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Orientation of Microcrystals in Abalone Shell near the Nacre-Prismatic Boundary

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Beamline(s): X20A

Introduction: The shell of the abalone (a mollusk, *Haliotis Rufescens*) is a canonical example of a biogenic organic-mineral composite with a hierarchical microstructure that lends it strength and toughness that are orders of magnitude higher than the inorganic calcium carbonates that form its fundamental building blocks [1]. The nacre (mother of pearl) layer of the shell is composed of aragonite (orthorhombic $CaCO_3$) platelets of 10-50 nm in thickness and about 10μm wide, which are stacked with organic material in a brick and mortar architecture in planes parallel to the shell's surface. The outer portion of the shell is composed of calcite (prismatic $CaCo_3$) mineral columns. Diffraction and microscopy studies up to now have identified the large-scale relative orientations of these two calcium carbonate mineral phases, which is that the crystallographic *c* axes of both are aligned normal to the boundary between the inner and outer shell sections. It has also been shown that the aragonite platelets exhibit twinning along {110} faces shared with the neighboring platelet. However, it is by no means clear that these orientational correlations persist close to the nacre-prismatic boundary, where the early growth stages of the crystals take place.

Methods and Materials: To investigate the relationships between calcite and aragonite orientations, we have performed x-ray microdiffraction studies of cut pieces of abalone shell at the IBM microdiffraction beamline X20A. The measurements were done in reflection geometry at a wavelength of 1.45 Å, with an illuminated spot size of 10-20 μm. The results shown here were obtained with the nacre-prismatic boundary aligned along the beam direction, so that a rocking curve within the reflection plane (i.e. a theta scan) nominally rotated the crystallites about the *c* axis. Measurements with the boundary line oriented along the theta axis were also investigated.

Results: A large scale mapping in the x and y translations was performed at calcite peak positions, to identify these grains and find the boundary region. The region $x \geq 0.2$ corresponds to the nacre, as identified by optical miscroscopy and by identification of peaks in long two-theta scans. Contours of Bragg peak intensities for different sample orientations are shown in Figure 1a. The black, red and blue contours show intensities from the calcite (220) peak, while the green contours come from a calcite (300) peak. The long axes of the calcite grains have a range of orientations, and are not strictly perpendicular to the region identified as the boundary. Also, smaller calcite crystals are found in the boundary region (i.e. the green spot at the upper right in the figure). On the nacre side, some intensity is seen (black contours) since the calcite (330) peak is close enough to the aragonite (204) to allow the tails of aragonite peaks to appear. A clear change in texture is observed, with the long grains giving way to smaller crystals. To examine the calcite-aragonite boundary more closely, we took a closer look at the calcite grain plotted as green contours near $x = 0.3$, $y = -2.75$ (box in Figure 1a). The same calcite (300) peak is shown again as green contours in Figure 1b. Black contours show aragonite grains having their (330) axes aligned parallel to the calcite (300). This contour map is typical of others we observed, and we can make the following general statements. First: groups of aligned crystals rarely extend more than 20-30 μm along any direction. Second: aligned crystals have so far not been observed to get any closer to the calcite boundary than what is shown. Instead, collections of weak peaks in two-theta are sometimes found but with only weak dependence on the sample orientation, suggesting that the aragonite has a poor powder texture close to the calcite. Third: rocking curves within the reflection plane on aligned grains were performed. Previous studies of abalone nacre nanostructure found a 3.5° twinning relationship between neighboring crystals [1]. Therefore, rocking curves in theta performed in one spot would be expected to show sets of peaks that are multiples of 3.5° apart. We have preliminary signatures of sets of peaks 7±1° apart in a few cases. But, the above interpretation presupposes that the aragonite planes are indeed aligned close to the reflection plane, and this has not been shown. Further work will investigate these structural relationships for a more complete set of angular orientations.

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References:

[1] M. Sarikaya and I. A. Aksay, Results and Problems in Cell Differentiation **19** (1992) 1.

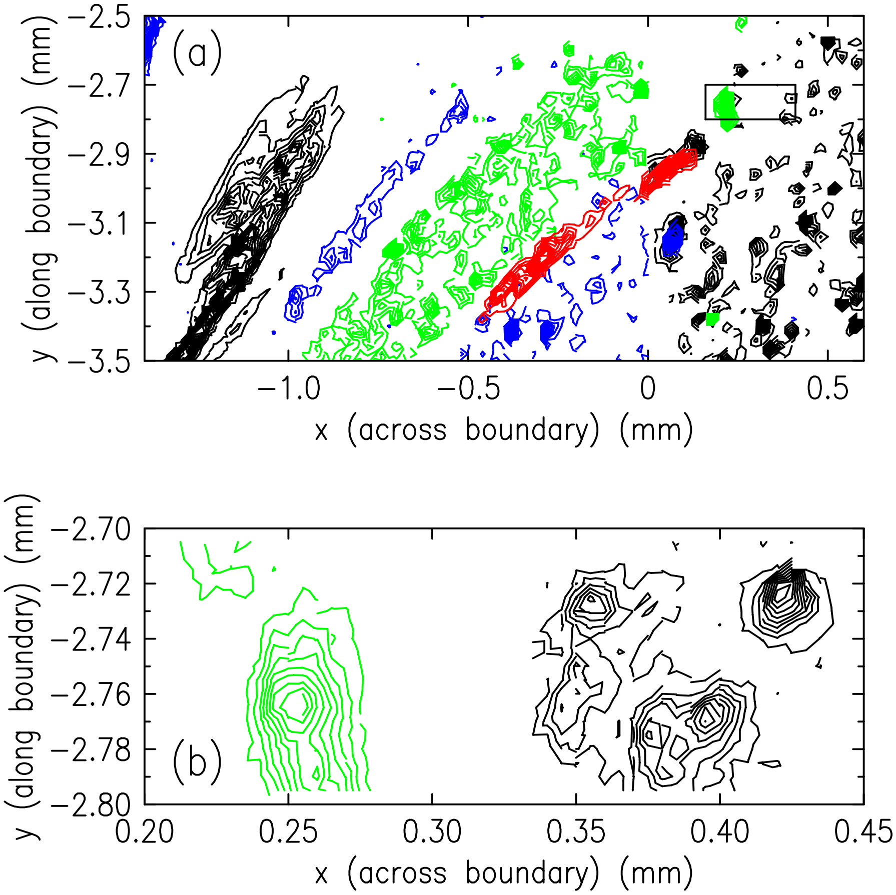

Figure 1. Bragg peak intensity maps for locations on abalone shell on the prismatic ($x \leq 0.2$) and nacre ($x \geq 0.2$) sides of the cut face containing the boundary line. (a) Intensity contours at the calcite (300) (green) and (220) (other colors) peak positions, where each color corresponds to differently oriented sets of crystallites. The black contours also show aragonite (204) intensity on the nacre side of the boundary, where the texture changes to being much smaller crystallites. (b) A closer look at the region bounded by the box in (a). Green: calcite (300) intensity. Black: aragonite (330) intensity at the same sample orientation.