II -Some applications of high-resolution TEM to porous non-conventional minerals

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Fourth Winter School on Multiscale Porous Materials – January, 2017-Marseilles, France

structural nanopores in minerals

Nanostructure of the EMT zeolite (Elf Mulhouse Two) with faujasite intergrown lamellae: an acidic catalyzer for fuel oil

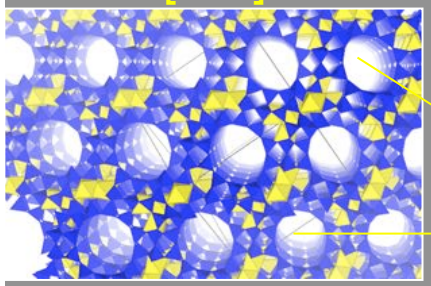
please tell the story !

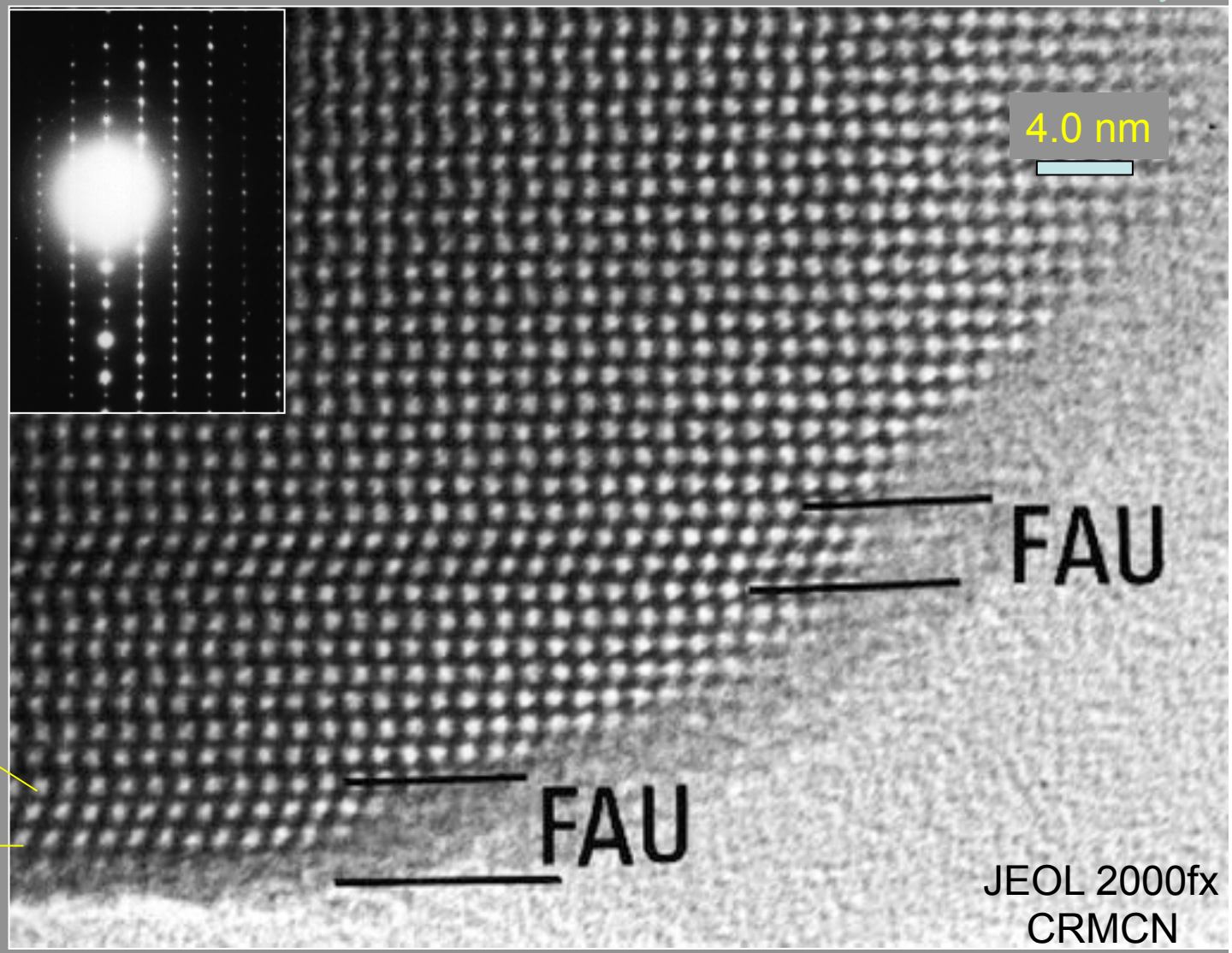
"lateral" nanopore network

EMT: AB stacking hexagonal structure

Faujasite: ABC stacking cubic structure

faujasite structure [110]





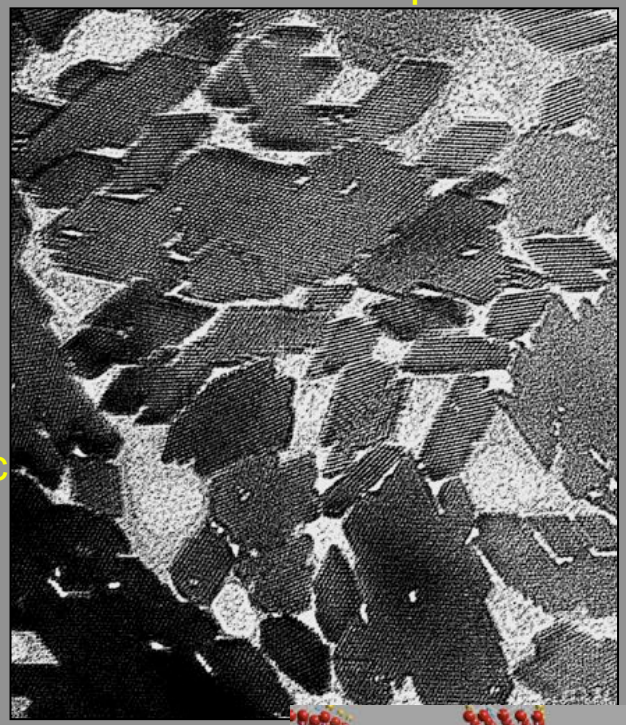
Palygorskite/attapulgite $(Mg,Al)_2Si_40_{10}(OH)$ -4(H_2O): a nanoporous fibrous clay

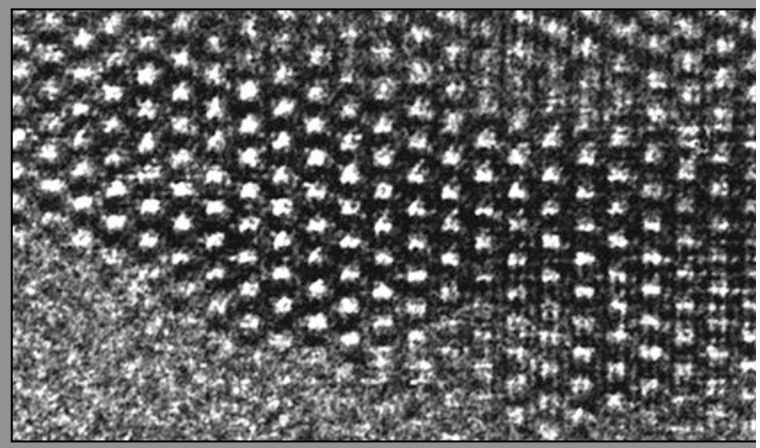
Highly absorbing material

A widespread drug

that binds to acid and toxic substances in the stomac and digestive tract

Also to treat diarrhea!!

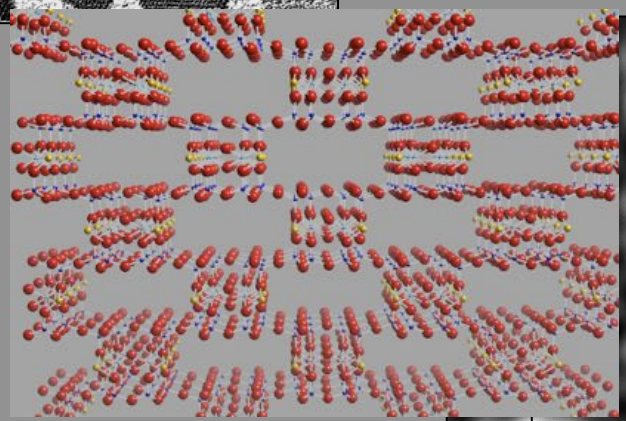




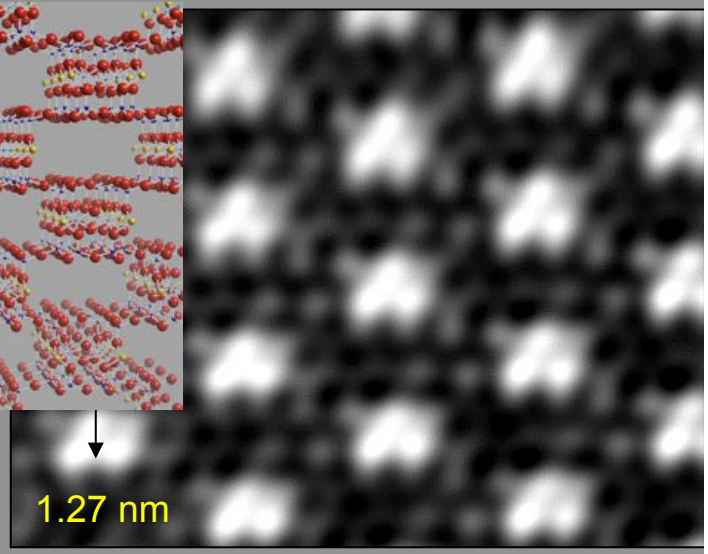
Raw
JEOL 3010
CINaM
Fourier-filtered

Cat beds

The eternal « Maya blue »
= trapped indigo molecules



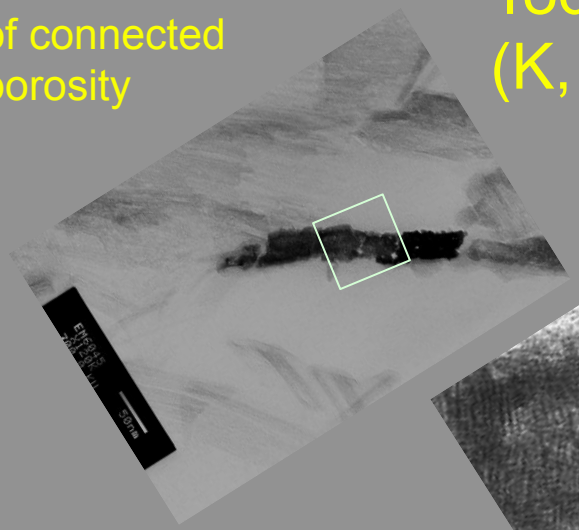
Ball-and-stick model

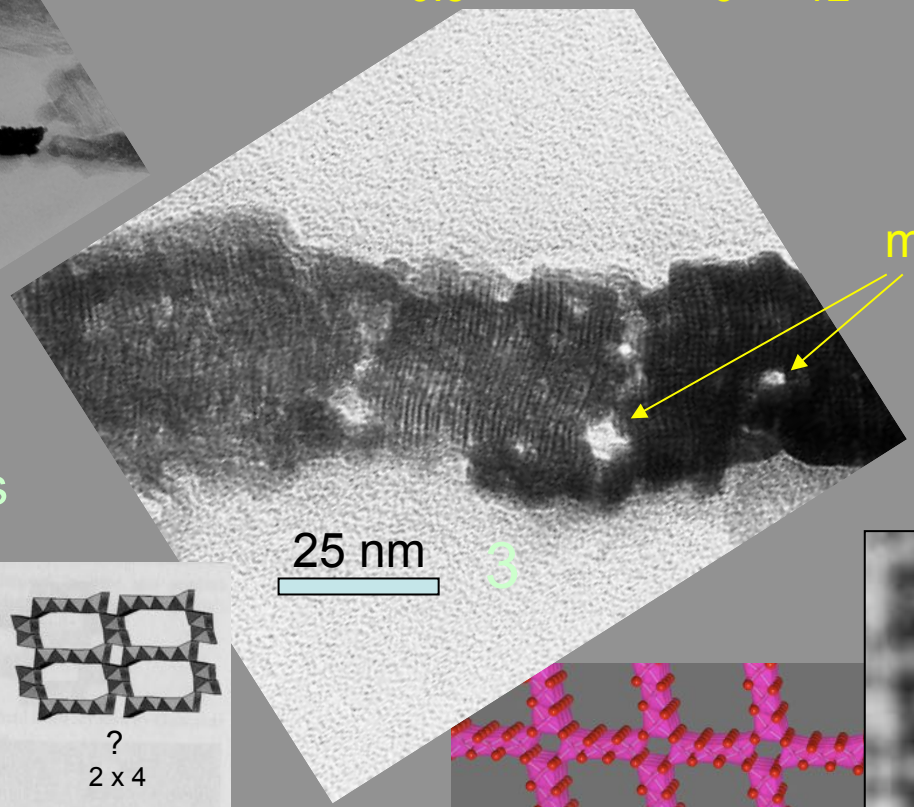


Todorokite - A tunnel manganese oxide

$(K, Ca, Na)_{0.5}\ Mn^{(3+,4+)}{}_6\ O_{12} - 4H_2O$

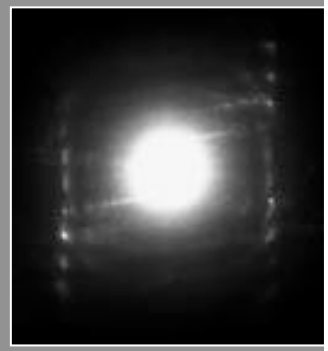
Three levels of connected porosity



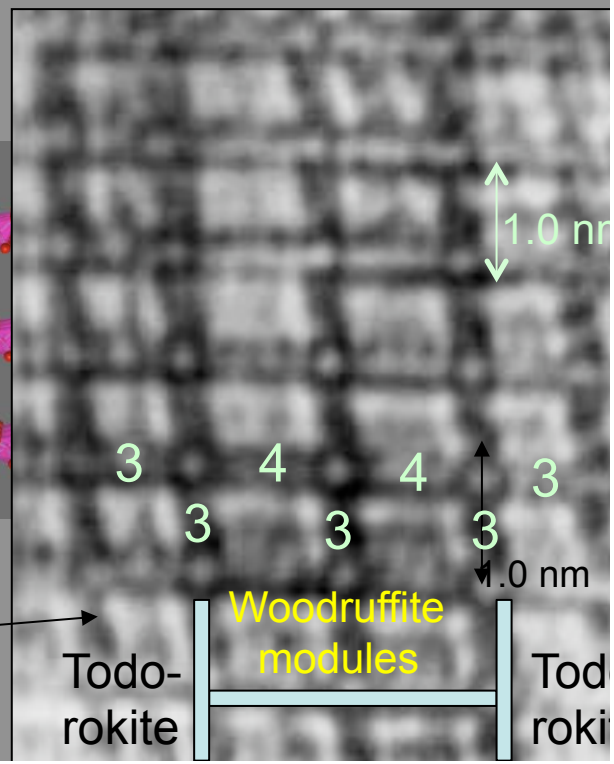


macropores

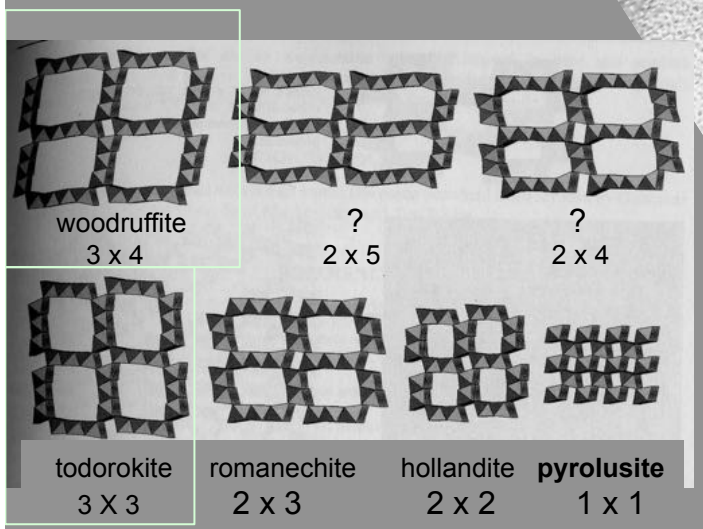
SAED pattern



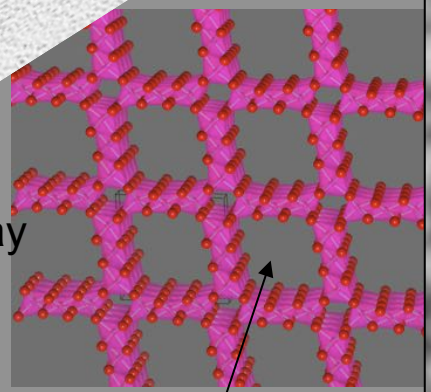
CINaM-JEOL 3010
Fourier-filtered image



Modular structures



mean X-ray structure



nanopores

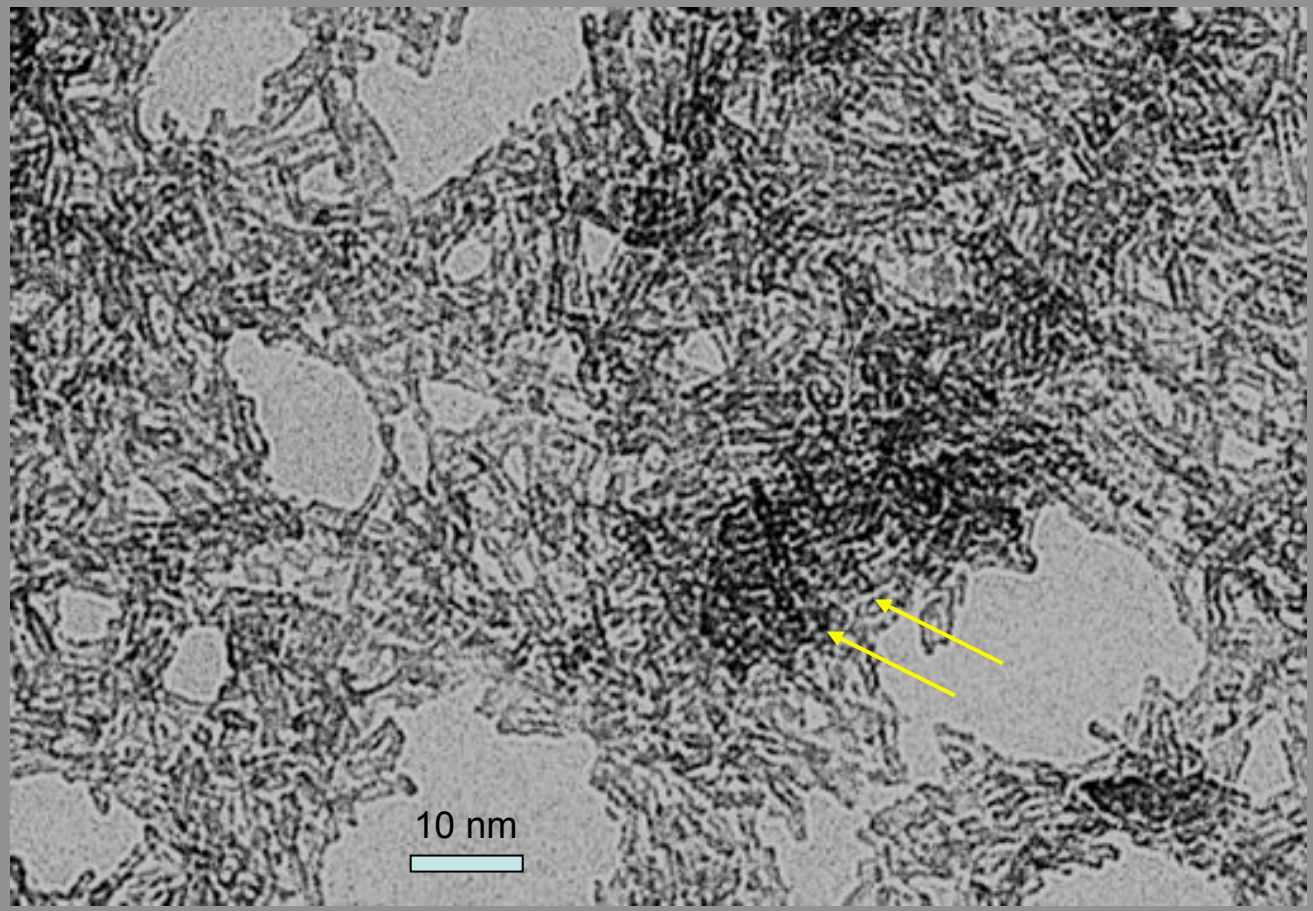
in polymetallic nodules on the sea floor

Synthetic imogolite $Al_2SiO_3(OH)_4$ short nanotubes SWNT

in soils derived from volcanic ash

tubule: external diameter ≈ 2 nm

layers of tubules resembling panpipes (arrows)



Used as template for synthesis of nano composites

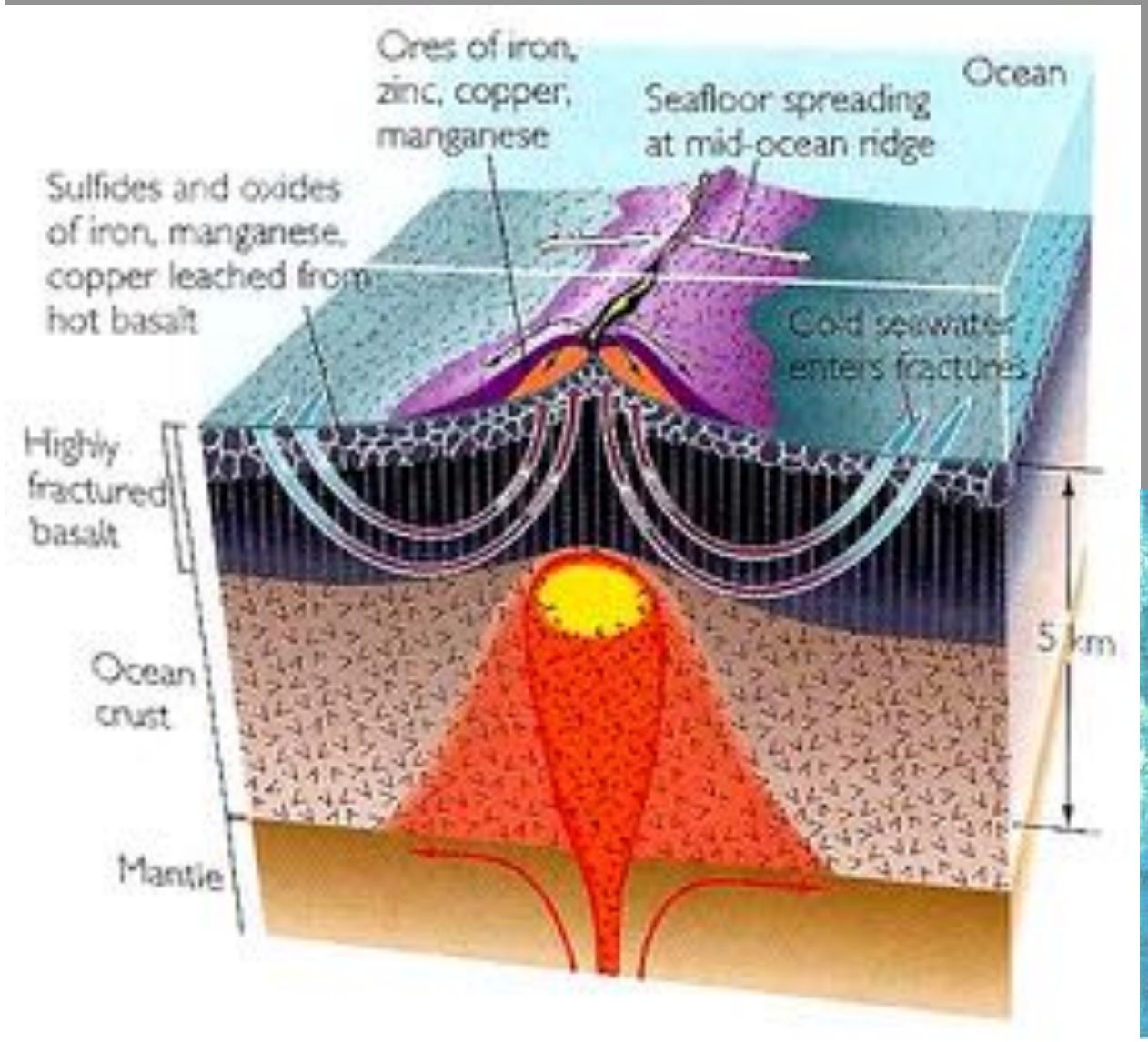
Chrysotile - asbestos

“Crack – seal“ veins in a serpentinite

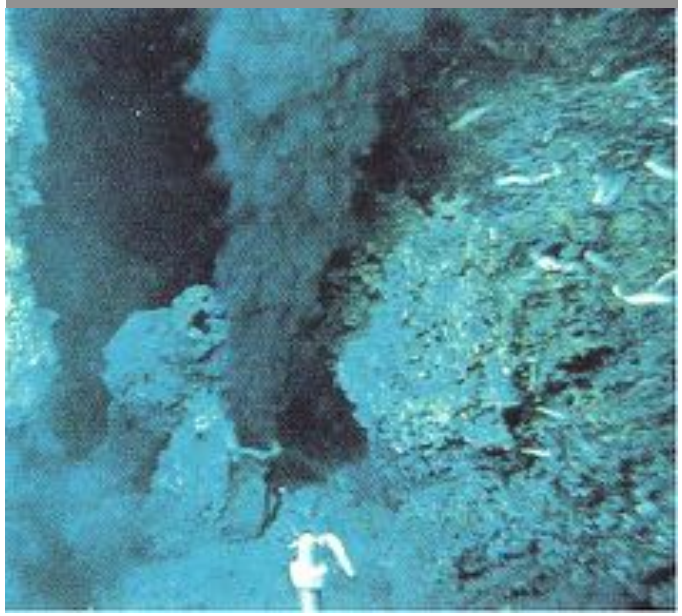
The longest chrysotile fibers In close-packing

Zoom on the mid-ocean ridge

The hardest quench on Earth
(exclusive of fulgurites)

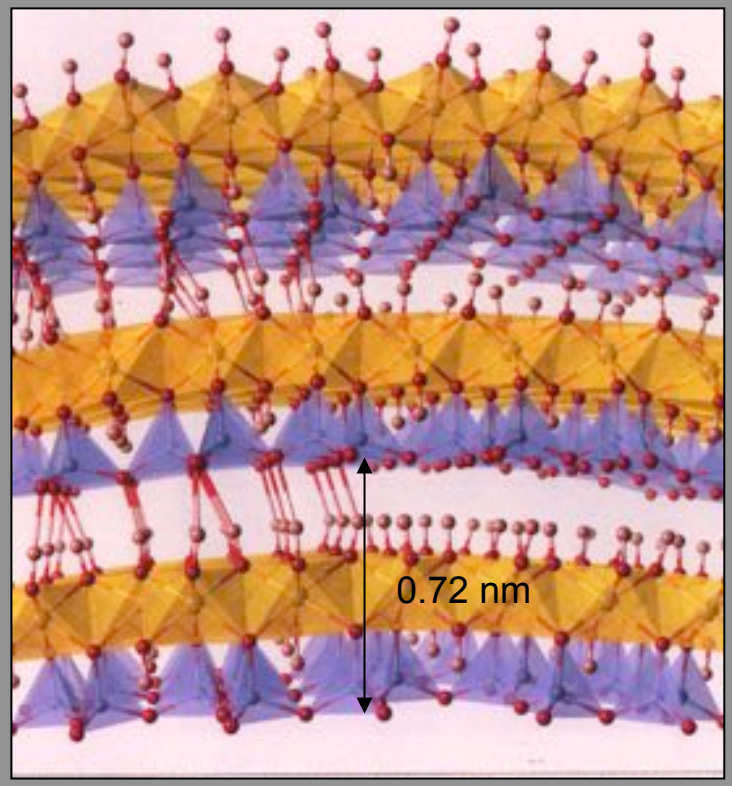


A black smoker

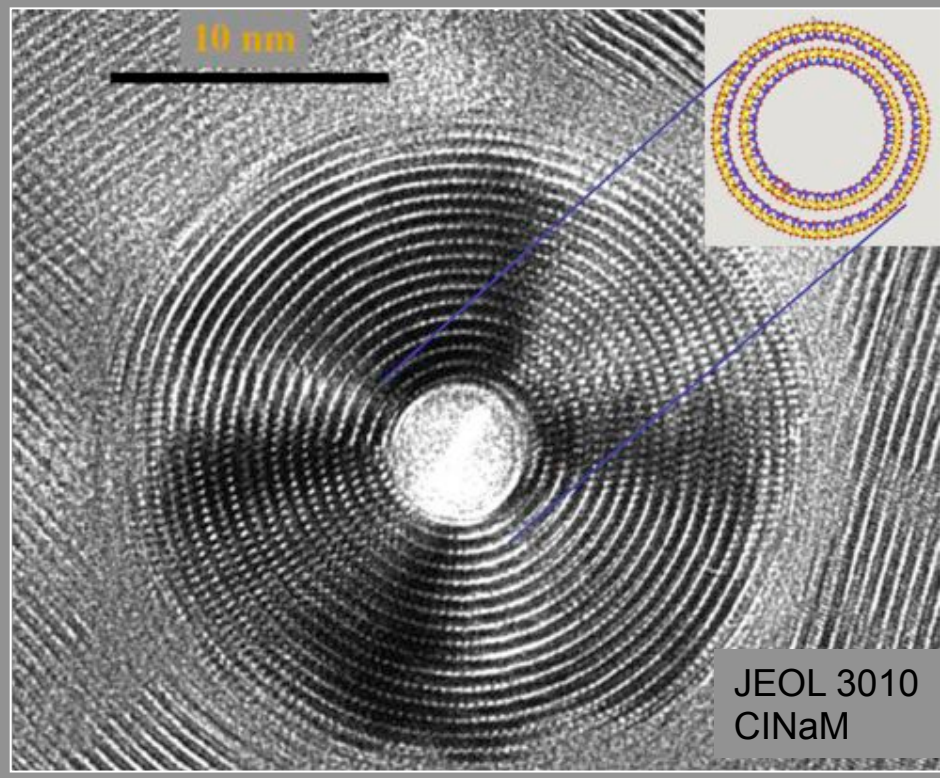


Chrysotile $Mg_3Si_2O_5(OH)_4$: a nano tubular silicate structure

O
T
O
T
O
T



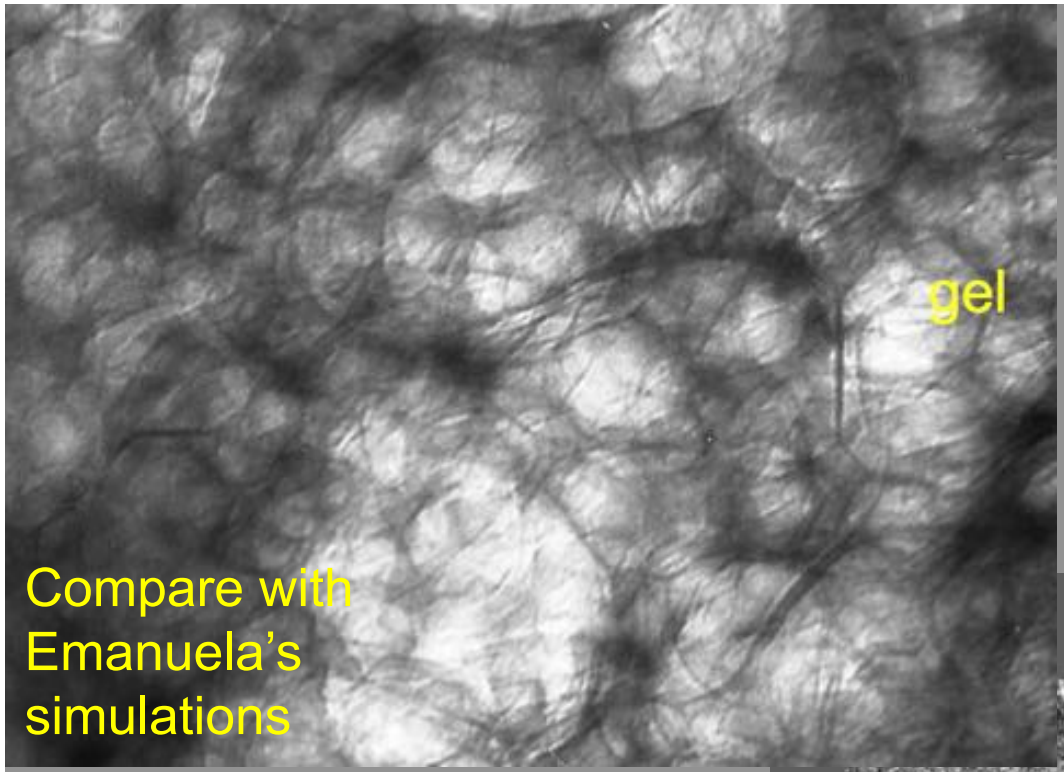
Polyhedral model of the polar structure of chrysotile



Cross-section of a chrysotile nanotube

A microstructural pore in the centre

Textural nanopores



Compare with Emanuela's simulations

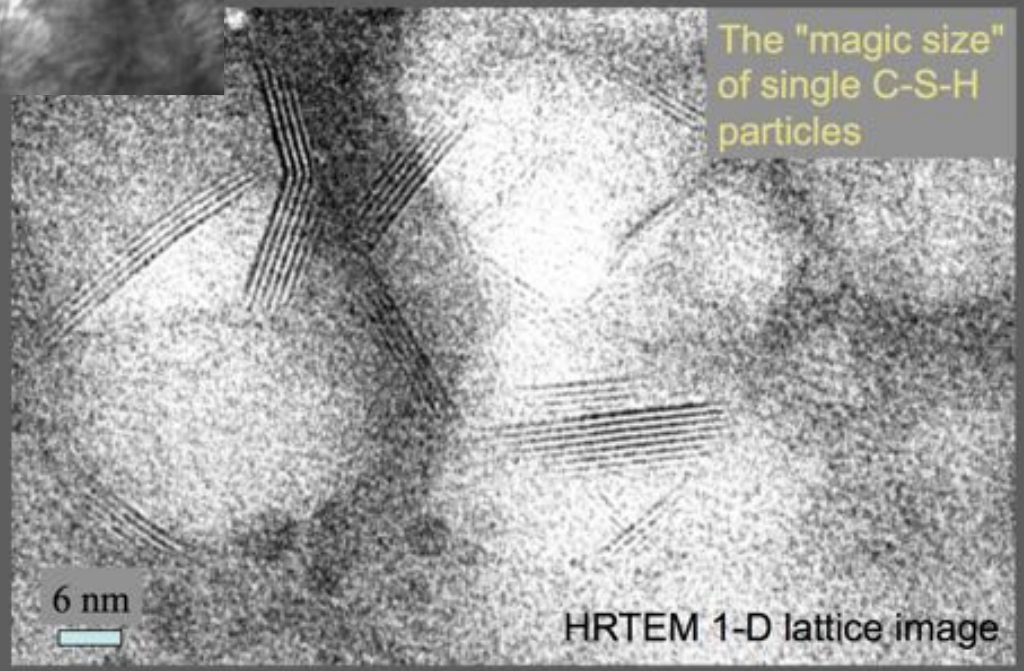
The glue of cement:

The Calcium Silicate Hydrate (CSH)

Inside high-density CSH

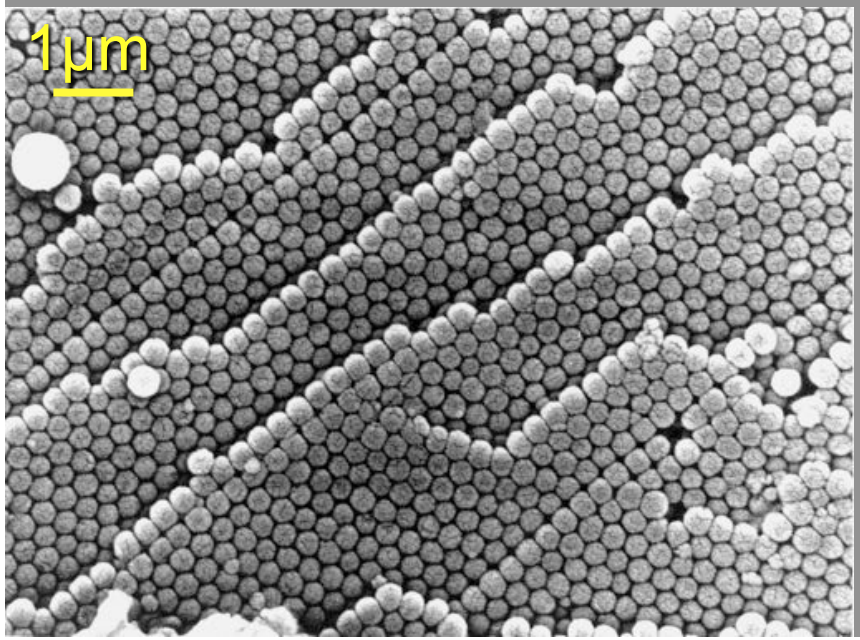
An house-of-card Texture

A nanoporous material



Opal A: a photonic, colloidal crystal

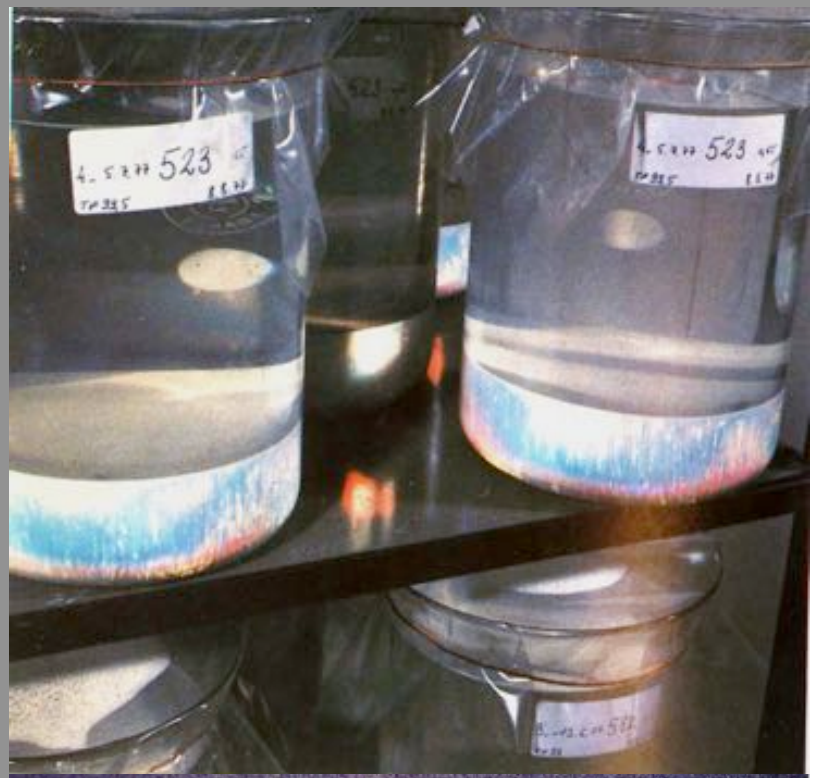
amorphous SiO_2



SEM image

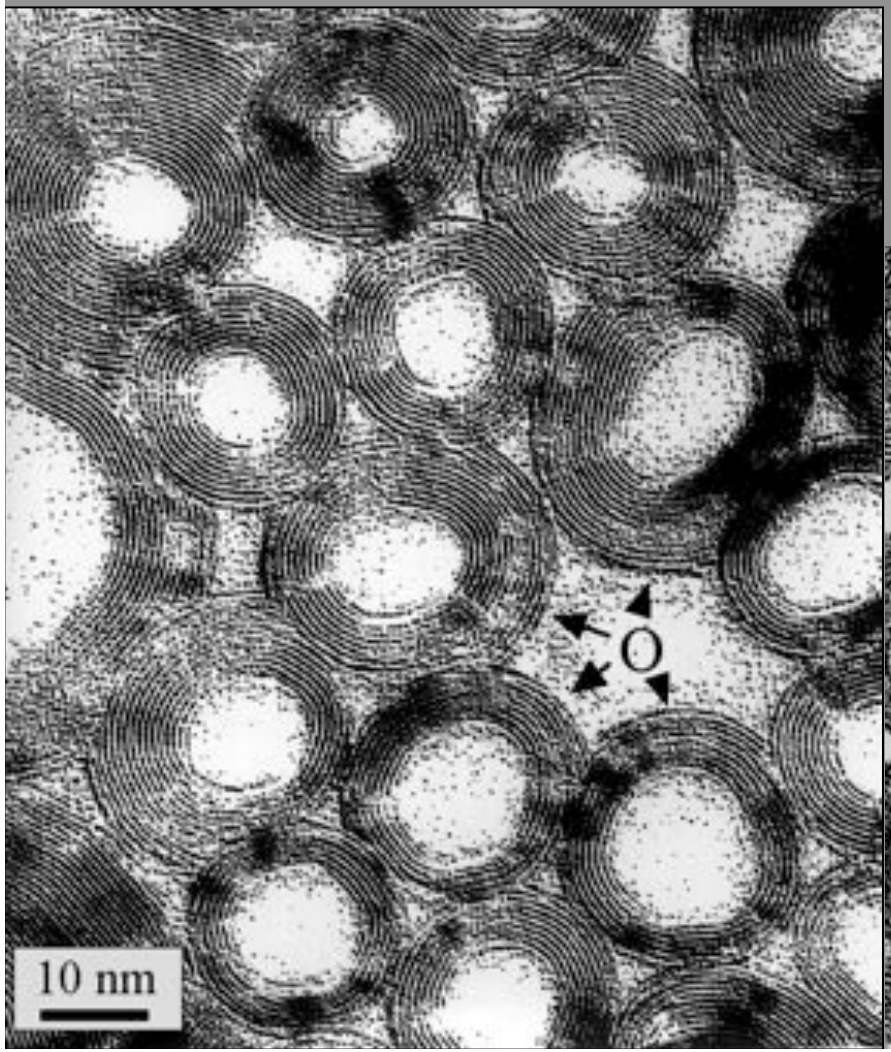
Opal structure (courtesy JP Gauthier)

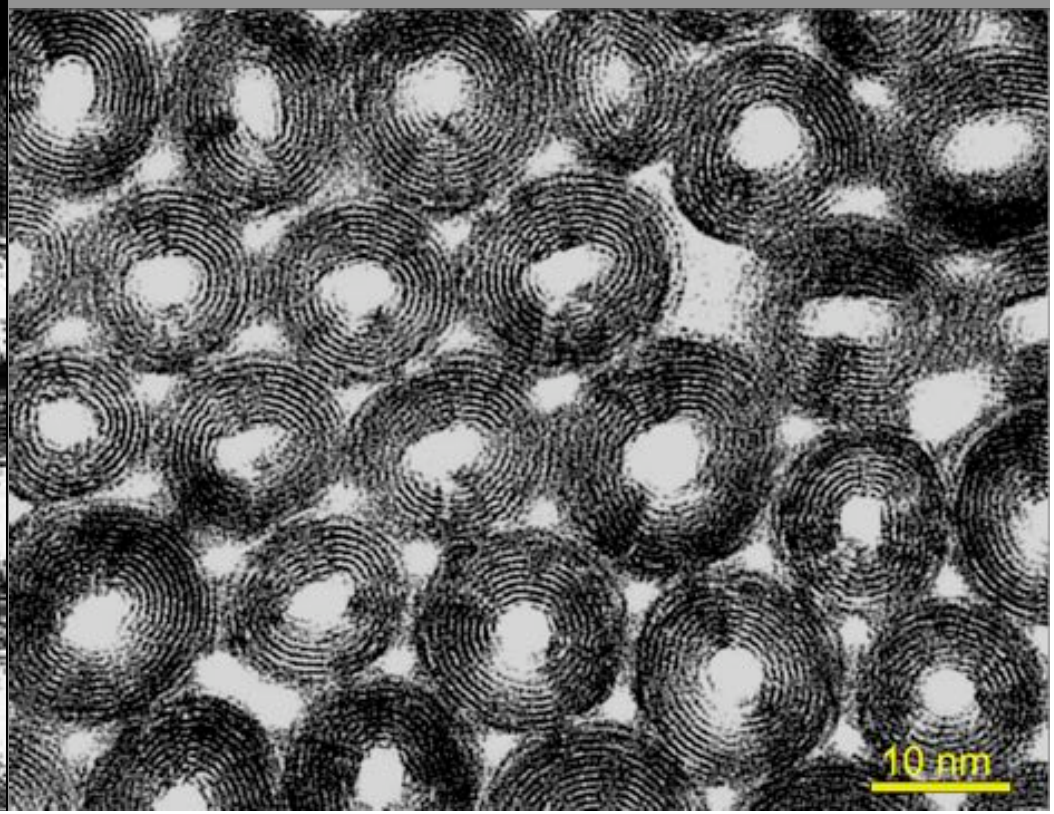
Gilson's synthesis of opal



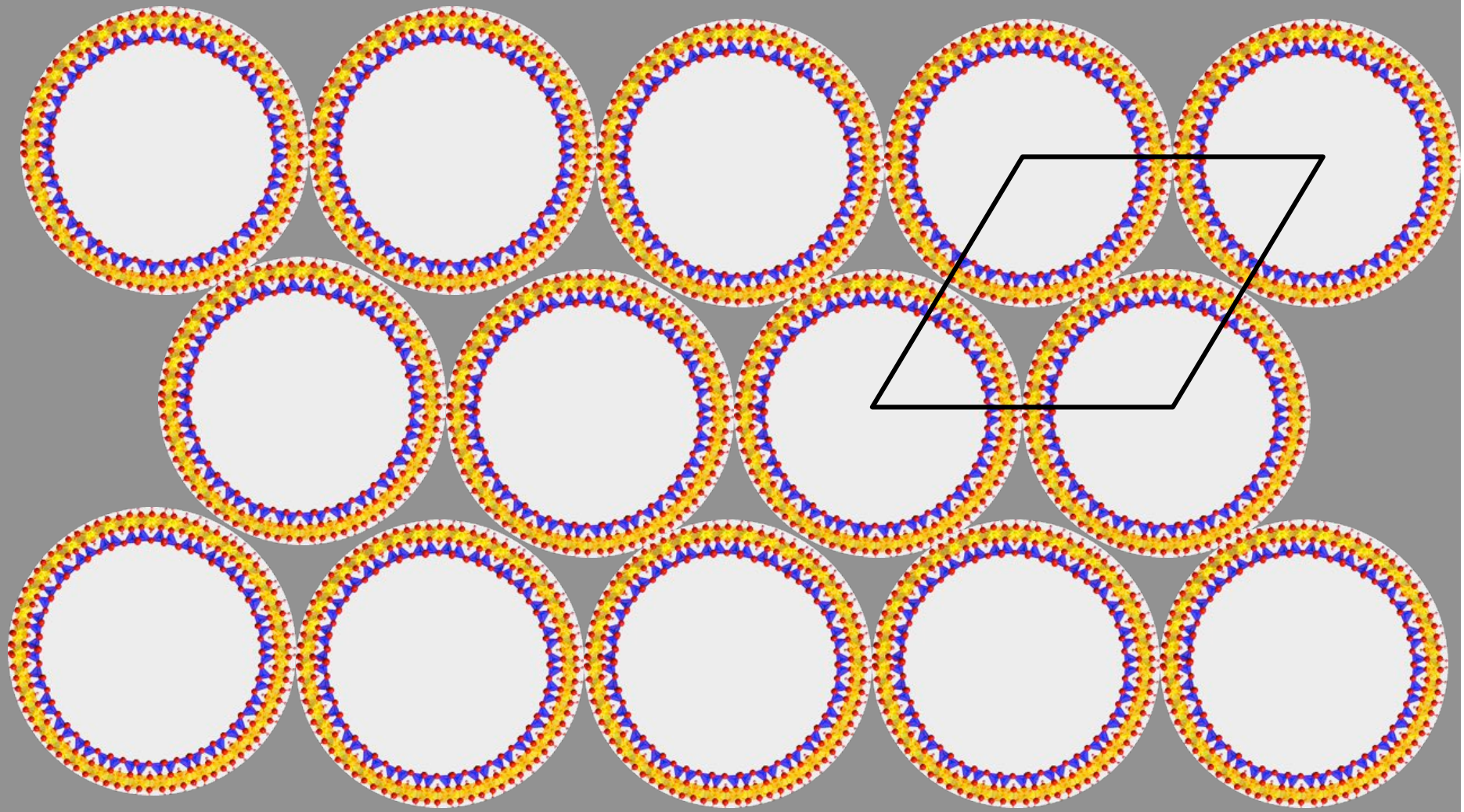
Cabochons from Gilson's opa

A colloidal 2-D glass of serpentine nanotubes





Nanopores in colloidal chrysotile crystals



two triangular channels bordered by $Mg(O,OH)_6$ octahedra per one cylindrical channel bordered by SiO_4 tetrahedra

A potential "two-function" molecular sieve?
An UV photonic crystal

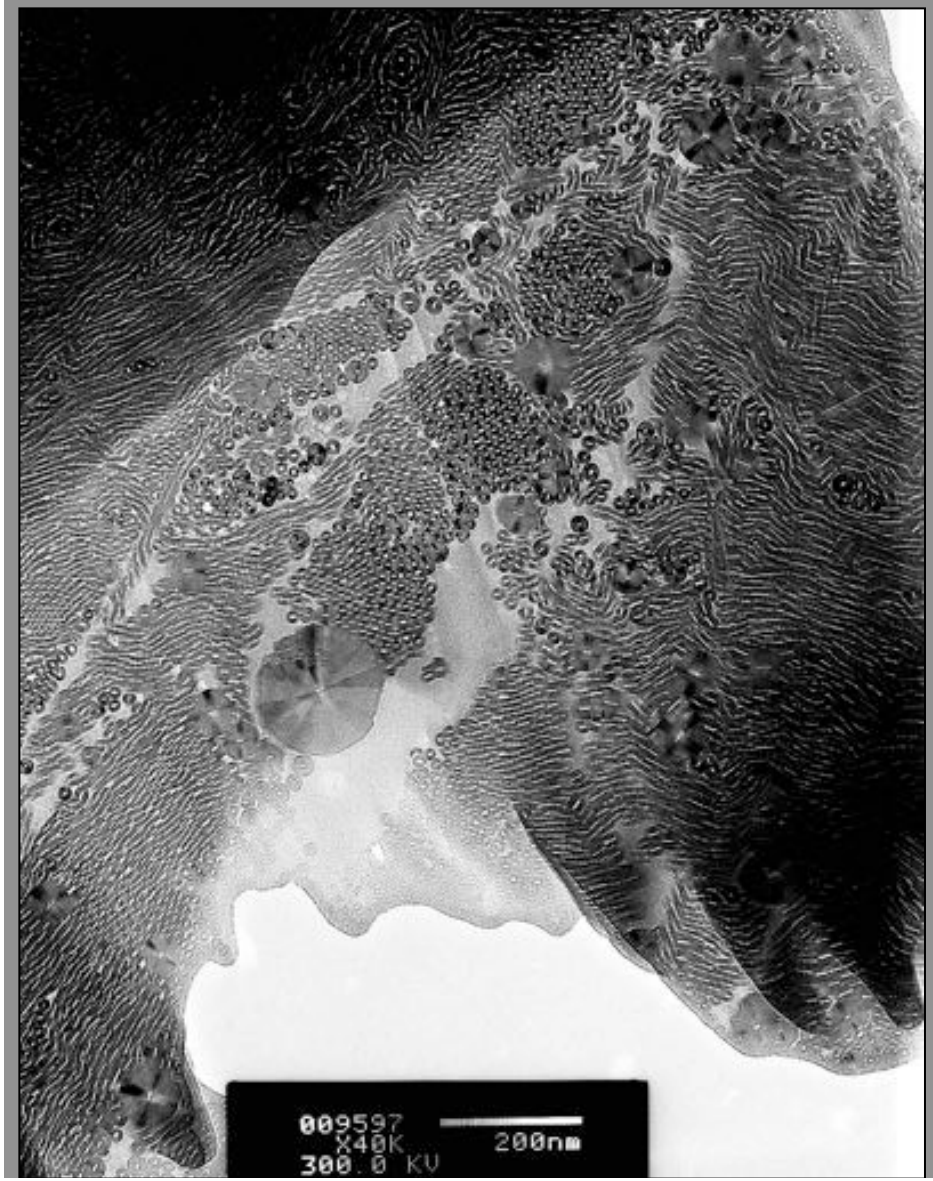
A mosaic of colloidal crystals formed by 2-D "assemblage" of chrysotile nanotubes

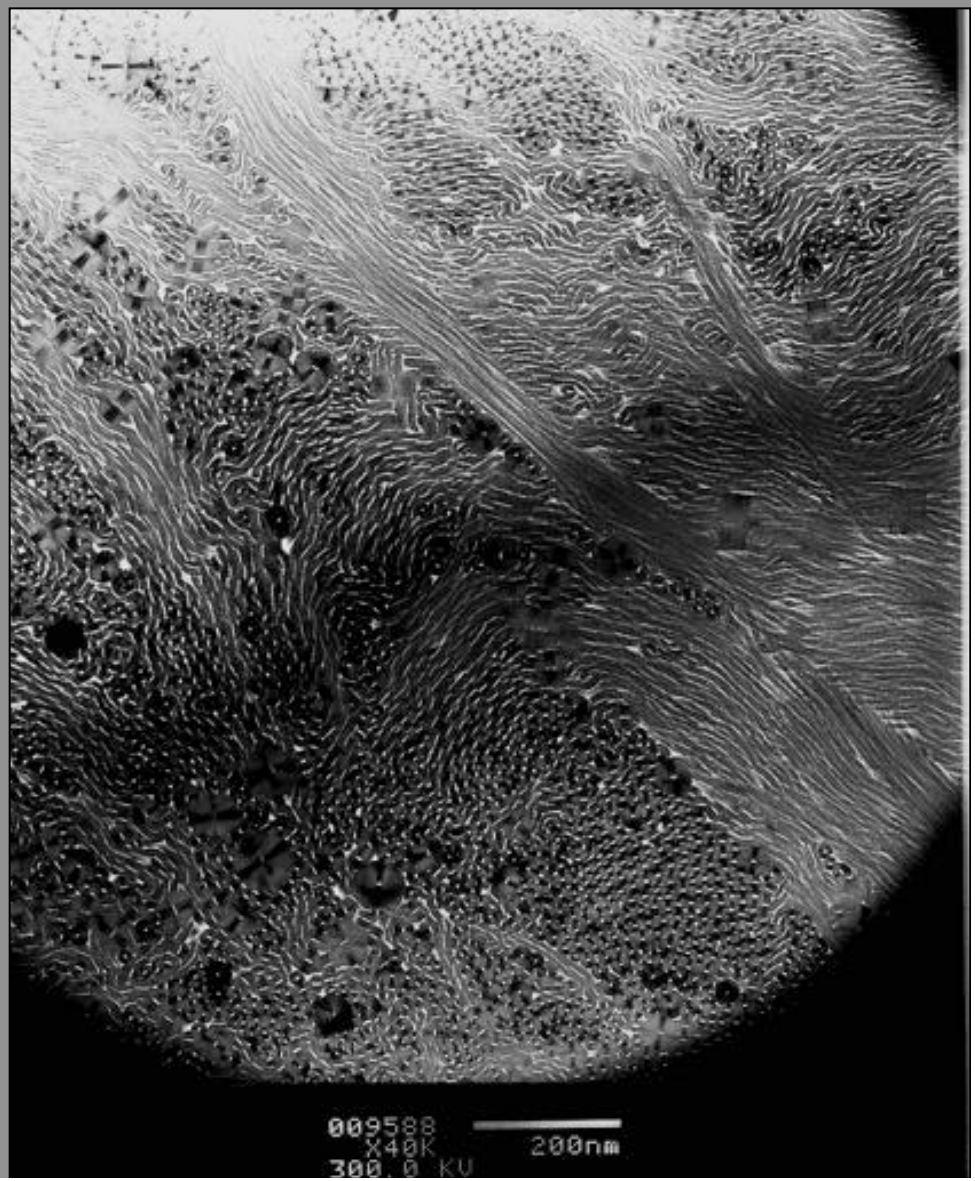
Repeated "Twinning"
of colloidal chrysotile
crystals on dense
tubule planes

A "supra-crystallography"
at work?

For fun

Textures of short chrysotile nanotubes:
arabesques of serpentine:
closer-and-closer to biological microstructures



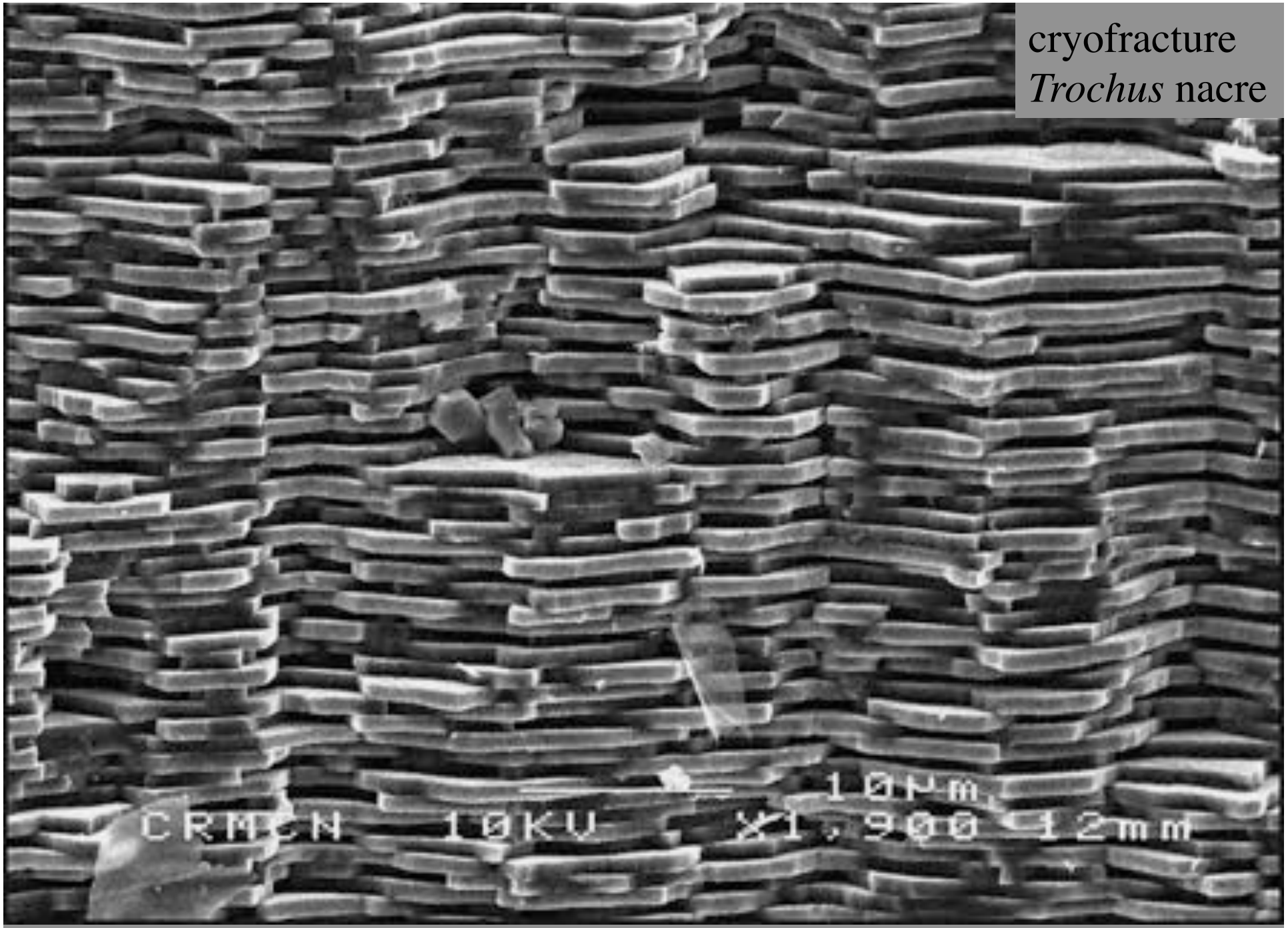


Last news

Biologically-controlled, Ca-carbonate biominerals are all

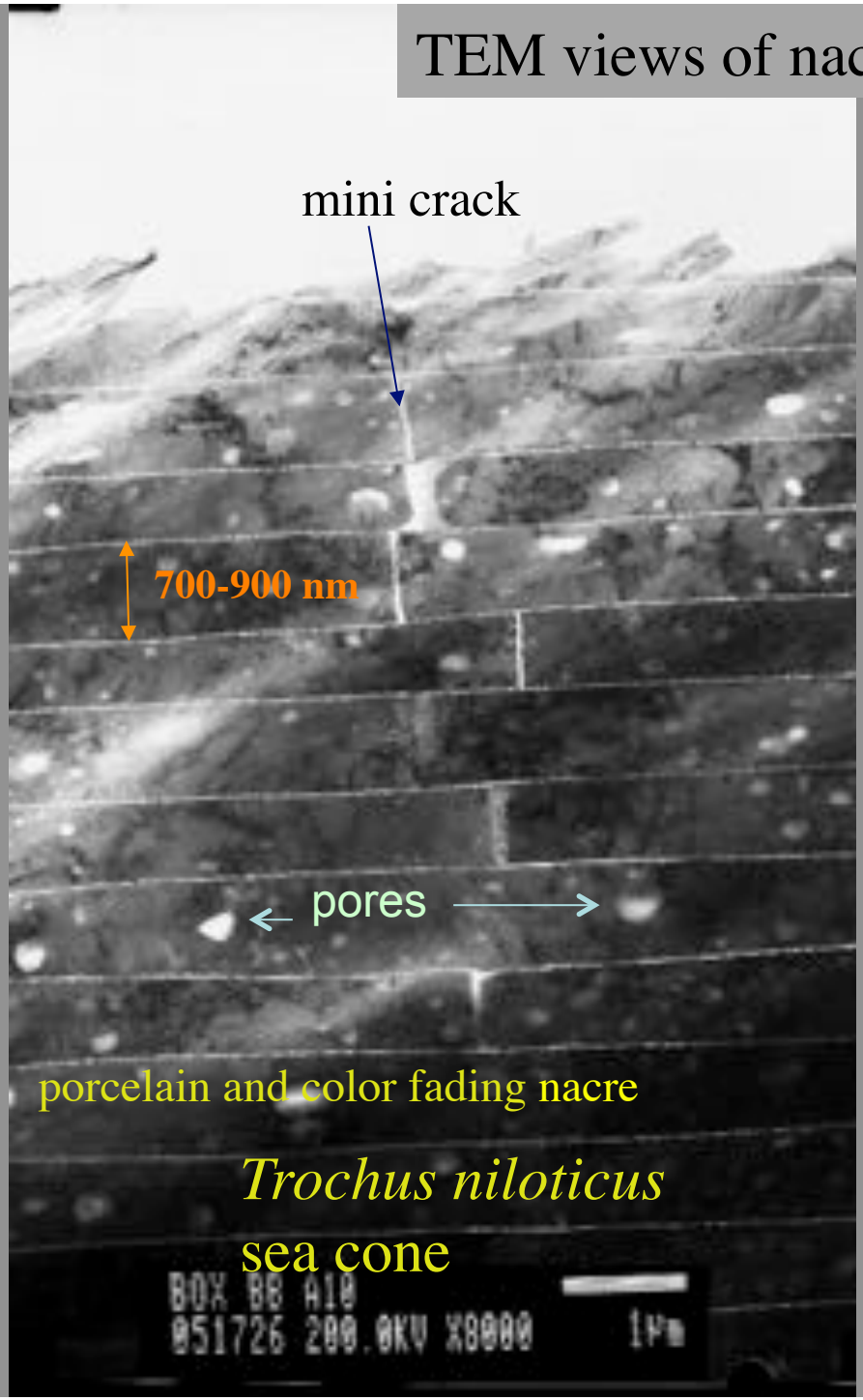
nanoporous organo-mineral composites

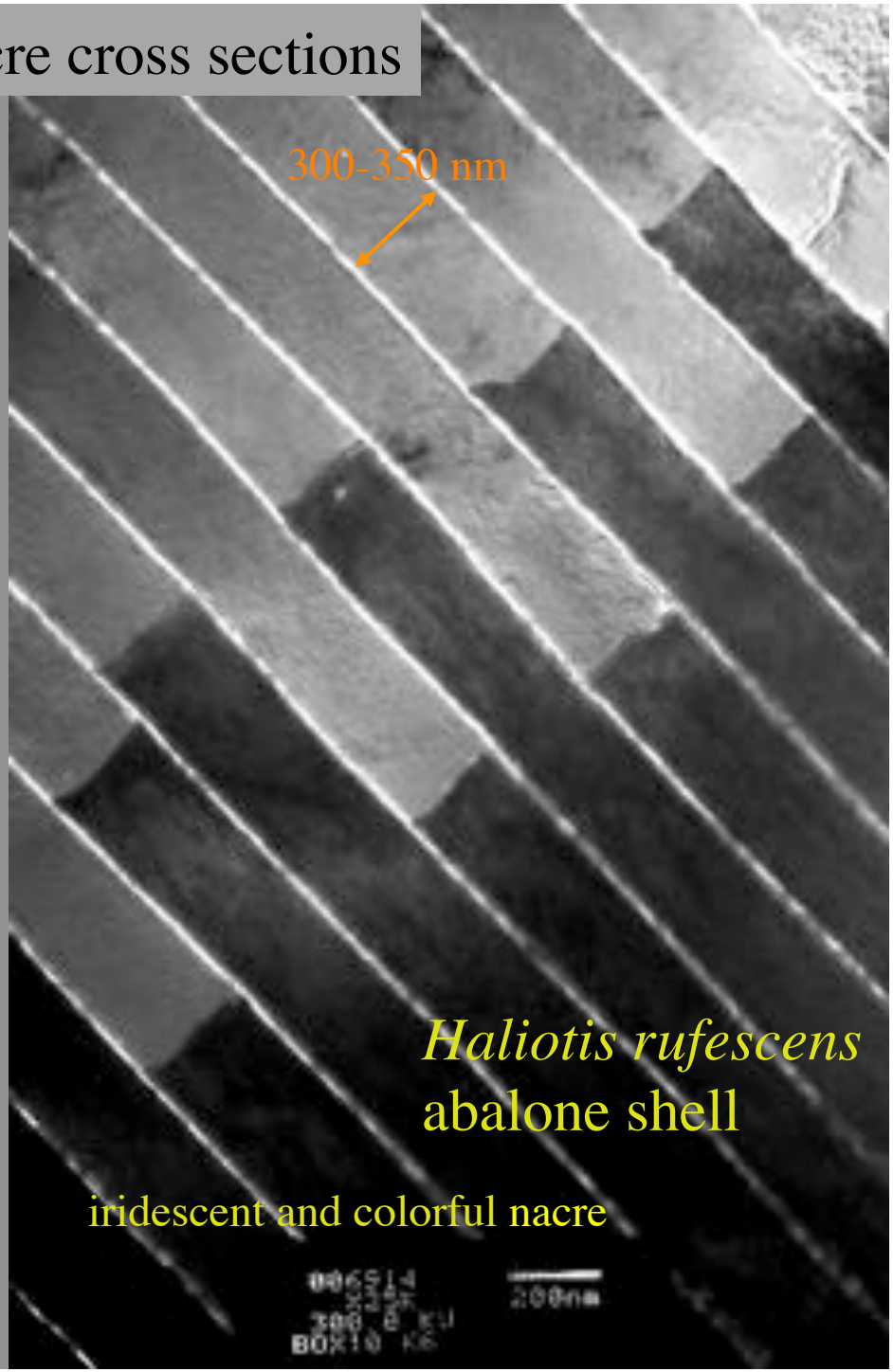
Example of mollusc sea shells



cryofracture
Trochus nacre

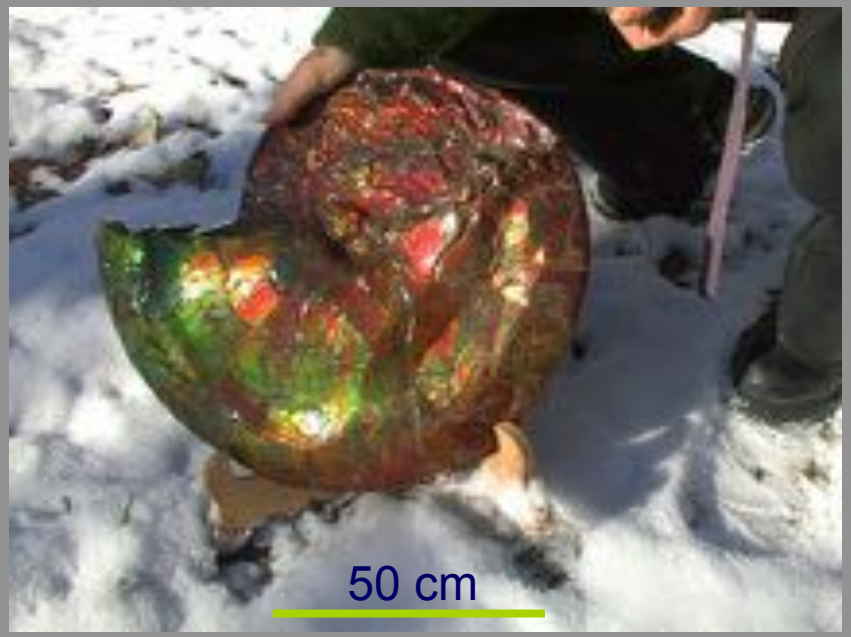
TEM views of nacre cross sections





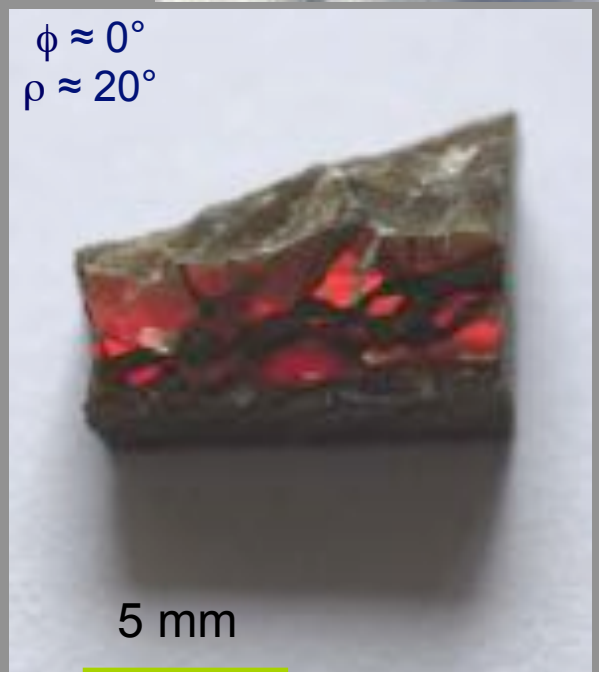
Ammolite as a new gem (bio) stone

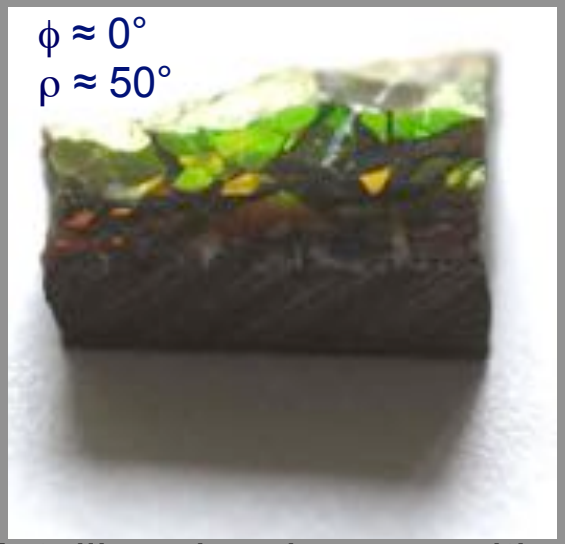
Ammolite pendant



Placenticeras Meeki
Cretaceous
(≈ 80 Mya)
Alberta (Canada)

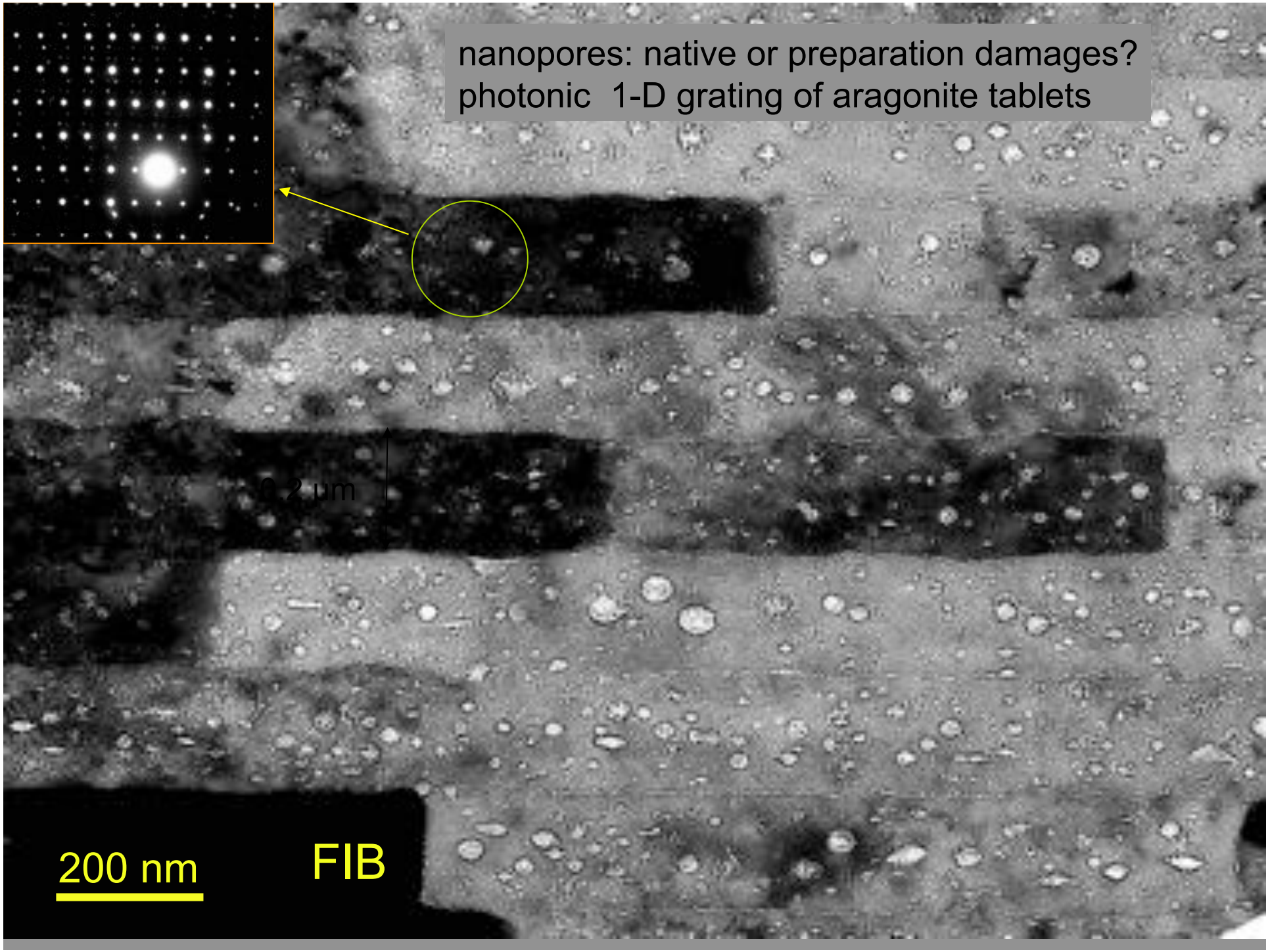
Iridescent ammonite
Cleoniceras (albian)
Madagascar



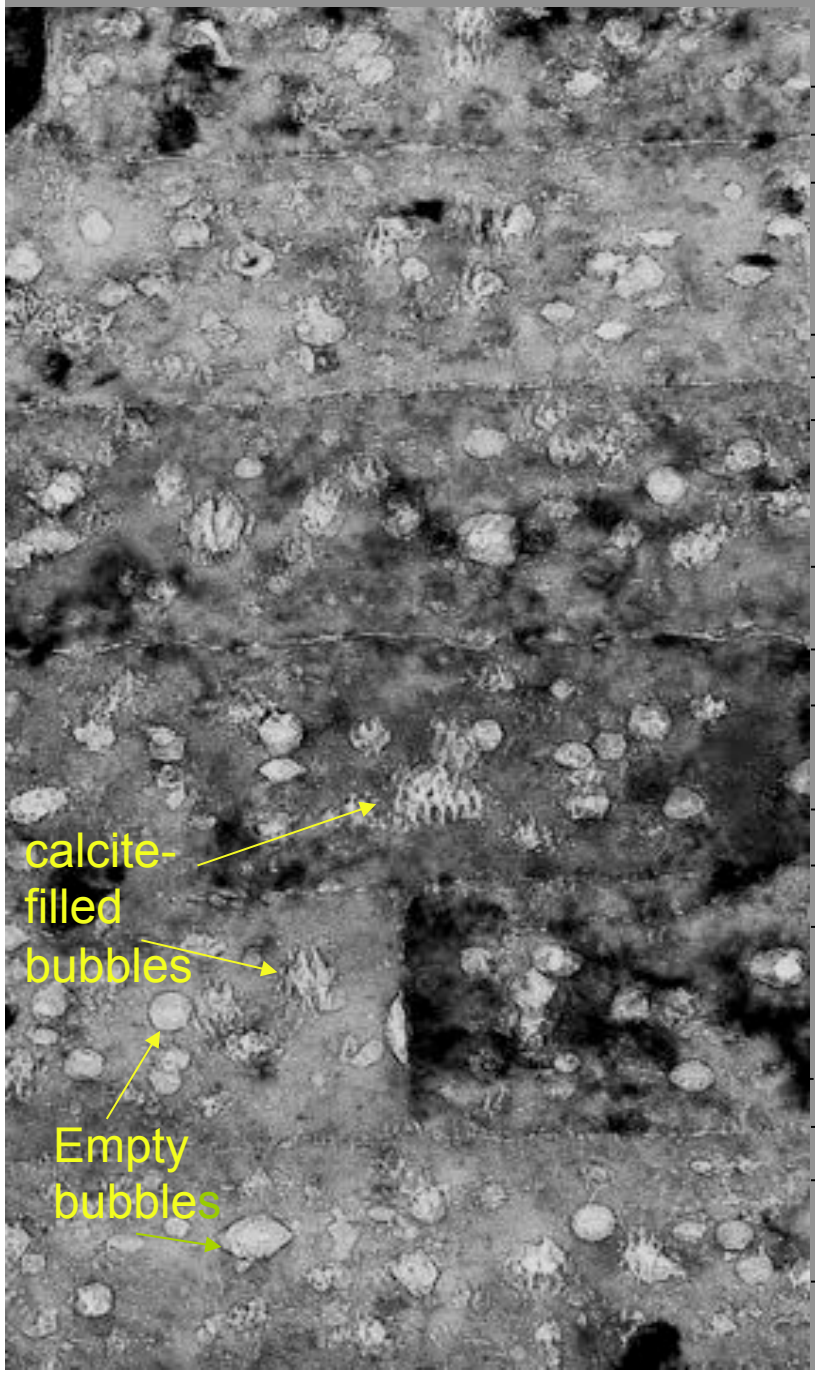


Metallic color changes with viewing incidence

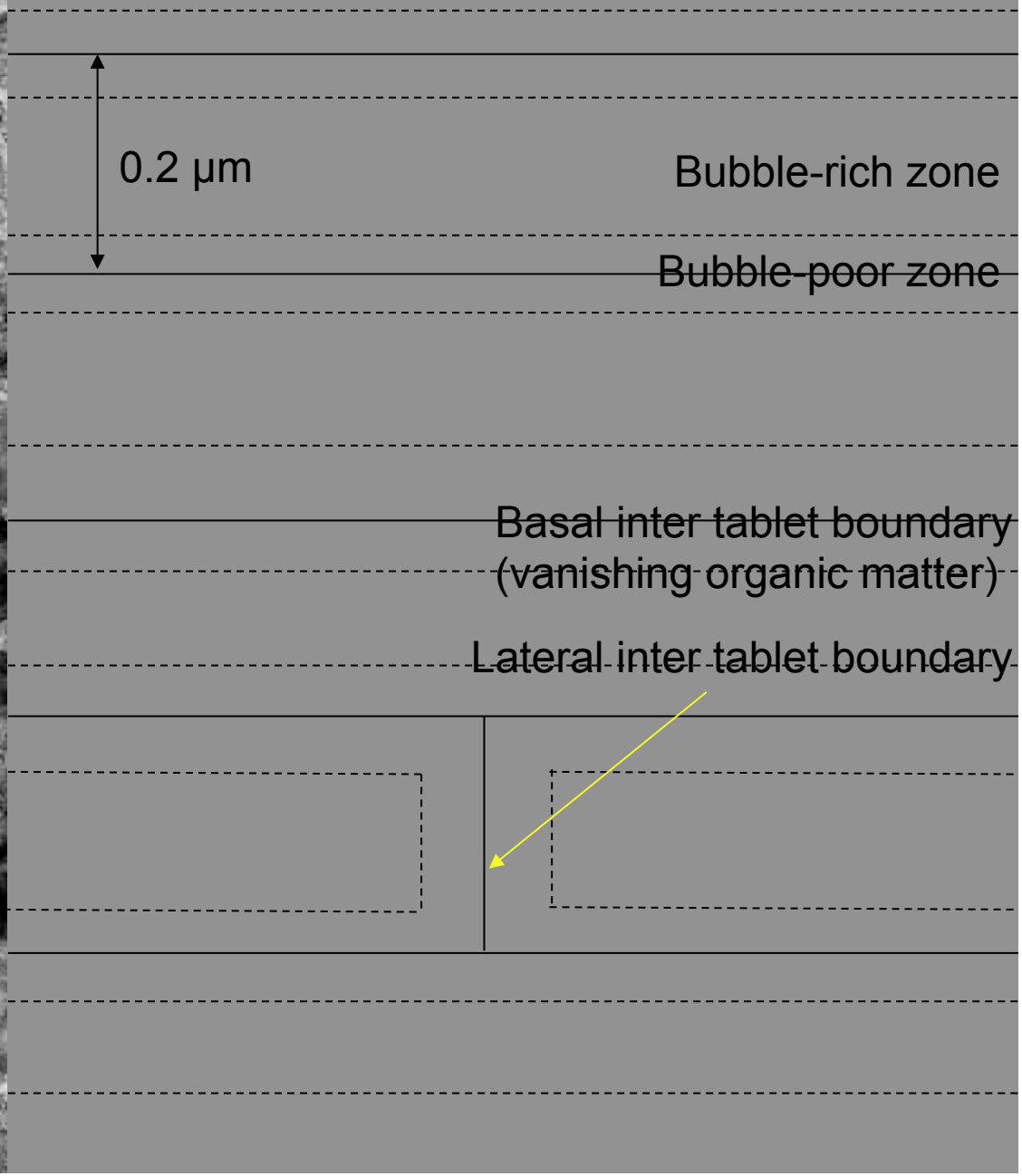
gift from
J.P. Gauthier


nanopores: native or preparation damages?
photonic 1-D grating of aragonite tablets
0.2 µm
200 nm
FIB

FIB cross-section of ammolite nacre



Ammolite = a photonic crystal involving a 1D-modulated grating of bubbles?



Nanomechanical properties of nacre

Collaboration: Dept Materials Sciences and Engineering - MIT(B. Bruet & C. Ortiz)

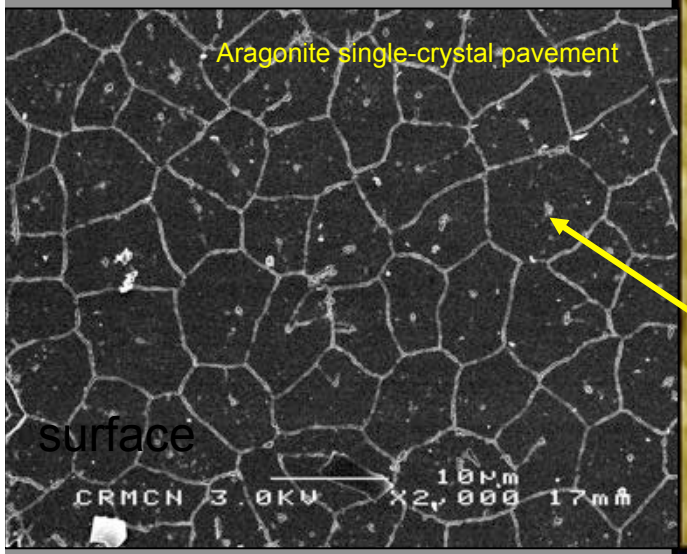
-Nano indentation of single tablets under AFM --> nano hardness

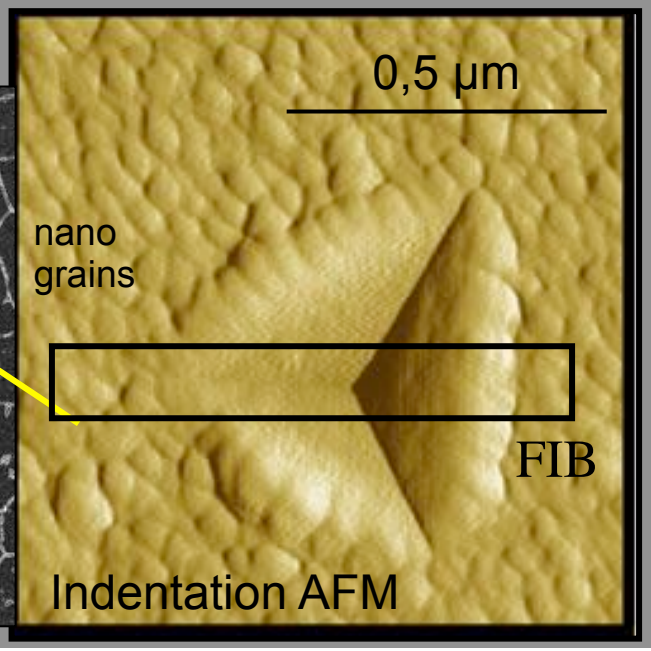
balistic absorber--> inside bullet-proof vests of the GI ?

Origin of the plastic deformation behaviour?

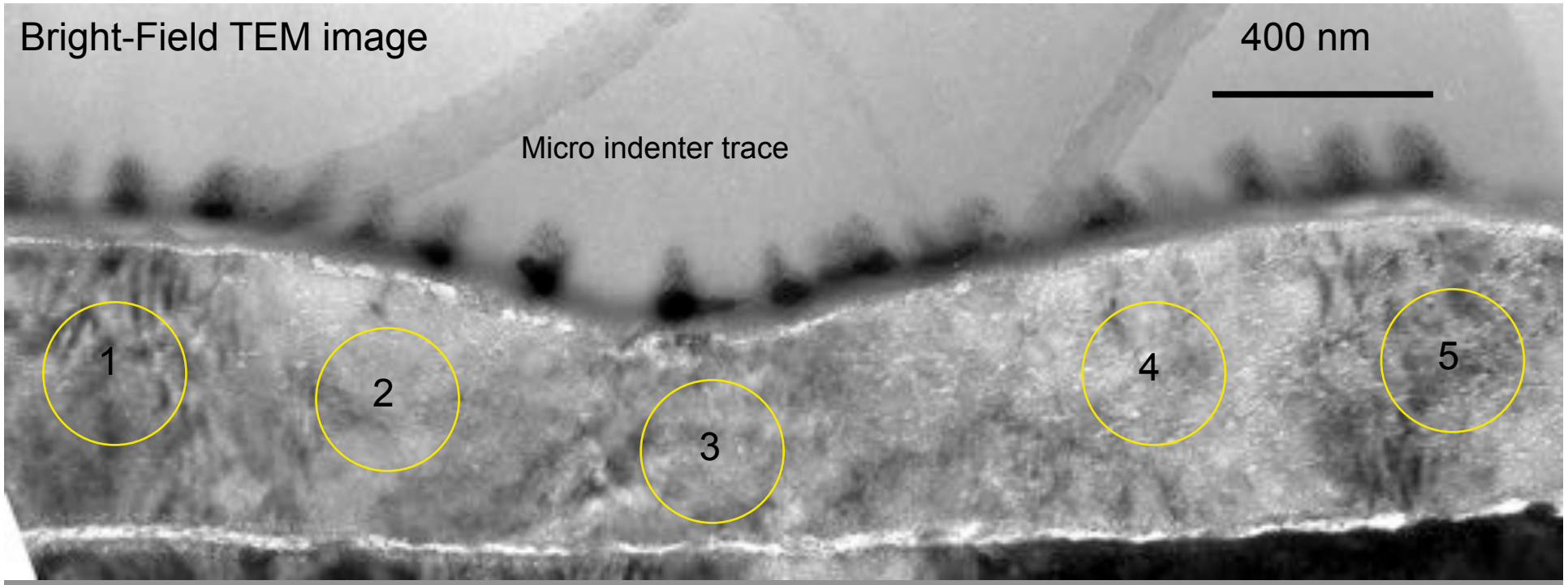
Collab. B.Bruet & C. Ortiz
DMSE - MIT

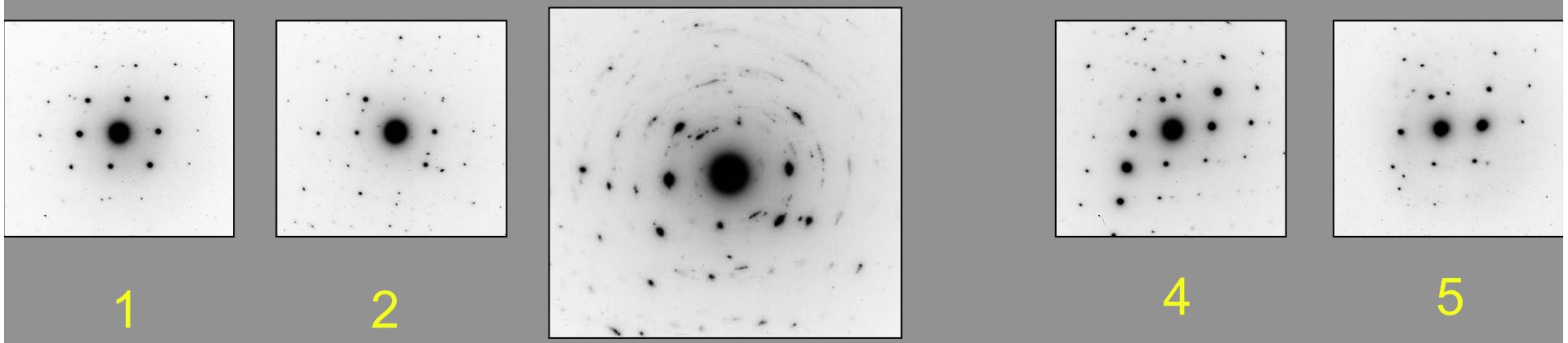
The sea cone





Outstanding mechanical properties:
-toughness
-strength
-stiffness





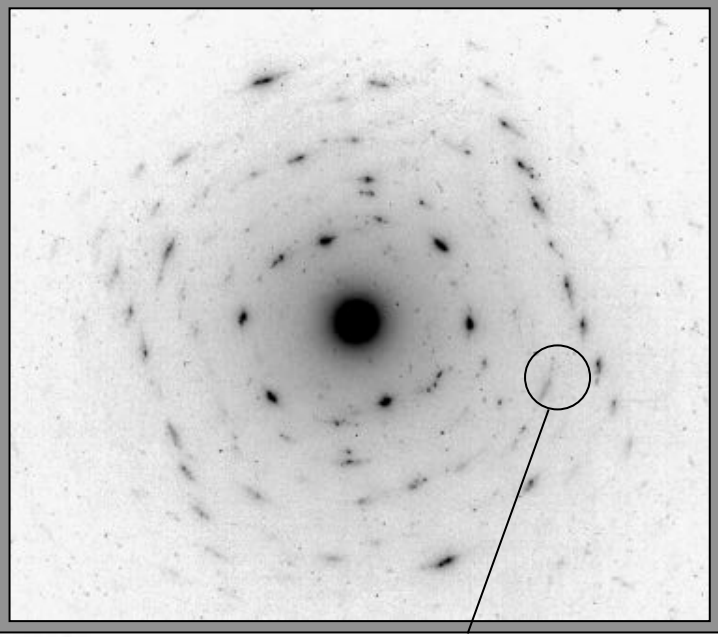
1 2 3 4 5

SAED patterns

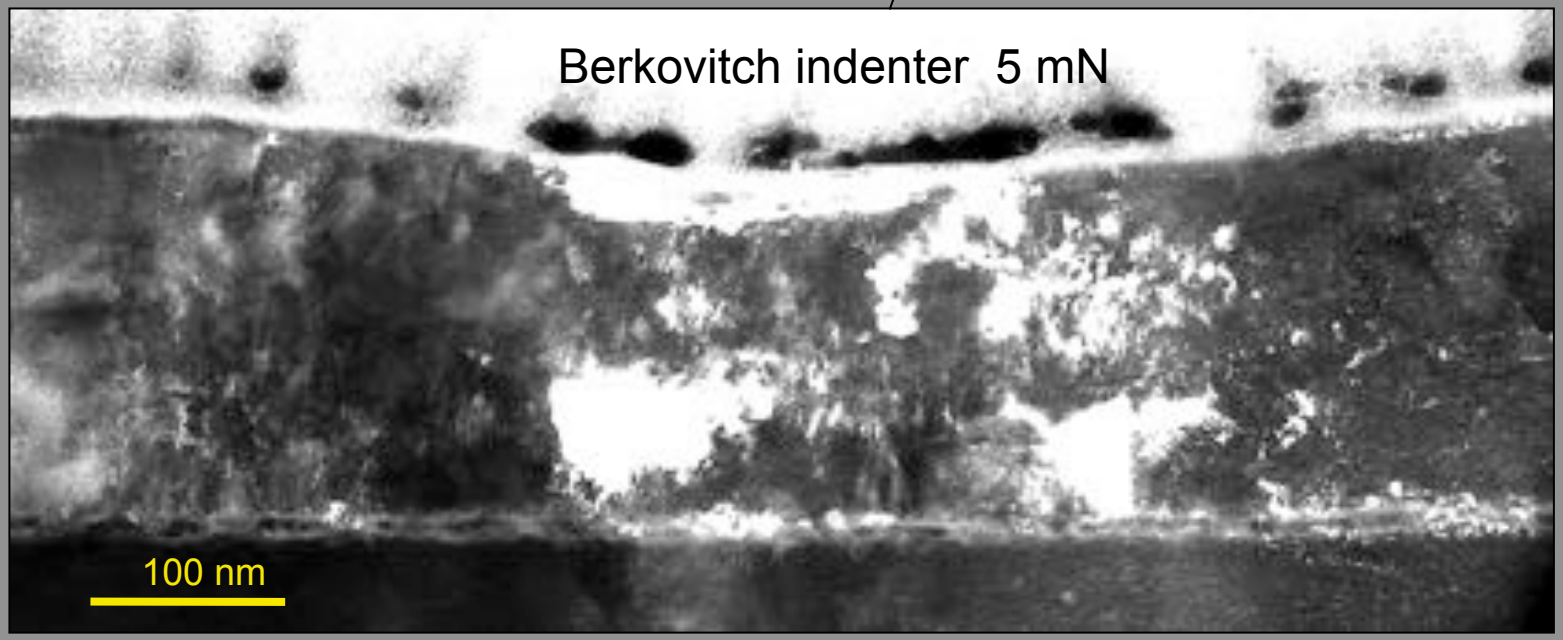
Berkovitch 10 mN

- rotation of nanograins
- collapse of intertablet OM

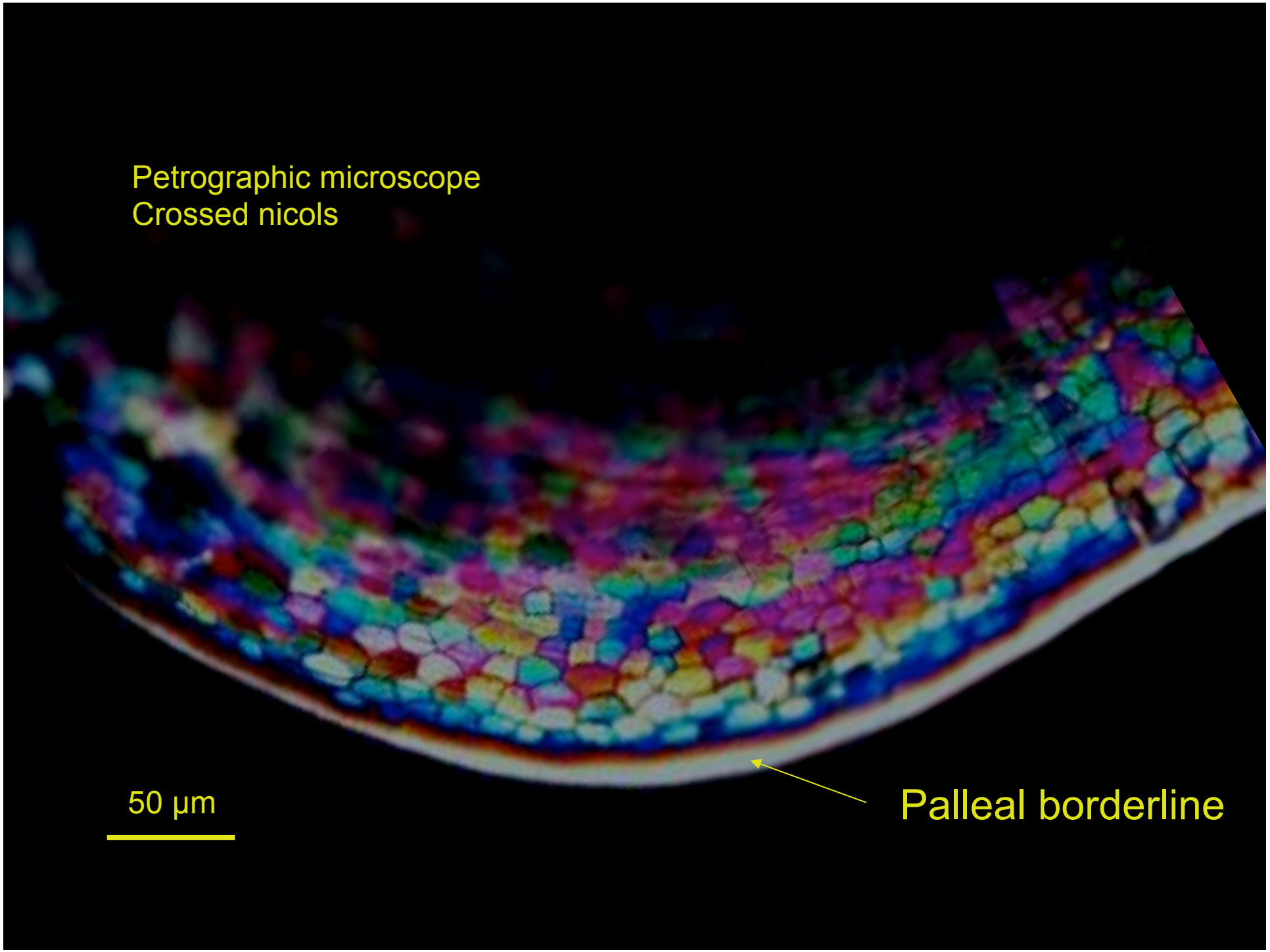
Electron diffraction pattern just below the indent



Where are rotating grains in the tablet?



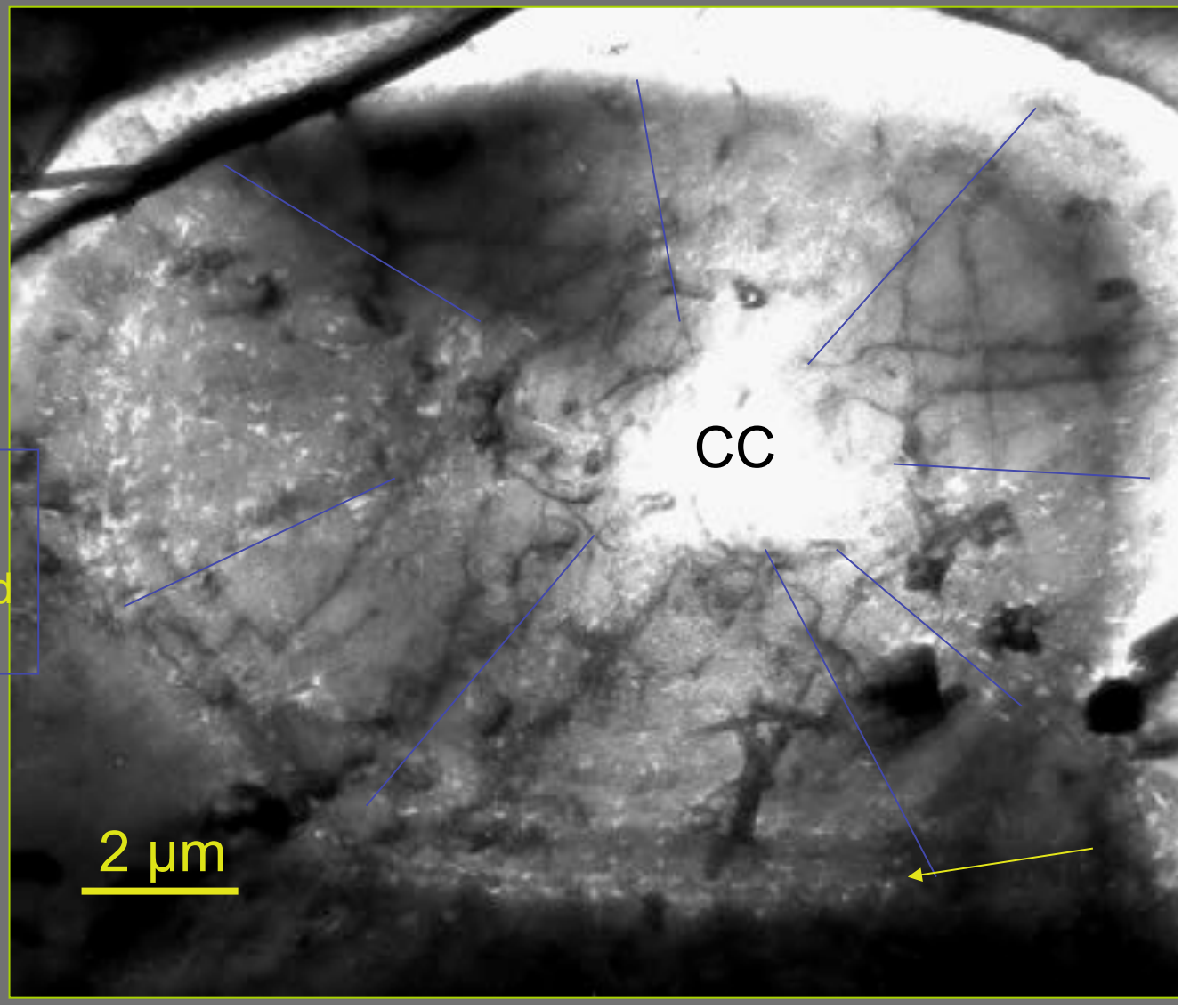
Dark-field TEM image made with the tails of selected diffraction arcs


Petrographic microscope
Crossed nicols
50 µm
Palleal borderline

Back-thinned outer surface of a single prism of *Pincatada margaritifera* – bright-field TEM view

Alternating sectors around the « nucleation centre »

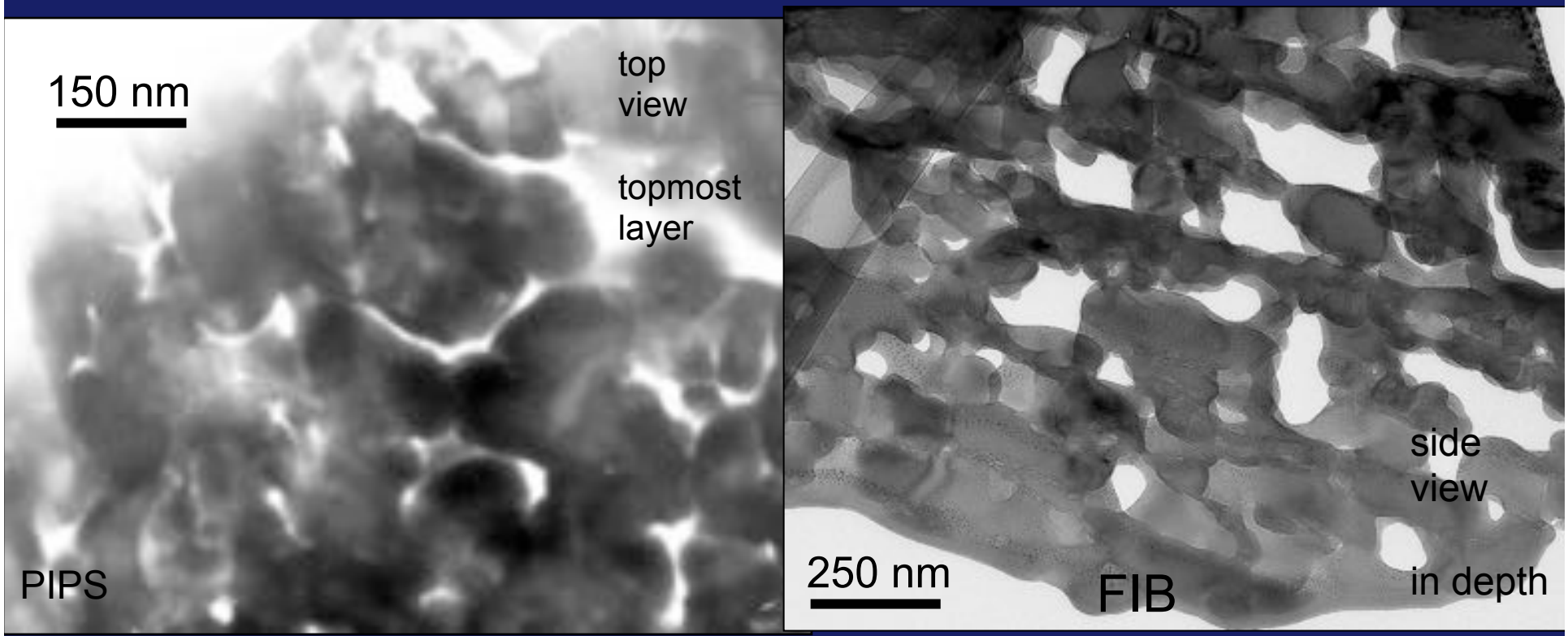
Radial and circumferential variations of porosity
In a single crystal controlled by mantle cells



Prism of *Ostrea edulis (flat oyster)*

BF-TEM

amorphous granules → crystallized granules

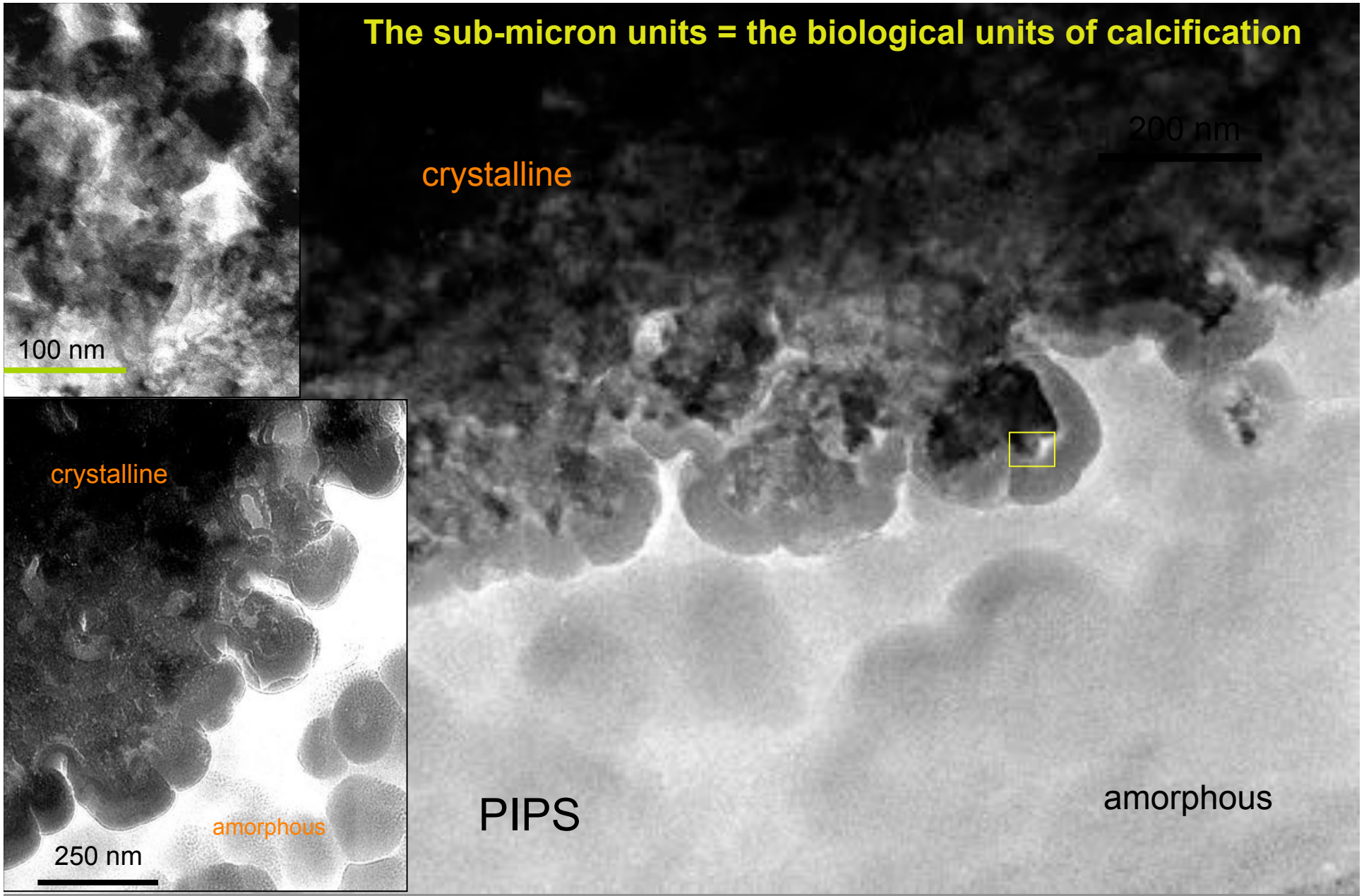


highly porous "single" crystal

non wetting → wetting

A wetting transition before/during crystallization?

The sub-micron units = the biological units of calcification



Arrested fronts of calcite crystallization close to the organic « mould » of prims

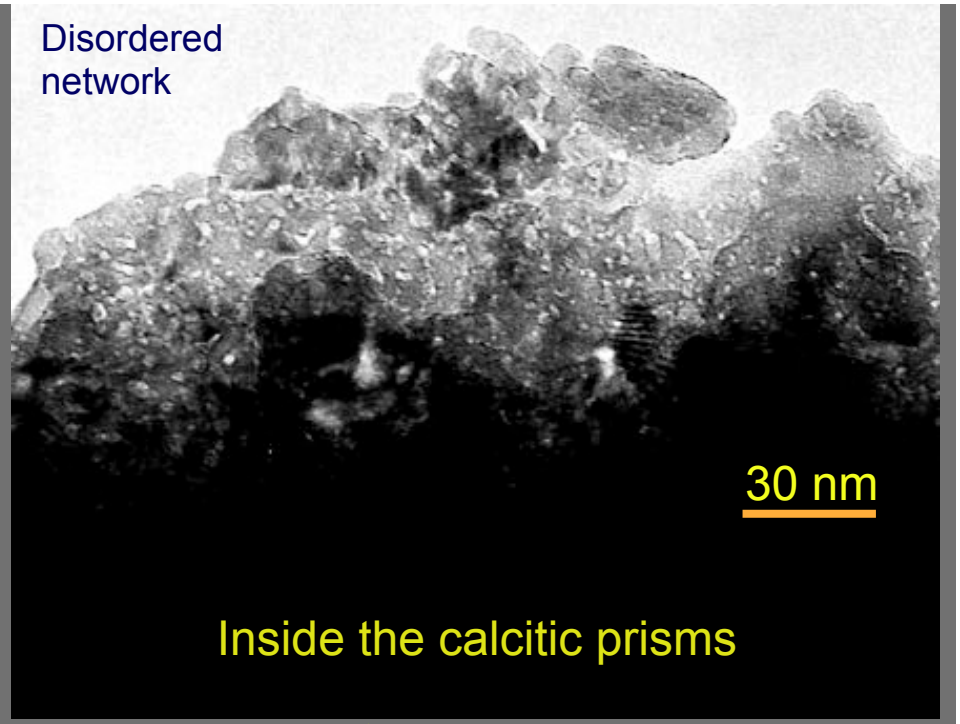
Vermicular nanoporosity (3-7 nm) running inside single biocrystals

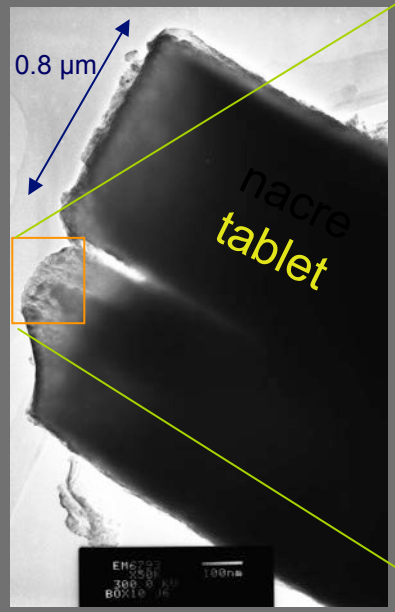
Trochus niloticus farmed *in the US*

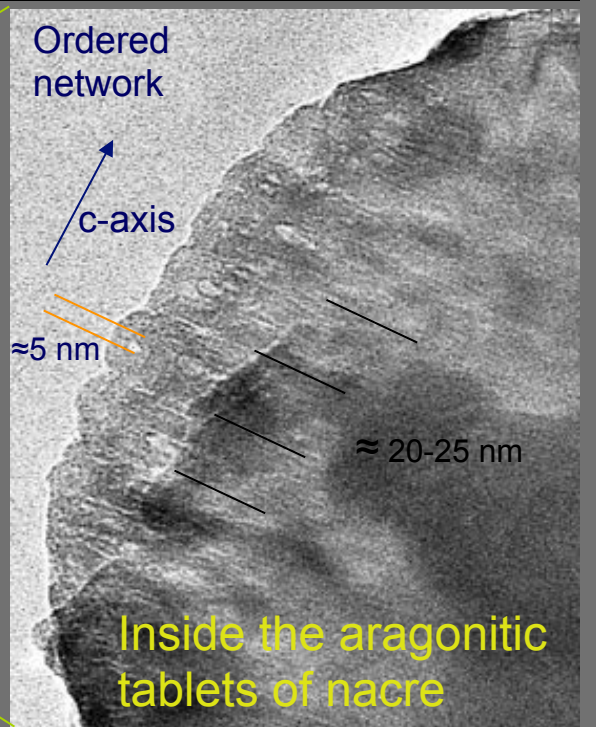
-killed in liquid N_2
-shell pieces Immersed in ethanol
-rapid mail in air-dried parcel (MIT-DMSE-->CRMCN)
-detached µm-sized particles by shear with a diamond-coated wire saw under dry N_2
-particles spread dry on a holey C-film
-TEM imaging using mostly absorption contrast (transmitted beam only of a SAED without strong reflections) , and low electron dose

Towards the pristine nanostructure of the shell

A framework to host fibrous (silk)proteins?



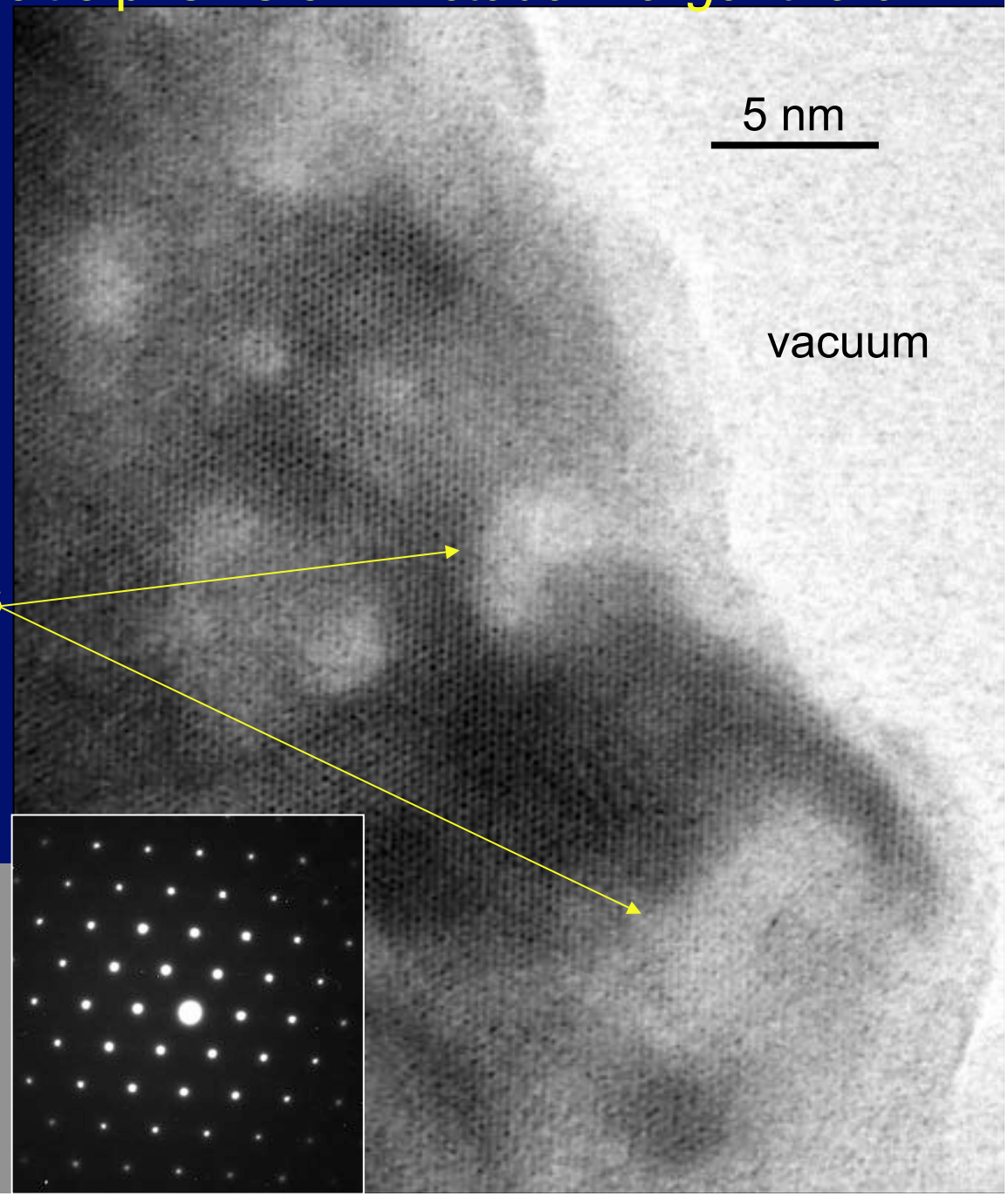




The ultra structure of calcitic prisms of *Pinctada margaritifera*

A single-crystal sponge!

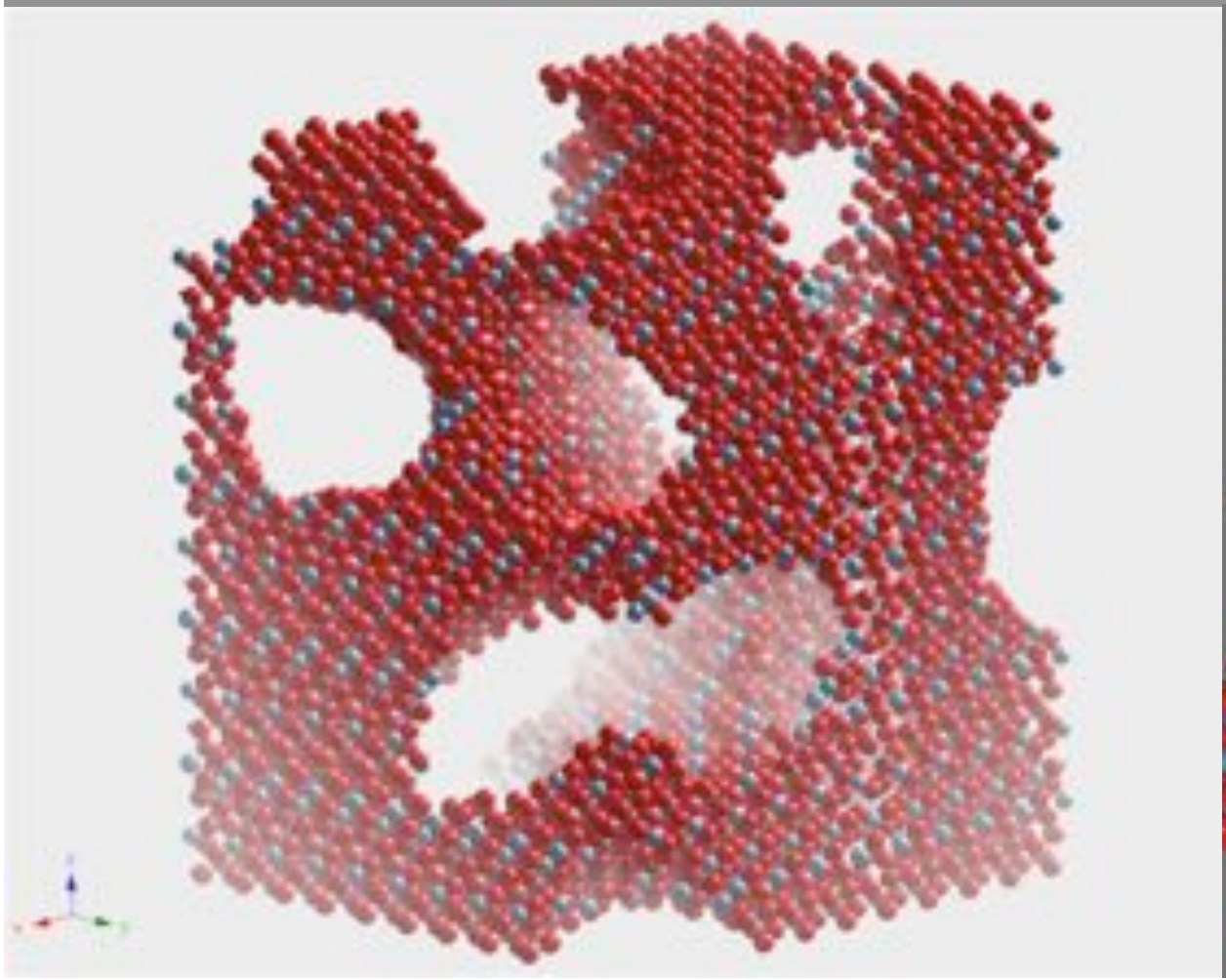
nano pores/nano channels



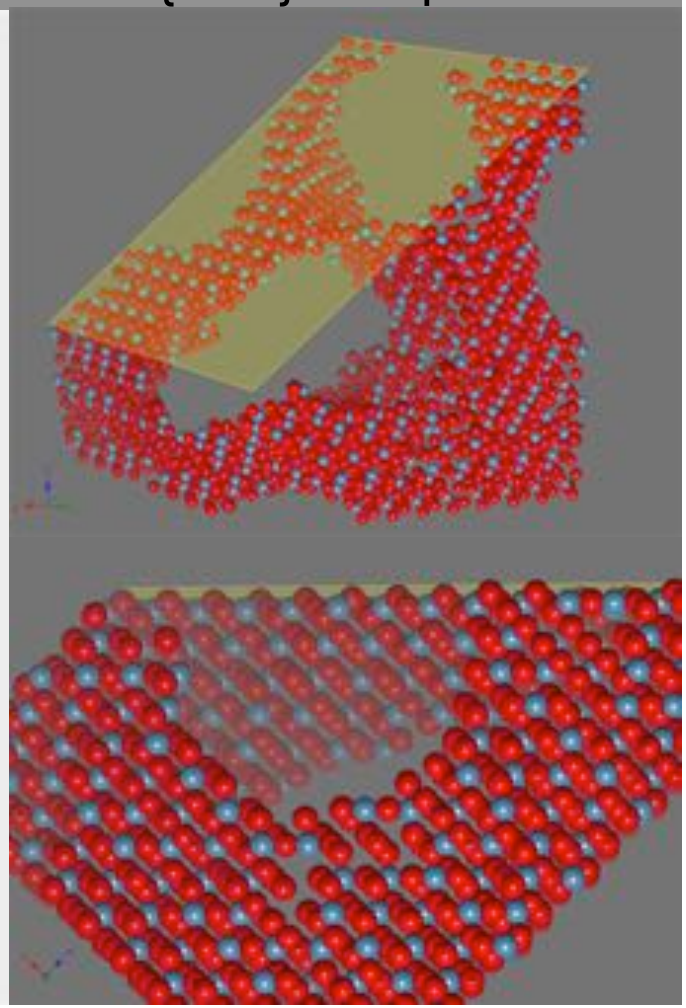
JEOL 3010
HRTEM; atomic resolution
<001> calcite
Detached shards overhanging on a holey carbon membrane

The sponge-like, nanoscopic model of bio-calcite single crystal

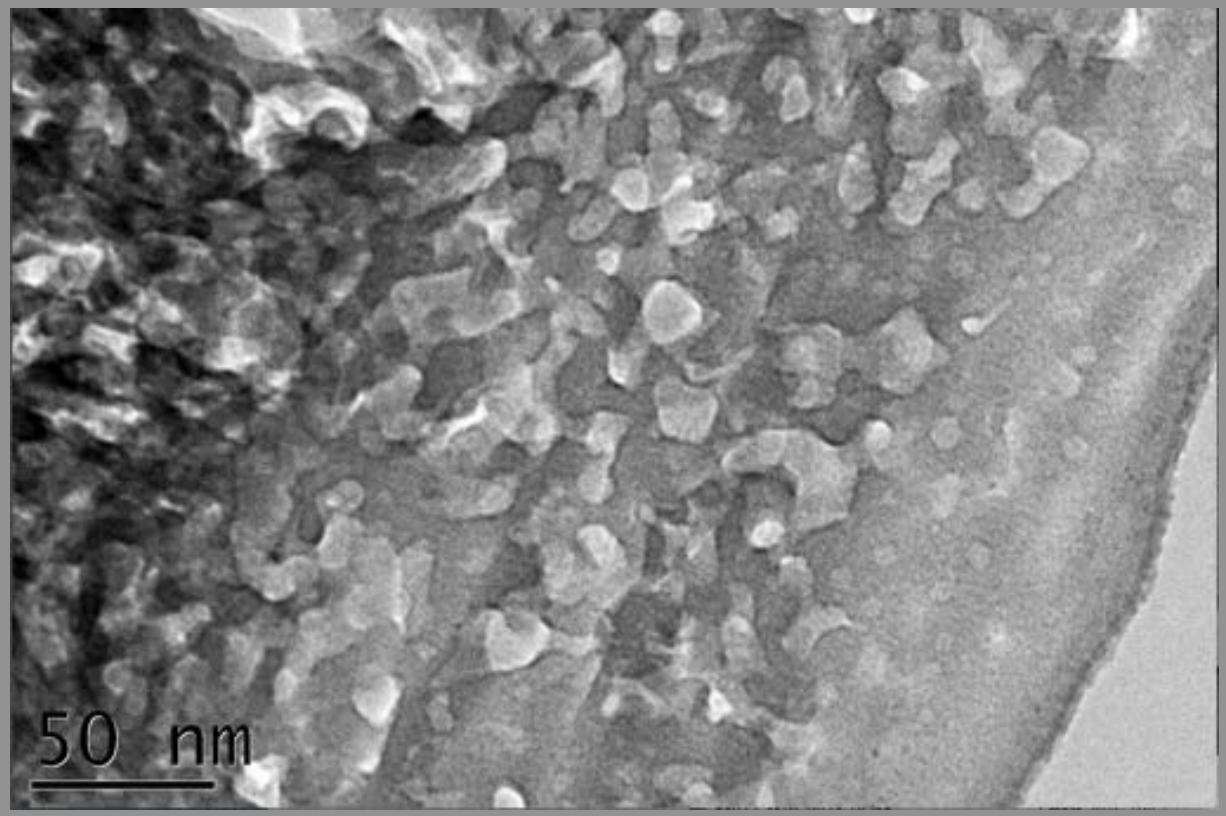
Size range 0.1 nm - 100 nm



percolation of a
{10.4} twin plane



Need of electron tomography to
know better and quantify nanopores



Nanopore network in a geopolymer shard
seen by bright-field TEM

Don’t worry, Jérémie B. will fill up this gap of knowledge
tomorrow evening