Structural distortion of biogenic aragonite in strongly textured mollusc shell layers

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Structure determination on real (textured) samples

Structure and QTA: correlations:

\( f(g) \) and \( |F_h|^2 \) are different!

\( f(g) \):
- Angularly constrained: \([h_1k_1l_1]^*\) and \([h_2k_2l_2]^*\)
  make a given angle: more determined for large texture strengths
- lot of data (spectra) needed

\( |F_h|^2 \):
- Position, \( f_i \), and Debye-Waller constrained
- work on the sum of all diagrams on average
Grinding to obtain powders

Grinding: removes angular relationship, adds correlations

Texture:
- not measured
- removed? hope to get a perfect powder
Strains, defaults, anisotropy … :
- some removed, some added

Same sample?
Rare samples?
Why not benefit of texture in Structure determination?

**Perfect powders:**
- overlaps (intra- and inter-
- no angular constrain
- anisotropy difficult to resolve

**Single crystals:**
- reduced overlaps
- max angular contrains
- Perfect texture: max anisotropy

**Single pattern**

**Many individual diffracted peaks**

**Textured powders:**
- reduced overlaps
- angular constrain = f(texture strength)
- Intermediate anisotropy

**Many patterns to measure and analyse**
**Simplified algorithm for Combined Analysis**

\[ P_k(\chi, \phi) = \int f(g, \varphi) d\varphi \]

\[ I_{i}^{\text{calc}}(\chi, \phi) = \sum_{n=1}^{N_{\text{phases}}} S_n \sum_{k} L_k |F_{k,n}|^2 S(2\theta_i - 2\theta_{k,n}) P_{k,n}(\chi, \phi) A + bkg_i \]
Minimum experimental requirements

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

+ ~1000 experiments (2θ diagrams)
in as many sample orientations

+ Instrument calibration
  (peaks widths and shapes, misalignments, defocusing …)
**Calibration**

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

KCl, LaB$_6$ ...

FWHM ($\omega$, $\chi$, $2\theta$ ...)
2$\theta$ shift
gaussianity
asymmetry
misalignments ...


Natural biogenic aragonitic crystals

Aplanarity of carbonate groups in $\text{CaCO}_3$

$\Delta Z_{C-O1} = c(z_C - z_{O1})$

Calcite

Biogenic aragonite

Mineral aragonite

0 Å

Intermediate ?

0.05744 Å
Aragonitic layers in mollusc shells

Gastropods
Crossed lamellar layers
Charonia lampas lampas (triton or trumpet cousin)

Columnar Nacre

Haliotis tuberculata (common abalone)

Bivalves
Sheet Nacre

Pinctada maxima (Mother of pearl oyster)
IRC layer of *Charonia lampas lampas* for selected \((\chi, \varphi)\) sample orientations
for all $(\chi, \varphi)$ sample orientations

refined experiments

GoF: 1,72
Rw: 28,0%
Rexp: 21,3%
Outer CL
43 mrd\(^2\)

Interm Radial CL
47 mrd\(^2\)

Inner Com CL
721 mrd\(^2\)

Inner Columnar Nacre
211 mrd\(^2\)

Inner Sheet Nacre
1100 mrd\(^2\)
### Unit-cell distortions

<table>
<thead>
<tr>
<th></th>
<th>OCL</th>
<th>Charonia</th>
<th>Pinctada</th>
<th>Haliotis</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>IRCL</td>
<td>ICCL</td>
<td>ISN</td>
</tr>
<tr>
<td>a (Å)</td>
<td>4,98563(7)</td>
<td>4,97538(4)</td>
<td>4,9813(1)</td>
<td>4,97071(4)</td>
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<tr>
<td>b (Å)</td>
<td>8,0103(1)</td>
<td>7,98848(8)</td>
<td>7,9679(1)</td>
<td>7,96629(6)</td>
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<tr>
<td>c (Å)</td>
<td>5,74626(3)</td>
<td>5,74961(2)</td>
<td>5,76261(5)</td>
<td>5,74804(2)</td>
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<tr>
<td>Δa/a</td>
<td>0,0047</td>
<td>0,0026</td>
<td>0,0038</td>
<td>0.0017</td>
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<tr>
<td>Δb/b</td>
<td>0,0053</td>
<td>0,0026</td>
<td>0,0000</td>
<td>-0.0002</td>
</tr>
<tr>
<td>Δc/c</td>
<td>0,0004</td>
<td>0,0010</td>
<td>0,0033</td>
<td>0.0007</td>
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<tr>
<td>ΔV/V (%)</td>
<td>1,05</td>
<td>0,62</td>
<td>0,71</td>
<td>0.22</td>
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</tbody>
</table>

Anisotropic cell distortion - depends on the layer
Only nacres exhibit (a,b) contraction
Due to inter- and intra-crystalline molecules
Distortions and anisotropies larger than pure intra- effect (Pokroy et al. 2007)
# Elastic stiffnesses

<table>
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<tr>
<th></th>
<th>Single crystal</th>
<th>ICCL</th>
<th>RCL</th>
<th>OCL</th>
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<tr>
<td>Elastic stiffness</td>
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<tr>
<td></td>
<td>160</td>
<td>96.5</td>
<td>130.1</td>
<td>111.1</td>
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<tr>
<td></td>
<td>37.3 87.2</td>
<td>31.6 139</td>
<td>32.6 103.3</td>
<td>32.9 119</td>
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<tr>
<td></td>
<td>1.7 15.7 84.8</td>
<td>13.7 9.5 87.8</td>
<td>10.3 14.1 84.5</td>
<td>13.2 11.8 84.8</td>
</tr>
<tr>
<td></td>
<td>41.2</td>
<td>29.8</td>
<td>36.3</td>
<td>32.8</td>
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<tr>
<td></td>
<td>25.6</td>
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<td>34.6</td>
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<td>42.7</td>
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<td>40.5</td>
<td>40.9</td>
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### Atomic Structures

<table>
<thead>
<tr>
<th></th>
<th>Geological reference</th>
<th>Charonia lampas OCL</th>
<th>Charonia lampas IRCL</th>
<th>Charonia lampas ICCL</th>
<th>Strombus decorus mixture</th>
<th>Pinctada maxima ISN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>y</td>
<td>0.41500</td>
<td>0.41418(5)</td>
<td>0.414071(4)</td>
<td>0.41276(9)</td>
<td>0.4135(7)</td>
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<tr>
<td></td>
<td>z</td>
<td>0.75970</td>
<td>0.75939(3)</td>
<td>0.76057(2)</td>
<td>0.75818(8)</td>
<td>0.7601(8)</td>
</tr>
<tr>
<td>C</td>
<td>y</td>
<td>0.76220</td>
<td>0.7628(2)</td>
<td>0.76341(2)</td>
<td>0.7356(4)</td>
<td>0.7607(4)</td>
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<tr>
<td></td>
<td>z</td>
<td>-0.08620</td>
<td>-0.0920(1)</td>
<td>-0.08702(9)</td>
<td>-0.0833(2)</td>
<td>-0.0851(7)</td>
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<tr>
<td>O1</td>
<td>y</td>
<td>0.92250</td>
<td>0.9115(2)</td>
<td>0.9238(1)</td>
<td>0.8957(3)</td>
<td>0.9228(4)</td>
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<tr>
<td></td>
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<td>-0.1018(2)</td>
<td>-0.0905(9)</td>
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<td>O2</td>
<td>x</td>
<td>0.47360</td>
<td>0.4768(1)</td>
<td>0.4754(1)</td>
<td>0.4864(3)</td>
<td>0.4763(6)</td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>0.68100</td>
<td>0.6826(1)</td>
<td>0.68332(9)</td>
<td>0.6834(2)</td>
<td>0.6833(3)</td>
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<tr>
<td></td>
<td>z</td>
<td>-0.08620</td>
<td>-0.08368(6)</td>
<td>-0.08473(5)</td>
<td>-0.0926(1)</td>
<td>-0.0863(7)</td>
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<tr>
<td>ΔZ_{C-O1} (Å)</td>
<td>0.05744</td>
<td>0.00029</td>
<td>0.04335</td>
<td>0.1066</td>
<td>0.031</td>
<td>0.054</td>
</tr>
</tbody>
</table>

Carbonate group aplanarity specific to a given layer
Aplanarity decreases from inner to outer shell layers (CL layers)
-> up to quite ΔZ=0 outside (nearly the calcite value)
Average aplanarity on the whole shell = geological reference (Strombus)
In Haliotis nacre: large ΔZ=0.08, + strong anisotropy: less stable nacre
Conclusions

a) Texture affects phase ratio and structure determination

b) Microstructure (crystallite size) affects texture (go to a)

c) Stresses shift peaks then affects structure and texture determination

d) Combined analysis may be a solution, unless you can destroy your sample or are not interested in macroscopic anisotropy ...

e) If you think you can destroy it, perhaps think twice

f) more information is always needed: local probes ...

g) www.ecole.ensicaen.fr/~chateign/texture/combined.pdf