Does the polymorphism control the boron isotopic composition of biocarbonate?

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The past variations of the atmospheric partial pressure of CO_2 can be constrained either from direct measurements in air bubbles trapped in ice cores or by geochemical proxies from oceanic sedimentary records. Among these geochemical proxies, the boron isotopic composition ($\delta^{11}B$) of carbonates is one of the most used. Indeed, carbonates are supposed to incorporate borate ions of the solution from which they precipitate, and thus their $\delta^{11}B$ depends on solution pH (and so on dissolved atmospheric CO_2) (eg Vengosh et al, 1991; Hemming and Hanson, 1992). However, Noireaux et al (2015) showed that the crystallography of the calcium carbonate inorganically precipitated could also control the boron isotopic composition; aragonite $\delta^{11}B$ values reflect the $\delta^{11}B$ of solution borate, whereas calcite $\delta^{11}B$ values are enriched in ^{11}B compared to the $\delta^{11}B$ of solution borate, likely because of the partial incorporation of boric acid. Intriguingly, the published data on biogenic carbonates (corals, foraminifera, brachiopods…) show the opposite behaviour with a larger boron isotopic fractionation relative to seawater borate ion for bio-aragonite compared to bio-calcite. To see if this different behaviour between inorganic and biogenic carbonates is linked to the crystallography and/or to biological processes, we will measure the $\delta^{11}B$ and B/Ca ratios of various shells presenting both aragonitic and calcitic layers (*Mytilus edulis*, *Haliotis rufescens*, *H. laevigata*, *Patella* sp., *Nerita* sp.). The first results show a clear difference in boron content, the aragonitic layer being 3 to 10 times enriched in boron compared to the calcitic layer, as expected from inorganic precipitation experiments (Mavromatis et al, 2015).

Hemming and Hanson (1992), GCA, 56, 537-543.
Mavromatis et al (2015), GCA, 150, 299-313.
Noireaux et al (2015) EPSL, 430, 398-407.
Vengosh et al (1991), GCA, 55, 2901-2910.