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TEM INVESTIGATION OF THE SHELL OF THE BRACHIOPOD *THECOSPIRA TYROLENSIS* (LORETZ): A CLUE TO UNDERSTANDING GROWTH AND REPLACEMENT OF PRISMATIC AND/OR FIBROUS LOW MG-CALCITE?

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Riassunto. Il guscio di *Thecospira tyrolensis* (Loretz) (Brachiopodo) è composto da 3 strati calcitici a basso tenore di Mg: uno strato primario, spesso diageneticamente alterato, uno strato secondario fibroso, con fibre allungate parallelamente alla superficie, uno strato terziario prismatico. Quest'ultimo è composto da prismi di calcite allungati perpendicolarmente rispetto all'epitelio esterno del mantello ed è generato da cellule epiteliali invertite alla secrezione inorganica. Per questo motivo e per i suoi caratteri morfologici può essere paragonato ad alcune calciti a basso tenore di Mg che riempiono i pori nei sedimenti carbonatici, per cui la sua formazione potrebbe forse seguire la teoria della nucleazione e della crescita inorganica.

Le osservazioni condotte con il microscopio elettronico a trasmissione hanno rivelato che gusci di calcite a basso tenore di Mg sono soggetti a processi di dissoluzione e riprecipitazione, che avvengono in corrispondenza di difetti cristallini (piani di microgeminazione e dislocazione). Questi difetti determinano gradini e depressioni sulla superficie del cristallo, che riducono l'energia libera di superficie necessaria per la nucleazione. I nuovi elementi di calcite vi si depositano, favorendo la crescita del cristallo secondo piani (hkil), che determinano l'abito prismatico.

Infine il confronto tra lo strato prismatico *Thecospira tyrolensis* (Loretz) e cementi con abito e composizione simili, ma dovuti a sostituzione di un precursore (calcite a basso tenore di Mg) ha permesso di formulare criteri per distinguere la calcite a basso tenore di Mg di origine primaria da quella di origine diagenetica.

Abstract. The shell of *Thecospira tyrolensis* (Loretz) is characterized by three distinct layers consisting of low Mg-calcite. The primary layer consists of microcrystalline calcite and it is often diagenetically altered. The secondary layer is composed of imbricate fibres subparallel to the valve surface. The tertiary layer (prismatic) is made of calcite prisms perpendicular to the outer epithelium of the mantle and was formed by ephitelial cells that reverted to inorganic secretion. For this reason, as well as its morphology, the prismatic layer can be compared to some pore-filling low Mg-calcites, therefore we would expect it to follow inorganic nucleation and growth theory. Transmission electron microscopy allowed to recognize crystal defects (sets of microtwins and dislocations) which, by creating abutting surfaces and kinks, represent favourable sites where new "calcite seeds" attach themselves to the crystal surface. Stacking of (hkil) planes where growth is faster (in particular the basal plane), favoured by twinning, accounts for the prismatic habit. Furthermore, observations with the trans-

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mission electron microscope indicate that even in very well preserved shells consisting of "stable" low Mg-calcite, dissolution and reprecipitation occurs, especially along twin and grain boundaries. As a consequence, transmission electron microscopy is strongly recommended before proceeding to geochemical analysis.

Comparison with diagenetic fibrous and abiotic low Mg-calcite replacing high Mg-calcite, allowed to recognize criteria for the possible distinction of the former as opposed to diagenetic low Mg-calcite replacing original low Mg-calcite.

Introduction.

The shell structure of the carnian brachiopod *Thecospira tyrolensis* (Loretz), composed of low Mg-calcite, shows three distinct layers (Benigni & Ferliga, 1989): a primary layer, nearly always diagenetically altered and consisting of microcrystalline calcite; a fibrous secondary layer; a prismatic tertiary layer. This latter is the one which resembles most, from the morphological point of view, some inorganically precipitated, pore filling low Mg-calcites interpreted either as replacements after aragonite or high Mg-calcites (Kendall & Tucker, 1973) or as primary cements (Kendall, 1985). Given and Wilkinson (1985) demonstrated the relations between ambient fluid chemistry, carbonate crystal habit, composition and mineralogy for abiotic carbonates in terms of kinetically mediated processes (i.e. rate of crystal growth, rates of carbonate ion supply). These same relationships might be true also in the case of biologically precipitated calcites.

As for brachiopods, Gaspard (1978) ascribes the passage from secondary layer to prismatic layer to the ending of organic secretion and deposition of "carbonate elements" perpendicular to the outer epithelium of the mantle, thus forming prisms. Furthermore, observations on the aspects of biomineralization in modern terebratulids (Gaspard, 1986), put to evidence the presence of calcite seeds embedded in an impersistent organic matrix which disappears as the seeds become more numerous and coalesce. Each of these granules represents an elementary crystal seed, than the evolution of a fibre or prism continues with accumulation of seeds in intervals between growth rings and the subsequent piling up of these intervals. According to the theory of nucleation and growth we would expect to find preferential sites for the "attachment" of the "calcite seeds", such as dislocations and these can be easily observed by means of transmission electron microscopy (TEM).

Furthermore, the well known stability of low Mg-calcite led to the use of brachiopod shells in order to determine the isotopic composition of ancient oceans (Brand & Veizer, 1981; Brand, 1982; Veizer et al., 1986). However, the extent of possible recrystallization even in apparently perfectly preserved shells cannot be determined without the aid of electron microscopy. In fact, very small crystal defects, the dimension of which can be of the order of less than 1/10 of a micron, can be the sites of dissolution and precipitation of new carbonate phases at a very small scale (Frisia Bruni & Wenk, 1985). Nevertheless, if dissolution-reprecipitation occurred, the study of well preserved brachiopod shells give us a clue to the understanding of low Mg-calcite replacement by diagenetic low Mg-calcite.

Scope of this study was to observe the nature of the prismatic layer in *Thecospira tyrolensis* (Loretz), to determine eventual analogies or differences with known pore-filling diagenetic low Mg-calcites (the evinosponge, Jadoul & Frisia, 1988) and to detect if these brachiopods shell underwent recrystallization despite the fact that in the San Cassiano Formation even aragonite has been preserved (in order to understand the reliability of isotopic data). This required the use of transmission electron microscopy, which is becoming a necessary technique for the study of biomineralization processes.

Transmission electron microscopy.

Full explanations of the method are given in Amelinckx and Van Landuyt (1976), Thomas and Goringe (1979) and Wenk (1976). Here only the information necessary to understand the acquisition and meaning of the data will be given. The first step consists in the sample preparation: extreme care must be paid to this operation, especially when dealing with carbonates. These minerals are very fragile and, if the operator does not

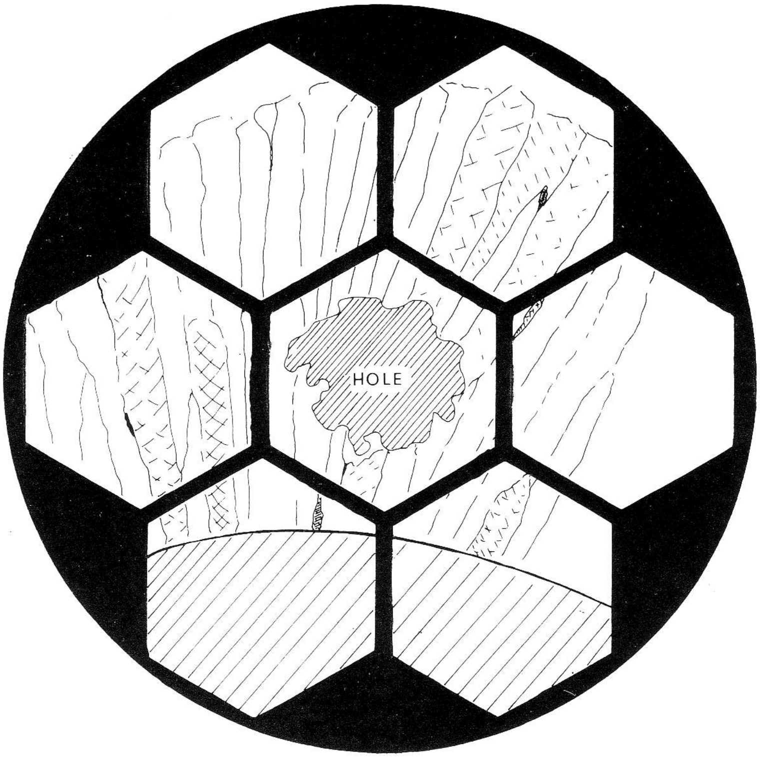

Fig. 1 - The specimen for transmission electron microscopy of carbonate samples. It consists of an ultrathin section prepared by means of ion thinning. Observations are carried out about the hole, where the section is transparent with respect to the electrons.

handle the specimen with proper gentleness, may break or develop crystal defects such as deformation twins. A thin section mounted on the glass support with crystal bond is prepared. Then the area of interest is chosen: for this study was a transverse section through the muscle field where the prismatic layer is well developed. On it a copper grid, with a diameter of 3 mm and consisting of six hexagonal holes, is glued by means of epoxy. The thin section is then detached from its support by immersion in acetone. Subsequently, the copper grid with the glued fragment is detached from the rest of the section with a sharp blade. The sample is now ready to be furtherly thinned by means of an ion beam thinner. Observations are carried out about a small hole where the material is transparent with respect to the electronic beam. Before proceeding to the final carbon coating, it is necessary to map the sample (Fig. 1): observations with the TEM are not simple, it is possible to loose track of what we want to see, especially when changing magnification (because as the strenght of the magnetic lens is varied, the image experiences a rotation).

In the TEM an electron beam traverses the specimen and then passes through a series of electromagnetic lenses by means of which a highly magnified image or a diffraction pattern can be obtained. This latter allows the immediate identification of different phases coexisting in the same specimen, such as calcite and aragonite, and their crystallographic relations (Frisia Bruni & Wenk, 1985).

The image mode (the resolution of which can be about 2 Å) allows us to study the internal structure of the mineral, i.e. to observe crystal defects, their nature and their possible role as preferential sites for nucleation and growth and/or dissolution. In other words, it gives an insight on how the crystal developed and if it underwent recrystallizations or tectonic stress, which might affect all our interpretations of isotope, trace element and also optical microscopy data.

Crystal nucleation and growth theory.

Before proceeding to the presentation and discussion of the data, it is useful to review, briefly, the theory of nucleation and growth of crystals, which holds for both organic and inorganic processes and might be the key to understanding shell structures. The formation of a crystal which precipitates from a solution requires an increase in free energy because the surface free energy dominates the process when very small volumes are involved (Fig. 2). When the maximum in free energy is attained we have nucleation and once the critical nucleus is formed, the crystal may spontaneously grow, by addition of further atoms and/or molecules. Growth is accompanied by a decrease in free energy because the surface free energy, at increasing volumes, is not any more the dominant factor. Furthermore, from Fig. 2 it can be observed that the activation energy for nucleation is also a function of supersaturation (for a more detailed discussion see Berner, 1980; Garside, 1982). Nucleation can be homogeneous and heterogeneous. In the first case, nucleation results from random collision of atoms in solution, while in the second case nuclei form on a substrate (such as other crystals) and, preferentially, on ac-

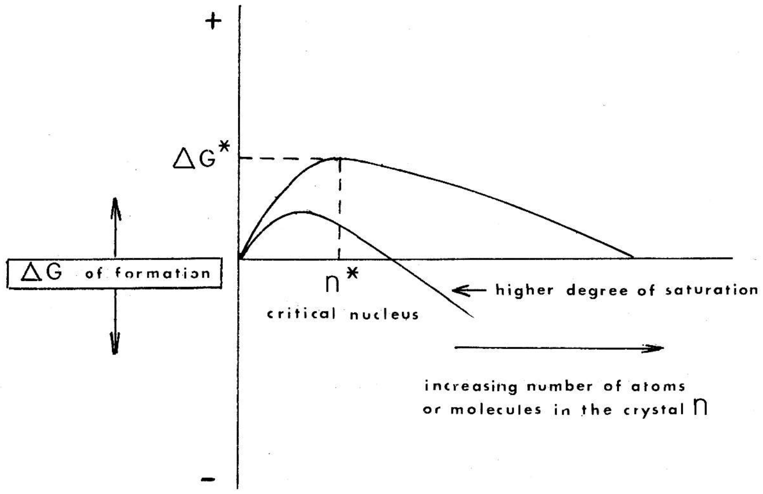

Fig. 2 - The diagram shows that the process of nucleation requires an increase of free energy of formation (Δ G) up to a maximum Δ G*, which depends on the degree of supersaturation. Once the Δ * is attained, the critical nucleus is formed and the crystal may grow by addition of atoms or molecules. Growth is accompanied by a decrease in free energy (redrawn from Berner, 1980).

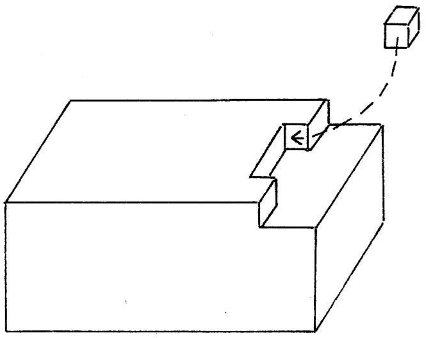

Fig. 3 - Example of kink in a step.

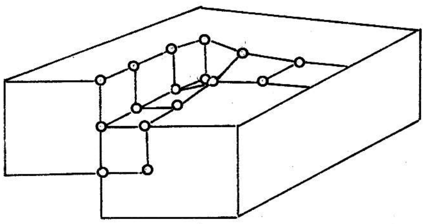

Fig. 4 - Screw dislocation as a source of step (redrawn from Nielsen & Christoffersen, 1982).

tive sites, i.e. kinks in steps (Fig. 3). In fact these "reduce" the surface free energy and, consequently reduce the critical size of the nuclei. Thus the process of nucleation may be more rapid and at lower degrees of supersaturation. Subsequently, the crystal will grow if the constituent material is present at its surface with a certain degree of supersaturation, whether this latter is maintained by means of biological processes or by diffusion or convection (Nielsen & Christoffersen, 1982). Growth sites are represented by steps with kinks on the surface of the crystal. A very efficient (in terms of energy) source of step is a screw dislocation (Fig. 4). During crystal growth the step winds itself to form a spiral with the centre fixed at the dislocation, in this way the step does not disappear and the crystal may grow continuously at very low supersaturation.

Furthermore, in inorganic processes crystals undergo distorsions of shape during their growth: this is especially true for twinning. In comparing data on twinned and untwinned crystals Becke (1911) found that:

1) twinned crystals grow larger than untwinned ones;

2) twinned crystals grow more rapidly than untwinned crystals along twin boundaries.

This can be explained by the idea that nucleation might be easier at a twin boundary, where a face abuts at an angle with another face (Smith, 1974; Frisia Bruni & Wenk, 1985). What has been said for growth, can also be adapted to dissolution processes (Nielsen & Christoffersen, 1982). The importance of crystal defects in nucleation and growth should now be clear. For our specific purpose the question is: can we observe structural defects such as dislocations and microtwins in biologically secreted low Mg-calcite crystals which form the brachiopod shells? Do these defects, if present, also represent sites for preferential dissolution and/or precipitation?

Ultramicrostructure of the shell of *Thecospira tyrolensis* (Loretz).

Optical microscope and Scanning Electron Microscope observations (see Benigni & Ferliga, 1989, for details) of transverse brachial valve sections through the muscle field of *Thecospira tyrolensis* (Loretz) from the Alpe di Specie outcrops permitted to ascertain the presence of three distinct layers, apparently well preserved. The external primary layer, which is generally corroded by dissolution phenomena, consists of calcite prisms, about 50-100 micron long, both inclined and/or perpendicular to the surface of the shell. The extinction is preferentially uniform and, sometimes, in patches, which might be due to calcite crystals precipitated in dissolution holes or filling borings. The passage to the secondary layer is abrupt. This latter is well preserved and composed of very fine fibres, about 20 micron long, subparallel to the shell surface. Each fibre is a single calcite crystal (Gaspard, 1978) and shows uniform extinction. The passage from the secondary layer to the tertiary layer is gradual. The tertiary layer prisms, up to 500 micron long and about 20-50 micron wide, show irregular boundaries, especially with the fibres of the secondary layer, and are perpendicular to the surface. The extinction is sligthly undulose, which might indicate that they are formed by subcrystals (sensu

Kendall, 1985). With the scanning electron microscope it is possible to observe a network of small holes (less than 1/10 of a micron) located within the crystals, possibly at the sites of crystal defects. Intergranular porosity is also well developed.

Transmission electron microscopy reveals the presence of pervasive microtwinning (Fig. 5). Particularly important is the fact some of the twins are developed on (0006) that are interpreted as *growth twins* (D. Barber, pers. comm.). These microstructures pertain to the mechanism by which the brachiopod itself builds its shell.

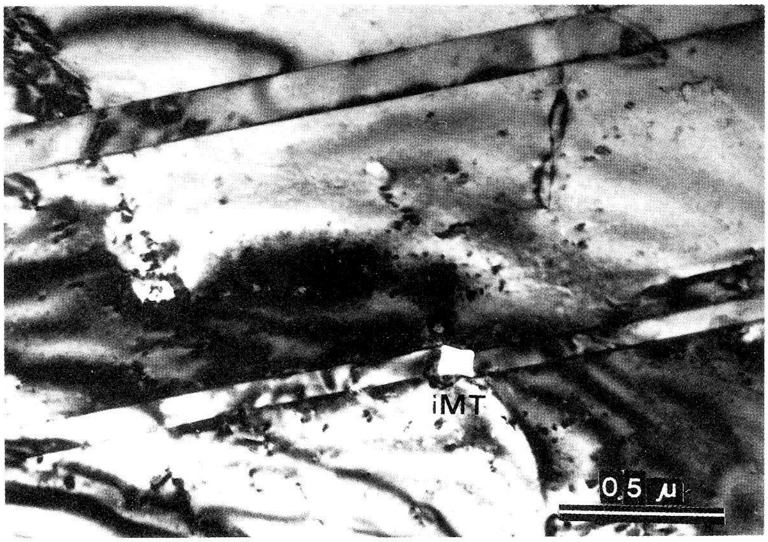

Fig. 5 - Transmission electron micrograph showing pervasive microtwinning in the prismatic layer of *Thecospira tyrolensis* (Loretz). Note that one of the microtwins is interrupted (iMT) and sligthly shifted thus forming a geometric hole. These shifts, as well as sets of twins, may account for the progressive enlargement of the prisms away from the outer epithelium.

Other microtwins develop on (01$\bar{1}$8), are interpreted as *deformation twins* (see Wenk et al., 1983) and are here interpreted as being due to growth processes since: 1) the San Cassiano fossils observed with the TEM (Frisia Bruni & Wenk, 1985) are not deformed by tectonics; 2) multiple twins developed by growth are characterized by parallel boundaries and abrupt terminations (Vernon, 1989), as observed in *Thecospira tyrolensis* (Loretz). Dislocations and dislocation loops are common (Fig. 6) and it is possible to distinguish climbing dislocations (cf, Wenk et al., 1983).

Often, at their junction, or at the junction dislocation-twin boundary, the development of small pores, about 1/100 of a micron in diameter can be observed. This pervasive porosity characterizes the shells and tests of several other organisms (Frisia Bruni, 1983). Fig. 6 shows that, at a very fine scale, dissolution and reprecipitation occurred. In fact it is possible to observe that a twinned crystal has undergone dissolution, which took place preferentially at twin boundaries. The neomorphic calcite bears cross-cutting relationship with that of the original prisms forming the tertiary layer, consists of smaller crystals, has a very high intergranular porosity and seems to have a greater

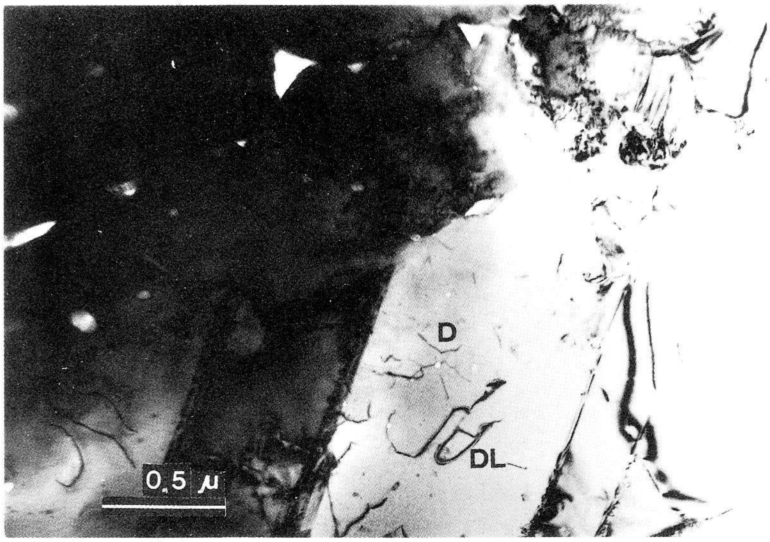

Fig. 6 - Twins showing dislocations (D) and dislocation loops (DL). Note that dislocation density is not high. The micrograph also shows that twin boundaries are favourable sites for dissolution and subsequent precipitation of new phase, characterized by higher dislocation density, cross cutting relationships with the primary calcite, high intergranular porosity.

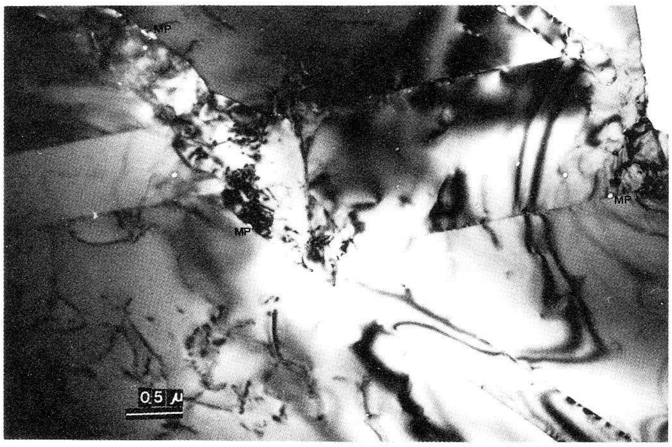

Fig. 7 - Micrograph showing two different sets of twins in the prismatic layer. Again, it is possible to see that twin junction might be the preferential sites for dissolution and reprecipitation. The diagenetic low Mg-calcite shows, as in Fig. 6, a higher dislocation density. Note diffuse microporosity (MP) along twin boundary, which besides favouring dissolution, could also represent the former site for soluble organic matter.

number of crystal defects with respect to the original biogenic calcite. Sometimes, this "diagenetic" calcite is "engulfed" between twins, and possibly recrystallization proceeds aided by the pervasive original microporosity of the shell. Fig. 7 shows a somewhat similar phenomenon: two adjacent individuals, which have the same crystallographic orientation, so that they could be a single crystal, are affected by dissolution and subsequent reprecipitation at their boundaries. Again dissolution and nucleation of neomorphic calcite took place at twin boundaries and at the junction between crystal surface and dislocations.

Comparison with "inorganically" precipitated fibrous low Mg-calcite: the evinosponge.

The structures known as "evinosponge" have been widely investigated by Jadoul and Frisia (1988) and Frisia Bruni et al. (1989). Therefore, here will be given a brief description in order to point out affinities and/or differences with the tertiary layer of *Thecospira tyrolensis* (Loretz) as well as some criteria to distinguish primary from replaced low Mg-calcite. The calcite fibres which form each isopachous concentric layer of the evinosponge structure, are 0.5-10 mm long and about 0.1-0.2 mm wide and show strong undulose extinction as well as deformed twin boundaries. Along with microdolomite inclusions and analogies with marine cements at Mururoa (Aissaoui et al., 1986) these characters have been considered as indicative of replacement after high Mg-calcite. Transmission electron microscope observations of the evinosponge fibrous calcite shows pervasive multiple microtwinning (Fig. 8a). Some of the twin boundaries are curved and terminations are lenticular (pointed), which is indicative of deformation (Vernon, 1989). The dislocation density (number of dislocations per unit area) is high, dislocation networks and dislocation tangles (intricate threads of dislocations) are present (Fig. 8b). Furthermore, each fibre seems to consist of several grains, in fact it is possible to observe Moire' fringes (Fig 8c), which occur at the interface between grains, accounting for even minor mismatch in crystallographic orientations (Oster, 1968).

Discussion.

As already mentioned the secretion of both fibres and prisms in modern brachiopods occurs in different phases: secretion of elementary crystal seeds and their organization in growth bands. The cells which secrete the fibres and the prisms should not be very different (Williams, 1968; Gaspard, 1978): however, the prismatic bodies are probably due to the breakdown of the orderly processes of secretion which control the growth of discrete fibres (Williams, 1968). Williams (1968) relates the deposition of prismatic calcite to the acceleration in carbonate secretion in several contiguous cells which caused an interruption in exudation of protein sheats defining individual fibres. The mature epitelial cells probably reverted to "inorganic secretion" allowing the growth of

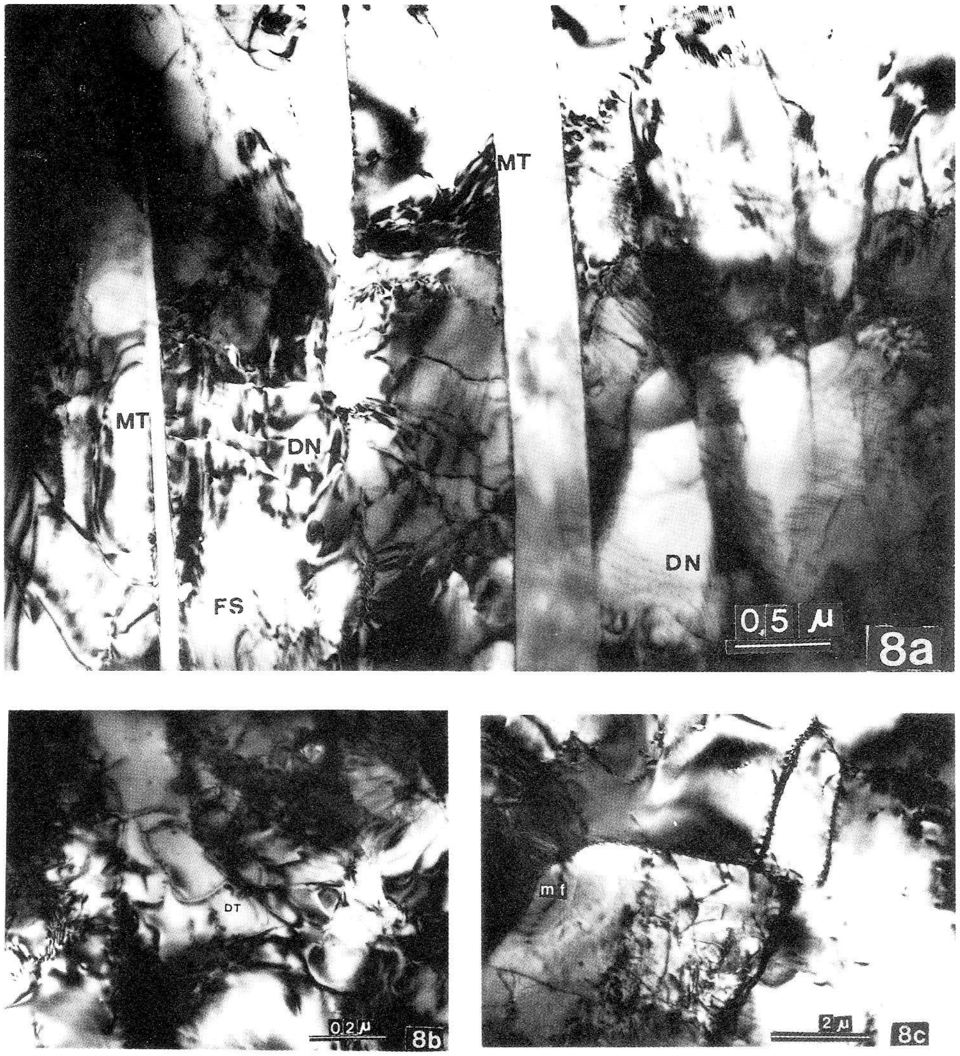

Fig. 8 - a) Micrograph of evinosponge fibre showing microtwins (MT), dislocation networks (DN) and fringe structures (FS). Note the pointed termination of the twin on the left.
b) Particular of (a) showing dislocation tangles (DT).
c) The evinosponge fibres show numerous subgrains as can be seen in this micrograph, pointed out by the pervasive presence of Moire' fringes (mf).

prisms perpendicular to the outer epitelium and not constrained by protein boundaries as the fibres are. The individuality of each prism might have been maintained by soluble organic matter within intergranular pores, and this hypothesis (Gaspard, 1978) seems to be a possibility if we consider the observed pervasive microporosity both at grain and twin boundaries.

The role of crystal defects in the development of calcite prisms.

According to "inorganic" nucleation and growth theory, it is possible that the development of the tertiary prismatic layer requires fewer nuclei with respect to the fibrous layer, and fast growth. The presence of extensive microtwinning could be indicative of the latter: in analogy to some inorganically precipitated fibrous calcites, the prismatic habit might be due either to repeated addition of basal planes (the 0006) or stacking of some (hkil) planar elements (such as $01\bar{1}8$, for example) or a combination of both (Given & Wilkinson, 1985). The brachiopod then, "utilizes" twin planes to obtain a fast growth of large crystals (Becke, 1911). Dislocations provide steps on crystal surfaces where the "calcite seeds" can attach without needing high supersaturations (Nielsen & Christoffersen, 1982, calculated that crystals do not grow by surface nucleation at 10% supersaturation). Twinning might be the rule in biogenic precipitation: Frisia Bruni (1983) observed microtwins in fibrous aragonite forming the shell of the gastropod *Fissurella* (Fig. 9) and the skeleton of corals. In doing this, organisms follow the rules of inorganic precipitation, trying to "save energy" during the process of nucleation and growth.

The observed systems of microtwins, coupled with dislocations (which create lattice distorsions) might also account for the deformation that occurs in creating a shell with a very complex morphology, such as that of *Thecospira tyrolensis* (Loretz). The presence of curved surfaces in the muscle field area could require the development of $01\bar{1}8$ twins (D. Barber, pers. comm.).

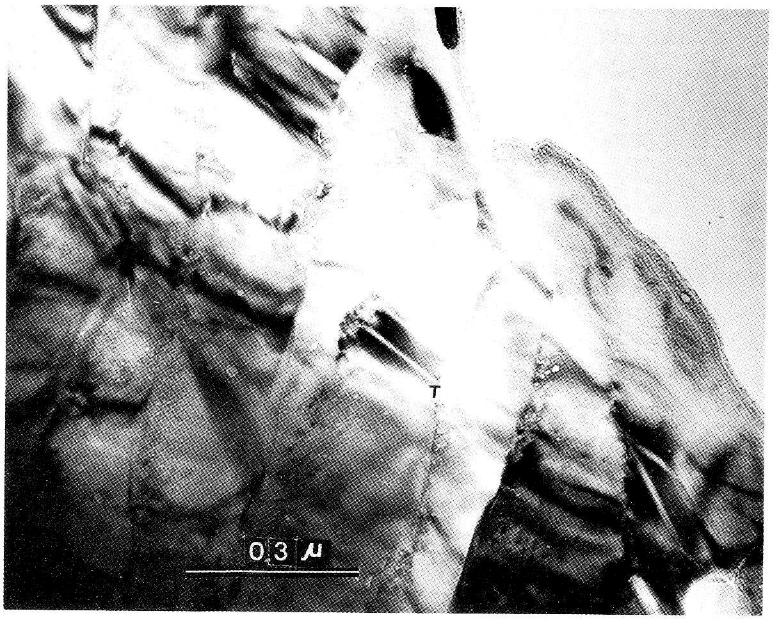

Fig. 9 - Micrograph showing the ultramicrostructure of the fibrous aragonitic layer of *Fissurella*. Note that aragonite crystals are twinned (T). Note also the pervasive intergranular porosity.

Role of crystal defects in diagenetic stabilization of both organically and inorganically precipitated calcites.

One of the most difficult problems facing both paleontologists and carbonate petrographers when dealing with shell structures and/or their geochemistry is the knowledge of the degree of alteration of the studied specimen. Conventional optical microscopy and scanning electron microscopy are not sufficient in that very small crystal defects, such as the forementioned ones, represent preferred pathways for diagenetic re-equilibration. The studied brachiopod, despite its well preserved morphology and structure, underwent some recrystallization. The new phase, diagenetic, very likely has a different geochemistry: in fact the ^{18}O value of the specimen is about -3.7‰ (PDB) which is considerably lower than the -2‰ (PDB) value calculated for a low Mg-calcite precipitated in equilibrium with Cassian waters (Scherer, 1977; Frisia Bruni et al., 1989). Transmission electron microscopy thus enables us to understand the degree of recrystallization, at least in well preserved low Mg-calcites: the neomorphic phase has cross-cutting relationships with the primary calcite, as well as a higher number of dislocations and develops preferentially at crystal defects.

Criteria for the distinction of primary vs. diagenetic low Mg-calcites.

Primary low Mg-calcite shows growth twins as well as dislocations, dislocation loops and climbing dislocations. Comparison with a probable diagenetic low Mg-calcite after original high Mg-calcite (that of the evinosponge) enables us to develop further criteria to recognize recrystallization. Gunderson and Wenk (1981) provide as a criterion of replacement after high Mg-calcite (or aragonite) the development of a modulated structure (fine bands, 100-200 Å wide, alternatively light and dark), however, these were not found in the evinosponge. On the other hand geochemical evidence pointed out to replacement. The compared study of *Thecospira tyrolensis* (Loretz) and the evinosponges indicates that a possible other criterion is: the presence of numerous subgrains within the same fibre. This pervasive presence of Moire' fringes within what appears to be a single crystal, is due to the presence of "sub-grains" the crystal lattice of which is slightly mismatched.

A further criterion of replacement could be the higher density of dislocations observed in the evinosponges. Dislocations tangles indicate that the evinosponges underwent tectonic deformation, accounting for the enhanced undulose extinction. It is difficult to ascertain if the observed twins are due to tectonics or not. Possibly we have both growth and stress acting: i.e. replacement calcite grew in a tectonic regime (Frisia Bruni et al., 1989). However, as in the studied brachiopod, microtwinning seems to be the rule in the evinosponge, which points out to a certain similarity between pore-filling fibrous calcites and prismatic biogenic calcites with respect to growth mechanisms. It is very interesting to note that only *Thecospira tyrolensis* (Loretz) prismatic calcite has sets of differently oriented microtwins. This might be a specific character of some "biogenic", which must adapt itself, during growth, to very complicated shapes. Furthermore, some fringe structures (Fig 8a,c) are present in the evinosponges, which have not been observed in the prismatic layer of the studied brachiopod, and could account for compositional variations in the diagenetic low Mg-calcite (Barber & Wenk, 1984), further evidence for replacement after a more Mg-rich phase.

Primary biogenic low Mg-calcite as a consequence to CO_3 availability.

A last puzzling question might be asked: why do some brachiopods precipitate low Mg-calcite? I suggest that, if the analogy with inorganic carbonates holds true, the scenario implying a discrete rate of supply of carbonate ions separating calcite and aragonite precipitation should be considered (Given & Wilkinson, 1985). Lower CO_3 availability gives rise to calcite, thus in water depleted of carbonate, low Mg-calcite is likely to precipitate as opposed to aragonite, which favours higher CO_3 availability. It is possible that calcite secreting brachiopods begun their evolution in a period of high pCO_2, i.e. low carbonate dissolved in sea water and are consequently "tuned" to these chemical parameters? It is a fascinating hypothesis, however, impossible to demonstrate. Nevertheless, during Cambrian the passage from high Mg-calcite and aragonite deposition to low Mg-calcite occurred (Sandberg, 1985; this calcite period lasted up to the Middle Carboniferous).

Conclusion.

TEM observations of the tertiary prismatic layer of *Thecospira tyrolensis* (Loretz) supports the hypothesis of its precipitation according to "inorganic-type" processes (Williams, 1968) as well as that of the presence of intergranular soluble organic matter (Gaspard, 1986). Nucleation and growth took place at crystal defects, the most important of which are sets of microtwins. It is possible that the prismatic shape of the tertiary layer calcite is due to progressive stacking of basal planes (which accounts for the perpendicular orientation with respect to the epithelium) and some (hkil) planes, probably $(01\bar{1}8)$ (which might be responsible for the "progressive" enlargement of the prisms away from the epithelium). Dislocations provide other favourable sites for the "attachment" of calcite seeds (sensu Gaspard, 1986). This study demonstrates that it is possible to determine the degree of recrystallization of low Mg-calcite shells. This process occurs preferentially at crystal defects, aided by the pervasive ultramicroporosity, which represents a passageway for diagenetic fluids. Before carrying out geochemical analysis (such as stable isotopes) on well preserved shells and tests of original low Mg-calcite, TEM observation of the specimens is strongly recommended. Comparisons with well known abiotic low Mg-calcites which replaced high Mg-calcites, point out both to similarities and diversities. Similar is the presence of microtwins and dislocations, which favours a faster crystal growth. The differences indicate some criteria by which we can distinguish different types of replacements:

1) diagenetic low Mg-calcite after high Mg-calcite shows:

- modulated structures (Gunderson & Wenk, 1981; Frisia Bruni & Wenk, 1985);

- higher dislocation density compared to original low Mg-calcites;
- a great number of "subgrains", as can be seen by the presence of Moire' patterns;
- other fringe structures (possibly accounting for compositional variations);

2) diagenetic low Mg-calcite after low Mg-calcite does not show the above mentioned microstructures. We should look at twin boundaries and grain boundaries for cross-cutting relationships, enhanced ultramicroporosity, grains with higher dislocation density with respect to the original calcite. We should also look for the absence of dislocation networks that may be indicative of tectonics, thus hindering isotopic as well as textural analysis.

Transmission electron microscopy applied to paleontological studies proves to be extremely useful for the interpretation of nucleation and growth of the carbonate phases which form the shell, and their subsequent alteration.

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