Chapter 3
Shell Microstructure and Shell Architecture

Abstract This chapter is focused on the analysis of the shell microstructure of different taxa and on how this information can be used for paleoenvironmental interpretations. A physic-chemical analysis on Modern, Holocene and Pleistocene shells of the purple clam *Amiantis purpurata* helps discern the structural changes during early diagenesis. In addition, the analyses of the microstructure of two other bivalves (*Glycymeris longior* and *Ameghinomya antiqua*) from the same region explain the differences in the degree of fragmentation in both species as a result of different structural features. Finally, cathodoluminiscence applied to *Tawera gayi* provides information on the skeletal growth cycles that is useful for evaluating changes.

Keywords Southern South America · Quaternary · Pleistocene · Holocene · Mollusca · Shell microstructure · Mechanical resistance · Early diagenesis

Shell microstructure refers to the arrangement of basic microstructural units, such as tablets, rods and blades, in a shell layer. Shell architecture deals with the larger aspect of the shell microstructure, such as the orientation of the largest units of shell microstructure with respect to the shell form (Carter 1980).

3.1 Inorganic-Organic Biocomposites

As seen in Chap. 2, mollusk shells have been used in comparative taphonomic studies because of their excellent potential for preservation. However, their resistant hard parts are subject to physical, chemical and biological agents or processes that can destroy these shells before and after burial e.g., (Lawrence 1968).

Bivalve shells are predominately composed of $CaCO_3$, in other words, calcite, variable proportions of aragonite, even vaterite, as well as organic polymers (Hare and Abelson 1965; Rhoads and Lutz 1980; Nehrke et al. 2012). As in other biomineralized exoskeletons, the orientation and growth of $CaCO_3$ crystals are strongly controlled by the organic matrices (which constitute about 1–5 wt% of the

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shell) forming compartments in which mineralization takes place. Most of the organic components are intercrystalline, with a smaller portion located within the crystal structure of calcium carbonate. This mixture, on a very fine scale of organic and bioprecipitated $CaCO_3$, modifies diagenetic processes and patterns in comparison with non-biogenic mineral features (Perrin and Smith 2007).

Mollusk shells can be considered inorganic-organic biocomposites, with excellent mechanical performance compared to non-biogenic material (Chateigner et al. 2010). Even though aragonite provides high mechanical strength to the valve (Chateigner et al. 2000), under the environmental conditions found on the Earth's surface, this phase is metastable, and is more susceptible to dissolution and recrystallization than calcite. In other words, during diagenesis, the alteration of aragonite skeletons commonly results in mineralogical and structural changes, as well as compression and postdepositional cementation (Brand 1989). For this reason, aragonitic fossils are usually poorly preserved in the geological record (Powell and Kowalewski 2002; Cherns et al. 2011). One exception is for the Cenozoic A-seas (aragonitic seas), in which a positive bias favoring aragonitic bivalves is recognized (De Renzi and Ros 2002).

This relative instability of aragonite when exposed to diagenesis introduces a bias in the fossil record, thus affecting its quality for paleoecological and paleobiological studies (Fernandez Lopez 2000; Cherns and Wright 2009). The detection of subtle postdepositional changes therefore becomes of utmost importance, especially in fossils that appear to retain their primary mineralogy when conventional screening techniques (such as X-ray diffraction) are used.

3.2 Chemical and Physico-Mechanical Changes from Fossil to Modern Shells

In a recent study, Bayer et al. (2013) described the chemical (trace element), textural, and physical–mechanical transformation that took place in shells of an aragonitic bivalve, the *Amiantis purpurata* venerid, during early diagenesis in a period of time that exceeds 100,000 years (i.e., from the Late Pleistocene up to the present day). The advantage of considering the same species from different outcrops of the same region is the elimination of interspecific variations associated with intrinsic factors (shell microstructure) and different environmental conditions that can occur when comparing shells of the same species collected from different regions.

Bayer et al. (2013) found that mineralogy remains constant, with aragonite as the only crystalline phase throughout the entire examined time interval, but texture (as revealed by XRD, SEM and optical microscopy; Fig. 3.1) is modified. The Pleistocene valve has more grains in a random distribution, compared with the twinning pattern evident in Modern and Holocene shells (Fig. 3.1). The approximate constant value of crystallite size suggests that the dissolved $CaCO_3$ does not

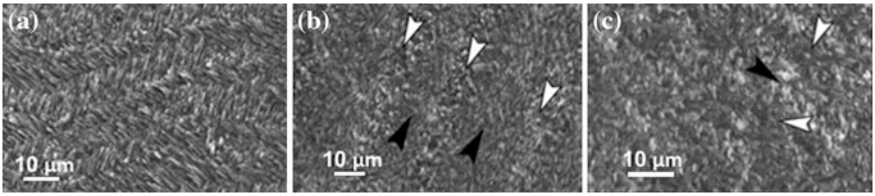

Fig. 3.1 SEM images (secondary electron mode) of *Amiantis purpurata* shells. **a** Details of the growth bands of a Modern shell, showing platy aragonite crystals defining a crossed-lamellar microstructure. **b** Growth bands from a Holocene shell that can still be observed. Some bands (marked with *white arrows*) have been replaced by a granular aggregate of aragonite crystals, whereas others (*black arrows*) still display the crossed-lamellar microstructure. **c** View of a Pleistocene shell where no growth bands can be discerned, showing a mixture of biogenic platy crystals (*white arrows*) with equant grains of aragonite of diagenetic origin (*black arrow*) (Modified from Bayer et al. 2013)

precipitate in crystallographic continuity with the preexisting crystals, as this would lead to a larger crystallite size (and narrower diffraction peaks) and a sharpening of the twinning pattern. A possible explanation which remains to be tested is that aragonite cement occupies voids left by degraded organic matrix, as found by Webb et al. (2007).

A comparison of the chemical composition of *A. purpurata* valves of different ages (Bayer et al. 2013) shows trends of decreasing Na, Sr and (to a lesser degree) Mg with increasing age. The authors correlate these variations with the dissolution and reprecipitation of aragonite through a thin film of solutions of meteoric origin in small-scale, semiclosed microenvironments (a vadose environment).

In terms of mechanical properties, a shell's resistance to fracture is characterized by the measurement of its strength (Zuschin and Stanton 2001; Yang et al. 2011). The mechanical properties of the valves, such as the ability to transfer charges between adjacent layers of aragonite (Liang et al. 2008), are associated with the structure and functions of the biological matrix, which also promotes the formation of crystalline layers (Rhoads and Lutz 1980). Bayer et al. (2013) found that Holocene and Pleistocene *A. purpurata* shells have a higher Vickers hardness and a more fragmented area than the Modern shells (Fig. 3.2). These differences indicate that over a period of less than 5,000 years the valves of *A. purpurata* have become harder but more brittle. These changes are also attributed to postdepositional modifications by dissolution-recrystallization processes mediated by a thin film of water in a vadose environment.

Microstructural adjustments are more sluggish than chemical modifications produced by diagenetic processes, whereas microhardness rapidly reaches high values, probably due to the early degradation of organic shell compounds.

In conclusion, this study shows that chemical and physico-mechanical changes in mollusk shells start early (at least before a shell reached the age of 5,000 year BP), increase with age and most probably occurred as a consequence of the degradation of the skeletal organic matrix.

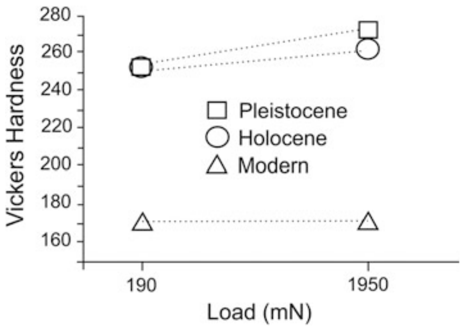

Fig. 3.2 Changes in mechanical resistance measured as microhardness of Modern, Holocene and Pleistocene samples of *Amiantis purpurata* (after Bayer et al. 2013)

3.3 The Intrinsic Properties of Taxa Lead to Differential Behavior Under Environmental Conditions

Boretto et al. (2013) described the microstructure of two bivalves (*Glycymeris longior* and *Ameghinomya antiqua*) from Puerto Lobos in northern Patagonia (Argentina), and provided arguments to explain the differences in the degree of fragmentation in both species as a result of different structural features. The associations of shells analyzed in these Holocene beach ridges can be classified as allochthonous (Kidwell and Bosence 1991), since they originated in the intertidal and subtidal zones (production areas) and were transported to the supralittoral area (settling zone). Taphonomic analyses, which evaluate the energy of the processes involved in the formation of these assemblages, indicate that *A. antiqua* and *G. longior* shells were drawn together during high energy storm events, and that these bivalve assemblages were affected by the same transport conditions and physicochemical characteristics as the depositional environment. Previous X-ray diffraction studies performed on samples of both taxa (Bolmaro et al. 2006; Boretto et al. 2013) indicate their aragonitic mineralogical composition. On the one hand, *A. antiqua* (Fig. 3.3a–c) is characterized by a dominant prismatic microstructure with two aragonitic layers: an outer prismatic layer and a homogenous inner layer, although sometimes a thinner, crossed-lamellar third layer can be observed (Carter 1990). This species shares the same attributes described for *Protothaca thaca* from Chile (Lazareth et al. 2006). On the other hand, in *G. longior* (Fig. 3.3d–f), two major shell layers can be distinguished: the inner and the outer layers, separated by the thin miostracal and middle layers. Additionally, the outer shell layer can be further subdivided into a middle layer and an outer layer. In this respect, *G. longior* shares the same attributes as *G. glycymeris* (Rogalla and Amler 2007). Boretto et al. (2013) described *G. longior* as composed of an inner shell layer which has a complex crossed lamellar structure, with interdigitating first order lamellar of lenticular shape that extend normal to the shell, and an area of homogeneous microstructure close to the apex. The miostracal layer of a fairly constant thickness (between 50 and 100 mm) and a prismatic structure is then developed, composed of elongated prisms with the long

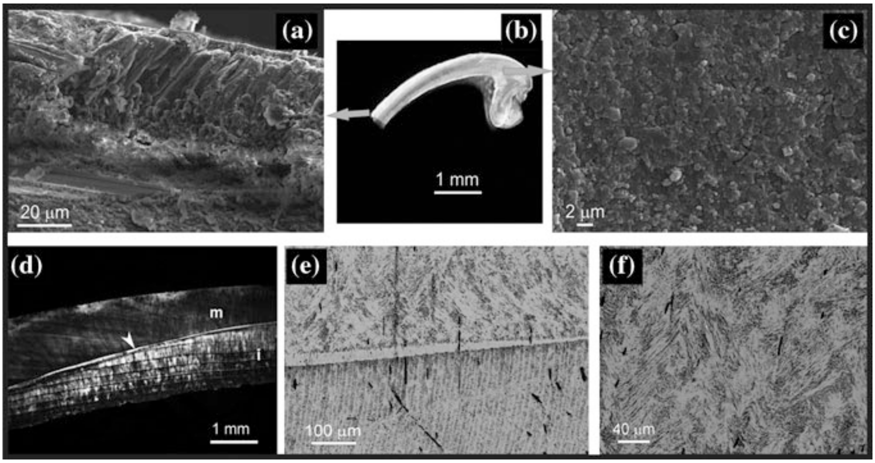

Fig. 3.3 Microstructural SEM images of *Ameghinomya antiqua* (**a–c**) versus *Glycymeris longior* (**d–f**). **a** Outer prismatic layer. **b** Cross-section from the umbo along the growth axis, showing the outer and inner layers. **c** Homogenous *inner* layer. **d** Cross-section of the shell showing the cloudy inner "i" and middle "m" layers which contrast with the *white arrow* point to the clear miostracal layer. **e** Contact of the miostracal layer with the inner and middle layers; note that the miostracal layer is homogeneous and lacks the *dark* spots which are interpreted as zones rich in organic material. **f** Close-up of the inner layer, showing complex *crossed* lamellar structure, first and second order lamellar (these defining a chevron pattern) (after Boretto et al. 2013)

axes oriented perpendicular to the layer margin. Below this, a crossed lamellar structure defines the middle layer, and finally these lamellar become thicker, torted and anastomosing, thus transitionally defining the outer zone. These differences in microstructure explain the different behavior of both species in relation to the taphonomic attributes analyzed in Chap. 2. Studies on the mechanical strength at break indicate that the crossed lamellar microstructure has a better performance in the elastic range, with a higher effective Young's modulus than the prismatic structure (Bolmaro et al. 2006). This explains the *G. longior* overall shell preservation as "whole and some broken", due to the complex cross lamellar microstructure, compared with the samples of *A. antiqua* from the Puerto Lobos site, which have a high degree of fragmentation.

3.4 Cathodoluminiscence Applied to Biogenic Carbonates

Although the X-ray examination of shells provides information on their mineralogical composition, there are other types of analysis, such as cathodoluminiscence (CL) applied to recent benthic biogenic carbonates (e.g., mollusk shells), through which information on the microstructure of shells and their growth can be obtained (Barbin 1992; Barbin and Gaspard 1995; Gordillo et al. 2011).

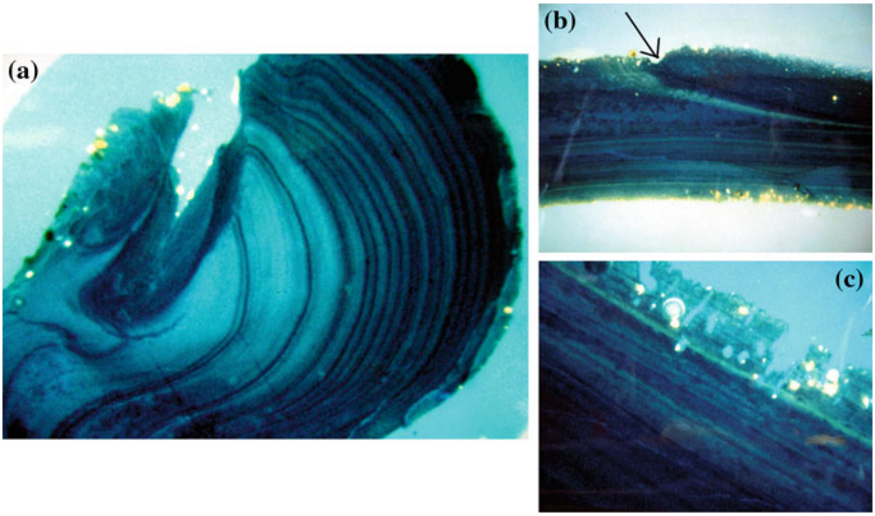

Fig. 3.4 View under cathodoluminiscence (CL) of sections of modern (**a**) and fossil (**b-c**) *Tawera gayi* shells from southern South America, showing a well-defined, almost concentric pattern of CL lines. Luminiscent bands border the winter (*dark*) growth rings; **c** high magnification (10x) of (**b**). A different luminescence (*light, bright yellow* luminescence) affecting *outer* and *inner* shell surfaces is interpreted as a bioeroded surface caused by external factors (i.e., bacteria and microboring organisms), but not produced by the mollusk biomineralization process

Gordillo et al. (2011) observed that under CL-microscopy, modern and fossil shells of the venerid *Tawera gayi* exhibit a well-defined pattern, with parallel spaced CL lines (Fig. 3.4). This zonation reflects the cycles of skeletal growth and luminescence intensity typical of aragonitic shells, and may be related to the alternating amount of manganese present in the aragonite (Barbin 1992). A rapid growth rate during the earlier life stages of *T. gayi* (Fig. 3.4a), and CL lines that terminate in an external growth line (Fig. 3.4b), as well as the regular repetition of CL with outlines approaching the shape of internal structures, indicate that these lines are related to the growth dynamics of the shell (see discussion in Tomasovych and Farkas 2005). The aragonitic *T. gayi* shells give a weak blue-green luminescence (probably due to a slower growth rate) alternating with dark areas associated with periods of a different growth rate (or a cessation of growth). In addition, a different luminescence (bright, light yellow luminescence) affecting outer and inner shell surfaces is interpreted as a bioeroded surface caused by external factors (i.e., bacteria and microboring organisms), but not produced by the mollusk biomineralization process (Fig. 3.4c). Although the data presented on the shell structure of *T. gayi* under CL is not enough to explain the true reasons behind the differences or changes among shells, it does indicate that CL lines correspond to zones recording changes in growth rate. Thus, the analysis of CL lines in this species can provide another important tool for the evaluation of *T. gayi* growth rates, in addition to external growth rates, isotopes and trace elements, since CL lines in bivalves are correlated with periods of slow growth, such as winter, spawning seasons or environmental disturbance (Barbin 1992; Barbin and Gaspar 1995). A systematic examination of CL line pattern in *T. gayi* can be useful for adding to our knowledge of changes during the Holocene.

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