

## ELNES Investigations of Interfaces in Abalone Shell

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A large number of living organisms produce an infinite variety of materials with excellent (physical, mechanical) properties that are superior when compared to modern, technologically advanced, man-made materials [1]. Their astonishing combination of biominerals (minerals formed inside living organisms) with organic compounds, that are arranged in complex architectures, leads to highly improved materials characteristics compared to their inorganic counterparts [2].

Calcium-containing minerals (carbonates and phosphates) are widespread constituents of different skeletal structures. 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 used mineral is in most of the cases calcium carbonate ( $\text{CaCO}_3$ ).  $\text{CaCO}_3$  forms three different polymorphs: calcite, aragonite and vaterite. The thermodynamically most stable forms, calcite and aragonite, are among the most frequently observed biominerals [3].

Abalone shell (*Haliotis rufescens*) was used in our study. The 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 layers of a protein-polysaccharide organic matrix [3, 4]. According to previous studies [5, 6], the aragonite platelets are vertically connected via mineral bridges, which are crossing the organic layers. This extraordinary nanoengineering work of molluscs has been intensively studied and several attempts have been made to mimic these structures aiming to achieve their incredible mechanical properties; however, producing such biomimetic materials still remains a challenge.

In the course of our work different interfaces and contacts in abalone shell were studied by investigating low-loss spectra and energy-loss near-edge structures (ELNES) of the C-K, Ca-L<sub>2,3</sub> and O-K edges in electron energy-loss spectroscopy (EELS). The mineral–organic interfaces and mineral bridges were of a special interest. A bright-field (BF) scanning transmission electron microscopy (STEM) image of a nacre with an alternating stacking of aragonite platelets and organic layers, and a high-angle annular dark field (HAADF)-STEM image of the mineral–organic interface are shown in Fig. 1 (a, b). The C-K, Ca-L<sub>2,3</sub> and O-K ELNES were acquired from an aragonite platelet, an organic layer and a mineral bridge (positions are marked in Fig. 1b) which are presented in Fig. 1c. There is no major difference in C-K, Ca-L<sub>2,3</sub> and O-K edges from the aragonite platelet and the mineral bridge. However, there is an obvious difference between the C-K edges recorded in the aragonite platelet and the organic layer. Additionally, the contacts of the self repaired parts of the damaged abalone shell were intensively studied at high energy and high spatial resolution using the Zeiss SESAM microscope [7]. These results will be compared to and discussed in context with the undamaged counterparts.

## References

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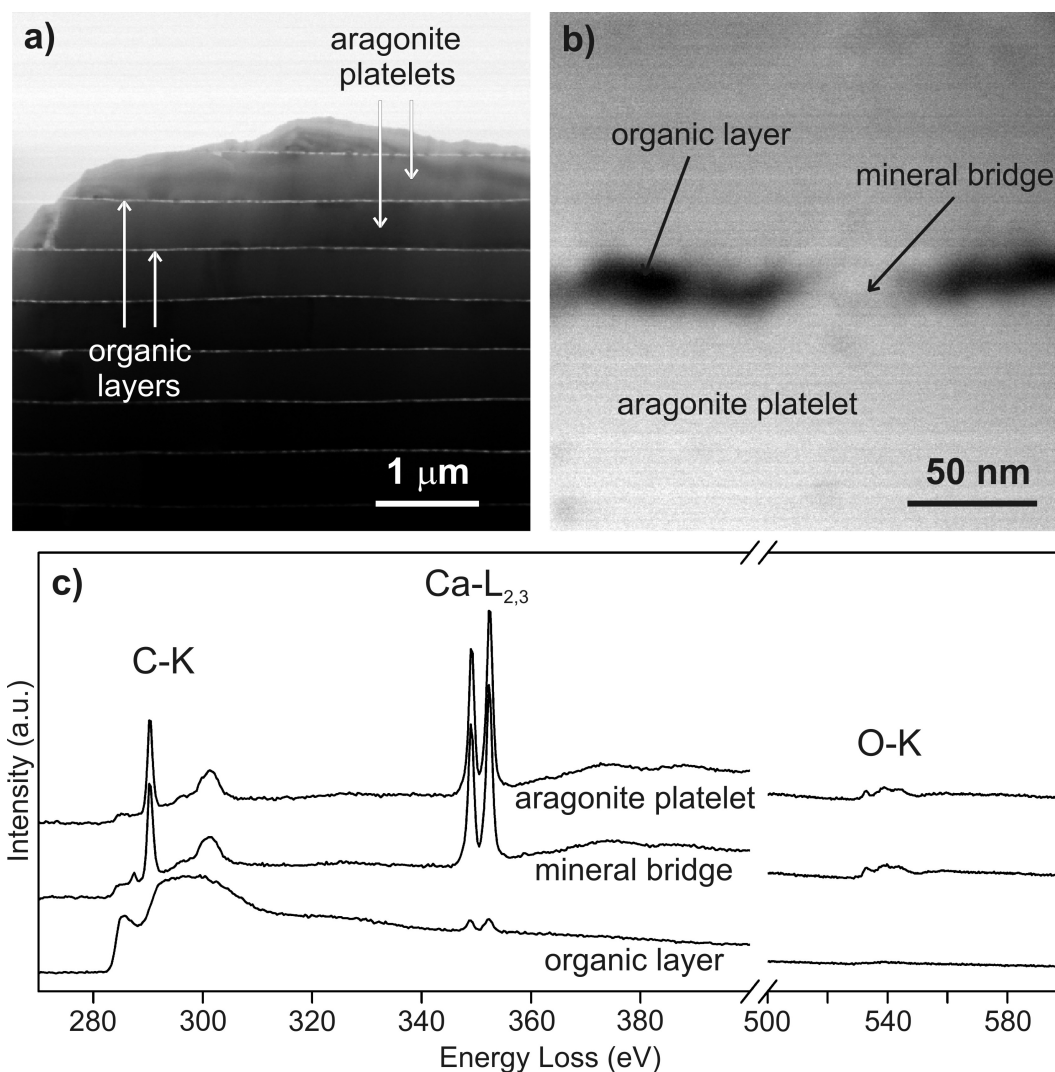


FIG. 1. (a) BF-STEM image of nacre with alternating aragonite platelets and organic layers. (b) HAADF-STEM image of the mineral–organic interface in nacre. (c) C-K, Ca-L<sub>2,3</sub> and O-K ELNES acquired from the aragonite platelet, the mineral bridge and the organic layer (positions marked in (b)).