Biomineralization

Pupa Gilbert
Departments of Physics (100%), Chemistry (0%), Materials Science (0%), Geoscience (0%)
UW-Madison
Radcliffe Institute for Advanced Study, Harvard University

http://www.lovethispic.com/image/14196/colorful-seashells

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NSF-DMR-BMAT DOE-BES-Geosciences US-Israel BSF Radcliffe Institute, Harvard


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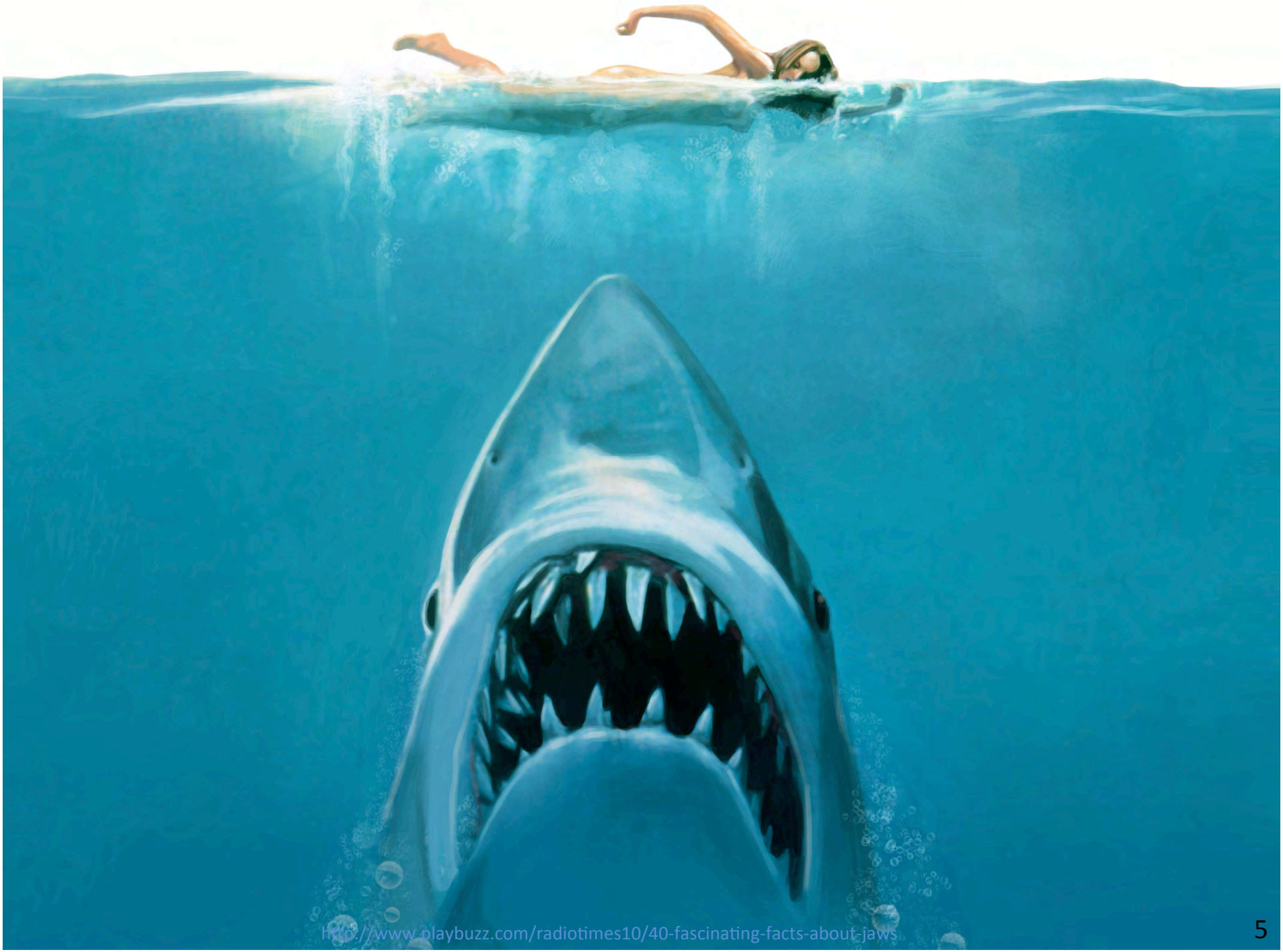
http://paulmerriman.com/facing-fears/



http://www.playbuzz.com/radiotimes10/40-fascinating-facts-about-jaws

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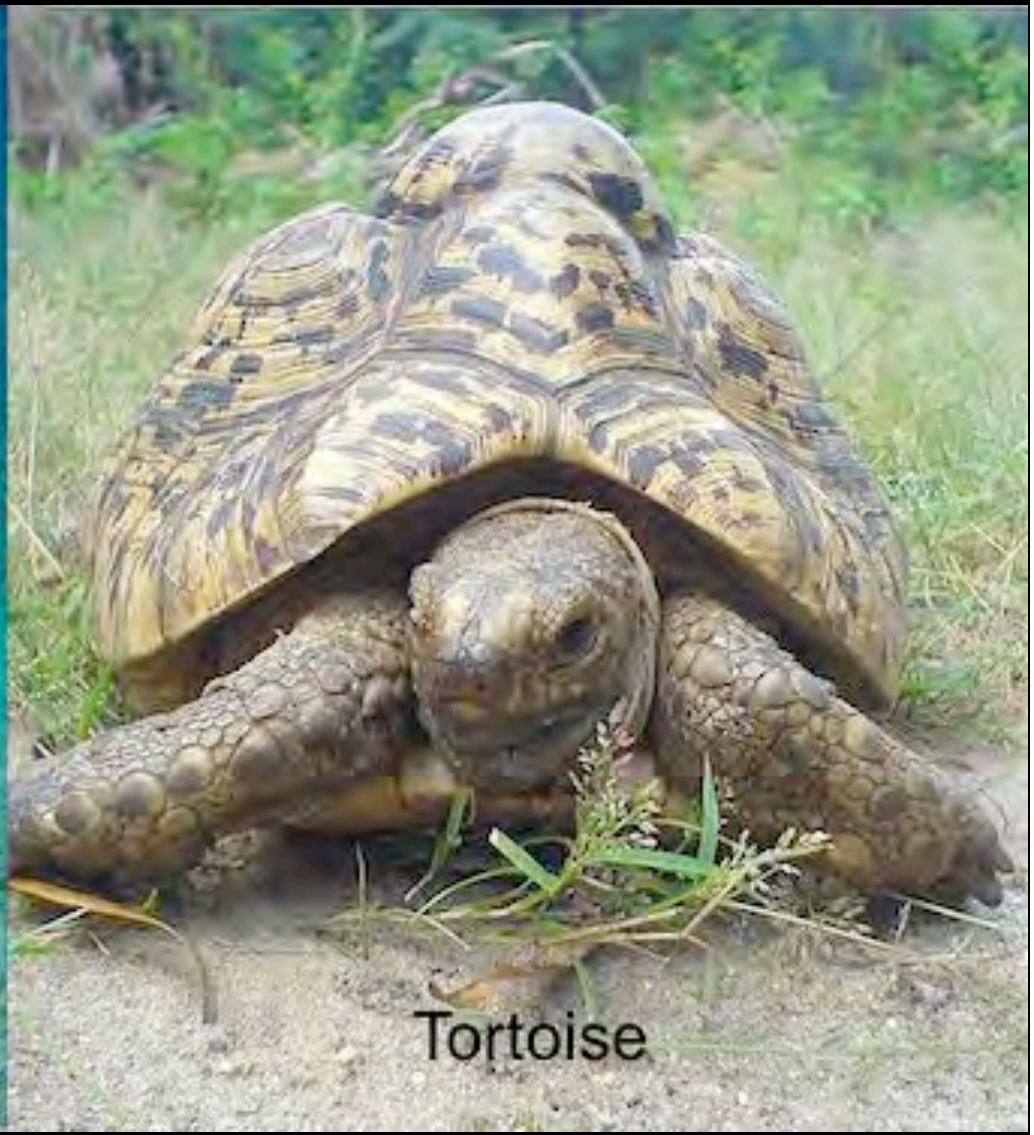
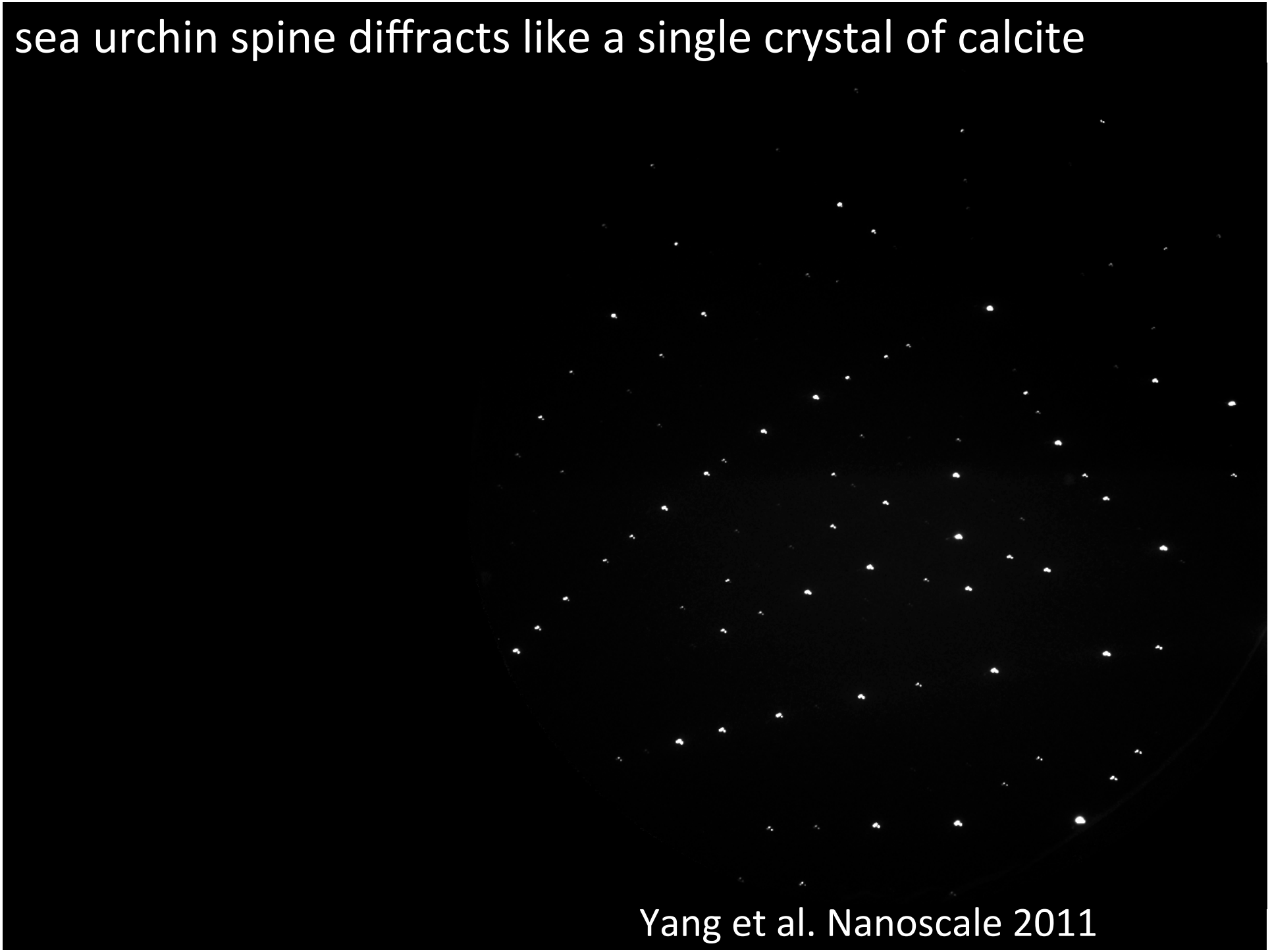


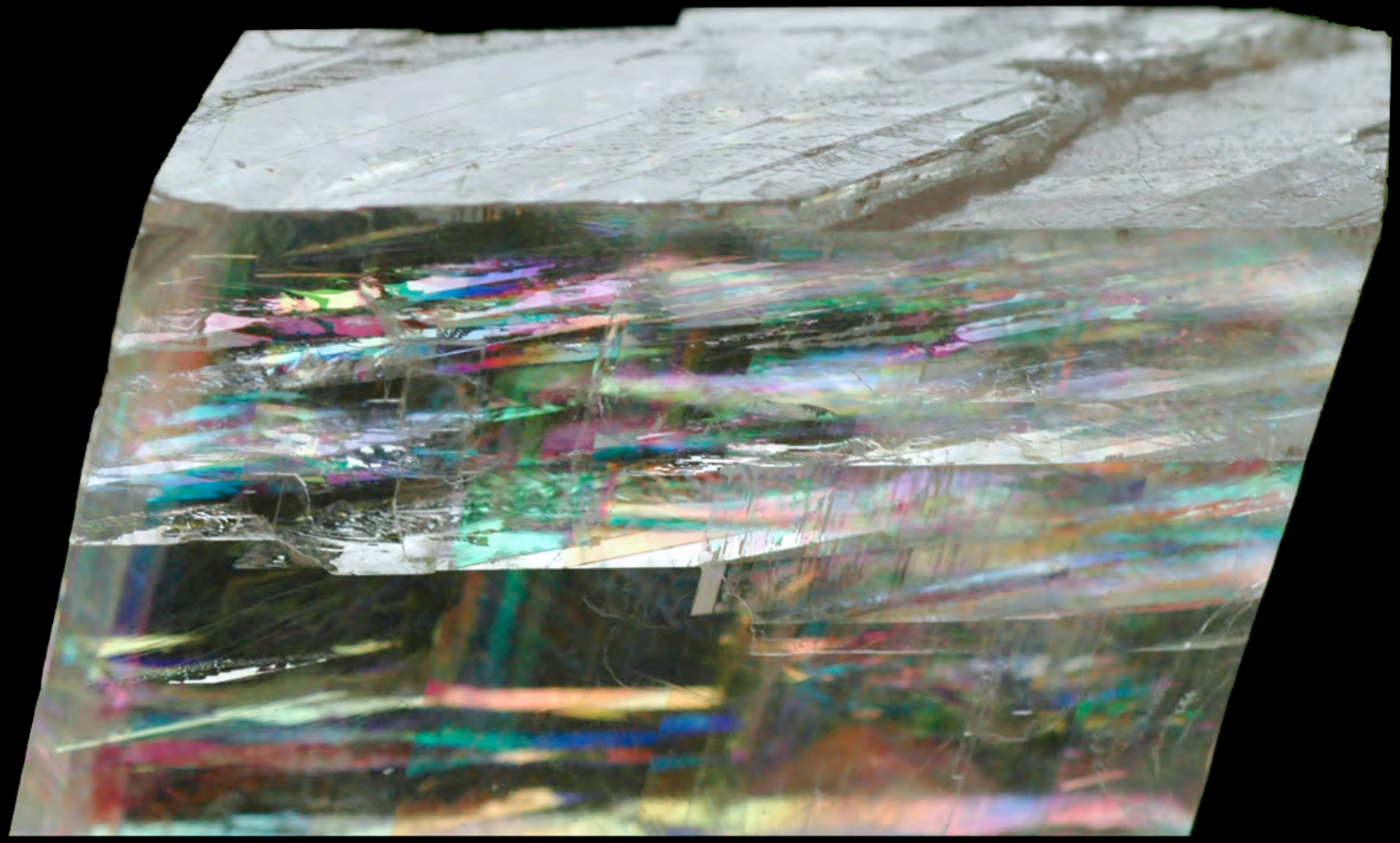
http://www.mnn.com/earth-matters/animals/photos/28-commonly-confused-animals/turtles-and-tortoises

sea urchin spine diffracts like a single crystal of calcite



Yang et al. Nanoscale 2011

calcite single crystal



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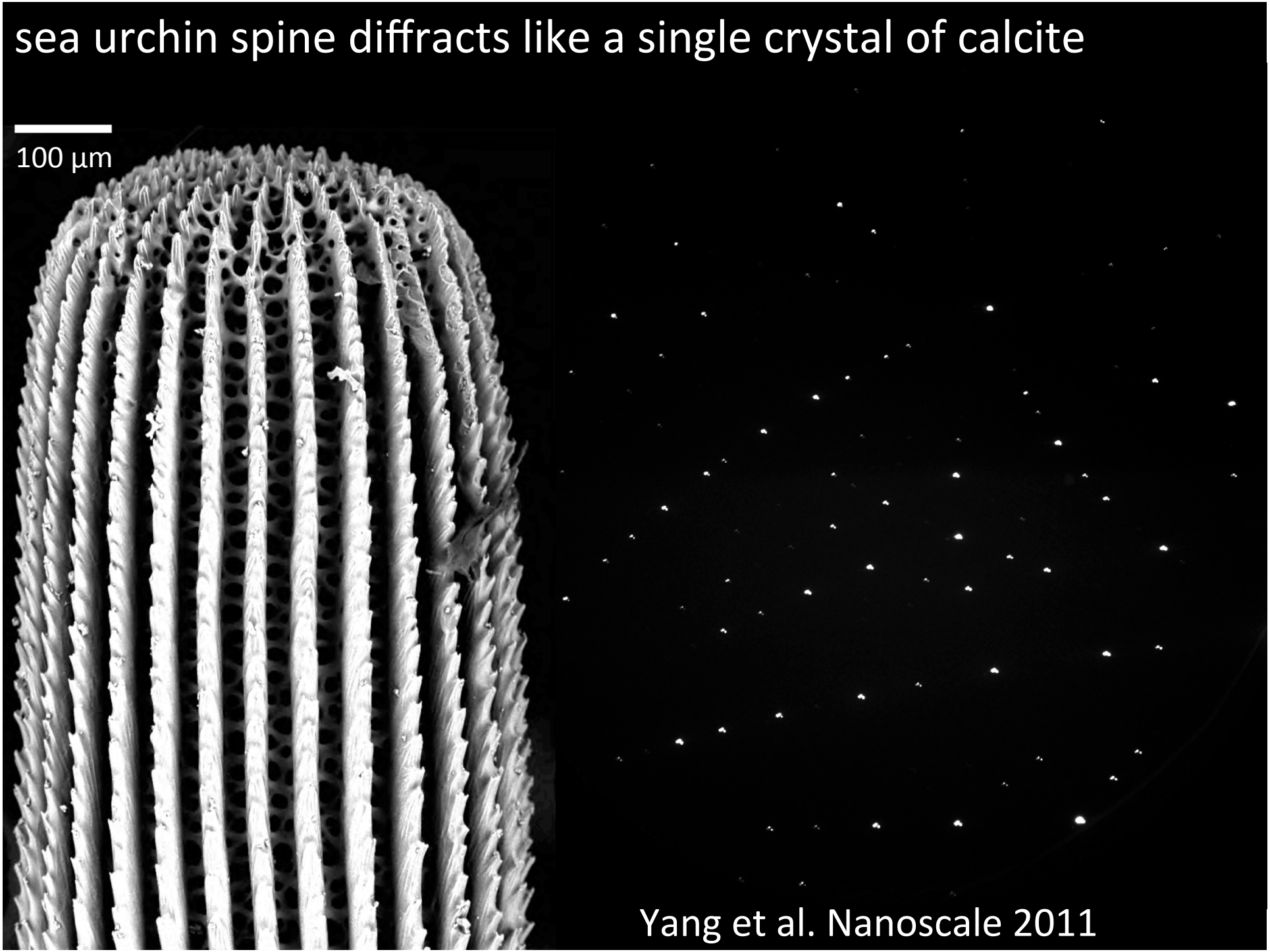
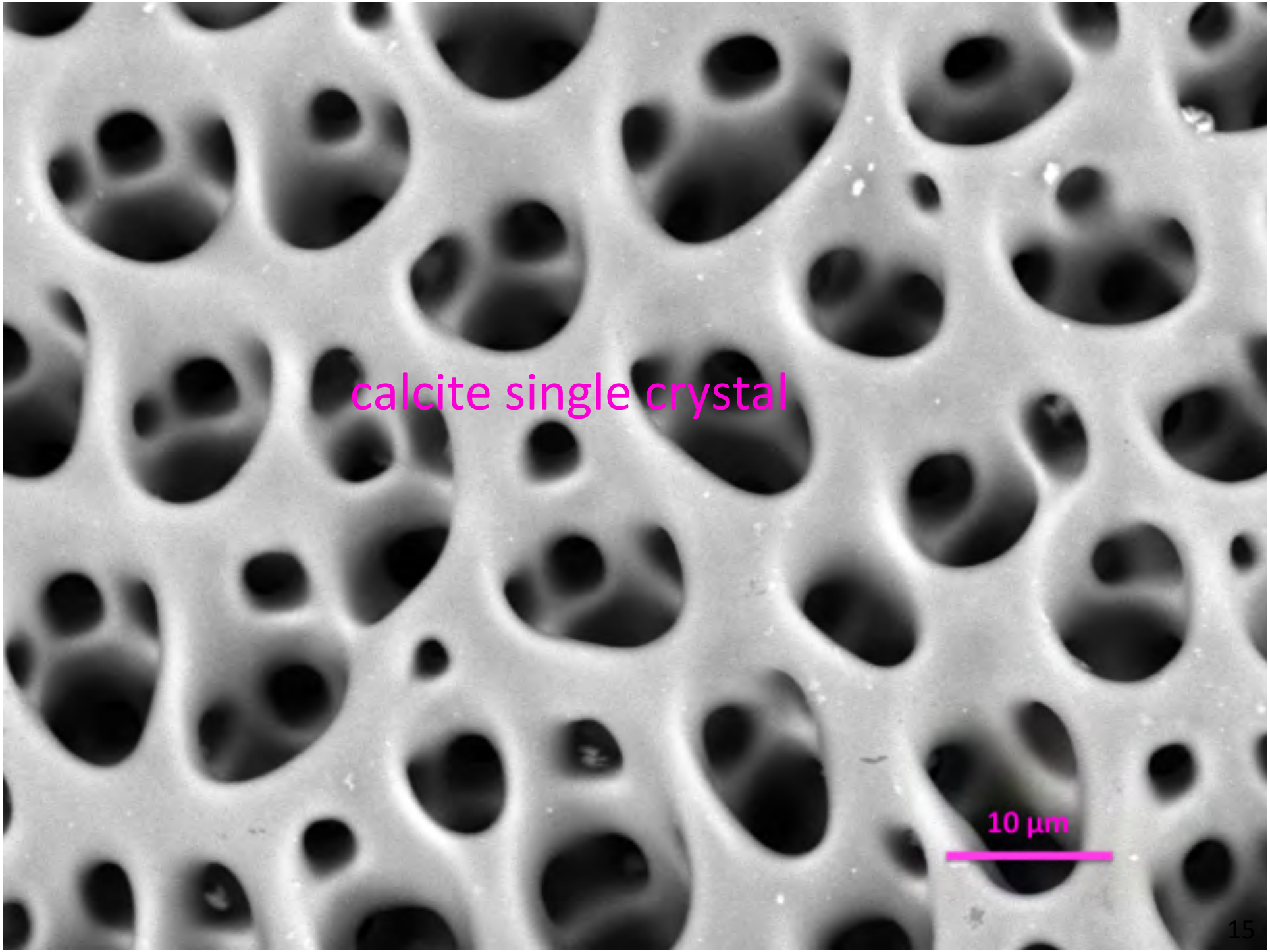
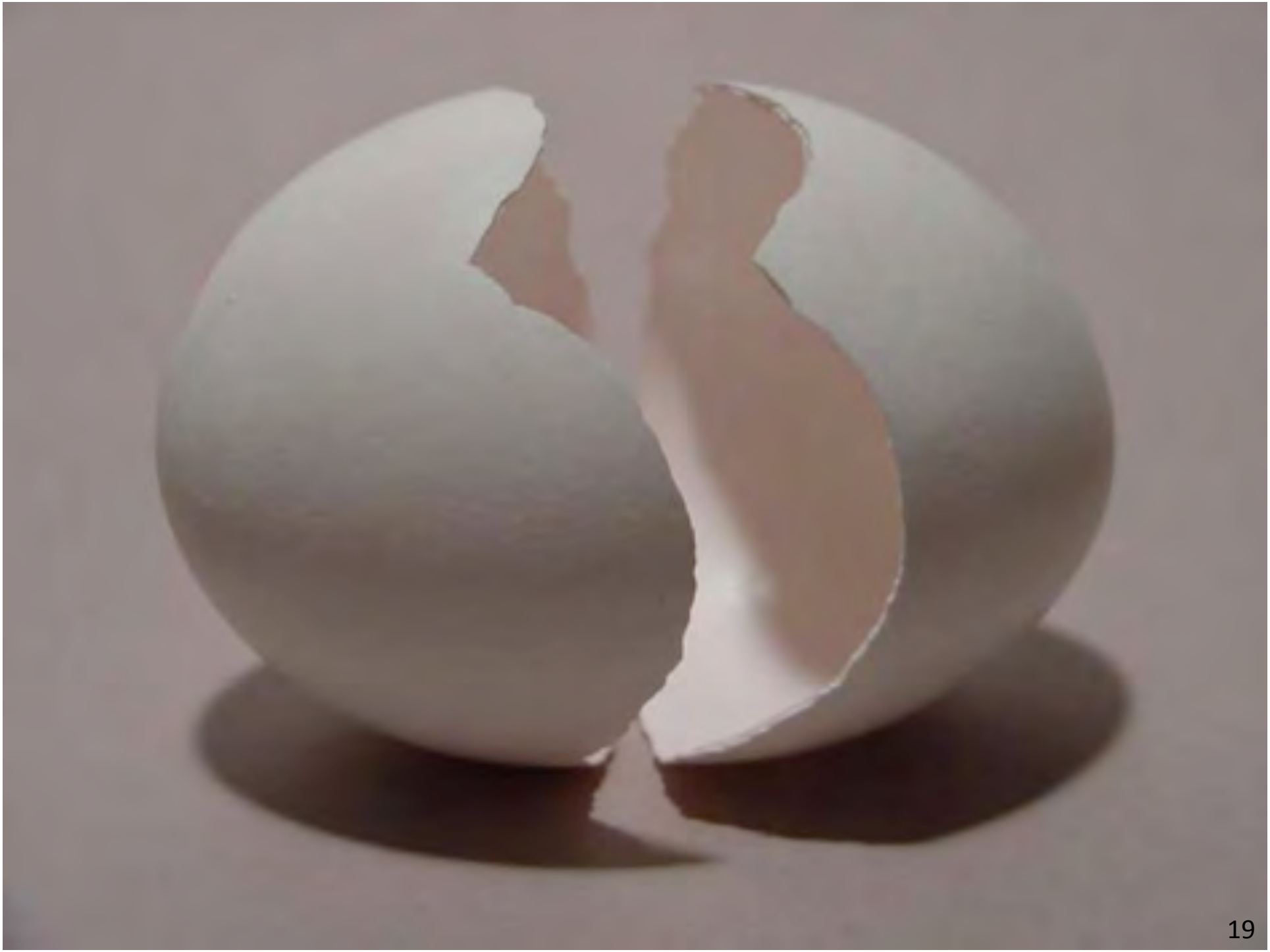



calcite single crystal
10 µm



biominerals

biomineralization = formation mechanisms

biomineralization

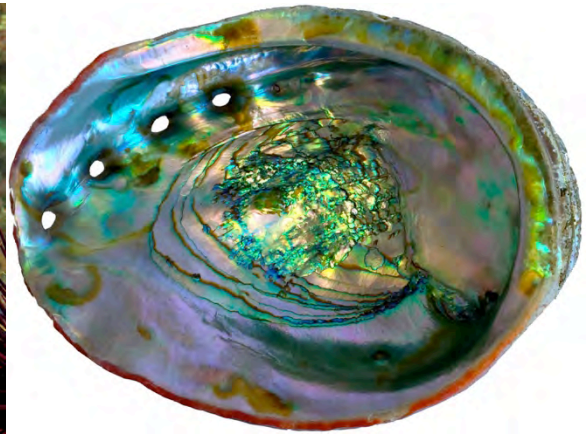
- why is it important?
- because it is a wide spread natural phenomenon
- useful for sleuthing into deep time (500,000 Myrs)
- mechanisms can be applied
    - large crystals for solar energy
    - amorphous drugs
    - 3D printing
    - bone implants
    - …

biomineralization mechanisms

- crystals grow by particle attachment (Science 2015)

amorphous particles (~100 nm) in fresh, forming biominerals

PNAS 2012

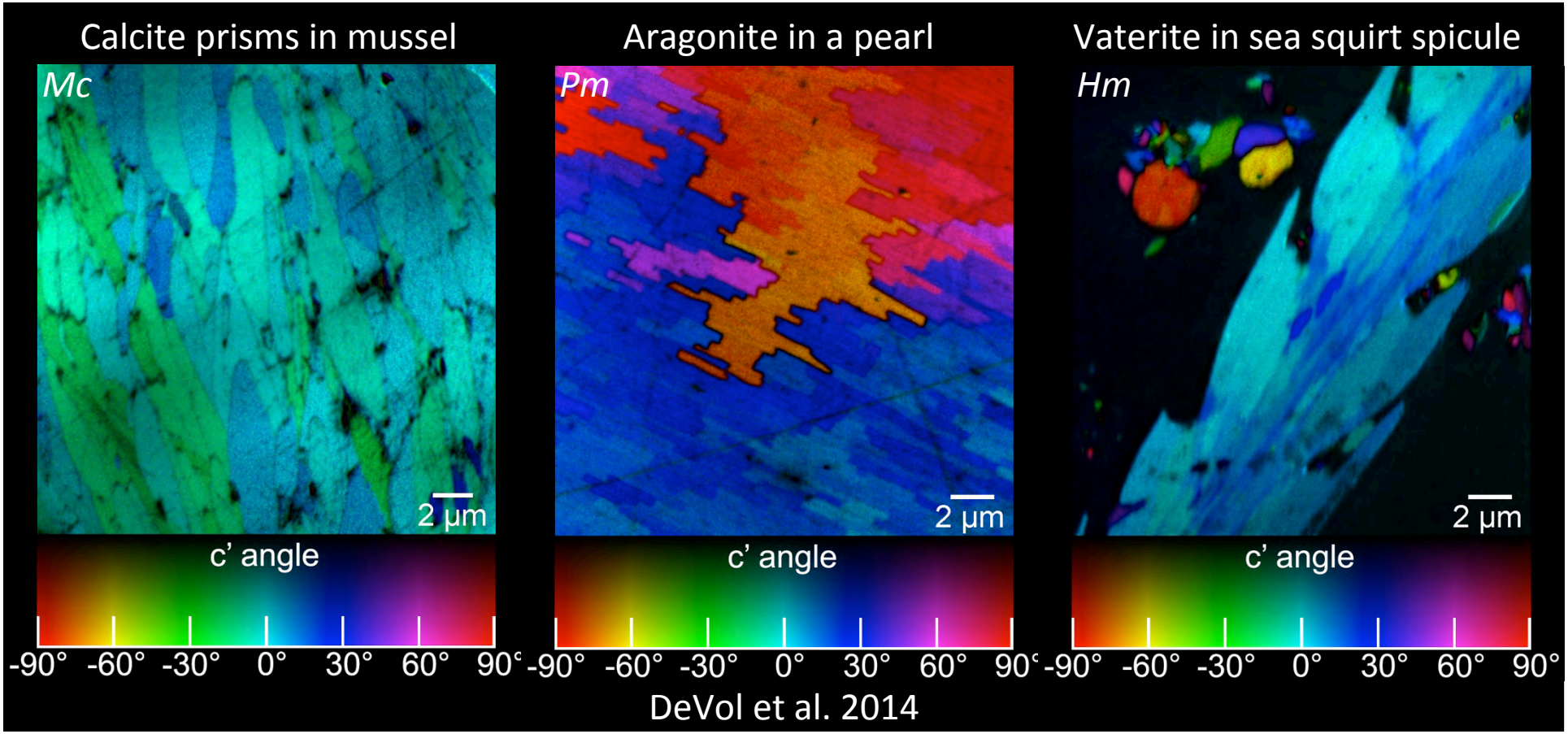


JACS 2015

Science 2017
under review

biomineralization mechanisms

- crystals grow by particle attachment
- orientation of crystals changes as the biomineral grows



Ca

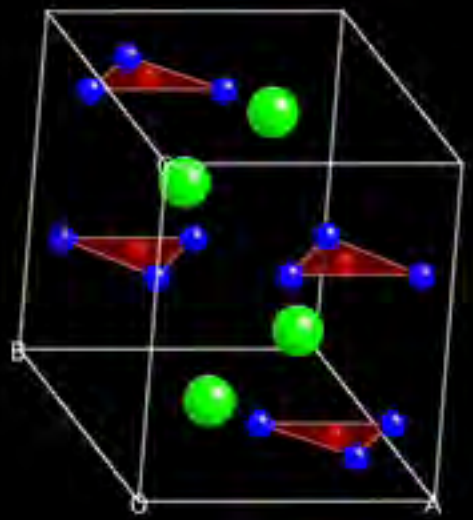
C

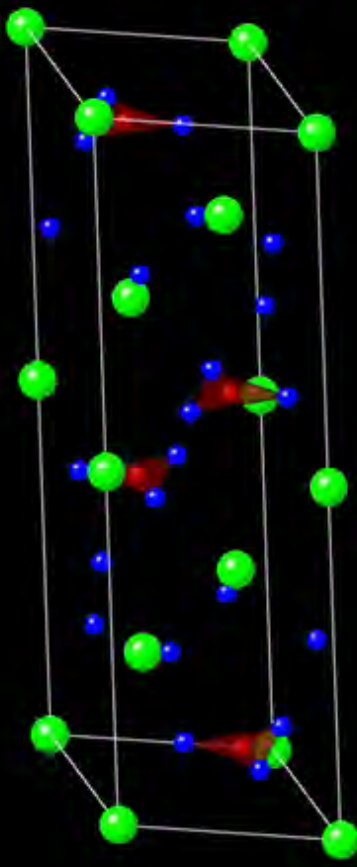
O

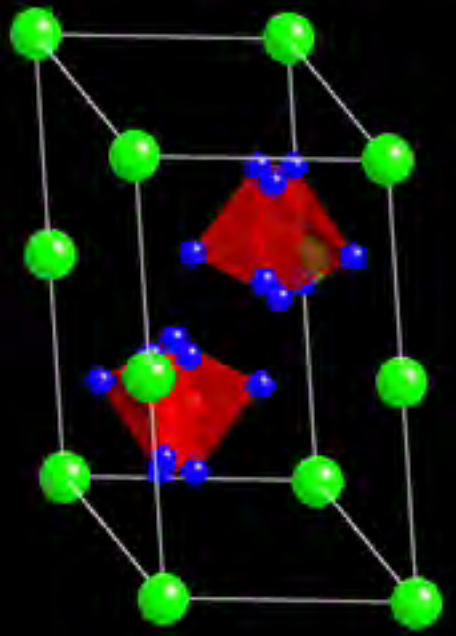
vaterite unit cell

calcite unit cell

aragonite unit cell

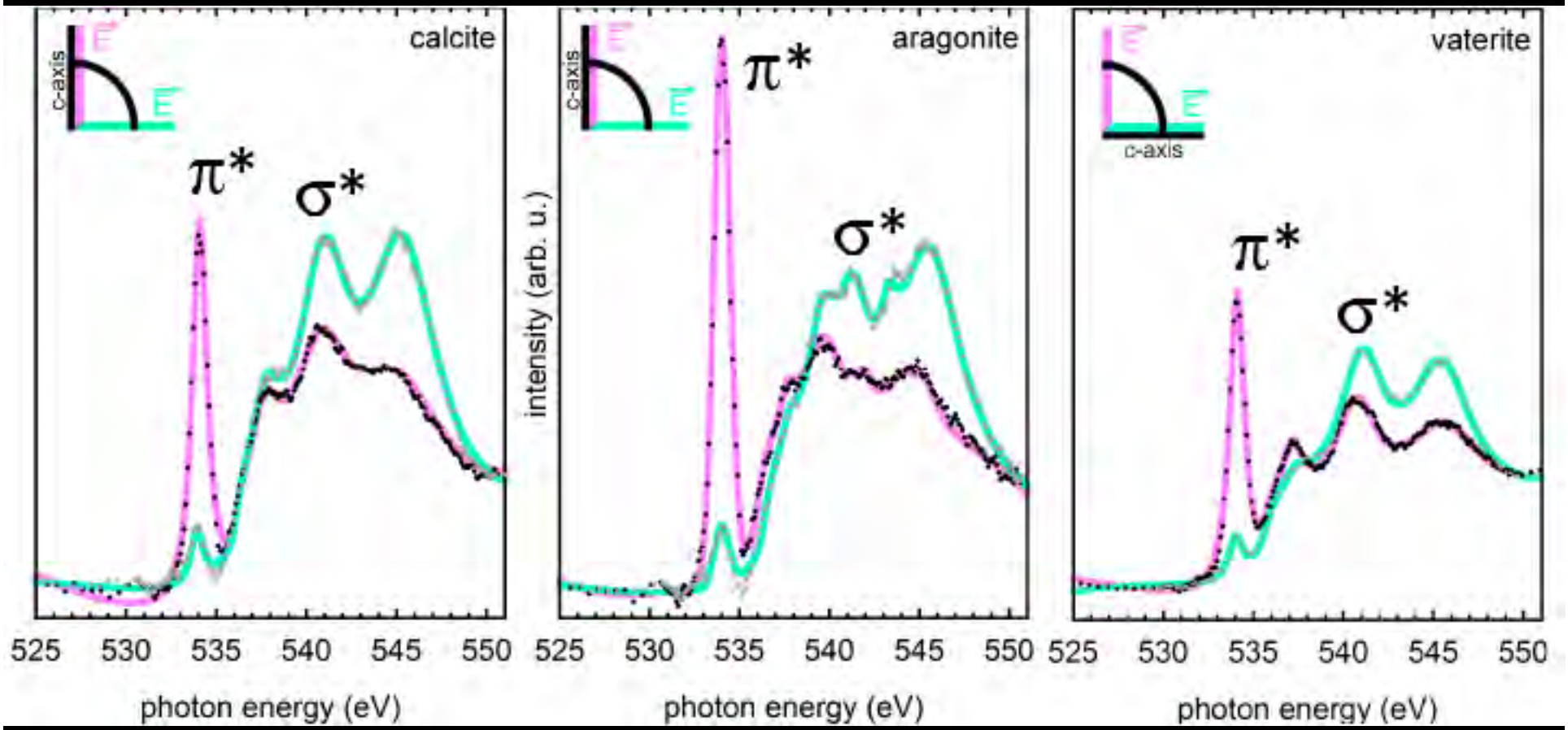






DeVol et al. 2014

x-ray linear dichroism
in O K-edge XAS spectra



Rebecca Metzler et al., PRL 2007

.....

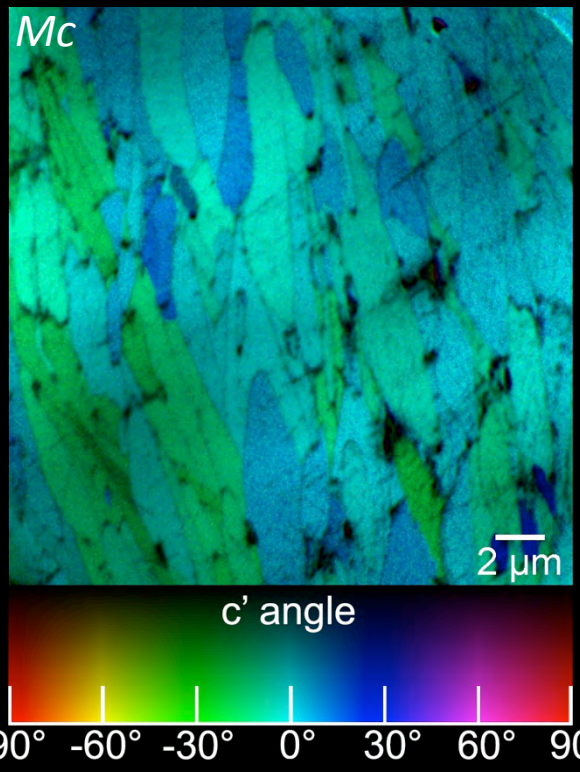
DeVol et al. 2014

PIC-mapping

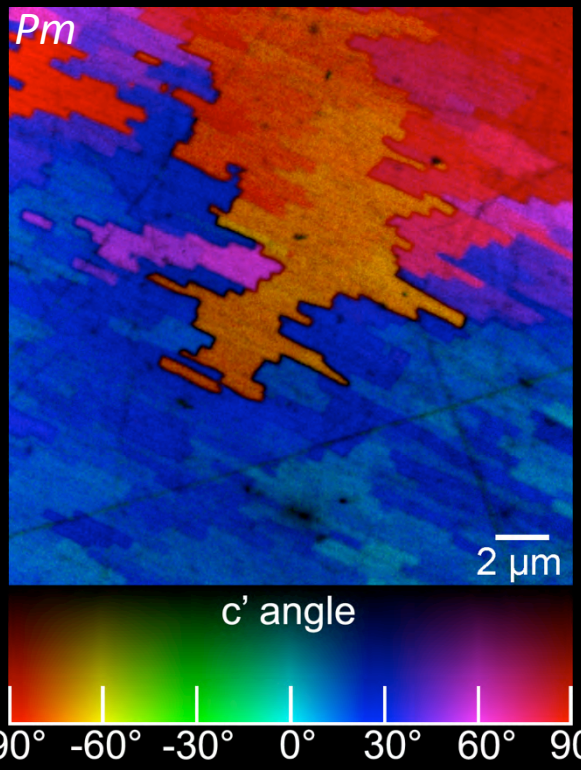
Polarization-dependent Imaging Contrast-mapping

color = c-axis orientation in 3D

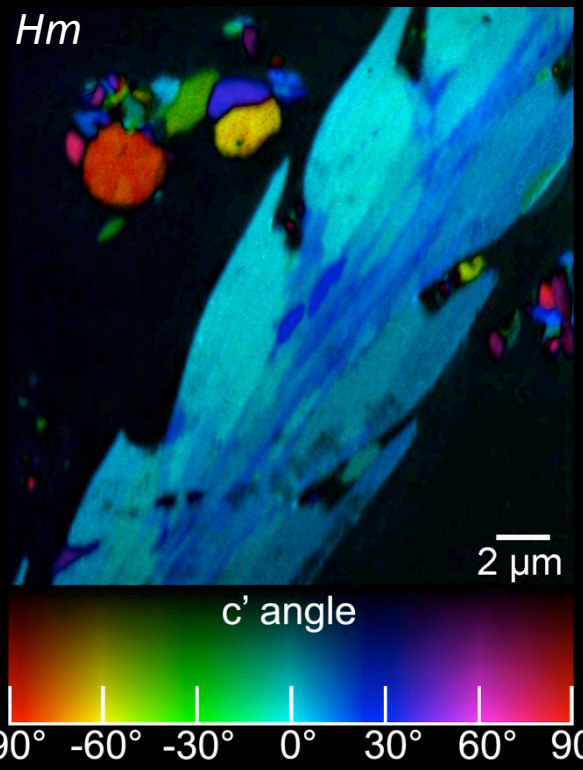
Calcite prisms in mussel



Aragonite in a pearl



Vaterite in sea squirt spicule



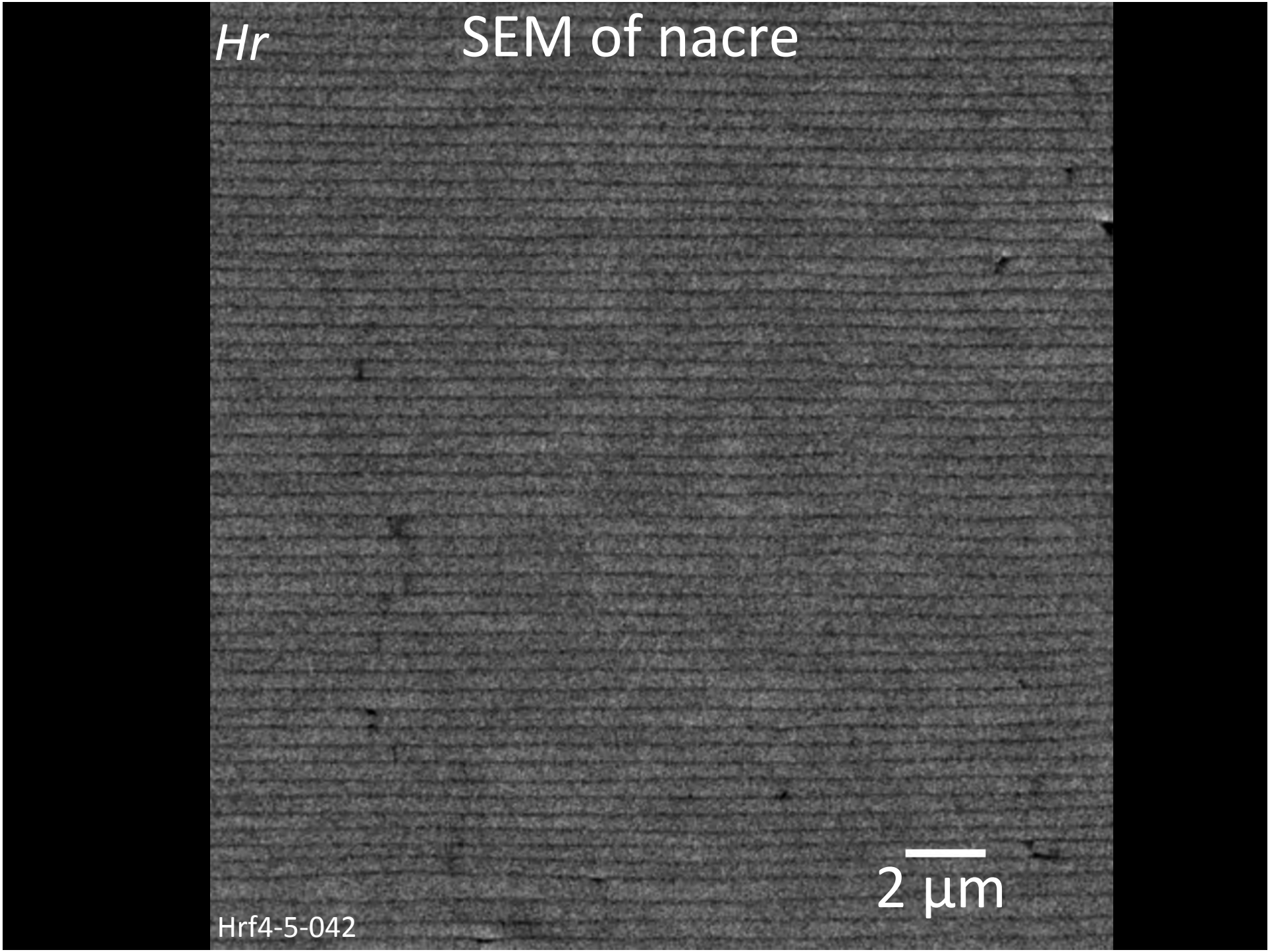
Rebecca Metzler et al., PRL 2007

.....

DeVol et al. 2014

nacre
(mother-of-pearl)

- lines the inside of many mollusk shells
- is widely studied because of its mechanical properties
- is iridescent


Hr
SEM of nacre
2 µm
Hrf4-5-042

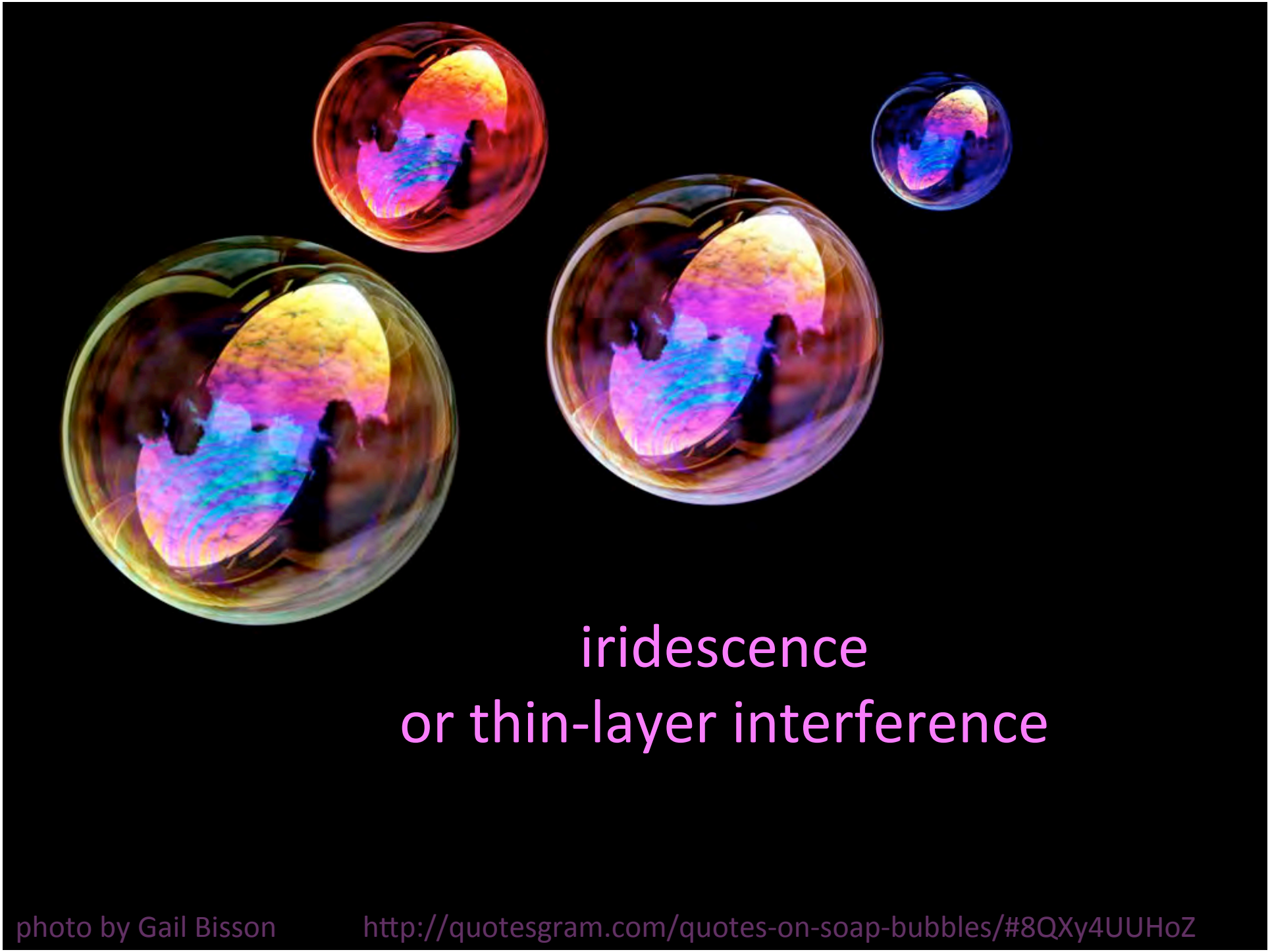
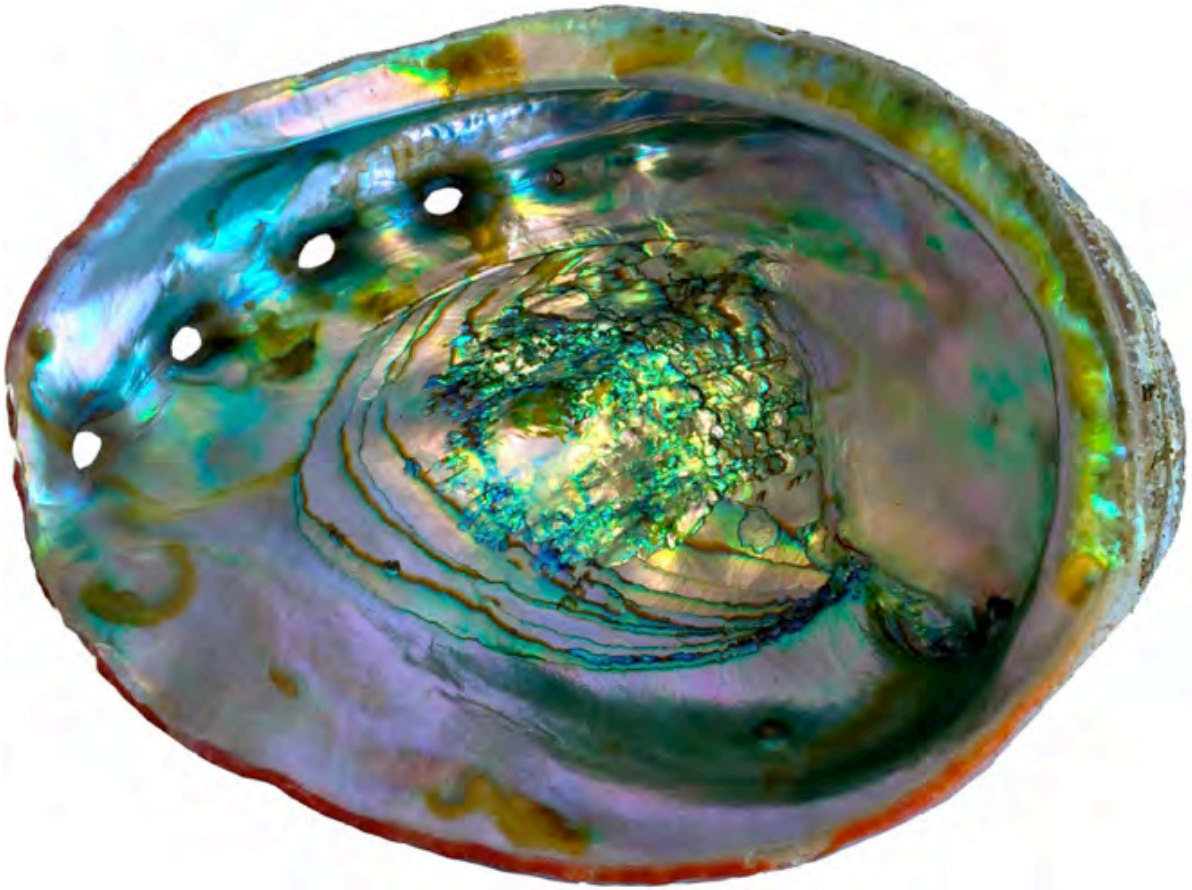
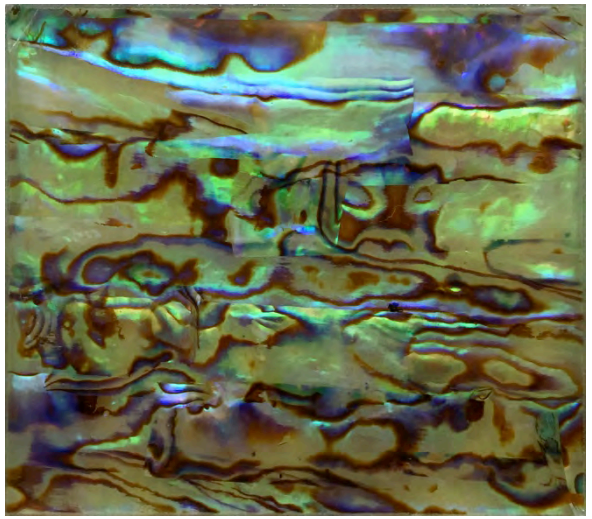


photo by Gail Bisson http://quotesgram.com/quotes-on-soap-bubbles/#8QXy4UUHoZ



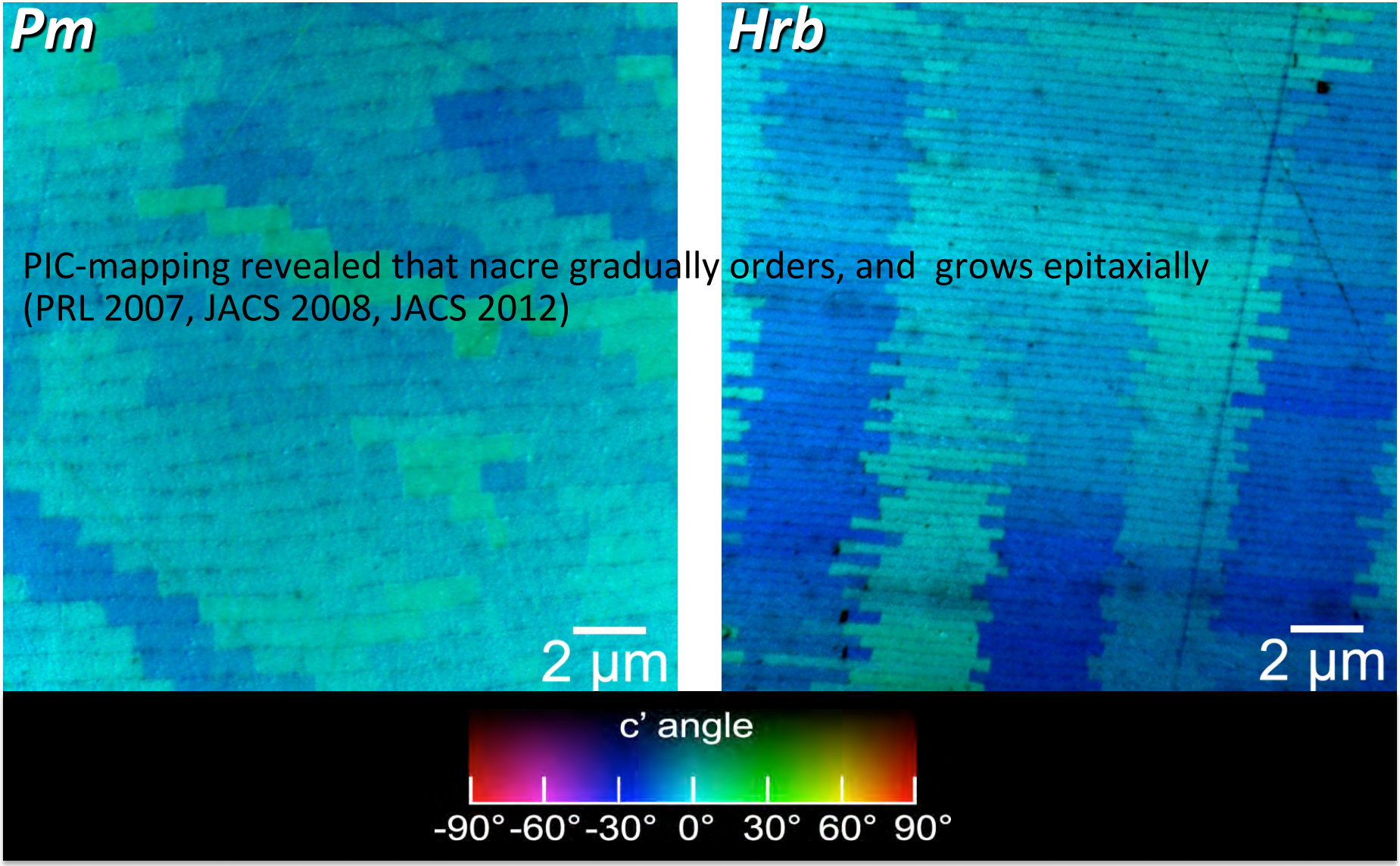


PIC-maps of nacre

(PIC=Polarization-dependent Imaging Contrast)

sheet nacre (bivalves)

columnar nacre (gastropods, cephalopods)

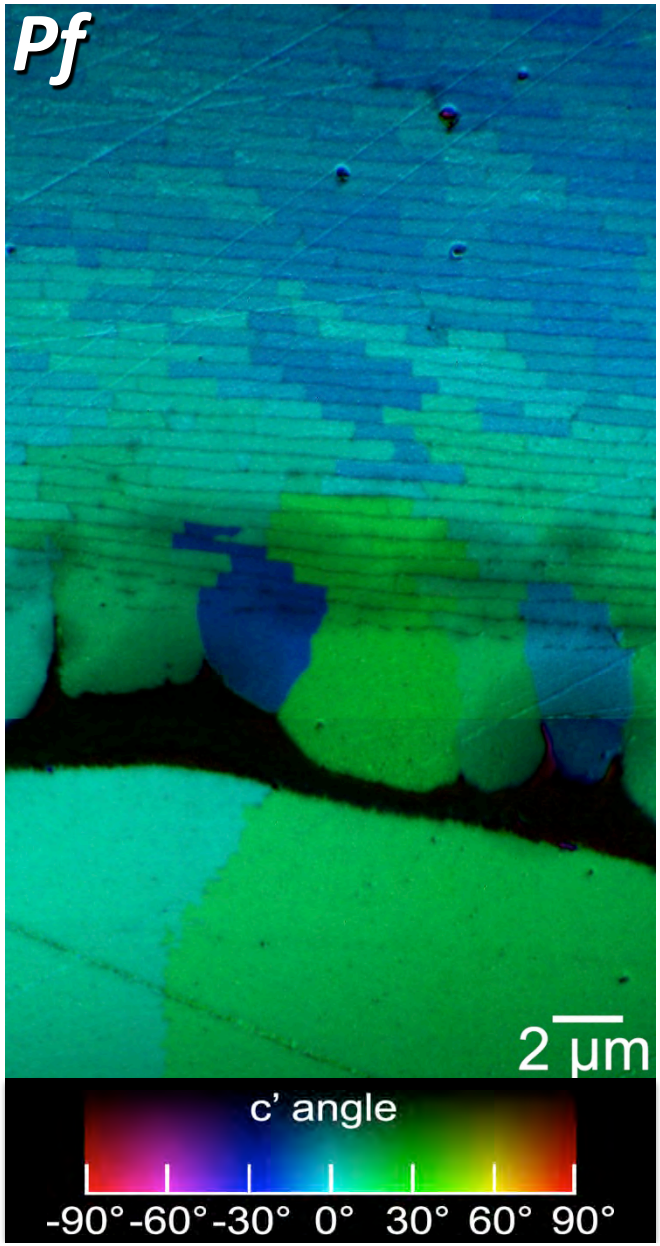


PIC-mapping revealed that nacre gradually orders, and grows epitaxially
(PRL 2007, JACS 2008, JACS 2012)

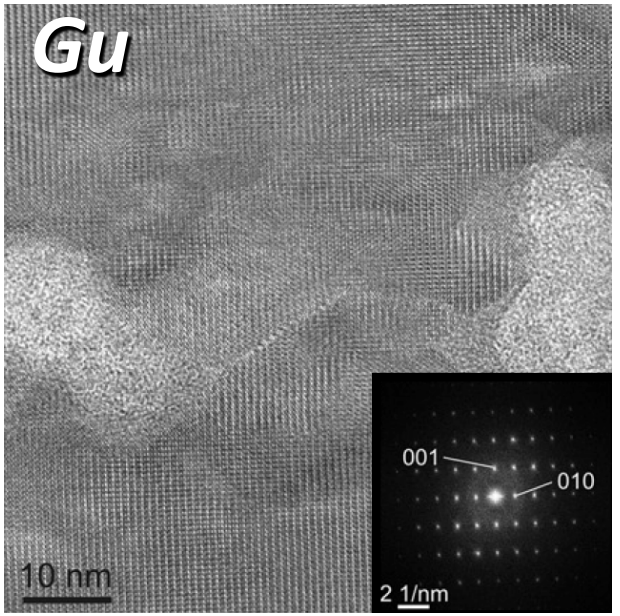
IC Olson et al. 2013

nacre gradually orders, and grows epitaxially

PIC-map (**P**olarization-dependent **I**maging **C**ontrast)



TEM

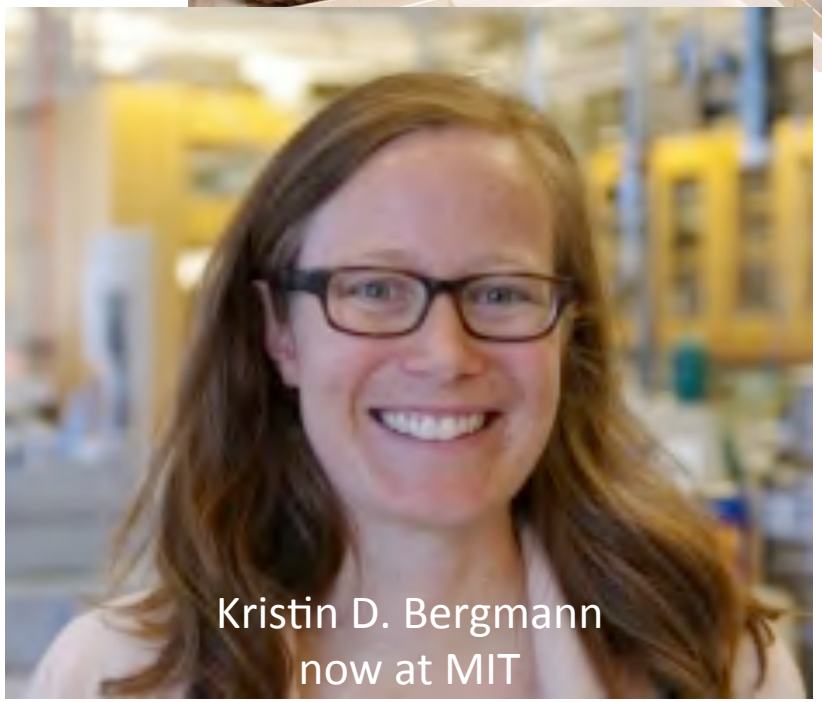


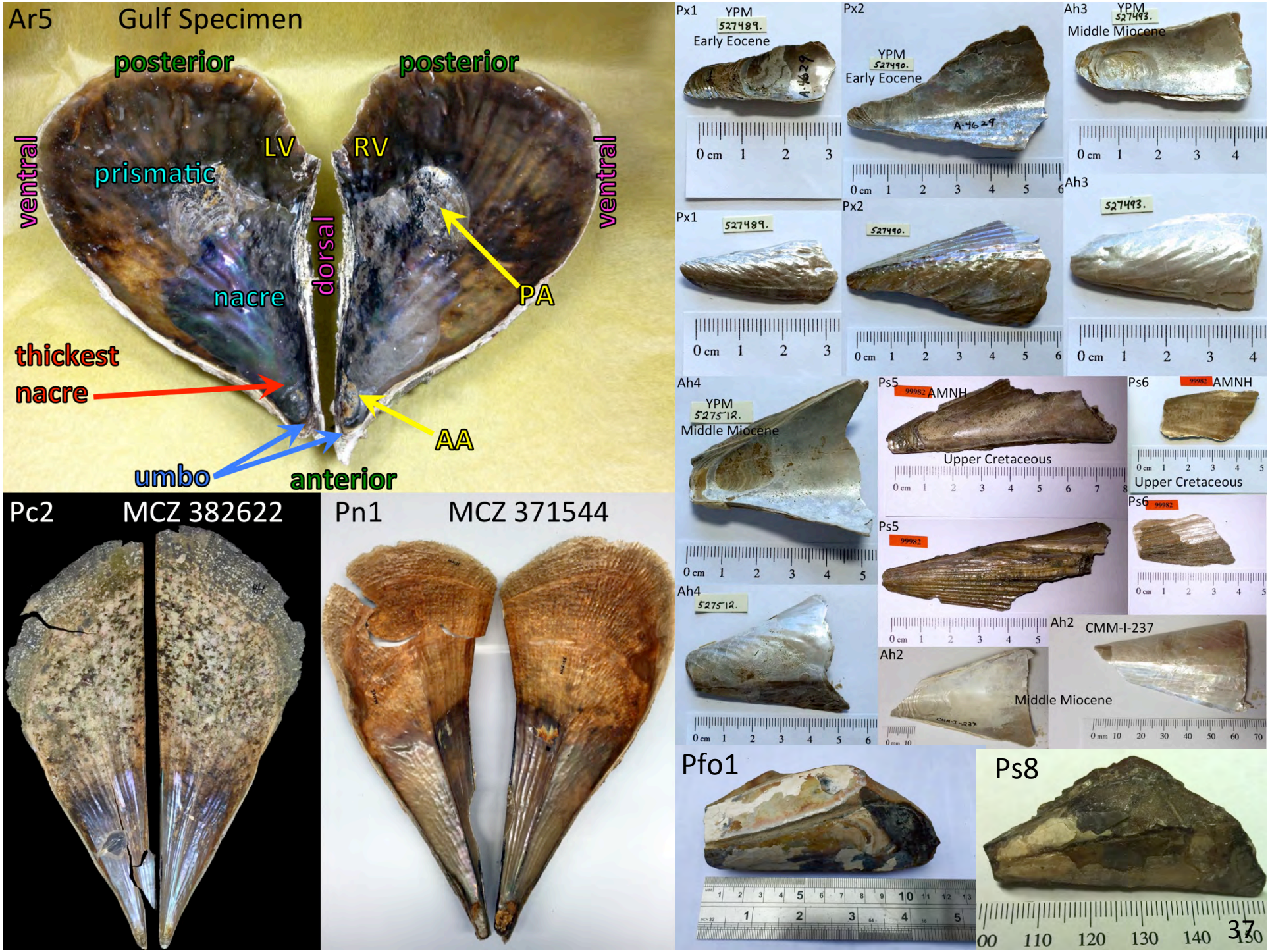
Checa et al. JSB 2011

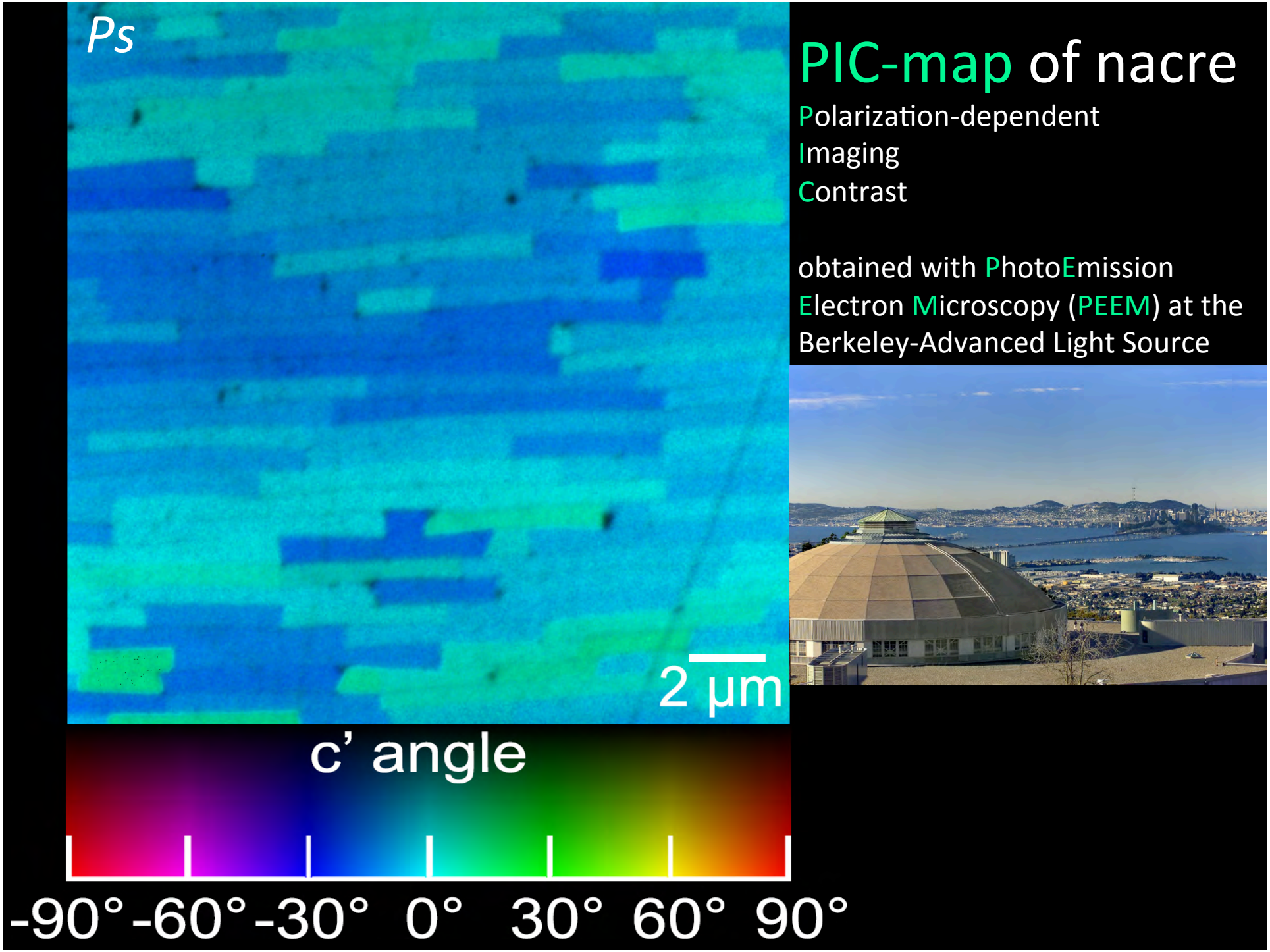
Gilbert et al. JACS 2008
Olson et al. JSB 2013


what controls tablet thickness
in nacre?
Atrina rigida shell, Florida

question at Harvard 2014-15:
does nacre TT record environmental temperature?




Ar5 Gulf Specimen
posterior
posterior
ventral
ventral
LV
RV
prismatic
dorsal
nacre
PA
thickest
nacre
AA
umbo
anterior
Pc2 MCZ 382622
Pn1 MCZ 371544
Px1 YPM 527489. Early Eocene
Px2 YPM 527490. Early Eocene
Ah3 YPM 527493. Middle Miocene
Px1 527489.
Px2 527490.
Ah3 527493.
Ah4 YPM 527512. Middle Miocene
Ps5 99982 AMNH Upper Cretaceous
Ps6 99982 AMNH Upper Cretaceous
Ah4 527512.
Ps5 99982
Ps6 99982
Ah2 CMM-I-237 Middle Miocene
Ah2
Pfo1
Ps8
37

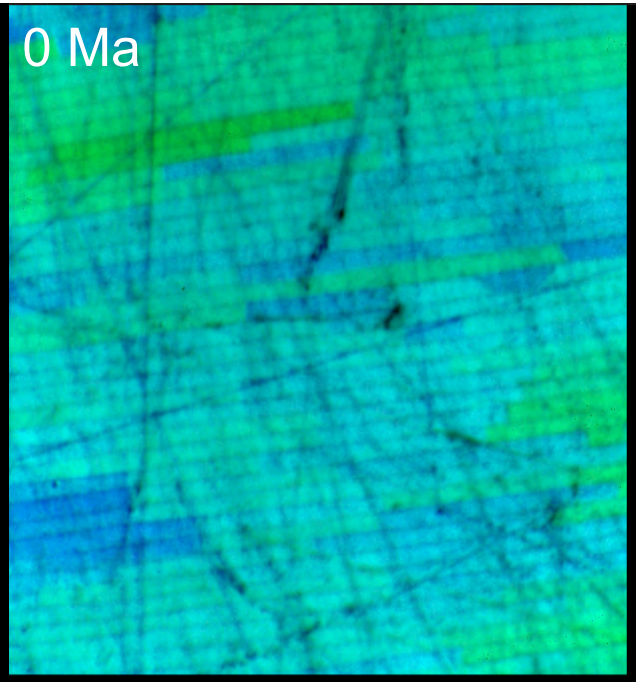


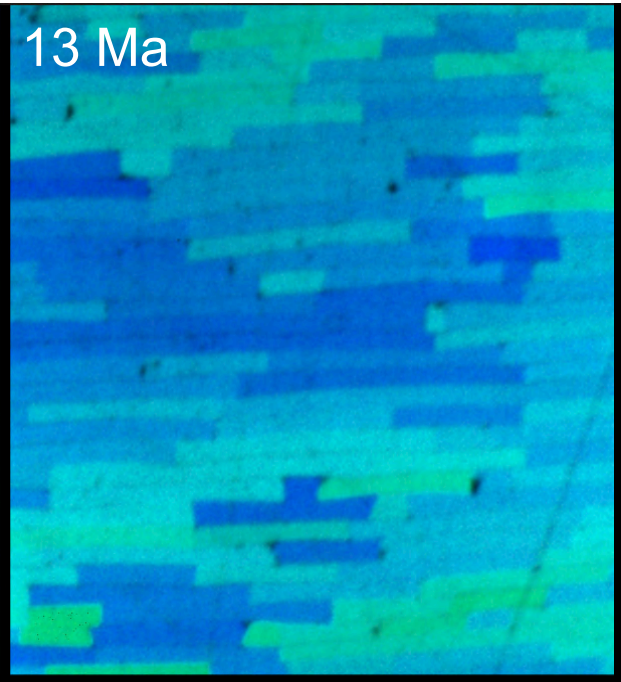
PIC-map of nacre

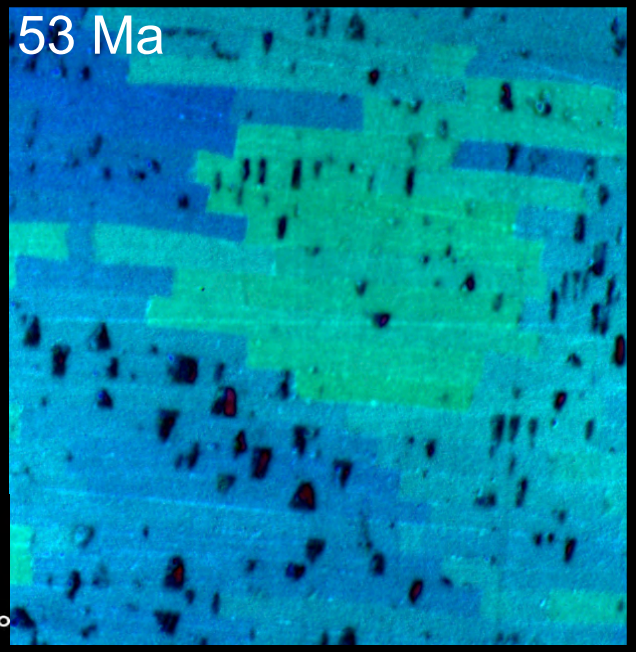
Polarization-dependent
Imaging
Contrast

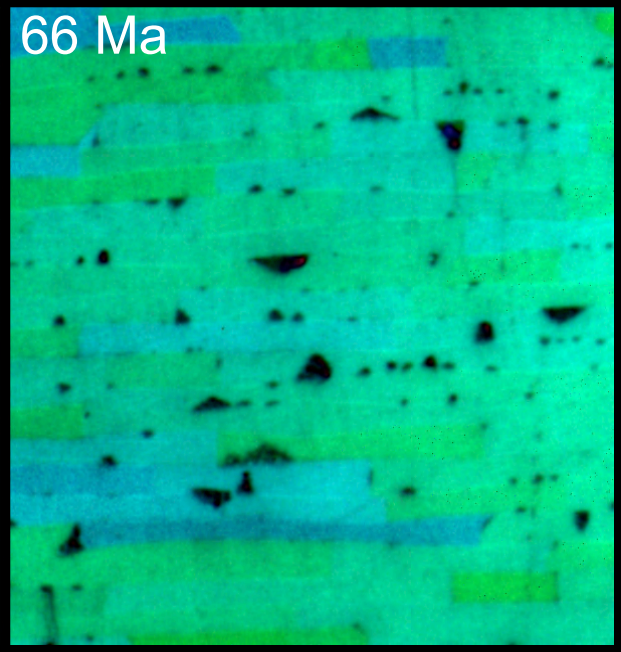
obtained with PhotoEmission Electron Microscopy (PEEM) at the Berkeley-Advanced Light Source

test of fossil preservation







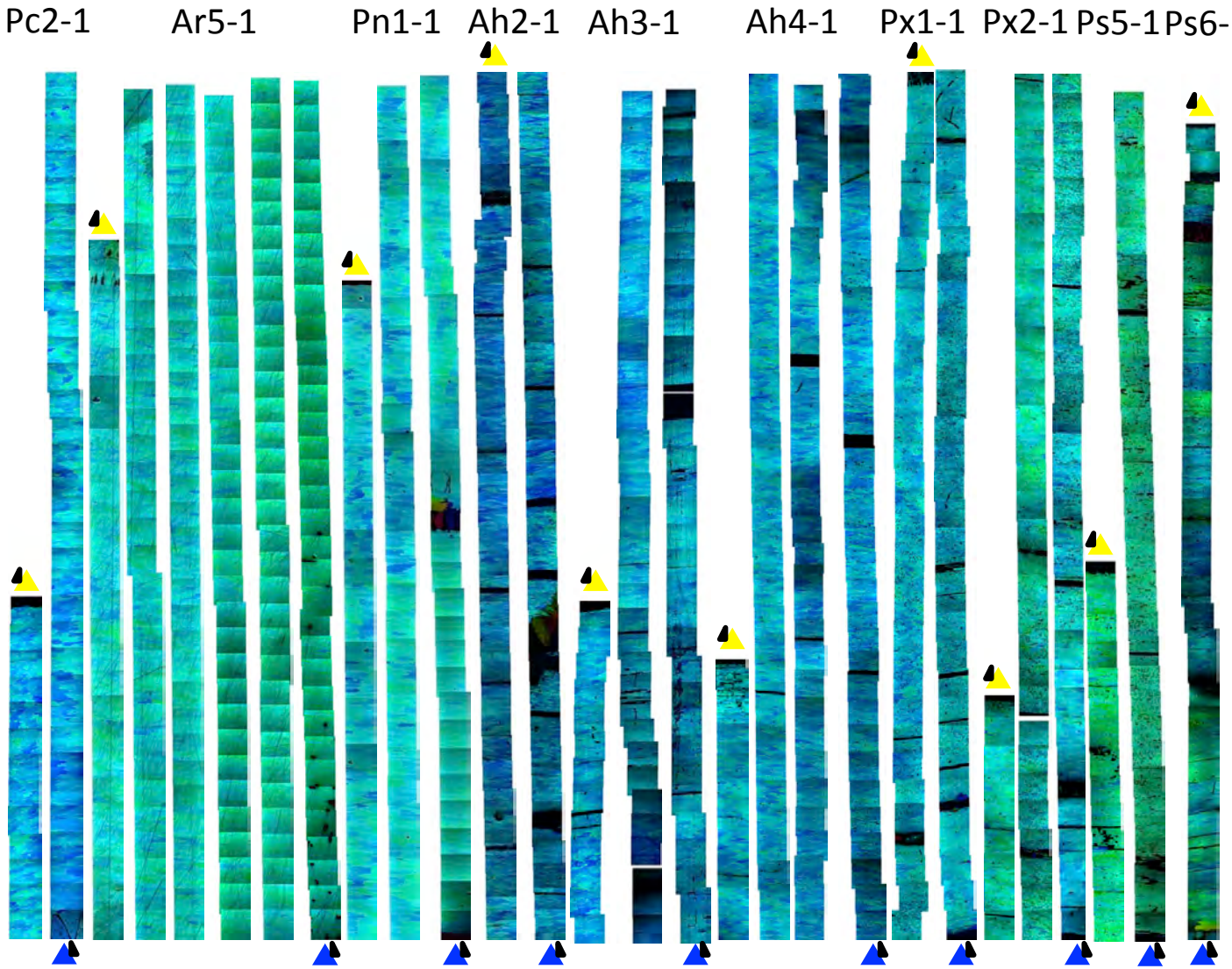


PIC-maps

(PIC=Polarization-dependent Imaging Contrast)

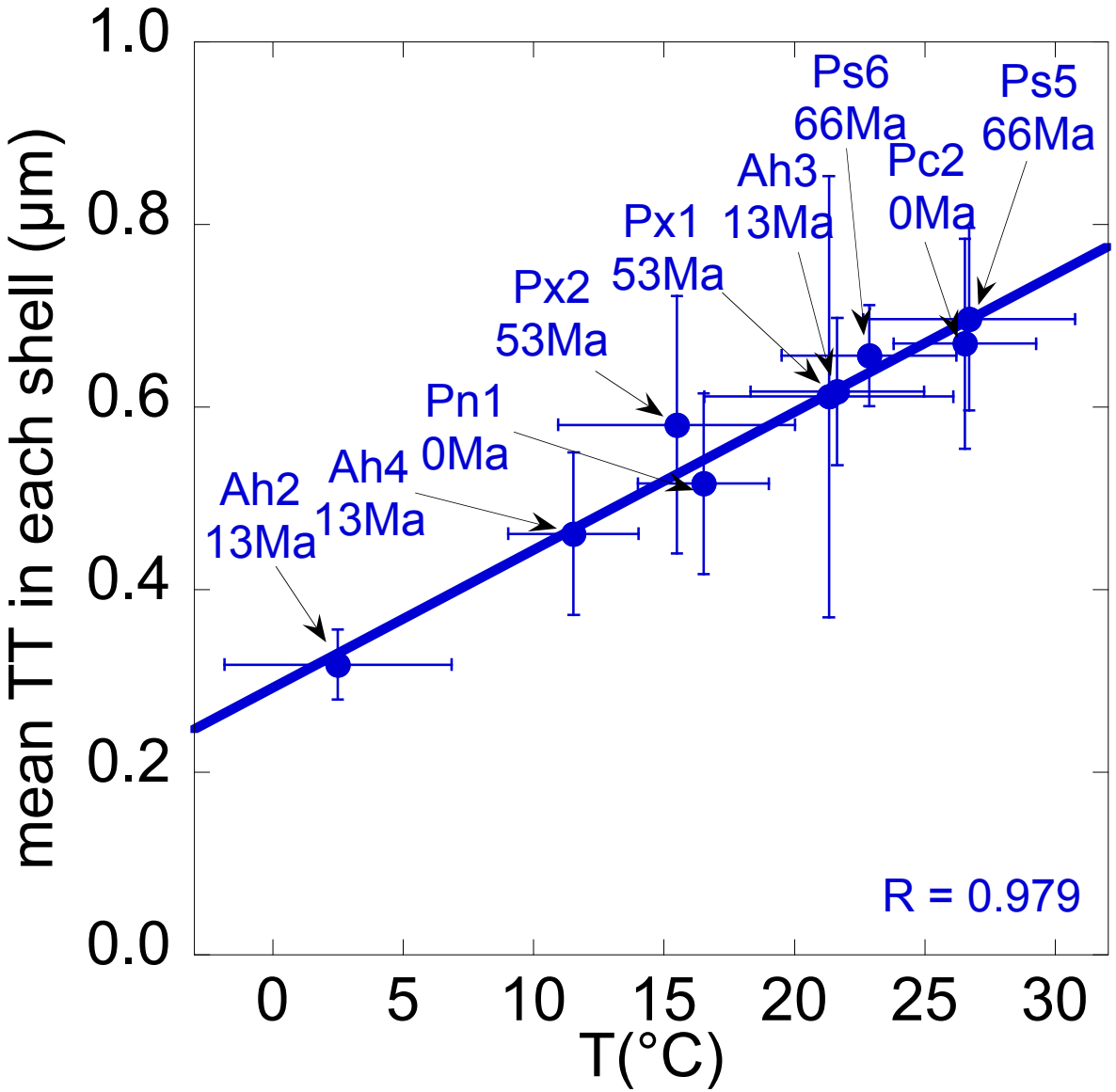
3 Recent + 7 Fossil shells

822 PIC-maps, partly overlapping to ensure continuity in position/time.



▲ = interior of shell, recent ▲ = exterior of shell, old

nacre tablet thickness (TT) vs temperature (T)



linear fit, with error bars NOT taken into account

PUPA Gilbert, KD Bergmann, CE Myers, MA Marcus, RT DeVol, C-Y Sun, AZ Blonsky, J Zhao, EA Karan, E Tamre, N Tamura, AJ Giuffre, S Lemer, G Giribet, JM Eiler, AH Knoll. Nacre tablet thickness records formation temperature in modern and fossil shells. EPSL 2017.

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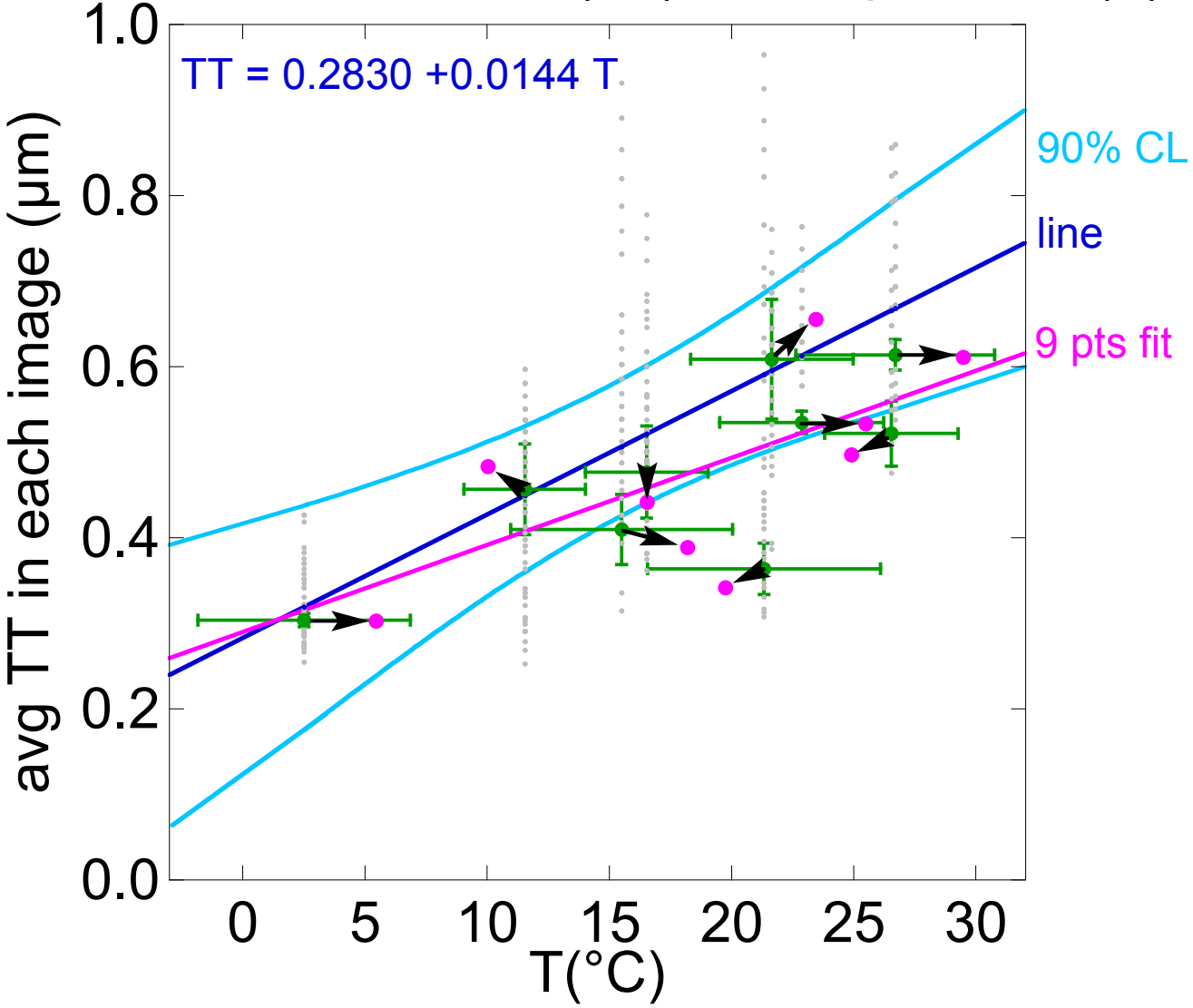

bootstrapping: fit 9 pts (1 per shell) displaced within the errors, repeat 10^5 times.

PUPA Gilbert, KD Bergmann, CE Myers, MA Marcus, RT DeVol, C-Y Sun, AZ Blonsky, J Zhao, EA Karan, E Tamre, N Tamura, AJ Giuffre, S Lemer, G Giribet, JM Eiler, AH Knoll. Nacre tablet thickness records formation temperature in modern and fossil shells. EPSL 2017.

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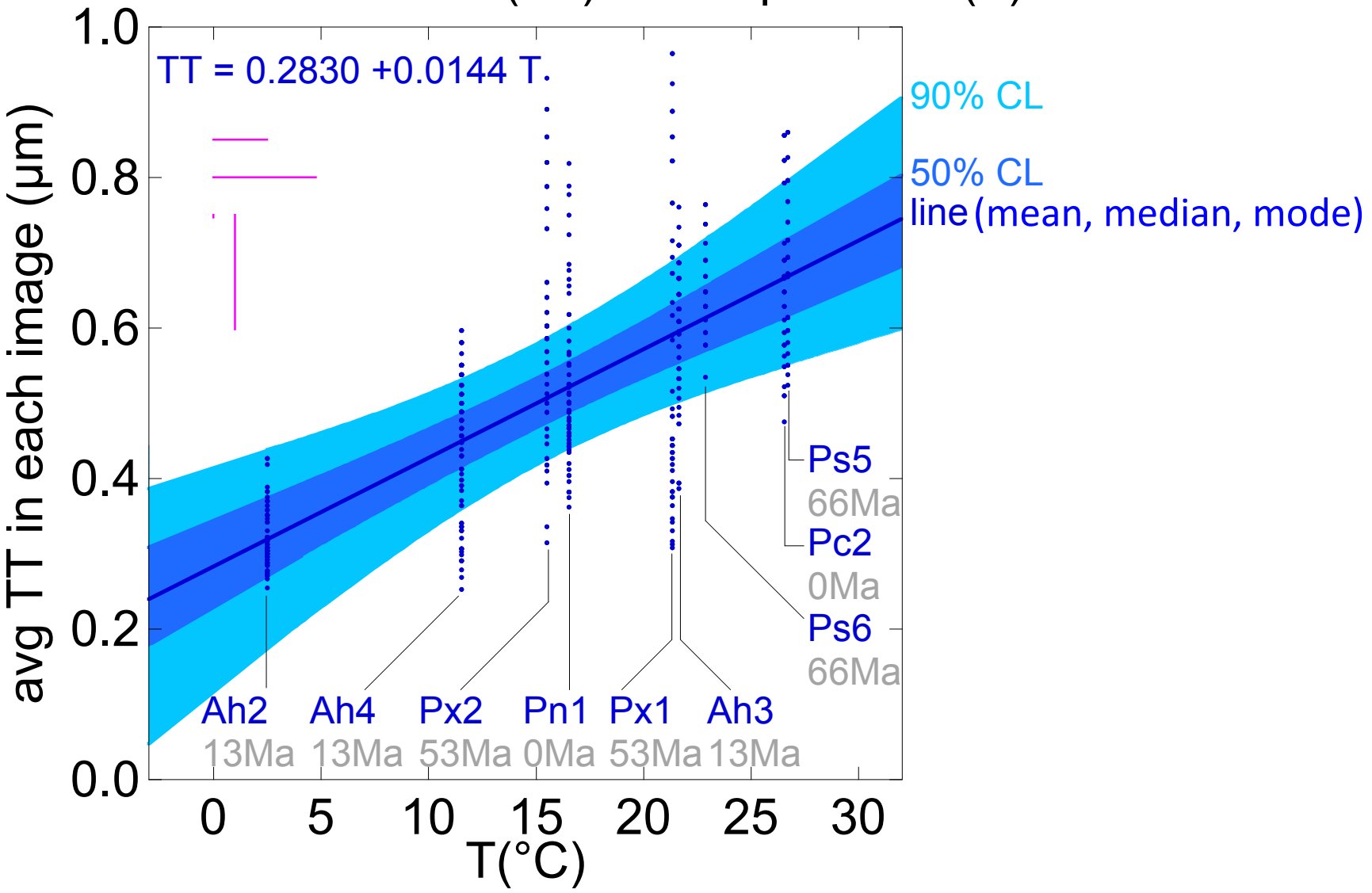
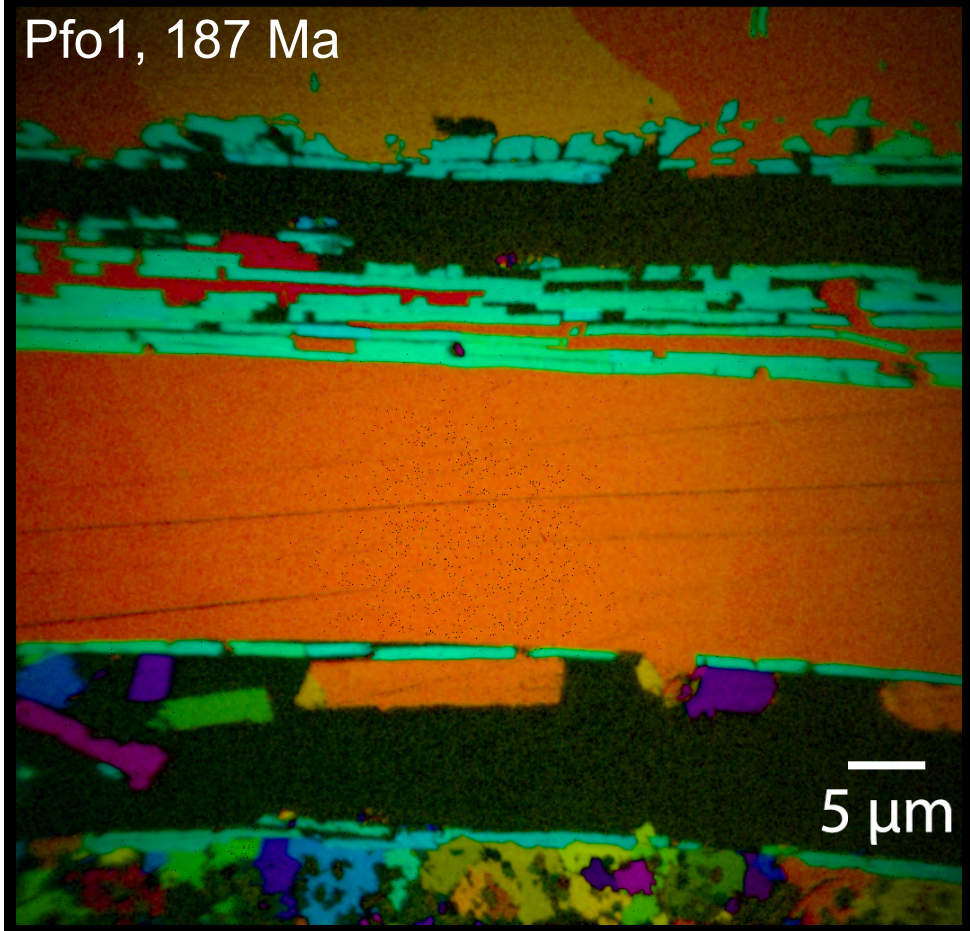
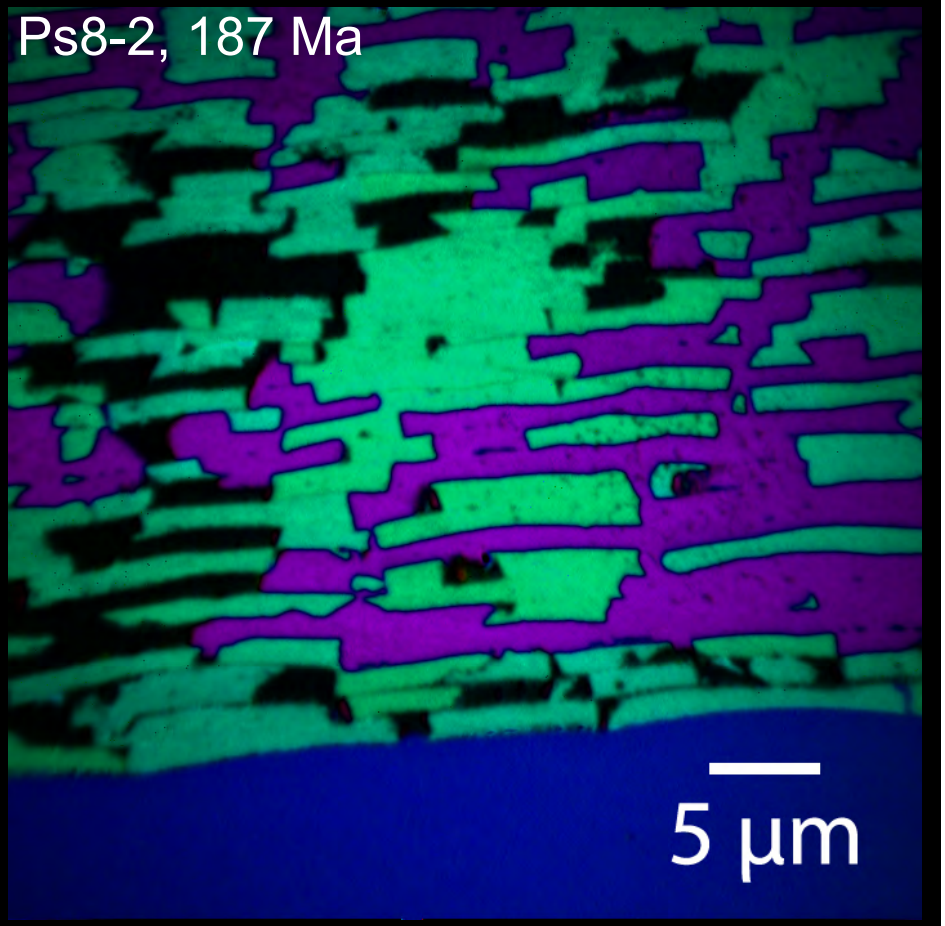
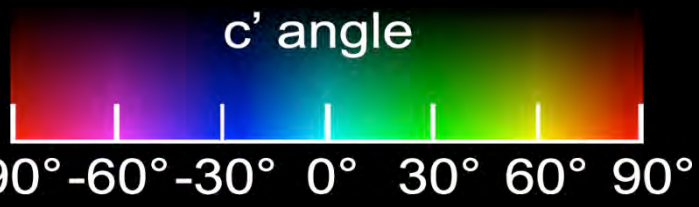


PUPA Gilbert, KD Bergmann, CE Myers, MA Marcus, RT DeVol, C-Y Sun, AZ Blonsky, J Zhao, EA Karan, E Tamre, N Tamura, AJ Giuffre, S Lemer, G Giribet, JM Eiler, AH Knoll. Nacre tablet thickness records formation temperature in modern and fossil shells. EPSL 2017.

using the nacre TT proxy for Jurassic *Pinna* with extensive diagenesis not accessible to elemental or isotopic analysis



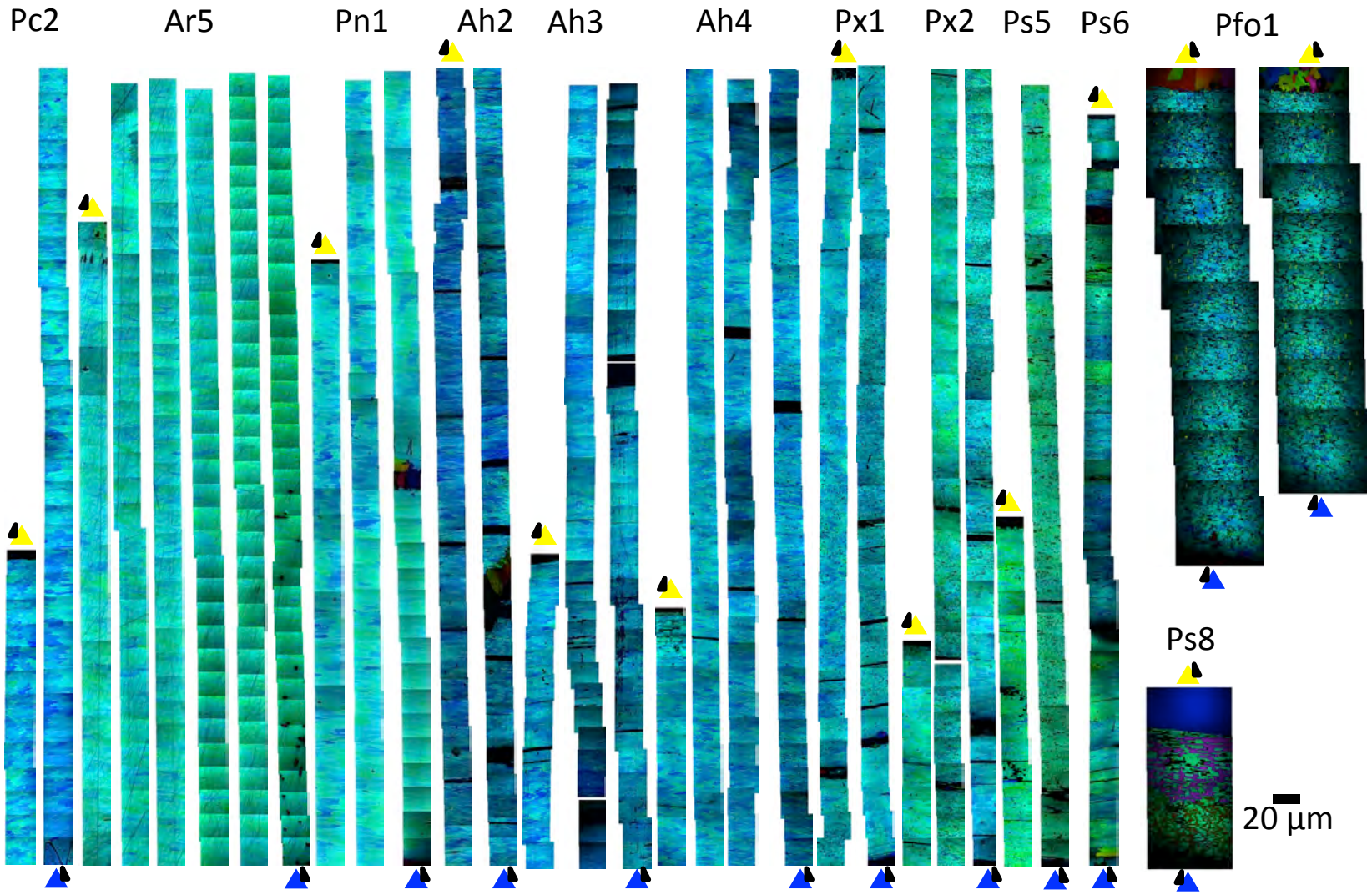




PIC-maps
(PIC=Polarization-dependent Imaging Contrast)

3 Recent + 9 Fossil shells

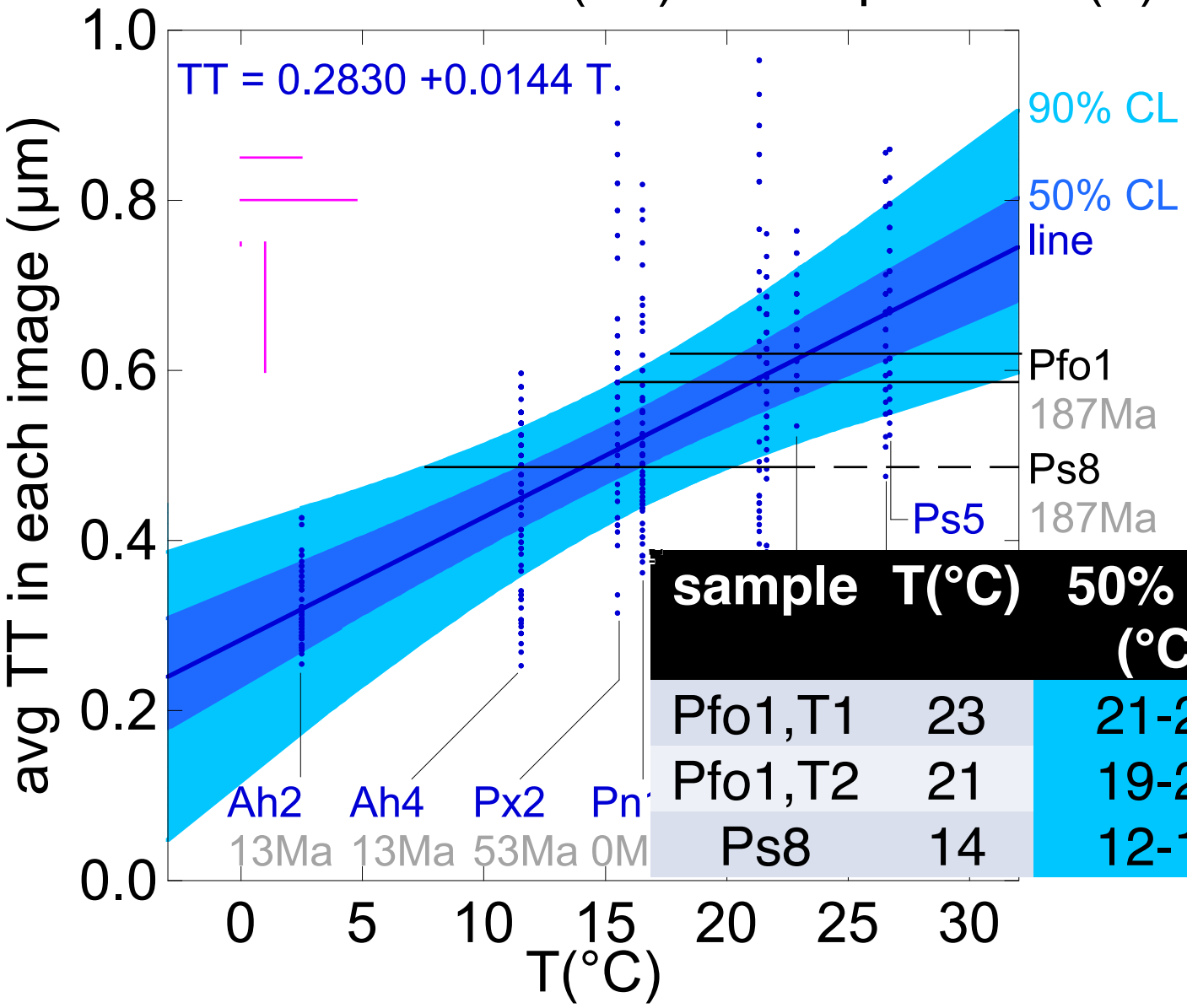
842 PIC-maps, partly overlapping to ensure continuity in position/time.



▲ = interior of shell, last deposited ▲ = exterior of shell, first deposited

measuring Jurassic T from TT:

nacre tablet thickness (TT) vs temperature (T)



sample	T(°C)	50% CL (°C)	90% CL (°C)
Pfo1,T1	23	21-27	18-34
Pfo1,T2	21	19-24	16-31
Ps8	14	12-14	8-20

conclusions

- biominerals, few formation mechanisms
- PIC-mapping
- TT vs. T correlation provides the first physical-structure proxy
- environment drives structure:
  metabolism − kinetics − thermodynamics
  biology − chemistry − physics

thanks to my group

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UW-Physics

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UW-Materials Science

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UW-Materials Science

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Associate Professor
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Audra L. Amasino
graduate student
MIT

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Harvard College OEB

Jessica Zhao
Harvard College
Appl Math

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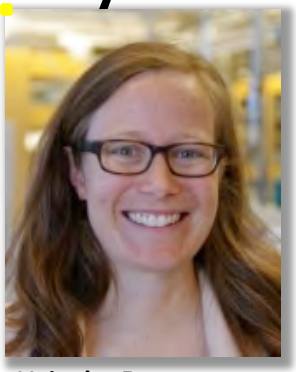


Kristin Bergmann
Harvard U

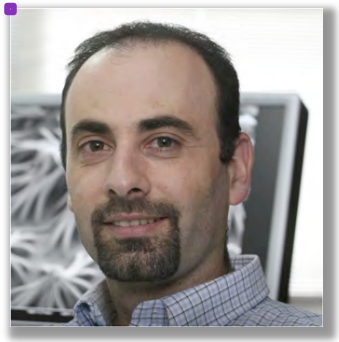
Corinne E. Myers

Lia Addadi
Weizmann, Israel

Steve Weiner

Yael Politi
Weizmann, now at MPI

Fred Wilt
UC-Berkeley

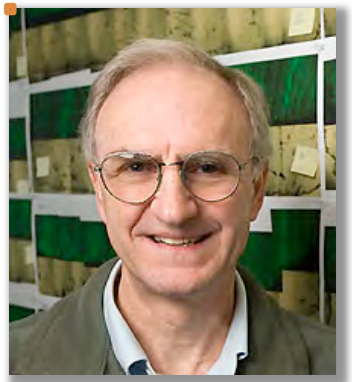


Boaz Pokroy
Technion, Israel

Susan N. Coppersmith
UW-Madison

Gonzalo Giribet
OEB-Harvard

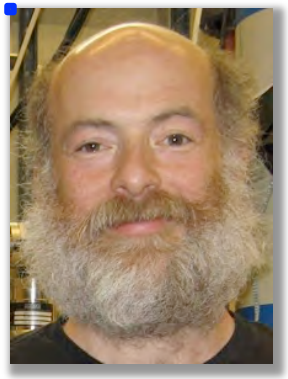
Sarah Lemer



John W. Valley
UW-Madison

Satish C. B. Myneni
Princeton

Nobumichi Tamura
Berkeley-ALS



Matthew A. Marcus
Berkeley-ALS

Alex Navrotsky
UC-Davis

Michele Parrinello
ETH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