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Dissolution of Phosphate and Precipitation of Carbonate in the Biomineralization of the Bivalve Shell Limnoperna fortunei

Antonio Valadão Cardoso[1]; Rodrigo Ferreira Novaes[2]; Rosana Aparecida Machado Souto[1]
1.Escola Design, UEMG; 2. Centro Microscopia, UFMG

Introduction

The mantle of bivalves plays a crucial role in the formation and maintenance of their shells through biomineralization .
Here we demonstrate that phosphate, whether absorbed as nano- and/or microparticles or synthesized within the mantle, is involved in shell formation in the bivalve *Limnoperna fortunei.*
To determine whether this phenomenon is exclusive to the freshwater species L. fortunei, shell samples from the marine bivalve *Perna perna* were analyzed using the same techniques and showed similar results.
Our findings suggest that calcium phosphate may act as a precursor during shell biomineralization. The subsequent transformation of calcium phosphate into calcium carbonate could provide an important biological advantage by releasing phosphate, an essential nutrient required for ATP production, nucleic acid synthesis, cellular repair, pH regulation, and nerve signal transmission.
In this way, phosphate remains available to the organism while calcium carbonate is incorporated into the shell structure.

Objectives

- To investigate the role of phosphate in shell biomineralization in the freshwater bivalve *Limnoperna fortunei*, including its possible transport via extracellular vesicles (EVs).
- To investigate whether calcium phosphate acts as a precursor to calcium carbonate during shell formation.
- To determine whether a similar biomineralization process occurs in the marine bivalve *Perna perna*.
- To evaluate the potential biological significance of the calcium phosphate → calcium carbonate transformation, particularly phosphate recycling during shell formation.

Methodology

Collection site: Grande River, Minas Gerais, Brazil

Sample preparation: Belo Horizonte, Minas Gerais, Brazil

ICP-OES

WDFRX

SEM/EDS

FTIR

DRX

Results and Discusson

Figure 1. The growing shell edges indicate the presence of calcium phosphate (see FTIR below). However, XRD analysis of the entire shell shows only calcium carbonate phases (see XRD below).

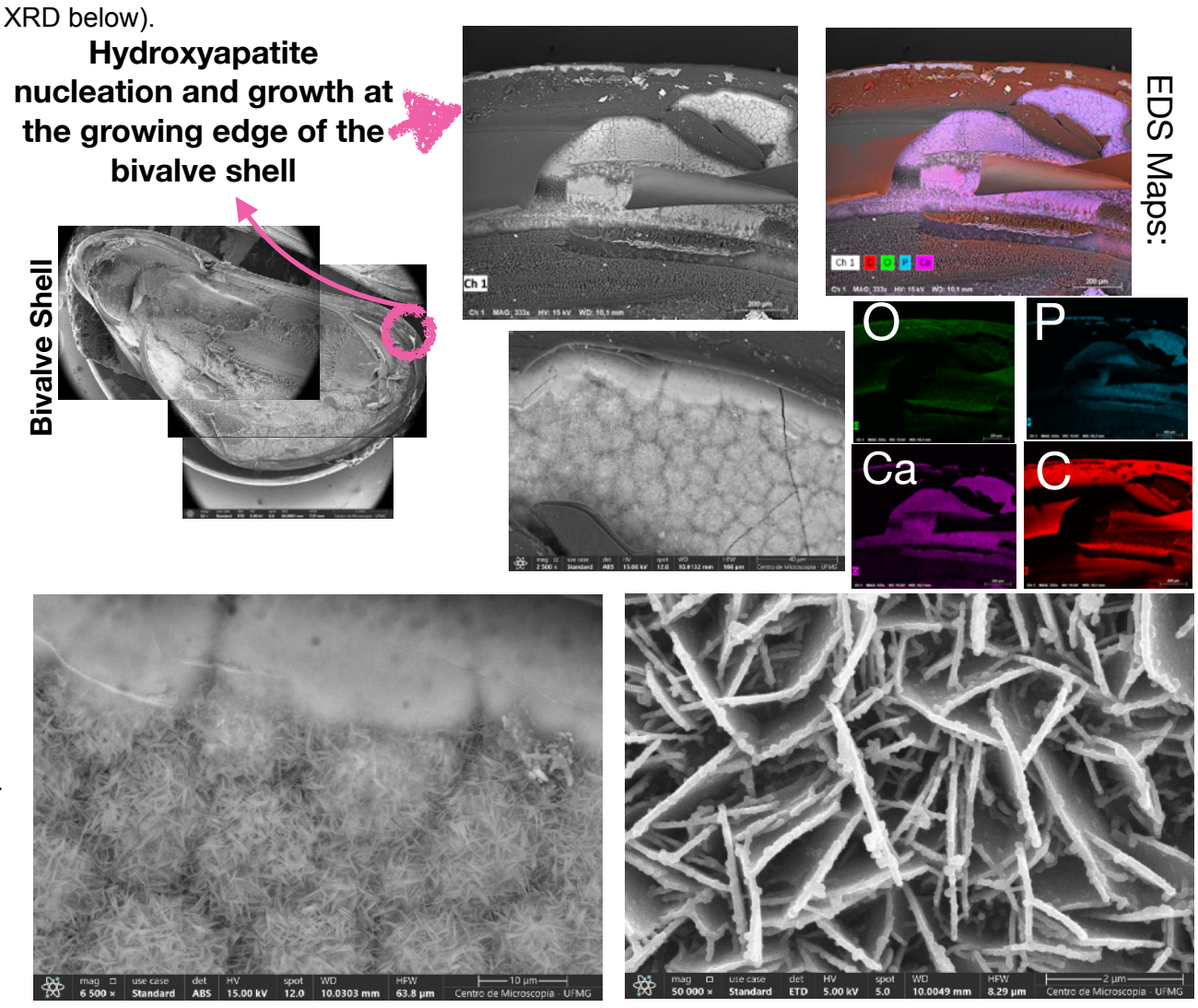


Table 3. Ca/P atomic ratios at selected points along the shell growing edge are close to the stoichiometric value for hydroxyapatite (Ca/P ≈ 1.67).

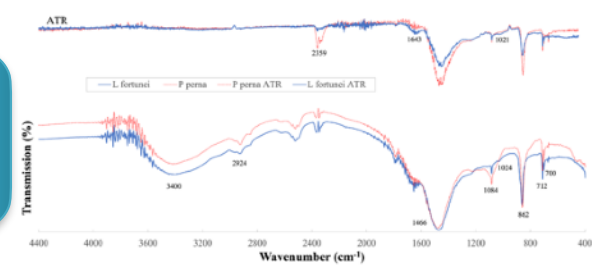
line	shell region	EDS quantification - Composition (weight %) C	O	P	Ca	Ca/P	EDS quant. (Atom %) P	Ca	Ratio Ca/P	Image of the Region
1	C1-A1	37.0	23.6	13.3	28.6	2.2	7.5	12.4	1.66	
2	C2-A1	13.8	36.6	15.5	33.1	2.1	10.4	17.2	1.65	

Molar ratio Ca/P

Hydroxyapatite (HA)	$Ca_{10}(PO_4)_6(OH)_2$	10	6	1.67

Composition (weight %)

		P	Ca	Ca/P			
Bone*	$CO_3^{-2}=6$	11.5	24.5	2.13	-	-	1.8



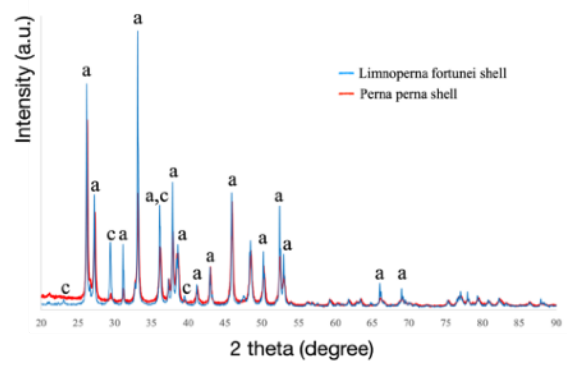


Table 1.

Sample (Shell)	Year	Ba	Ca	Fe	P	Mg	Na	Sr	Zn	K
		%								
Limnoperna fortunei	2016	0.0159	35.08	0.040	-	0.0235	0.220	0.059	0.0090	0.0032
Limnoperna fortunei	2022	0.0161	36.07	0.011	-	0.0180	0.537	0.120	0.0003	0.0037
Limnoperna fortunei	2023	0.0002	38.71	0.002	0.026	0.0190	0.640	0.120	0.0003	0.0190
Perna perna	2022	0.0003	38.64	0.002	-	0.0159	0.663	0.105	-	0.0133
Perna perna	2023	0.0340	39.05	0.043	0.039	0.0230	0.250	0.071	0.0008	0.0029

Table 2.

Sample (Shell)	Year	Al	Ba	Ca	Cl	Fe	Mg	Na	P	S
		%								
Limnoperna fortunei	2023	0.051	-	98.190	0.280	0.033	0.050	0.760	0.037	0.240
Perna perna	2023	0.110	0.490	98.100	0.420	0.230	0.062	0.430	0.089	0.210

Conclusions

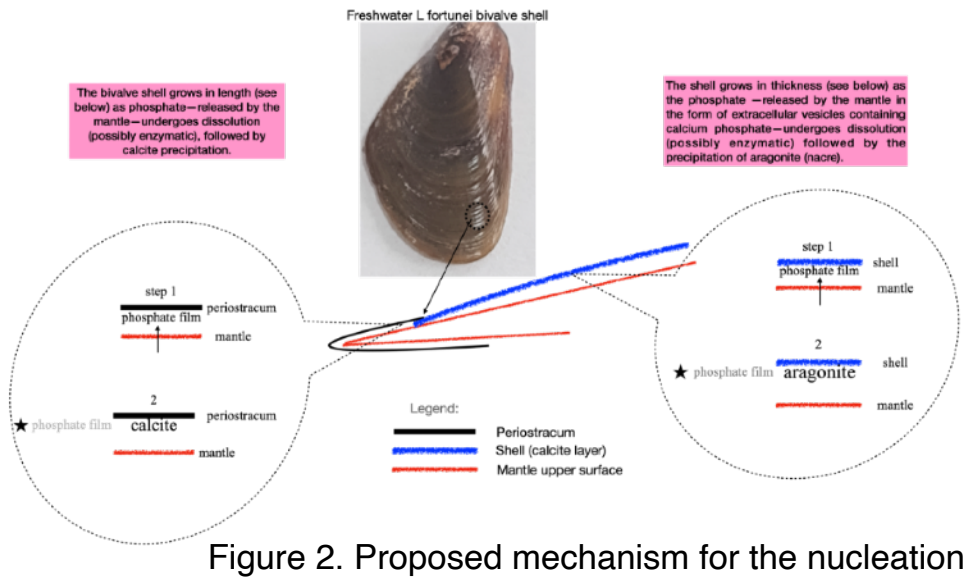


Figure 2. Proposed mechanism for the nucleation and growth of the composite that forms the shell.

References and Acknowledgments

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