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

Alain Baronnet, Jérémie Berthonneau & Olivier Grauby

Aix- Marseille Université (AMU)
Centre Interdisciplinaire de Nanosciences de Marseille (CINaM)

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

"lateral" nanopore network

EMT: AB stacking hexagonal structure

Faujasite: ABC stacking cubic structure

please tell the story!

4.0 nm

faujasite structure [110]
Palygorskite/attapulgite \((\text{Mg,Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_4(\text{H}_2\text{O})\): a nanoporous fibrous clay

Highly absorbing material

A widespread drug that binds to acid and toxic substances in the stomach and digestive tract

Also to treat diarrhea!!

The eternal « Maya blue » = trapped indigo molecules

Ball-and-stick model

Raw
JEOL 3010
CINaM
Fourier-filtered

1.27 nm
Todorokite - A tunnel manganese oxide
(K, Ca, Na)$_{0.5}$ Mn$^{3+,4+}_6$ O$_{12}$ - 4H$_2$O

Three levels of connected porosity

Modular structures

Mean X-ray structure

Macropores

Nanopores

in polymetallic nodules on the sea floor
Synthetic imogolite $\text{Al}_2\text{SiO}_3(\text{OH})_4$ short nanotubes SWNT

in soils derived from volcanic ash

tubule: external diameter $\approx 2$ 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 $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$: a nano tubular silicate structure

Polyhedral model of the polar structure of chrysotile

Cross-section of a chrysotile nanotube

A microstructural pore in the centre
Textural nanopores
The glue of cement: The Calcium Silicate Hydrate (CSH) Inside high-density CSH

A nanoporous material

An house-of-card Texture

Compare with Emanuela’s simulations

The "magic size" of single C-S-H particles

HRTEM 1-D lattice image
Opal A: a photonic, colloidal crystal
amorphous SiO$_2$

Coober Pedy, Australia

Gilson’s synthesis of opal

SEM image

Opal structure (courtesy JP Gauthier)

Cabochons from Gilson’s opal
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

defects
grain boundaries
long fibers; equal size

Serpentinite vein
Val d'Aosta
Piémont
Italy

JEOL 2000fx - CRMCN
Repeated "Twinning" of colloidal chrysotile crystals on dense tubule planes

A "supra-crystallography" at work?
Textures of short chrysotile nanotubes: arabesques of serpentine: closer-and-closer to biological microstructures
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

- Mini cracks
- Pores
- 700-900 nm
- 300-350 nm

**Haliotis rufescens**
abalone shell

**Trochus niloticus**
sea cone

Porcelain and color fading nacre

Iridescent and colorful nacre

**Haliotis rufescens**
abalone shell

Iridescent and colorful nacre
Ammolite as a new gem (bio) stone

Iridescent ammonite
Cleoniceras (albian)
Madagascar

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

Ammolite pendant

Metallic color changes with viewing incidence

φ ≈ 0°
ρ ≈ 20°

φ ≈ 0°
ρ ≈ 50°

φ ≈ 80°
ρ ≈ 20°

5 mm

gift from J.P. Gauthier
nanopores: native or preparation damages?
photonic 1-D grating of aragonite tablets
Ammolite = a photonic crystal involving a 1D-modulated grating of bubbles?

- Bubble-rich zone
- Bubble-poor zone
- Basal inter tablet boundary (vanishing organic matter)
- Lateral inter tablet boundary

(calcite-filled bubbles)

(Empty 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

Aragonite single-crystal pavement

nano grains

0.5 µm

FIB

Indentation AFM

Outstanding mechanical properties:
-toughness
-strength
-stiffness

The sea cone
Bright-Field TEM image

Micro indenter trace

1. Rotation of nanograins
2. Collapse of intertablet OM

SAED patterns

Berkovitch 10 mN
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
Extreme border of the valve (prismatic layer) of a *Pinctada margaritifera* 50 µm

Petrographic microscope
Crossed nicols

Palleal borderline

50 µm
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

150 nm  

250 nm  

top view  

topmost layer

PIPS  

FIB  

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