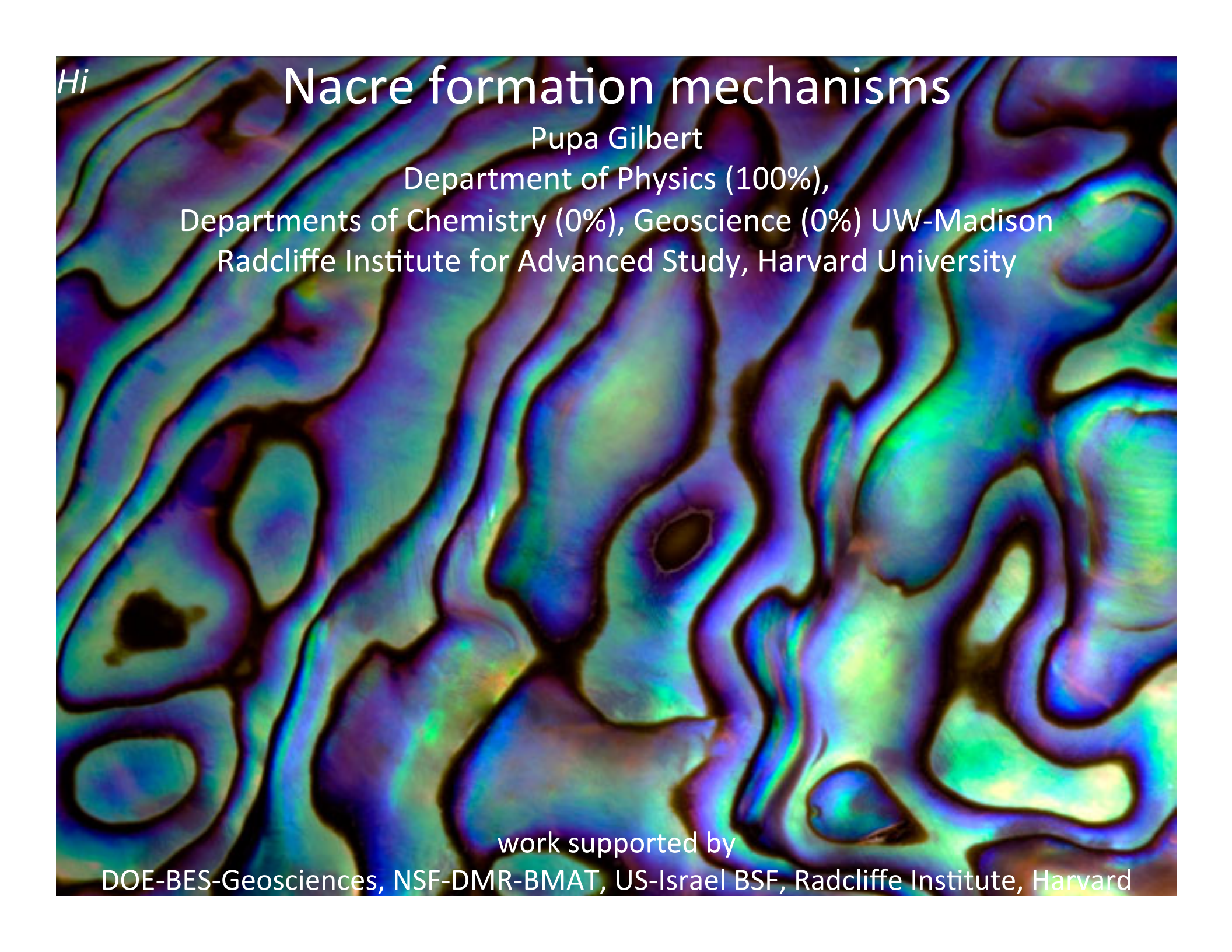




Hi Nacre formation mechanisms

Pupa Gilbert

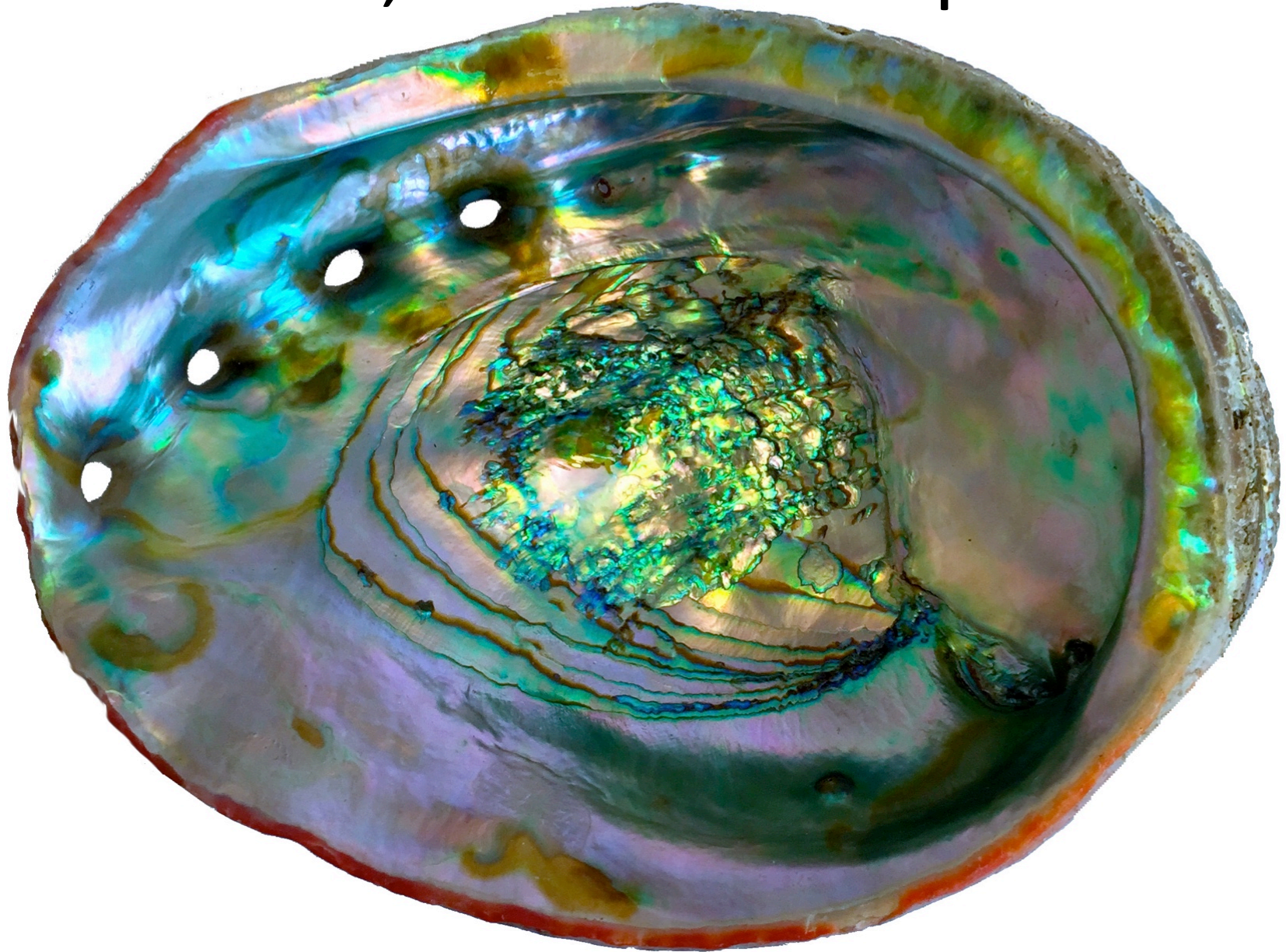
Department of Physics (100%),
Departments of Chemistry (0%), Geoscience (0%) UW-Madison
Radcliffe Institute for Advanced Study, Harvard University

work supported by

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

Hr

nacre, or mother-of-pearl



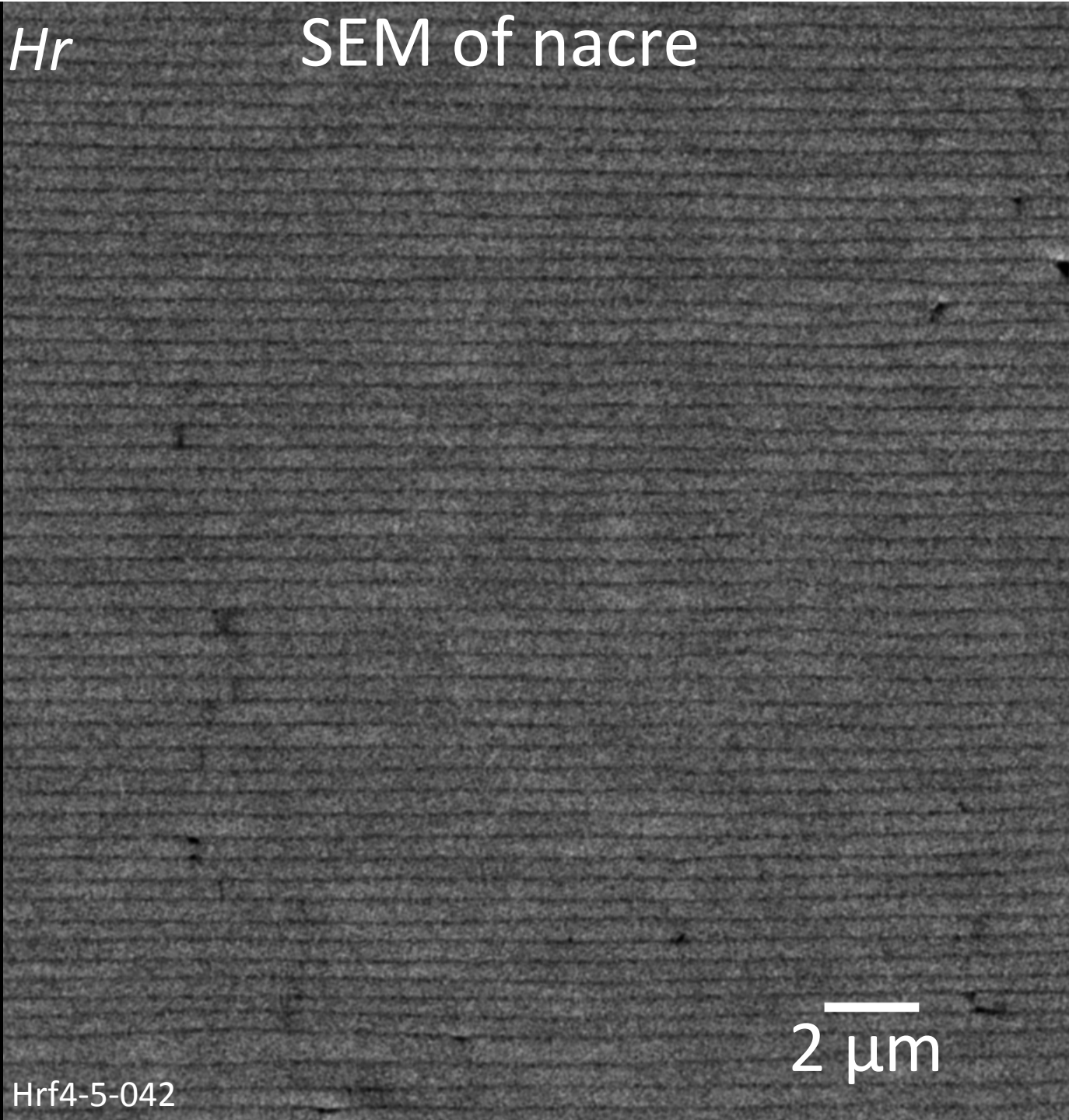
Haliotis rufescens, red abalone, CA

Hr

SEM of nacre

Hrf4-5-042

2 μm

This is a scanning electron micrograph (SEM) of a nacre surface. The image displays a highly regular, fine-grained texture consisting of numerous horizontal, parallel lines or striations. These lines are closely spaced and run across the entire width of the image. The overall appearance is that of a smooth but finely textured surface. The image is framed by black bars on the left and right sides.

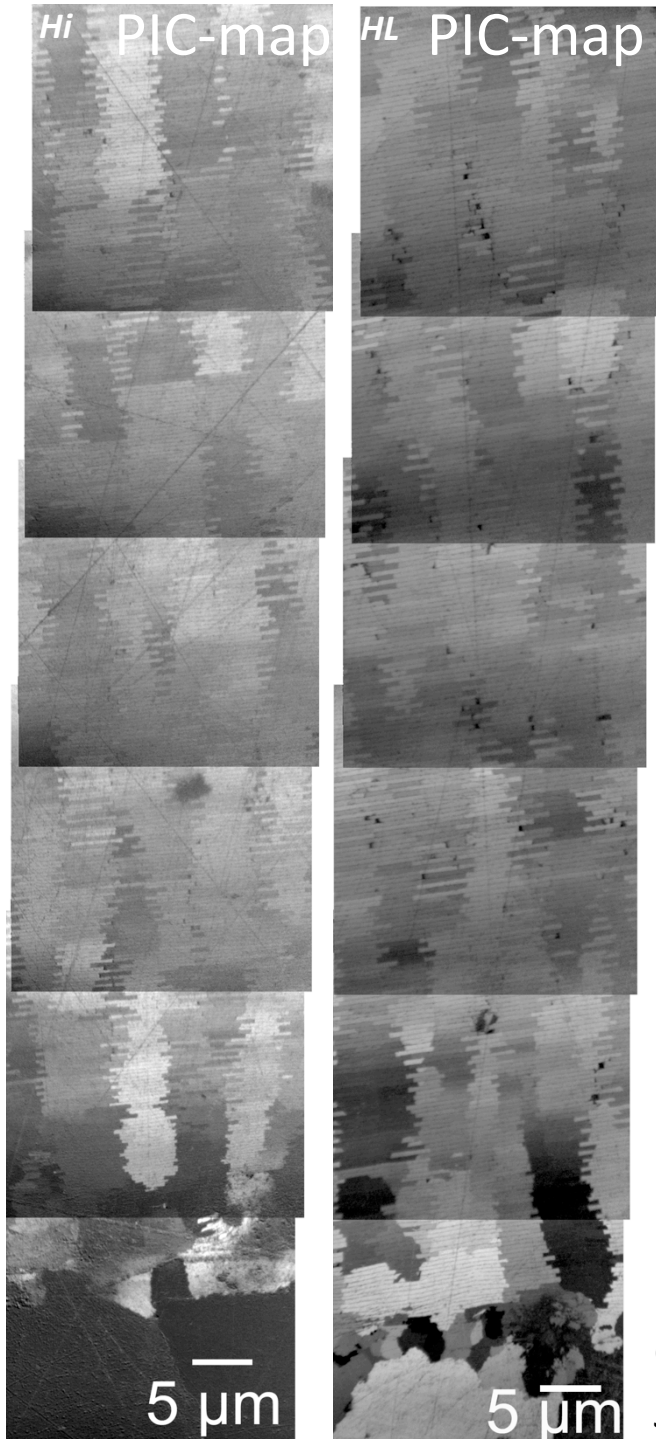
PIC-maps of nacre

(PIC=Polarization-dependent Imaging Contrast)
obtained with PhotoEmission Electron Microscopy (PEEM)

myth: the orientation of nacre tablets is
templated by organic molecules

experiments and theory show that
nacre *gradually* orders as it grows.
2 order parameters change with distance from
nacre-prismatic boundary:

- tablet contrast (= angle spread)
- tablet width



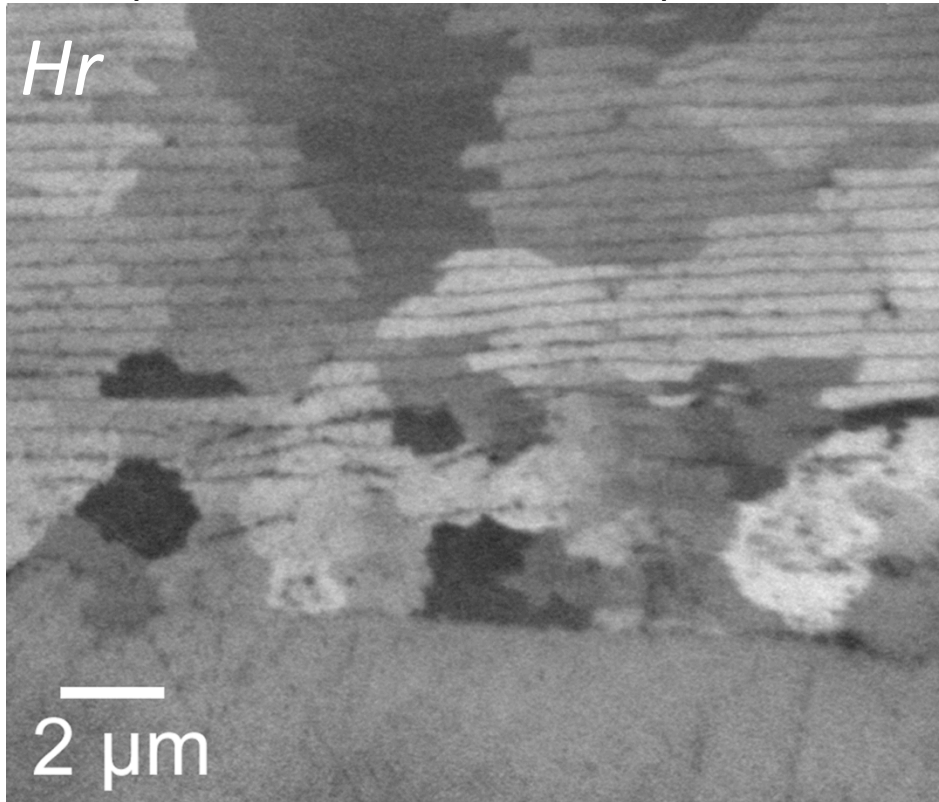
PUPA Gilbert, RA Metzler, D Zhou, A Scholl, A Doran, A Young, M Kunz,
N Tamura, [SN Coppersmith](#).

Gradual Ordering in Red Abalone Nacre.

J. Am. Chem. Soc. **130**, 17519-17527 (2008)

nacre *gradually* orders as it grows

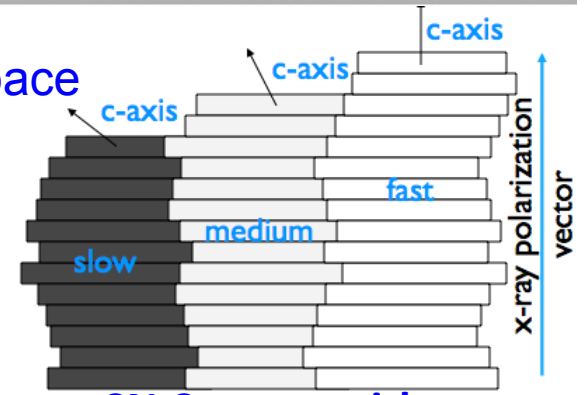
experimental data: PIC-map of nacre



simulation data: fast=bright, slow=dark



fast-growing crystal orientations prevail in a competition for space



PUPA Gilbert, RA Metzler, D Zhou, A Scholl, A Doran, A Young, M Kunz, N Tamura, [SN Coppersmith](#).
Gradual Ordering in Red Abalone Nacre. J. Am. Chem. Soc. **130**, 17519-17527 (2008)

Sue Coppersmith's model for nacre growth

nacre

population genetics

nucleation of new crystal orientation



mutation

in-plane growth rate



fitness

$$\frac{\varphi_l(\gamma)}{\varphi_{l-1}(\gamma)} = \frac{1}{N_l} \left(1 - \frac{\alpha\gamma^2}{2} \right) \approx \frac{1}{N_l} e^{-\alpha\gamma^2/2}$$

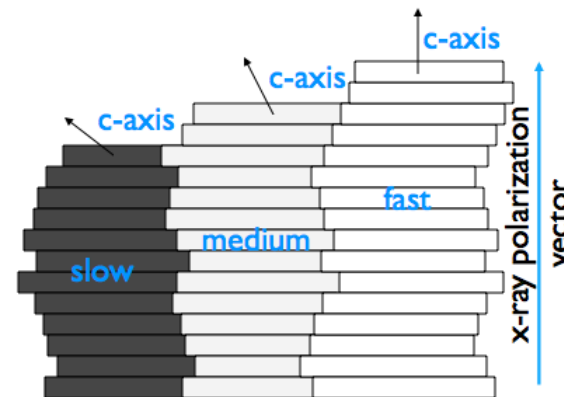
where α is a numerical coefficient and N_l is a normalization factor that is fixed by the normalization condition

$$1 = \int_0^\pi (2\pi\gamma) \varphi_l(\gamma) d\gamma = \frac{1}{N_l} \int_0^\pi (2\pi\gamma) e^{-\alpha\gamma^2/2} \varphi_{l-1}(\gamma) d\gamma$$

We also assume that there is a small probability ε that when a tablet nucleates, instead of adopting the same γ as the tablet below its nucleation site, it takes on a value chosen from a probability distribution $w(\gamma)$ that we will choose to be Gaussian, $w(\gamma) = ((\beta)/(2\pi))^{1/2} e^{-\beta\gamma^2/2}$. This misorientation process is analogous to mutation in population genetics.⁴² Therefore, the evolution is governed by the equation

$$\varphi_l(\gamma) = \varepsilon \left(\frac{\beta}{2\pi} \right)^{1/2} e^{-\beta\gamma^2/2} + (1 - \varepsilon) \frac{1}{N_l} \varphi_{l-1}(\gamma) e^{-\alpha\gamma^2/2}$$

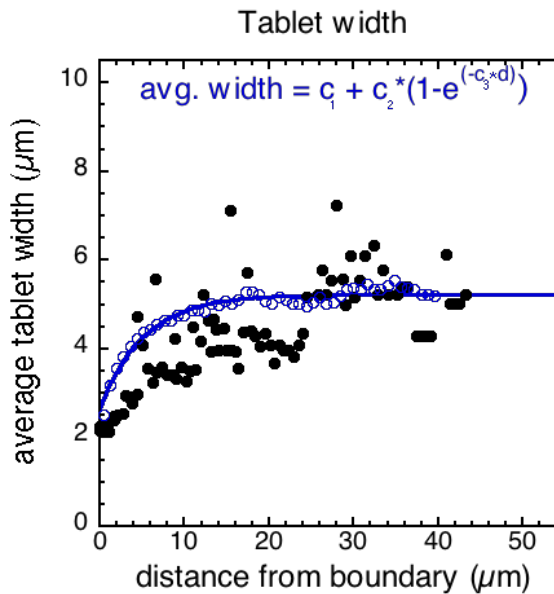
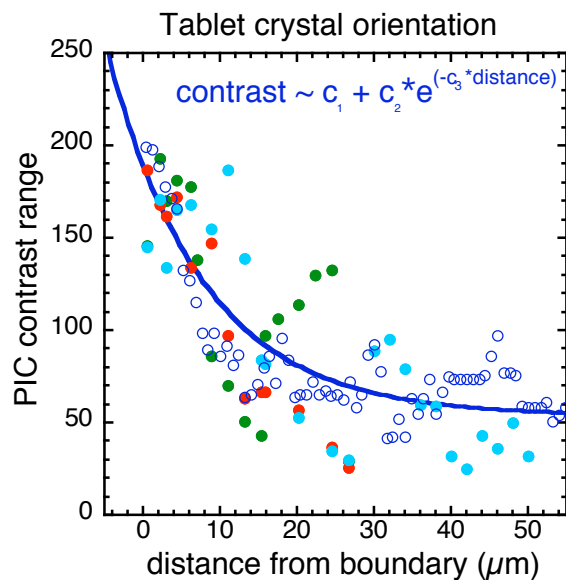
When the co-orientation of tablets in successive layers is perfect, so that $\varepsilon = 0$, the solution to this equation is $\varphi_{l+1}(\gamma) \propto \varphi_1(\gamma) e^{-l\alpha\gamma^2/2}$. Therefore, when $\varepsilon = 0$, for any α



PUPA Gilbert, RA Metzler, D Zhou, A Scholl, A Doran, A Young, M Kunz, N Tamura, **SN Coppersmith**.
Gradual Ordering in Red Abalone Nacre. J. Am. Chem. Soc. **130**, 17519-17527 (2008)

nacre *gradually* orders as it grows

Sue's kinetic growth model w/ 30% spread in growth rate, 3% new orientation

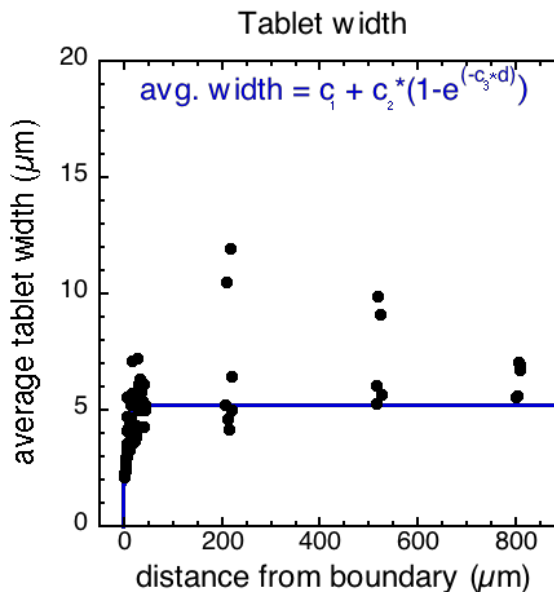
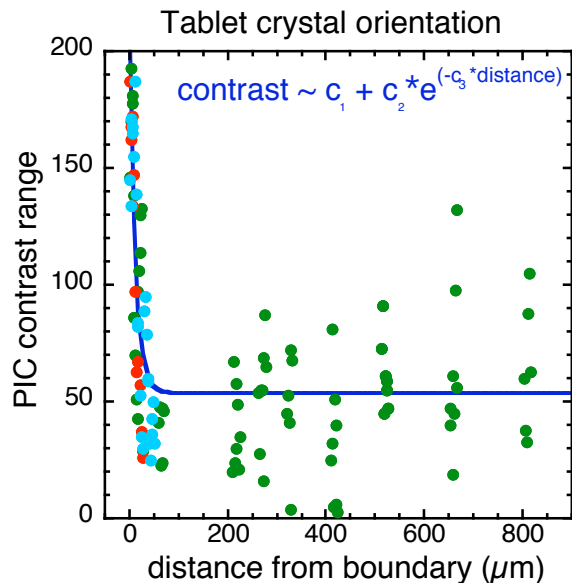


experiment results: ● ● ● ●

theory results: ○

fit of theory results: —

short-range: 0-50 μm



long-range: 0-800 μm

Gilbert et al. JACS 2008

Coppersmith et al. J. Phys. A 2009



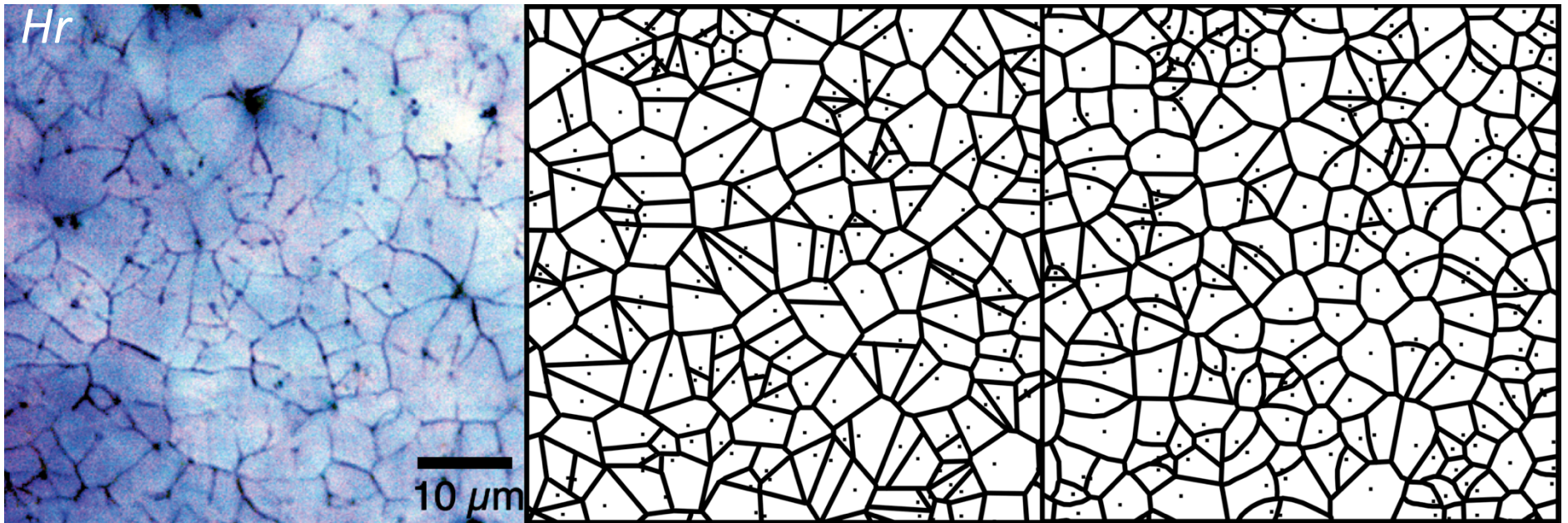
Another model by Sue Coppersmith for in-plane nacre growth

experimental data:
VLM of 1 nacre layer

simulation data: Voronoi constructions

isotropic growth rates

30% spread in growth rates



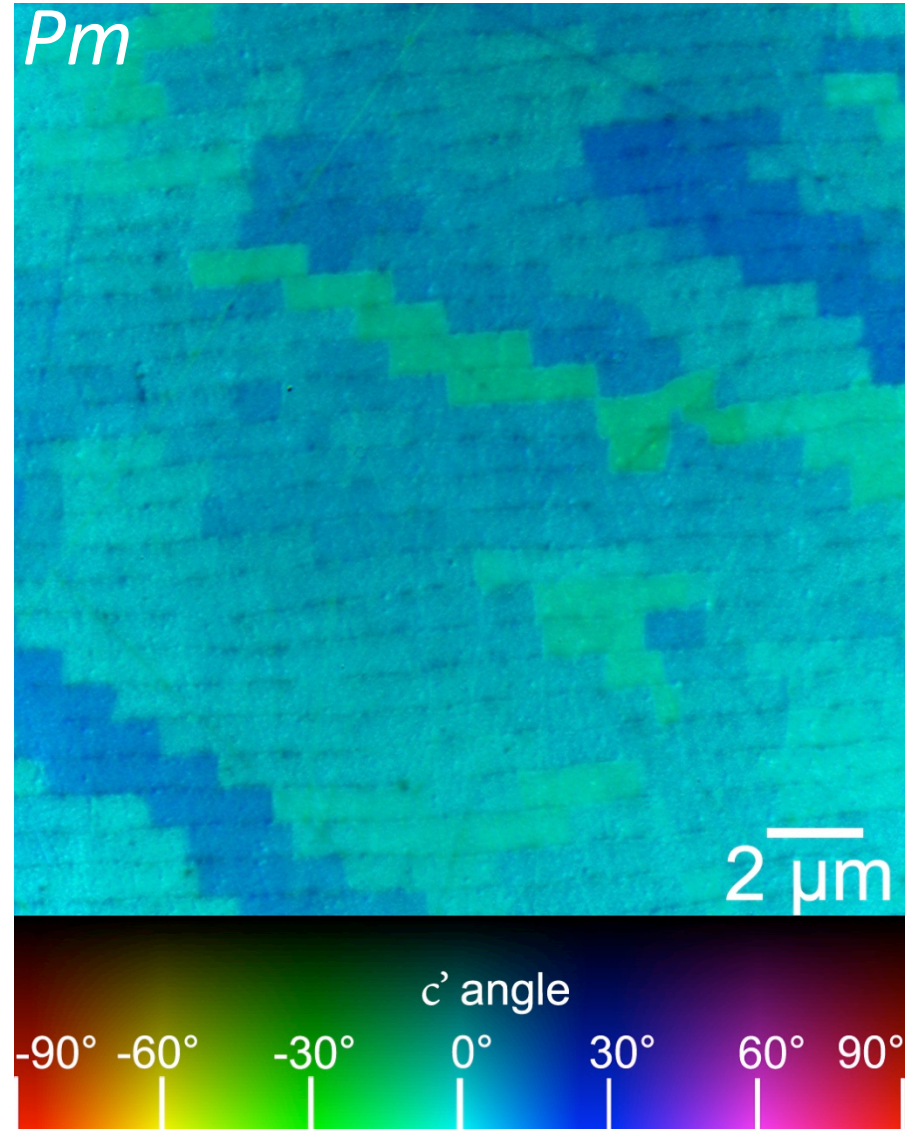
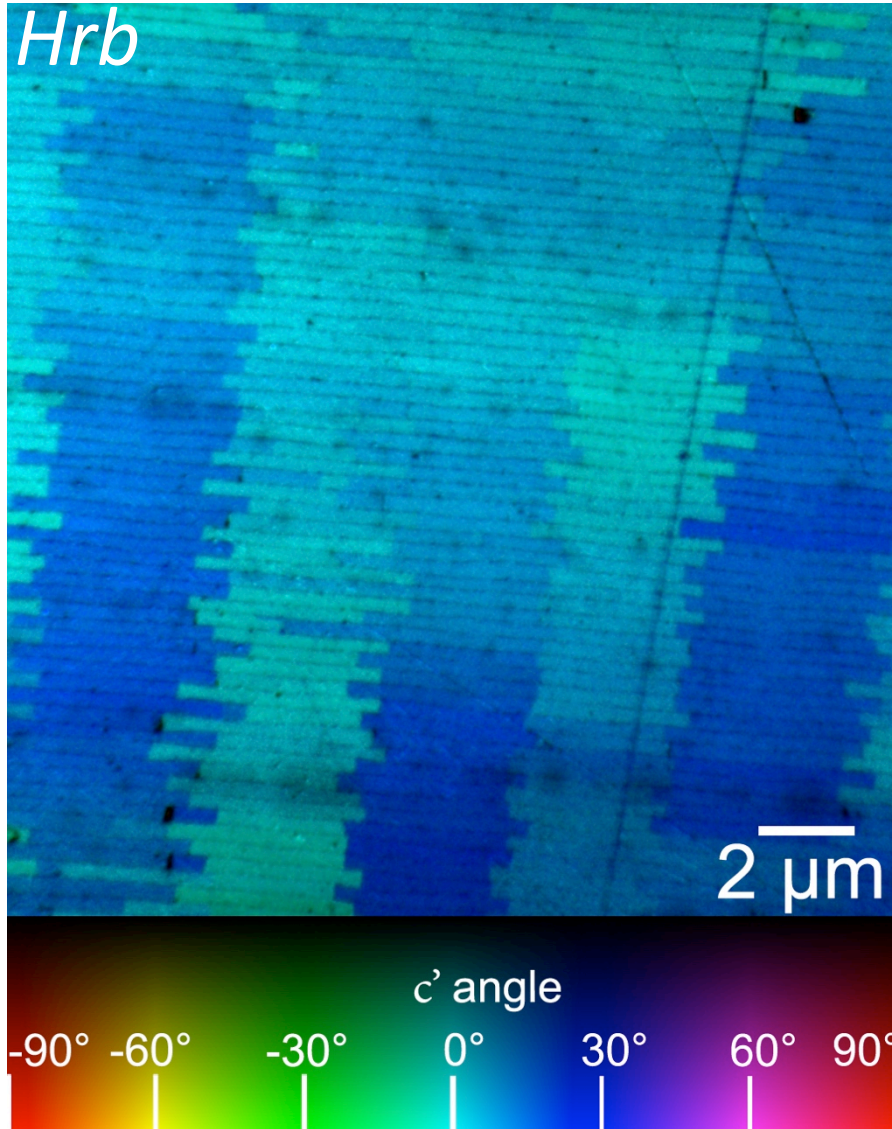
PUPA Gilbert, RA Metzler, D Zhou, A Scholl, A Doran, A Young, M Kunz, N Tamura, [SN Coppersmith](#).
Gradual Ordering in Red Abalone Nacre. J. Am. Chem. Soc. **130**, 17519-17527 (2008)

PIC-maps of nacre, fully quantitative, in color

(PIC=Polarization-dependent Imaging Contrast)

columnar nacre (gastropods, cephalopods)

sheet nacre (bivalves)

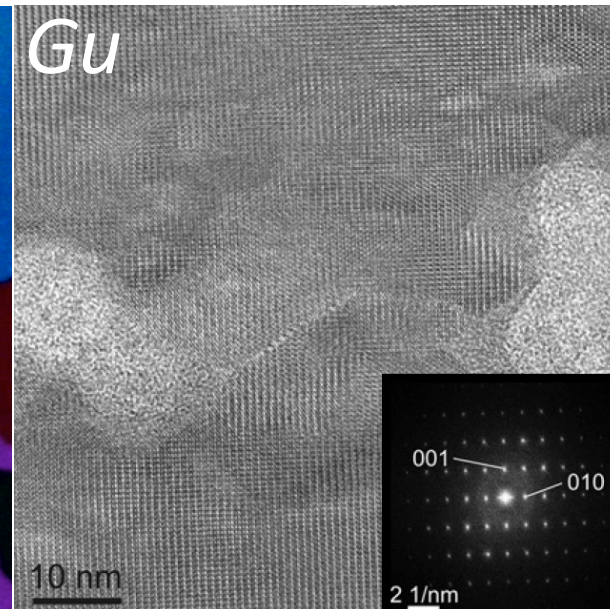
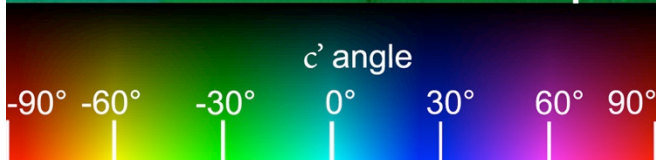
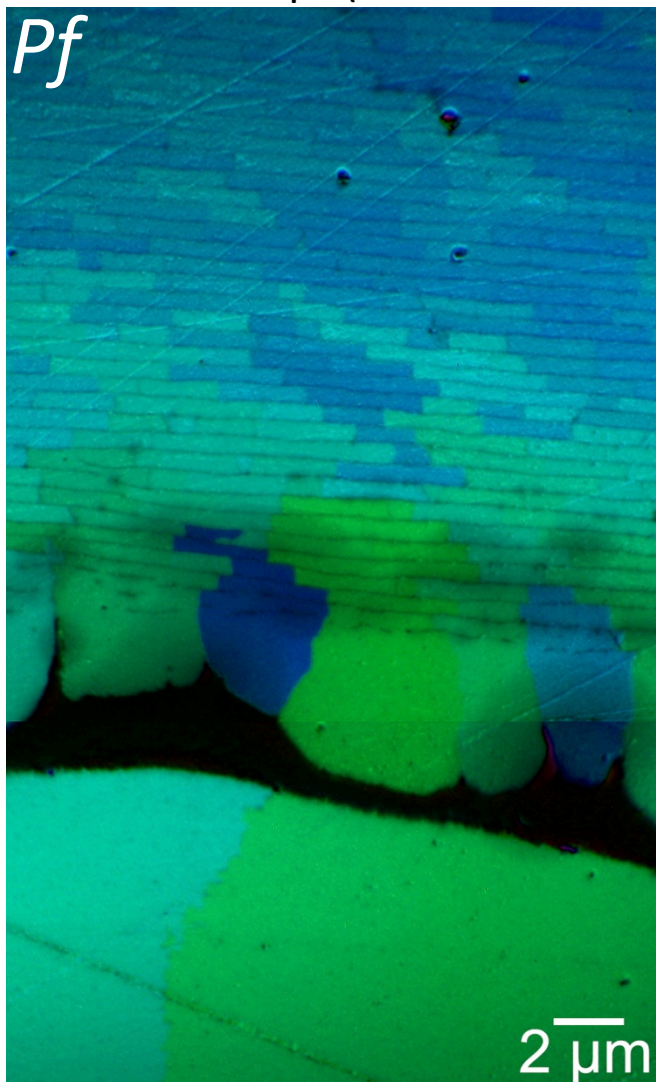


adapted from IC Olson et al. 2013

nacre gradually orders, and grows epitaxially

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

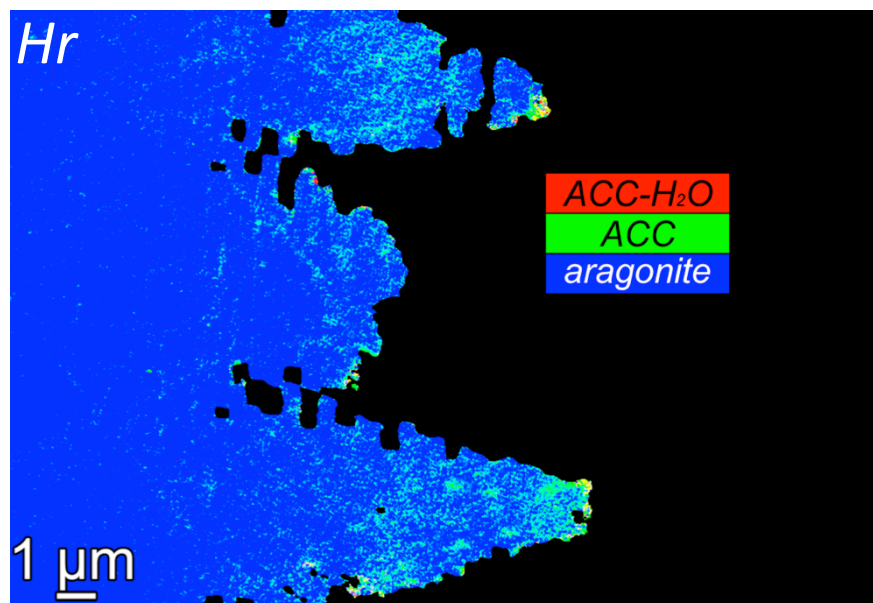
TEM



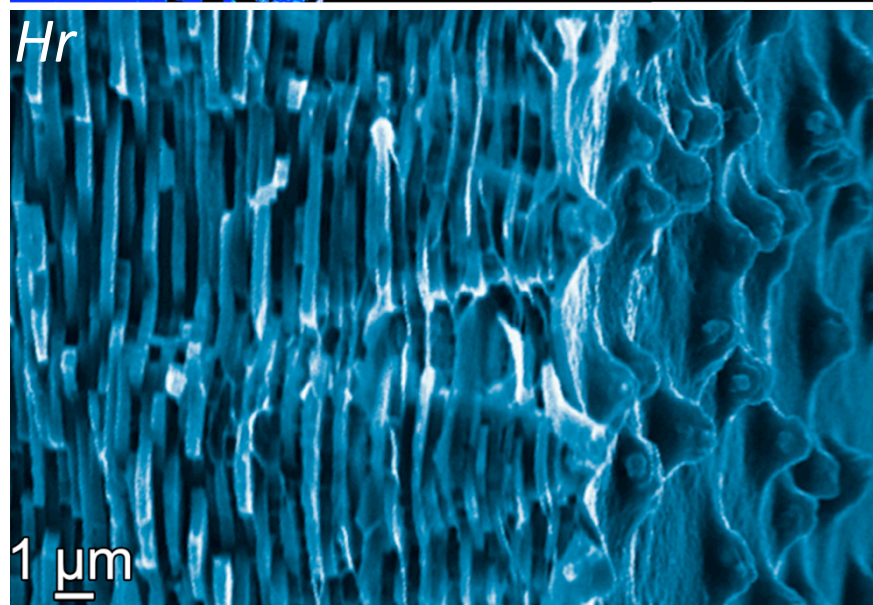
↑
Checa et al. JSB 2011

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

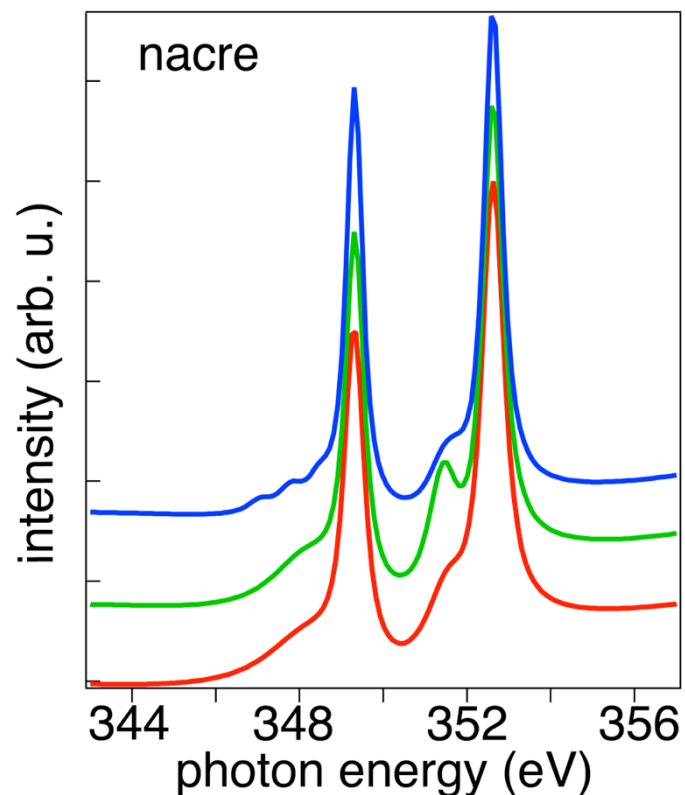
Nacre forms from 2 amorphous precursors: ACC-H₂O and ACC



component mapping, obtained with
PhotoEmission Electron Microscopy
(PEEM)



Ca L-edge XANES
spectral components



Nanoscale transforming mineral phases in fresh nacre

RT DeVol, C-Y Sun, MA Marcus, [SN Coppersmith](#), SCB Myneni, PUPA Gilbert. JACS 137, 13325 (2015)

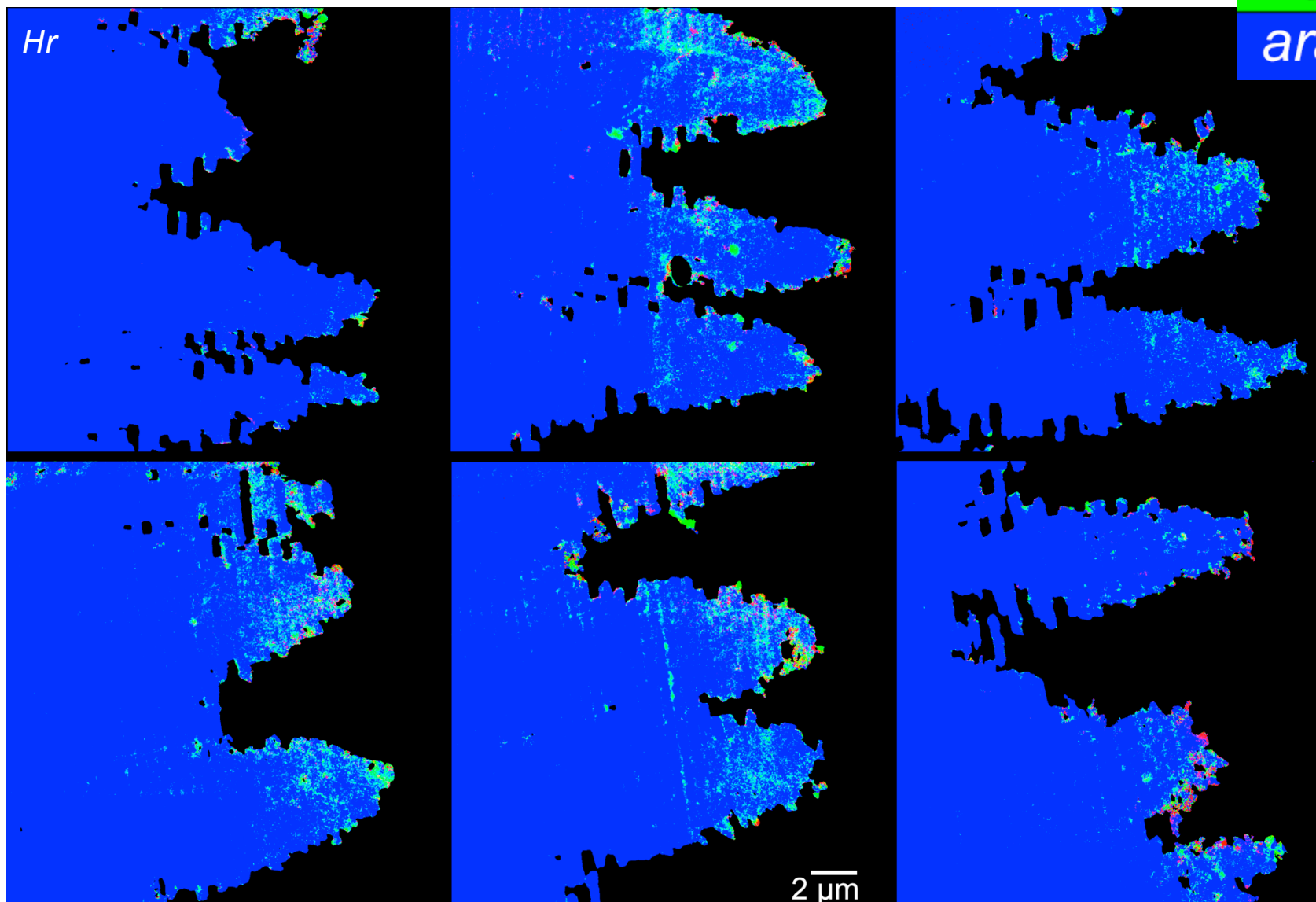
6 other regions of forming nacre, from 2 different shells

Conclusion: Nacre has calcite-like ACC precursors

ACC-H₂O

ACC

aragonite



Nanoscale transforming mineral phases in fresh nacre

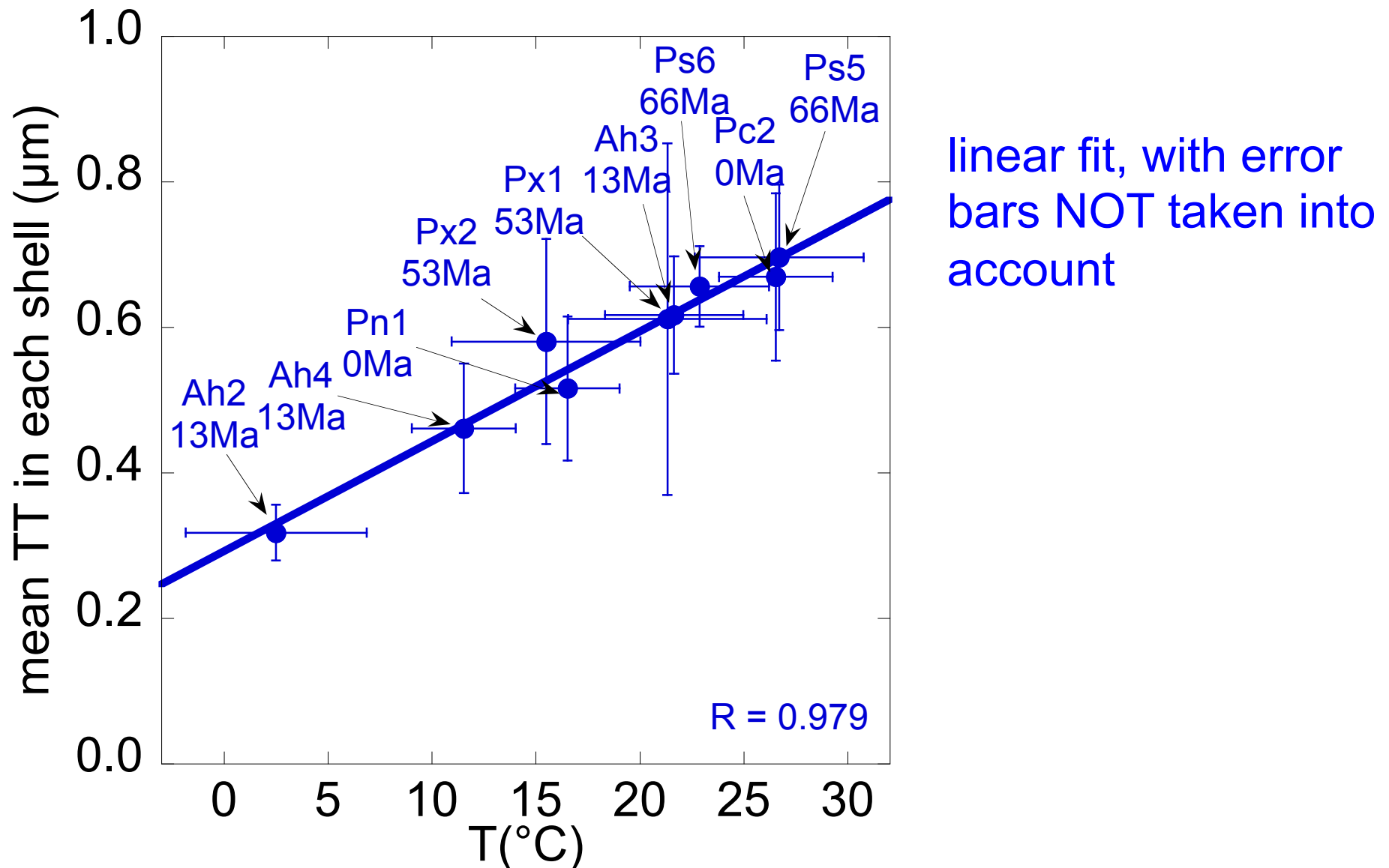
RT DeVol, C-Y Sun, MA Marcus, [SN Coppersmith](#), SCB Myneni, PUPA Gilbert. JACS 137, 13325 (2015)

Ar

what controls tablet thickness?

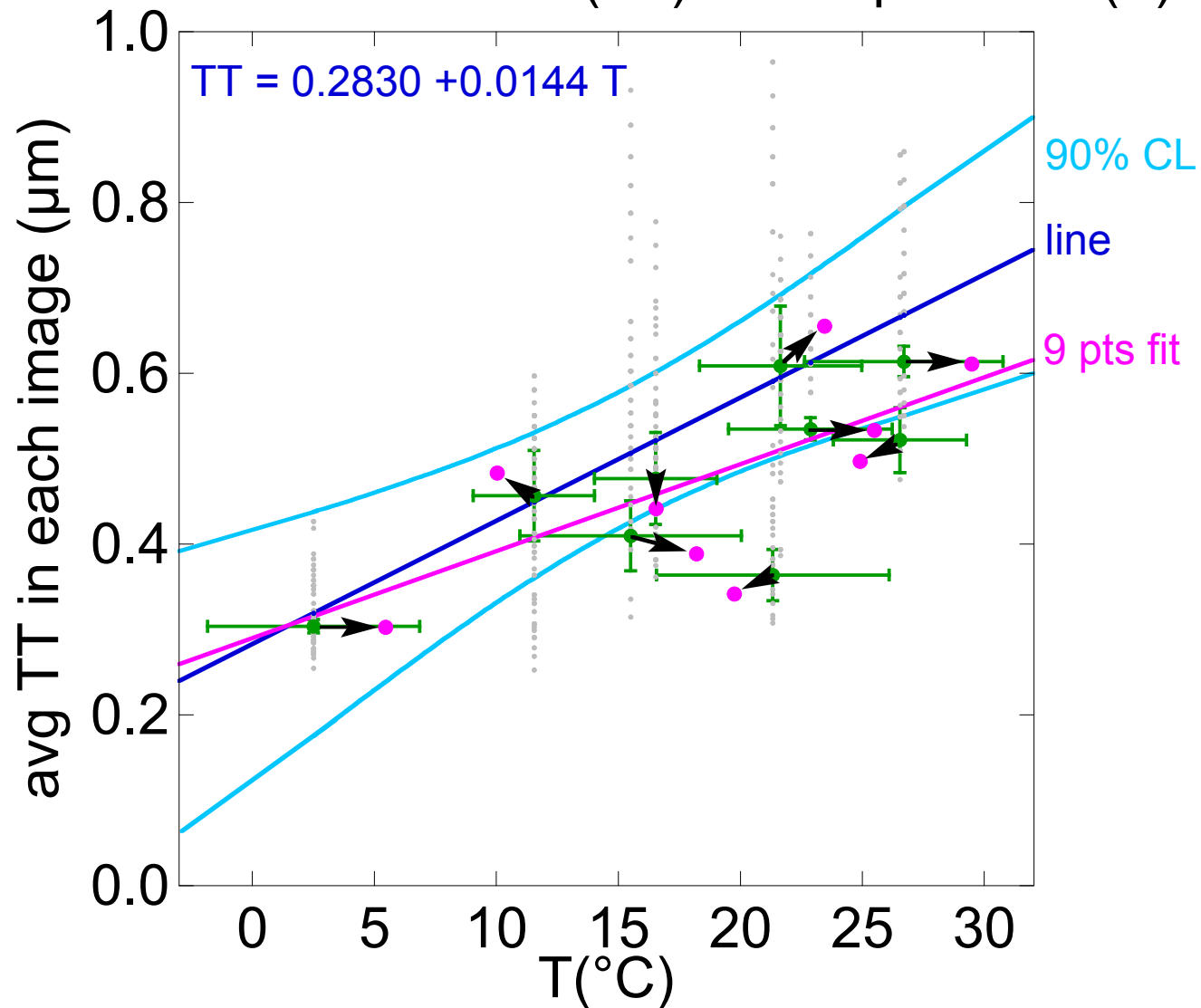


nacre tablet thickness (TT) vs temperature (T)



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, in press.

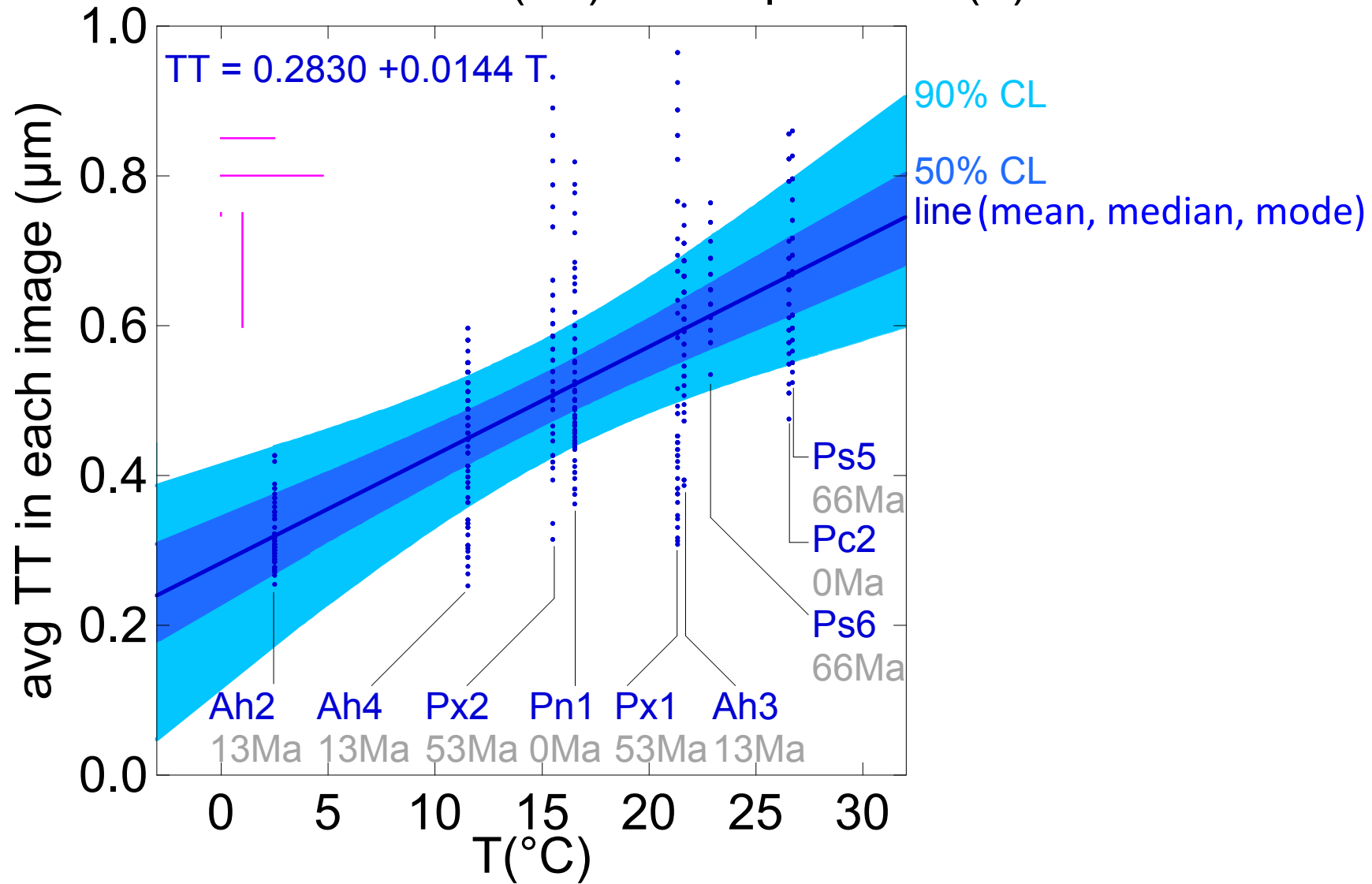
nacre tablet thickness (TT) vs temperature (T)



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

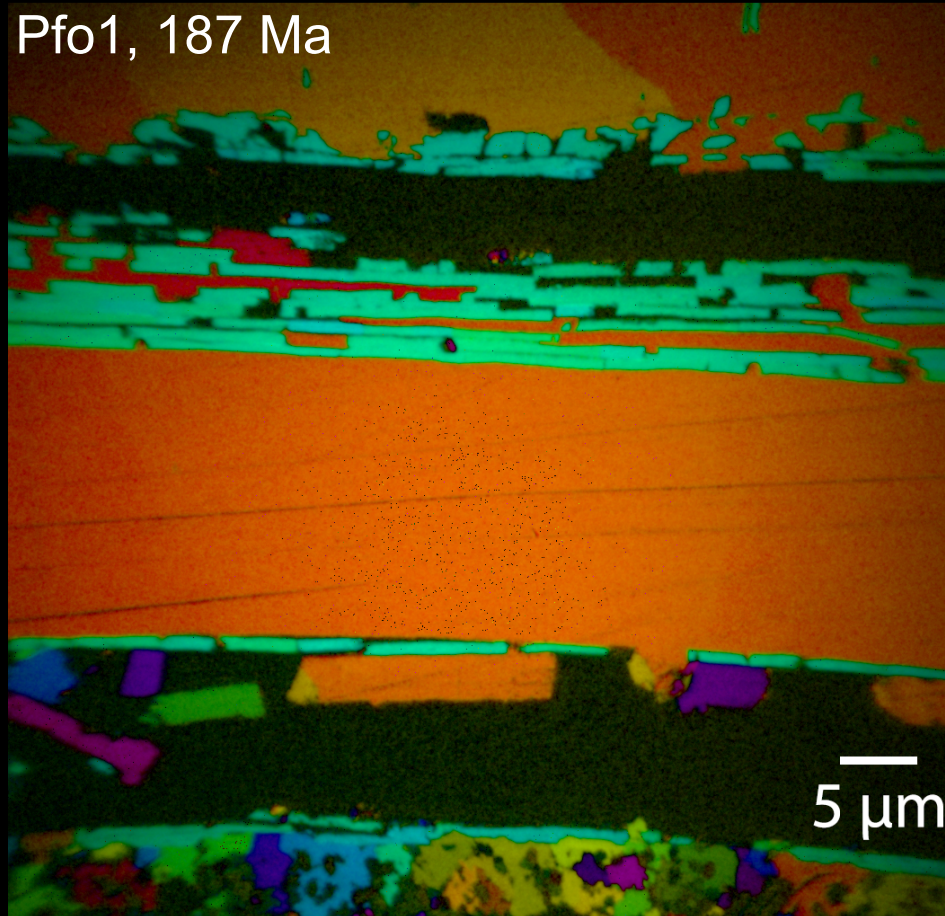
PUPA Gilbert, KD Bergmann, CE Myers, MA Marcus, RT DeVol, C-Y Sun, AZ Blonsky, J Zhao, EA Karan, E Tamre, N Tamura, AJ Giuffre, S Lemer, G Giribet, JM Eiler, AH Knoll. Nacre tablet thickness records formation temperature in modern and fossil shells. EPSL, in press.

nacre tablet thickness (TT) vs temperature (T)

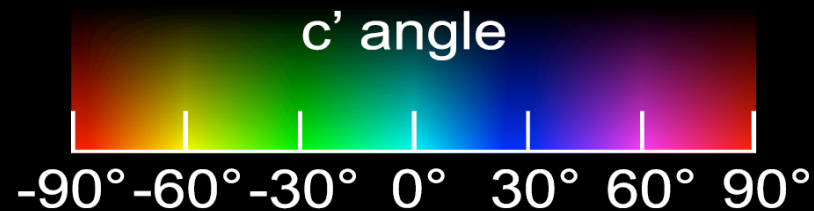
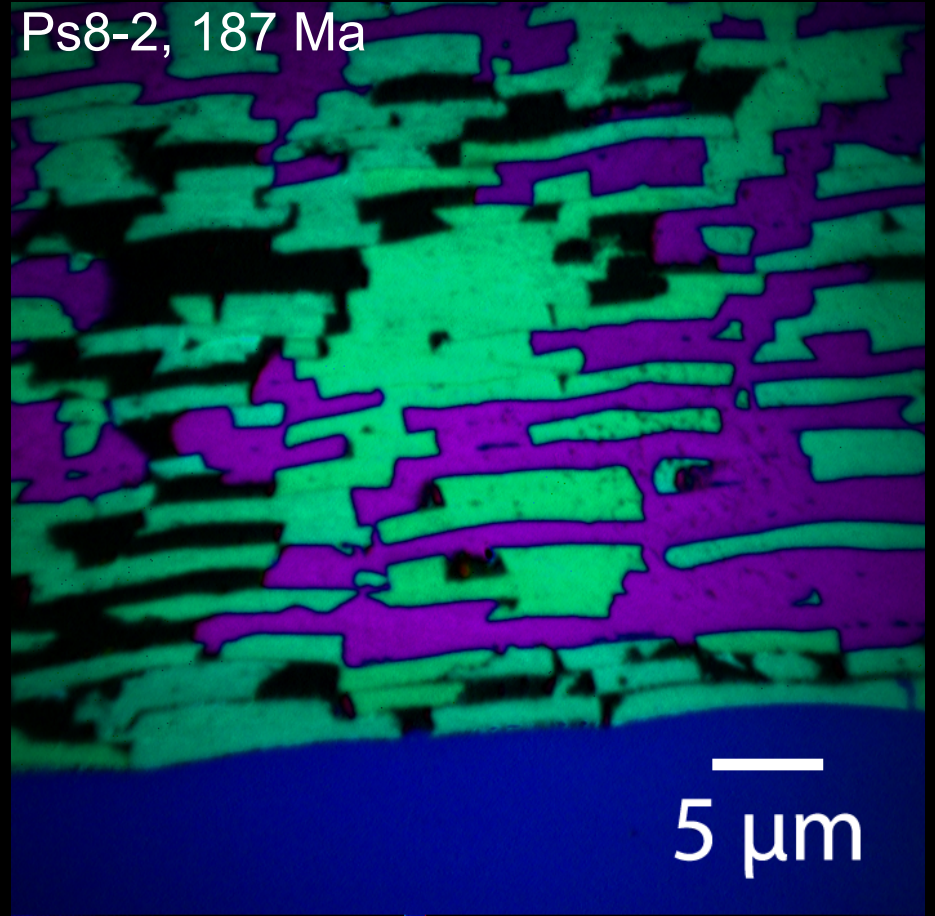


using the nacre TT proxy for Jurassic *Pinna* with extensive diagenesis

Pfo1, 187 Ma



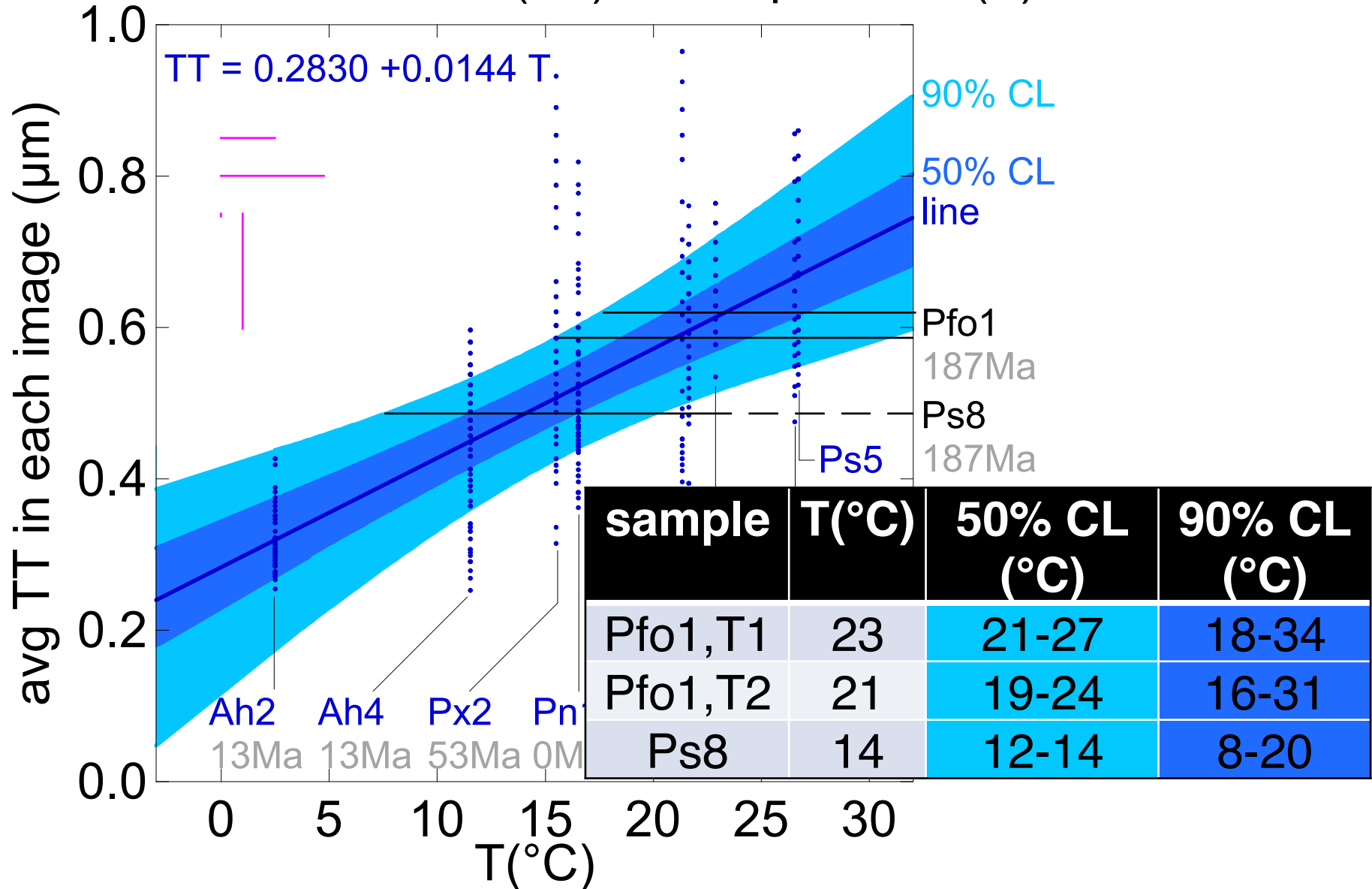
Ps8-2, 187 Ma



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

measuring Jurassic T from TT:

nacre tablet thickness (TT) vs temperature (T)



thanks to my group



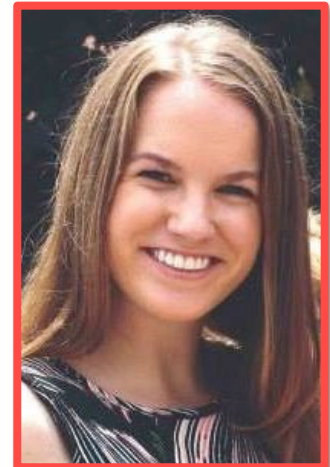
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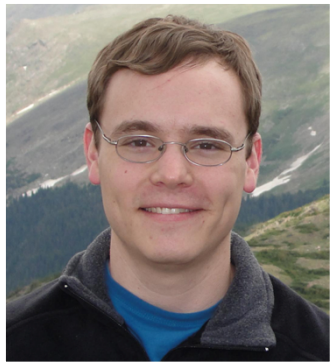
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many thanks to excellent collaborators



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Andrew H. Knoll



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Harvard U



Corinne E. Myers



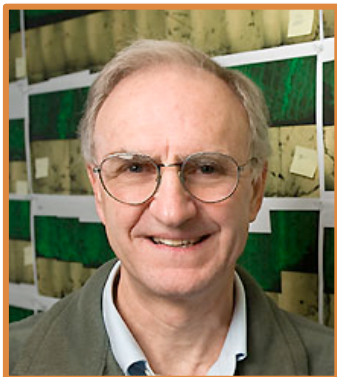
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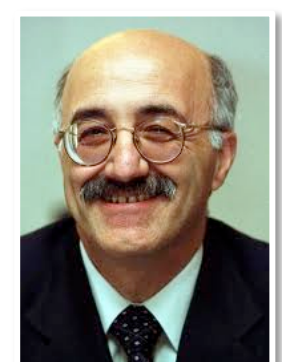
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UC-Davis



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ETH



thank you for your attention

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NSF: DMR-BMAT
US-Israel BSF
Radcliffe IAS