

ELNES studies of abalone shell and geological CaCO₃ polymorphs

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Living organisms produce a great variety of materials with extraordinary (physical, mechanical) properties that are far superior when compared to modern, technologically advanced, man-made materials [1]. Their combination of biominerals (minerals formed inside living organisms) with organic compounds leads to highly improved materials characteristics compared to their inorganic/geological counterparts [2]. This is because organism controlled and produced materials have unique microstructures; they are synthesized at ambient temperatures and atmospheric conditions [3].

Calcium containing minerals (Ca carbonates, Ca phosphates) are widespread constituents of skeletal structures such as shells and bones. They are thermodynamically stable within biological environments due to their high lattice energies and low solubility [3]. Different molluscs build shells of varying shapes and sizes, but surprisingly the involved mineral is in most of the cases calcium carbonate (CaCO₃). CaCO₃ forms three different polymorphs: calcite, aragonite and vaterite. The thermodynamically most stable forms, calcite and aragonite, are among the most frequently observed biominerals. On the other hand the metastable form vaterite has not yet been observed to be a constituent of adult molluscs shells [3, 4].

For our study, abalone shell (*Haliotis rufescens*) was used. Abalone shell consists of an outer prismatic layer (calcite) and an inner nacreous layer (aragonite). The nacre (mother-of-pearl) consists of polygonal aragonite platelets that are separated by sheets/layers of organic matrix [5]. This extraordinary nanoengineering work of molluscs has been intensively studied. Attempts have been made to imitate these structures aiming to achieve their incredible mechanical properties; however, producing such biomimetic materials remains a challenge. The aim of our work was the investigation and comparison of abalone shell and CaCO₃ polymorphs of geological origin by investigating the Ca-L_{2,3} electron energy-loss near-edge structures (ELNES). Bright field (BF) scanning transmission electron microscopy (STEM) images of a contact region between the prismatic calcite and nacreous aragonite as well as of the nacre are shown in Figure 1.

Ca-L_{2,3} ELNES acquired from prismatic calcite and nacreous aragonite of abalone shell are compared to the spectra recorded from calcite and aragonite of geological origin and are presented in Figure 2. There is no noticeable difference between the Ca-L_{2,3} edges of biological and geological origin (Fig. 2 a,b). However there is a clear difference between spectra recorded in aragonite (Fig. 2a) and calcite (Fig. 2b). The difference in Ca-L_{2,3} edges of aragonite and calcite arises due to the different coordination environment of calcium. The calcium atoms in calcite (and vaterite) are 6-fold coordinated by oxygen atoms and in aragonite the coordination of calcium is 9-fold [6].

In the course of our work also low-loss electron energy-loss experiments were performed and will be discussed. Additionally the healed parts of the damaged abalone shell were studied by investigating the ELNES at high energy and high spatial resolution.

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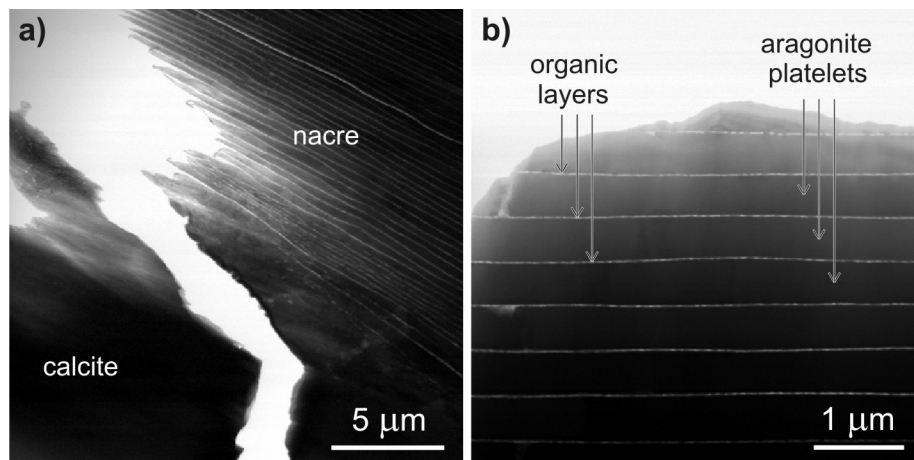


Figure 1. BF-STEM images of a contact region between outer calcite and inner nacreous layer (a) and nacreous aragonite platelets separated by organic layers (b). Images were acquired using a VG HB501UX microscope operated at 100 kV.

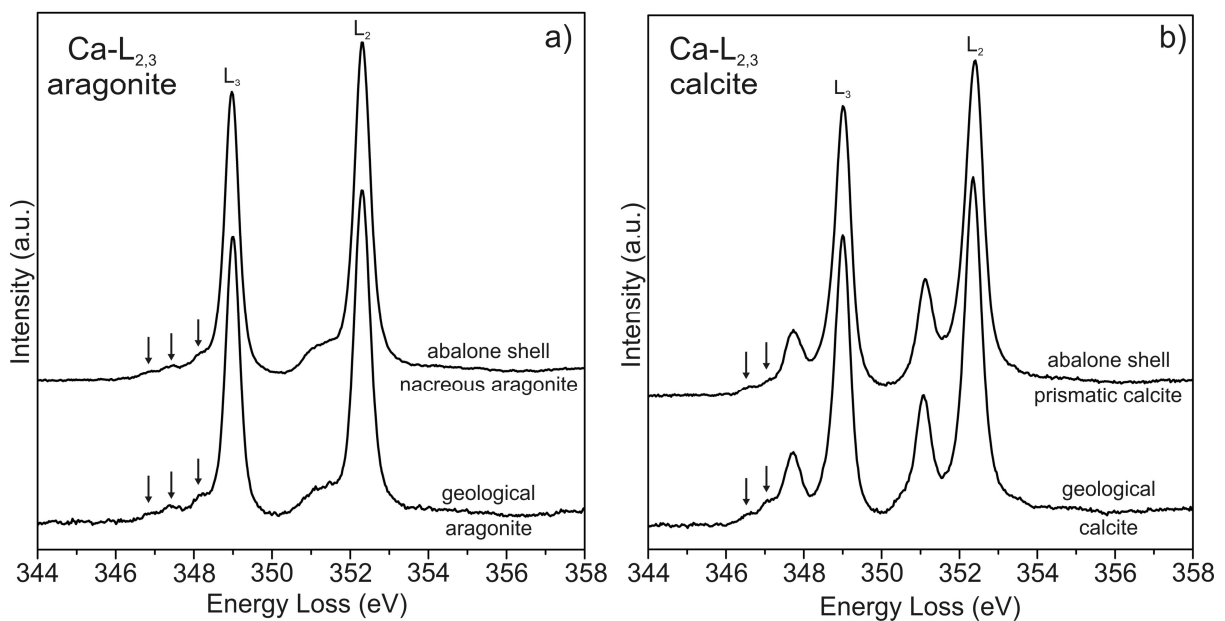


Figure 2. Ca-L_{2,3} ELNES from aragonite (a) and calcite (b) of biological and geological origins. Spectra were acquired using the Zeiss SESAM operated at 200 kV which is equipped with an electrostatic Ω -type monochromator and the MANDOLINE filter [7].