MORPHOLOGICAL AND STRUCTURAL STUDY OF SOME BLACK SEA SHELLS

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Introduction

Shells are extracellular, calcified structures composed of calcium carbonate crystals and organic material [1]. The primitive crystalline calcium carbonate polymorph for bivalve shells is aragonite. However, while some species are made of aragonite, others are constituted of calcite, and a number of species have both forms. The third calcium carbonate polymorph, vaterite, is also found in bivalves, but it is not common [2].

The purpose of the present study was the collection and identification of some shells from the Black Sea, followed by their grinding and physico-chemical characterization in order to find their structure and composition.

Shells identification

A number of molluscan shells were collected from the Black Sea and examined to determine their species. The examination revealed shell species belonging to various classes, subclasses, families and subfamilies of Mollusca:

- The Mediterranean mussel ***Mytilus galloprovincialis*** may be confused with *Mytilus edulis*, they are often difficult to distinguish. In addition, they may hybridize. However, in *Mytilus galloprovincialis* the umbones turn down, giving the basal line of the shell a concave appearance, the valves are higher and less angular and the mantle edges are darker, becoming blue or purple. All *Mytilus* species have distinctive shells ranging in colouration from black with blue or purplish hues to dark brown and occasionally light brown.
- ***Mya arenaria*** is bivalve with a dirty white or fawn shell with a fawn or light yellow periostracum. The shell is oval in outline, marked by conspicuous concentric lines with dissimilar valves, the right being slightly more convex than the left. The interior of the shell is white with a deep pallial sinus.
- ***Cerastoderma edule*** is thick, equivalve, globular and broadly oval in outline. Shell with 22-28 radiating ribs, crossed by concentric ridges may bear short, flat spines; the surface is off-white, yellowish or brownish. Both valves bear two cardinal teeth.

Experimental

The shells used in this study were collected from the Black Sea and they were identified. The most relevant taxonomic groups are presented in Table 1 [1,2].

Table 1. Identification and classification of molluscan shells collected from the Black Sea

Taxon details	***Mytilus galloprovincialis* (Lamarck, 1819)**	***Mya arenaria* (Linnaeus, 1758)**	***Cerastoderma edule* (Linnaeus, 1758)**
Domain:	Eukaryota	Eukaryota	Eukaryota
Kingdom:	Animalia	Animalia	Animalia
Phylum:	Mollusca	Mollusca	Mollusca
Class:	Bivalvia	Bivalvia	Bivalvia
Subclass:	Autobranchia	Heterodonta	Heterodonta
Order:	Mytilida	Myida	Cardiida

Superfamily:	Mytiloidea	Myoidea	Cardioidea
Family:	Mytilidae	Myidae	Cardiidae
Genus:	Mytilus	Mya	Cerastoderma
Species:	M. galloprovincialis	M. arenaria	C. edule

The samples are numbered in the following order: sample 1 - *Mytilus galloprovincialis;* sample 2 - *Mya arenaria;* sample 3 - *Cerastoderma edule*. Each type is ultrasonicated in distilled water at room temperature, after which the water is drained and the washing is repeated under ultrasound with a different amount of water. After the final rinsing, they are dried for 2 hours at 80°C. After that, the shells are broken one by one by pressing them between 2 steel cylinders with a diameter of about 50 mm at a pressure of 5 tons force (tf) for 30 seconds using the hydraulic press. After breaking, the samples are sieved with sieves of different meshes, of which the fractions: 1) 1-1.6 mm and 2) <200 µm are considered for this study. The obtained powder specimens are characterized in terms of structure by Scanning Electron Microscopy (SEM - Model Inspect S). X-Ray powder diffraction patterns are obtained using an X'Pert PRO MPD diffractometer.

Results and discussion

The structure of the shells was morphological investigated using the scanning electron microscopy, as depicted in figure 1. For the *Mytilus galloprovincialis* fraction 2 sample, the lamellar structure is visible, with well-defined parallel layers, while the other structures are more compact and the layers/lamellas are less well defined.

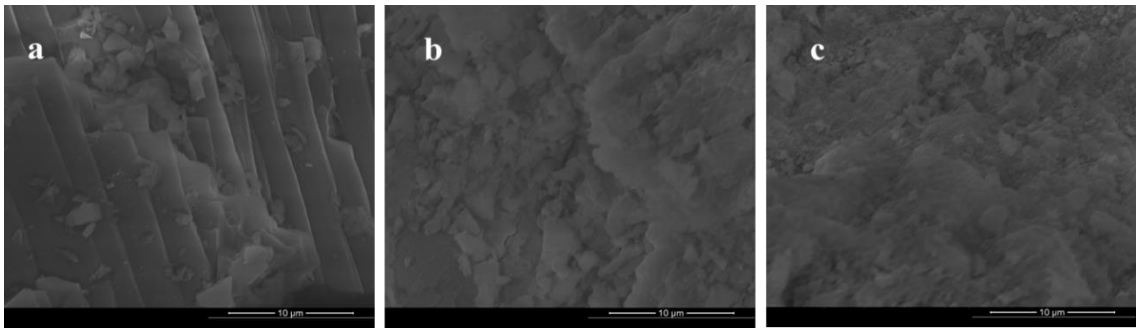

Figure 1. SEM images of a) sample 1 *Mytilus galloprovincialis*, fraction 2; b) sample 2 *Mya arenaria*, fraction 2; c) sample 3 *Cerastoderma edule*. fraction 2

The XRD analysis (Figure 2) was performed in the 2 Theta field 10 - 70 degrees, for fraction 2 (< 200 µm). Ethanol was used for placing the samples on zero background holders. All the samples present a good level of crystallinity, showing intense narrow peaks.

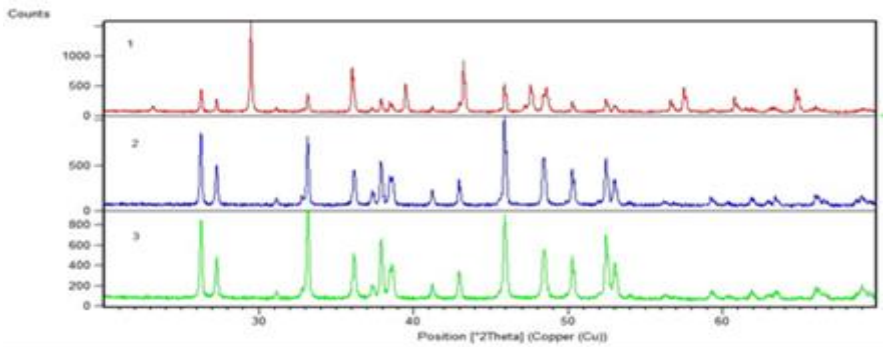

Figure 2. XRD patterns of fraction 1 for samples 1, 2 and 3.

Sample 1 contains aragonite and calcite and the other two specimens contain only aragonite, presenting identical XRD patterns. The identification of peaks belonging to the two phases

present in sample 1 is shown in Figure 3, similar to other results in literature [3].

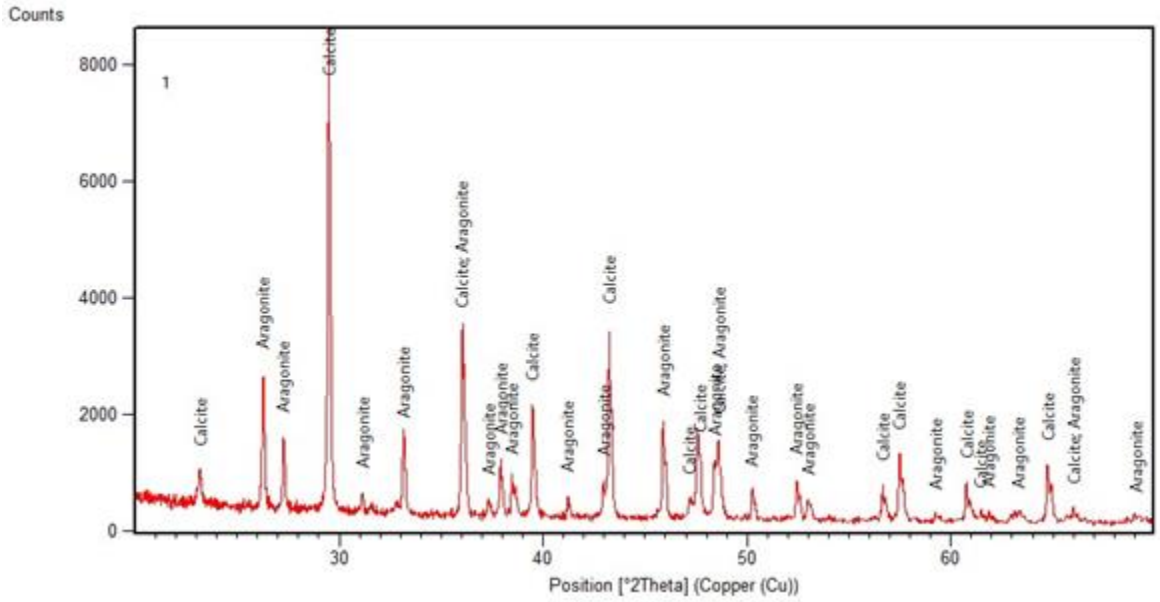

Figure 3. XRD spectrum of sample 1 *Mytilus galloprovincialis,* fraction 1

According to FullProf calculations, sample 1 contains: Phase 1- Aragonite 44.99%; Phase 2- Calcite 55.01%.

Conclusions

Shells collected from the Black Sea and identified in this study belong to the species: *Mytilus galloprovincialis, Mya arenaria and Cerastoderma edule*. Studying their structure and composition, the *Mytilus galloprovincialis* type (brown shells) presents a lamellar structure with well defined parallel layers, while the other two types (white and yellowish) present an inner structure which is less well shaped, compared to the first one. XRD analysis showed that the well defined structure is composed of aragonite and calcite, while the other two types are made of aragonite only. We presume the composition is a major factor in determining the shells outer aspect/color, as well as their properties. We will continue this study in order to find more interesting things and applications for the shells, based on their structure and composition.

Acknowledgements

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