Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.22764

Unexpected phases and phase transitions in biomineral aragonite

CONNOR A SCHMIDT[1], ERIC TAMBUTTÉ[2], ALEXANDER A VENN[2], ZHAOYONG ZOU[3], MARIA CRISTINA CASTILLO ALVAREZ[4], LAURENT DEVRIENDT[4], HANS BECHTEL[5], CAYLA A STIFLER[6], SAMANTHA ANGLEMYER[6], CP BREIT[6], CONNOR L FOUST[6], ANDRII HOPANCHUK[6], CONNOR N KLAUS[6], ISAAC KOEHLER[6], ISABELLE M LECLOUX[6], JAIDEN MEZERA[6], MADELINE R PATTON[6], ANNIE PURISCH[6], VIRGINIA QUACH[6], JADEN SENGKHAMMEE[6], TARAK SRISTY[6], SHREYA VATTEM[6], EVAN J WALCH[6], MARIE ALBERIC[7], YAEL POLITI[8], PETER FRATZL[9], SYLVIE TAMBUTTÉ[2] AND **PROF. PUPA GILBERT**[1,4]

[1]University of Wisconsin-Madison
[2]Centre Scientifique de Monaco
[3]Wuhan University
[4]Lawrence Berkeley National Laboratory
[5]Advanced Light Source
[6]UW-Madison
[7]Sorbonne Université
[8]TU-Dresden
[9]Max Planck Institute of Colloids and Interfaces
Presenting Author: pupa@physics.wisc.edu

Analyzing 200 million spectra with Myriad Mapping (MM) of nanoscale mineral phases we found expected and unexpected precursors on the surface of freshly deposited coral skeleton and nacre, but not on sea urchin spines. The expected phases, found on all biominerals (1-11), were amorphous calcium carbonate hydrated ($ACCH_2O$) and anhydrous (ACC). The unexpected crystalline precursors were calcium carbonate hemihydrate ($CaCO_3 \cdot ½H_2O$, CCHH) and monohydrocalcite ($CaCO_3 \cdot 1H_2O$, MHC)(12). These results demonstrated that biomineralization pathways are more complex and diverse than previously understood, opening new questions on the effect of multiple metastable precursor phases on isotopic and trace element compositions that are commonly used as proxies for paleo-environmental reconstructions.

1. E Beniash, . . . S Weiner 1997 DOI: https://doi.org/10.1098/rspb.1997.0066
2. M Najman, . . . GD Stasio 2004
3. Y Politi, . . . L Addadi 2004 DOI: 10.1126/science.1102289
4. Y Politi, . . . PUPA Gilbert 2008 DOI: https://doi.org/10.1073/pnas.0806604105
5. YUT Gong, . . . PUPA Gilbert 2012 DOI: https://doi.org/10.1073/pnas.1118085109
6. RT DeVol, . . . PUPA Gilbert 2015 DOI: https://doi.org/10.1021/jacs.5b07931
7. MA Marcus, . . . PUPA Gilbert 2017 DOI: https://doi.org/10.1021/acsnano.7b05044
8. T Mass, . . . PUPA Gilbert 2017 DOI: https://doi.org/10.1073/pnas.1707890114
9. C-Y Sun, . . . PUPA Gilbert 2017 DOI: https://doi.org/10.1021/acsnano.7b00127
10. C-Y Sun, . . . PUPA Gilbert 2020 DOI: https://doi.org/10.1073/pnas.2012025117
11. CA Stifler, . . . PUPA Gilbert 2021 DOI: https://doi.org/10.1021/acs.cgd.1c00865
12. CA Schmidt, . . . PUPA Gilbert 2024 DOI: https://doi.org/10.1038/s41467-024-46117-x

Figure 1. Metastable transient precursors to coral skeleton and nacre formation. These Myriad Maps (MMs) show that amorphous and crystalline precursors are both present, but only on the forming surface of fresh, forming aragonite ($CaCO_3$) biominerals, including coral skeletons (A1, A2, A3) and abalone nacre (B1, B2, B3). Calcite biominerals, including sea urchin spines (C1, C2, C3) only have amorphous precursors. Legend: red is amorphous calcium carbonate hydrated (ACC-H_2O), green is amorphous calcium carbonate dehydrated (ACC), cyan is calcium carbonate hemihydrate (CCHH), and magenta is monohydrocalcite (MHC). Data from (12).