

## Clumped isotope signatures of Silurian brachiopod shells: pristine signals or diagenetic overprints?

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We are addressing the carbonate clumped isotope thermometer to Silurian brachiopod shells from Gotland (Sweden) to decipher temperature and  $\delta^{18}\text{O}$  of ocean water. The sedimentary sequence is characterized by pronounced shifts in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  with similar trends of the isotope curves being measured for brachiopod shell calcite (Samtleben et al., 1996; Wenzel & Joachimski, 1996), micritic limestones (Munnecke et al., 2003) and biogenic phosphates (Wenzel et al., 2000). This correlation and the fact that three of the excursions are determined globally, support the assumption that bulk carbon and oxygen isotope signatures are pristine.

Ultrastructural and chemical pre-analyses (CL, SEM, trace element concentrations) indicate that no or at least minor diagenetic processes had affected the shells. Therefore, a reset of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of the brachiopods from Gotland, which were considered for the published isotope curves, was excluded (e.g., Samtleben et al., 1996; Wenzel & Joachimski, 1996). However, our SEM investigations on 60 brachiopods from Gotland indicate that recrystallization occurred at least partially, with the typical round shaped fibres being replaced by angular shaped crystals.

Carbonate clumped isotope thermometry is based on the ordering of isotopes, i.e. on the concentration of  $^{13}\text{C}$ - $^{18}\text{O}$  bondings within carbonate groups of minerals. The measure of temperature is  $\Delta_{47}$ , which describes the deviation of the 47/44 abundance ratios in  $\text{CO}_2$  derived from  $\text{H}_3\text{PO}_4$  digestions of carbonates from the corresponding stochastic 47/44 ratios. We receive apparent crystallization temperatures of 30 - 70°C and 30 - 60°C, respectively, applying our own calcite calibration and the Ghosh calibration recalculated by Dennis et al. (2011). These results may indicate that isotopic clumping of  $^{13}\text{C}$  and  $^{18}\text{O}$  inside the brachiopod shells was at least partly altered during diagenesis. In contrast to  $^{13}\text{C}$ - $^{18}\text{O}$  clumps, recrystallization may not be visible in the bulk carbon and oxygen isotopic composition due to the much higher abundance of carbonate groups containing  $^{12}\text{C}$ - $^{18}\text{O}$  and  $^{13}\text{C}$ - $^{16}\text{O}$  bondings. We are currently applying additional methods such as CL, nanofocus-CT and a screen for trace elements to distinguish between primary and secondary calcite. Furthermore, a comparison of  $\Delta_{47}$  values of micritic/sparitic infillings and shell calcite will help to receive a better understanding of the diagenetic history of these sedimentary rocks and their components within.

### References:

- Dennis et al. (2011), *GCA* **75**, 7117-7131  
Munnecke et al. (2003), *PPP* **195(1-2)**, 99-124  
Samtleben et al. (1996), *IJES* **85(2)**, 278-292  
Wenzel and Joachimski (1996), *PPP* **122(1-4)**, 143-166  
Wenzel et al. (2000), *GCA* **64(11)**, 1859-1872