Residual Stresses and Crystal Orientation in Biominerals revealed by Dark Field X-ray Microscopy

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Workshop on DFXM
Complex Architectures of Biominerals

CALCIUM PHOSPHATE:
Structural Support

CALCIUM CARBONATE:
Structural Support, Protection, Optical Functions
Correlative analysis of the spatial arrangement and crystallographic properties of biominerals allows us to analyze mechanical properties, to analytically describe the morphogenesis and to evaluate the thermodynamic and kinetic parameters governing its formation.
The morphology of these biological structures can be predicted with simple thermodynamic principals → adds a fundamentally new perspective to the field of biomineralization, the shells evolution and biomimetic material design.
Residual Stresses

Residual strains in biogenic calcite and aragonite


Residual strains prevents crack propagation


Toughening of calcite optical brittle star lenses

Bragg Ptychography reveals domains in calcite prisms


The role of residual stresses in biomineral formation has never been investigated
Techniques

**HRTEM**
High Resolution Transmission Electron Microscopy

+ High spatial resolution (sub ångström)
- Excessive sample prep
- Low strain resolution
- Sample environment
- Small field of views

**3D XRD / DCT**
3D X-Ray Diffraction / Diffraction Contrast Tomography

+ Polycrystalline materials
+ Bigger volumes
- Lower spatial resolution (usually microns)

**CDI/Bragg Ptychography**
Coherent Diffraction Imaging / Ptychography

+ High spatial resolution (~ 10 nm)
+ High angular resolution (~ 0.005 °)
- Small sample sizes (100 nm-2 µm)

**DFXM**
Dark Field X-Ray Microscopy

+ Adjustable resolution range (30 nm–300 nm)
+ High angular resolution (~ 0.001 °)
+ Bigger sample sizes (< 0.5 mm)
+ In-situ setups
Samples

Calcite prisms of *Pinna nobilis*:

- Single-crystal-like with very small misorientation distribution (< 1°)

150 µm
Samples

**Calcite prisms of *Pinctada nigra***:

- Initially prisms appear single-crystal-like
- Crystals rotate gradually and split while maintaining the gradual change in orientation
- Total misorientation distribution 10°-20°
Dark-Field X-Ray Microscopy


calcite
Results *Pinna nobilis*

Radiograph of the tip of an isolated *P. nobilis* prism.

Sample was tilted 45° to fit Bragg conditions for 104 plane. Line scans were collected starting at the tip upwards:

- 78 nm x and 310 nm y resolution
- < 0.01° angular resolution
- 200 nm line beam in 1 µm steps

### MOSAICITY

- θ: -0.05° to 0.15°
- η: -0.15° to 0.15°

### LATTICE

- 100 rotation axis
- 120 rotation axis
- Calcite slip systems
Results *Pinna nobilis*

GROWTH LINES:

Elemental Variations:


Organic Variations:

Results *Pinctada nigra*

Radiograph of the *P. nigra* prism.

Sample was positioned horizontally to fit bragg conditions for 104 plane and line scans were collected starting at the tip upwards:

- 4x4 binned
- 310 nm x and 1.2 µm y resolution
- < 0.4 ° angular resolution
- 200 nm line beam in 1.5 µm steps
Results *Pinctada nigra*

d-space

120 rotation axis

100 rotation axis
Conclusions

**Results:**

- Reveal mosaicy and orientational gradients in *P. nobilis*
- Correlate specific crystallographic rotations to residual strain
- Similar lattice distortion patterns in *P. nobilis* and *P. nigra*, despite crystallographic differences
- Correlate shape and strain patterns in P. nigra and compression with initial grain splitting

**DFXM for biomineral characterization:**

- Adjustable spatial and high angular resolution → large field of views & and minor sample preparation allow comprehensive and correlative analysis of strain orientation and shape
- Single and polycrystalline
- Adjustable sample environment → no vacuum

*Multiscale correlative approaches are essential for biomineral studies*
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Thank you for your attention!