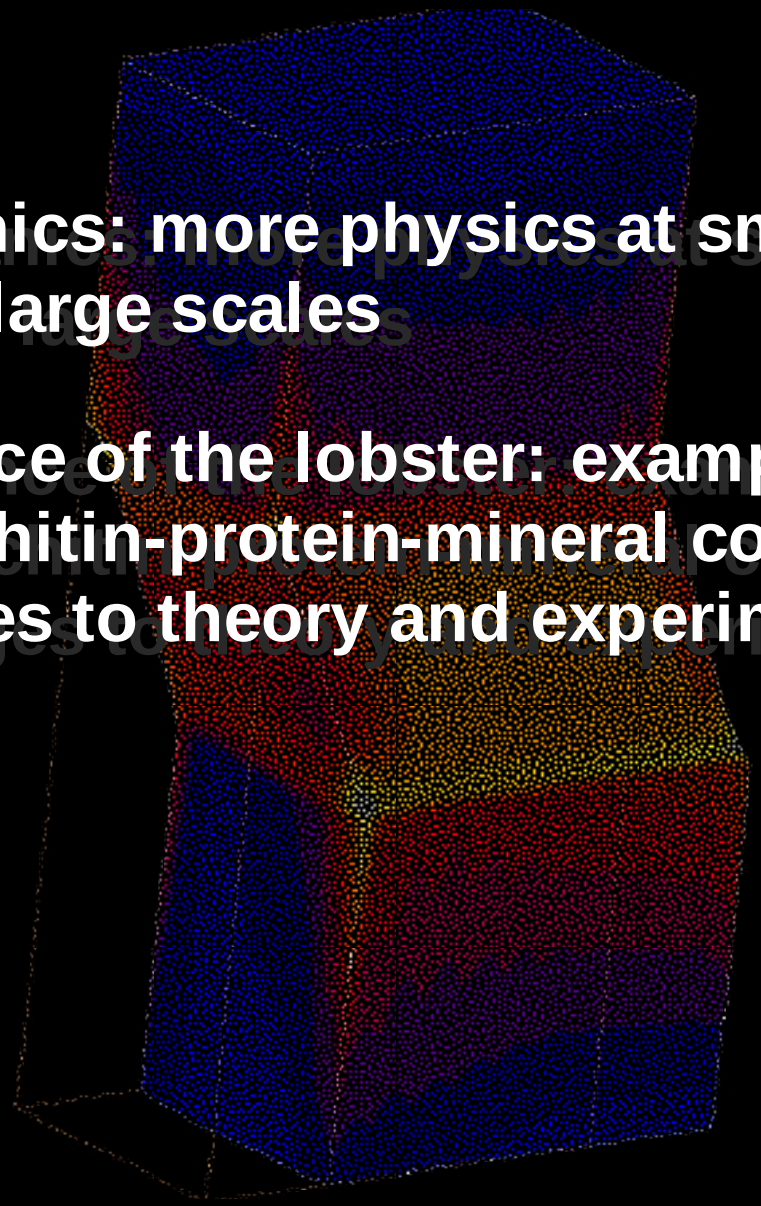
Horseshoe crab, FIB+EBSD, Ca, no Kikuchi



Messages of the day

Crystal mechanics: more physics at small scales; more maths at large scales

Materials science of the lobster: example of an extraordinary chitin-protein-mineral composite with many challenges to theory and experiment



!! Thanks !! to the team

Roters, Ma: crystal mechanics
Sachs, Romano, Al-Sawalmih, Fabritius: chitin-composites
Zaefferer, Bastos: 3D Microscopy
Neugebauer, Petrov, Limperakis: ab initio and MD

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DFG