Isostructural exclusion of elements between aragonite and calcite layers in the shell of the Pacific oyster *Crassostrea gigas*

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Sections of the shell of the farmed Pacific oyster *Crassostrea gigas* that are available commercially in Wellington, New Zealand, showed a distinct alternating pattern in the shell mineral when observed by reflected light (Figure 1).

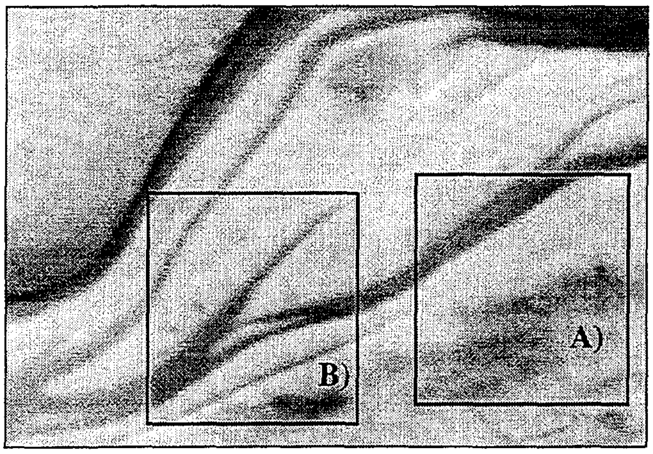

Figure 1: Distinct alternating pattern in the shell mineral observed by reflected light. The positions where two 2D maps were measured are indicated by the regions A and B

The layers were identified by Raman scattering as alternating bands of the calcite and aragonite mineral forms of calcium carbonate using the micro-Raman facility at the Hawaii Institute of Geophysics and Planetology [1]. The differences in the unit cell structure of calcite and aragonite favour different trace elements in the two minerals. Aragonite is iso-structural with Strontianite $SrCO_3$, and calcite is isostructural with Smithsonite $ZnCO_3$ [2]. As a result, Sr deposition should be favoured in the aragonite layer and is excluded from the calcite layer; and, conversely, Zn deposition should be favoured in the calcite layer and is excluded from the aragonite layer. However, up to today, significant differences in the pattern of Sr and Zn in microprobe scans are not discovered.

In order to obtain high-resolution two dimensional (2D) maps of the trace elements proton microprobe scans were performed using the microprobe facility in Melbourne [3]. The proton beam was focused to 6µm in diameter and particle induced X-ray emission (PIXE) analyses were made across the calcite and aragonite layers of the shell of C. gigas.

The measurements show sharply divided boundaries reflecting the inverse occurrence of Zn and Sr. The 2-D target area of the shell cross section was a 400µm thick section mounted in Zn-, Sr-free resin on glass.

Figures 2 to 4 show Ca, Sr, and Zn maps measured at position A (refer to figure 1.). The Ca map of the 2-D cross section in figure 2 shows only minor Ca density changes corresponding to the pattern (viewed by reflected light) of the light (calcite) and dark (aragonite) layers.

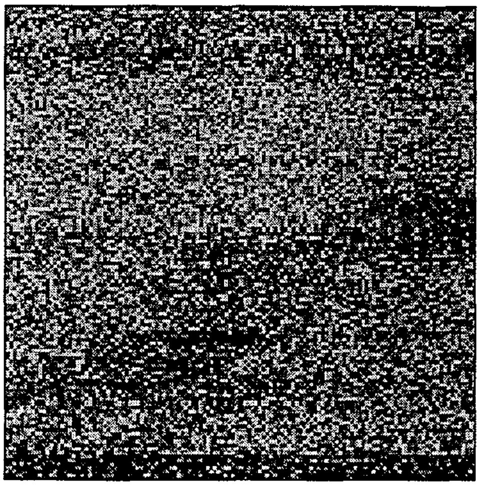

Figure 2: Ca map of the 2-D cross section

However, the Sr map in figure 3 shows clear Sr peaks occupying the dark layer areas in figure 1. The Zn map in figure 4 shows clear Zn peaks occupying the light layer areas in figure 1.

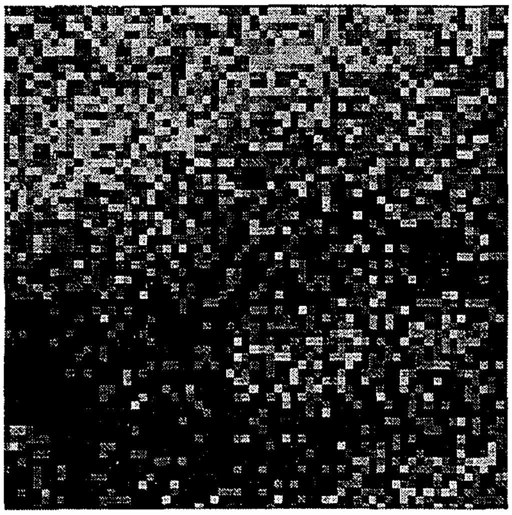

Figure 3: Sr map of the 2-D cross section

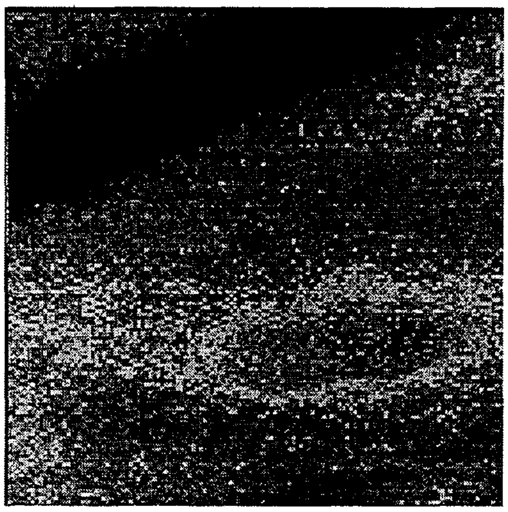

Figure 4: Zn map of the 2-D cross section

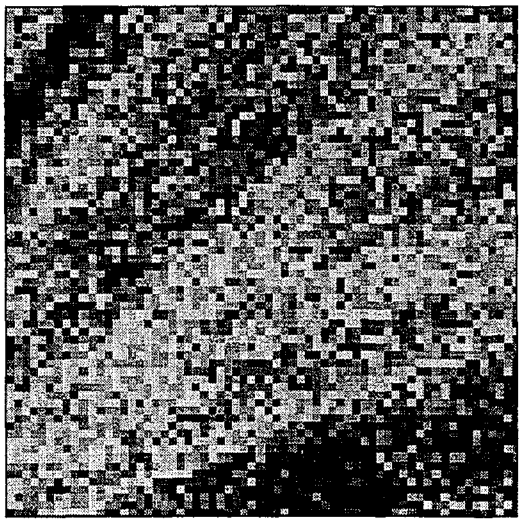

Figure 5: Sr map of the 2-D cross section

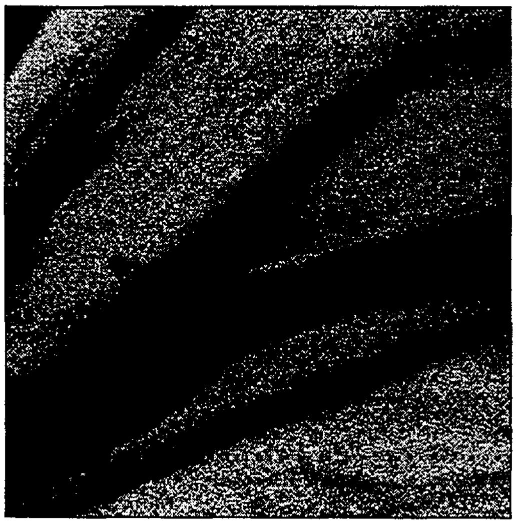

Figure 6: Zn map of the 2-D cross section

Additional maps were recorded to confirm the findings described in figures 3 and 4. Figures 5 and 6 show Sr and Zn maps measured at position B (refer to figure 1).

By the ion microprobe analysis of the oyster shell it is shown that differences in the unit cell structure of calcite and aragonite definitively favour different trace elements in the two minerals. The microprobe maps confirm that aragonite is iso-structural with $SrCO_3$, and calcite is isostructural with $ZnCO_3$.

References:

[1] Gauldie, R. W., S. K. Sharma and E. Volk. 1997. Micro-Raman spectral study of vaterite and aragonite otoliths of the Coho salmon *Oncorhynchus kisutch.* Comp. Biochem. Physiol. 118: 753-757

[2] Mason, B. and Berry, L. G. 1968. Elements of Mineralogy. W. H. Freeman and Company, San Francisco. 330 pp

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