doi:10.1017/S1431927620013379
Microsc. Microanal. 26 (Suppl 2), 2020

Resolving Internal Structures and Composition of Biominerals: The Case of Calcitic Prisms of Mollusk Shells

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Biominerals are organo-mineral materials produced by living organisms. More than 50 mineral phases are identified [1]. Biominerals based on $CaCO_3$ are found in a large number of organisms, such as mollusks, corals, echinoderms. The prismatic layers of mollusk shells are the historical references because of their large size [2, 3]. Although they are not frequent, they are among the best-known biominerals.

Prismatic layers are, depending on the taxonomy, aragonite or calcite [4, 5]. Calcite prisms of Pteriomorpha have geometrical shape, with polygonal sections (Fig. 1A-L), but their inner structure differs. The longitudinal faces of *Pinna* prisms are smooth (Fig. 1C), those of *Pinctada* are smooth, then corrugated (Fig. 1H) [6, 7], so that the growth mechanisms are not identical in these two taxa. Both species show growth layers (Fig. 1D, I) when etched using acidic or enzymatic solutions. Polarised light images show that the prisms are "monocrystalline" in *Pinna*, polycrystalline in *Pinctada* (Fig. 1E, F, J, K). Etched transverse sections clearly show the differences (Fig. 1G, 1L). Growth layers are also visible in chemical distribution maps (Fig. 1M, N), and every chemical element has its own deposition rhythm [8]. Organic envelopes surrounding the prisms of *Pinna* are rich in S (Fig. 1N). In *Pinctada*, the envelopes are poor in Ca associated components (Fig. 1O), rich in S (Fig. 1P), S being mainly associated with amino acids (Fig. 1Q) [9]. µXRF also shows the presence of Br in *Pinctada* (Fig. 1R), and the 3-layered structure of the envelope of *Pinna* (Fig. 1S). The complex structure of the interprismatic envelopes is also demonstrated using FTIR and TOF SIMS [9]. AFM images display the irregularity of the layers of the envelopes in *Pinna* and *Pinctada* (Fig. 1T, U). Although the main part of $CaCO_3$ is crystalline (calcite), the inner structure of the prisms comprises rounded granules (Fig. 1V, W), without the angles or facets typical of non biogenic calcite. DRX and EBSD analyses have shown that the *c* axis is parallel to the long morphological axis in *Pinna*, and is perpendicular in *Pinctada* [10]. Thus, it can be said that the morphology of biogenic calcitic prisms is determined not only by atomic structure of calcite, but largely by organic components, the presence or absence of which are drastically changing the growth mode.

Structures and compositions of calcareous biominerals differ from those of their non-biogenic counterparts. Morphological similarity of the structural units is not sufficient enough to describe a biomineral. *In situ* observations show structural and compositional differences, usually confirmed by analyses of the extracted organic components. The structure and composition are dependent upon the taxonomy. Prismatic layers are not the only example. The main features of the nacreous layer of Bivalvia, Gastropoda and Cephalopoda differ. Moreover, the nacreous tablets of every taxa have specific shapes, inner structure and composition. In a given layer, the shape, inner structure and composition of tablets, prisms or laths depend on the taxa, and in a given shell, they depend on the structure [4, 5, 11, 12]. Only a progressive study using a large range of observations allows us to understand the organo-mineral interplay from a macro to a nanoscale. The strong control of the organisms on the shell secretion in Mollusks is not unique. Similar process exist in corals, brachiopods, etc.

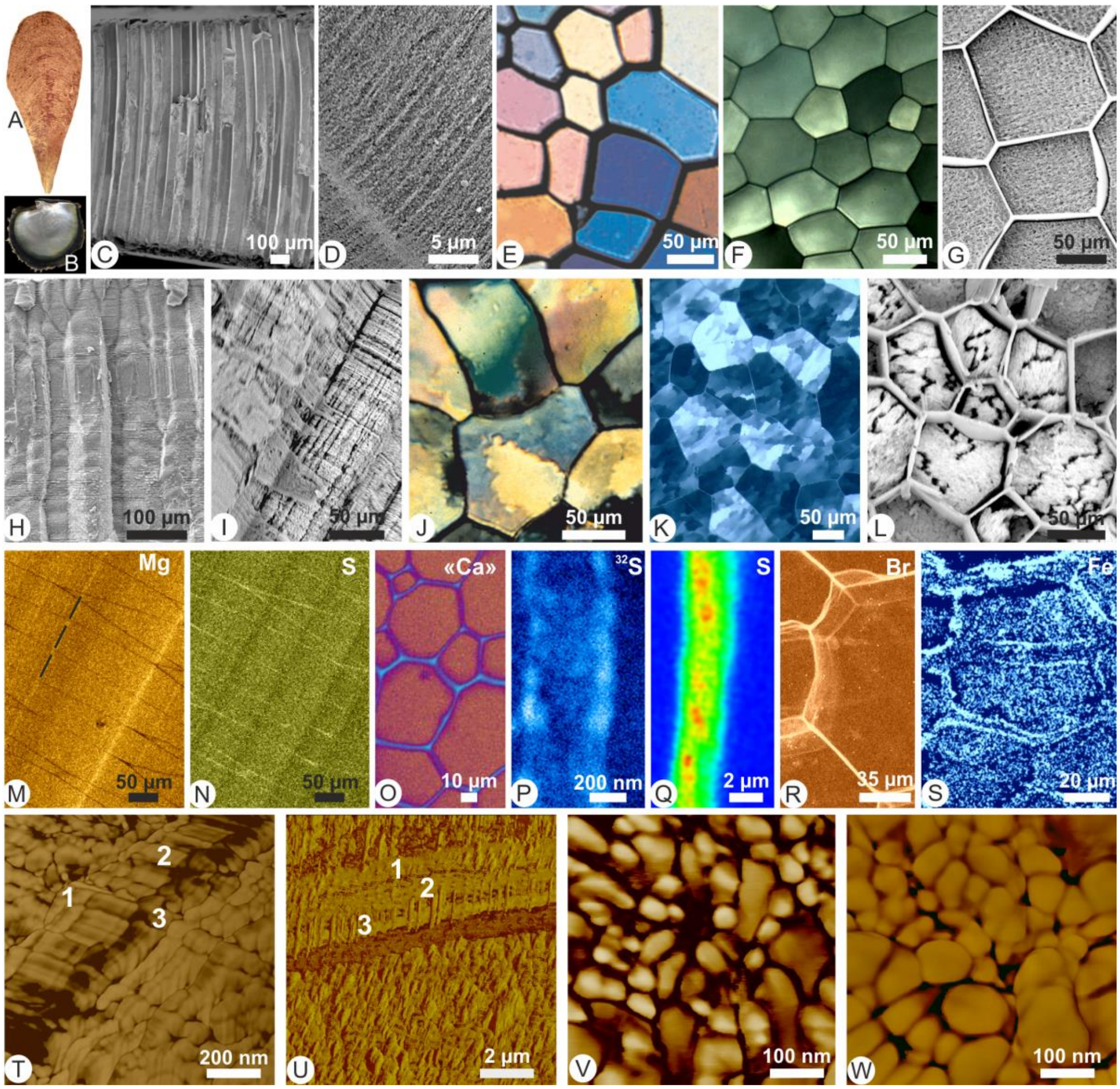

Figure 1. Figure 1. A) Outer surface of Pinna shell. B) inner surface of *Pinctada*. C) Fracture showing the parallel long prisms of *Pinna*. D) Growth layer in the prisms of *Pinna*. R) Thin section observed in transmitted polarized light showing the "monocrystalline" prisms of *Pinna*. F) Epipolarisation image of the prisms of *Pinna*. G) Polished and etched section showing the interprismatic organic envelopes in *Pinna*. H) fracture showing the smooth (top) and corrugated (bottom) surface of the prisms of *Pinctada*. I) Polished and etched section showing growth layers in *Pinctada*. J) Thin section observed in transmitted polarized light showing the polycrystalline prisms of *Pinctada*. K) Epipolarisation image of the prisms of *Pinctada*. L) Polished and etched section showing intraprismatic membranes in *Pinctada*. M, N) WDS distribution maps of Mg and S in *Pinna*. O) TOF SIMS map of Ca based ions in a transverse section of the calcitic prisms of *Pinctada*. P) NanoSIMS map showing 3 layers in the interprismatic envelopes of *Pinctada*. Q) µXRF map showing the high S amino acids content of the interprismatic envelopes of *Pinctada*. R) µXRF bromine map of the prisms of *Pinctada*. S) µXRF Fe map showing the multilayered organic envelopes of *Pinna*. T, U) AFM images of the interprismatic envelopes of *Pinna* (T) and *Pinctada* (V), showing 3 irregular sublayers. V, W) Rounded granules of *Pinna* (V) and *Pinctada* (W).

https://doi.org/10.1017/S1431927620013379 Published online by Cambridge University Press

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https://doi.org/10.1017/S1431927620013379 Published online by Cambridge University Press