

# Coral reef formation from nanometers to kilometers



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  - Chemistry (0%),
  - Materials Science (0%),
  - Geoscience (0%)
- **Lawrence Berkeley National Lab**
  - Chemical Sciences Division

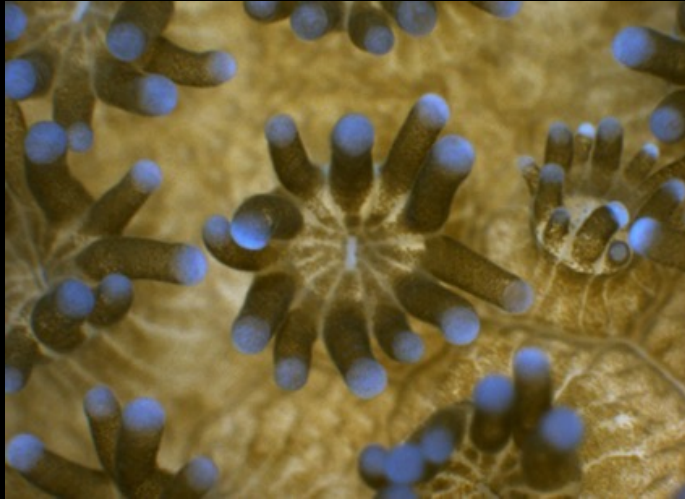
**work supported by**

- **DOE: BES-Geosciences**
- **NSF: DMR-BMAT**
- **BSF, Radcliffe**

*Great Barrier Reef, Australia, 2016*

## hexacorals

*Stylophora pistillata*



## octocorals

*Corallium rubrum*



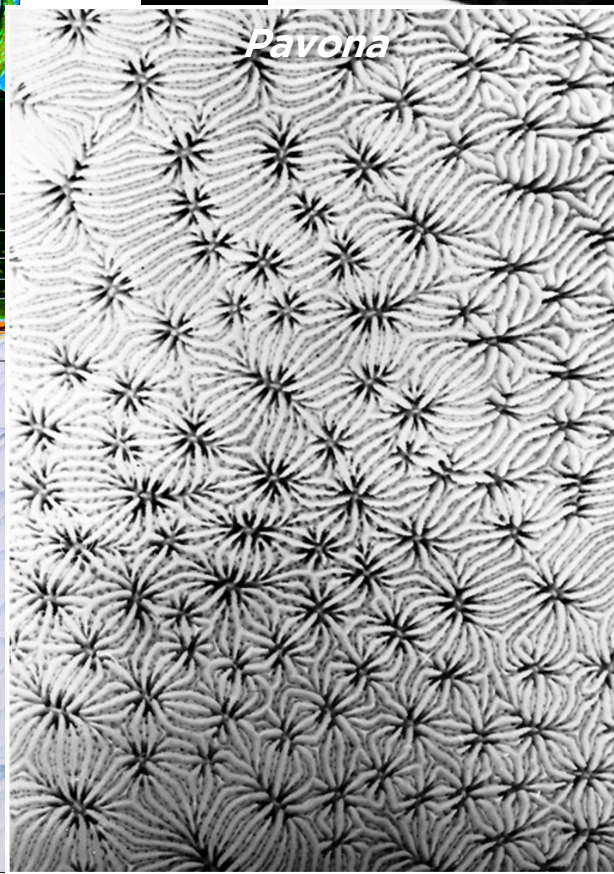
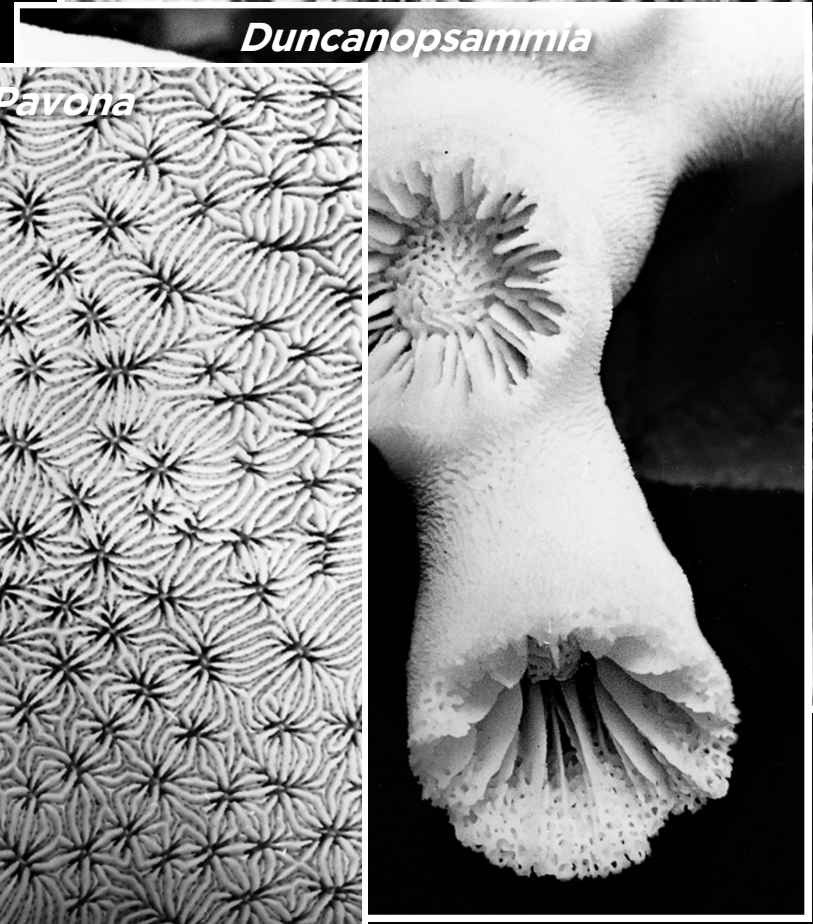
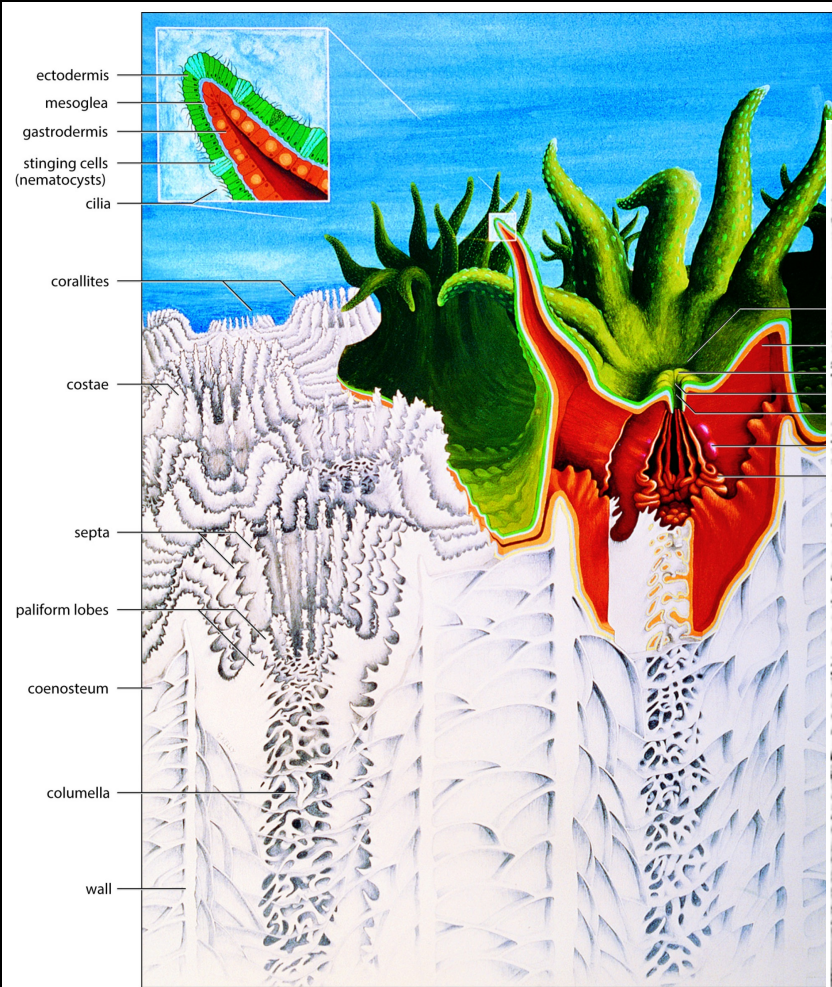
<https://phys.org/news/2018-06-coral-ocean-acidification.html>

[https://goodmoocsk.life/product\\_details/24856555.html](https://goodmoocsk.life/product_details/24856555.html)

[https://en.wikipedia.org/wiki/Balanophyllia\\_elegans](https://en.wikipedia.org/wiki/Balanophyllia_elegans)



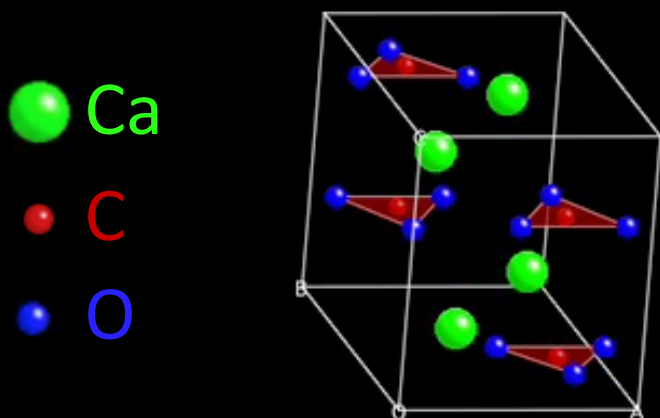
# introduction to corals



JEN Veron, MG Stafford-Smith, E Turak, and LM DeVantier. Corals of the World, 2016.  
<http://www.coralsoftheworld.org/page/structure-and-growth/>

coral skeletons are 99% aragonite ( $\text{CaCO}_3$ ), 1% proteins

aragonite unit cell



DeVol et al. J Phys Chem B 2014

geologic aragonite



<https://www.britannica.com/science/aragonite>



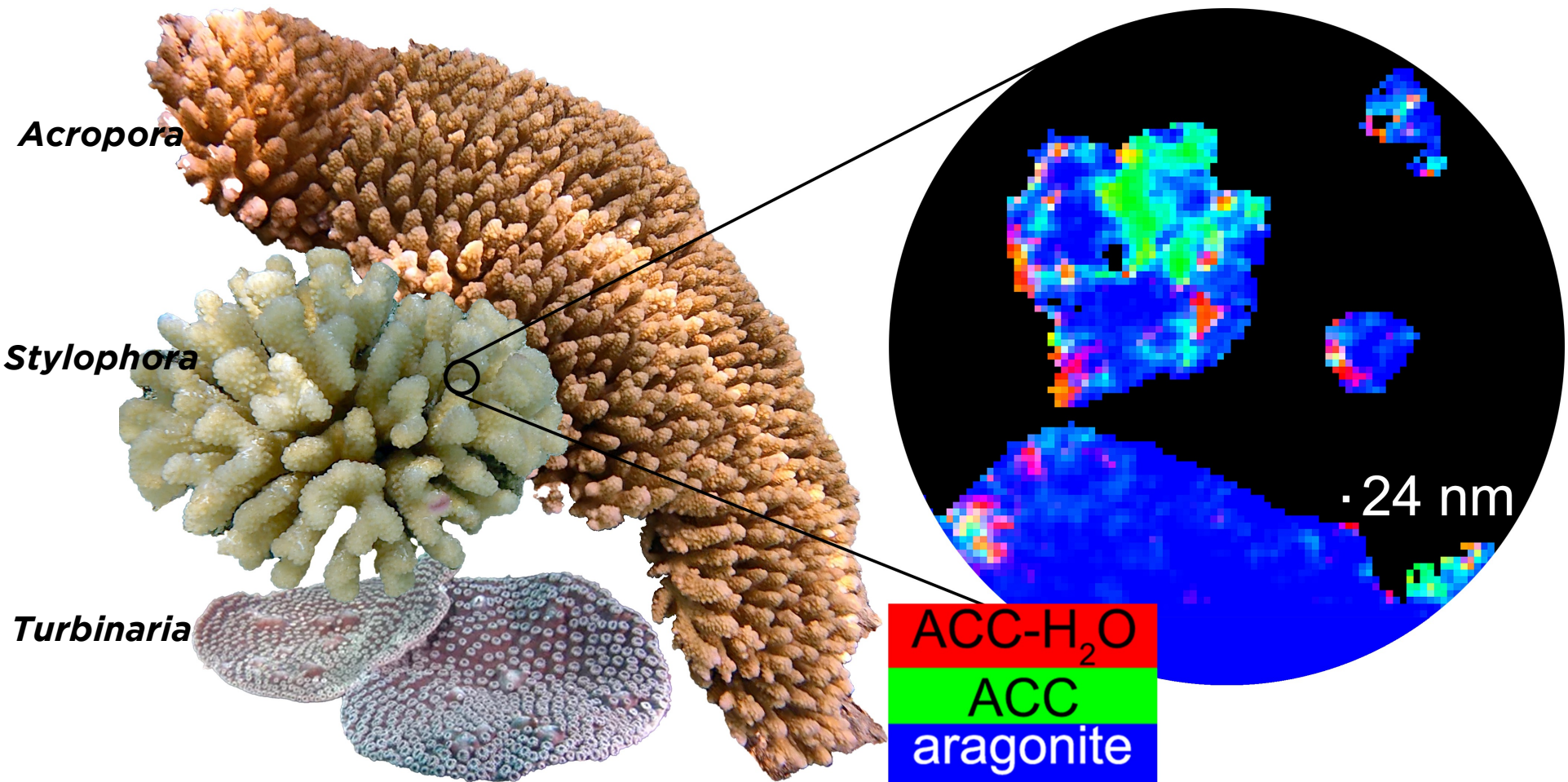


aragonite ( $\text{CaCO}_3$ ) coral skeletons provide the structure of coral reefs

- coral reefs only cover 1% of all ocean floors
  - yet they host 25% of all known marine species
  - they provide coastline protection
  - fishing
  - tourism
  - \$3 billion/year to US economy
  - \$3 trillion/year to world economy
- they are threatened by ocean acidification and warming

*Great Barrier Reef, Australia, 2016*

# amorphous calcium carbonate (ACC) precursors



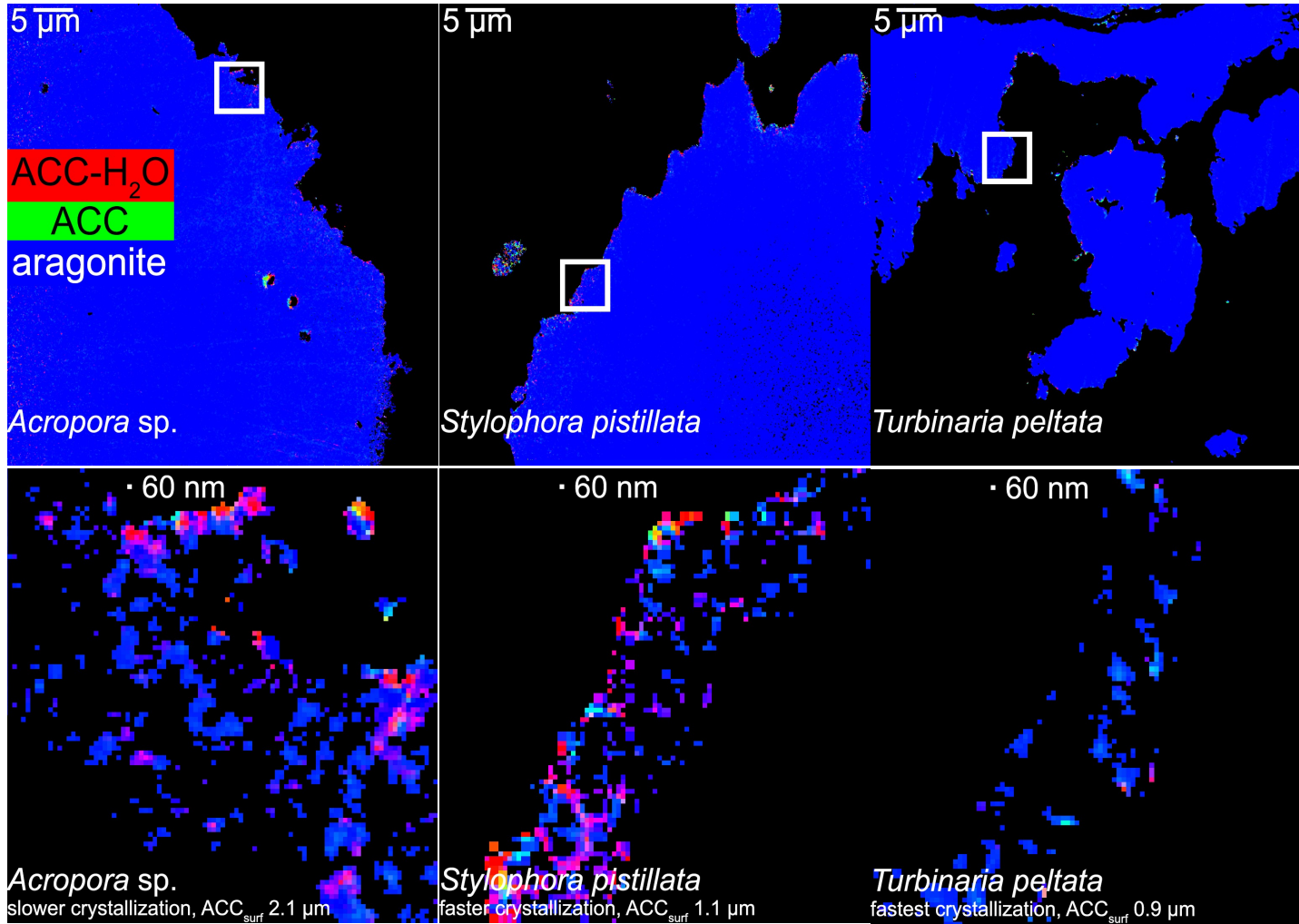
CA Schmidt, CA Stifler, EL Luffey, BI Fordyce, A Ahmed, G Barreiro Pujol, CP Breit, SS Davison, CN Klaus, IJ Koehler, IM LeCloux, C Matute Diaz, CM Nguyen, V Quach, JS Sengkhamee, EJ Walch, MM Xiong, E Tambutté, S Tambutté, T Mass, PUPA Gilbert. JACS 2022



# amorphous precursors on the surface of coral skeletons



Connor A. Schmidt  
UW-Physics, Chemistry



CA Schmidt, CA Stifler, EL Luffey, BI Fordyce, A Ahmed, G Barreiro Pujol, CP Breit, SS Davison, CN Klaus, IJ Koehler, IM LeCloux, C Matute Diaz, CM Nguyen, V Quach, JS Sengkhamee, EJ Walch, MM Xiong, E Tambutté, S Tambutté, T Mass, PUPA Gilbert. JACS 2022

the key to saving coral reefs from climate change is to understand how corals form their skeletons



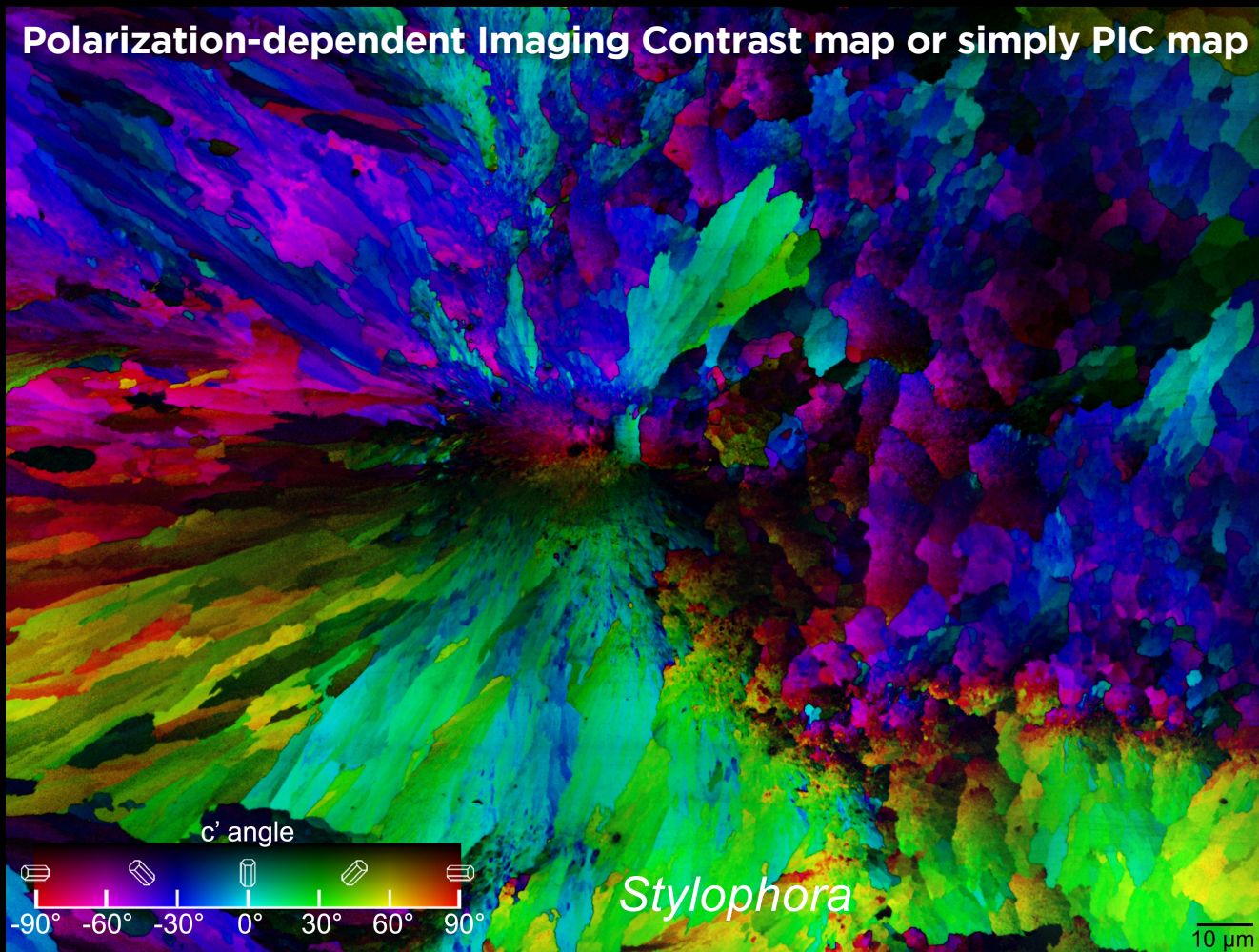
Dr. Chang-Yu Sun  
UW-Physics, Materials Science

20 nm

*Micromussa*

C-Y Sun, CA Stifler, RV Chopdekar, CA Schmidt, G Parida, V Schoeppler, BI Fordyce, JH Brau, T Mass, S Tambutte, PUPA Gilbert. PNAS 2020

Polarization-dependent Imaging Contrast map or simply PIC map

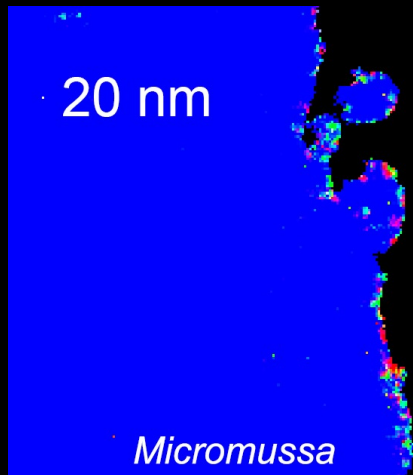


C-Y Sun, L Gránásy, CA Stifler, JAY Zhang, T Zaquin, T Mass, S Goffredo, G Falini, MA Marcus, R Chopdekar, T Pusztai, JC Weaver, PUPA Gilbert. Acta Biomaterialia 2021

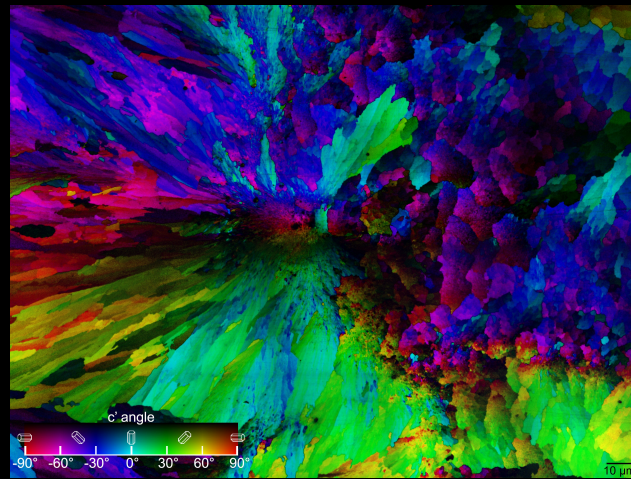


they all work at the nanoscale, but many corals in parallel form entire reefs

nm



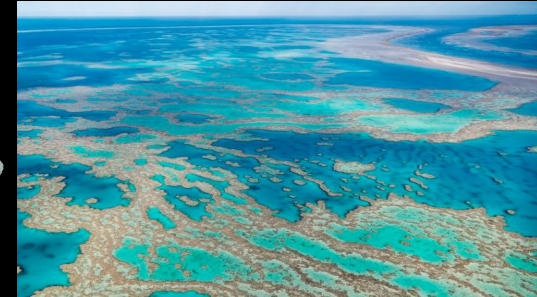
μm



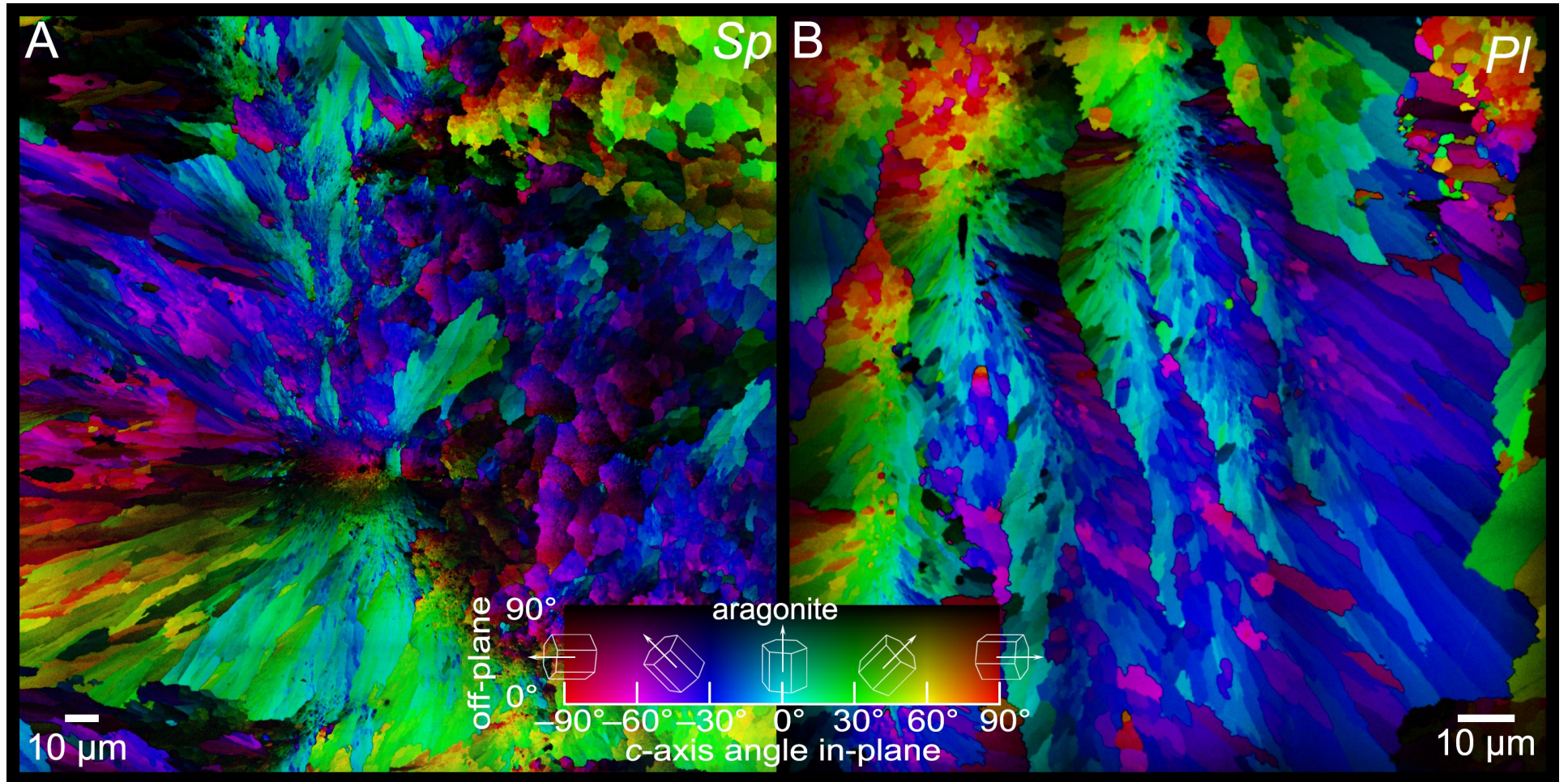
cm



km



**all coral skeletons are spherulitic**  
**Polarization-dependent Imaging Contrast maps (PIC maps)**

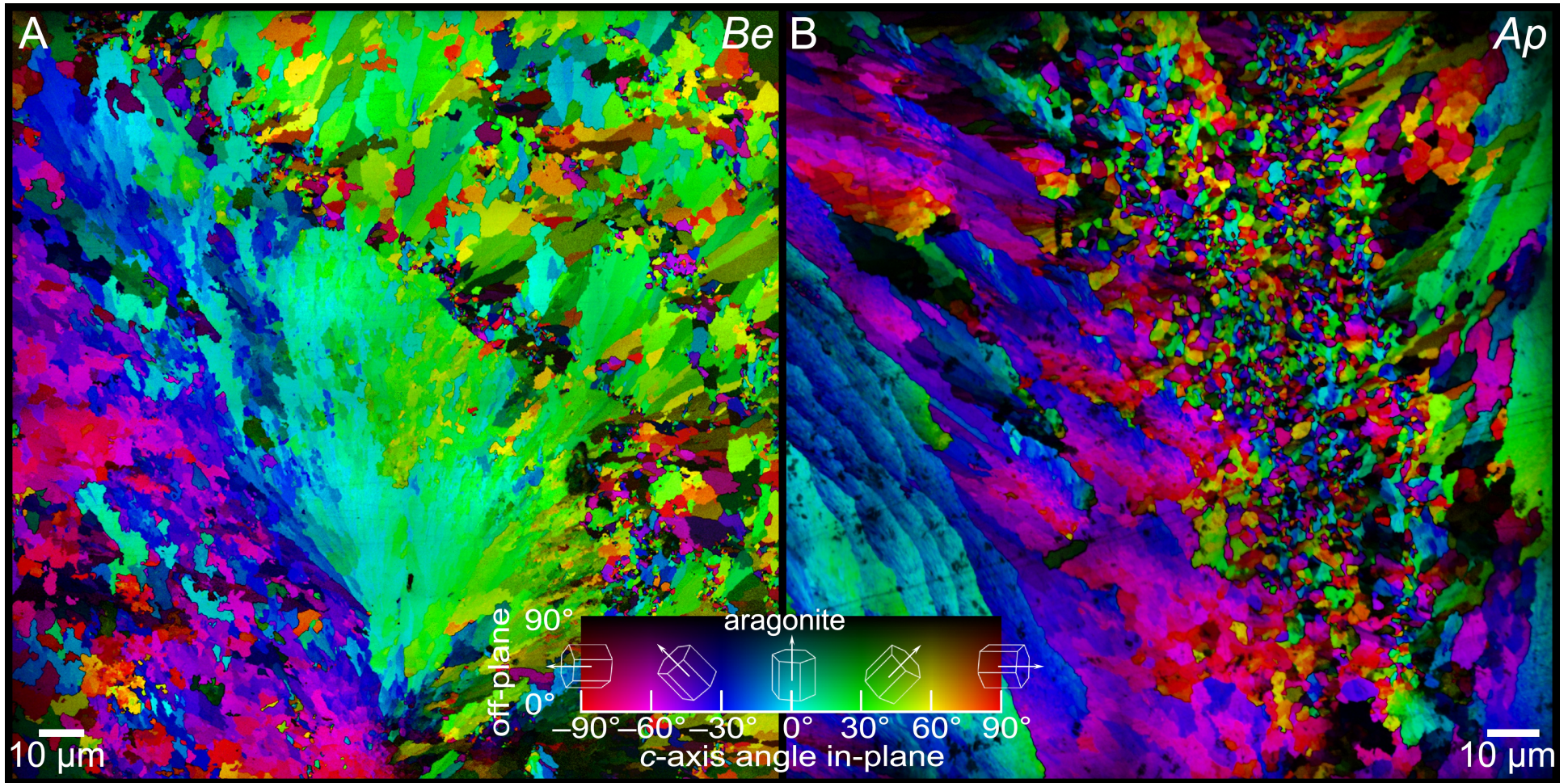


**PUPA Gilbert, MRS Bulletin 2023**

**Sun et al. PNAS 2020, Sun et al. Acta Biomaterialia 2021**



**all coral skeletons are spherulitic**  
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**PUPA Gilbert, MRS Bulletin 2023**

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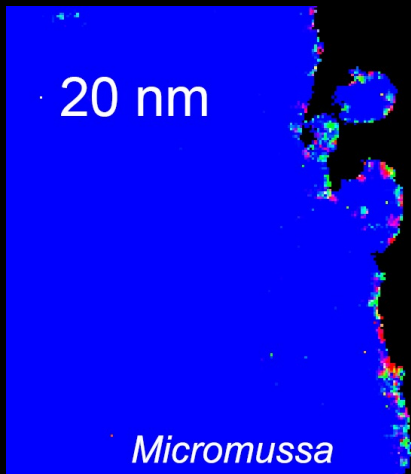
## why spherulites?

materials properties are better along c-axis than a,b-axes

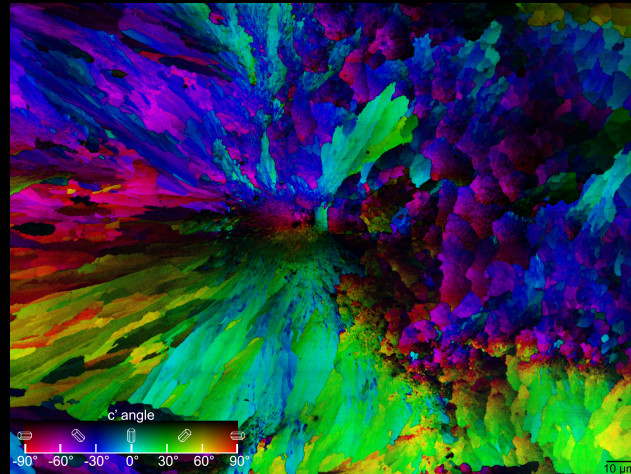
- hardness (resistance to indentation)
- stiffness (AKA Young's modulus or E, resistance to bending or stretching)
- yield strength (resistance to permanent deformation)
- tensile strength (resistance to breaking)
- toughness (resistance to fracture)

thus, spherulitic structure of coral skeletons makes it possible to build entire reefs, from nm to km

nm



μm



cm



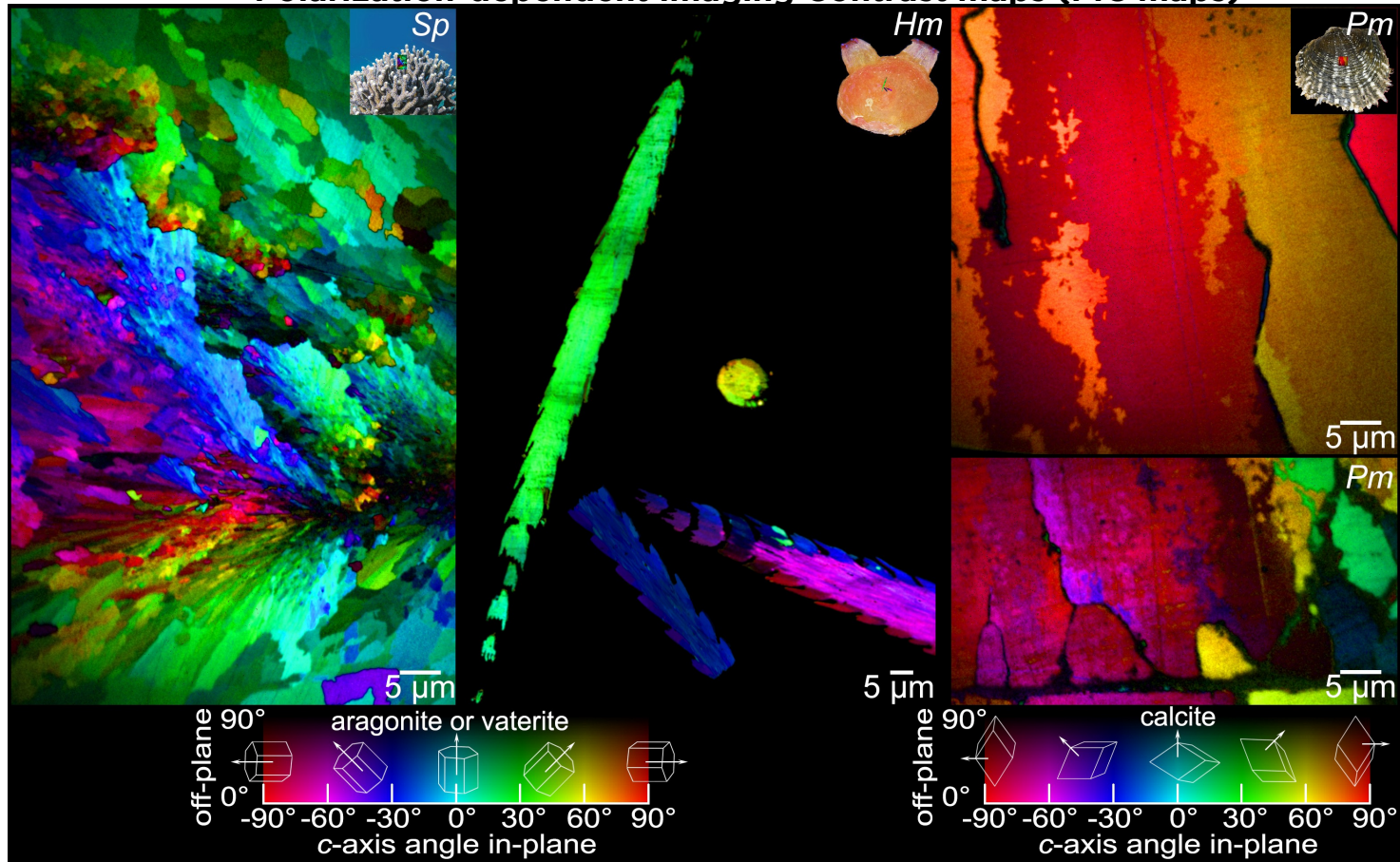
km





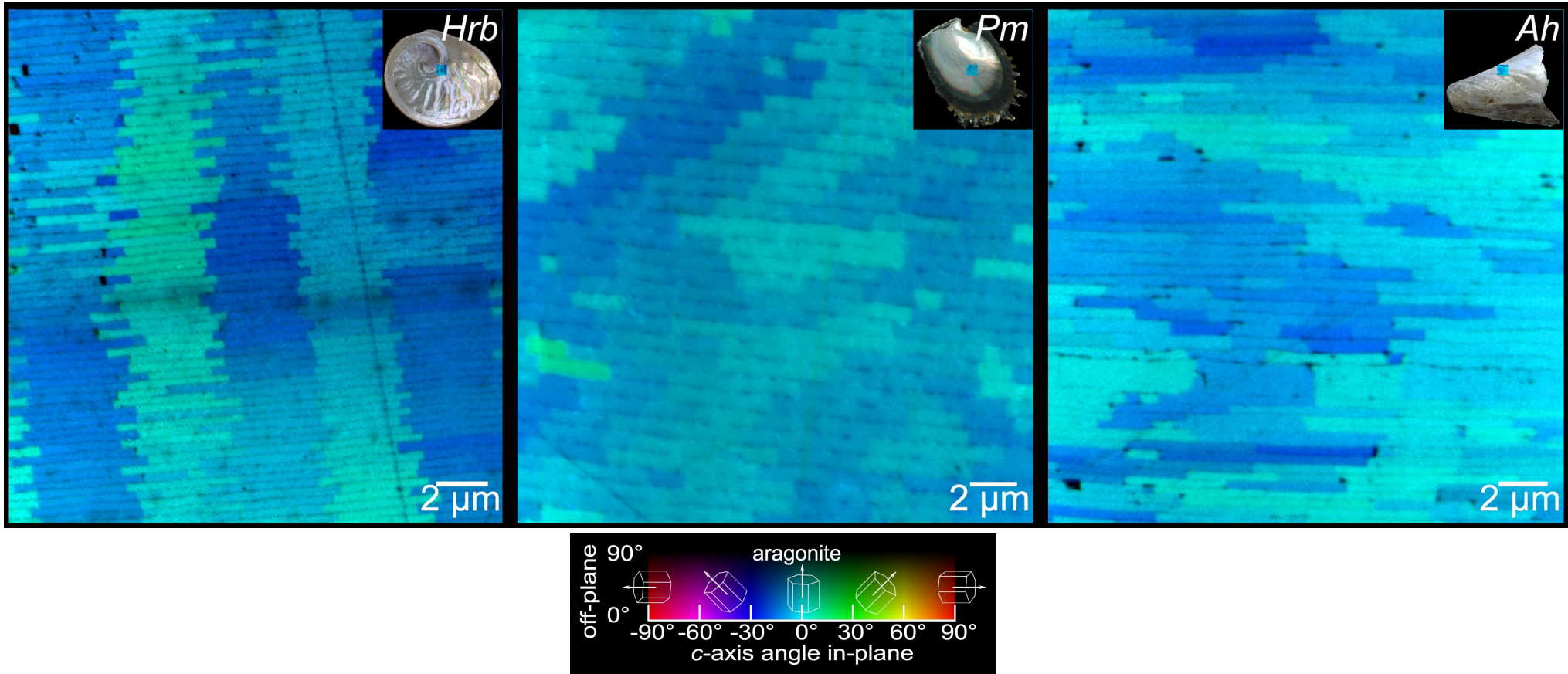
not only coral skeletons, many other biominerals have slight misorientation of adjacent crystals.

Polarization-dependent Imaging Contrast maps (PIC maps)



AJ Lew, CA Stifler, A Tits, CA Schmidt, A Scholl, A Cantamessa, L Müller, Y Delaunois, P Compère, D Ruffoni, MJ Buehler, PUPA Gilbert. *Advanced Materials* 35, 2300373 (2023)

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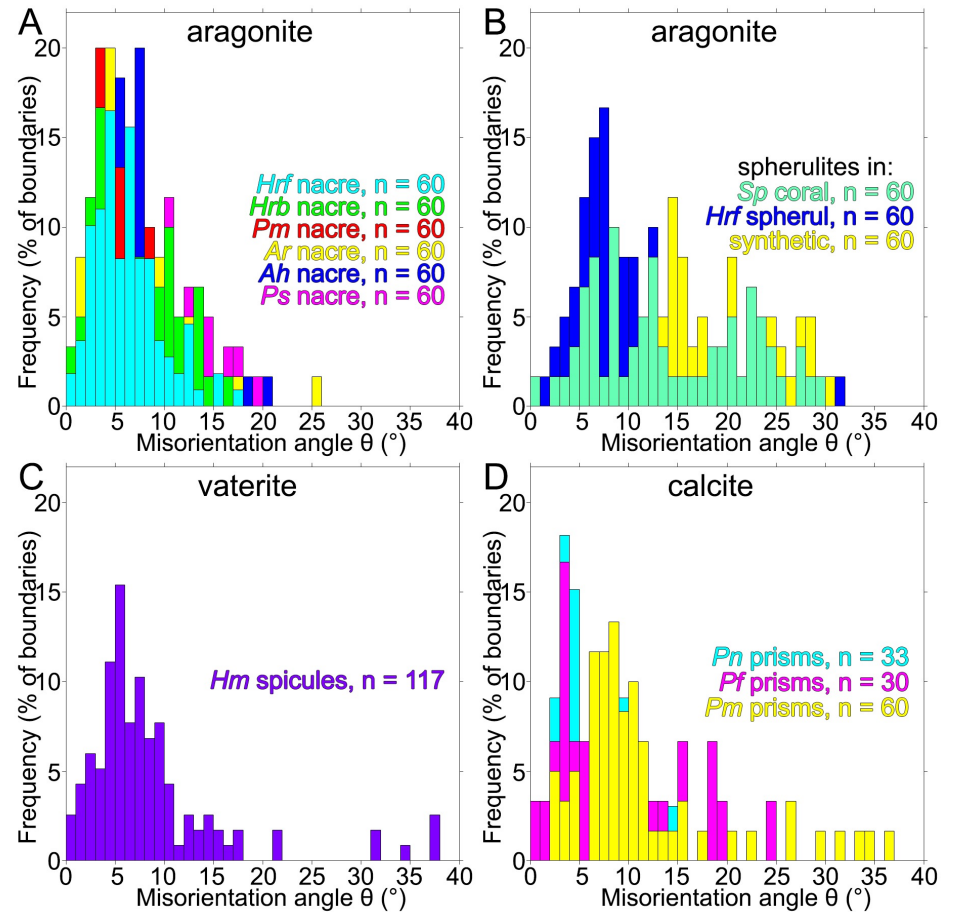
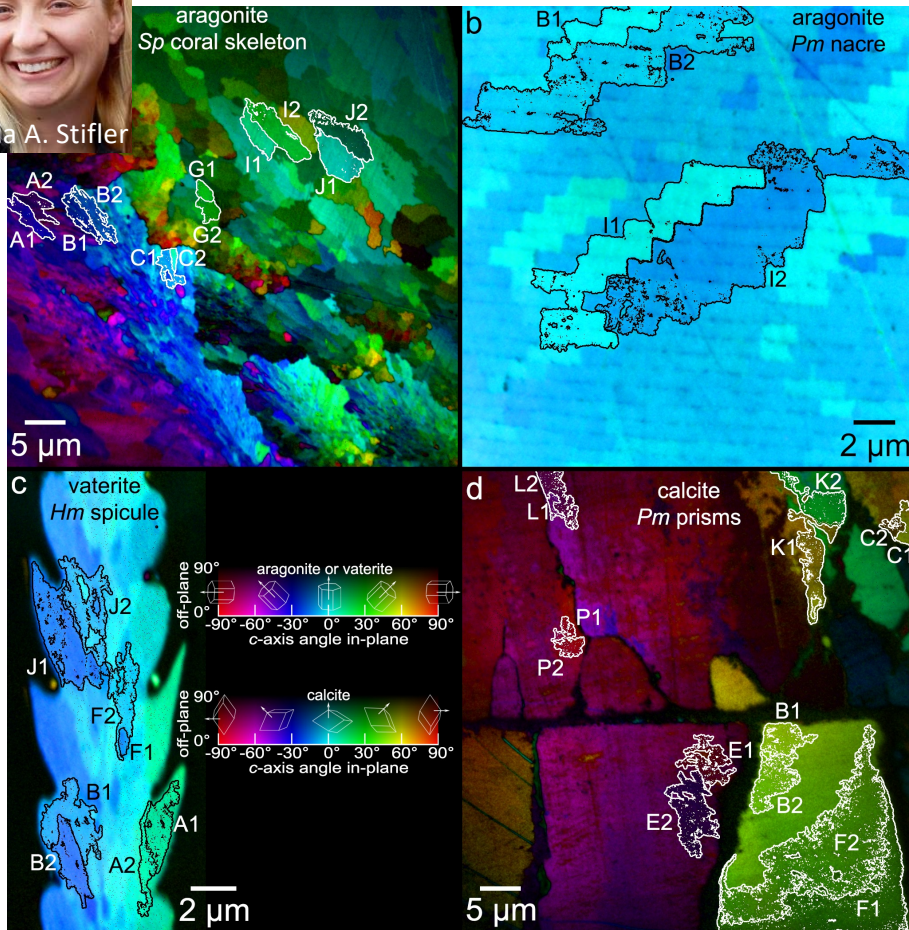
AJ Lew, CA Stifler, A Tits, CA Schmidt, A Scholl, A Cantamessa, L Müller, Y Delaunois, P Compère, D Ruffoni, MJ Buehler, PUPA Gilbert. *Advanced Materials* 35, 2300373 (2023)





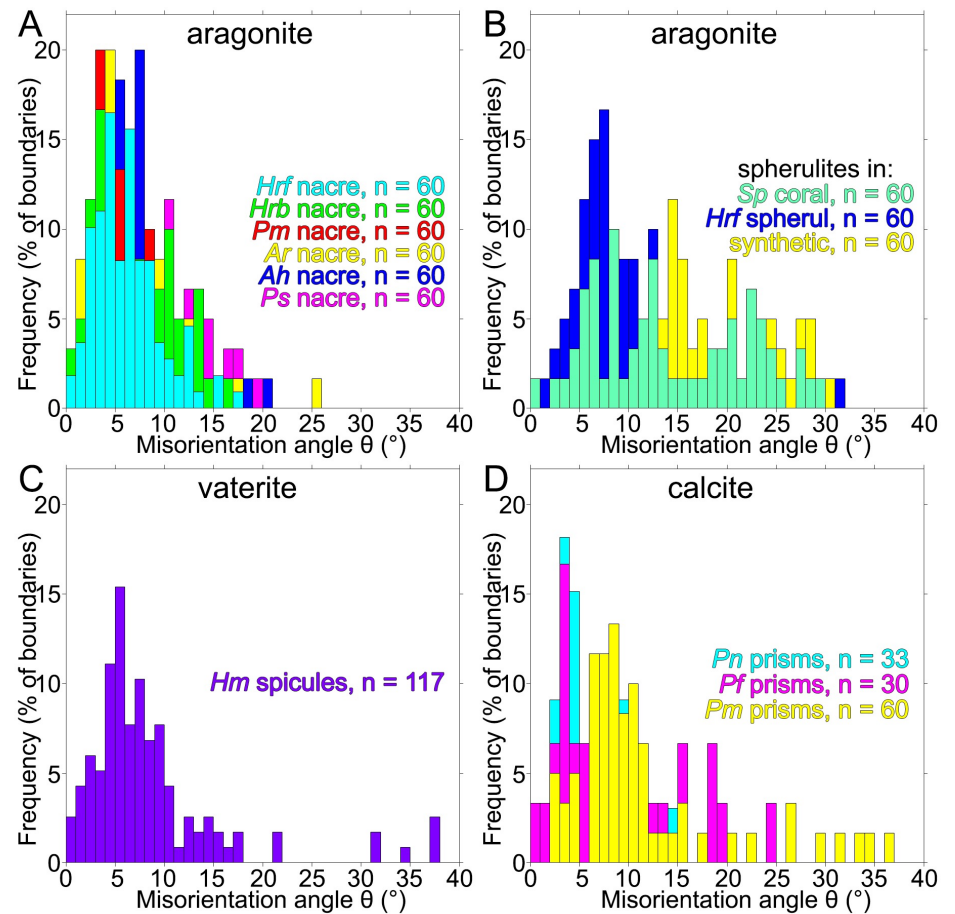
Cayla A. Stifler

## diverse biominerals have slight misorientation (1°-40°) of adjacent crystals



AJ Lew, CA Stifler, A Tits, CA Schmidt, A Scholl, A Cantamessa, L Müller, Y Delaunois, P Compère, D Ruffoni, MJ Buehler, PUPA Gilbert. *Advanced Materials* 35, 2300373 (2023)

diverse biominerals have slight misorientation ( $1^{\circ}$ - $40^{\circ}$ ) of adjacent crystals



is slight misorientation useful?  
 does it improve a materials property?

AJ Lew, CA Stifler, A Tits, CA Schmidt, A Scholl, A Cantamessa, L Müller, Y Delaunois, P Compère, D Ruffoni, MJ Buehler, PUPA Gilbert. *Advanced Materials* 35, 2300373 (2023)



**slight misorientation (<40°) of aragonite (CaCO<sub>3</sub>) bicrystals makes cracks deflect at grain boundaries, toughens the biomineral**

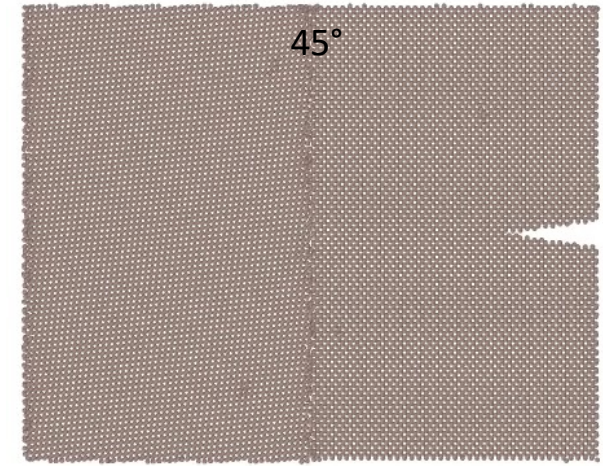
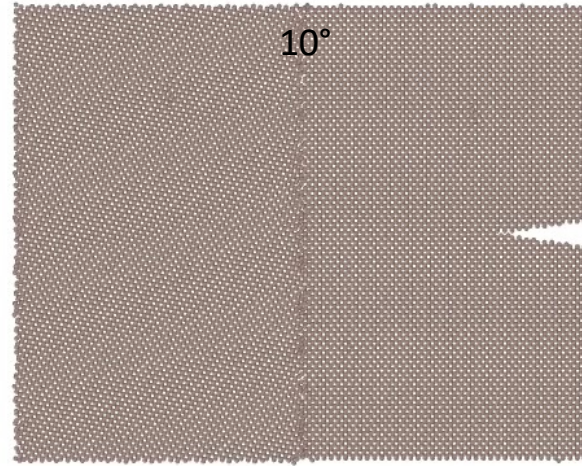
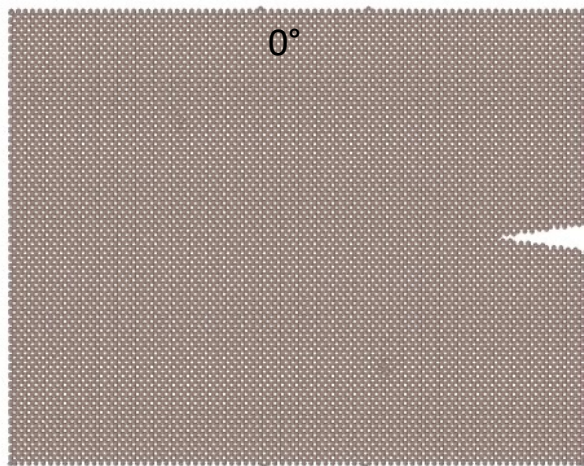
**MD simulations done by Andrew J. Lew, Markus J. Buehler (MIT)**



Andrew J.  
Lew



Markus J.  
Buehler



**AJ Lew, CA Stifler, A Tits, CA Schmidt, A Scholl, A Cantamessa, L Müller, Y Delaunois, P Compère, D Ruffoni, MJ Buehler, PUPA Gilbert. *Advanced Materials* 35, 2300373 (2023)**

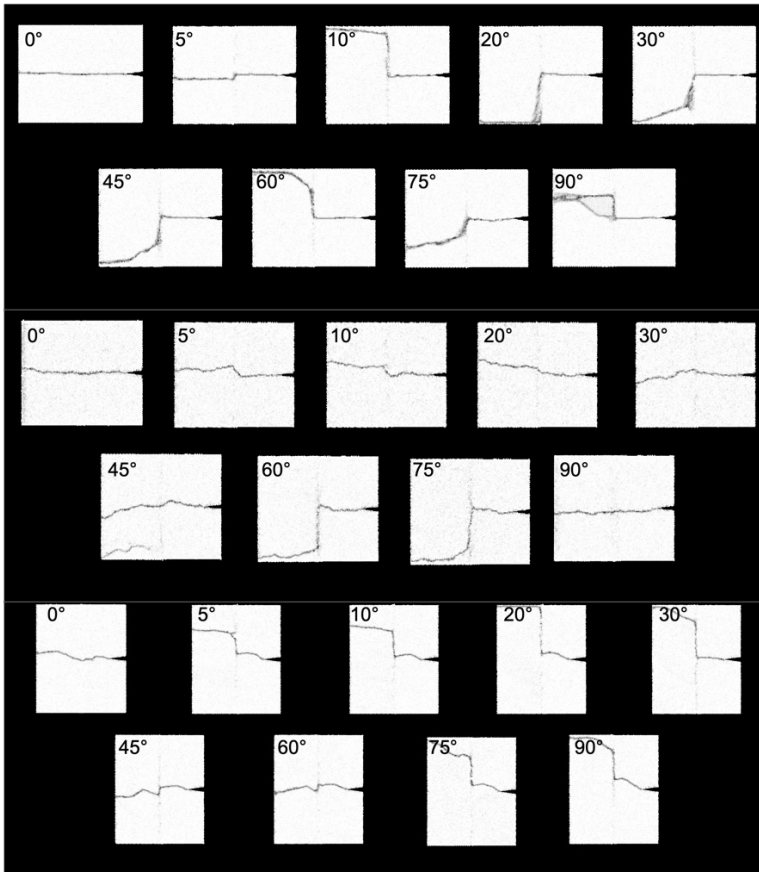
**toughness = area under the stress-strain curve (MD simulations)**  
**from zero strain to complete fracture**

Lew et al. *Adv Mater* 2023

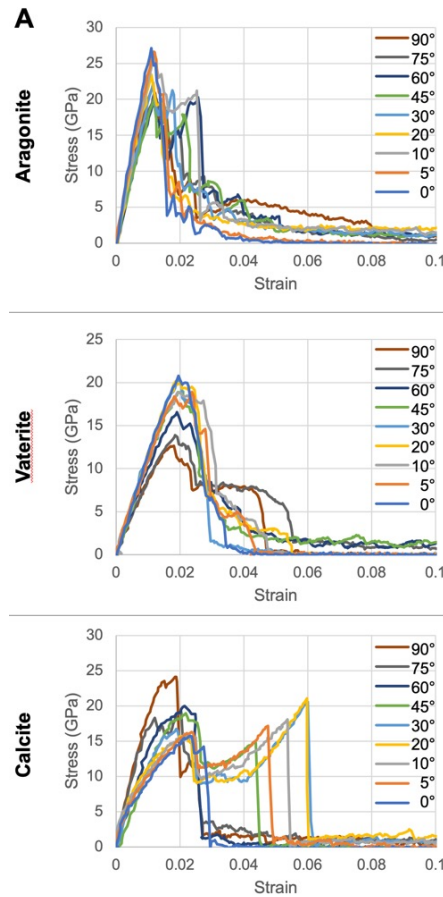


Andrew J. Lew

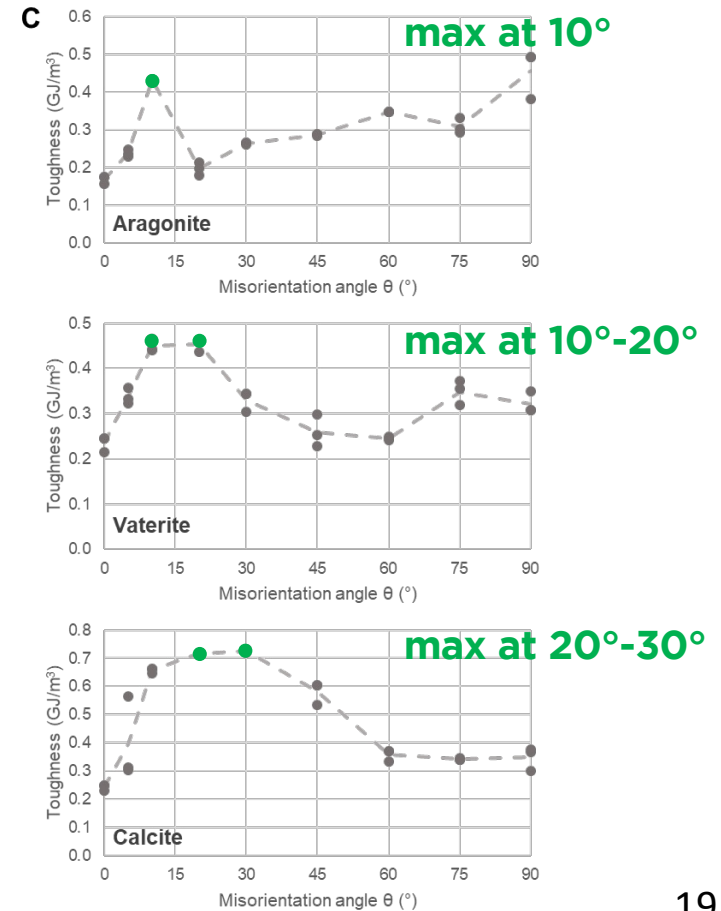
**MD simulations of bicrystals**



**stress-strain curves**



**toughness vs.  $\theta$**





**Thus, slight misorientation ( $1^{\circ}$ - $40^{\circ}$ ) in coral skeletons makes them tougher  
contributing coral skeletons' evolutionary success,  
and formation of entire coral reef ecosystems**



**Image from Wikimedia**



# thanks to my group



Connor A. Schmidt  
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Isabelle M. LeCloux  
UW-Physics, Chem E



Chang-Yu Sun  
UW-Physics, Mat Sci



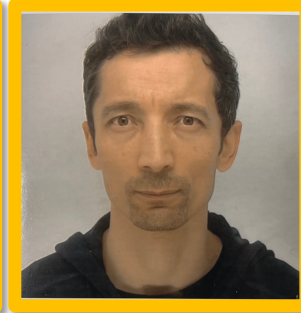
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Advanced Light Source



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Evan J. Walch



Maddie Patton



Annie Purisch



Jaden Sengkamee



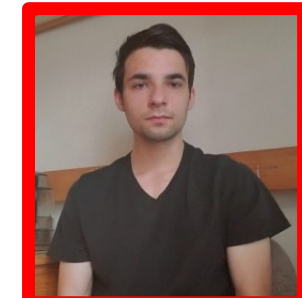
Virginia Quach



CP Breit



Connor L. Foust



Andrii Hopanchuk



Isaac Koehler



Samantha Anglemeyer



Christopher Fan



Mengtian Yang



Tarak Sristy



Shreya Vattem



Gwen Wieland 21



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Yael Politi  
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Andreas Scholl  
Advanced Light Source



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MIT



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U Pittsburgh



László Gránásy  
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Budapest, Hungary





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