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Are fossil brachiopod geochemical analyses biased by cement-filled puncta?

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Due to their resistance to diagenesis, fossil brachiopods have extensively been used as archives in paleoenvironmental studies. Most analyses on fossil brachiopods focus on carbon and oxygen stable isotopes, minor and trace elements, and most of the analyses are still done on the bulk of the shell's low-Mg calcite (LMC). Despite the huge progress made over the years on the cleaning procedures in order to avoid contaminations, analytical biases caused by the brachiopod puncta, filled with diagenetic carbonate cement, has not been addressed so far. Here we present a preliminary investigation on the chemical differences that this secondary cement might have if compared to the biogenic calcite nucleated by the brachiopod. Cenozoic specimens of Megerlia truncata, one Gryphus kickxi and one of Terebratula sinuosa were studied from different locations and outcrops. Electron microprobe analysis in wavelength dispersive mode was done in order to measure the Ca, Mg, Sr, Mn, Fe, Ba, Al, P and Si content in a valve's thin section, targeting both biogenic calcite of the shell and the cement in the puncta. Results show a clear offset only in G. kickxi, with all the targeted puncta having much higher Fe and Mg contents. M. truncata and T. sinuosa specimens are more homogeneous and with less distinct chemical differences between puncta and shell calcite. Such differences might be easily explained by different diagenetic stages: e.g. similar in M. truncata and T. sinuosa, and basically different in G. kickxi. The case of G. kickxi points at the possible analytical biases that puncta might cause even in well preserved specimens. The differences in chemical composition that we observed are not species specific, although they might be influenced by puncta size, but rather related to the depositional environment and geological history of the depositional basin. A large scale survey is needed to more accurately understand the influence of infilled puncta across a large variety of geological settings. This will ultimately lead to a better calibration of geochemical proxies when using brachiopod shell geochemistry as environmental archives.