



Lipids from the nacreous and prismatic layers of two Pteriomorpha Mollusc shells

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Mollusc shells are the best-known Ca-carbonate biominerals. They are commonly described as a mineralized two layered structure: an outer layer composed of calcite prismatic units, and an internal layer composed of tablets of aragonite: the nacreous layer.

An external organic layer (periostracum) is present in most taxa. However, the most common structure in the Mollusc shell is the aragonite crossed lamellar layer, but aragonite prisms, calcite foliated layers and homogeneous layers have been also described by Boggild (1930) in all the Mollusc orders. Since, more detailed descriptions of Bivalve shells have been done (Taylor et al., 1969, 1973). Despite the nacropismatic arrangement is rare, calcite prismatic and aragonite nacreous layers are the best studied because of their simple 3D structure and large units. Among these Molluscs, some Bivalve species composed of these two layers are of commercial interest, such as the pearl oyster, *Pinctada margaritifera*, cultivated in French Polynesia to produce black pearls.

It is well established that Mollusc shells are composite structures of organic and inorganic components (Hatchett, 1799; Grégoire et al., 1955; Beedham, 1958; Simkiss, 1965; Mutvei, 1969; Cuif et al., 1980; Berman et al., 1993; Kobayashi and Samata, 2006). Numerous studies are concerned with the organic matrix of the shell. Organic components are commonly obtained after a strong or mild decalcification process. They are said to consist of both a soluble and insoluble fraction. The main part of studies is dedicated to the soluble components, and among them, proteins (Grégoire et al., 1955; Grégoire, 1961; Krampitz et al., 1976; Samata et al., 1980, 2004; Weiner, 1983; Miyamoto et al., 2006). Despite the pioneering work of Wada (1980) sugars are usually neglected despite their role in biomineralization. The third component of the organic matrix of calcareous biominerals is lipids. To date, there is a paucity of information concerning the presence, abundance and composition of these components in Mollusc shells. Gouletquer and Wolowicz (1989) have estimated that proteins represent 90% of the organic matrix of the shell, carbohydrates vary from 0.15 to 0.29%, while lipids vary from 0.8 to 2.9%. Fatty acids, cholesterol, phytadienes and ketones have been described in modern and fossil shells (Cobabe and Pratt, 1995). Using a procedure to extract intra- and intercrystalline organic matrices, Collins et al. (1995) have detected n-alkanes, n-alcohols, fatty acids and sterols in modern shells.

It is suggested that the contents and ratios of these components are dependant on the environment and phylogeny. Lipids of the nacreous layer of *Pinctada* are diverse, with cholesterol, fatty acids, triglycerides and other unknown components (Rousseau et al., 2006). It has been established that the main part of the soluble organic matrices of the nacreous layer is composed of acidic proteins (Samata, 1988, 1990), whereas the prismatic layer of *Pinna* is mainly composed of acidic and sulphated polysaccharides (Dauphin, 2002; Dauphin et al., 2003). The amino acid compositions of the two layers are also different (Samata, 1990).

Because the organic matrices extracted from the aragonite nacre and calcite prisms are the best known materials, the lipids extracted from the calcite prisms of *Pinna nobilis* and *Pinctada margaritifera* and the aragonite nacre of *P. margaritifera* have been chosen as test material for characterisation of the lipid fraction of mollusk shells. The nacreous layer of *Pinctada* is thick, whereas its prismatic layer is thin, and the prisms display complex structures. On the opposite, the calcitic prismatic layer of *Pinna* is thick, with no intraprismatic membranes, and its nacreous layer is thin and present only in the oldest part of the shell. Moreover, these layers have a simple geometry so that some organic components (membranes, wall. . .) said to be insoluble, are clearly visible.

Lipids were extracted from the calcite prismatic and aragonite nacreous layer of two mollusc shells thanks organic solvents. Two methods were used for the characterisation of the lipid obtained Fourier Transform Infrared Spectrometry and thin layered chromatography. Fourier Transform Infrared Spectrometry shows that lipids are present

in both samples, but they are not similar. Thin layer chromatography confirms that lipids are different in the two studied layers, so that it may be suggested they are species-dependant, but also structure-dependant. Although not yet deciphered, their role in biomineralization and fossilisation processes is probably important.