Biomineralization
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sea urchin spine diffracts like a single crystal of calcite
calcite single crystal
sea urchin spine diffracts like a single crystal of calcite
calcite single crystal
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
calcite unit cell

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
SEM of nacre

Hr

2 µm
iridescence
or thin-layer interference
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 (Polarization-dependent Imaging Contrast)

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

Checa et al. JSB 2011
what controls tablet thickness in nacre?

Atrina rigida shell, Florida
question at Harvard 2014-15: does nacre TT record environmental temperature?
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.
nacre tablet thickness (TT) vs temperature (T)

linear fit, with error bars NOT taken into account

mean TT in each shell (µm)

T(°C)

Y = M0 + M1*x + ... M8*x8 + M9*x9

Y = M0 + M1*x + ... M8*x8 + M9*x9

R = 0.979

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

nacre tablet thickness (TT) vs temperature (T)

$TT = 0.2830 + 0.0144 T$

90% CL line

9 pts fit

nacre tablet thickness (TT) vs temperature (T)

TT = 0.2830 + 0.0144 T.

avg TT in each image (µm)

T(°C)

TT = 0.2830 + 0.0144 T

Y = M0 + M1*x + ... M8*x8 + M9*x9

0.10527
0.025387
-0.00029935
0.99998R

90% CL
50% CL
line (mean, median, mode)

Ps5
66Ma
Pc2
0Ma
Ps6
66Ma

Ah2
13Ma
Ah4
13Ma
Px2
53Ma
Pn1
0Ma
Px1
53Ma
Ah3
13Ma

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

Pfo1, 187 Ma

Ps8-2, 187 Ma

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)

\[ TT = 0.2830 + 0.0144T \]

<table>
<thead>
<tr>
<th>sample</th>
<th>T(°C)</th>
<th>50% CL (°C)</th>
<th>90% CL (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pfo1,T1</td>
<td>23</td>
<td>21-27</td>
<td>18-34</td>
</tr>
<tr>
<td>Pfo1,T2</td>
<td>21</td>
<td>19-24</td>
<td>16-31</td>
</tr>
<tr>
<td>Ps8</td>
<td>14</td>
<td>12-14</td>
<td>8-20</td>
</tr>
</tbody>
</table>
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
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