(Transmission) Electron Microscopy for Multi-Scale Porous Materials

I- Basic principles and techniques

A. BARONNET, J. BERTHONNEAU & O. GRAUBY
Aix-Marseille Université
Centre Interdisciplinaire de Nanoscience de Marseille (CINaM)

Fourth Winter School on Multiscale Porous Materials – January, 2017-Marseilles, France
I – Basic principles of Transmission Electron Microscopy (TEM)

The TEM machine

- Of what it is made of, and how it works
- Some attached techniques

Sample preparation techniques

Very high-resolution Imaging and diffraction

Use of the (Fast) Fourier Transform (FFT) in TEM at very high resolution

II - Some applications of high-resolution TEM on non conventional minerals

-Ultrastructures and pores down to the atomic scale
The transmission electron microscope upside down = a "light" microscope in which electrons replace photons

- **air**
  - Fixed lens focal distances

- **vacuum** $10^{-5} - 10^{-9}$ torr
  - Varying lens focal distances
  - Fixed equipment

- **high tension** $100 - 400$ Kv
  - Moving equipment
Complexity due to:
- Bad electron optics
- Need of vacuum anywhere inside
The complex electron path through a TEM

In a TEM, you may switch immediately from the direct space (image) to the reciprocal space (diffraction).
Bigger and bigger?
Better and better?

1.25 MV HRTEM
RUCA
(Anvers)

Image-corrected 300 keV HRTEM
Aix-Marseille Université

To pass through « thick » samples

Desperate guy (red face)) trying to image antigorite

Not suited for beam-sensitive materials
Electron sources and acceleration voltage

Classical tungsten filament

Cold and warm cathode field emission tip

A LaB₆ tip

coherent beam

not so coherent beam

suited for beam-sensitive materials

acceleration voltage 300keV = best against beam damages
Material responses under electrons

Incident beam e^−

Backscattered e^−
(SEM Z-imaging
Electron Back Scattering Diffraction (EBSD))

Secondary e^−
(std SEM imaging)

specimen

Cathodaluminescence

X-rays
Energy Dispersive Spectroscopy (EDS)
Wavelength Dispersive Spectroscopy (WDS)

Auger e^−
Surface chemical analysis

Inelastically scattered e^−
High-Angle Annular Dark Field (HAADF) imaging
Electron Energy Loss Spectroscopy (EELS)

Unscattered e^−
(transmitted beam)
Bright-Field (BF) imaging
Electron Tomography

Elastically scattered e^−
(Selected Area)
Electron Diffraction (SAED)
Dark-Field (DF) imaging
Sample volumes analyzed with Electron microprobe/ TEM EDS (ATEM)

Detector ($\lambda$ analysis) 30 keV Sample

Analysed zone

EDS (hv analysis) 300 keV Sample

Quantitative data for oxygen and above; $Z \geq 8$

X-ray energy 0-20keV

$V_{\text{analyzed}} = 10 \, \mu m^3$

$V_{\text{analyzed}} = 10^{-6} \, \mu m^3$

$V_{\text{analyzed}} = 10^{-6} \, \mu m^3$

ATEM is a satellite tool absolutely needed for complex material studies dealing with micro to nano size of crystals

5 µm
### An ideal sample to enter the TEM should be:

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent</td>
<td>for standard acceleration (200-300 kV) =&gt; 0 &lt; thickness &lt; 500 nm for oxides (silicates) HRTEM --&gt; 5-10 nm</td>
</tr>
<tr>
<td>Manipulable</td>
<td>(support inscribed in diam. 3 mm)</td>
</tr>
<tr>
<td>Conductive</td>
<td>or rendered conductive by metallization =&gt; amorphous C-coating</td>
</tr>
<tr>
<td>Representative</td>
<td>of the bulk of the materials =&gt; structures, microstructures, defects, chemical compositions, …be saved (preparation and observation)</td>
</tr>
</tbody>
</table>
The thin-sample preparation techniques

Which materials do you want to look at?

organic, mineral, hard, soft, coherent, porous, granular, fibrous, composite,, hydroxylated, hydrated,..................

What do you want to see in this material?

shape, size, crystallinity, chemical composition, defects, texture, ultrastructure, .........................
TEM grids and slots

Where should I put the specimen?

Conducting: Cu, Ni, Mo, Au,.....

3 mm

Mesh grids

"Bivalve" grids

Supporting C film + amorphous C sample coating

Honeycomb grid

"Stadium" slots for ion thinning

Evacuation of electric charges = image stability
The "drop deposition" technique

Advantages
- the simplest and quickest
- for powder characterization
- (size, shape, diffraction, composition)

Drawbacks
- not for water soluble minerals
- Particle density adjustment
- drift and tilt under the beam (no clean HRTEM)
- + - noise from C-film background (holey, lacey C-films- C-film wettability

Celadonite mica crystals (O. Grauby)

synthetic chrysotile charge
Ultramicrotomy
Cutting a « pencil » with
A diamond knife
Ultramicrotoming (continue)

**Advantages**
- unique for powders, fibers, synthesis charges
- chemically extremely clean
- ready for the TEM

**Drawbacks**
- not for big and hard materials
- sample bent and cracked: avoid for microstructure and defect observations
- Long training for embedding samples and to cut well
- expensive diamond knives
- mechanical drift under the e-beam: not good for HRTEM
Focused ion beam (FIB) milling

Advantages
- sample below a surface feature ready for TEM
- normal to the surface
- soft and hard, porous samples

drawbacks
- chemically dirty: Ga & Pt implantations
- smearing of chemical composition
- strong structural damages

Slicing the nacreous layer of an oyster shell - O. Grauby
Recent FIB specimen holder

3 mm

half slot

10 nm
**A phytolithe:** a mesoporous material made of amorphous silica

*Storage of Si by plants*

See Jérémie B. to morrow for electron tomography of this slice
The royal road

*From the rock to the atomic image by TEM*

- **uncovered rock slate**
  - double face 1µm polish
  - 30-50 µm-thick

- **Thermofusible resin**
  - (Lakeside, crystalbond)

- **glass plate**

- **diamond saw**

- **the rock slice**

- **sugar piece**

- **thin section**

- **polishing machines**

- **diamond wire saw**

- **300 µm**

- **a special thin section**
Crossed nicols light microscopy to place the slots

- recognize the minerals from their optical properties (refringence & Birefringence)
- crystallographic orientation with 15° accuracy (for HRTEM)

microdrilling around the slot and melt the glue underneath (< 200°C)

detach with a twizzer and wash the glue with alcohol

ready for the PIPS milling
Ion-milling systems

Precision ion polishing system (PIPS)
Ar⁺ ions, 5 --> 2 keV, two guns 7-4° incidence. Polishing time 0.5h to 5 days for 50µm-thick thin section

Advantages
- Large and thin surfaces to look at
- Wedge-shaped sample: extra-thin zones
- Gentle heating
- High mechanical stability
- Reasonable damages (amorphisation)

Drawbacks
- Pollution by sputtering: grid, specimen holder
- Needs to be trained for optimum use
Around the hole: hours of TEM exploration to come

Ultra thin wedge around the hole border
Only part suitable for TEM
Preparation of TEM specimens:

The sampling problem: to be representative for up scaling to be useful

"All thinned samples of the Earth crust for TEM enter a thimble while the crust volume is roughly 75. $10^7$ km$^3$. So, be careful with sampling! “

David Veblen,
Johns Hopkins University, Baltimore
Electron diffraction by crystals

The direct lattice (blue) and the reciprocal lattice (green)

A 2-D case

Perpendicular rows

Inverse metrics
Electron diffraction by crystals

Bragg's law

\[ 2d_{(hkl)} \sin \theta = n\lambda \]

and for high-energy electrons:

\[ 2d_{(hkl)} \theta \approx n\lambda \]

\[ \theta \approx < 1-2^\circ \text{ ------> only lattice planes // to the incident beam are diffracting} \]

very thin specimen ----> elongation of reciprocal lattice nodes ----> relaxation of Bragg's conditions ----> many reflections at a time
Slight curvature of the Ewald's sphere (R = 1/\(\lambda\))
intersecting the 3D arrangement of the reciprocal lattice (RL)
The SAED pattern = Visualisation of sub planar sections of the reciprocal lattice
Tilting the sample in diffraction mode is exploring the RL in 3-D

Double tilt, high-resolution, specimen holder \(\pm 15^\circ\)

Procedure of alignment of a single crystal:
find a crowdly SAED,
put the zero-order Laue zone (ZOLZ) perfectly symmetrical around the transmitted beam
by centring the first-order Laue zone (FOLZ) when visible!
Microdiffraction patterns of some states of matter

- Amorphous
- Polycrystalline
- Single crystal + disorder
- Cylindrical lattice
- Quasi crystal seen along a 2-fold axis

B. Devouard
Toward very high-resolution TEM (HRTEM)

Introducing

Atomic structure images
A biperiodic image
= discrete sum (truncated)
of sine variations of fringe contrast along
diffraction vectors

The Graal: the charge density projection
of the crystal structure

In the trigonometric form:

$$\rho(y,z) = \sum_k \sum_l |F_{0kl}| \cos 2\pi (ky + lz + \alpha_{0kl})$$

$$= |F_{000}|$$

$$+ |F_{010}| \cos 2\pi (y + \alpha_{010}) + |F_{020}| \cos 2\pi (2y + \alpha_{020}) + \ldots$$

$$+ |F_{001}| \cos 2\pi (z + \alpha_{001}) + |F_{002}| \cos 2\pi (2z + \alpha_{002}) + \ldots$$

$$+ |F_{011}| \cos 2\pi (y + z + \alpha_{011}) + |F_{022}| \cos 2\pi (2y + 2z + \alpha_{022}) + \ldots$$
Point-to-point resolutions at CINaM:
2.8 Å for 200 kV TEM
1.6Å or 2.1Å for 300kV TEM
0.5Å somewhere in the world

Electronic image = recombination of discrete diffracted beams that keep amplitudes and phases of diffracted waves

but:
dynamical diffraction + phase offsets due mainly to spherical aberration

The Scherzer defocus (critical underfocusing) roughly compensate for those phase offsets within the transfer window toward the structure image

\[ d_r = 0.65 \lambda^{3/4} C_s^{1/4} \]
Semi-random layer stacking in a 2M1 phengite mica

Out of focus

Scherzer defocus

Same thickness

The structure image
Correct phases are essential to get a correct structure image.
Very HR numerical scan of the image «nuclear» film circular selection

Quasi-atomic image of the biotite mica seen along <1 0 0>

Recorded Diff pattern

FFT processing (FIJI application)

FFT now realistic substitute to the microdiffraction
The high-resolution TEM Image of a 2M1 phengite

From lattice images to structure images
Atomic image of a white mica: muscovite
\( \text{K(Al}_2\text{)AlSi}_3\text{O}_{10}(\text{OH})_2 \) a two-layer polytype 2\( \text{M}_1 \)

polyhedral model

strongly diffusing atoms

JEOL 3010 - CRMCN

charge density projection

2.0 nm

oxygen does not appear
Raw or Fourier-filtered images for HRTEM?

raw, quasi atomic image of mica

K-deficient atomic row
However point defects hard to see

Fourier space background filtered

Smooth but not so pleasant, isn't it?
no more chance to see localized defects
Everything looks perfect! Information lost
Toward the 3D view with a TEM

Stereo imaging

Electron tomography
(Jérémie B. tomorrow)

See Jérémie Berthonneau tomorrow

See Timm Weitkamp Wednesday evening