Controlled growth of mollusc shells: Quantitative Crystallographic Texture Analysis input

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## Overlook

- Generality on QTA by diffraction
- Complex growth of layers: microstructure versus texture
- **a** and **c**-axes patterns of aragonitic layers, twinning
- QTA: global versus local probes
- QTA and Mollusc's Phylogeny
- QTA and calcitic fossils
- QTA and Mollusc's prothaetics
- QTA and mechanical behaviour



We measure pole figures  $P_{hkl}$ , statistical representation of crystallite orientation in a sample frame XYZ:



 $\{\alpha,\beta,\gamma\}$  three Euler angles,  $\gamma$  accessed by refinement of the Orientation Distribution Function (ODF)



## Reference frame in mollusc shells



 Crystal: CaCO<sub>3</sub>, aragonite (Pmcn) or calcite (R3c), for thousands of crystallites:



## Typical x-ray diffraction pattern

#### Mytilus edulis (common mussel)



#### Crassostrea gigas (common oyster)



Measured for around 1000 sample orientations, using x-rays, neutrons or electrons, depending on the desired probed volume

ODF-reliability (x-rays: point detector): *Helix pomatia* (Burgundy land snail: Outer com. crossed lamellar)





#### Inner sheet nacre of *Anodonta cygnea* (river mussel): no intra-mineral epitaxy



Bathymodiolus thermophilus (-2400m deep mussel): no inter-mineral epitaxy



Euglandina sp.: different crystallite shapes, close orientations !



Inner sheet nacre of *Cypraea testudinaria* (cowry): no inter-layer epitaxy



*Cyclophorus woodianus*: different crystal orientations look like single crystal from diffraction !





#### c-axes texture patterns



#### a-axes texture patterns



## Twinning in aragonite ...



 $\alpha = 2 \arctan(a/b) = 63.8^{\circ}$ 

## ... forms nacre platelets ...





#### Bragg, 1937

Mutvei, 1980

## ... that rearrange ...



*Pinctada margaritifera* (black pearl oyster)





Haliotis cracherodi (black abalone)



#### Neutrons or x-rays: global approach Electrons: local, like with EBSD

### Crassostrea gigas (common oyster: Inner foliated calcite) Electrons



x-rays

Global analysis is coherent with local ones like synchrotron microfocus x-rays (*Aizenberg*, J. et al. (1996) Connective Tissue Research **34(4)**, 255-261)



From 70 mollusc species (gastropods, bivalves and cephalopods), around 150 layers studied

In collaboration with C. Hedegaard (*DGB Aarhus, Denmark*) and H.-R. Wenk (DEPS Berkeley, *USA*) Closely related species, close textural characters, but significant variations: textural parameters can serve character analysis



# Phylogenic interest: nacre = ancestral (Carter & Clarck, 1985)





#### nacre not ancestral



## In collaboration with L. Harper (*DESC Cambridge, UK*) and M. Morales (*LERMAT-ENSICAEN, France*)

#### Pinnoid and Pterioid prismatic layers



#### Pinna nobilis

c-axes // N a-axes at random

Pteria penguin

#### Mussels prismatic layers



Mytilus edulis c-axes ∠ N a-axes single-crystal like

c-axes  $\perp N$ , // G Bathymodiolus thermophilus

#### Scallop and trichite prismatic layers



Amussium parpiraceum (scallop) c-axes ⊥ N, // G a-axes single-crystal like

Trichites (fossil) c-axes ∠ N a-axes random

#### Texture Analysis results

|                   | Layer | ODF   | ODF min | RP0 | RP1 | c-axis | a-axis  | <b>{001} Max</b> | $\mathbf{F}^2$      | - S |
|-------------------|-------|-------|---------|-----|-----|--------|---------|------------------|---------------------|-----|
|                   | type  | Max   | (mrd)   | (%) | (%) |        |         | (mrd)            | (mrd <sup>2</sup> ) |     |
|                   |       | (mrd) |         |     |     |        |         |                  |                     |     |
| Pinna nobilis     | OP    | 303   | 0       | 50  | 29  | // N   | random  | 68               | 29                  | 2.3 |
| Pteria penguin    | OP    | 84    | 0       | 29  | 15  | // N   | random  | 31               | 13                  | 1.9 |
| Amussium          | OP    | 330   | 0       | 53  | 33  | // G   | <110>// | 20               | 31                  | 2.6 |
| parpiraceum       |       |       |         |     |     |        | М       |                  |                     |     |
| Bathymodiolus     | OP    | 63    | 0       | 25  | 18  | // G   | // M    | 27               | 13                  | 1.9 |
| thermophilus      |       |       |         |     |     |        |         |                  |                     |     |
| Mytilus edulis    | OP    | 207   | 0       | 41  | 25  | 75°    | <110>// | 23               | 21                  | 2.2 |
|                   |       |       |         |     |     | from N | М       |                  |                     |     |
| Trichites         | Р     | 390   | 0       | 52  | 28  | 15°    | random  | 56               | 41                  | 2.2 |
|                   |       |       |         |     |     | from N |         |                  |                     |     |
| Crassostrea gigas | IF    | 908   | 0       | 45  | 31  | 35°    | // M    | >100             | 329                 | 5.1 |
|                   |       |       |         |     |     | from N |         |                  |                     |     |

No DNA is available on fossils like in Trichites, but Trichite's textural parameters are close to the ones of *pinnoids* or *pterioids*: interesting for the classification of extinct species c

Chateigner, Morales, Harper, Materials Science Forum, 408-412, 2002, 1687-1692



Pinctada margaritifera and P. maxima nacres: Bio-compatible and bio-inductive layers for rabbit bones (E. Lopez (MNHN, Paris)





**Bivalvia** 

P. Margaritifera

|   | Atrina maurea          | $\left< \perp \left  \text{ISN} \right  \ast_{44}^{\text{a, 20}} \right>$ |                    |
|---|------------------------|---------------------------------------------------------------------------|--------------------|
|   | —— Pinna nobilis       | $\left< \perp \left  \text{ISN} \right  \ast^{a,95}_{25} \right>$         |                    |
|   | Lampsilis alatus       | $\left< \perp \left  \text{ISN} \right  \ast^{\text{a},90}_{25} \right>$  |                    |
|   | Fragum fragum          | $\langle \forall, 15   \text{ICCL}   \times_{50}^{<110>} \rangle$         |                    |
|   | Glycymeris gigantea    | $\langle \forall, 15   \text{ICCL}   \times_{50}^{<110>} \rangle$         |                    |
|   | Spondylus princeps     | $\langle v, 10   ICCL   \times_{50}^{<110>}$                              | , -15              |
|   | Paphia solanderi       | $\left< \perp  \text{ICCL} O \right> \left< \angle, 2 \right>$            | $20 OSiP O\rangle$ |
| _ | Neotrigonia sp.        | $\left< \perp \left  \text{ISN} \right  \ast_{12}^{a,90} \right>$         |                    |
|   | Pinctada margaritifera | $\left< \perp \left  \text{ISN} \right  \ast_8^{a,90} \right>$            |                    |
|   | Pinctada maxima        | $\left< \perp \left  \text{ISN} \right  \ast_{14}^{\text{a},90} \right>$  |                    |
|   | Pteria penguin         | $\left< \perp \left  \text{ISN} \right  \ast_{15}^{\text{a},-30} \right>$ |                    |
|   |                        |                                                                           | 4                  |



## C<sub>ijkl</sub> (Gpa)

#### P waves





#### Single crystal (Gpa)

123

| 151 | 151               |                    |                                      |
|-----|-------------------|--------------------|--------------------------------------|
| 251 | 151               |                    |                                      |
| 151 | 251               |                    |                                      |
|     |                   | 123                |                                      |
|     |                   |                    | 123                                  |
|     | 151<br>251<br>151 | 151151251151151251 | 151 151<br>251 151<br>151 251<br>123 |

#### CoNi alloy

| 298 | 127 | 126 | -0. | 0.  | -2 |
|-----|-----|-----|-----|-----|----|
| 127 | 305 | 118 | 0.  | 0.  | -1 |
| 126 | 118 | 307 | -0. | -0. | 3  |
| -0. | 0.  | -0  | 78  | 2.8 | 0. |
| 0.  | 0.  | -0  | 2   | 85  | -0 |
| -2  | -1  | 3   | 0.  | -0. | 86 |



QTA + Simulation Geometric Mean

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## Some conclusions

- Shells exhibit a large variety of texture patterns, in their aragonite and calcite layers
- Textural parameters are similar for close species, different for distant species, they confirm organically driven growth and refute mineral epitaxy
- Texture and microstructure analyses give nonredundant information in shells
- "Texture" characters can be relevant for classification and phylogenetic interpretation, either for living or extinct species
- Texture may serve as a tool to predict bio-compatible species, and mechanical behaviours of shells