Prof. Giorgio Sartor

Conchiglia

Versione 2.0 - apr 2012

Phylum: Mollusca

- Classes:
  - Aplacophora:
    - Senza conchiglia, *Helicoradomenia juani*
  - Polycophora:
    - LOricati, *Chiton magnificus*
  - Monoplacophora:
    - Una conchiglia, *Neopilina galatheae*
  - Gastropoda:
    - Lumache
  - Scaphopoda:
    - shovel-footed, *Antalis vulgaris*
  - Bivalvia:
    - Due valve, *Mytilus galloprovincialis*
  - Cephalopoda:
    - Molluschi nuotatori, *Nautilus belauensis*

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Slug-like aplacophoran mollusc is covered with tiny spicules that make it look "furry".

Marine molluscs whose shell is composed of eight articulating plates or valves. It has a perfect knife (radula) to scrape rocks.

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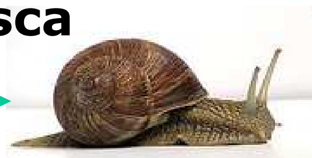

Helix pomatia

Lunatia palida

Buccinum Elatior

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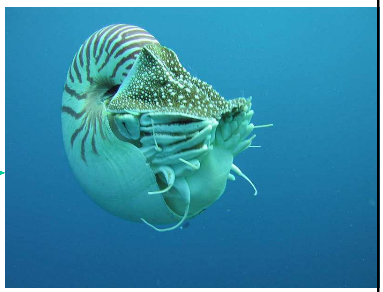


Molluschi bivalvi

Umani e molluschi

Molluscs are slow (food)

Umani e molluschi

- Curtis WilliamMarean e Peter Nilsen, nel 2001 scoprirono, nel promontorio di Pinnacle Point nei pressi di Mossel Bay, una grotta, denominata poi PP13B, ricca di reperti risalenti al periodo compreso fra 165000 e 48000 anni fa.
- Alcuni reperti, in particolare alcuni piccoli strumenti litici di silcrete la cui lavorazione richiedeva un attento controllo del fuoco da parte dei primi uomini (tecnica che in precedenza si riteneva avesse avuto origine molto più tardi, nel Solutreano in Francia), e la nutrizione con mitili (la cui raccolta, possibile solo durante le basse maree sigiziali, presupponeva la conoscenza di calendari lunari) hanno permesso a di ipotizzare che le capacità cognitive avanzate dell'uomo si sono evolute in tempi molto più antichi di quanto si pensasse fino ad allora.

Come gli umani usano i molluschi


Cozze gratinate


Spaghetti alle vongole


Ostriche gratinate


Impepata di cozze


Capesante gratinate


Lumache alla bourguignonne

Come gli umani usano le conchiglie

Haliotis rufescens

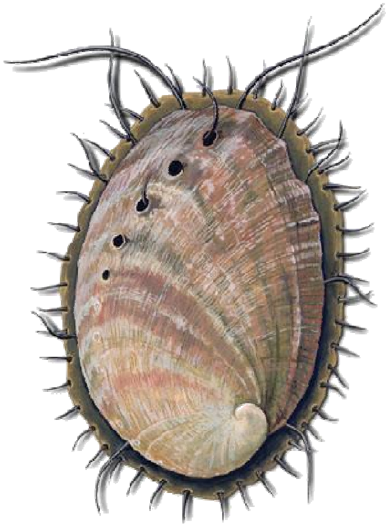
Taxonomy

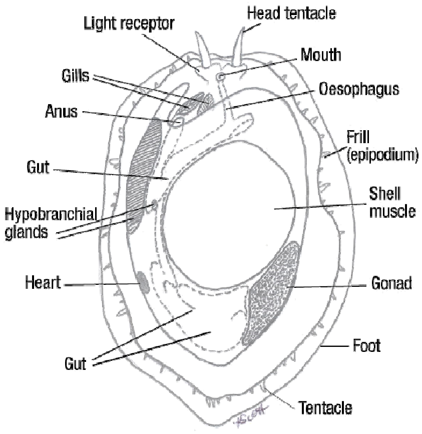
- Kingdom ***Animalia*** Linnaeus, 1758 - animals
  - Subkingdom ***Bilateria*** (Hatschek, 1888) Cavalier-Smith, 1983 - bilaterians
    - Branch ***Protostomia*** Grobben, 1908 - protostomes
      - Infrakingdom "***Lophotrochozoa***" - lophotrochozoans
        - Superphylum ***Eutrochozoa***
          - Phylum ***Mollusca*** (Linnaeus, 1758) Cuvier, 1795 - molluscs
            - Class ***Gastropoda*** Cuvier, 1795 snails and slugs
              - Subclass ***Orthogastropoda*** Ponder & Lindberg, 1996
                - Superorder ***Vetigastropoda*** Salvini-Plawen, 1980
                  - Superfamily ***Haliotoidea*** C.S. Rafinesque, 1815
                    - Family ***Haliotidae***™ C.S. Rafinesque, 1815 - abalones
                      - Genus ***Haliotis***™ C. Linnaeus, 1758
                        - ***Haliotis aquatilis***
                        - ***Haliotis coccinea*** Reeve, 1846
                        - ***Haliotis cracherodii*** Leach, 1814 - black abalone
                        - ***Haliotis diversicolor*** Reeve, 1846
                        - ***Haliotis jacnensis*** Reeve, 1846
                        - ***Haliotis kamtschatkana*** Jones, 1845 - pinto abalone
                        - ***Haliotis lamellosa*** Lamarck, 1822
                        - ***Haliotis midae*** Linnaeus, 1758
                        - ***Haliotis pustulata*** Reeve, 1846
                        - ***Haliotis rufescens*** Swainson, 1822 - red abalone
                        - ***Haliotis subg. Haliotis***™ {Linnaeus, 1758}
                        - ***Haliotis subg. Ovinotis*** {Cotton, 1943}
                        - ***Haliotis subg. Sanhaliotis*** {Iredale, 1929}
                        - ***Haliotis subg. Schismotis***
                        - ***Haliotis subg. Sulculus*** {H. & A. Adams, 1854}
                        - ***Haliotis tuberculata*** Linnaeus, 1758 European ormer
                        - ***Haliotis varia*** Linnaeus, 1758
                        - ***Haliotis virginea*** Gmelin, 1791
                        - ***Haliotis walallensis*** Stearns, 1899 - northern green abalone

Haliotis rufescens (red abalone)

- The red abalone is a gastropod (univalve) having a large, oval shell shaped like a shallow bowl.
- The shells of some archaeological specimens are close to 30 cm in length, and lengths around 20 cm are common.
- Most of the abalone's body under its shell consists of a "foot" for attaching itself to a rock surface and sometimes for locomotion, although a mature abalone generally resides in one spot.
- Abalone feed on algae, and the red or coral color of the outer surface of a red abalone shell (the shell's epidermis) results from consumption of red algae.

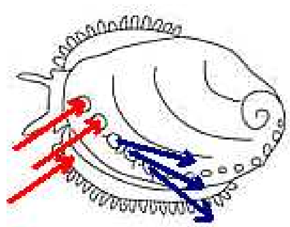
Anatomy



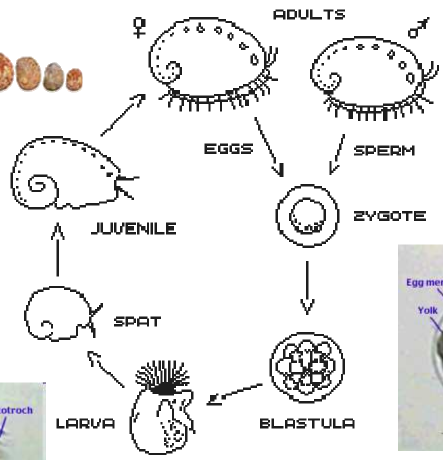


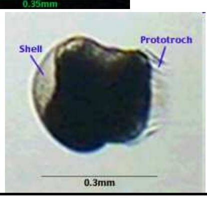
Respiration

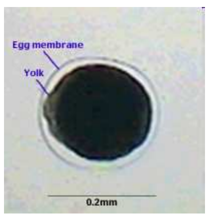
- Water taken in by the abalone and passed over its gills exits through a row of holes along one side of the shell (the hole nearest the front edge of the shell may be used for water intake).
- As the shell grows larger, new and larger holes are added and the old holes on the opposite (exterior) end of the row are plugged with nacre.
- Typically, four such holes are open, but the holes filled with nacre are easily seen on the shell.

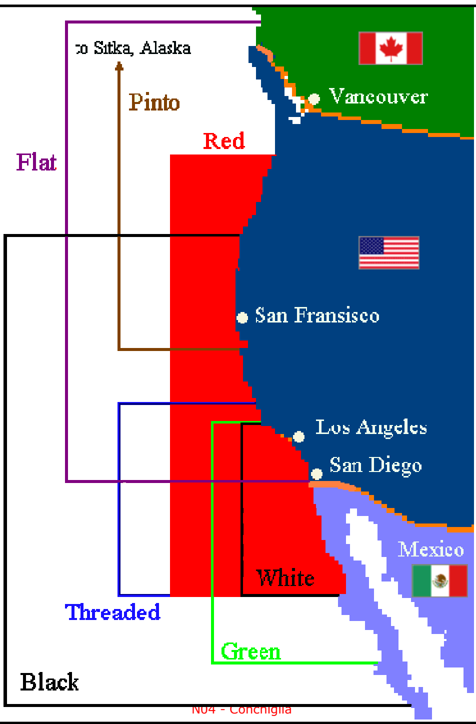


Life cycle









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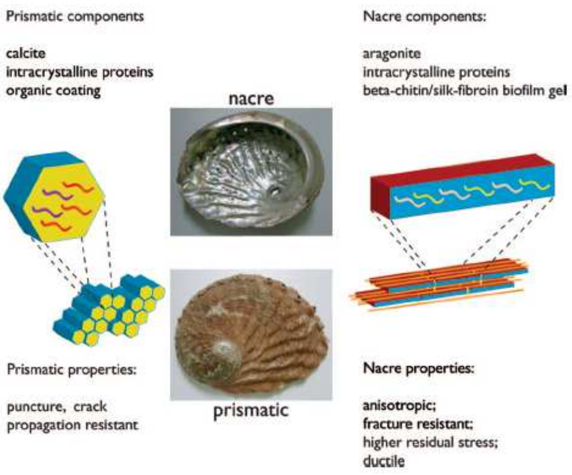
The Shell

Natural, high-performance, microlaminate composite of inorganic crystals and biopolymers;

The shell



Both the prismatic and nacre layers contain a number of proteins, some of which are intracrystalline, i.e., incorporated within the inorganic phase, and some which form biofilms around the mineral phase.

J. S. Evans, Chemical Reviews, 2008, Vol. 108, No. 11

Molluscan shell proteins

Frédéric Marin *, Gilles Luquet
C. R. Palevol 3 (2004) 469–492

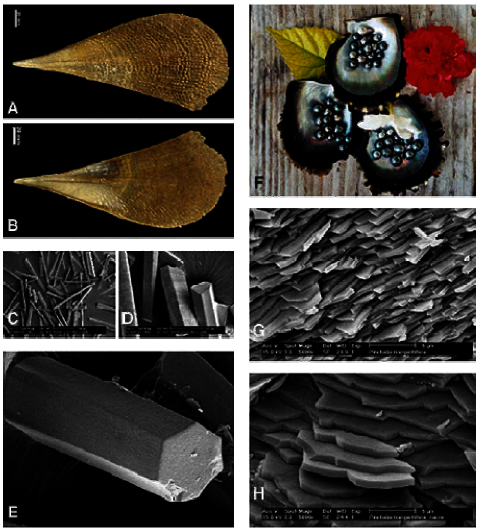
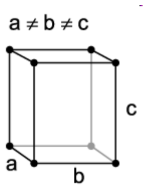
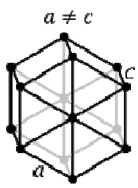


Fig. 1. The shell of two nacroprismatic bivalve genera and their corresponding shell microstructures, observed with ESEM. A, B : Shell of the Mediterranean fan mussel, ***Pinna nobilis***, two-year-old specimen (length of the shell: 25 cm). **A**: Right valve, external surface, showing the prismatic layer. **B**: Right valve, internal surface. The internal nacreous layer is only present in the first half of the shell. **C**: When treated with sodium hypochlorite, the outer layer can be dissociated in calcitic prism units. **D**: Isolated prisms, higher magnification. **E**: Detail of one single prism (diameter : 40 μm, length 100 μm). **F**: Right and left shell valves and pearls of the 'black-lip' pearl oyster, ***Pinctada margaritifera***, from French Polynesia (Manihi, Tuamotus). **G**: Nacreous layer of ***Pinctada margaritifera***. **H**: Idem, higher magnification. The nacreous layer is made of superimposed aragonitic flat tablets, which are arranged in a 'brick-wall' microstructure.

$CaCO_3$



- Aragonite:
  - Orthorhombic, pseudohexagonal.
  - *Point Group:* 2/m 2/m 2/m.



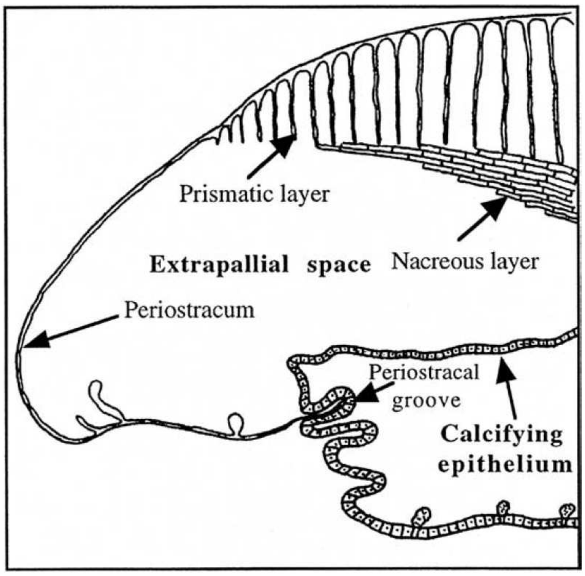
- Calcite:
  - Hexagonal.
  - *Point Group:* 3 2/m.

The shell

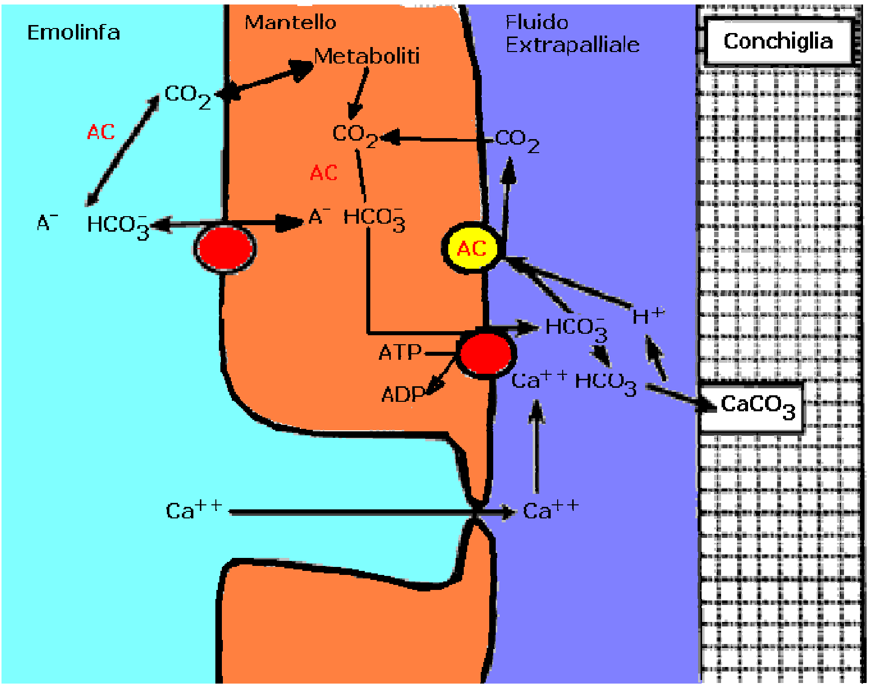
- Fracture toughness estimated to be 3,000-times greater than that of the constituent mineral alone;
- The content of organics represents only ~ 1% of the mass of the composite.

Inner side of a green abalone (*Haliotis fulgens*) shell, showing the iridescent nacre. Shell diameter is ~20 cm.

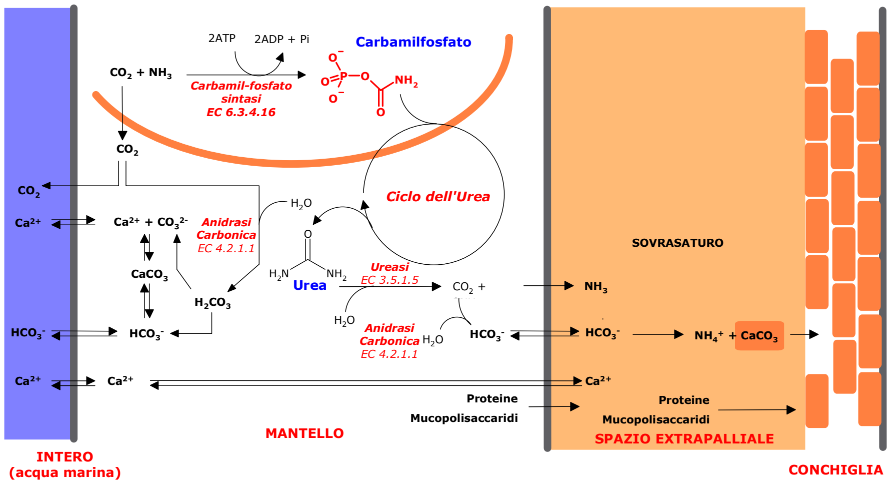
Shell formation



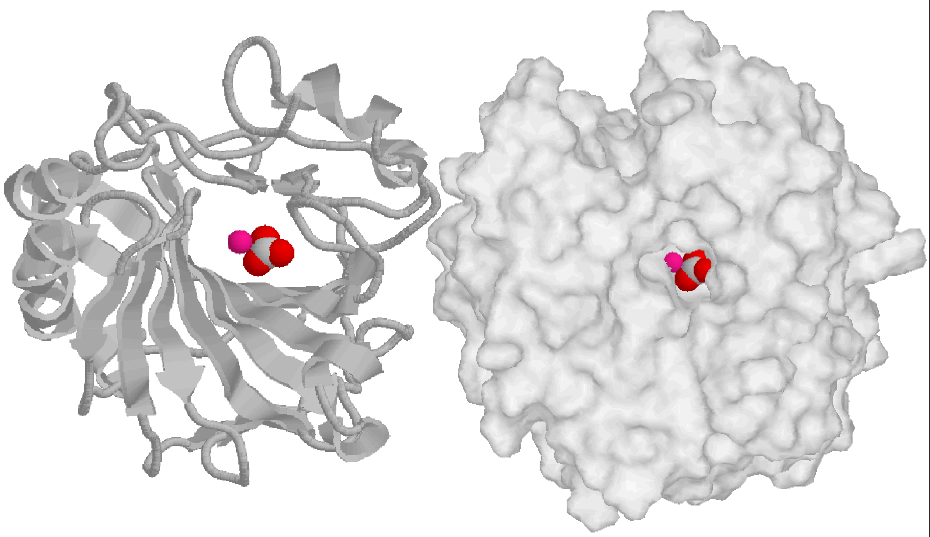
F. Marin, G. Luquet - C. R. Palevol 3 (2004) 469–492



Urea, CO_2 e NH_3



Anidrasi carbonica (EC 4.2.1.1)



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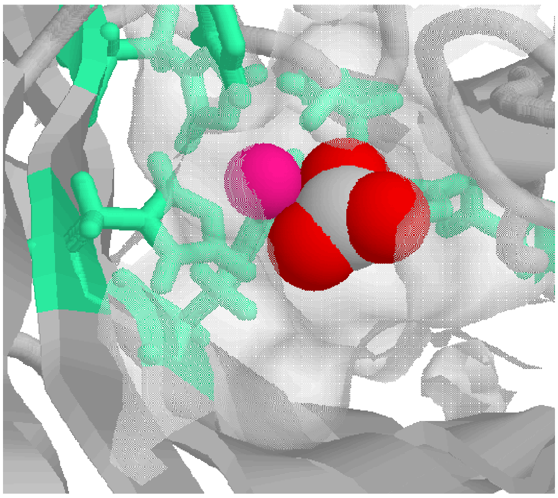
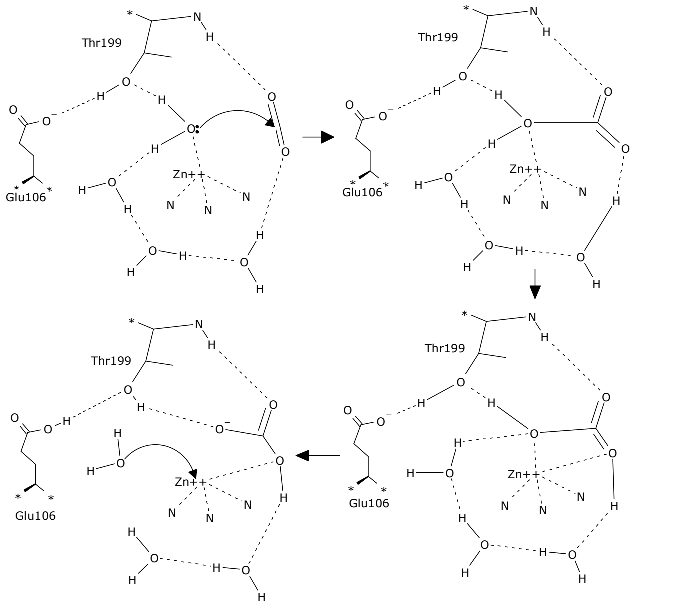


Anidrasi carbonica (EC 4.2.1.1)



Chem. Mater., Vol. 8, No. 3, 1996 Zaremba et al.

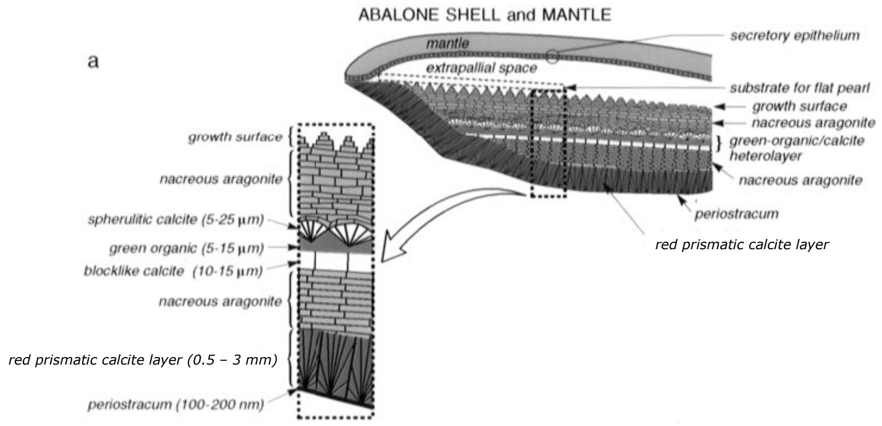


Figure 1. (a) Schematic (not drawn to scale) of a vertical section of the outer edge of the shell and mantle of a red abalone (*Haliotis rufescens*) with an enlargement indicating thickness dimensions of the shell structures. The size of the extrapallial space is exaggerated for clarity.

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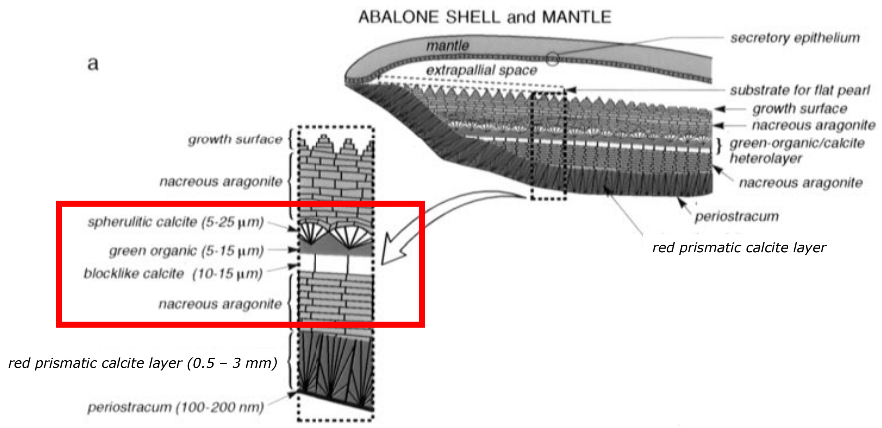

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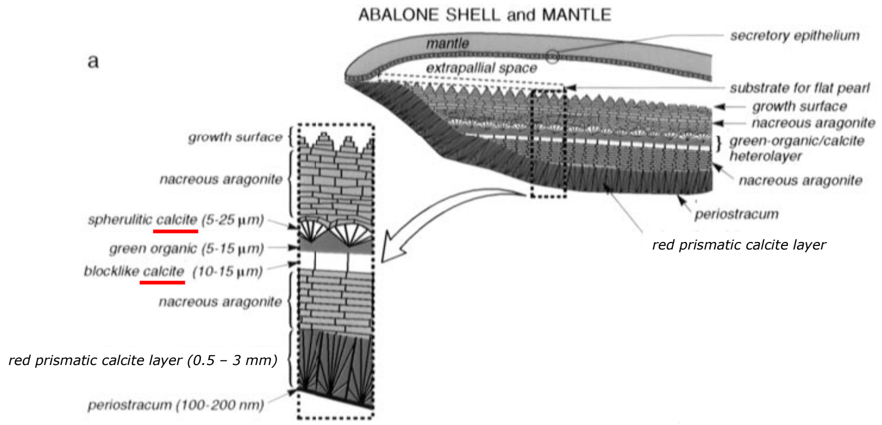

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A.Y.-M. Lin et al. Acta Biomaterialia 4 (2008) 131–138

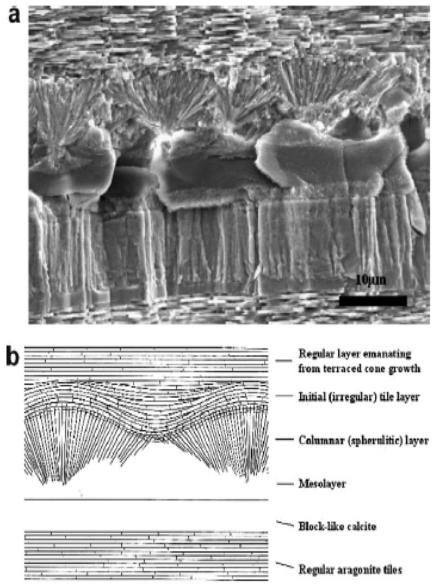


Fig. 2. Cross-sectional view of spherulitic to tile transition after growth interruption: (a) SEM and (b) schematic diagram.

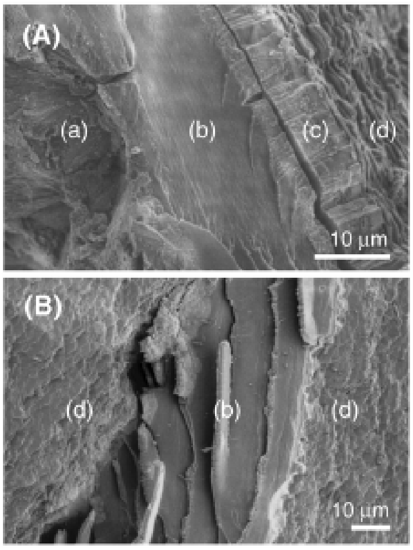
The green layer

- The interstitial polymeric sheet is itself a microlaminate composite;
- It contain distinct sub layers;
- The purified green sheets can be split by cleavage when a mechanical force is applied parallel to the plane of the sheet

The interstitial nucleating sheet

- is colored (green) and fluorescent;
- it stains with Coomassie brilliant blue: it contains proteins;
- it stains with cationic carbocyanin dye: it contains high local concentrations of anionic groups;
- it resists to a wide range of denaturing agents and proteolytic enzymes: high degree of covalent cross-linking.

Green layer



A. Scanning electron micrograph of a cross section of abalone shell nacre. Asymmetry of the interstitial composite polymer sheet is visible.
B. SEM of two sublayers from the interstitial composite polymer sheet.

(a) aragonitic spherulitic region;
(b) interstitial polymeric sheet;
(c) prismatic aragonitic region.
(d) aragonitic nacre region.

Asymmetry

	Spherulitic Crystal-Facing Surface	Prismatic Crystal-Facing Surface
Coomassie blue	reactive	reactive
Schiff reagent	reactive	not reactive
DOPA assay	less reactive	more reactive
Cationic carbocyanin	more reactive	less reactive

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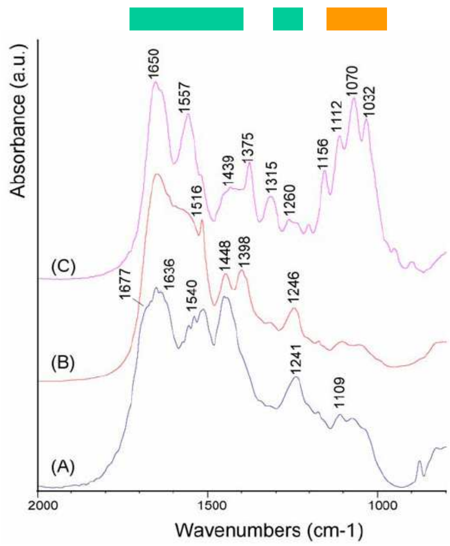
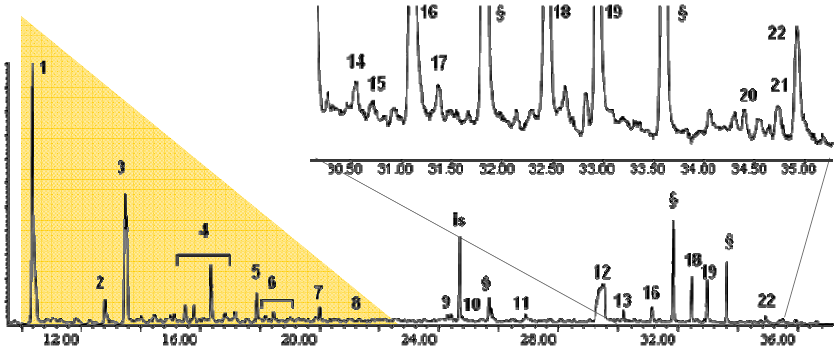
FTIR spectra



A. Interstitial polymer sheet.
B. Soluble NaOH fraction.
C. Insoluble NaOH fraction.

Amide bonds

C-C-O-C and C-C-OH stretching and bending



GC-MS trace of products evolved from flash pyrolysis of alkaline extract. Tentative structural assignment:

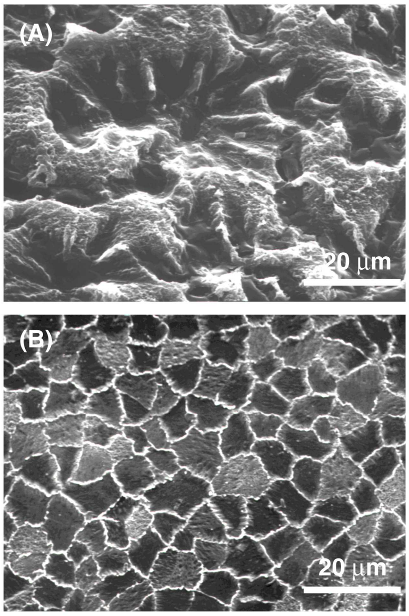
1, phenol; 2, *o*-phenol; 3, *m,p*-phenol; 4, C2-phenols; 5, 4-vinylphenol; 6, C3-phenols; 7, indole; 8, 4-(2-propenyl)-phenol; 9, unknown (*m/z* 69, 137, 152); 10, 4-hydroxy benzeneacetonitrile; 11, 3-[4-hydroxyphenyl]proprionitrile; 12, cyclo(Gly-Val); 13, diketodipyrrole; 14, cyclo(Val-Val); 15, cyclo(Pro-Ala); 16, cyclo(Pro-Gly); 17, unknown (*m/z* 80,107, 120, 187); 18, cyclo(Pro-Val); 19, cyclo(Pro-Val); 20, cyclo(Pro-Ile); 21, cyclo(Pro-Leu); 22, cyclo(Pro-Pro). i.s., internal standard (2-bromonaphthalene); §, contaminants (plastic additives).

Asymmetry

“Physical” Asymmetry

Scanning electron micrographs of the surfaces of the interstitial composite polymer sheet after demineralization.

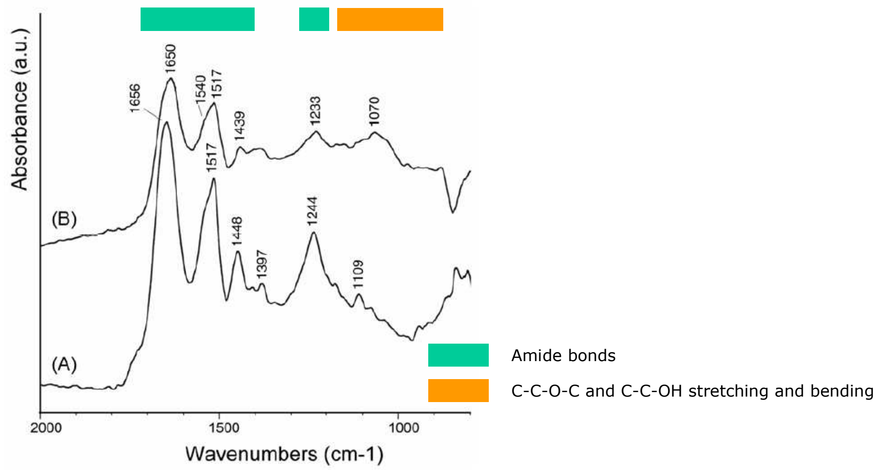
A. Surface facing spherulitic crystals.
B. Surface facing prismatic crystals.



“Physical” Asymmetry

- The surface that lies adjacent to the prismatic crystal layer has a higher apparent density of surface features,
- The surface associated with the nucleation of the spherulitic crystals appears more spongy.

“Chemical” asymmetry



ATR-FTIR spectra of the two sides of the interstitial composite polymer sheet. **(A)** Prismatic side. **(B)** Spherulitic side.

Green layer composition

Amino Acids			
Cys	1.3	Val	5.5
Asx	9.6	Ile	0.6
$MetSO_2$	0.1	Leu	1.9
Thr	5.2	Tyr	21.8
Ser	7.4	Phe	0.1
Glx	9.9	His	5.5
Pro	24.3	Lys	3.7
Gly	20.3	Arg	4.9
Ala	2.1		

Sugars	
N-acetylglucosamine	3.0 (5)
Glucose	13.0(8)
Galactose	12.5(8)
Mannose	3.9(5)
Xylose	8.5(8)
Arabinose	14.0(2)
Other	35.0

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Galactose	12.5 (8)
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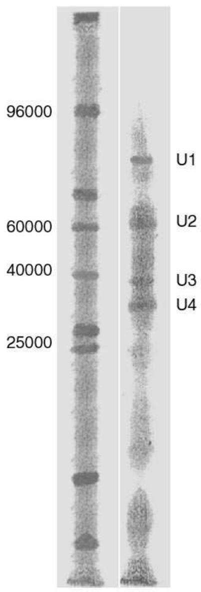
Xylose	8.5 (8)
Arabinose	14.0 (2)
Other	35.0

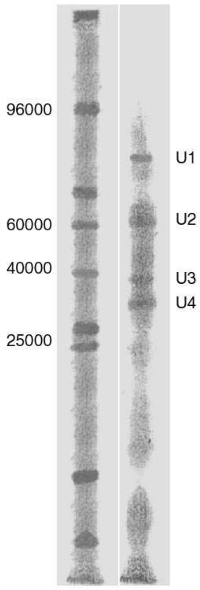
Proteins



	U1*	U2*	U3*	U4*	NaOH-soluble§
Cys	2.1	2.6	2.2	2.1	0.1
Asx	16.1	18.3	16.2	15.4	14.6
$MetSO_2$	1.1	(n.d.)	1.6	1.0	0.1
Thr	7.6	3.1	5.1	5.2	6.0
Ser	10.4	9.0	9.1	9.8	7.4
Glx	14.9	14.8	14.2	17.9	16.0
Pro	7.1	5.4	6.7	5.0	32.3
Gly	13.6	19.6	18.5	18.1	12.4
Ala	5.6	5.6	6.0	5.2	2.9
Val	5.6	4.0	5.0	4.3	8.7
Ile	3.6	2.9	4.1	3.4	1.2
Leu	6.3	5.8	6.0	6.0	3.0
Tyr	1.0	0.6	0.1	0.1	17.8
Phe	2.0	2.1	2.4	0.2	1.3
His	1.8	2.0	1.9	0.2	8.4
Lys	3.5	4.7	4.2	3.8	4.6
Arg	6.2	6.0	6.2	5.2	5.0

(*) Urea extracted; (§) 3500 MW cutoff

Proteins



	U1*	U2*	U3*	U4*	NaOH-soluble§
Cys	2.1	2.6	2.2	2.1	0.1
Asx	16.1	18.3	16.2	15.4	14.6
$MetSO_2$	1.1	(n.d.)	1.6	1.0	0.1
Thr	7.6	3.1	5.1	5.2	6.0
Ser	10.4	9.0	9.1	9.8	7.4
Glx	14.9	14.8	14.2	17.9	16.0
Pro	7.1	5.4	6.7	5.0	32.3
Gly	13.6	19.6	18.5	18.1	12.4
Ala	5.6	5.6	6.0	5.2	2.9
Val	5.6	4.0	5.0	4.3	8.7
Ile	3.6	2.9	4.1	3.4	1.2
Leu	6.3	5.8	6.0	6.0	3.0
Tyr	1.0	0.6	0.1	0.1	17.8
Phe	2.0	2.1	2.4	0.2	1.3
His	1.8	2.0	1.9	0.2	8.4
Lys	3.5	4.7	4.2	3.8	4.6
Arg	6.2	6.0	6.2	5.2	5.0

(*) Urea extracted; (§) 3500 MW cutoff

Conclusions

- The interstitial nucleating sheets in abalone shell nacre are trilaminate, with glycoprotein layers sandwiching a central layer of chitin.
- The architecture of the interstitial sheets resembles that of the insoluble organic matrix of the nacre, although the proteins are very different in the two materials.

Conclusions

- During shell formation, prismatic and spherulitic aragonite precedes and follows the deposition of the interstitial green polymeric composite sheets;
- these sheets demark the interruption of nacre synthesis and serve to nucleate the resumption of calcium carbonate crystal growth.

Conclusions

- The surface of the interstitial sheet that is richest in anionic and phenolic groups functions, a nucleator of calcite crystal growth *in vitro*.
- The interstitial sheet modulate the crystal growth of $CaCO_3$ to obtain a very resistant biomaterial.

Referenze sul WEB

- Vie metaboliche
  - KEGG: http://www.genome.ad.jp/kegg/
    - Degradazione degli xenobiotici: http://www.genome.ad.jp/kegg/pathway/map/map01196.html
- Struttura delle proteine:
  - Protein data bank (Brookhaven): http://www.rcsb.org/pdb/
  - Hexpasy
    - Expert Protein Analysis System: http://us.expasy.org/sprot/
    - Prosite (protein families and domains): http://www.expasy.org/prosite/
    - Enzyme (Enzyme nomenclature database): http://www.expasy.org/enzyme/
  - Scop (famiglie strutturali): http://scop.berkeley.edu/
- Enzimi:
  - Nomenclatura - IUBMB: http://www.chem.qmw.ac.uk/iubmb/
  - Proprietà - Brenda: http://www.brenda.uni-koeln.de/
  - Expasy (Enzyme nomenclature database): http://www.expasy.org/enzyme/
- Database di biocatalisi e biodegradazione: http://umbbd.ahc.umn.edu/
- Citocromo P450: http://www.icgeb.org/~p450srv/
- Metallotioneine: http://www.unizh.ch/~mtpage/MT.html
- Tossicità degli xenobiotici: Agency for Toxic Substances and Disease Registry http://www.atsdr.cdc.gov

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