

Pteropod shell mineral and structure: one of the major calcifiers in the oceans

Steve Weiner

Odelia Sibony-Nevo

Bracha Viviana Farstey, Iddo Pinkas, Linda J.W Shimon Katya Rechav, Eyal Shimoni, Neta Varsano and Lia Addadi

Weizmann Institute of Science, Israel



The Peterson Experiment (1966)

Many Questions



Will their shells dissolve as they fall

Which organisms produce CaCO₃

in the surface waters?

3700m in the sediments, dissolved? Are all the CaCO₃ shells below

the same way as geological calcite? Does biologically produced CaCO₃ dissolve in

Major producers of calcium carbonate in the surface waters



CMarZ.org



Aragonite











Coccolithophores

Foraminifera

Nordic Microalgae

Calcite

Dinoflagellate cysts



Both are polymorphs of calcium carbonate. Aragonite is the less stable polymorph and therefore more soluble.

Pteropods (sea butterflies)

(nektonic gastropods; abundant in the surface waters of all oceans)



• The name pteropod derives from the fact that the gastropod (snail) foot (poda) has been modified to form paired swimming wings (ptero-)

Thin transparent aragonitic shells

- Size: 0.6 6 mm
- Two different taxonomic groups



columnella Cuvierinia

Creseis virgula



http://www.arcodiv.org/simple_viewer/PelagicSnails

Limacinoidea



Limacina helicina

Shell microstructure



Cavolinioidea



Structure?

Single crystals similar in size and shape.

Many organisms form their minerals by first depositing an unstable and disordered precursor phase

ACP to carbonated apatite Ferrihydrite to magnetite

Amorphous calcium

carbonate (ACC) to calcite



Chiton (mollusk)

teeth 1967, Weiner 1985. Chiton Lowenstam and **Towe and Lowenstam**



Sea urchin larva

Beniash et al. 1997.





Weiss et al 2002

columnella Cuvierinia

Pteropods

Mollusk larval shell

ACC to aragonite

Two Questions

- What is the 3-dimensional structure of the Cavoliniidae shell?
- Does the Cavoliniidae aragonite form through a disordered precursor geological aragonite? phase? Does the adult shell aragonite have the same solubility as



Creseis acicula (Red Sea, caught live)

Growing edge



Protoconch



Though SEM images contains many details, we were not able to define any consistent 3D structure. Nor did we ever see a complete helical



FIB SEM: 3D Structural Determination



Low organic matter (0.01%)

Zeiss FIB SEM Crossbeam. 2017

Densely packed fibers

FIB-SEM - It actually worked!





K. Rechav

Cannot trace one crystal fiber throughout the structure

Try reconstructing the structure in an oblique plane







3D volume OS- outer shell surface

The 3D packing of the S shaped fibers-the model



arrays in a plane oblique to the natural surface. A continuous S-shaped crystal fiber is organized into nested

These nested arrays are stacked one on top of another to form the 3D structure of one layer.

N. Varsano

The 3D packing of the S-shaped fibers in the shell

OS- outer shell surface

Part 2: The Formation of the Mineral

Creseis acicula shell growth and development

Pteropod shells grow and thicken throughout the animal's life

Protoconch

shelled pteropod Creseis acicula using mainly in vivo Study mineral deposition and maturation in the micro-Raman spectroscopy.

O. Sibony-Nevo, I. Pinkas, V. Farstey, H. Baron, L. Addadi and S. Weiner, Cryst. Growth Des. 19, 2564 (2019).

Does C. acicula form its shell via a precursor phase?

Pteropod shells grow and thicken throughout the animal's life

Growing edge Calcein staining 20 uM

Is ACC a precursor for aragonite mineral formation in pteropods?

A nanosphere texture is indicative of crystalline biominerals that formed via an amorphous mineral phase, but not proof

Shell microstructure observed in cryo SEM

Micro-Raman spectroscopy

Raman is a spectroscopic technique based on light scattering used to observe

I. Pinkas

- vibrational modes in different compounds
- 2. Aragonite has large numbers of vibrational modes
- ယ The lattice mode region in the spectra is the most sensitive to the level of order.
- 4 We use the 785 nm laser as it is less sensitive to fluorescence and has Therefore if there is long distance order the peaks will be more distinct

low energy and therefore minimizes crystallization artifacts

What is the mineral composition in the shell of *C. acicula*?

Experimental limitations

RAMAN depth of field is 1 μ m in relation to the experimental optical setting

We are only able to measure the entire volume of the growing edge, but can measure through the volume in thicker parts of the shell

The C. acicula Raman spectra clearly show that the mineral phase becomes more ordered over time.

In vivo micro Raman spectroscopy- Results

in spectra obtained from more mature regions of the shell, relative to the ratio at the growing edge in both developmental stages of C. acicula We observed that the peak height ratios increase

In vivo micro Raman spectroscopy- Results

Pteropods and Foraminifera in the Deep-sea Sediments

I have concluded that roughly half of the mass of calcium carbonate falling to the bottom of the ocean consists of aragonite, almost all of which is dissolved away. (Berner 1979)

What does this distribution represent?

- Where the foraminifera and pteropods live in the surface waters?
- Areas where they do not dissolve as they fall to the bottom of the ocean?
- Sea water saturated with respect to aragonite for pteropods and calcite for foraminifera?
- All these options contribute, but the possibility that calcite, has probably not been considered. be more soluble than geological aragonite and pteropod aragonite (and foraminiferal calcite) may

Conclusions

composed of nested arrays of S-shaped aragonite fibers (what are the mechanical implications?) The micro-structure of the Cavoliniidae shell is not helical, but is

Pteropod aragonite forms via a nascent disordered precursor phase.

aragonite and is therefore more soluble The aragonite of adult pteropod shells is not as ordered as geological

chemistry, pteropod preservation in marine sediments?) (what are the implications for sea water "aragonite" saturation

Acknowledgments

Odelia Sibony-Nevo

Lia Addadi

Bracha Viviana Farstey Iddo Pinkas

Katya Rechav Eyal Shimoni Linda J.W. Shimon Neta Varsano Emeline Raguin

Raquel Isidoro

