Understanding structure and mechanical properties of the arthropod cuticle using multiscale simulation: Example of Homarus Americanus

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Overview

- Motivation
- Structure and property overview
- Ab initio prediction of chitin (structure, stiffness)
- Ab initio prediction of calcite (dopant effects on structure)
- Multiscale modeling of stiffness
- Summary and conclusions

Raabe: Adv. Mater. 14 (2002)

Chitin: Exoskeleton component of >90% of all animals on earth:

Arthropods: insects; crustaceans (lobsters, crabs, shrimp); chelicerates (spiders, scorpions)









The materials science of chitin composites: motivation

Arthropods have adapted to every habitat on earth: adaptive material → candidate for bio-inspired material

Chitin basics unknown → ab initio

Influence of dopants on biominerals → ab initio

Common feature: hierarchical cuticle → composite design

Good mechanical properties → multiscale modeling and bioinspired carbon-based compounds

Nikolov et al. :Adv. Mater. 22 (2010) 519

Building units

- Organic matrix in most parts of the cuticle
  - the organic material (chitin, proteins) is combined with inorganic nano-particles

- Inorganic nano-particles
  - consists of amorphous or crystalline (calcite) $CaCO_3$
  - $CaCO_3$ doped by Mg
  - arrangement according to the organisation of the chitin-protein fibres

- Cuticle
  - is a hierarchical composite material that combines high mechanical strength with a high functional versatility

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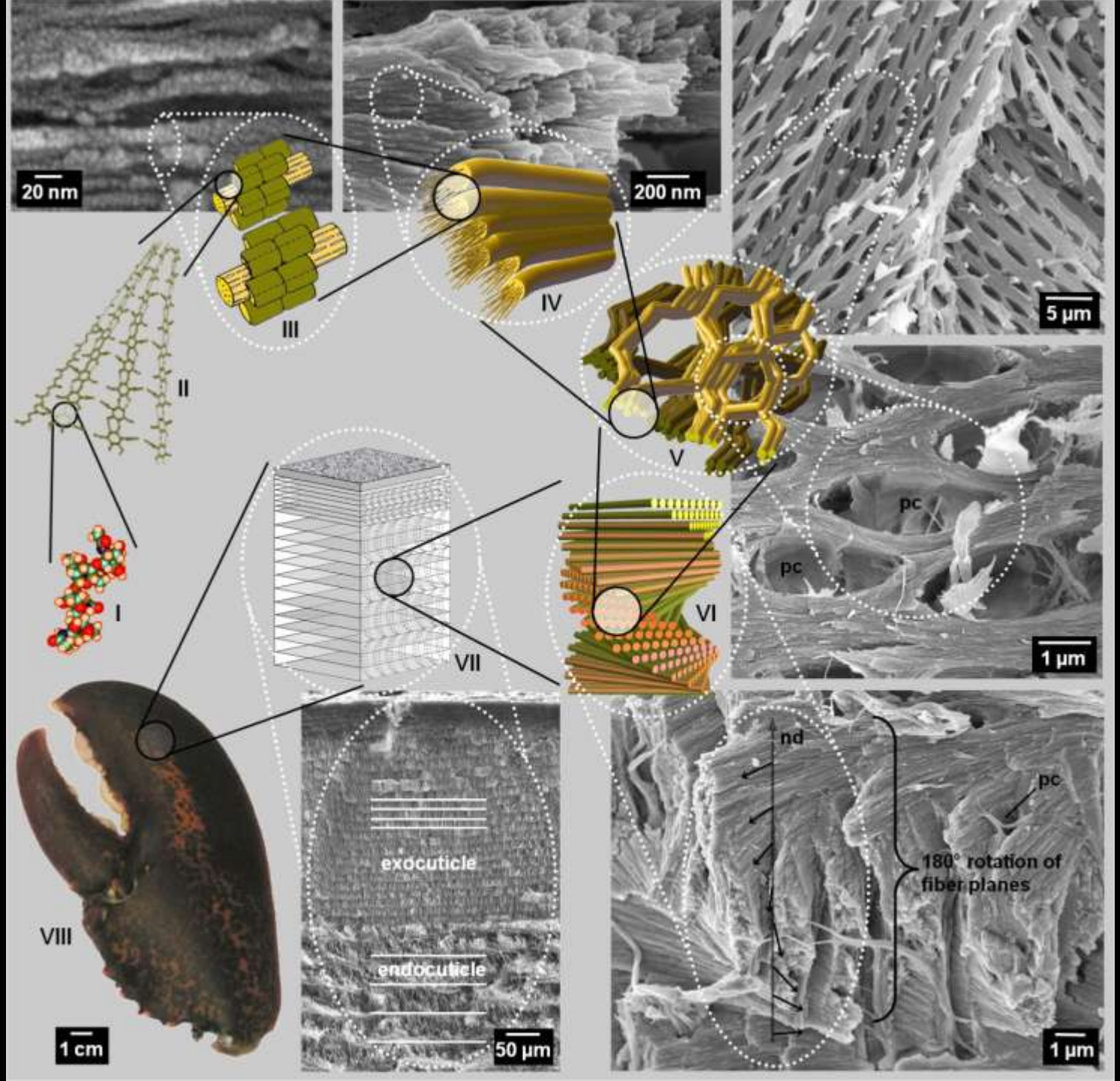
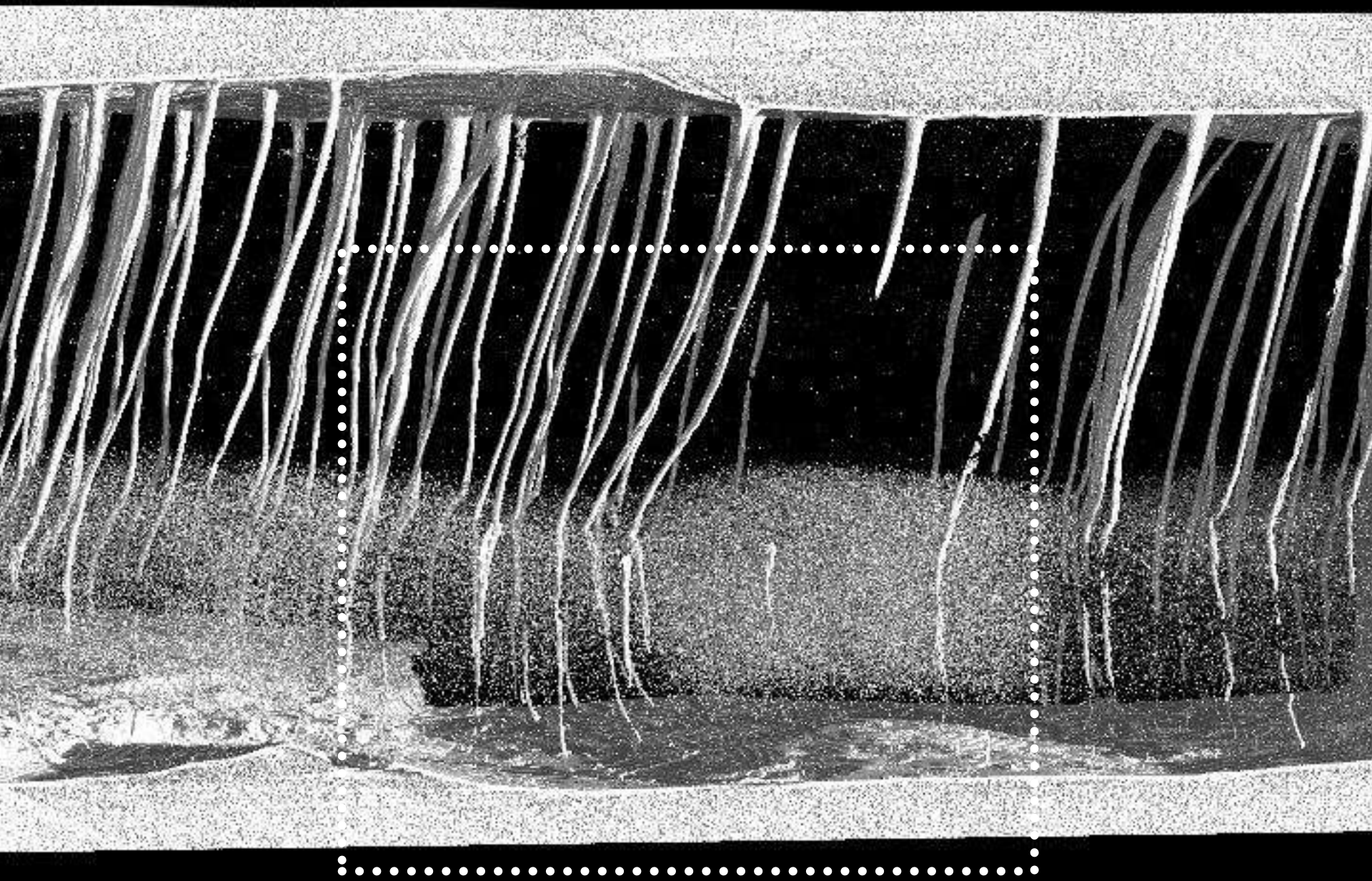
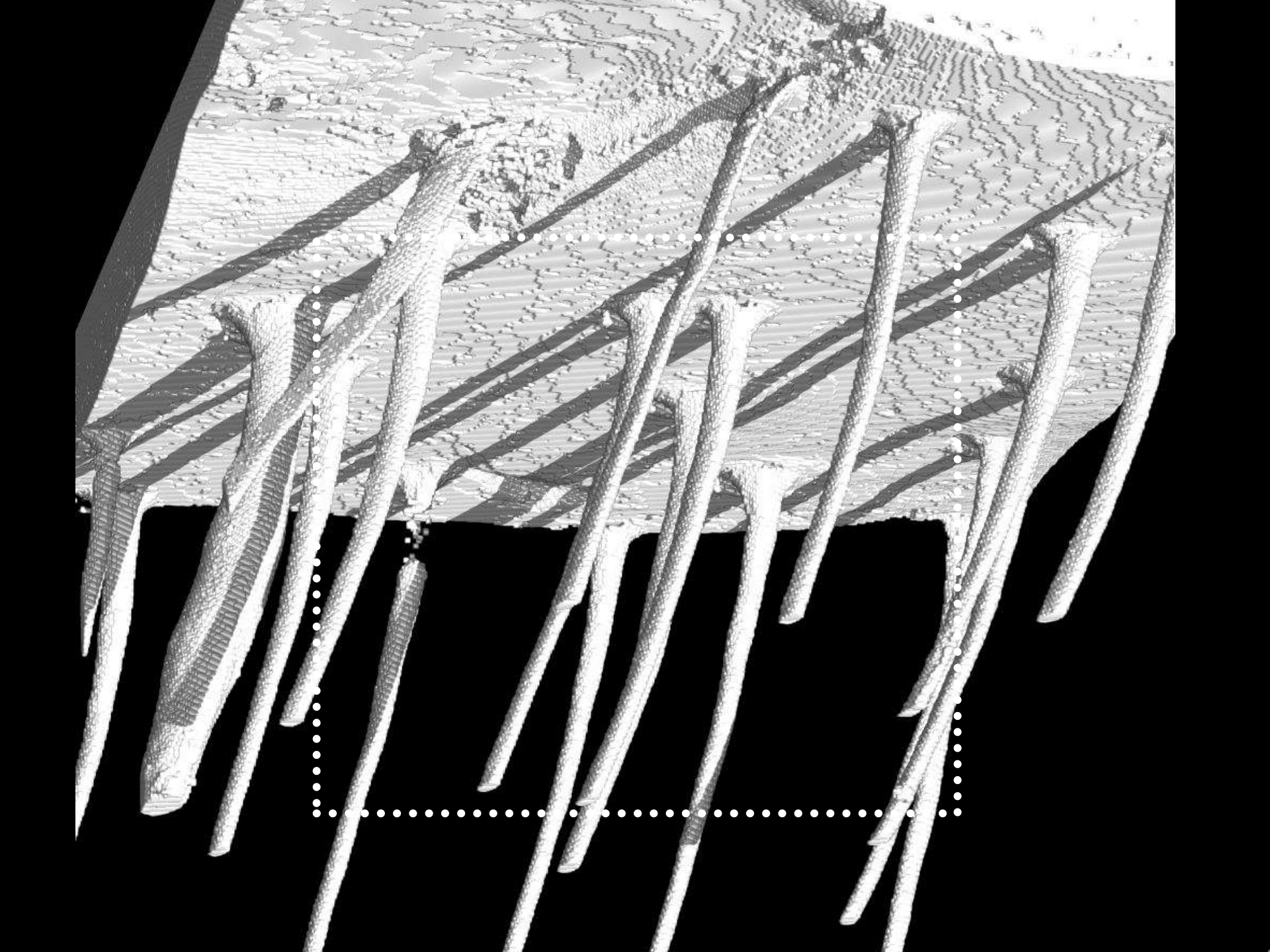
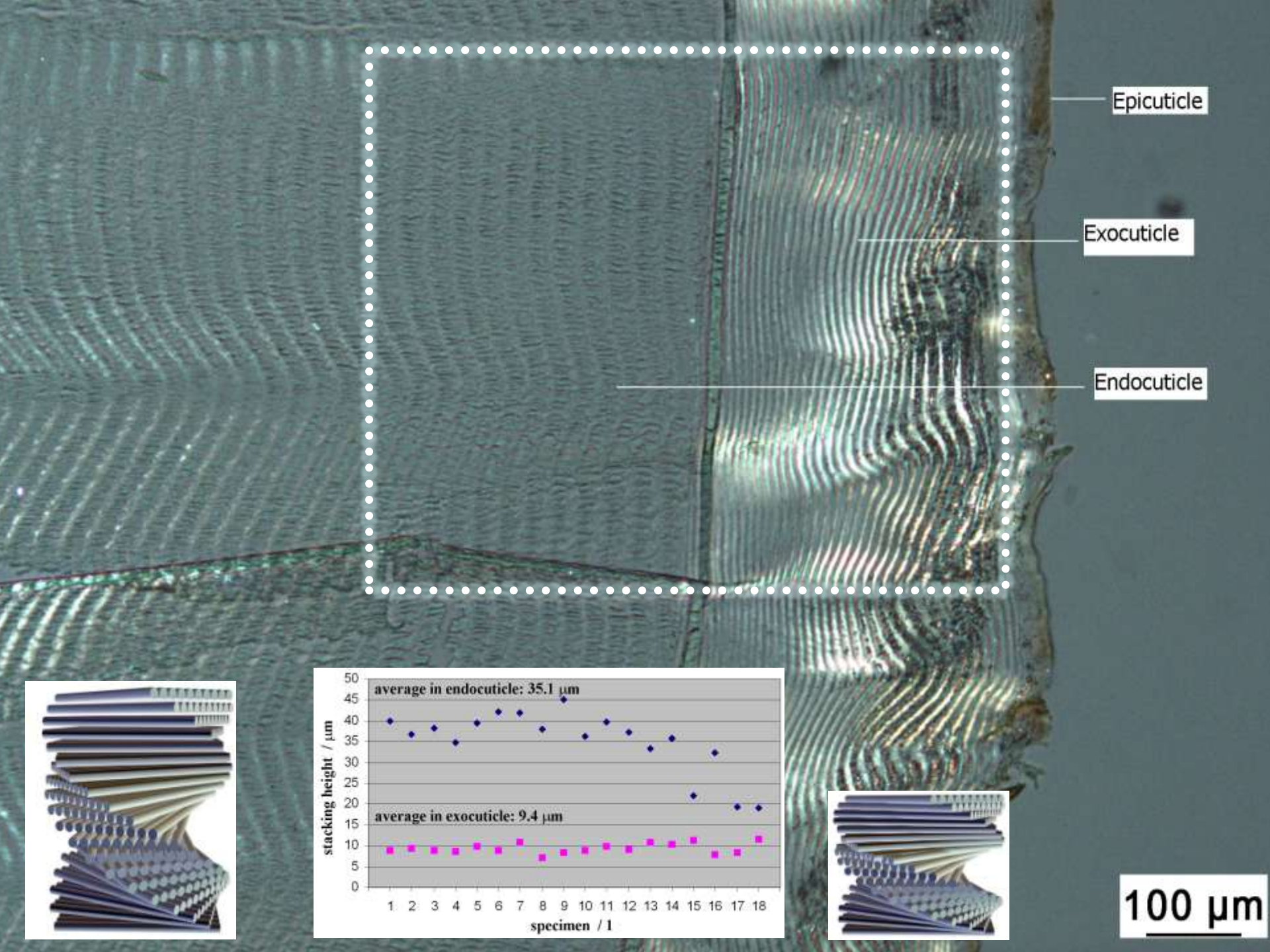
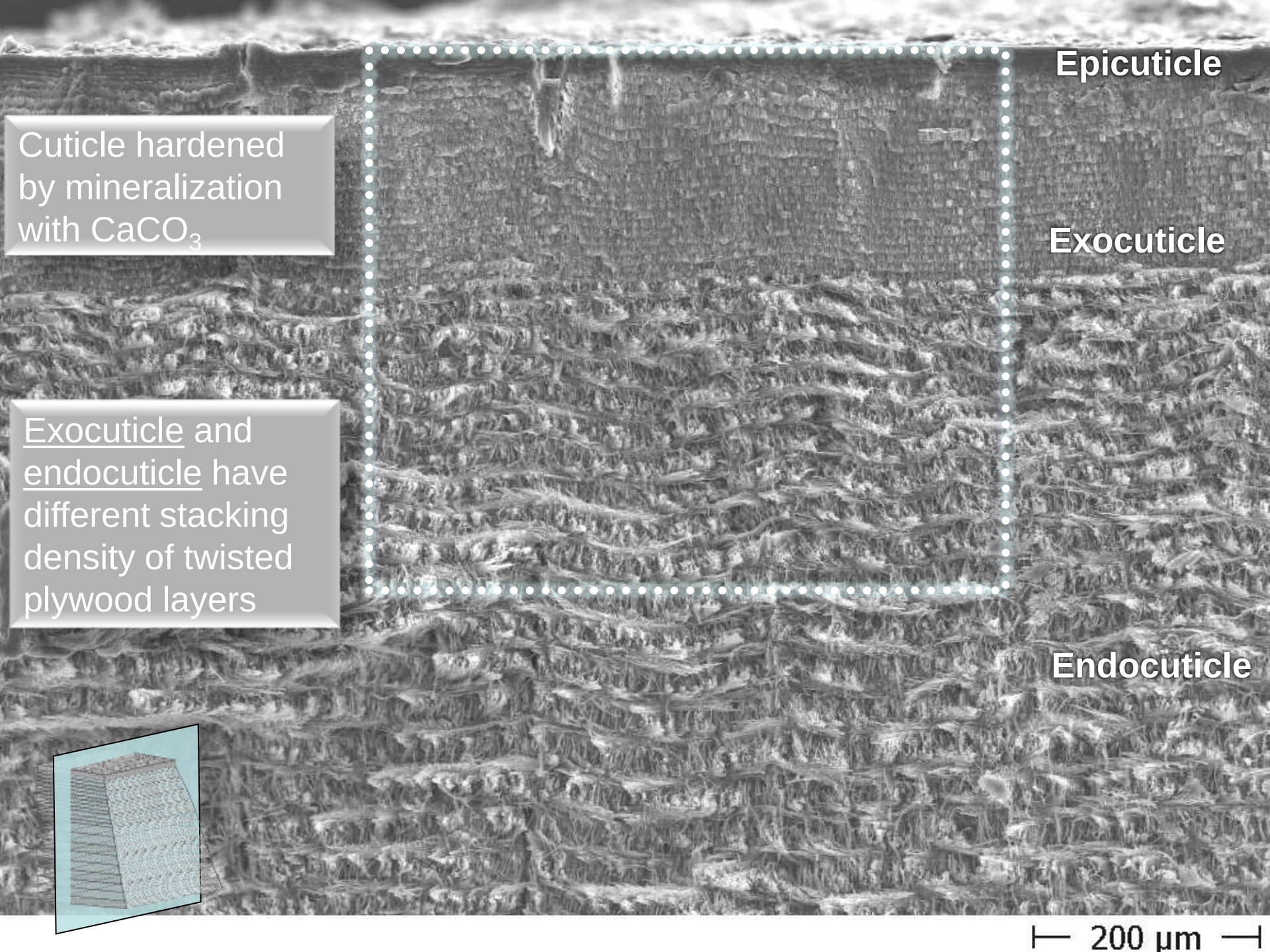

20 nm
200 nm
5 µm
I
II
III
IV
V
VI
VII
VIII
pc
pc
1 µm
nd
pc
180° rotation of fiber planes
1 µm
exocuticle
endocuticle
50 µm
1 cm



measurement by Astrid Haibel, BESSY

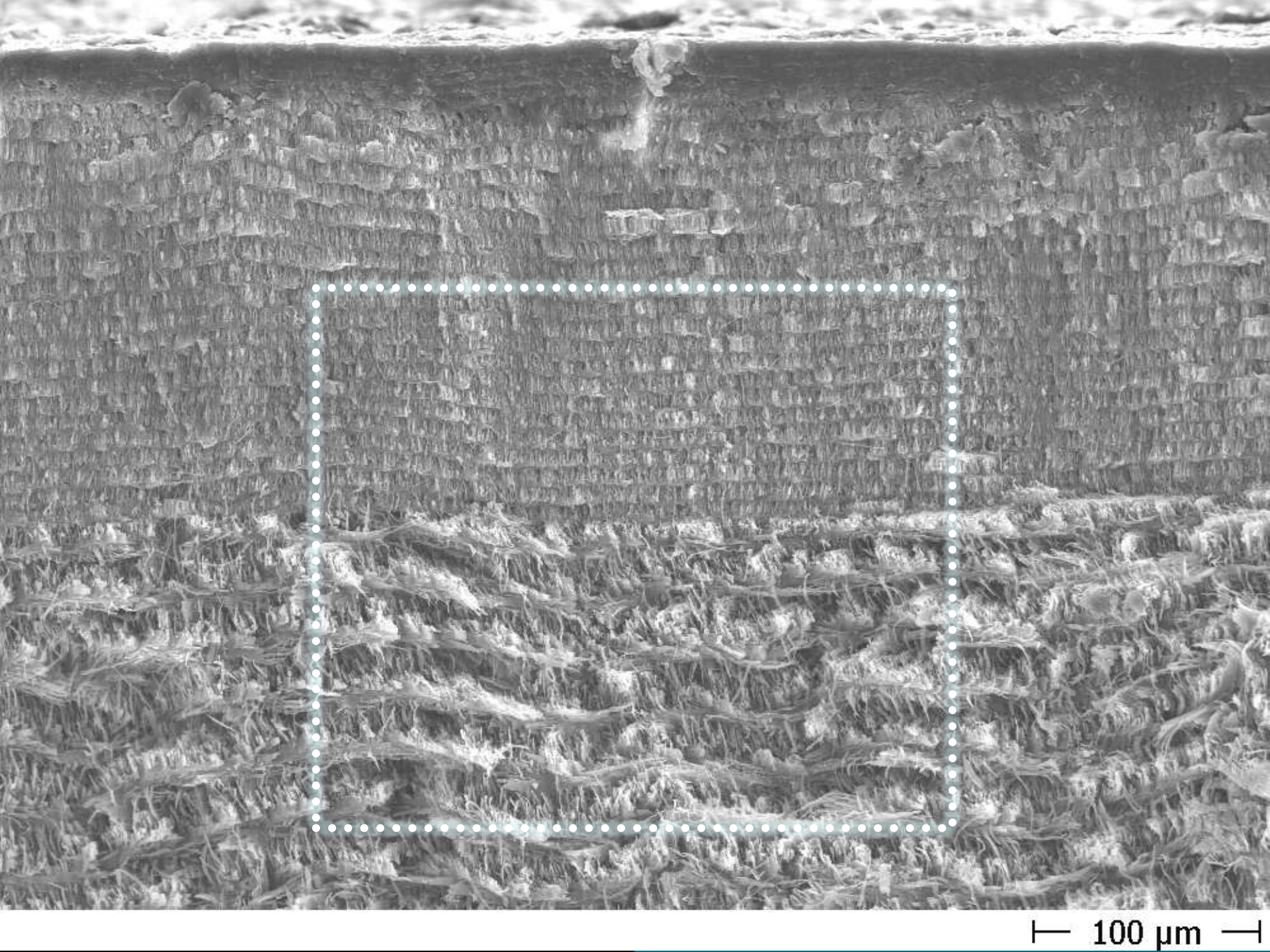


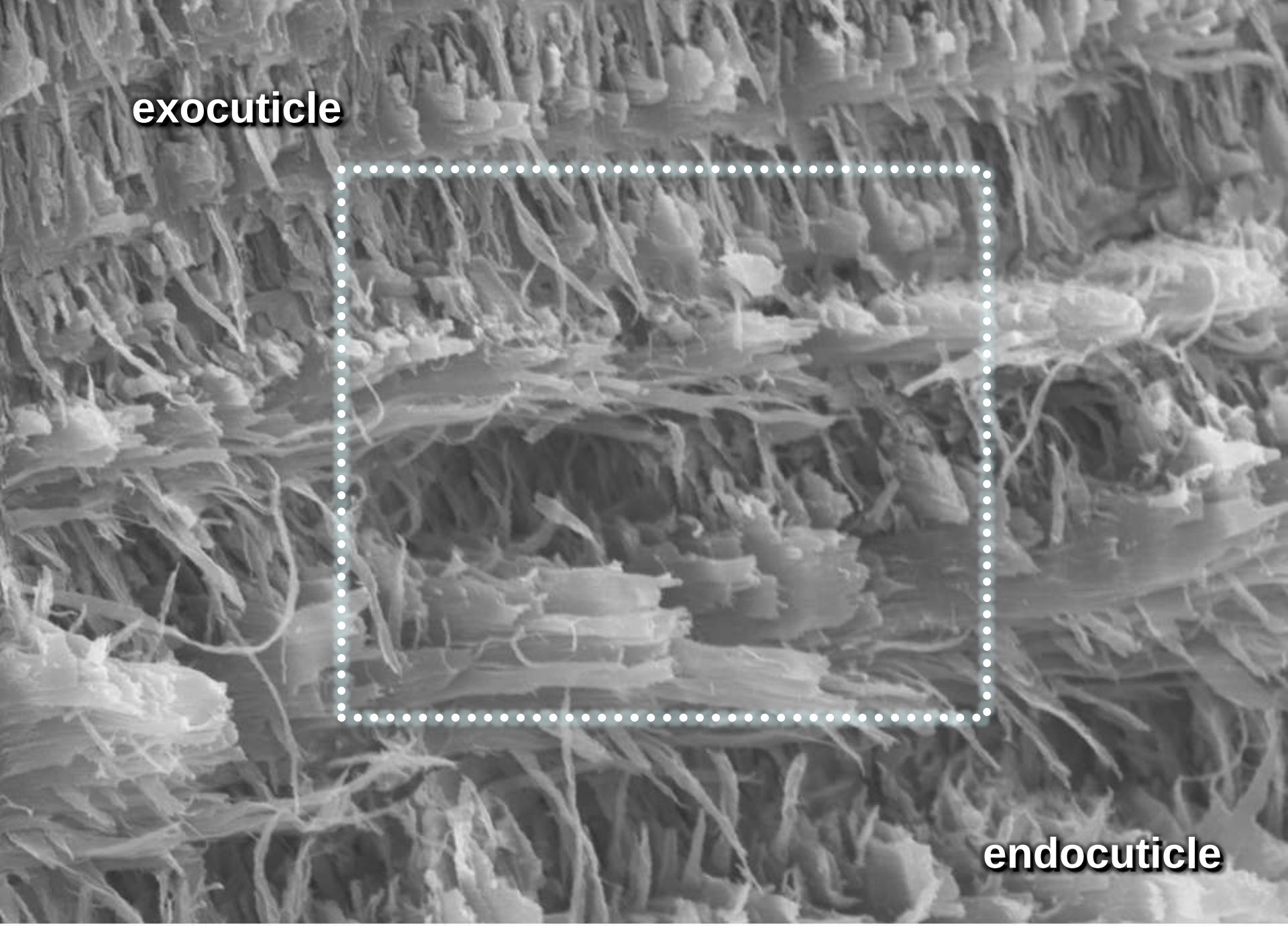

Epicuticle
Exocuticle
Endocuticle
average in endocuticle: 35.1 µm
average in exocuticle: 9.4 µm
stacking height / µm
specimen / 1
0
5
10
15
20
25
30
35
40
45
50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
100 µm



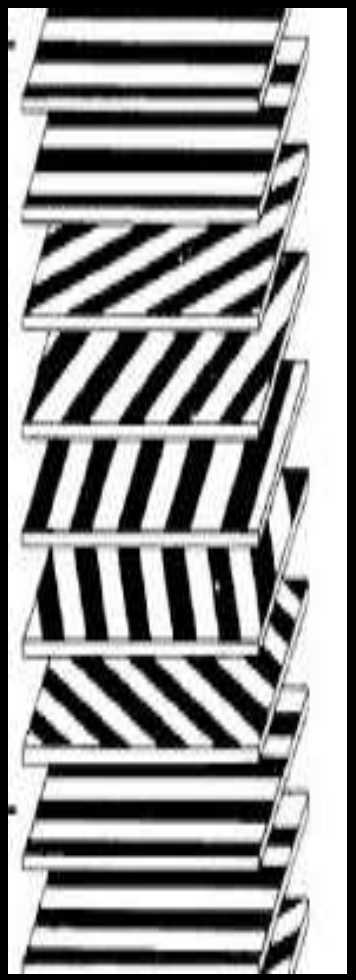
Cuticle hardened by mineralization with $CaCO_3$

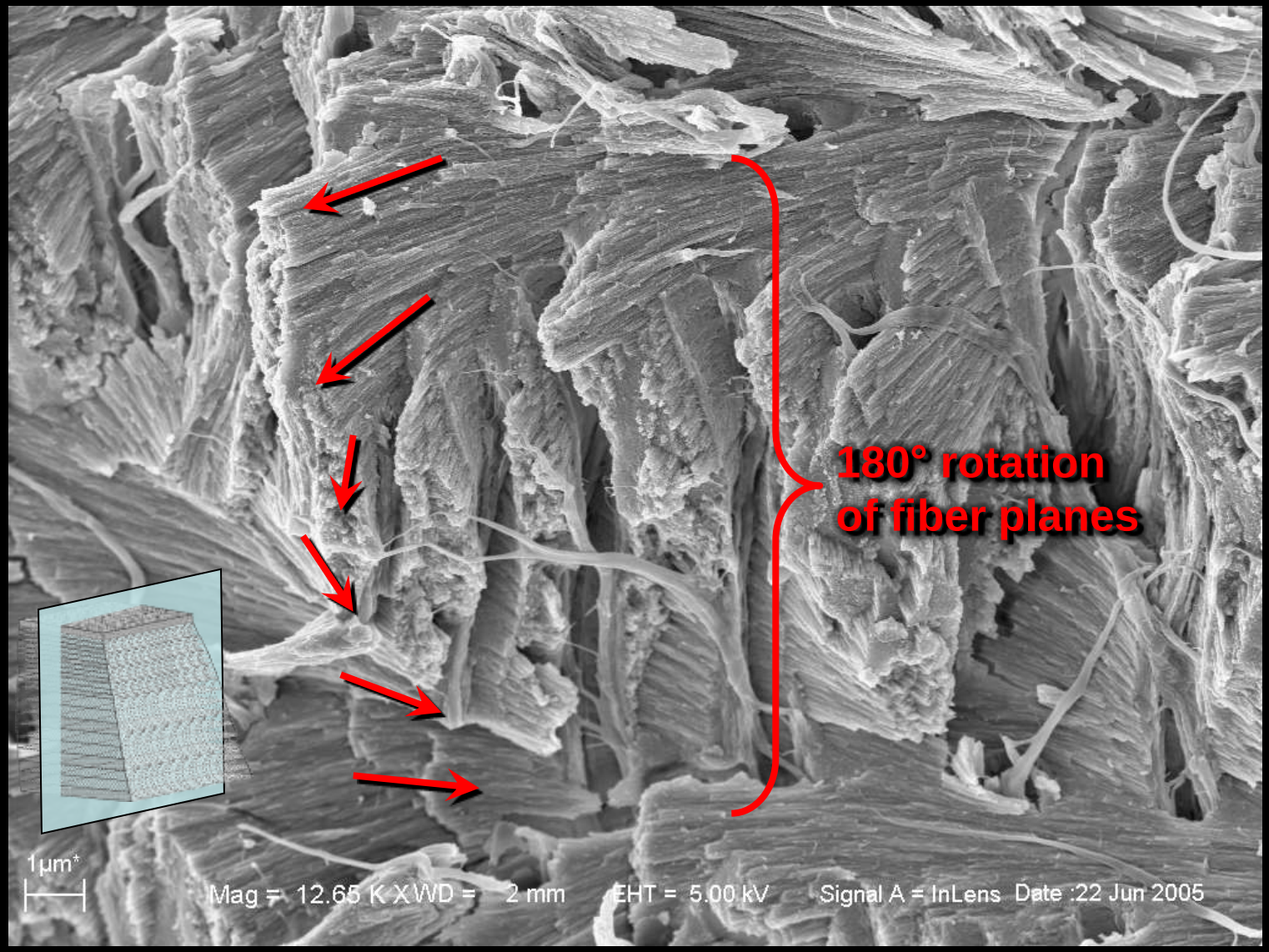
Exocuticle and endocuticle have different stacking density of twisted plywood layers

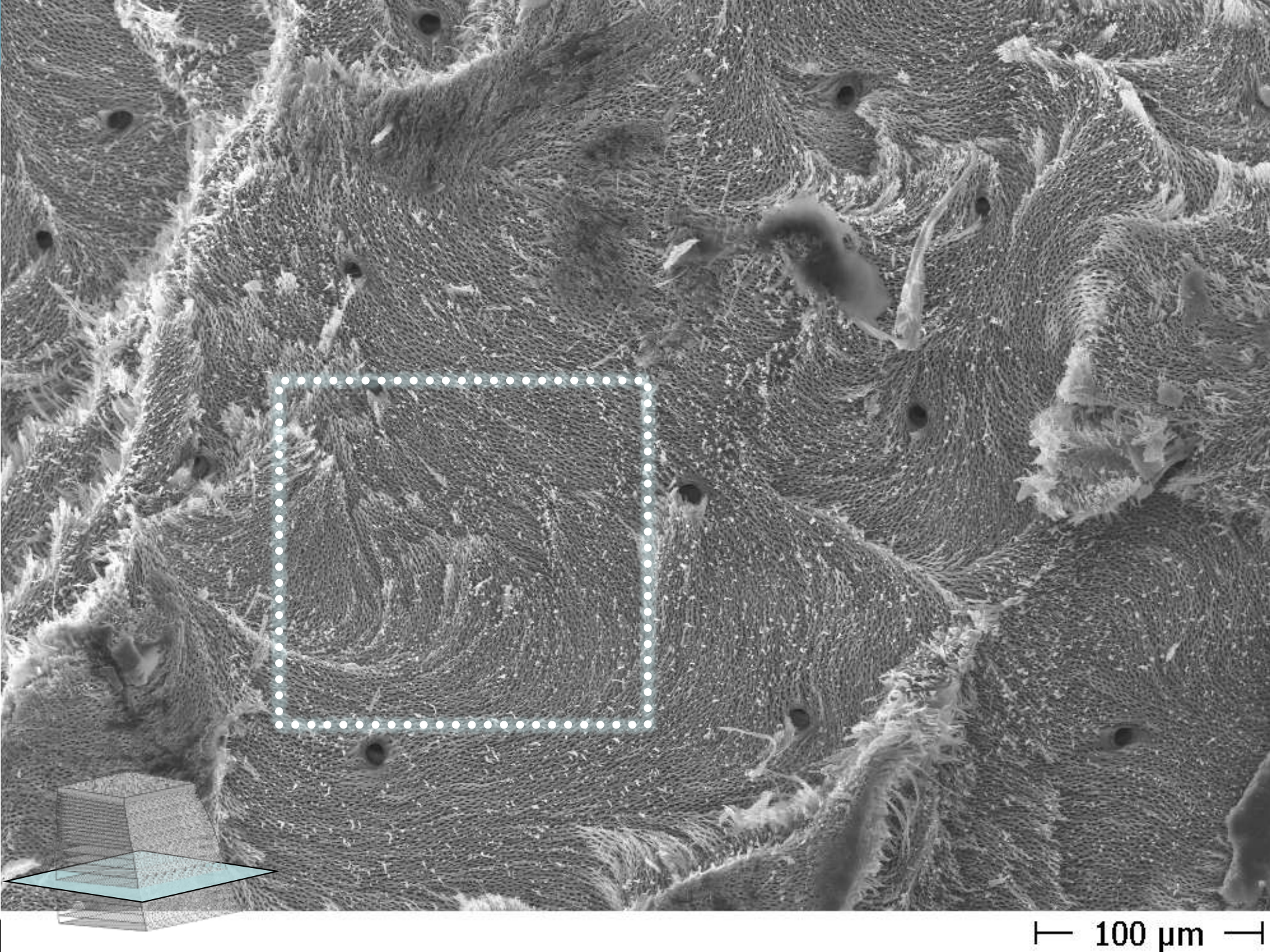

100 µm

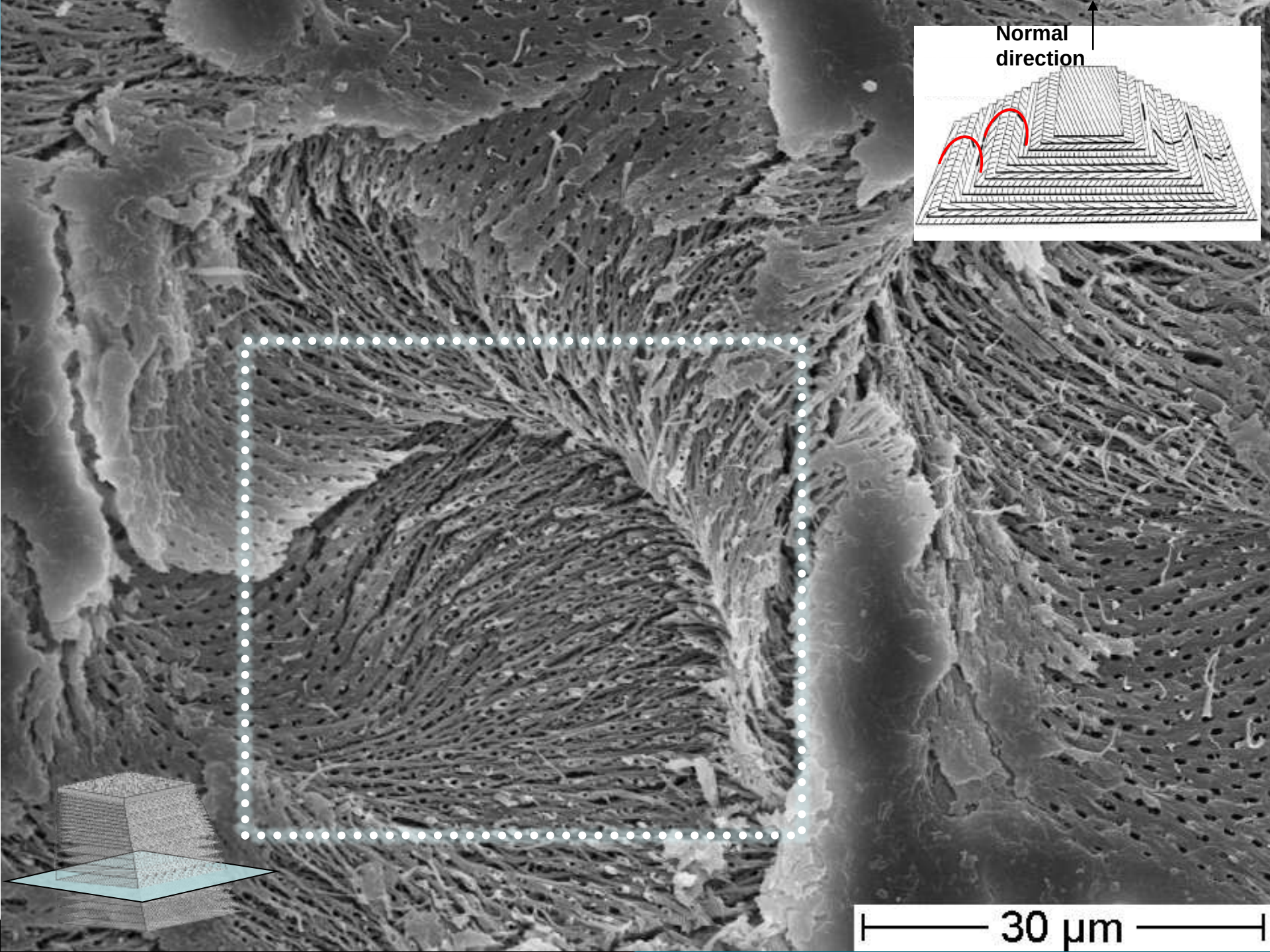


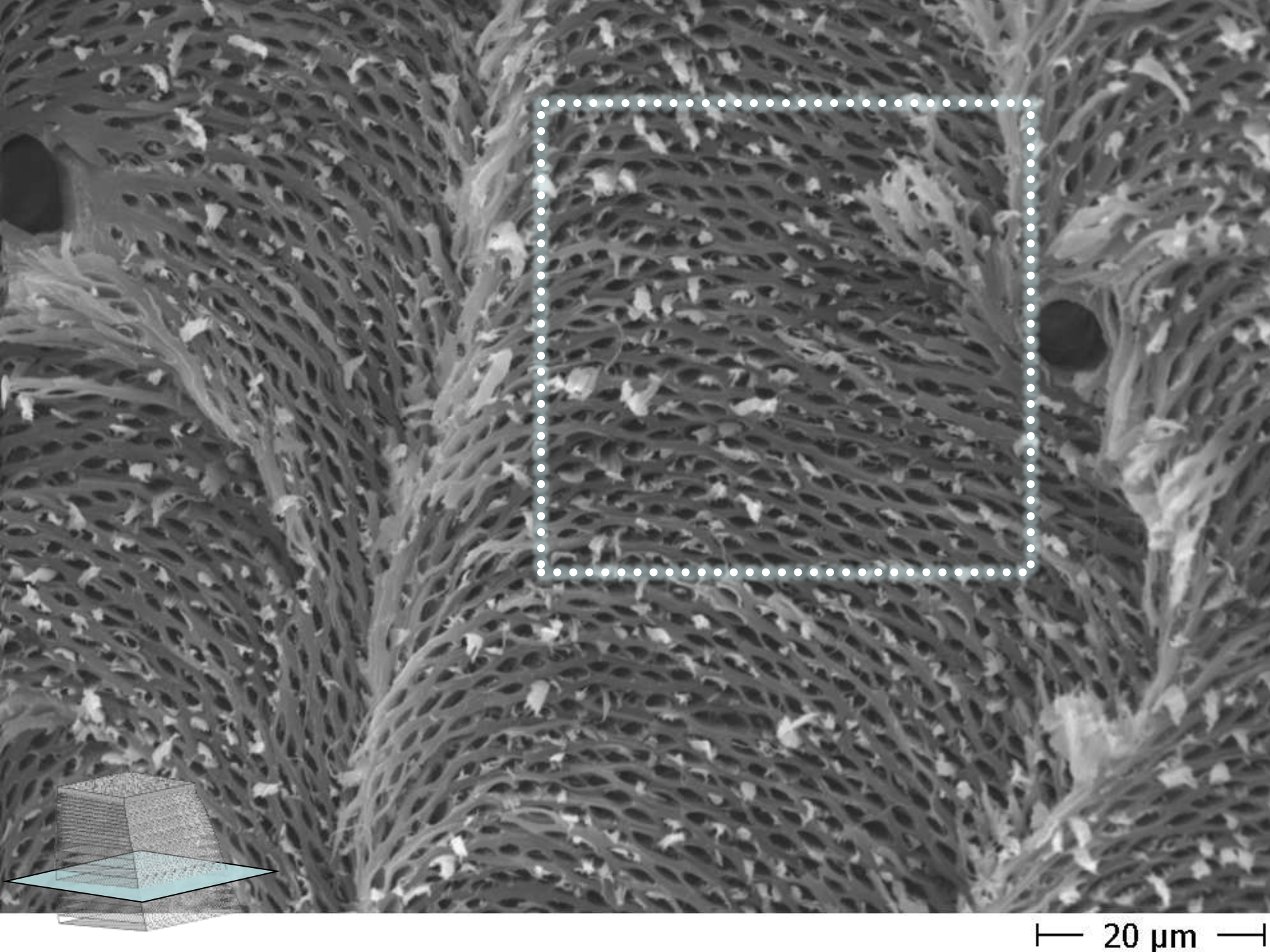
Nikolov et al.: Adv. Mater. 22 (2010) p. 519; Al-Sawalmih et al.: Adv. Funct. Mater. 18 (2008) 3307

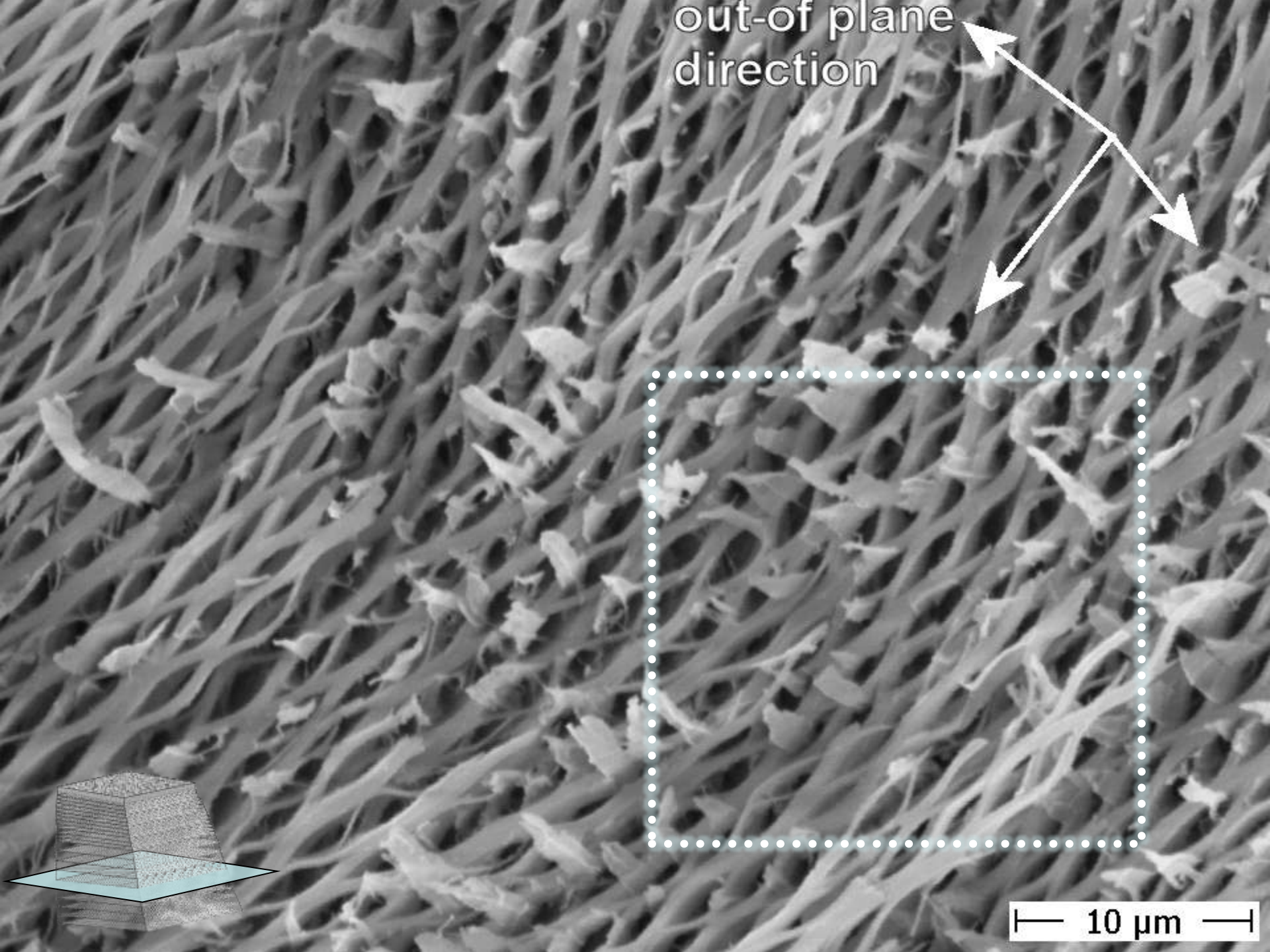


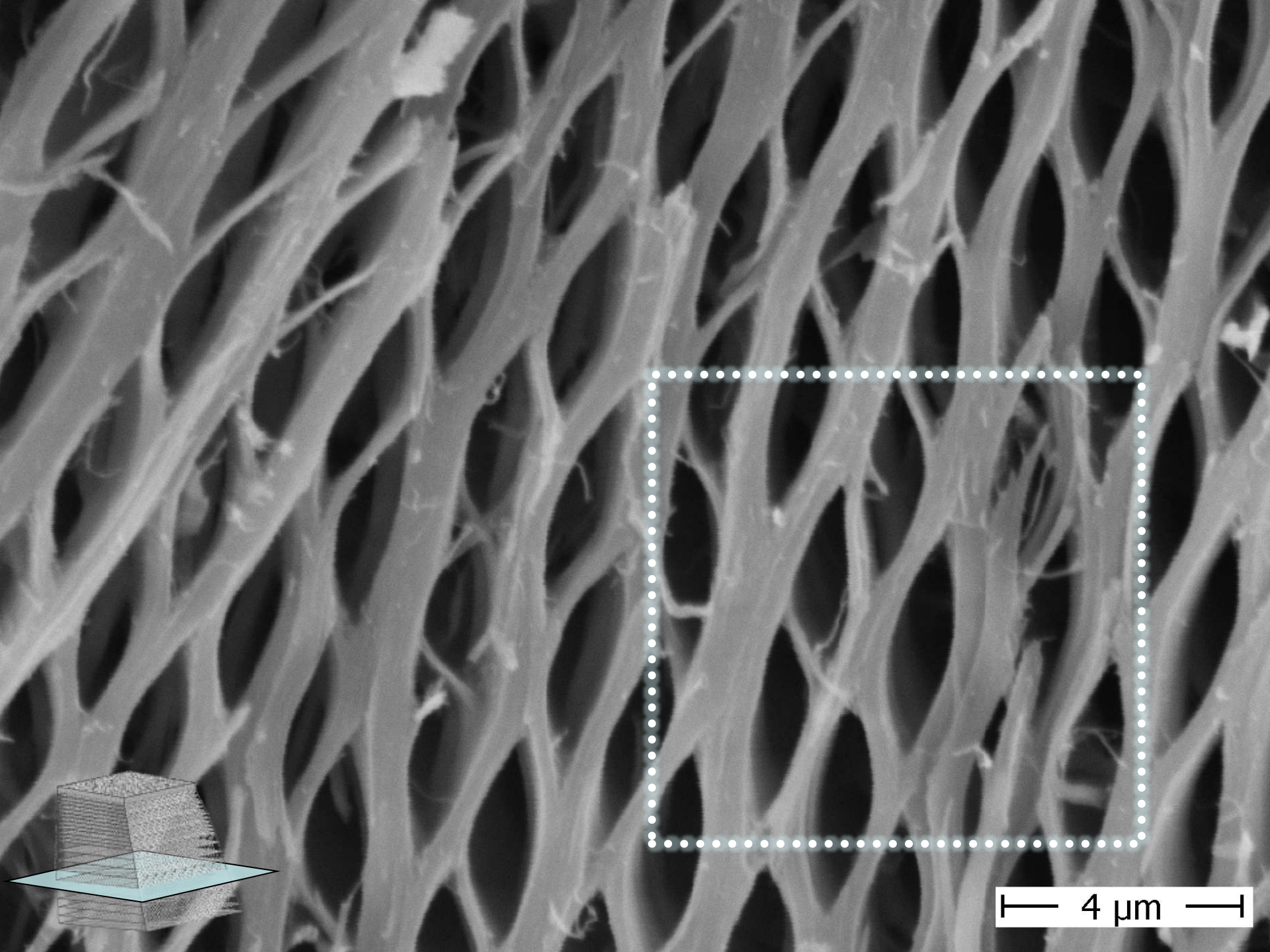

180° rotation
of fiber planes
1µm*
Mag = 12.66 K X WD = 2 mm
EHT = 5.00 kV
Signal A = InLens Date :22 Jun 2005

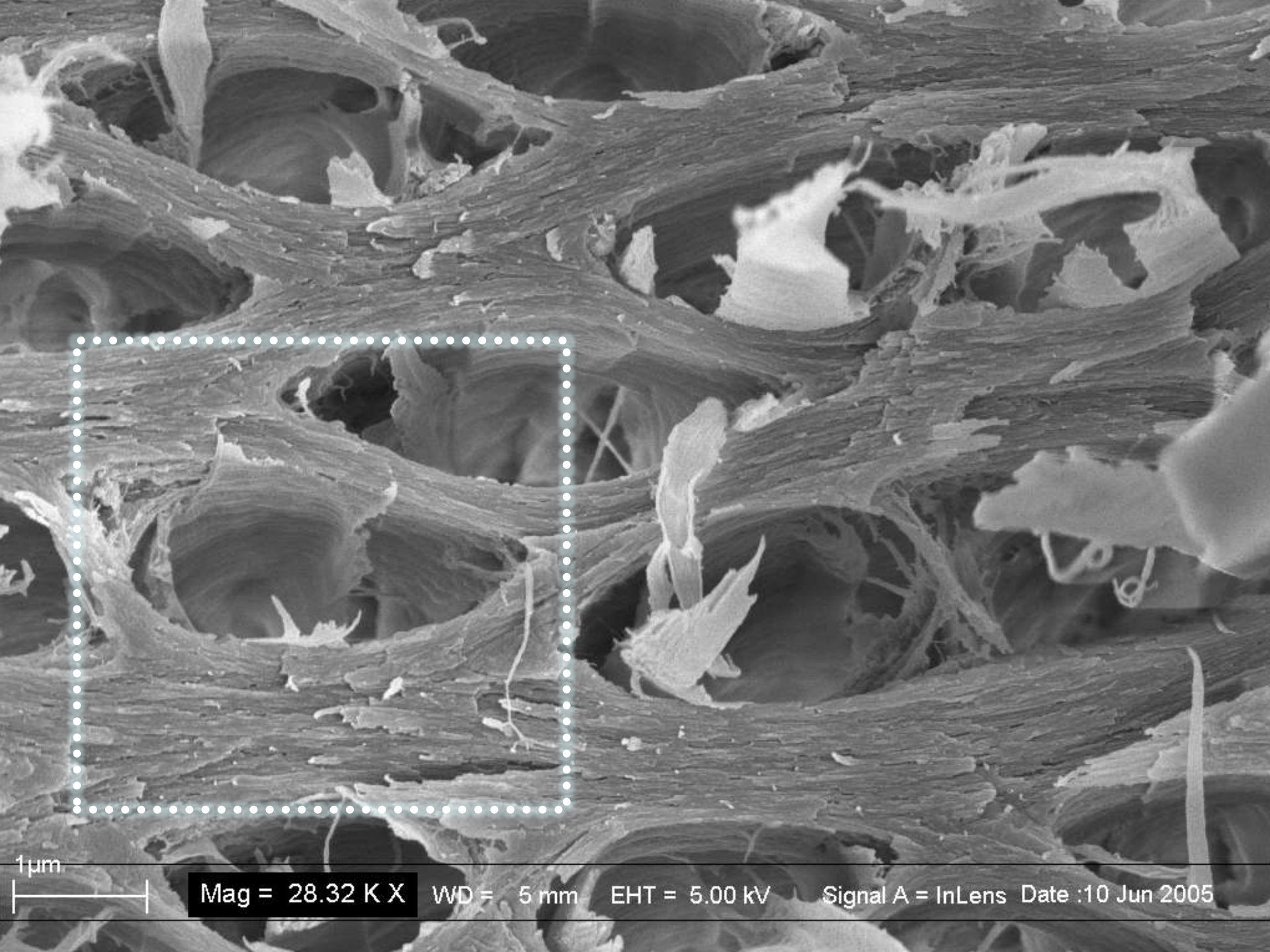

100 µm

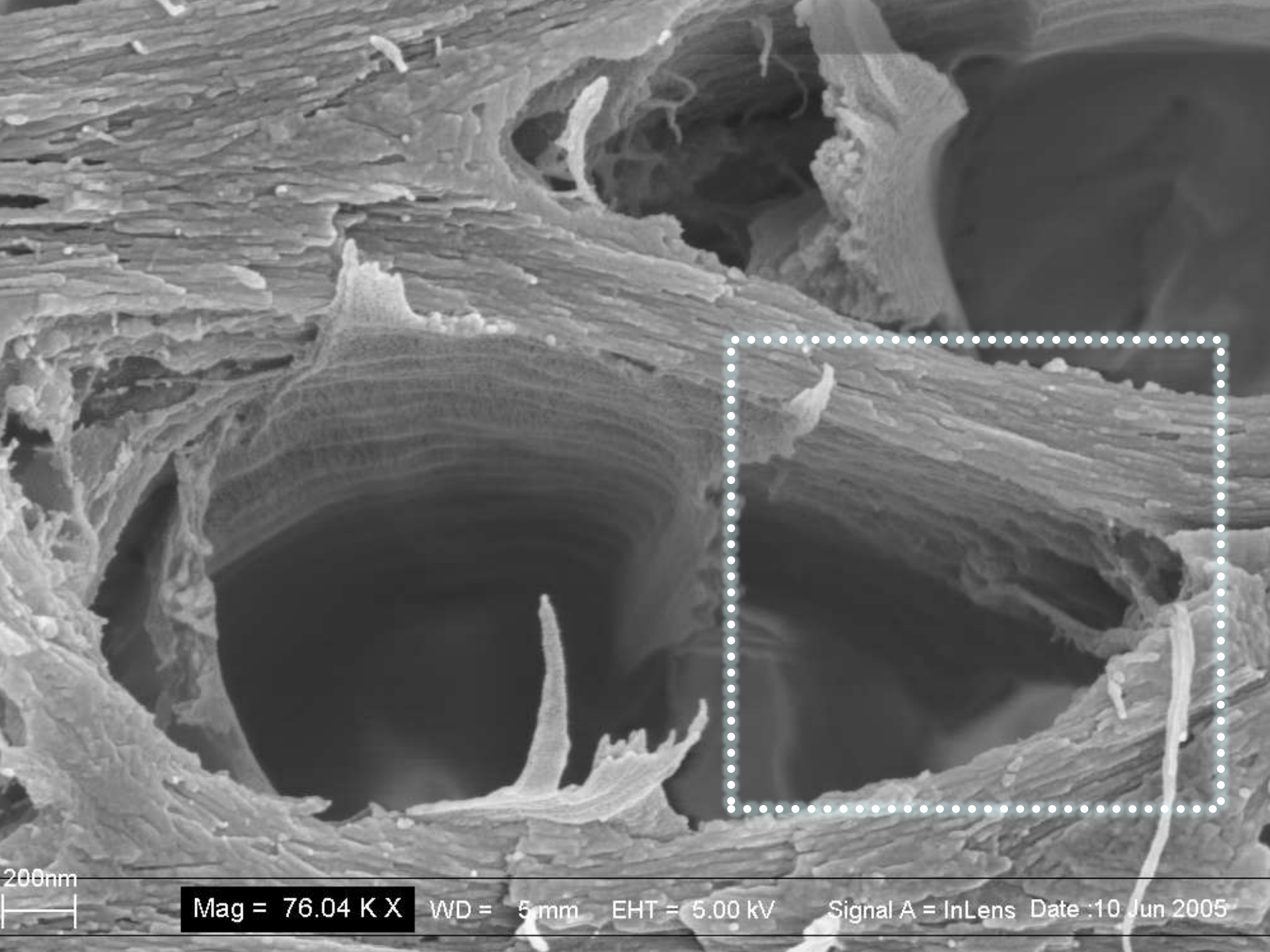

Normal
direction
30 µm


20 µm


out-of plane
direction
10 µm

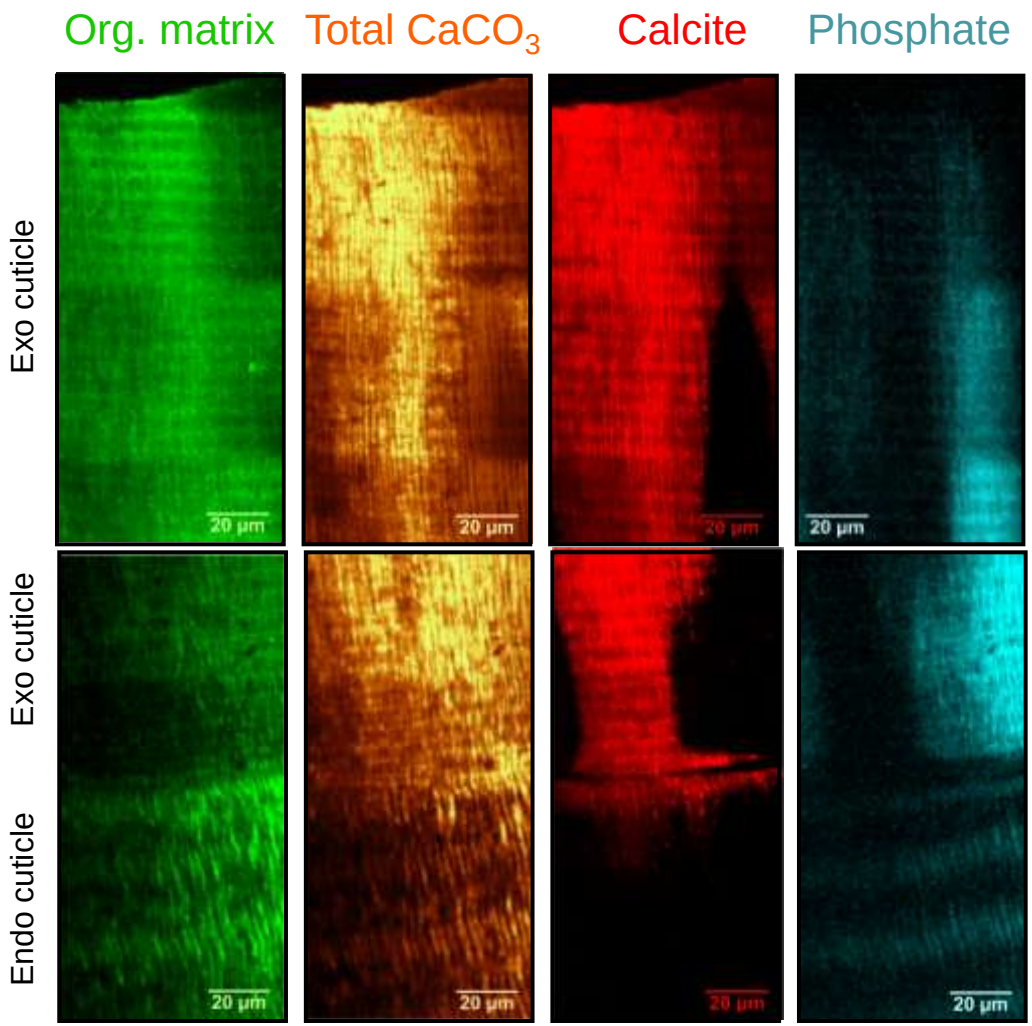

4 µm


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

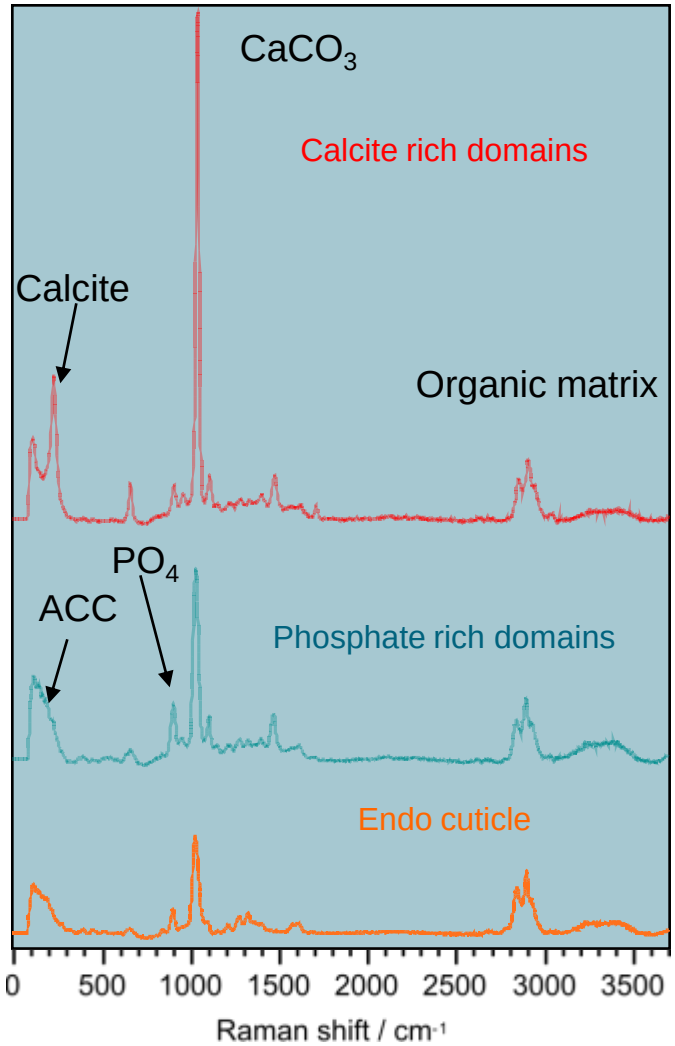

200nm
Mag = 76.04 K X
WD = 5 mm
EHT = 5.00 kV
Signal A = InLens
Date :10 Jun 2005


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

Raman imaging of the claw cuticle of H. americanus



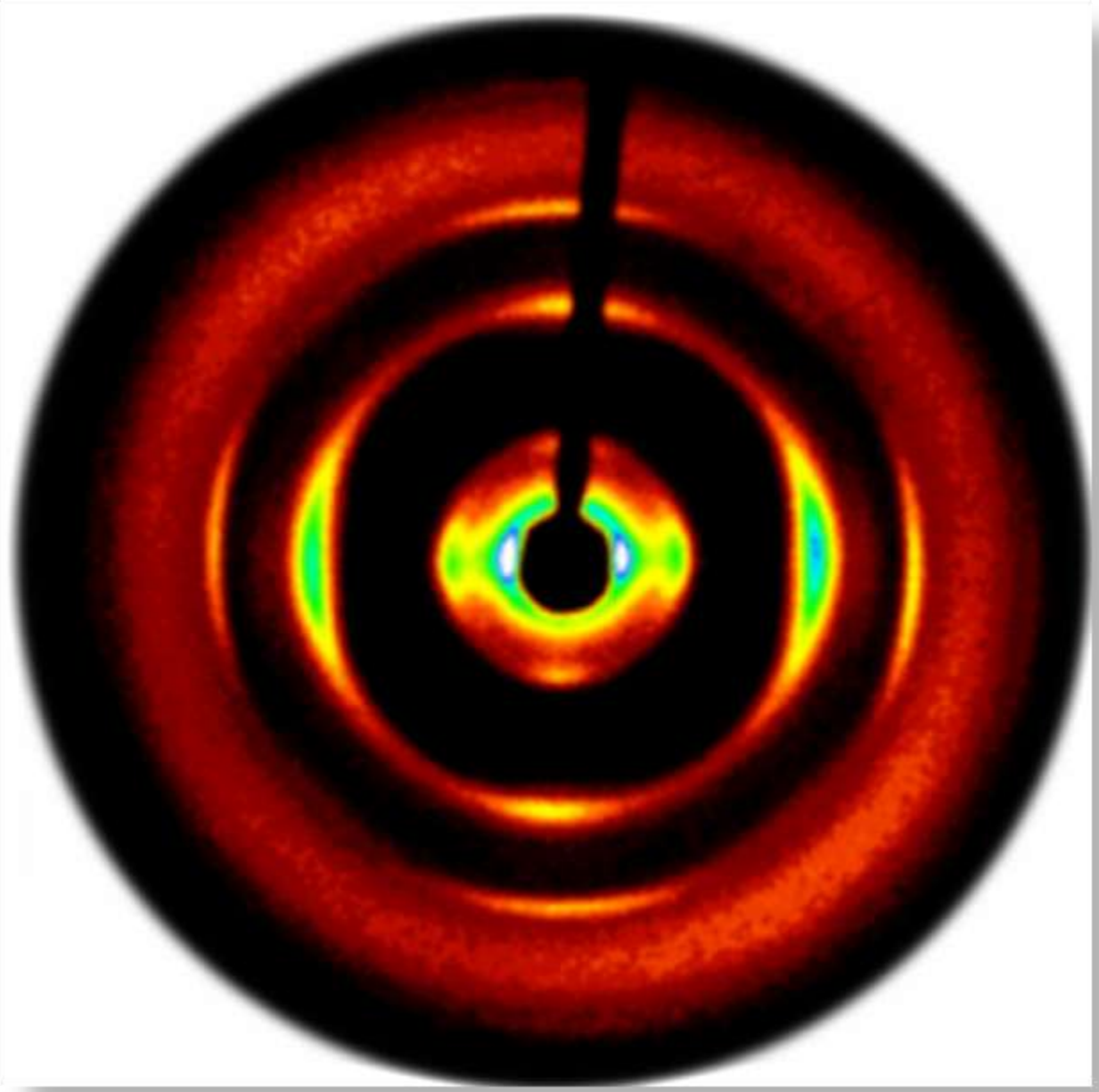
Averaged Raman spectra
normalized to organic matrix



S. Hild, Linz

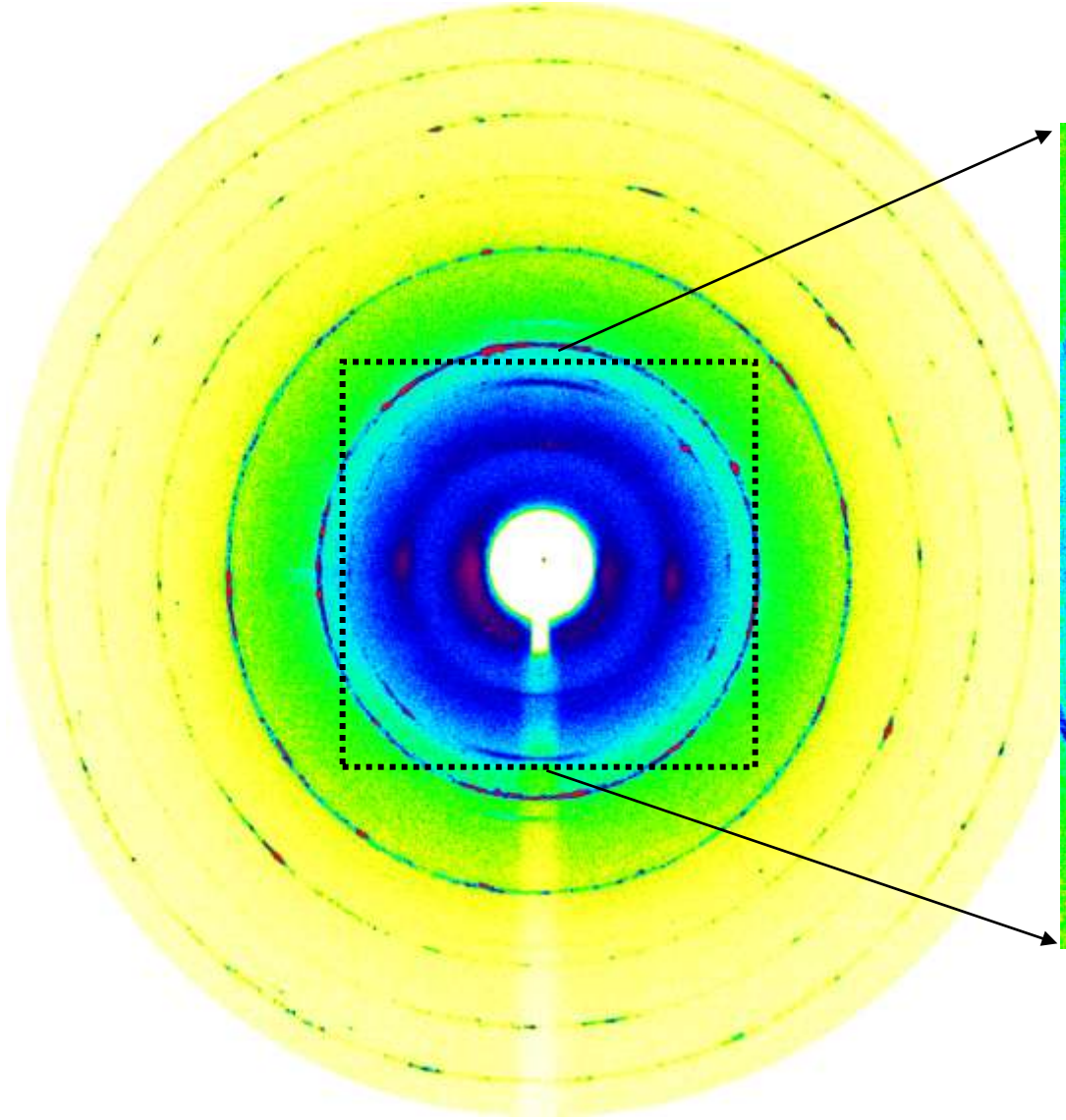
Sachs, Fabritius, Raabe: J Material Research 21 (2006) 1987

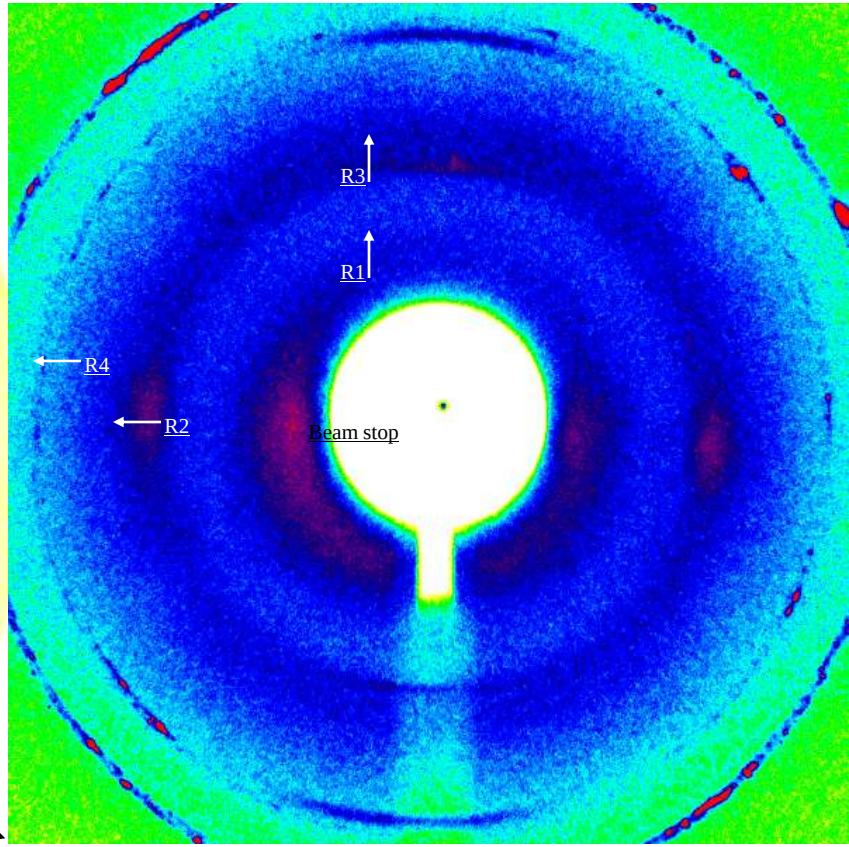
X-ray wide angle diffraction, lobster



λ= 0,9995 Å.

X-ray wide angle diffraction, lobster

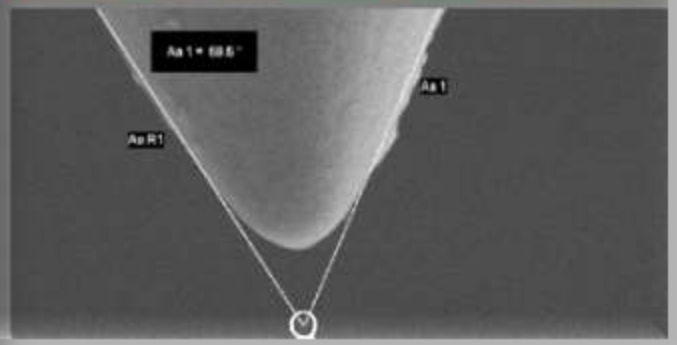




very strong chitin textures
clusters of calcite

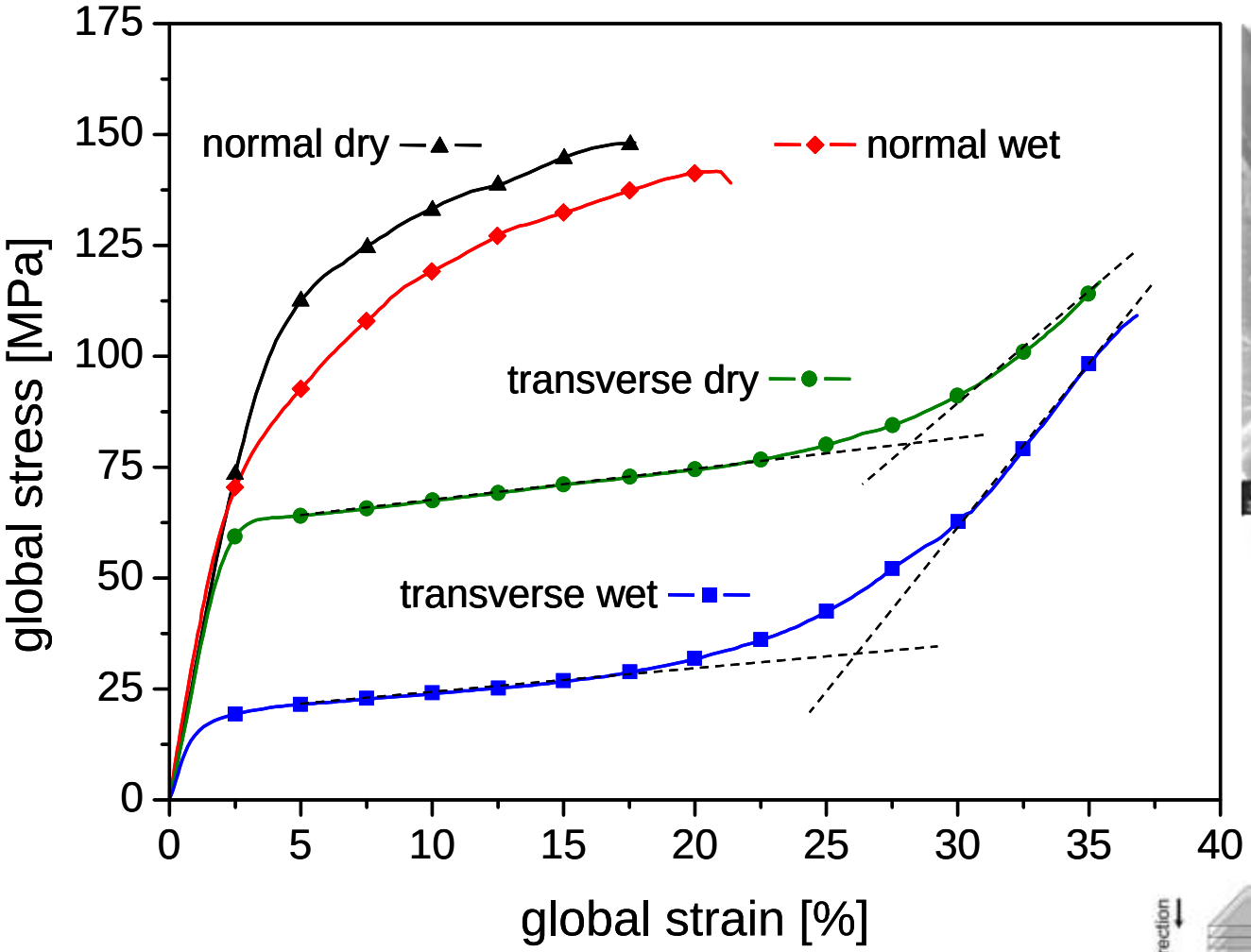
DESY (BW5), λ=0.196 Å.

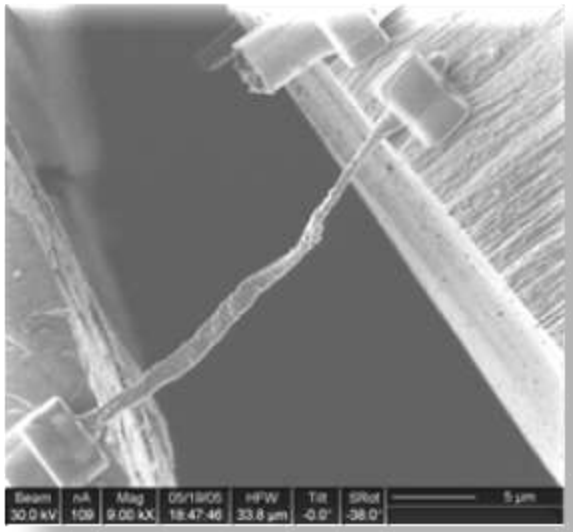
The materials science of chitin composites

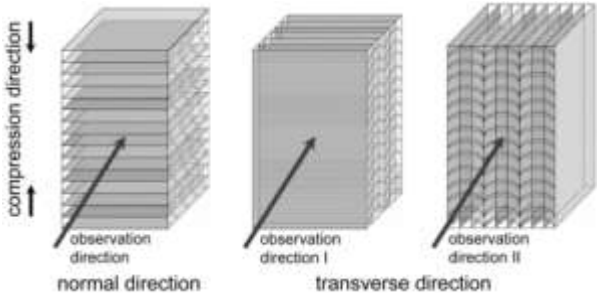


Fabritius, Sachs, Romano, Raabe : Adv. Mater. 21 (2009) 391

Compression tests (macroscopic), lobster

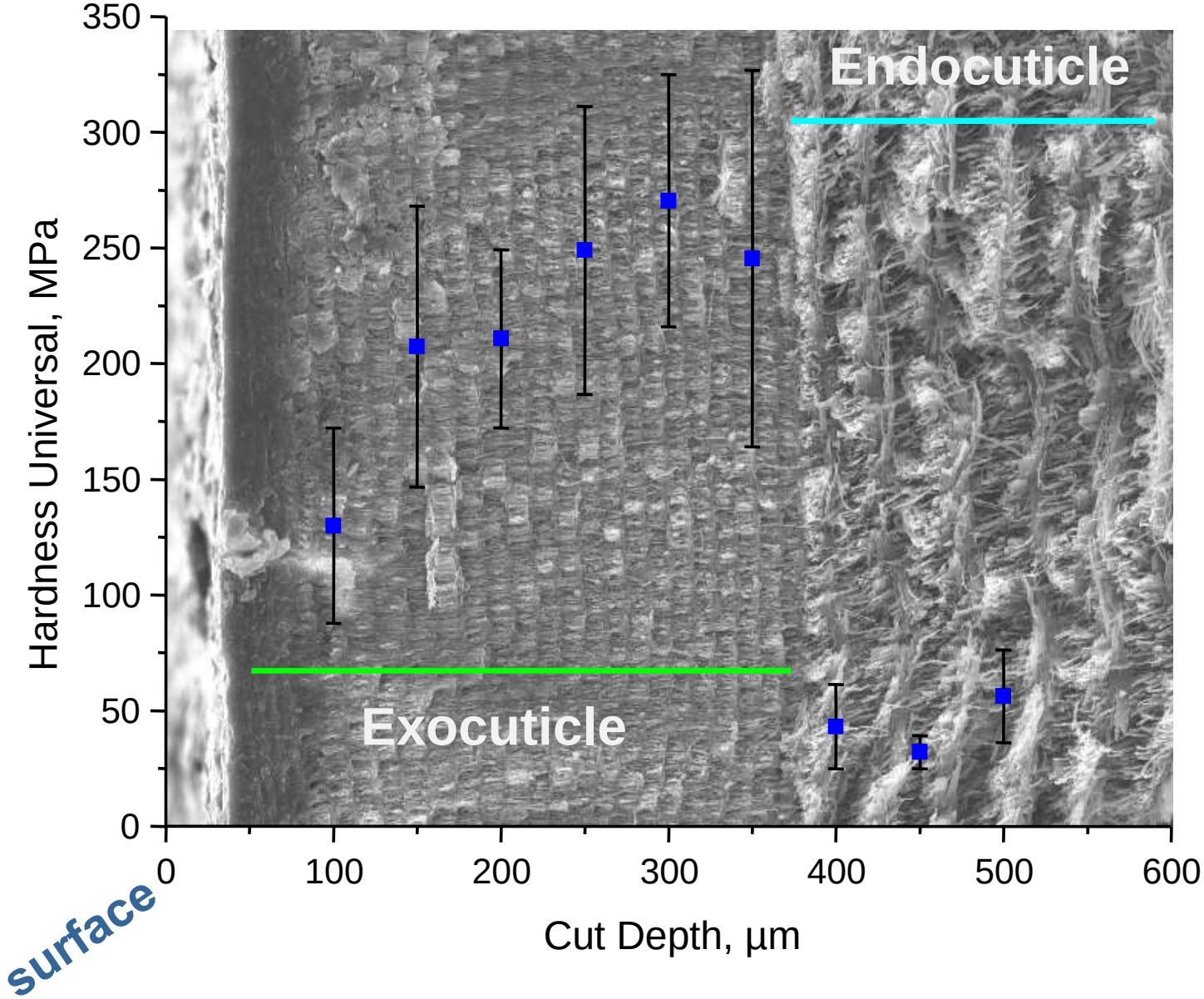






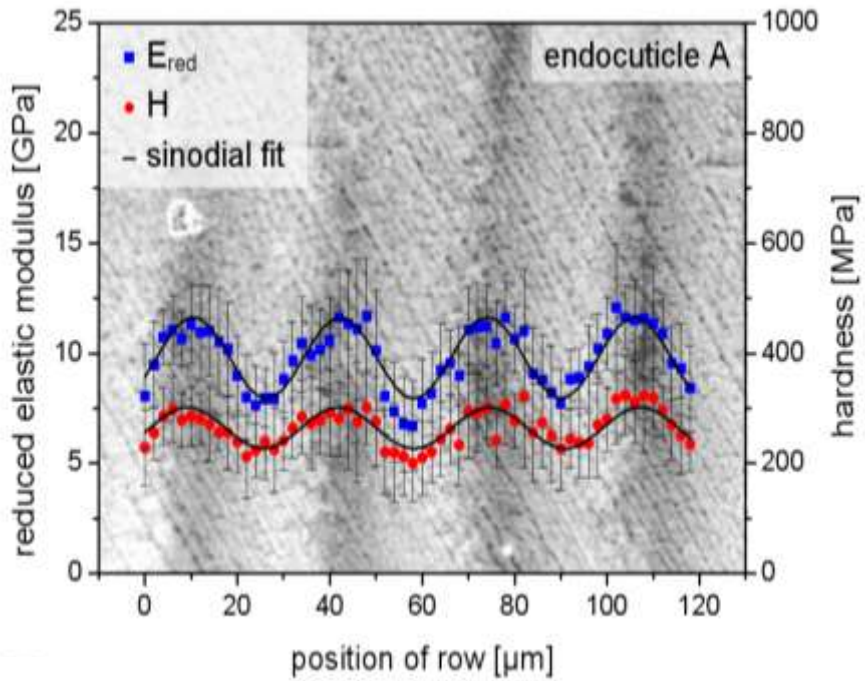
P. Romano, H. Fabritius, D. Raabe: Acta Biomaterialia. 3 (2007) 301

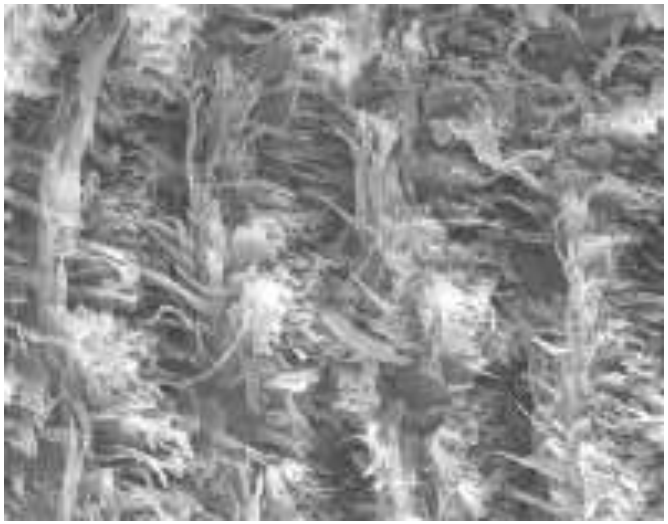
Hardness (mesoscopic)

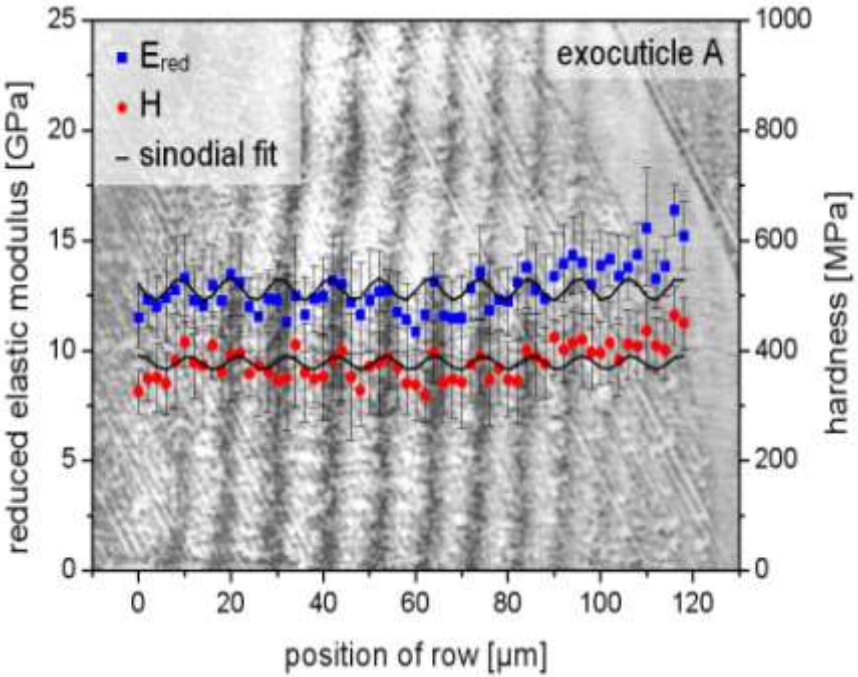


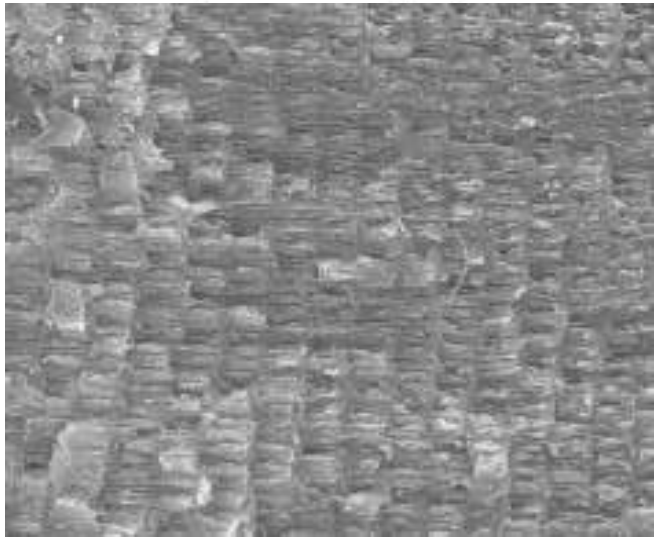
Raabe, Sachs, Romano: Acta Mater. 53 (2005) 4281

Mechanical properties (microscopic, nanoindentation)









Sachs, Fabritius, Raabe: J Material Research 21 (2006) 1987

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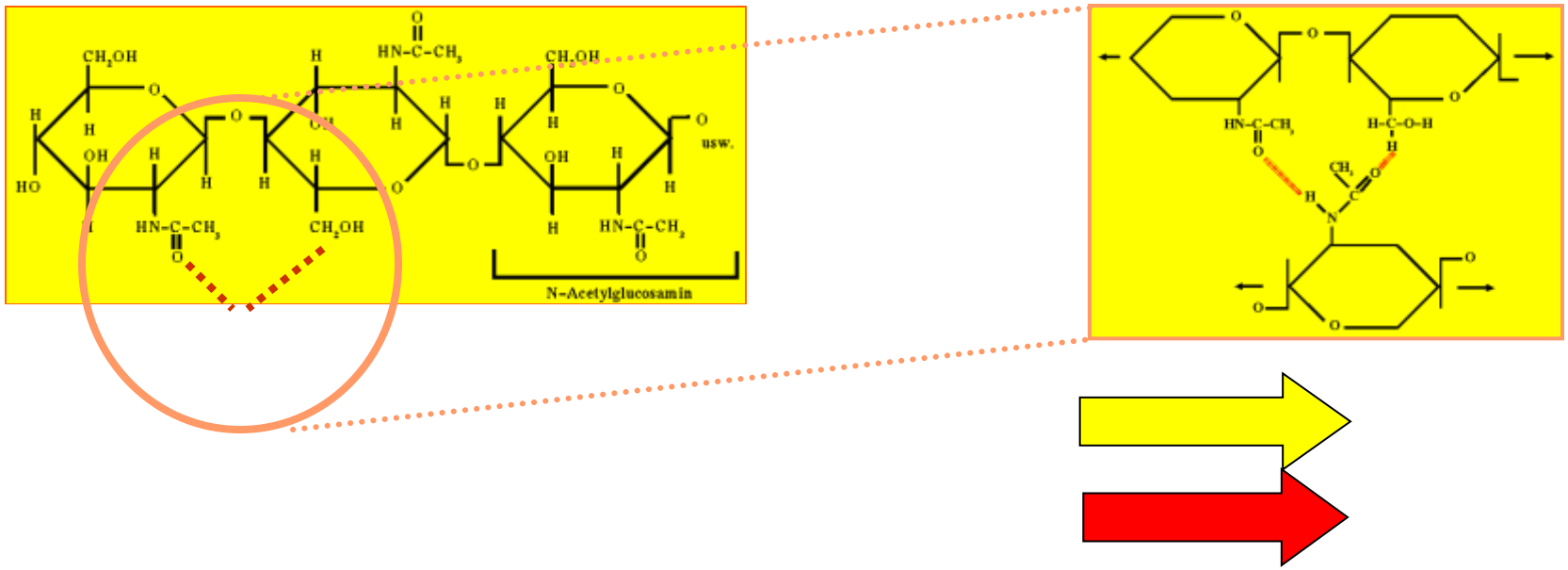
Raabe: Adv. Mater. 14 (2002)

What is α-chitin?



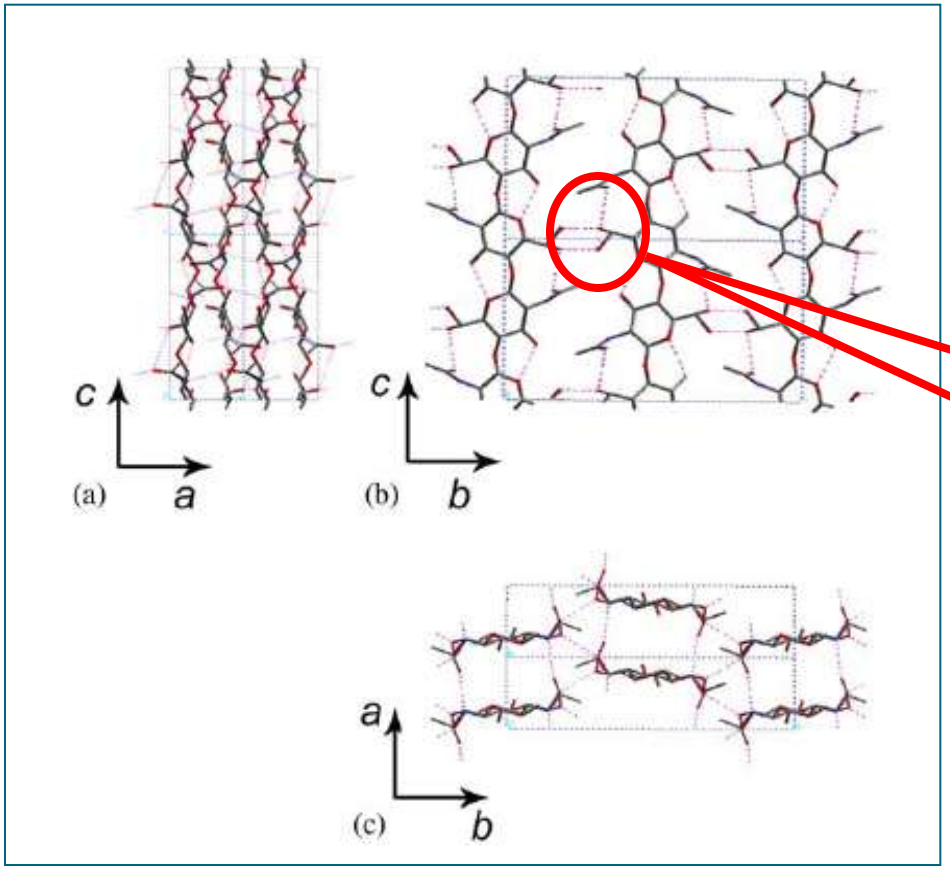
*J. Biochem Biophys. Cytol., 1957, **3**, 669 - 683.*

The crystal structure of α -chitin

Carlstrom, D.

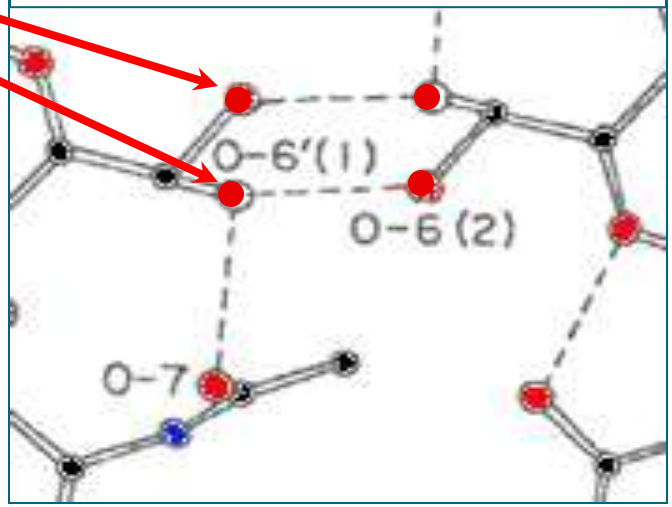
Polymer	Unit cell dimensions (Bohrradius) a b c γ	Space group
α-Chitin	8.96 35.64 19.50 90°	P21

108 atoms / 52 unknown H-positions



Hydrogen positions?
H-bonding pattern ?

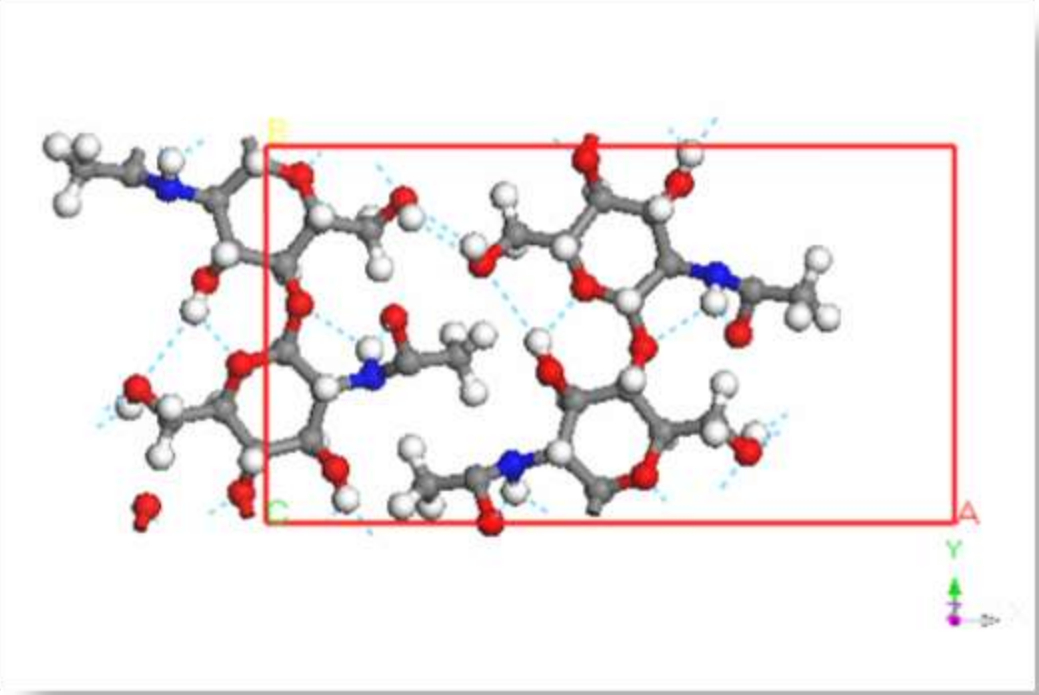
two conformations of α-chitin



Minke and Blackwell, J. Mol. Biol. 120, (1978)

Hierarchy of theoretical methods

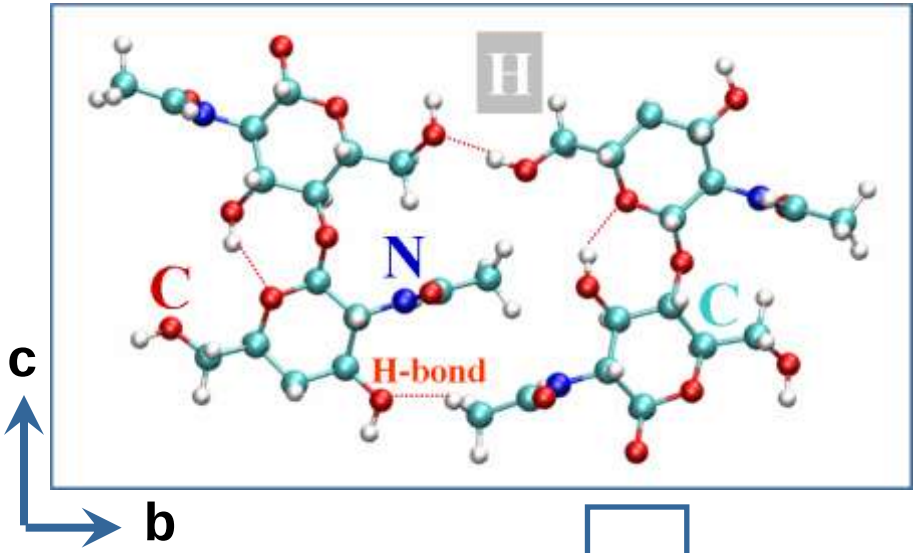
	CPU time	Accuracy	Resulting structures
•**Empirical Potentials** Geometry optimization Molecular Dynamics (universal force field)	~10 min	Low	**~10^3**
•**Tight Binding** (SCC-DFTB) Geometry optimization (SPHIngX)			
•**DFT** (PWs, PBE-GGA) Geometry Optimization (SPHIngX)			



C, C N H

Nikolov et al. Adv. Mater. 22 (2010), 519

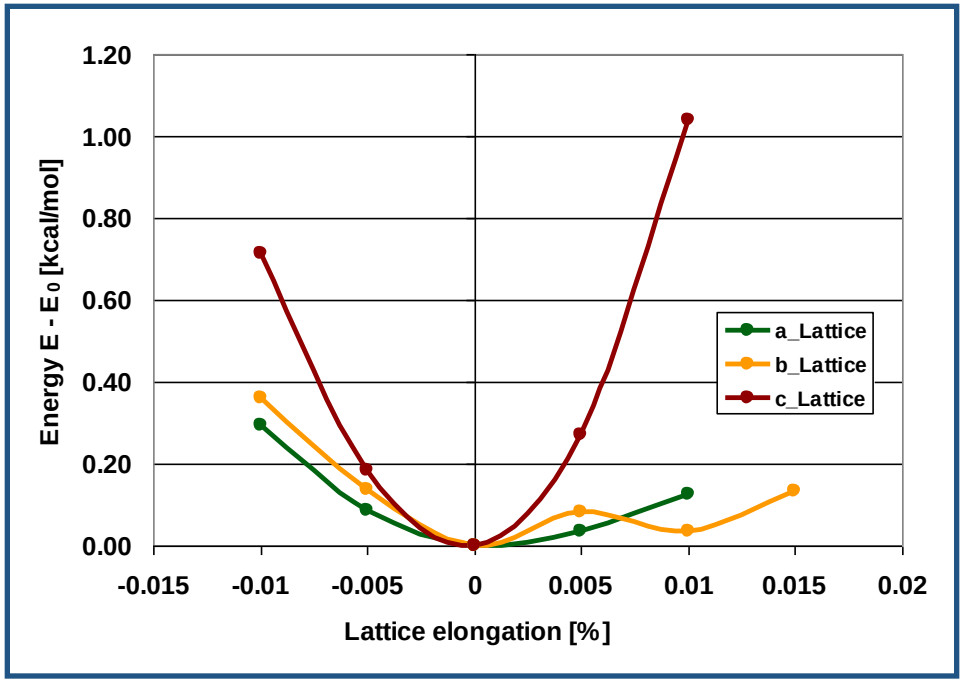
Ab initio prediction of α-chitin elastic properties



C, C N H

Ab initio calculations:
a = 4.98 Å; *b* = 19.32 Å; *c* = 10.45 Å
(this study)

Exp. measured
a = 4.74 Å; *b* = 18.86 Å; *c* = 10.32 Å
(Minke & Blackwell J. Mol. Biol. 1978)



$$\underline{\underline{C_{CH}}} = \begin{bmatrix} 119 & 0.1 & 1.1 & 0 & 0 & 0 \\ 0.1 & 28 & 2 & 0 & 0 & 0 \\ 1.1 & 2 & 24 & 0 & 0 & 0 \\ 0 & 0 & 0 & 5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{bmatrix} GPa$$

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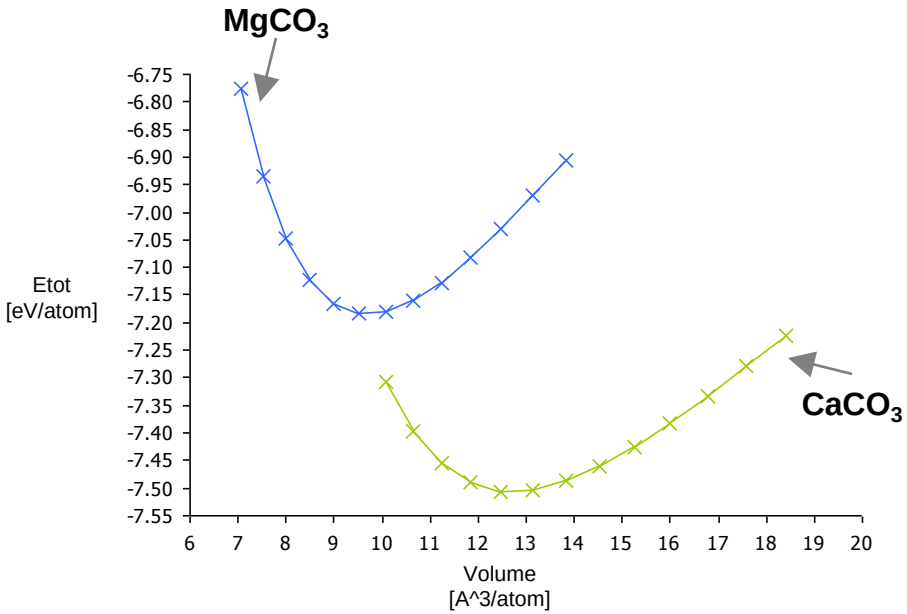
$Mg_mCa_n(CO_3)_6$: energy vs. volume changes



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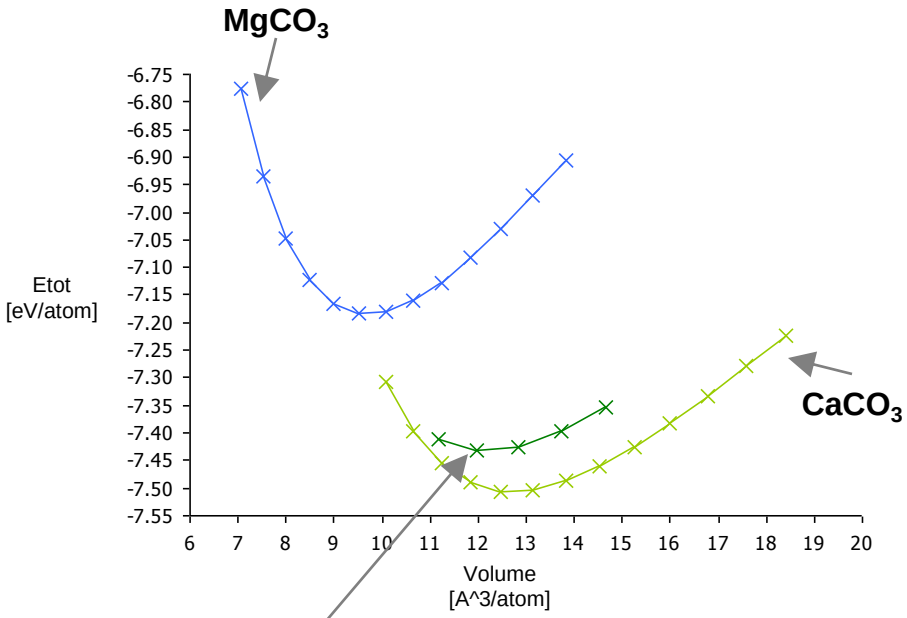
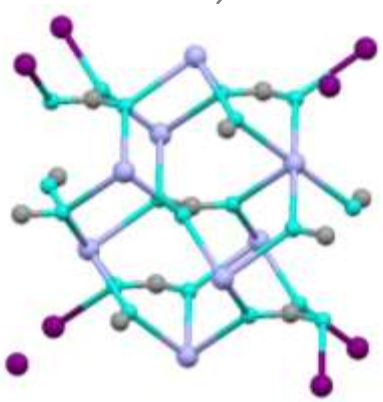
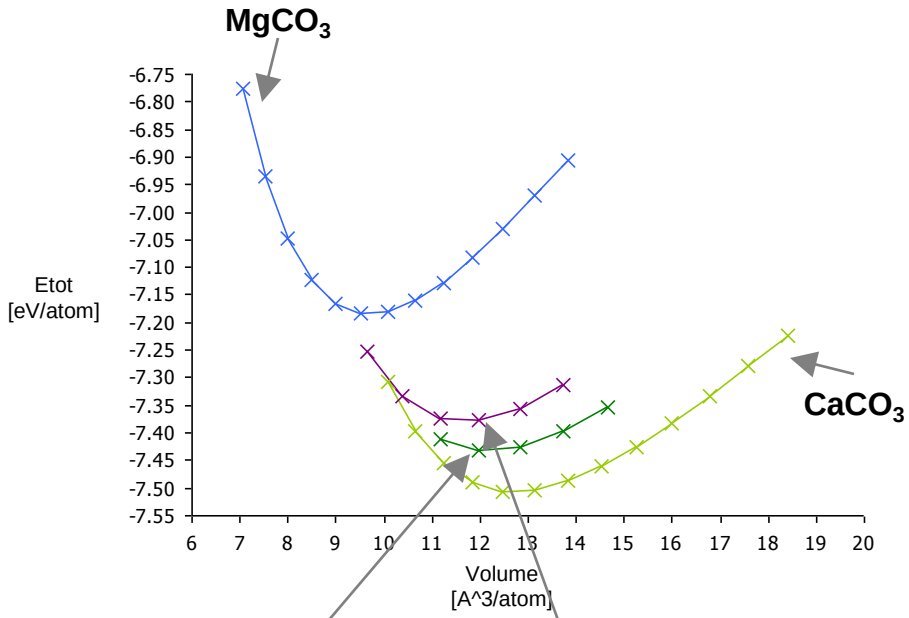
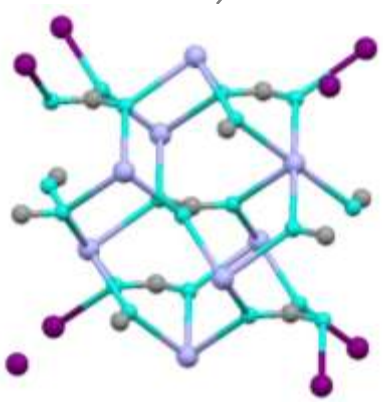




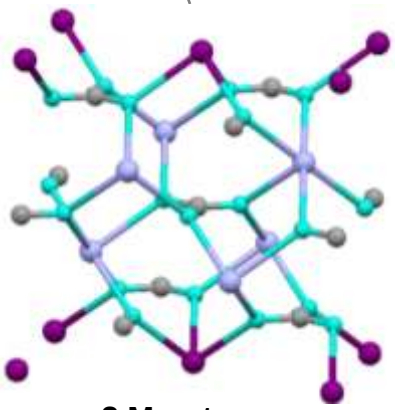
1 Mg-atom

$Mg_mCa_n(CO_3)_6$: energy vs. volume changes



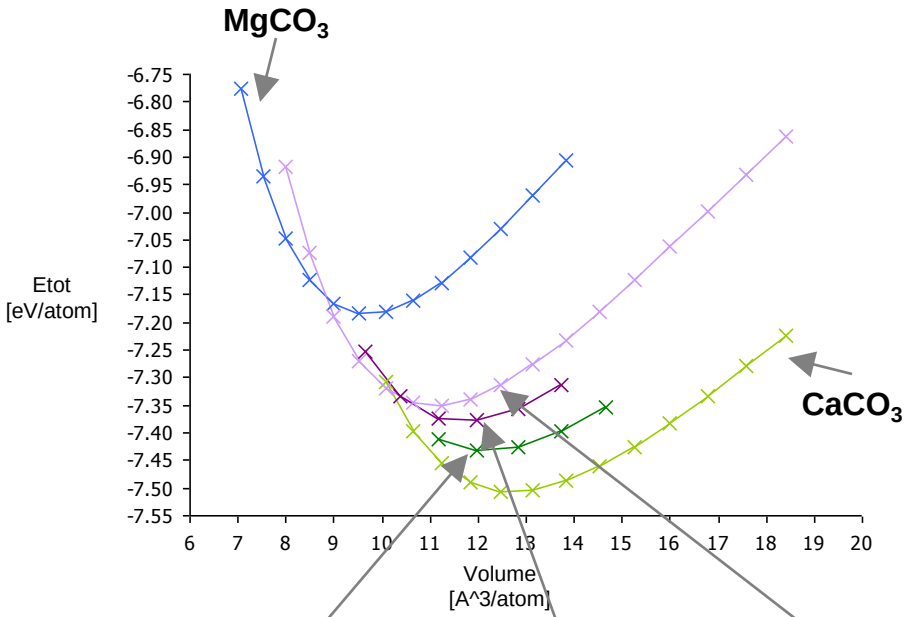


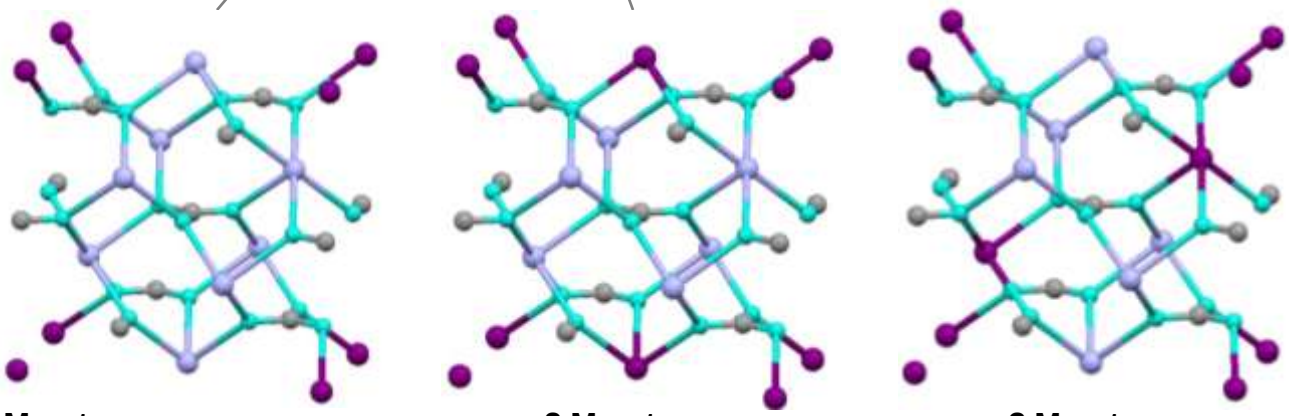
1 Mg-atom



2 Mg-atoms

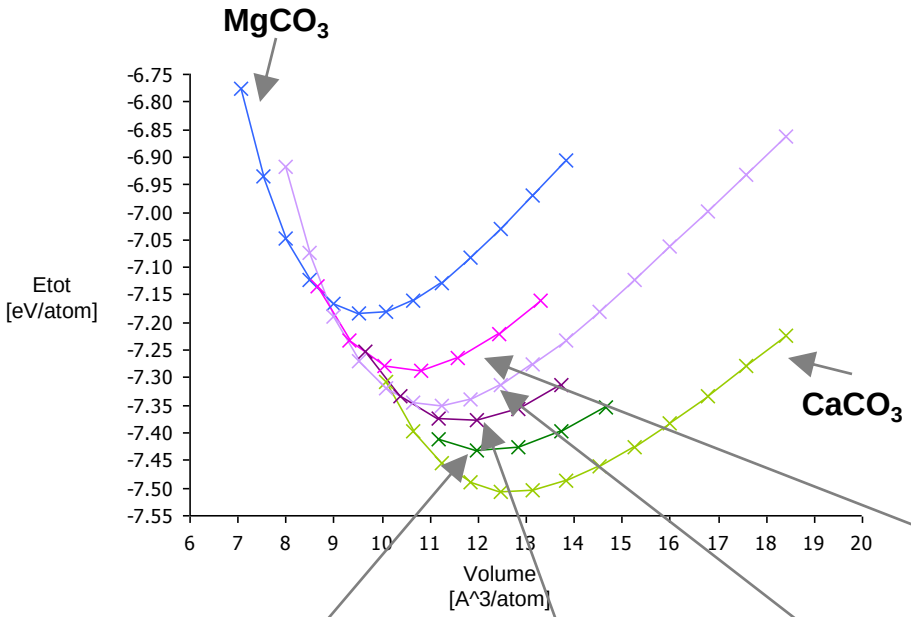
$Mg_mCa_n(CO_3)_6$: energy vs. volume changes

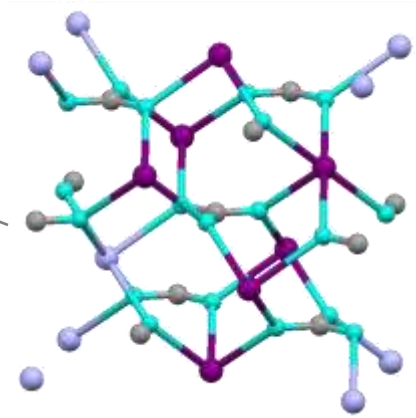




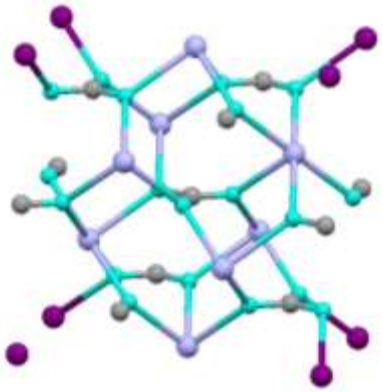
1 Mg-atom **2 Mg-atoms** **3 Mg-atoms**

$Mg_mCa_n(CO_3)_6$: energy vs. volume changes

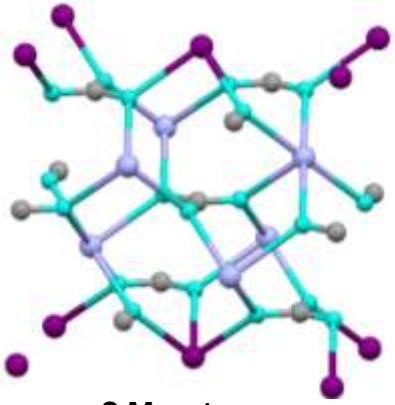




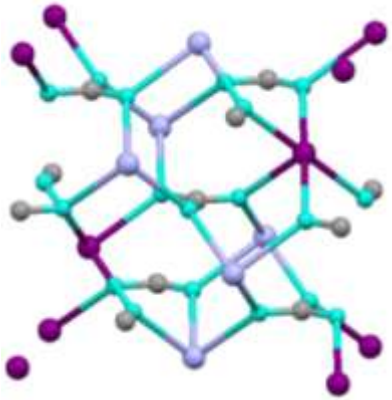
4 Mg-atoms



1 Mg-atom

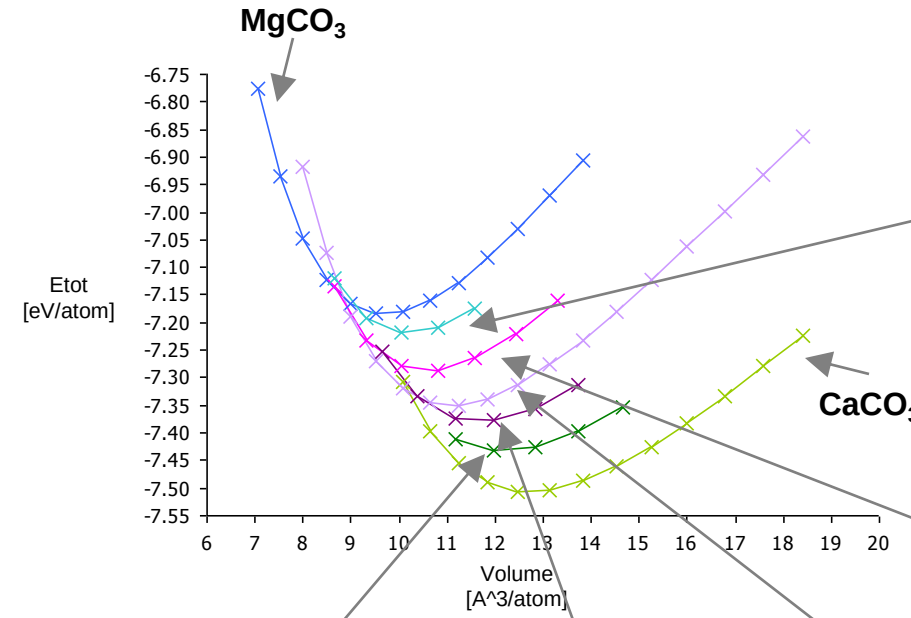


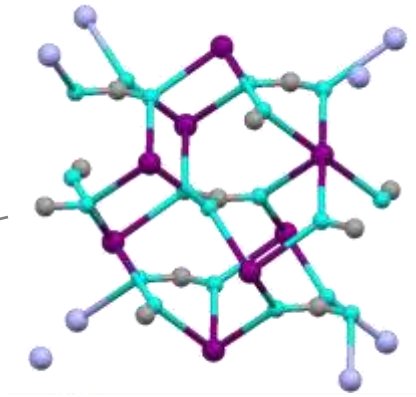
2 Mg-atoms



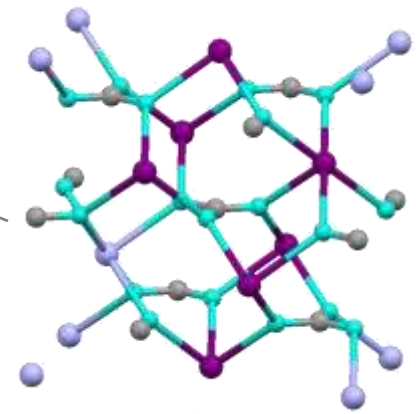
3 Mg-atoms

$Mg_mCa_n(CO_3)_6$: energy vs. volume changes

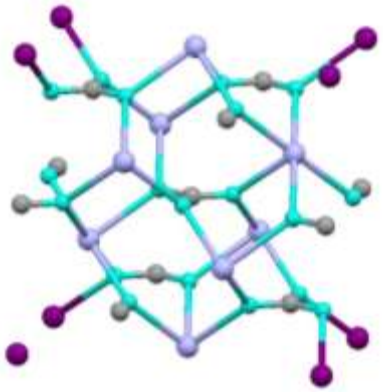




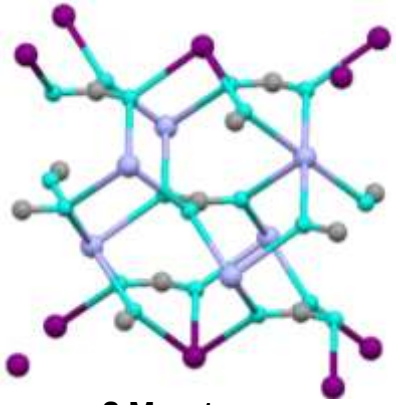
5 Mg-atoms



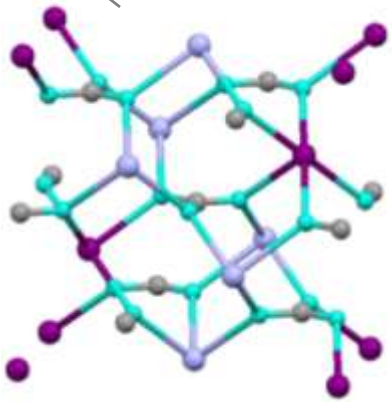
4 Mg-atoms



1 Mg-atom



2 Mg-atoms



3 Mg-atoms

Overview

- Motivation
- Structure and property overview
- Ab initio prediction of chitin (structure, stiffness)
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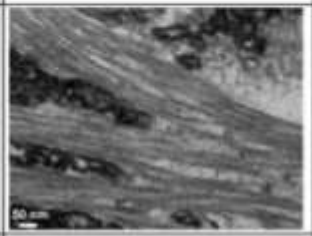
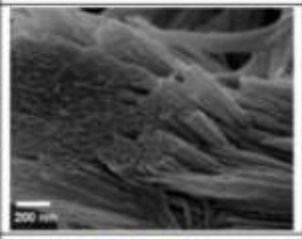
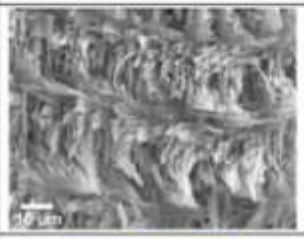
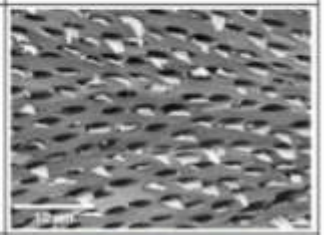
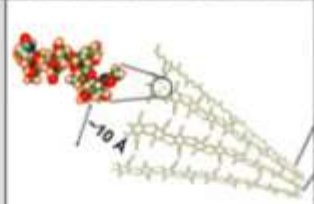
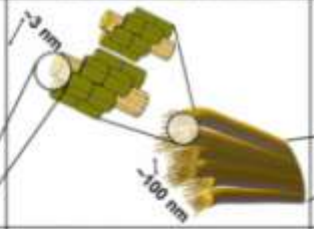
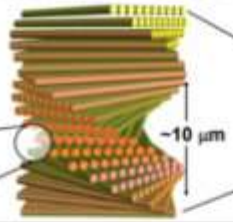
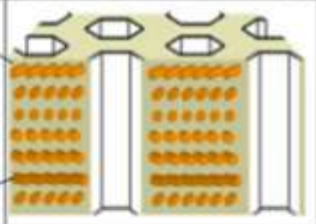
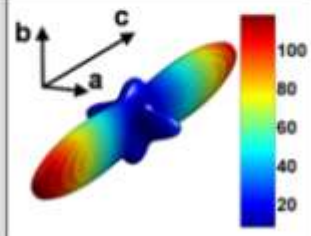
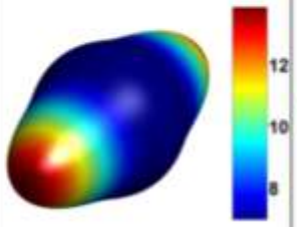
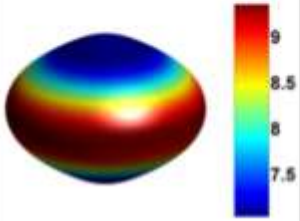
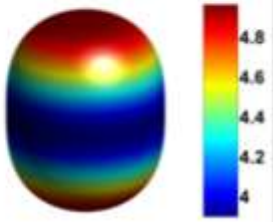
Hierarchical modeling of stiffness starting from ab initio

Scale	0.1 nm – 10 nm	10 nm – 100 nm	100 nm – 10 μm	10 μm – 1 mm
Hierarchical structure unit	α-chitin (H-bonded anti-parallel N-acetyl-glucosamine molecular chains)	Mineralized chitin-protein nanofibrils in a planar array	Twisted plywood stack of mineralized chitin-protein planes without pore canals	Twisted plywood stack of mineralized chitin-protein planes with pore canals
Experimental method	Transmission electron microscope	Field emission scanning electron microscope	Field emission scanning electron microscope	Field emission scanning electron microscope
Microstructure				
Schematic				
Simulation method	Ab initio; density functional theory	Mori-Tanaka scheme (chitin-protein fiber); Torquato 3-point scheme (mineral-protein matrix)	Voigt estimate, tensor rotation	Torquato 3-point homogenization
Elastic behavior, 3D map of Young's modulus [GPa] a,b-axis: basal directions of chitin cell c-axis: longitudinal axis of molecule				

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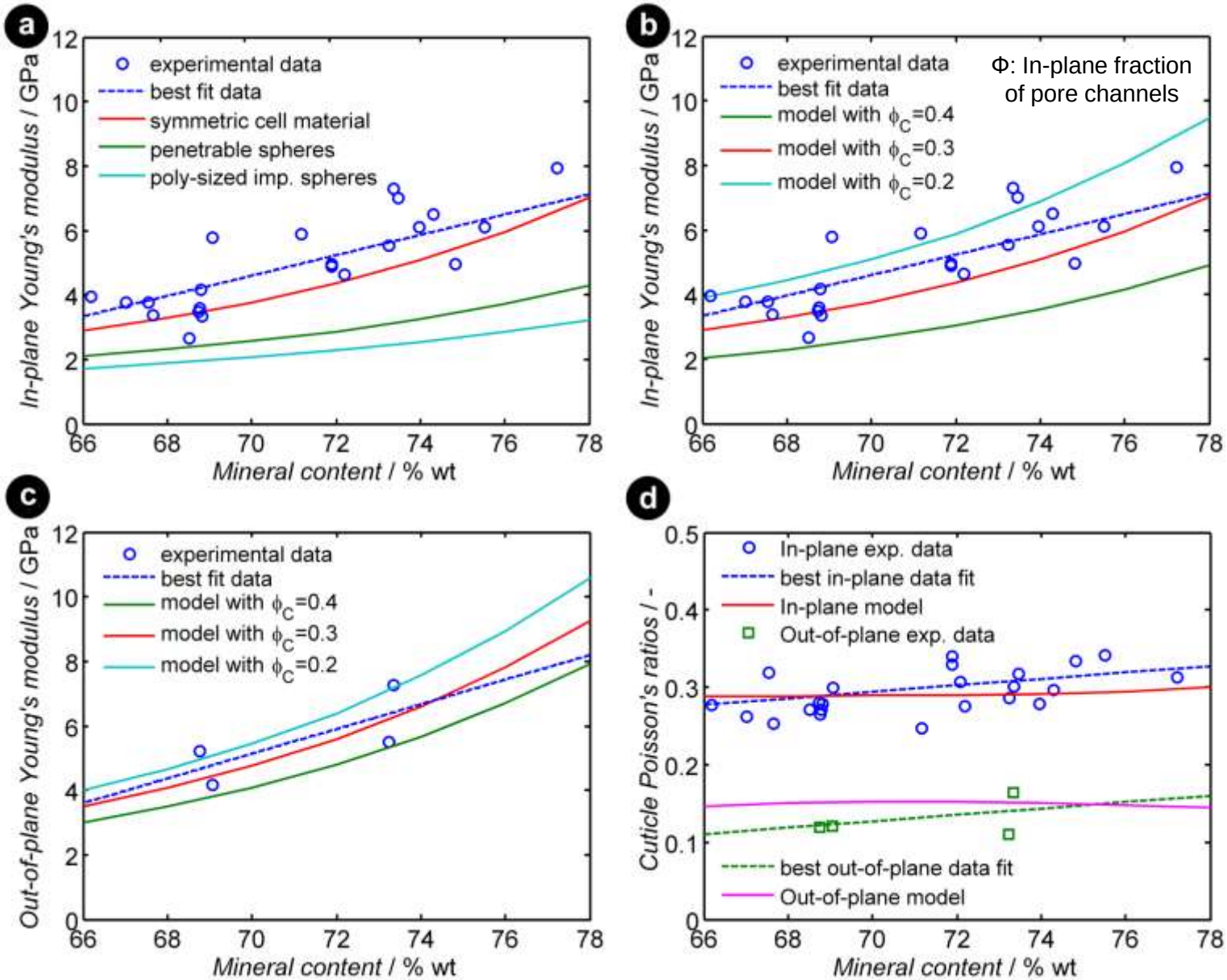
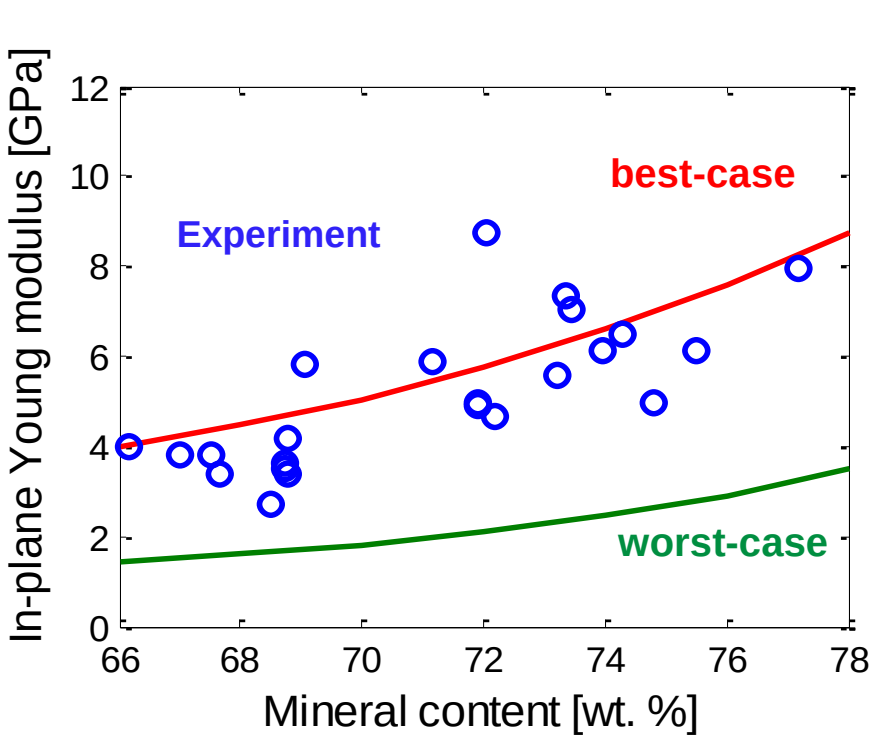
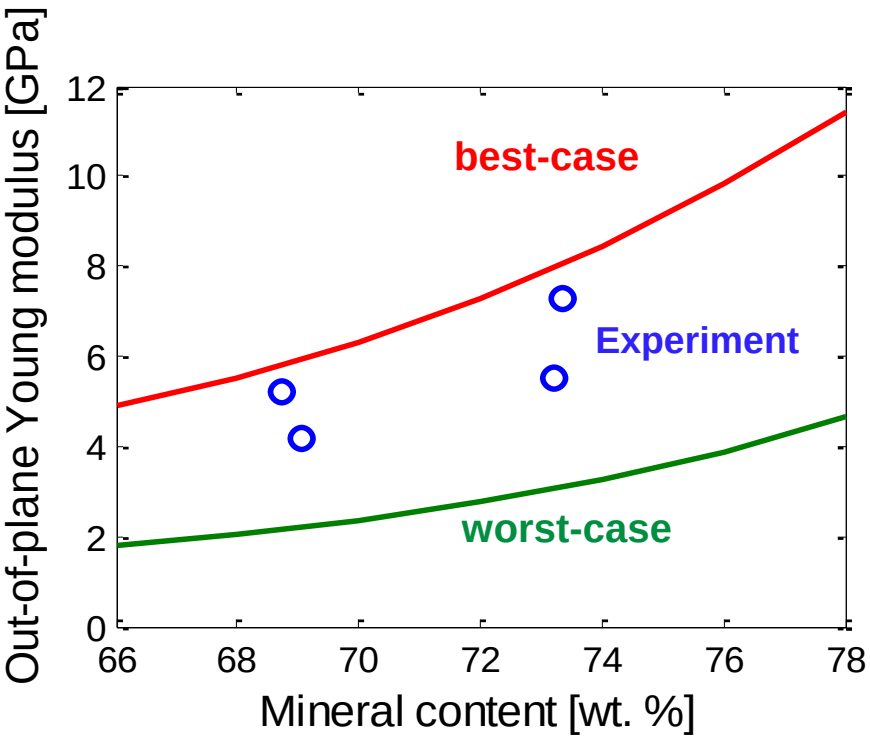
Predictions and comparison to experiments



Comparison between model and experiment: error propagation





Cases obtained by accumulative changes that maximize (red) / minimize (green) the elastic overall moduli.

The experiments suggest that the hierarchical organization of the material provides an optimal use of the properties of the underlying ingredients.

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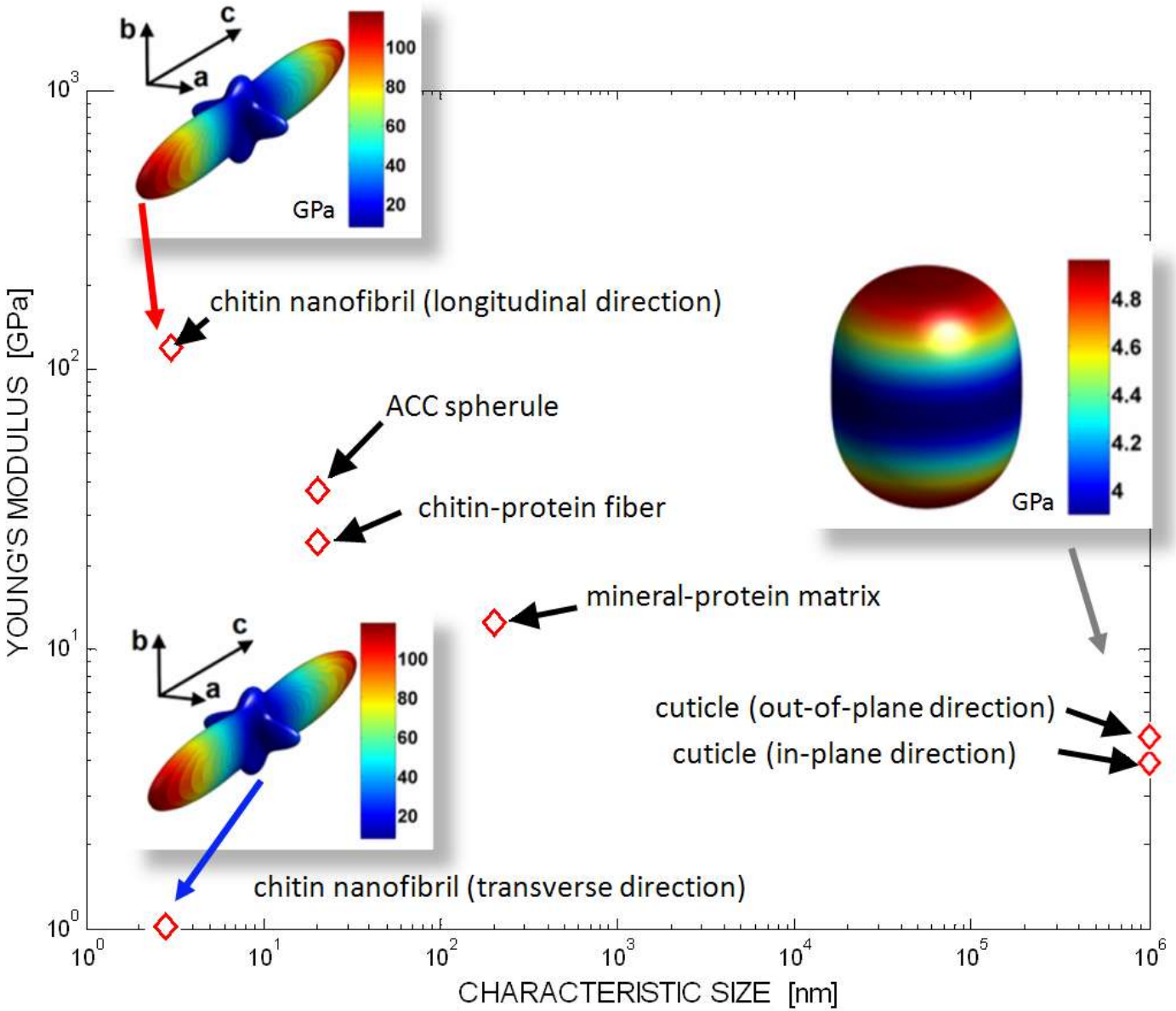
Hierarchical modeling of stiffness starting from ab initio



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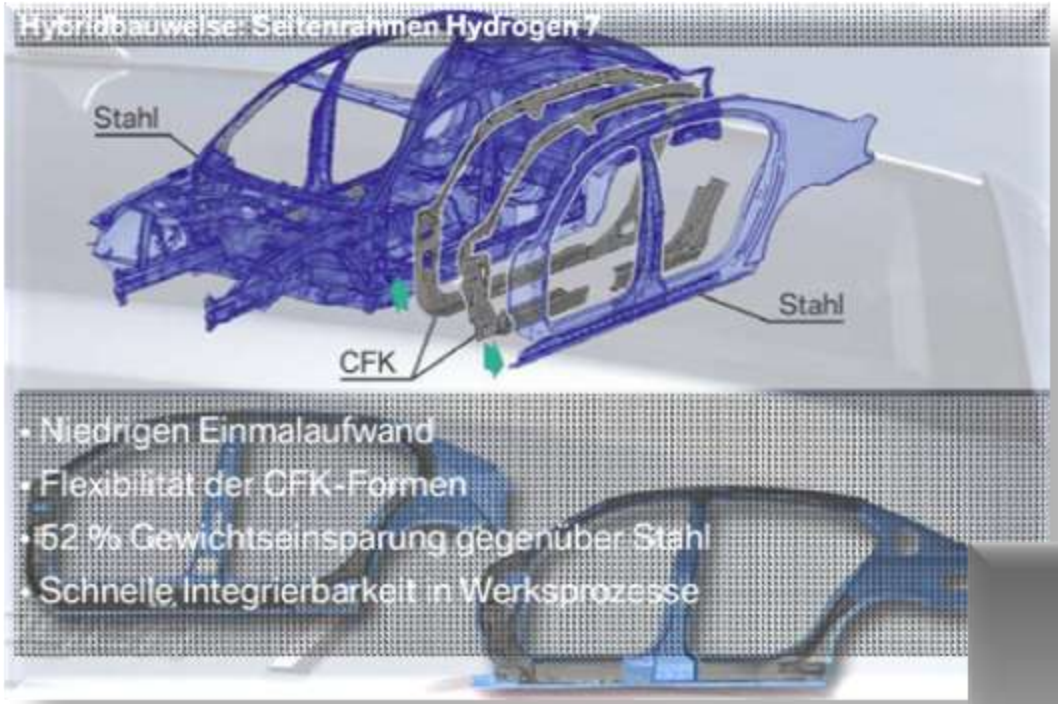
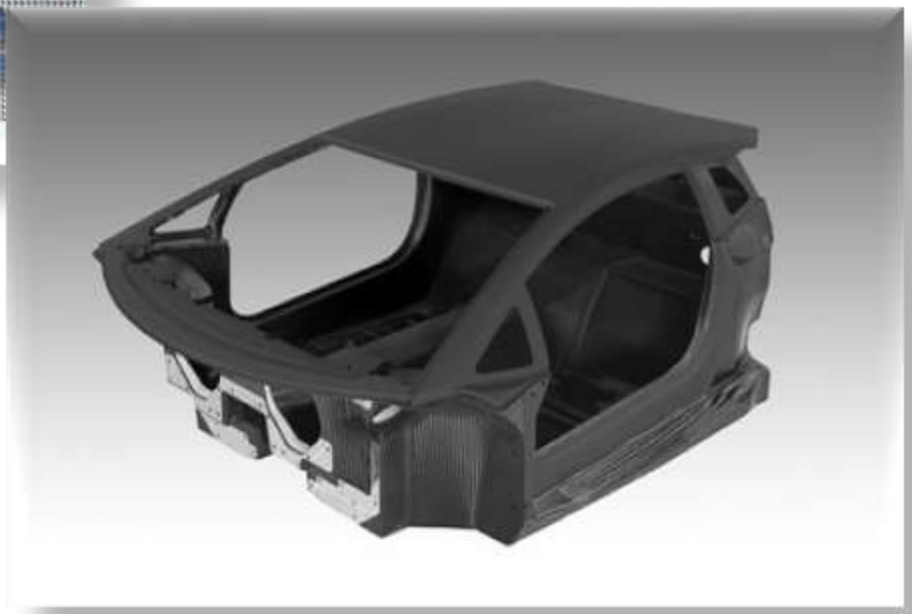
New composite concepts for transportation



courtesy BMW



courtesy Lamborghini

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