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

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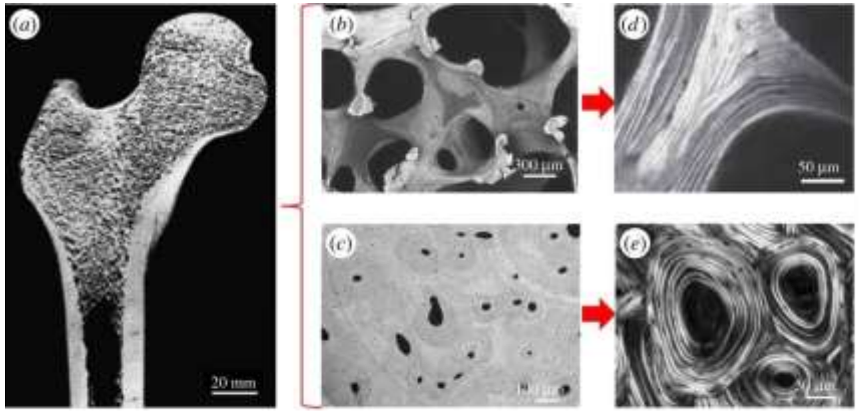
TECHNISCHE UNIVERSITÄT DRESDEN

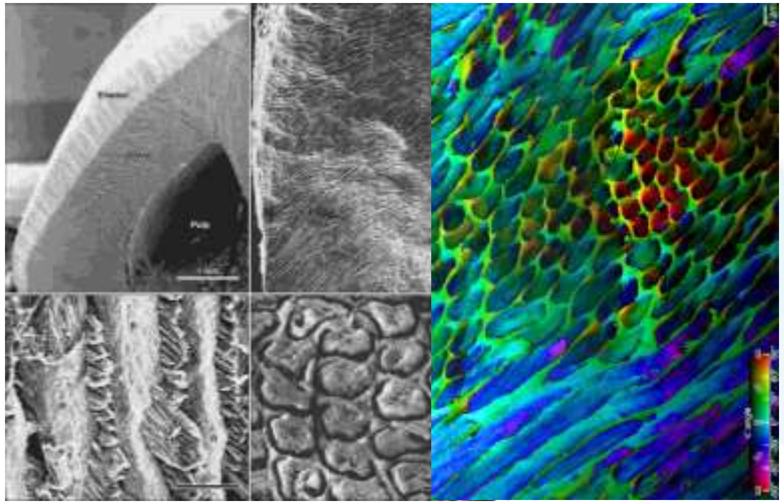
Workshop on DFXM

Complex Architectures of Biominerals

CALCIUM PHOSPHATE:

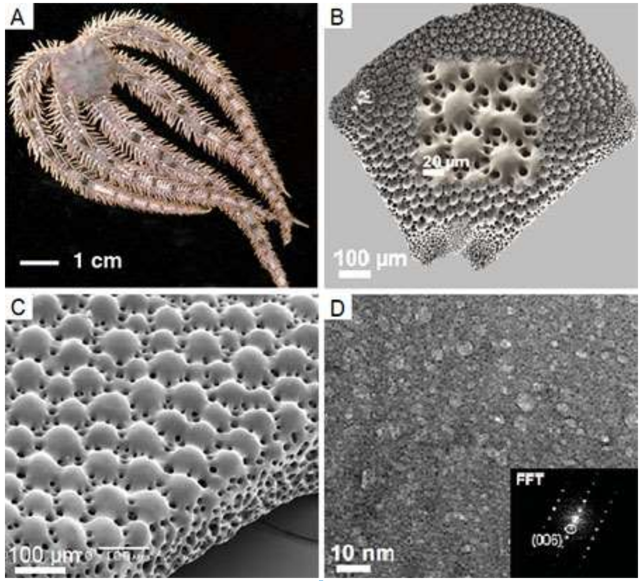
Structural Support

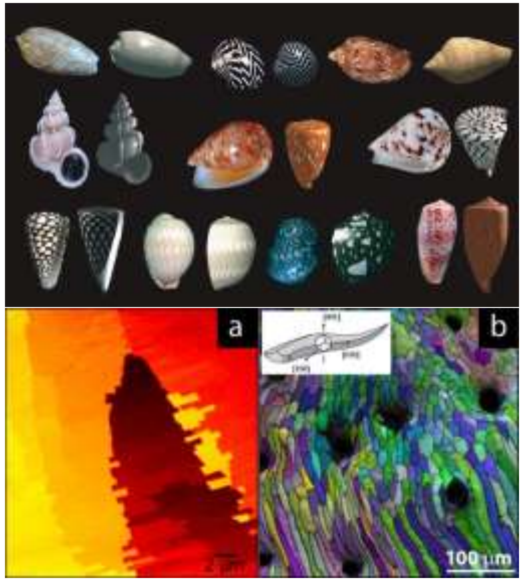


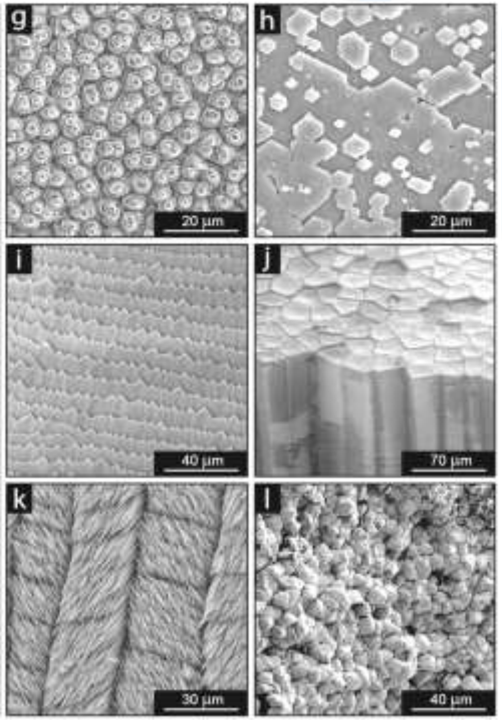


CALCIUM CARBONATE:

Structural Support, Protection, Optical Functions

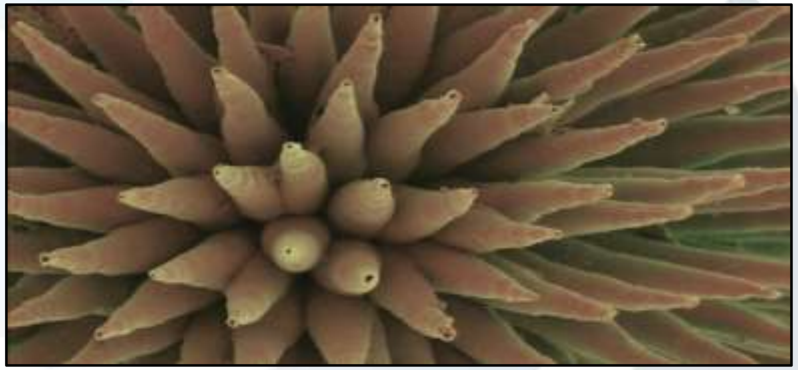


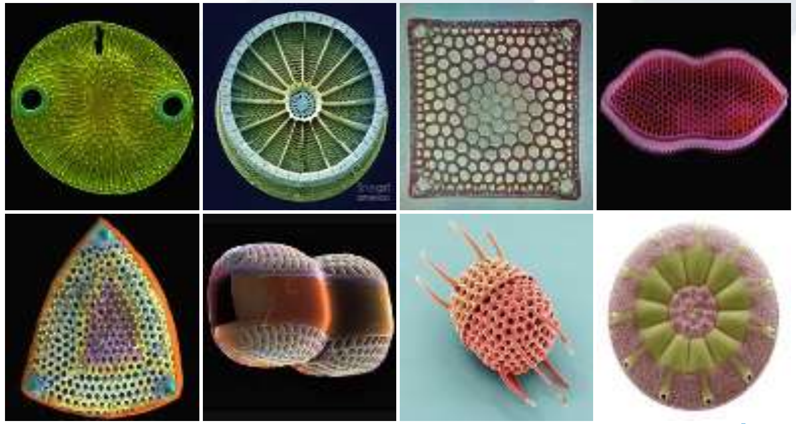




AMORPHOUS SILICA:

Structural Support, Filtering

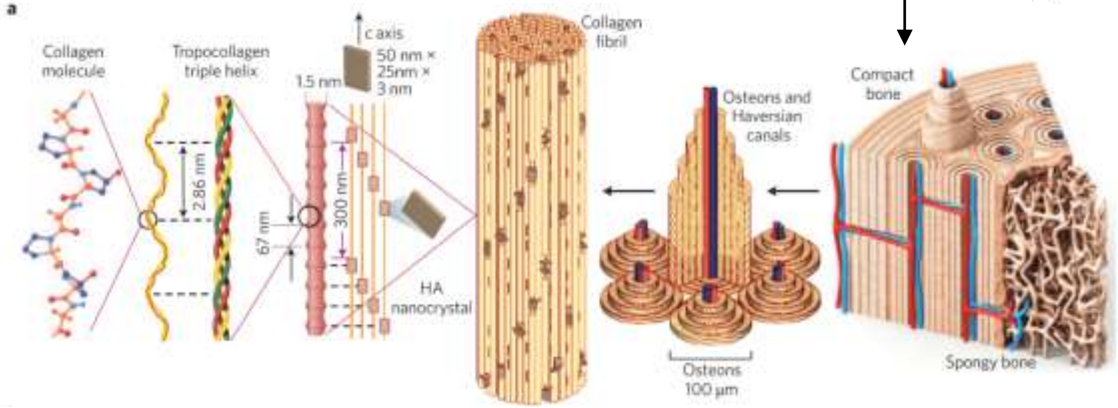




From Structure to Function

3D HIERARCHY:

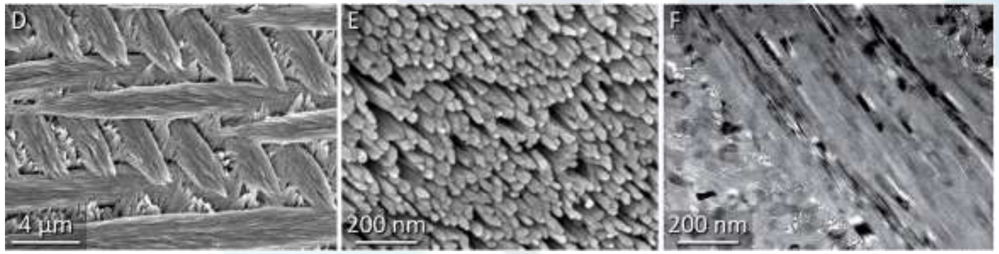
Composition, orientation, structure

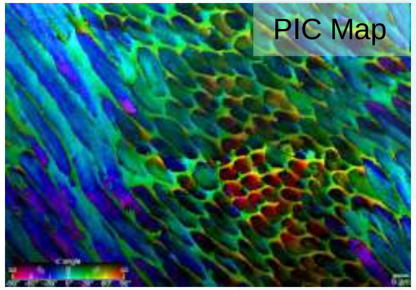


Wegst et al., Nature Materials, 2014

STRUCTURE:

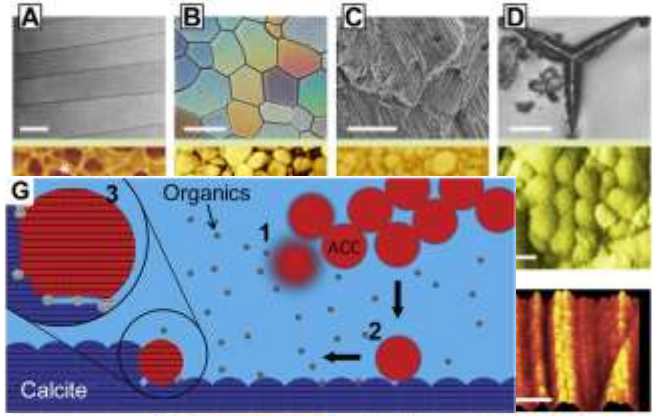
Misorientation prevents crack propagation



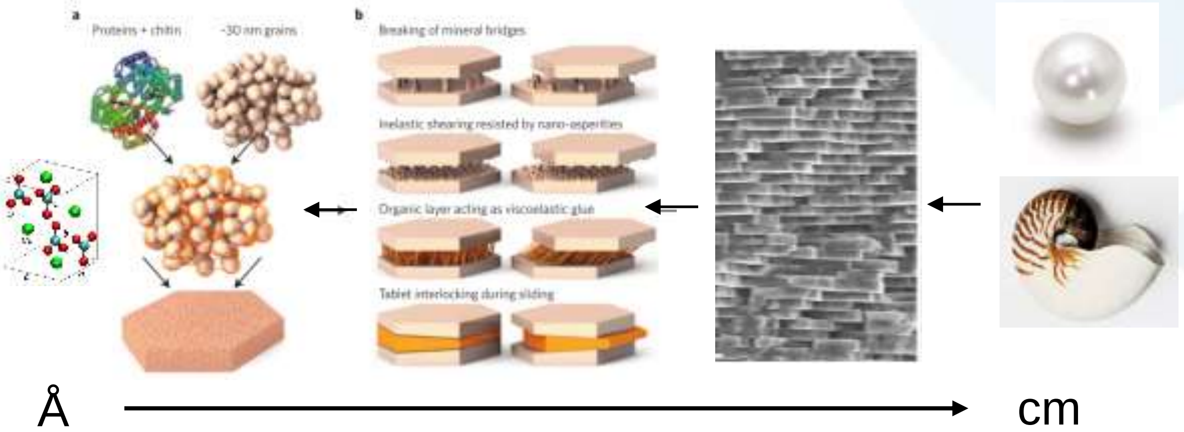


Stifler C. et al, Acta Biomaterialia, 2020
Beniash E., et al., Nat. Comm. 10, 4383 (2019)

Nanogranular substructure

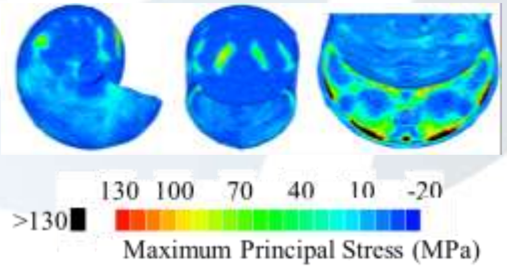


Wolf et al., Journal of Structural Biology, 2016



STRUCTURE:

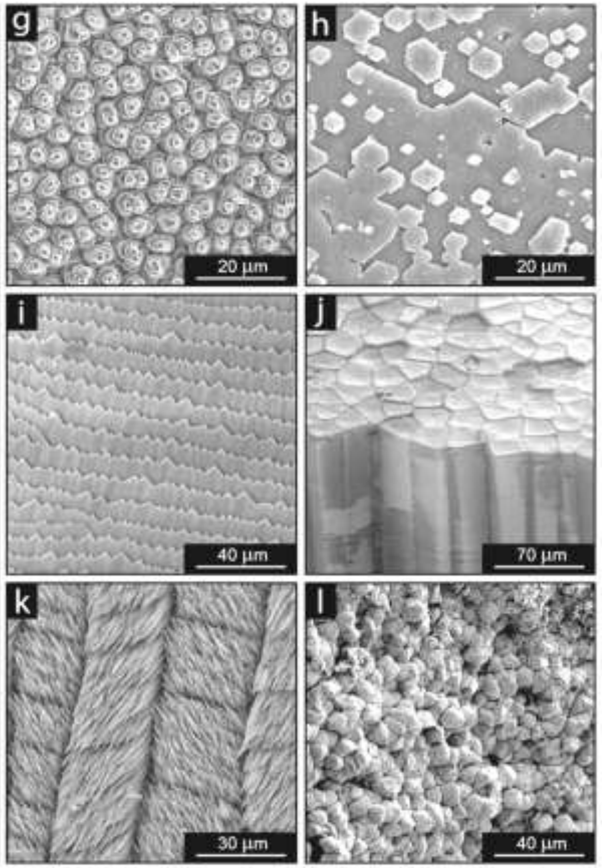
FEI Analysis of microstructure

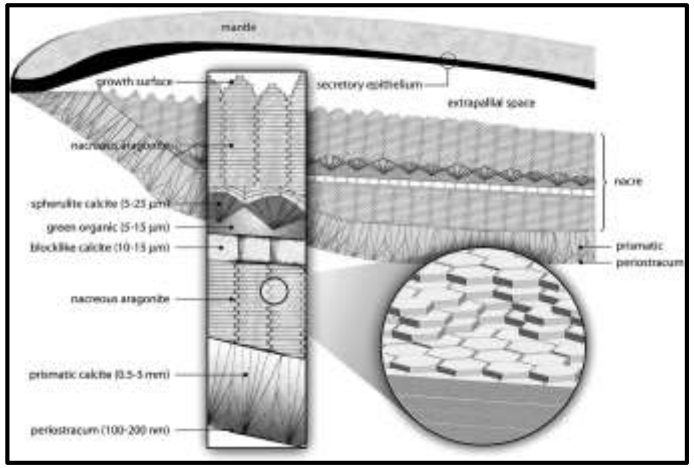


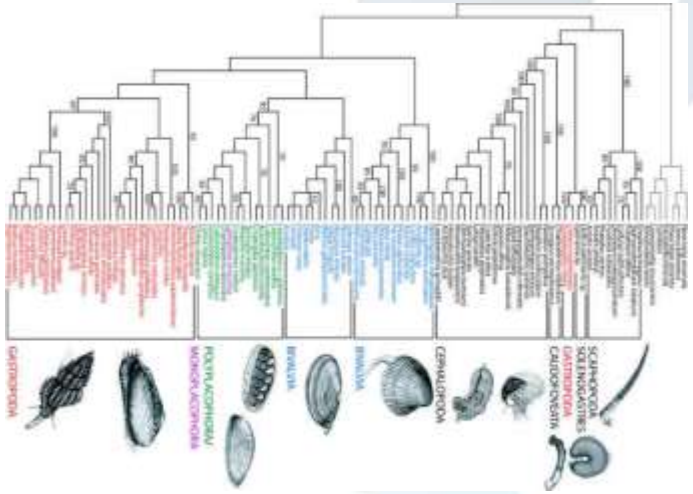
Lemanis R., et al., PeerJ 4:e2434 (2016)

Correlative analysis of the spatial arrangement and crystallographic poperties of biominerals allows us to analyze mechanical properties, to analytically describe the morphogenisis and to evaluate the thermodynamic and kinetic parameters governing its formation

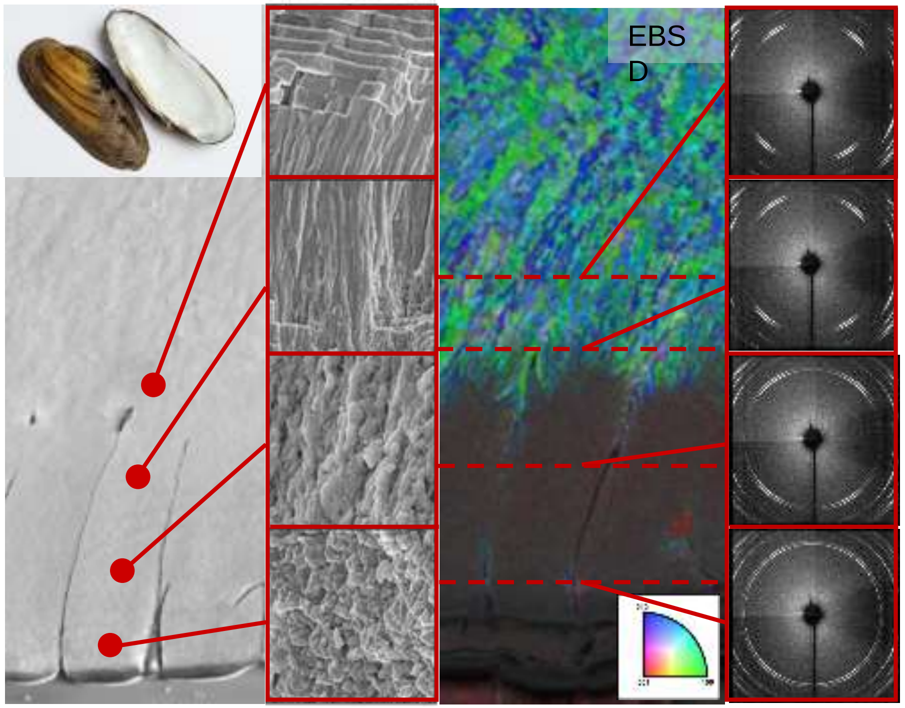
Biomineralization of Molluscan Shells

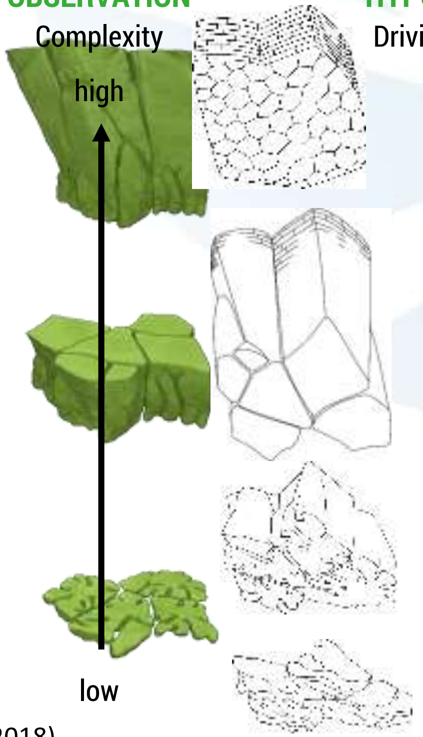




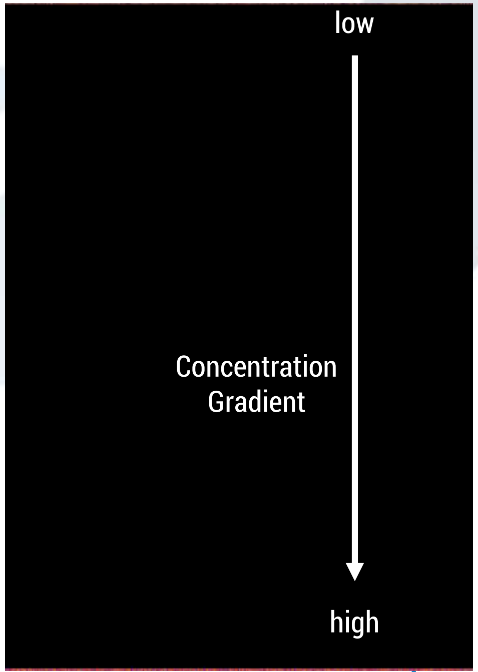


The morphology of these biological structures can be predicted with simple thermodynamic principals → adds a fundamentally new perspective to the field of biomineralization, the shells evolution and biomimetic material design





SIMULATION



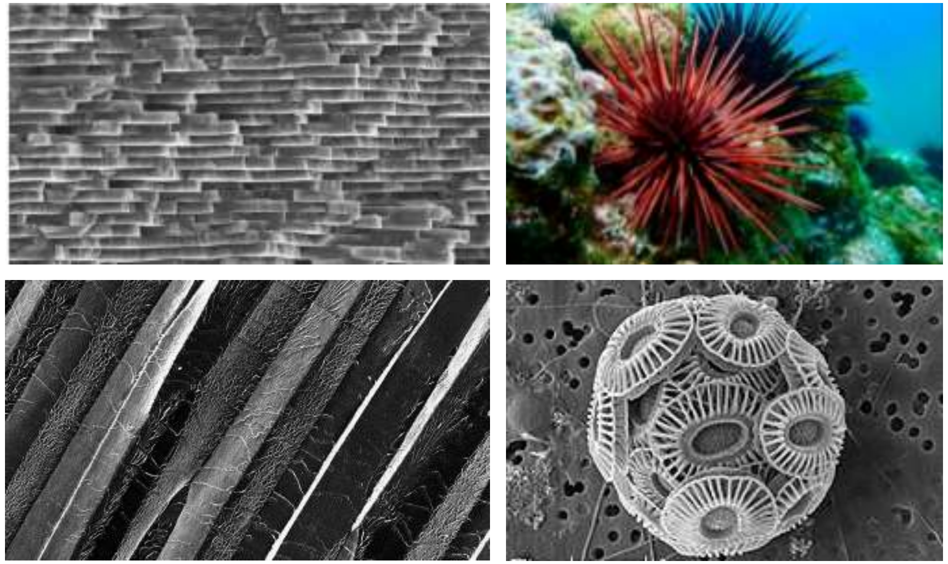
CELLULAR CONTROL
Genetics
Genomics
Proteomics
Secretion

SELF-ASSEMBLY
Mineralogy
Chemistry
Physics

V. Schoeppler, et al., Adv. Mater. 1803855 (2018)
V. Schoeppler, et al., PNAS, 116 (41) 20388-20397 (2019)

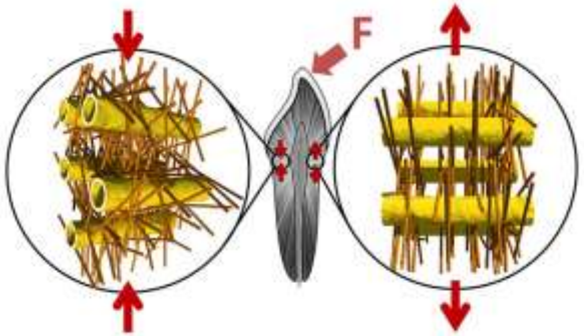
Residual Stresses

Residual strains in biogenic calcite and aragonite



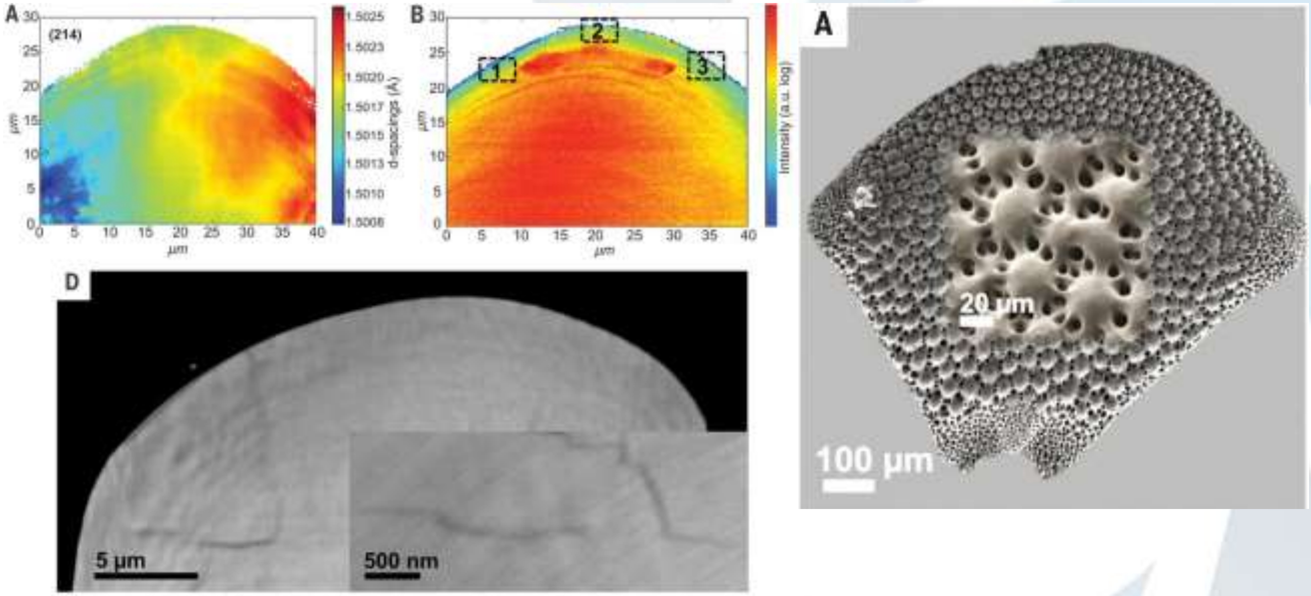
Zolotoyabko E., Adv. Mater. Interfaces, 4, 1600189 (2017)

Residual strains prevents crack propagation



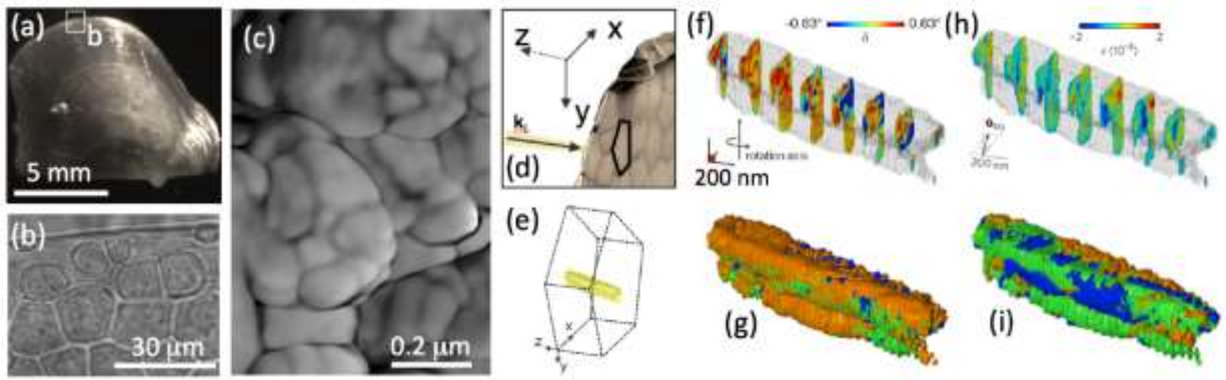
Forien J.B. et al., Nano Letters, 15, 3729–3734 (2015)

Toughening of calcite optical brittle star lenses



Polishchuk I. et al., Science, 8, 358 (2017)

Bragg Ptychography reveals domains in calcite prisms



Mastropietro F. et al., Nature Mat., 16, 946–952 (2017)

BERKELEY LAB | ADVANCED LIGHT SOURCE

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)

non-destructive methods
structure
fast
sensitive methods
“big” volumes
STRESSES
multiscale
lattice information
orientation

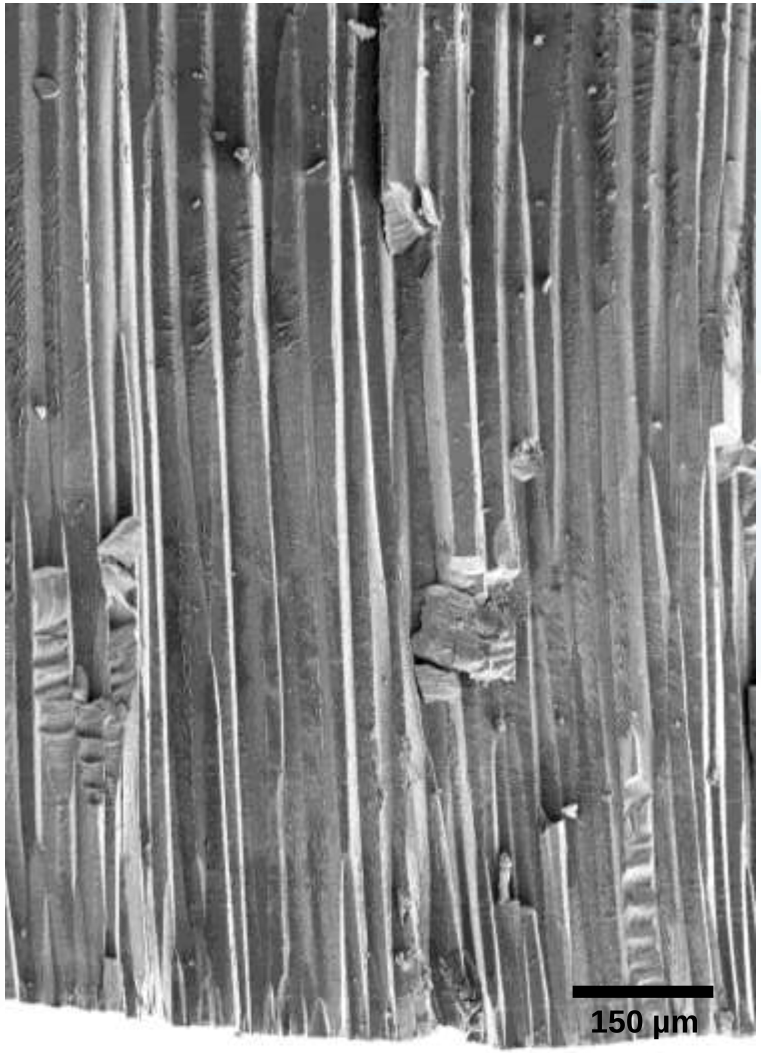
DFXM
Dark Field X-Ray Microscopy

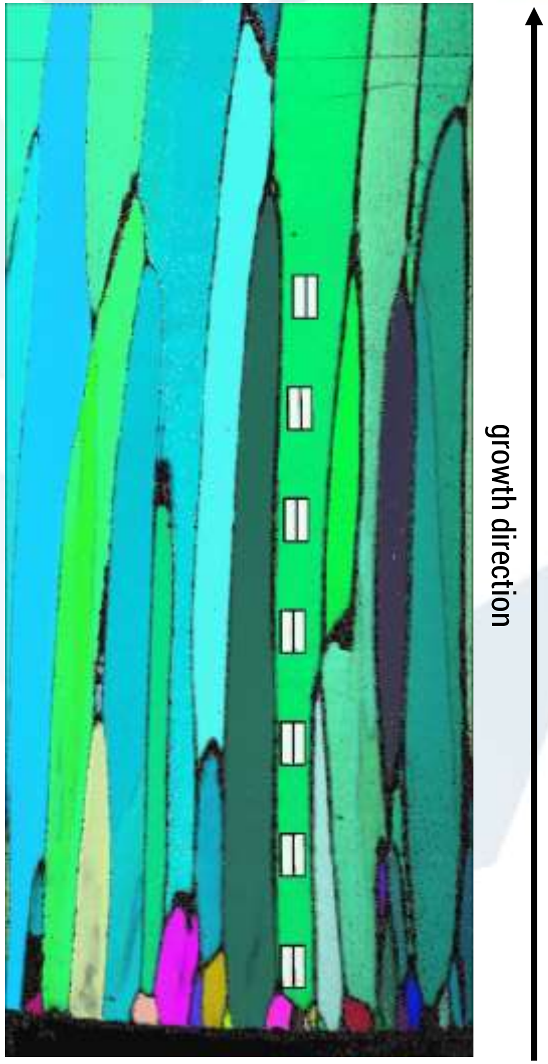
+ Adjustable resolution range (30 nm–300 nm)
+ High angular resolution (~ 0.001 °)
+ Bigger sample sizes (< 0.5 mm)
+ In-situ setups

Samples

Calcite prisms *of Pinna nobilis:*

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

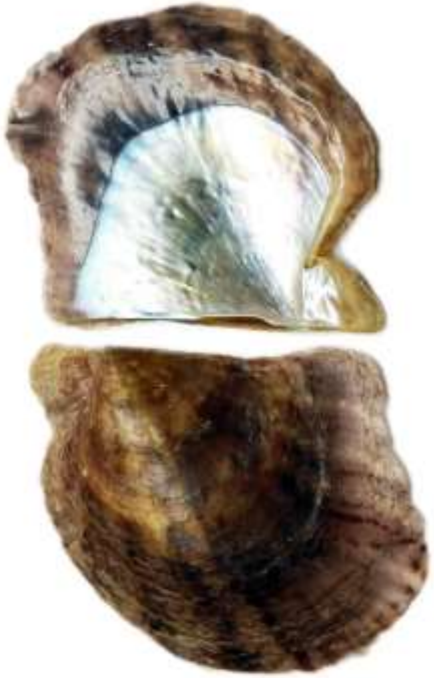


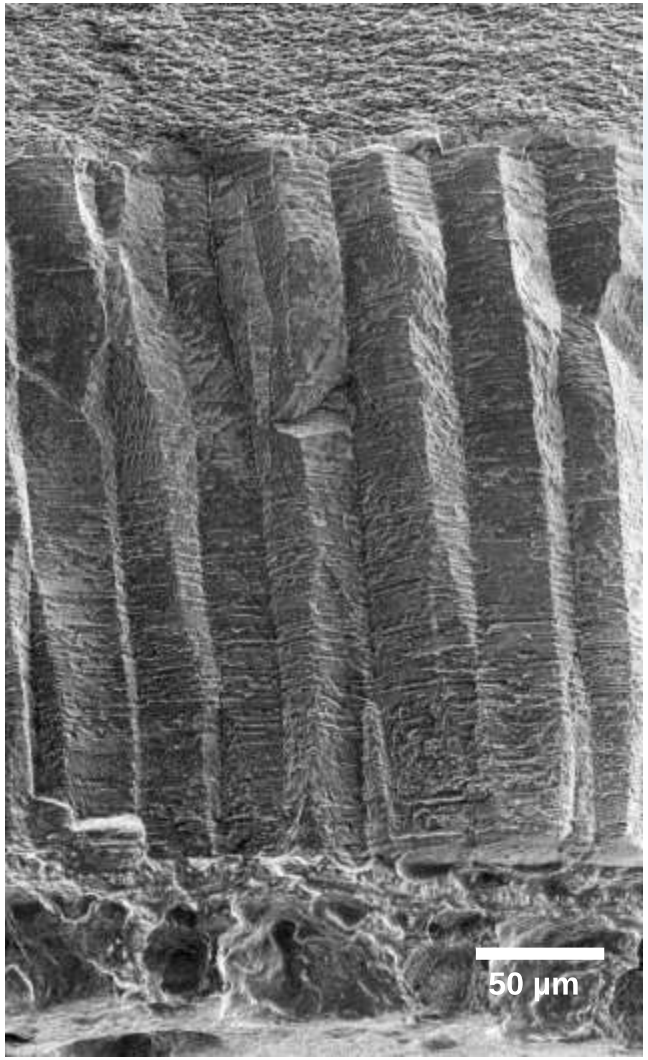


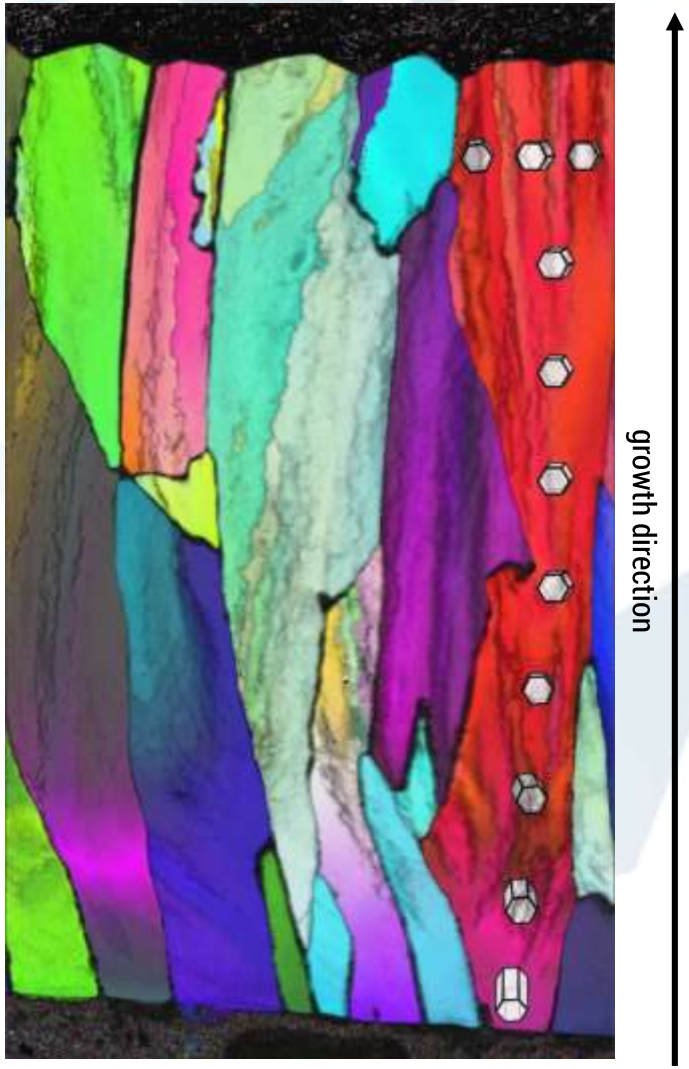
Samples

Calcite prisms *of Pinctada nigra:*

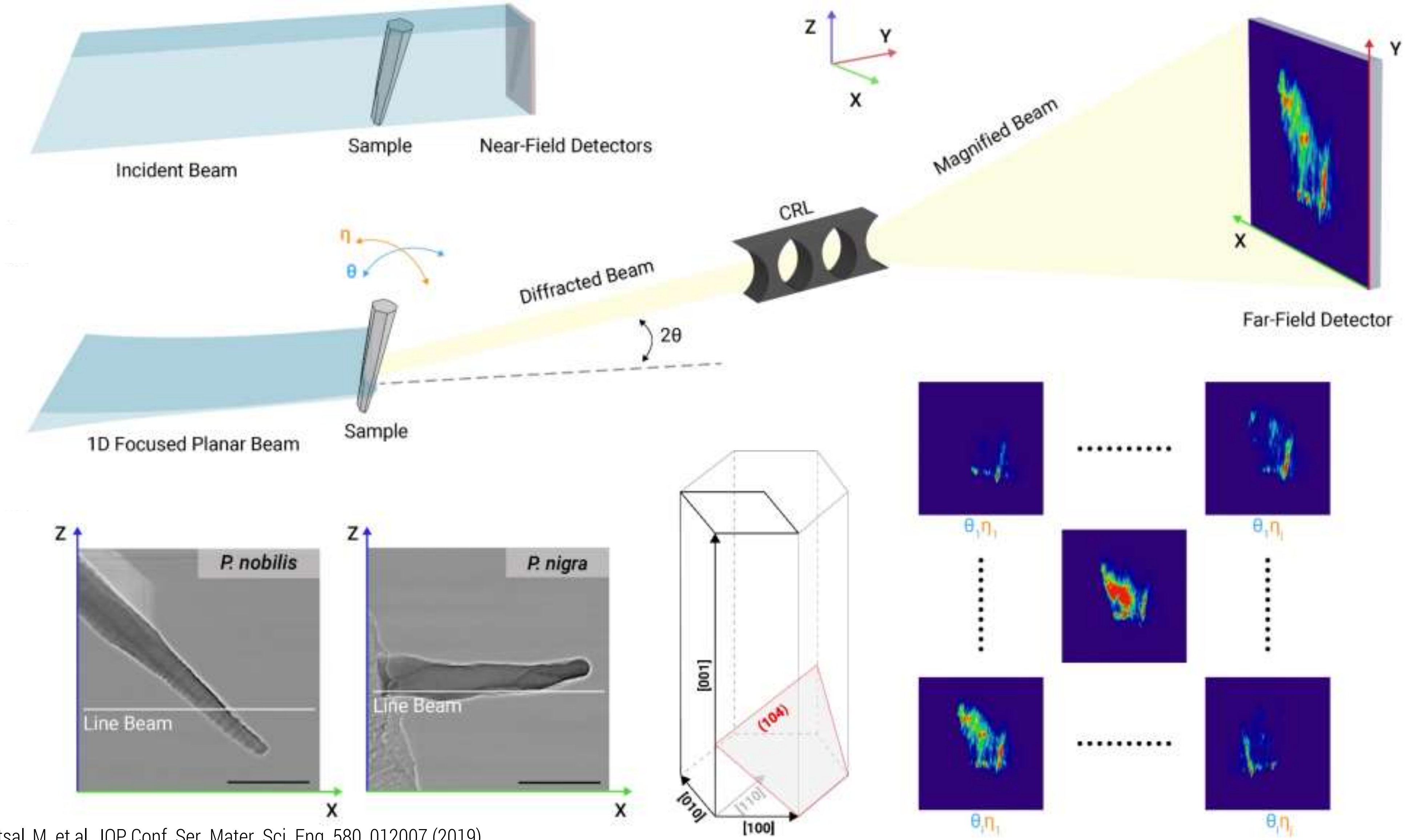
- Initially prisms appear single-crystal-like
- Crystals rotates gradually and split while maintaining the gradual change in orientation
- Total misorientation distribution 10 -20 °







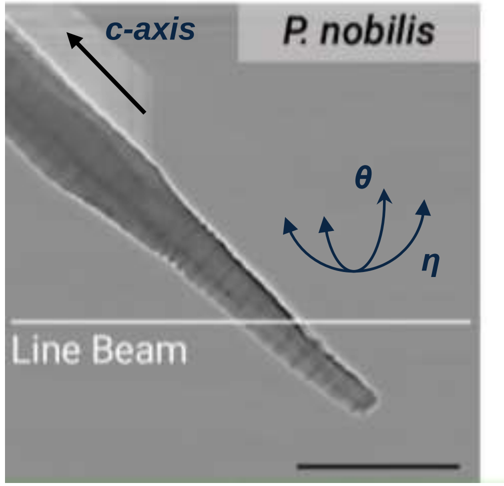
Dark-Field X-Ray Microscopy



Kutsal, M. et al., IOP Conf. Ser. Mater. Sci. Eng. 580, 012007 (2019).

calcite

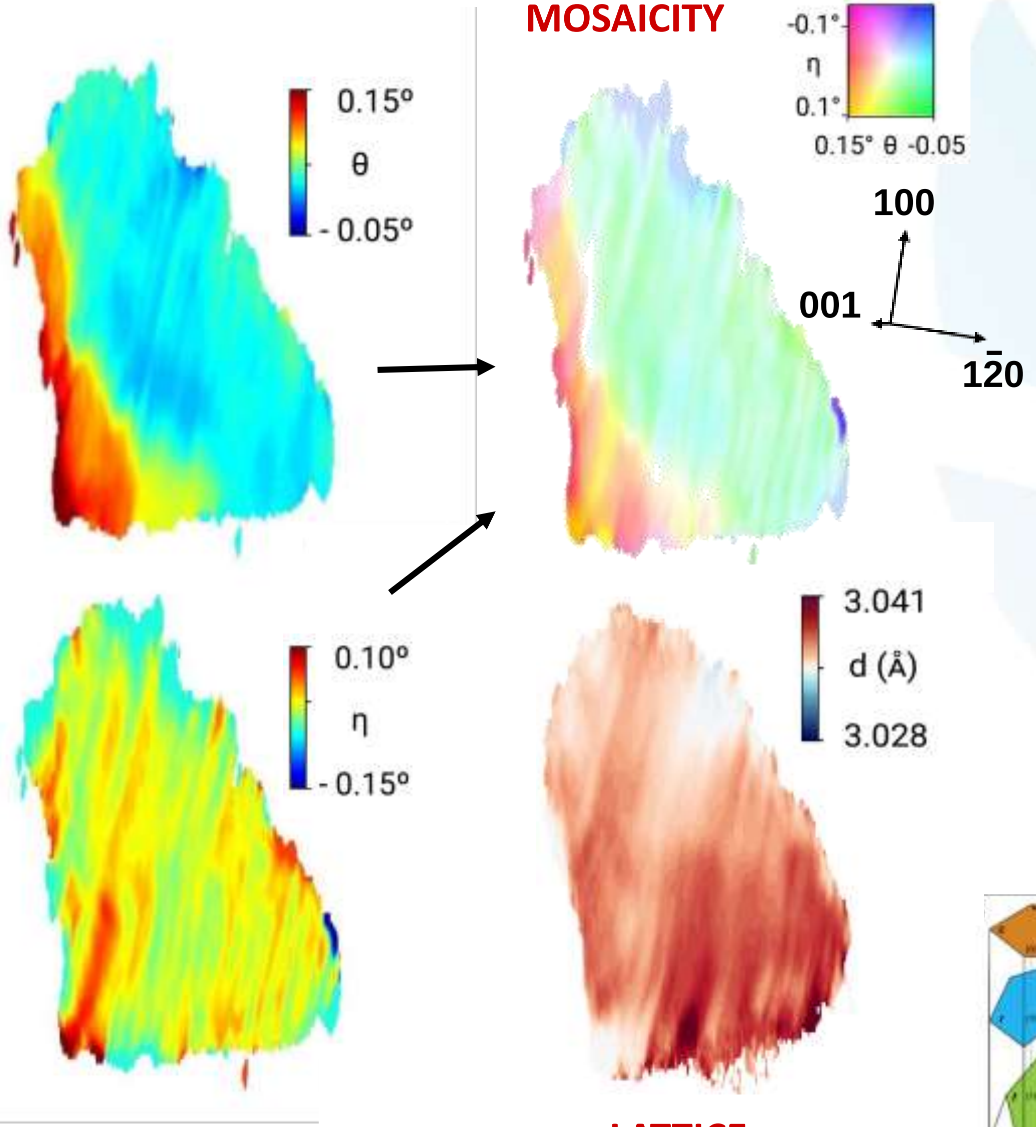
Results *Pinna nobilis*

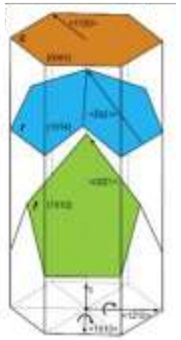


Radiograph of the tip of an isolated *P. nobilis* prism.

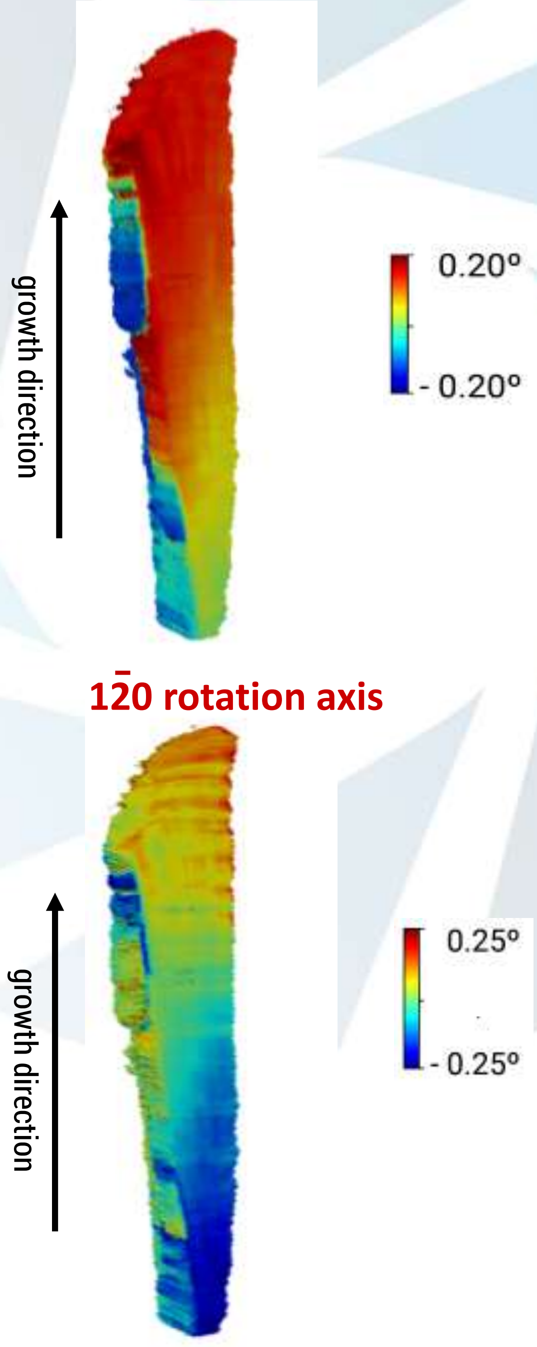
Sample was tilted 45° to fit Bragg conditions for 104 plane. Line scans were collected starting at the tip upwards

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

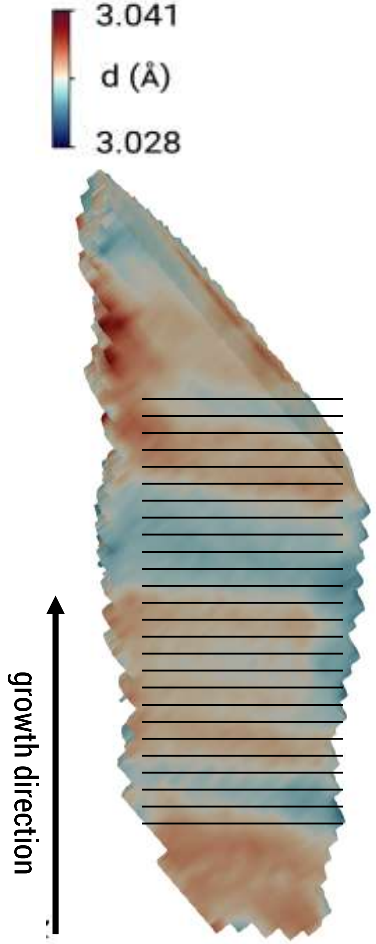




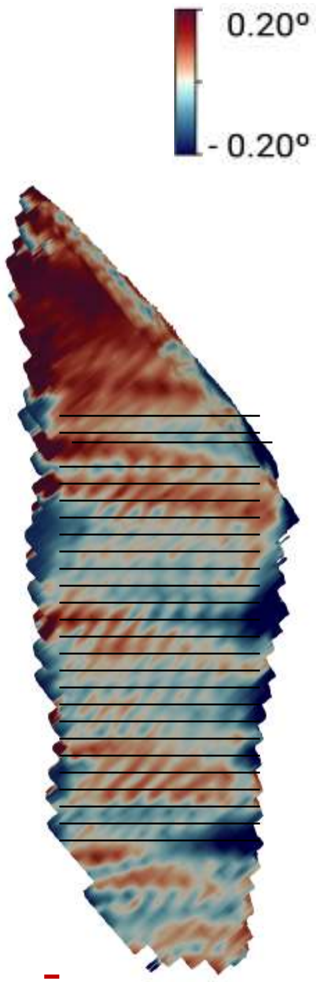
Calcite slip systems



Results *Pinna nobilis*



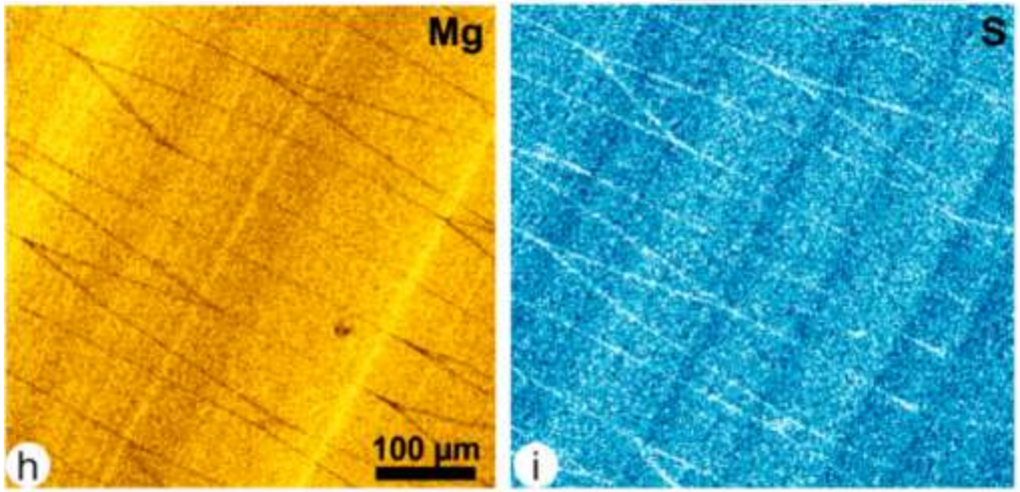
D-space



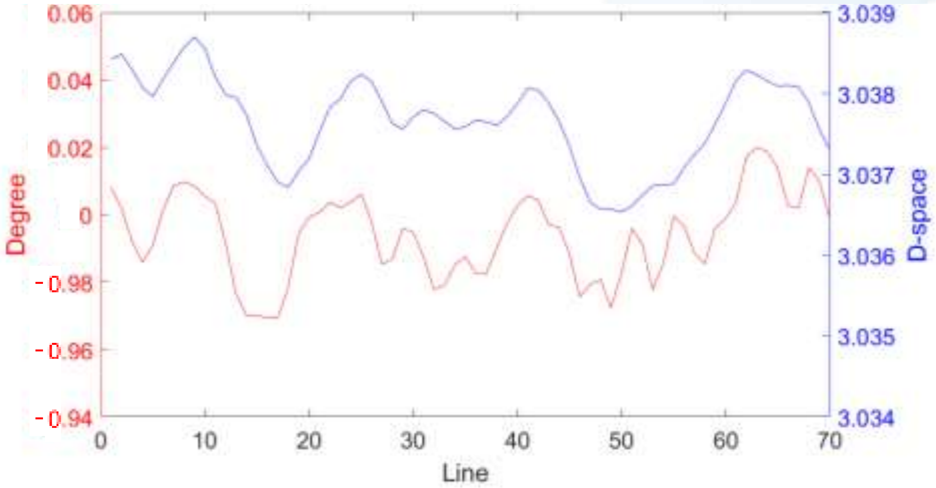
$1\bar{2}0$ rotation axis

GROWTH LINES:

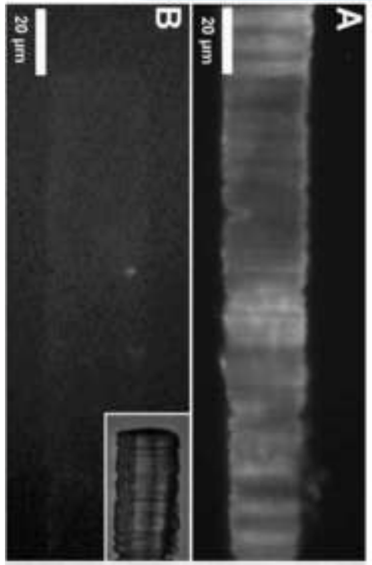
Elemental Variations:



Dauphin, Y. et al., Minerals,8,365 (2018).

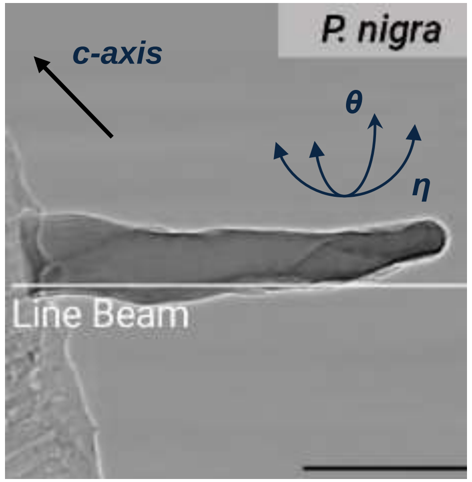


Organic Variations:



Nudelman, F., et al., Faraday Discuss., 136, 15168, (2007)

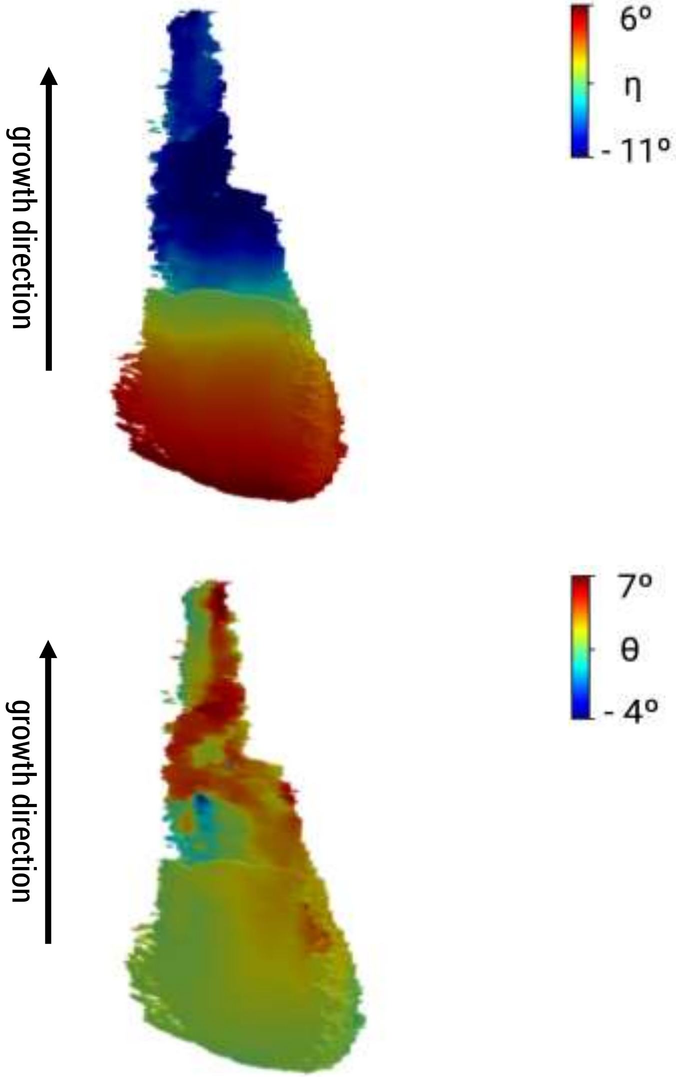
Results *Pinctada nigra*

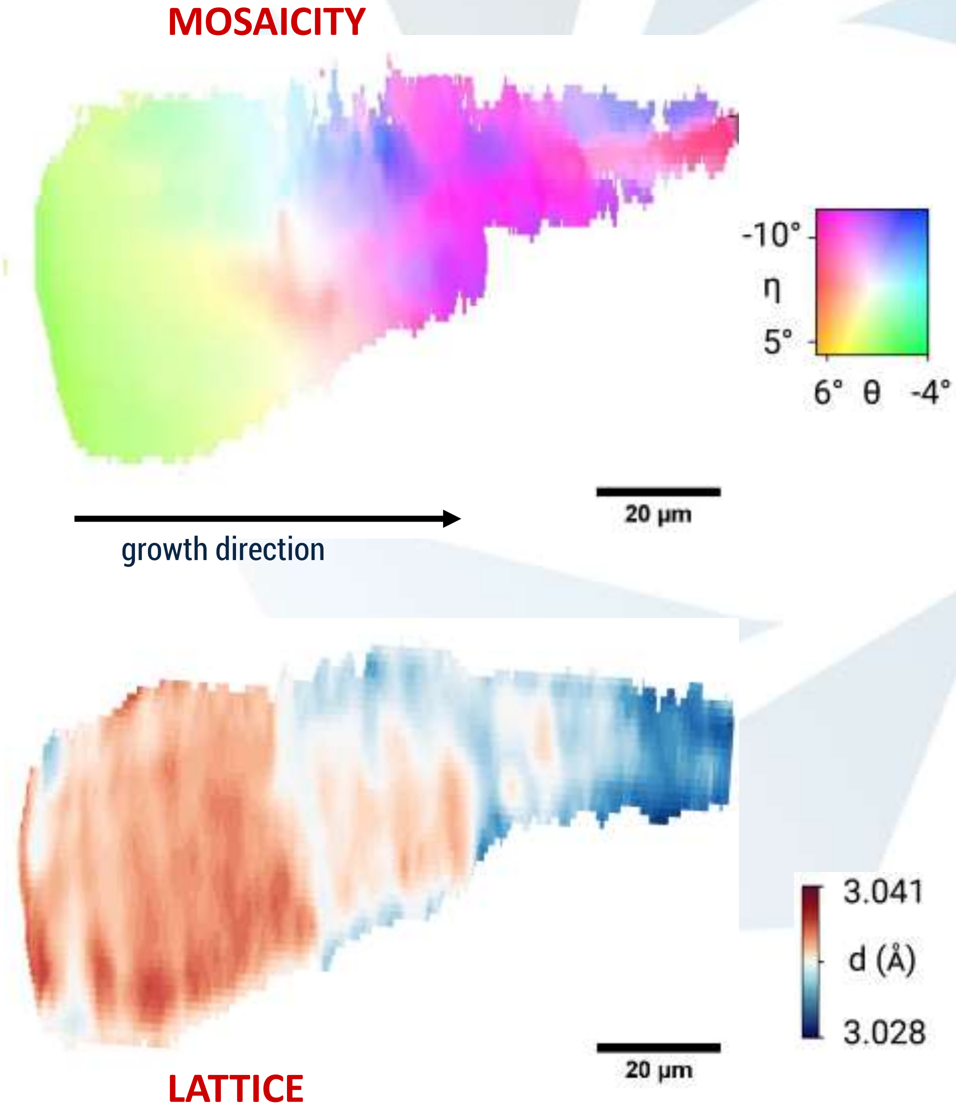


Radiograph of the *P. nigra* prism.

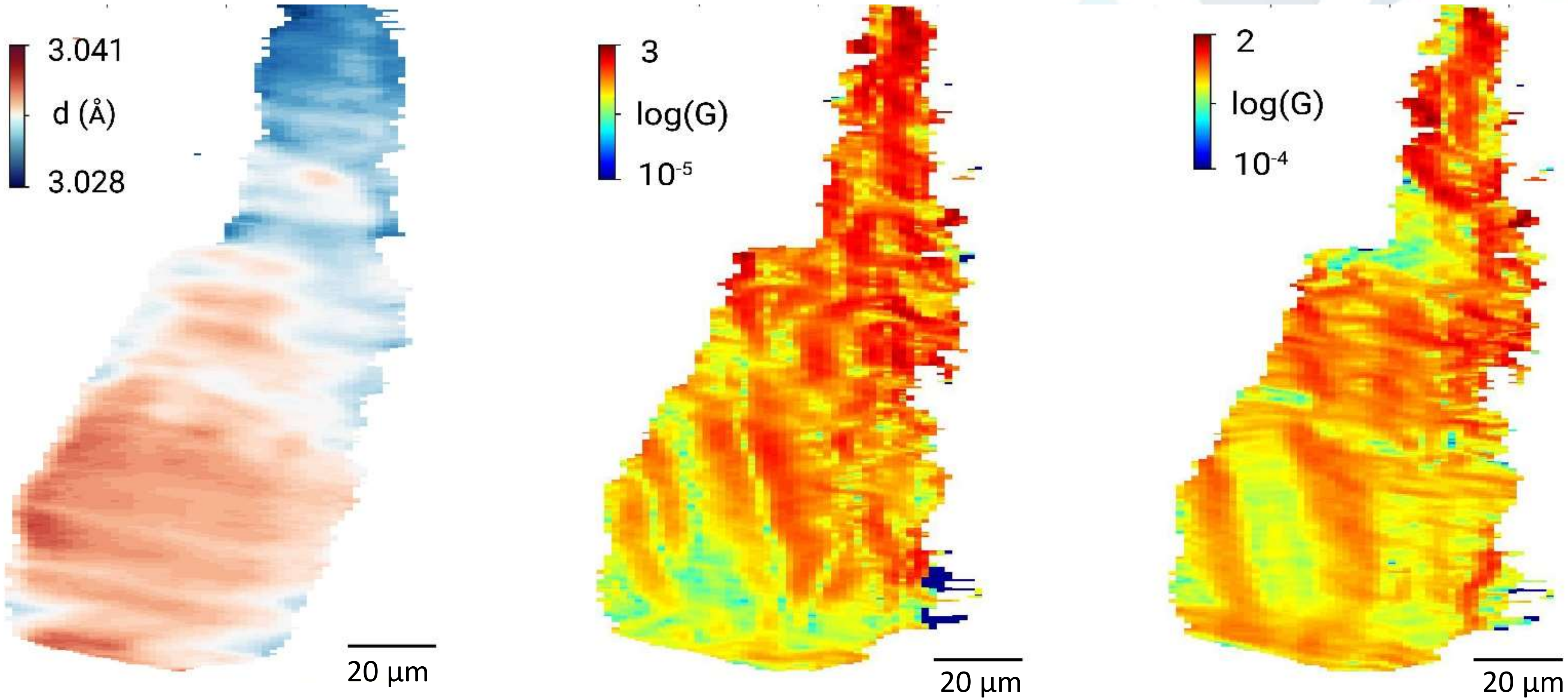
Sample was positioned horizontally to fit bragg conditions for 104 plane and line scans were collected starting at the tip upwards

- ***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 **1$\bar{2}$0 rotation axis** **100 rotation axis**

Conclusions

Results:

- Reveal mosaicity 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

Acknowledgements

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UC Berkeley

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Deputy Director and co-PI
UC Los Angeles

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Thank you for your attention!