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Stable carbon and oxygen isotope values from Silurian brachiopod shells from Gotland (Sweden): primary or diagenetically altered signals?

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Fossil brachiopods are commonly used for stable isotope analysis especially of Palaeozoic and Mesozoic sediments. The $\delta^{18}O$ and $\delta^{13}C$ signals are used for both stratigraphic correlation and palaeoenvironmental reconstructions since it is assumed that brachiopods secrete shell calcite in near-isotopic equilibrium with ambient sea water.
The aim of this study is to reconstruct high-resolution isotope records from preserved shells. Brachiopod shells derive from the Silurian of Gotland where brachiopods are known to be well- preserved (Fig. 1). The investigated organisms lived in tropical shallow water in the Baltic Sea.

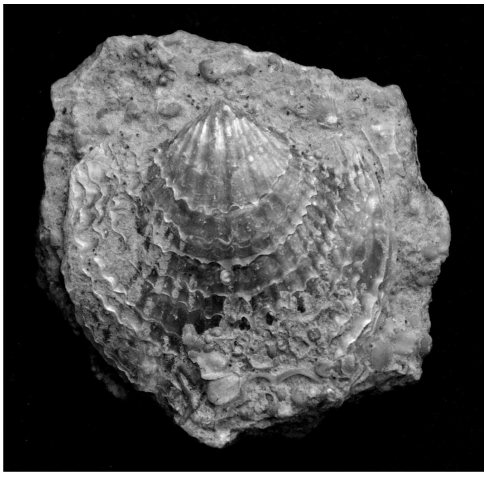

Fig. 1: Brachiopod from Follingbo.

To determine the state of preservation, the shells were screened by cathodoluminescence (CL) and scanning electron microscopy (SEM; Figs. 2, 3). Out of 100 brachiopod shells, four specimens were chosen for high-resolution sampling (300µm steps) of the secondary (fibrous) shell calcite. Samples were taken from longitudinal sections which were first analysed by CL. The shells were mostly non-luminescent but small areas of Mn^{2+}-induced luminescence were noticed in every shell. SEM analyses were performed in transverse sections. From every sampled brachiopod shell, four or five SEM-sections were prepared perpendicular to growth direction in order to get a better overview on the preservation state of the entire shell (Figs. 2, 3). Only oxygen isotope values will be discussed because they are more prone to diagenetic alteration than $\delta^{13}C$ values.

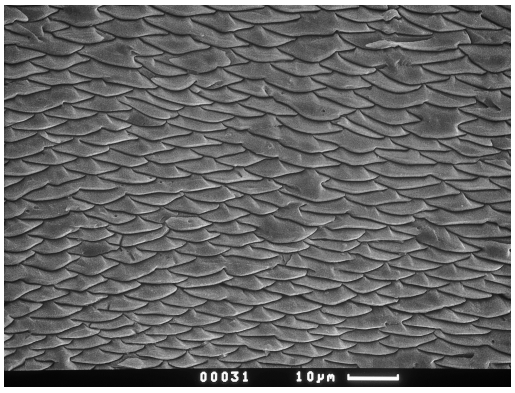

Fig. 2: Well-preserved secondary shell layer.

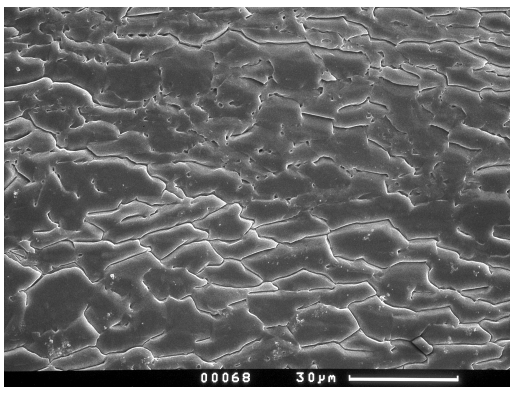

Fig. 3: Secondary shell layer diagenetically altered.

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The high-resolution isotope curves of the four brachiopod shells are remarkably similar. $\delta^{18}O$ values of all brachiopods decrease from the umbo to the margin (Fig. 4). Three shells show a pronounced positive shift in $\delta^{18}O$ in the anterior part and a decrease towards the margin (Fig. 4), which, however, is less clear in the fourth example.

One potential explanation for the observed pattern is that brachiopods do not secrete shell calcite in isotopic equilibrium with sea water (vital fractionation effect) and that this oxygen isotope fractionation changed systematically during the lifetime of the brachiopod. Another explanation is that the signals are diagenetically overprinted. The maximum oxygen isotope variation measured in a single shell is 1.8 ‰. This variation translates into a change of water temperatures of nearly 8°C (assuming constant salin ity). Though there are areas in modern tropical shallow water where such large changes are observed it seems unrealistic that the

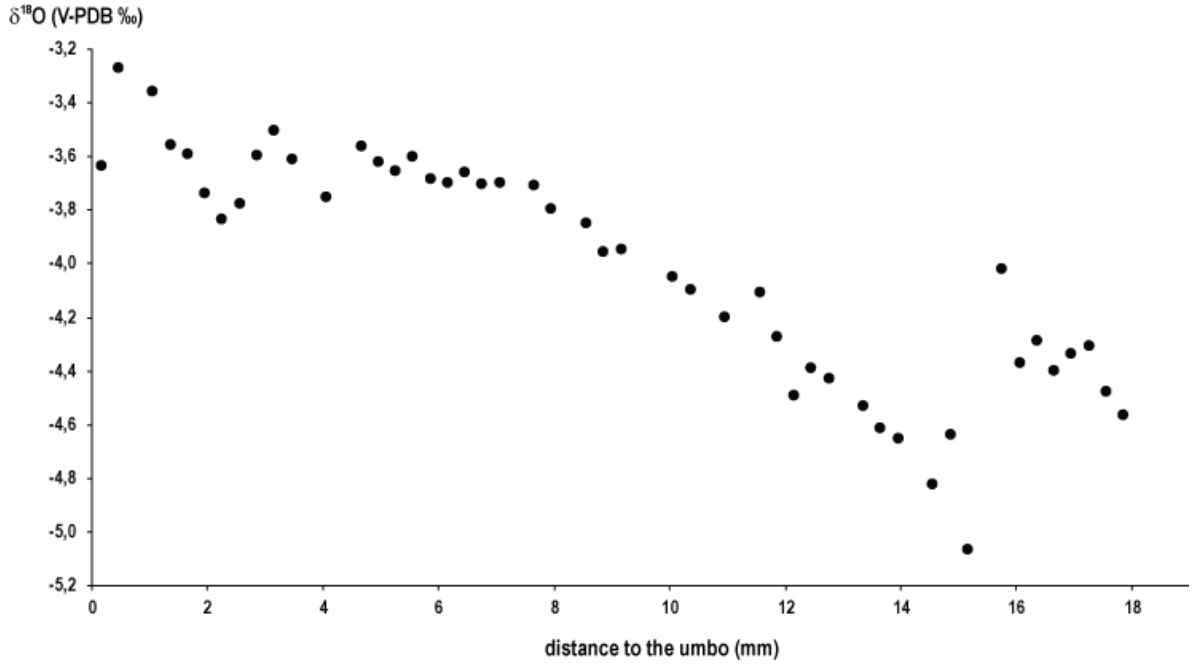

Fig. 4: $\delta^{18}O$ values along a brachiopod shell.

curves indicate a systematic warming during the lifetime of the brachiopods since these organisms most probably lived for several years. A diagenetic alteration for the observed decrease in $\delta^{18}O$ appears a more realistic explanation since the changes in $\delta^{18}O$ coincide with a change in the ultrastructure of shell, from well-preserved fibres near the umbo (Fig. 2) to altered fibres near the margin (Fig. 3). However, two observations argue against this possibility. First, the increases of the $\delta^{18}O$ values close to the margin of the shells are difficult to explain by diagenetic processes, and secondly, the changes in ultrastructure observed along the shells do not correlate with an increase of cathodoluminescence.

Because a diagenetic influence especially close to the margin of the shells cannot be excluded at the present state of knowledge, the brachiopod $\delta^{18}O$ records should be interpreted critically. High- resolution trace element ratios will give further information on the preservation state and will help to answer the question if the Silurian brachiopods from Gotland preserved their primary isotopic signals.