X-ray and neutron full profile analysis for texture, structure and phase determination of natural samples and more: “Combined analysis approach”

M. Morales, D. Chateigner, L. Lutterotti
Combined analysis approach presentation

- Experimental needs
- Problems on ultrastructures: typical ferroelectric film example
- Methodology-Algorithm
- Ultrastructure implementation
- Results on a case study on typical ferroelectric film
- Residual stresses, Rietveld and texture
- MAUD program implemented codes
- Example showing correlations between stress and texture
- Example showing correlations between anisotropic sizes and texture.

Combined analysis approach illustration through various textured examples: multiphase bulks and thin films

- Geological samples
- \textit{CaCO}_3 mollusc shells
- Biomimetic \textit{CaCO}_3 thin films for medical applications
- Shell fossils: Texture and phylogeny
- Multiphased \textit{Cr}^{2+}:\textit{ZnSe} films: combined analysis approach actual limitations
Random powder: \( I_{RX\,\text{calc}}(2\theta) = \sum I_{hkl,\text{phases}}(2\theta) S_{hkl}(2\theta) + bkg\ (2\theta) \)

\[ I_{hkl}(2\theta) = AS |F_{hkl}|^2 m_{hkl} \frac{L_p}{V_c^2} \]

- Lorentz- polarisation factor
- unit-cell volume
- multiplicity
- structure factor (includes Debye-Waller term)
- scale factor (phase abundance)
- absorption

\[ S_{hkl}(2\theta) = S_{hkl}^I(2\theta) * S_{hkl}^S(2\theta) \]

Sample aberrations = crystallite sizes (isotropic or anisotropic) +

\( \text{rms microstrains } \varepsilon^* = < \varepsilon >^2 \) due to linear and point defects, stacking faults...

Combined analysis approach
Texture:

Correction of intensities for texture:

\[ I_{hkl}(2\theta, \chi, \varphi) = I_{hkl}(2\theta) P_{hkl}(\chi, \varphi) \]

Orientation Distribution Function (ODF): WIMV or E-WIMV methods

From spectra: pole figures \( P_{hkl}(\chi, \varphi) \)

ODF = statistical distribution of orientations

Combined analysis approach
Minimum experimental requirements:

1D or 2D Detector + 4-circle diffractometer (X-rays and neutrons)
CRISMAT, ILL

\[ \lambda_{\text{Cu } \alpha} = 1.5418 \text{ Å} \]

\[ \lambda_{\text{neutron}} = 2.533 \text{ Å} \]

~1000 experiments (2θ diagrams) in as many sample orientations
Instrument calibration:

instrumental resolution function

mapping spectrometer space with:
• KCl or LaB$_6$ powder standards for X-rays
• Belemnite rostrum having large calcite grains for neutrons

peaks widths and shapes FWHM ($\omega$, $\chi$, $2\theta$ ...), misalignments, defocusing ($2\theta$ shift, Gaussianity, asymmetry) ...

Combined analysis approach
Problems on ultrastructures: example of Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ (PTC) ferroelectric films

Ferroelectric properties optimisation: polarisation vector along c \( \equiv \langle 001 \rangle / \equiv \mathbf{n}_{\text{film}} \)

<table>
<thead>
<tr>
<th>PTC film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode (Pt)</td>
</tr>
<tr>
<td>Antidiffusion barrier (TiO$_2$)</td>
</tr>
<tr>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Substrate (Si)</td>
</tr>
</tbody>
</table>

Sum X-ray diagram ($\chi$, $\varphi$)

Pt and PTC strong peak overlaps + mixture of strong and lower textures

Pseudo cubic phase of PTC

♦ texture effect not fully removable: **structure and microstructure**
♦ structure and microstructure unknown: **texture**

combined analysis approach necessary !!!

X-ray combined analysis approach
Algorithm and methodology

Intensity corrections for textured samples:

\[
I_{hkl}(2\theta, \chi, \varphi) = I_{hkl}(2\theta) P_{hkl}(\chi, \varphi)
\]

**MAUD program** (Material Analysis Using Diffraction) : (Marquardt non linear least squares fit, for instance)

**Rietveld cycle** : Structure, microstructure

**QTA cycle** : WIMV or E-WIMV Orientation distribution function

1\textsuperscript{st} cycle: integrated intensities (Le Bail extraction) ➔ Pole figure construction \( P_{hkl}(\chi, \varphi) \).
Ultrastructure PTC/Pt implementation

Corrections are needed for volumic/absorption changes when the samples are rotated.

With a CPS detector:

PTC : $C_{\chi}^{\text{top film}} = g_1 \frac{(1 - \exp(-\mu T g_2 / \cos \chi))/(1-\exp(-2\mu T / \sin \omega \cos \chi))}{1}$

Pt : $C_{\chi}^{\text{cov layer}} = C_{\chi}^{\text{top film}} \frac{\exp(-g_2 \sum \mu \prime i T' i / \cos \chi))/(\exp(-2 \sum \mu \prime i T' i / \sin \omega \cos \chi))}$

Gives access to individual thicknesses in the refinement
**Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ (PTC) film**

- **R$_{Bragg}$ = 6%**
- **R$_w$ = 5%**

- **a = 3.945(1) Å, c = 4.080(1) Å**
- **T = 4080(10) Å, t$_{iso}$ = 390(7) Å**
- **ε = 0.0067(1)**

- **a' = 3.955(1) Å, T' = 462(4) Å**
- **t'$_{iso}$ = 458(3) Å, ε' = 0.0032(1)**

- **R$_{Bragg}$ = 6%**
- **R$_w$ = 5%**

- **15% of c axes non oriented in film plane → some weak polarization properties**

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**Ricote, Morales et al. TSF 450, (2004) 128.**

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**X-ray combined analysis approach**
Residual stresses, Rietveld and texture

- peak shifts bias structure and texture determination → residual stress must be determined

- different deformation of differently oriented crystallites → texture influences residual stress

combined analysis approach necessary !!!

Non-linearity in \( \sin^2 \psi \) relation observed due to stress gradients or texture → Reuss, Voigt, Hill, Bulk geometric mean approaches.
MAUD implemented codes: parameter interdependency + formalism

Extracted Intensities

WIMV, E-WIMV Harmonics

Orientation Distribution Function

Specular Reflectivity

Roughness, electron
Density & EDP, Thickness

Pole figures
Inverse pole figures

Structural parameters
atomic positions, substitutions, vibrations
Cell parameters

Multiphased, layered samples:
Thickness,
Anisotropic Sizes
and μ-strains (Popa),
Stacking faults (Warren),
Phase ratio (amorphous + crystalline)

Le Bail
Rietveld

Rietveld

Combined analysis approach

Geometric mean approach

Structure + Microstructure + phase %

Le Bail

Residual stresses
Strain Distribution Function

Popa-Balzar, sin²ψ

Fresnel, Matrix (Parrat), DWBA
Combined analysis approach on PTC films: Substrate influence on residual stress and texture

Enhancement of <001> texture

PTC on Pt/TiO$_2$/ (100)Si

PTC on Pt/(100)MgO

PTC on Pt/(100)SrTiO$_3$

Tensile stress

Compressive stress

Texture Index (m.r.d.$^2$)

- PTC on Pt/TiO$_2$/ (100)Si: Texture Index 2.1
- PTC on Pt/(100)MgO: Texture Index 5.1
- PTC on Pt/(100)SrTiO$_3$: Texture Index 7.9

Ferroelectric PTC X-ray combined analysis
Anisotropic sizes and texture: nanocrystallized Si thin film example


Texture helps the "real" mean shape determination

- Determination by peak deconvolution + Popa formalism

Anisotropic crystallite shape:

Popa formalism

\[
< R_h > = R_0 + R_1 P_2^0 (x) + R_2 P_2^1 (x) \cos \varphi + R_3 P_2^1 (x) \sin \varphi + R_4 P_2^2 (x) \cos 2\varphi + R_5 P_2^2 (x) \sin 2\varphi + \ldots
\]

\[
< e_h^2 > E_h^4 = E_1 h^4 + E_2 k^4 + E_3 \ell^4 + 2E_4 h^2 k^2 + 2E_5 \ell^2 k^2 + 2E_6 h^2 \ell^2 + 4E_7 h^3 k + 4E_8 h^3 \ell + 4E_9 k^3 h + 4E_{10} k^3 \ell + 4E_{11} \ell^3 h + 4E_{12} \ell^3 k + 4E_{13} h^2 k \ell + 4E_{14} k^2 h \ell + 4E_{15} \ell^2 k h
\]

→ microstrain

Combined analysis approach : nc –Si films
fibre texture with multiple orientations never reaching pure <111> texture component whereas [111] elongated crystallite → in agreement with HRTEM observations

Combined analysis approach : nc –Si films
Illustration of the combined analysis approach

QTA = important tool in geology to describe anisotropy of fabrics, the mollusc and fossils phylogeny and geophysics.

1) Metamorphic Amphibolites from Alps:
   (M. Zucali, G. Gosso, DES, Milano)

X-ray and neutron diffractions applied to QTA analysis of naturally deformed glaucophanite from the Western Italian Alps

= winchitic amphiboles ($\geq 97\%$)

Comparison of two techniques reveals limits and problems of texture analysis related to strongly deformed polymineralic samples.

ODF measured and computed with 3 methods:

- Direct X-ray peak integrations
- X-ray combined analysis
- Neutron combined analysis
Geological samples

$(\chi, \varphi)$ summed X-ray diagrams

$\omega = 16^\circ$

Diagrams approximately close to random powder due to defocusing effect: pole figures incompletely measured!

Compared to a direct integration + some overlaps treated by WIMV method (intensity contribution assigned to each component of the multi-pole figure) Rietveld texture analysis is better to solve overlaps!
Neutron diagrams (D1B, ILL)

Summed diagram close to a random powder (no defocusing effect) even if blind areas remain!

<table>
<thead>
<tr>
<th></th>
<th>Glaucophane (Comodi et al.)</th>
<th>Winchite (Ghose et al.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$ (°)</td>
<td>10°</td>
<td></td>
</tr>
<tr>
<td>$\chi$ (°)</td>
<td>60°</td>
<td></td>
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<tr>
<td>$\phi$ (°)</td>
<td>0°</td>
<td></td>
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</table>

Lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>Glaucophane</th>
<th>Winchite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>9.5355 (7)</td>
<td>9.7573</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>17.7060 (2)</td>
<td>17.9026</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.2823 (7)</td>
<td>5.2886</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>103.780 (9)</td>
<td>103.81</td>
</tr>
</tbody>
</table>

Few overlaps in comparison with X-rays!

Texture correction: neutron combined analysis approach with only one phase present (amphibole)

$\omega = 10^\circ$, $\chi = 60^\circ$, $\phi = 0^\circ$
Grain size problems + heterogeneity of individual amphibole minerals → Neutron radiation better to probe the whole rock!! (more penetrative + large volume sample tested → better statistic)

Texture comparable with those described in amphiboles deformed at ≠ pressure and temperature: [001]* and [110]* directions mainly // and ⊥ to lineation
Texture of amphiboles collected at ≠ places and in ≠ lithologic types

White mica and chlorite partially replace amphibole or fill small fractures with quartz and carbonates

Combined approach allows to access to pole figures for most of the rock-forming minerals (even for mica)

Geological samples

Fig. 1: Tectonic sketch map of the Alpine chain: shaded areas correspond to continental Alpine crust. Legend: 1 = Southalpine basement, 2 = Auro, 4 = Helvetic basement, 5 = Tertiary intrusive bodies. Also included: Triassic Group occurrences in the Vicenza nappes (a), the Eastern Alps of the Swiss jura (b) and the Montebello Pass area in Central Austroalpine domain of the Lombardy-Carnic Nappes (c).
Degree of fabric evolution due to:
- deformation partitioning at metric-scale
- degree of chemical changes within amphiboles
- evolving metamorphic conditions during Alpine subduction (60-100 Million years).
crystallite orientations strong incidence on deformations occurring during geological processes + mutual deformations of several phases may play important rules in the global phenomena.

rock sample from Palm Canyon = low symmetry polyphase materials deformed in the Santa Rosa mylonite zone during the late Cretaceous.

Texture resolved with neutrons (D1B, ILL) for polyphase rock (quartz, biotite and plagioclase considered as pure albite).
Strongly overlapped peaks intra- and inter-phases + textured sample → Combined analysis approach

<table>
<thead>
<tr>
<th>PC 82 mylonite</th>
<th>Biotite</th>
<th>Quartz</th>
<th>Albite</th>
<th>Anorthite</th>
<th>K-spar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (weight %)</td>
<td>9.0</td>
<td>24.2</td>
<td>31.7</td>
<td>17.4</td>
<td>14.1</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/m</td>
<td>R3</td>
<td>C-1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Only 3 phases considered

Geological samples
**Biotite:**

010 axes // lineation direction

**Quartz:**

Max. ODF with c-axes in the foliation plane + a-axes // lineation direction

**Albite:**

a-axes // lineation + b- and c-axes randomly distributed around a-axes.

Orientationnal relationships

// Lineation:

<100>*-quartz // <100>*-albite

// foliation:

<001>*-quartz // <100>*-biotite
Illustration of the X-ray combined analysis approach


Tremendous work on mollusc shell growth + mollusc shell = fascinating examples of high resistant biocomposite materials.
Mollusc shell = two polymorphs of CaCO$_3$: aragonite + calcite + organic phases

For example: the organic part of the red Abalone *Haliotis rufescens* shell represents around 1 to 5% of the total weight and shell is 3000 time more resistant than pure geological aragonite!

Nacre (aragonite) is significant in medicine (orthopedics) due to high osteoinductive properties. Maya Indians of Honduras already used nacre for dental implants 2000 years ago!

In modern orthopedic medicine, aragonite of Pinctada maxima stimulates bone growth by human osteoblasts.
a) *Charonia lampas lampas*: Aragonitic shell

Mediterranean sea and Eastern Atlantic carnivorous gastropod mollusc. Protected species in mediterranea.

$N = \text{normal}, \ M = \text{margin} \text{ and } G = \text{growth directions}$

Microstructure never reported → determination by using SEM and X-ray combined analysis approach allowing to work with the real shell!

SEM studies: 3 crossed lamellar layers of biogenic aragonite

- **OCL**: Outer Comarginal Crossed Lamellae: lamellae plane // $M$
- **IRCL**: Intermediate Radial Crossed Lamellae: lamellae plane $\perp M$
- **ICCL**: Inner Irregular Complex Crossed Lamellae

$CaCO_3$ mollusc shells
X-ray measurements with a large scanning grid of 5°x5° → 936 X-ray diagrams for each layer (no residual stress evidenced)

Combined analysis approach: texture, cell parameters, atomic positions, \( \Delta Z \), \( C-O1 \) distance related to aplanarity of \( \text{CO}_3 \) groups.

<table>
<thead>
<tr>
<th>Layer</th>
<th>OCL</th>
<th>IRCL</th>
<th>ICCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>4.98563(7)</td>
<td>4.97538(4)</td>
<td>4.9813(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.0103(1)</td>
<td>7.98848(8)</td>
<td>7.9679(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.74626(3)</td>
<td>5.74961(2)</td>
<td>5.76261(5)</td>
</tr>
</tbody>
</table>

\[ \Delta V/V \]

<table>
<thead>
<tr>
<th></th>
<th>OCL</th>
<th>IRCL</th>
<th>ICCL</th>
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</thead>
<tbody>
<tr>
<td>OD max</td>
<td>299</td>
<td>196</td>
<td>2816</td>
</tr>
<tr>
<td>OD min</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Texture index (m.r.d.)

- OD reliability factors:
  - \( R_w \) (\%): 14.3, 11.2, 32.5
  - \( R_B \) (\%): 15.6, 12.7, 47.8

- Rietveld reliability factors:
  - GoF (\%): 1.72, 1.72, 3.05
  - \( R_w \) (\%): 29.2, 28.0, 57.3
  - \( R_B \) (\%): 22.9, 21.7, 47.2
  - \( R_{exp} \) (\%): 22.2, 21.3, 32.8

Largest crystallite organisation closer to the animal

\( \text{CaCO}_3 \) mollusc shells
Recalculated pole figures

Fiber texture: \( \mathbf{c} \parallel N \)

Split of \( \mathbf{c} \) axes around \( N \) + two contributions // (G,N) plane.

Split of \( \mathbf{c} \) axis from \( N \) + two contributions // (M,N) plane.

Texture information coherent with usually admitted gastropods phylogeny for this taxon!

\( \text{CaCO}_3 \) mollusc shells
Combined analysis: access to cell parameters and distortion of aragonite shell without needs of powdering specimen!!

<table>
<thead>
<tr>
<th></th>
<th>Geological reference</th>
<th>Charonia lampas OCL</th>
<th>Charonia lampas IRCL</th>
<th>Charonia lampas ICCL</th>
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<tbody>
<tr>
<td><strong>a (Å)</strong></td>
<td>4.9623(3)</td>
<td>4.98563(7)</td>
<td>4.97538(4)</td>
<td>4.9813(1)</td>
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<td></td>
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<tr>
<td></td>
<td>5.7439(3)</td>
<td>5.74626(3)</td>
<td>5.74961(2)</td>
<td>5.76261(5)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>4.98563(7)</td>
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<td>5.76261(5)</td>
<td>5.76261(5)</td>
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<tr>
<td><strong>c (Å)</strong></td>
<td>4.97538(4)</td>
<td>7.98848(8)</td>
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<td>5.76261(5)</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>y</th>
<th>z</th>
<th>y</th>
<th>z</th>
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<tbody>
<tr>
<td><strong>Ca</strong></td>
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<td>0.75970</td>
<td>0.41418(5)</td>
<td>0.75939(3)</td>
</tr>
<tr>
<td></td>
<td>0.76220</td>
<td>-0.08620</td>
<td>0.7628(2)</td>
<td>-0.0920(1)</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>0.76220</td>
<td>-0.08620</td>
<td>0.7628(2)</td>
<td>-0.0920(1)</td>
</tr>
<tr>
<td></td>
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<td>-0.08702(9)</td>
<td>0.76341(2)</td>
<td>-0.08702(9)</td>
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<tr>
<td><strong>O1</strong></td>
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</tr>
<tr>
<td></td>
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<td>-0.09456(6)</td>
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<tr>
<td><strong>O2</strong></td>
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<td>0.4754(1)</td>
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<tr>
<td></td>
<td>0.4864(3)</td>
<td>0.6834(2)</td>
<td>0.4864(3)</td>
<td>0.6834(2)</td>
</tr>
<tr>
<td><strong>ΔZ_{C-O1} (Å)</strong></td>
<td>0.05744</td>
<td>0.00029</td>
<td>0.04335</td>
<td>0.1066</td>
</tr>
</tbody>
</table>

ΔZ_{C-O1} ↗ from outer to inner layer correlated to the organic macromolecules presence + coherent with the ∆ of texture strength → control loss from macromolecules on aragonite stabilization farther from animal!

Anisotropic cell distortions yet observed in biogenic aragonite powderised layers

CaCO₃ mollusc shells
b) *Pinctada maxima*:
shell nacre of giant oyster = biomaterial that stimulates bone regeneration + in vivo studies show its biocompatibility and that nacre also able to induce new bone formation

- Geological nacre composition = pure aragonite (orthorhombic Pmcn)
  - Microstructure = strongly textured pseudo hexagonal nacre tablets

- *Pinctada maxima* nacre = aragonite and organic phases (2% – 5%) : biogenic nacre

X-ray Combined analysis approach : 2.5°*2.5° grid
Better understanding of the “natural” nacre structure and microstructure in order to deposit synthetic nacre
<table>
<thead>
<tr>
<th>Geological reference</th>
<th>Pinectada maxima</th>
</tr>
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<tbody>
<tr>
<td>a (Å)</td>
<td>4.9623(3)</td>
</tr>
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<td>b (Å)</td>
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<tr>
<td>c (Å)</td>
<td>5.7439(3)</td>
</tr>
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<td>4.97071(4)</td>
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<tr>
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<td>0.75939 (2)</td>
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<td>C</td>
<td>y: 0.76220</td>
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<td></td>
<td>z: -0.08620</td>
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<td>0.7676 (1)</td>
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<td></td>
<td>-0.0831 (1)</td>
</tr>
<tr>
<td>O1</td>
<td>y: 0.92250</td>
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<td>z: -0.09620</td>
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<tr>
<td>ΔZ_{c-O1} (Å)</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>0.054</td>
</tr>
</tbody>
</table>

Cell parameter distortions due to the presence of organic molecules like in Charonia lampas:

\[ R_w = 21.95\% \]
\[ R_b = 24.92\% \]

Normalized pole figures: strong texture with c-axis orientation weakly tilted from the normal shell

\[ \text{CaCO}_3 \text{ mollusc shells} \]
Nacre tablets of *Pinctada maxima* perfectly aligned with shell large domains showing common alignment of c-axes resembling a single-crystal or textures observed in epitaxial films:

**Observed texture ≠ from the columnar nacre evidenced in some gastropod (fiber textures) and Cephalopoda (double “twinned” textures) shells**
4) Biomimetic CaCO₃: Electrodeposited aragonite (Thesis of C. Krauss)

Medical European law: forbids animal proteins in human body → mimic textured hexagonal like aragonite

Synthetic nacre for osteopathy on Ti substrate:
- prostheses mainly in titanium subjected to bone resorption
- Ti substrate: high strength, inertia and immunity to corrosion

CaCO₃: 3 allotropic forms
- Calcite (R3c - trigonal): too much stable form but non osteoinductive
- Vaterite (P63/mmc - hexagonal): non-stable form not good for applications
- Aragonite (Pmcn - orthorhombic): metastable form; Gibbs energy $\Delta G_0(C\rightarrow A) = -1$kJ/mol

Electrodeposition of CaCO₃ in aragonitic form on titanium foil + microstructure and texture characterizations: SEM and X-Ray diffraction
Corresponding X-ray diagram: only aragonite is evidenced with a pronounced (00l) texture.

SEM backscattering images of deposited aragonite on Ti foils:

Nonoptimized deposited films: cauliflower-shaped aragonite + calcite + vaterite.

Optimized deposited films with nacre like pseudo hexagonal shaped crystals.

Recalculated pole figure: <00l> fiber like texture.

Texture strength far from natural nacre → differences can be associated to organic driven processes.

Biomimetic CaCO$_3$
Addition of Pinctada maxima organic molecules to the electrolyte: 2 types of organic phases (polar and apolar)

**Apolar phase**: cauliflower-shaped aragonite + calcite + vaterite

**Polar phase**: compact cauliflower-shaped aragonite + calcite + vaterite

Unexpected reduction of the <001> texture!
Crystallite shape and texture strength must be improved!
Illustration of the X-ray combined analysis approach

5) Biomimetic CaCO₃: synthesis of CaCO₃ polymorphs with polyacrylic acid (PAA) (S. Ouhénia thesis – December 2008)

Some studies show that surfactants can influence CaCO₃ nucleation, growth and grain shapes and consequently control crystal phases formation not usually stabilized under natural environment.

Aragonite (nacre) metastable at room temperature transforms to calcite in natural environment.

Many attempts to mimic aragonite, biological synthesis using different organic substrates and additives: for example aragonite thin films form on polyvinyl alcohol matrices in presence of polyacrilic acid (PAA)…

This work: CaCO₃ crystallization from aqueous solutions in presence of PAA at various temperatures (25°C to 80°C). PAA’s effects studied by SEM and X-ray diffraction.
At 25°C with and without PAA

**Vaterite**

- Spherical particles: 3µm
- Rhombic interpenetrated particles: 4µm
- \( R_b(\%) = 6.53\% \)
- \( R_w(\%) = 8.18\% \)

**Calcite**

- Calcite: 71(1)%
- Vaterite: 29(1)%

2 non textured polymorphs of CaCO₃ are present

**Biomimetic CaCO₃**
At 25°C with and without PAA

**Vaterite**
- Deformed spheres agglomerated in raspberry particles: 15 µm

**Calcite**
- Rhombic particles with less regular faces and porosity: 10 µm

With PAA,

\[ R_b (\%) = 9.79\% \quad R_w (\%) = 12.34\% \]

Calcite: 49.5(6)%; volume decrease: 0.075%
Vaterite 50.5(6)%; volume increase: 0.23%

With PAA, \( \uparrow \) \% of vaterite
At 50°C without PAA

**Vaterite**: raspberries  
**Calcite**: regular rhombs  
**Aragonite**: califlowers

3 non textured polymorphs of CaCO$_3$ are present + anisotropic crystallite shape → Popa formalism

$R_b (\%) = 6.81\%$;  $R_w (\%) = 8.40\%$

- Calcite: 47%
- Vaterite: 46%
- Aragonite: 7%

**Biomimetic CaCO$_3$**
At 50°C with PAA

Vaterite flowers
Calcite: porous rhombs
Aragonite: dendrites

\( R_b (\%) = 6.81\% ; \ R_w (\%) = 8.40\% \)
Calcite: 10.2\%
Vaterite: 79\%
Aragonite: 10.8\%

With PAA, strong \( \geq \) % of vaterite
+ \( \geq \) % of aragonite

Biomimetic CaCO_3
Anisotropic crystallite shapes at 50°C without and with PAA

Vaterite

- c-elongated needles with $c/a \sim 0.76$

Without PAA

Aragonite

- c-elongated needles with $c/b \sim 0.11$

With PAA

- flatness along $c$-axis with $c/a \sim 1.36$

- Idem aragonite!

Calcite

- Quasi-cubic crystallites

Ca-PAA complex adsorption on carbonate group faces blocks growth along $c$-axis + prevents transformation in calcite!

Quasi-cubic crystallites → no site for Ca-PAA complex adsorption

Biomimetic $\text{CaCO}_3$
At 80°C without PAA

3 non textured polymorphs of CaCO$_3$ are present

$R_b (%) = 5.05\%$; $R_w (%) = 6.86\%$

Calcite : 7.3\%
Vaterite : 12.7\%
Aragonite : 80\% !!

Biomimetic CaCO$_3$
At 80°C with PAA

SEM backscattered images: only aragonite needles are observed.

3 non textured polymorphs of CaCO$_3$ are present.

$R_b(\%) = 7.25\%$; $R_w(\%) = 9.17\%$
Calcite: 8.5\%  
Vaterite: 1.5\%  
Aragonite: 89\% !!

With PAA, $\geq \%$ of vaterite + $\geq \%$ of aragonite

Conclusions: PAA and temperature $\geq$ favor non textured aragonite growth: shift of chemical equilibrium of 3 polymorphs!

Biomimetic CaCO$_3$
greatest abundance and diversity during the Jurassic and Cretaceous periods. *Belemnites* ranged at the largest genetic distance from actually measured species + can serve as an outgroup for a phylogenetic classification.

The most common fossilised part of the internal shell = "rostrum" consists of massive calcite. The rostrum served as a counter-weight to the buoyancy provided by the chambered shell and also for protection of that delicate shell.

Quantitative Texture Analysis provides a set of new characters usable as a complement for a phylogenetic interpretation in cladistic or phenetic approaches + in case of calcitic shell layers QTA is able to link extinct and living molluscs via fossilised species!

*Morales et al.* (2002), *Mat. Sci. For.* 408, 1687
**Neutron diagram (D1B-ILL line):**
sum over 1368 scans over as many sample orientations.

- Pure calcite is observed

**Intra-phase peak overlaps + texture → combined analysis approach**

**Main pole figures:**
As in other cephalopod, calcite c-axes randomly distributed around belemnite rostrum cylindrical axis.

**Presence of large grains** (sizes range from few cm to over 1 meter for Belemnitae americanus)

- X-ray diffraction can’t properly probe texture!!

**Correlated to the c-axes of Nautilus sp. aragonite layers →**
Nacre not ancestral and might have evolved from original calcite: on the contrary of the common hypothesis!

*Shell fossils: Texture and phylogeny*
Combined analysis approach actual limitations:

7) Multiphased Cr\(^{2+}\):ZnSe films: texture, anisotropic crystallite sizes, residual stresses, twin faults and phase analysis

Mid-IR region (2 – 5 \(\mu\)m) « molecular fingerprint region » → environmental, medicine, biological and defense applications

1996 : transition-metal doped II-VI zinc chalcogenide compound for room-temperature laser materials in the mid-IR.

Realization of compact optically and electrically pumped mid-IR micro-lasers.

fluorescence and stimulated emission optimization = production of quality films

Multiphased Cr\(^{2+}\):ZnSe films : combined analysis approach actual limitations
Figure: RX θ-2θ diagrams

- ZnSe hexagonal

- Cubic (C) and hexagonal (H) ZnSe

- H-ZnSe more marked at higher $P_{RF}$

- Highly textured with in majority $<111>_{C-ZnSe} // n_{film}$

Figure: $\chi$-scans with $\omega = 13.65^\circ$

Anisotropic crystallite shapes

- $\chi = 20^\circ$
- $\chi = 40^\circ$
- $\chi = 20^\circ$

Multiphased $Cr^{2+}:ZnSe$ films: combined analysis approach actual limitations
\[ \omega = 13.65^\circ, \ P_{RF} = 200W \]

Residual strains for both C-ZnSe and H-ZnSe! Biaxial model with \( \sigma_{11} = \sigma_{22} \) due to fibre like texture.

Fibre strong textures + 2 phases + anisotropic crystallite shape + residual strains \( \rightarrow \) combined analysis approach is necessary!

Multiphased \( \text{Cr}^{2+}:\text{ZnSe films} \) : combined analysis approach actual limitations
### Phase Cell parameters (Å)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cell parameters (Å)</th>
<th>In-plane stress (MPa)</th>
<th>Anisotropic sizes (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[111]</td>
</tr>
<tr>
<td>C-ZnSe</td>
<td>$a = 5.6497(3)$</td>
<td>263 (14)</td>
<td>112 (1)</td>
</tr>
<tr>
<td>H-ZnSe</td>
<td>$a = 3.9527(6)$</td>
<td>436 (25)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$c = 6.7154(8)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fibre strong textures + 2 phases + anisotropic crystallite shape + residual strains!

$R_{exp} = 11.1\%$

$R_W = 25.7\%$

% H-ZnSe = 45.4%

Tensile in plane stress ≠ Rizzo et al.

Multiphased Cr$^{2+}$:ZnSe films: combined analysis approach actual imitations
\( \text{C-ZnSe texture:} \)

strong <111> fibre texture with some residual orientations

\( \text{H-ZnSe texture:} \)

unique <001> strong fibre texture

*Multiphased \( \text{Cr}^{2+}\cdot\text{ZnSe films}: \) combined analysis approach actual limitations*
Refined fibre like textures independent of the substrate choice!

Strong <111> texture for the C-ZnSe + twin faults evidenced in H-ZnSe

Multiphased Cr\textsuperscript{2+}:ZnSe films: combined analysis approach actual limitations
χ - sum diagram at $\omega = 13.65^\circ$ with residual strains:
fit still not optimum!!

Discrepancies not resolved with introduction of stacking faults and micro-strains!!
→ another still unidentified phenomenon?!

Intergrowth between C-ZnSe and H-ZnSe must play a rule + need to be implemented in MAUD!

Necessity of incorporation of twin faults in H-ZnSe as evidenced in TEM images

Better reproduction for $2\theta > 35^\circ$ with H-ZnSe twin faults probability of 45.7 (6)%;
but still discrepancies for $2\theta < 35^\circ$ !!!

Multiphased Cr$^{2+}$:ZnSe films: combined analysis approach actual limitations
THANK YOU FOR YOUR ATTENTION !!!