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Study of bryozoan mineralogic polymorphisms and isotopic signature: from the individual scale to that of the whole colony.

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Given the current physical and chemical state prevailing at Earth's surface, aragonite and high Mg calcite (> 5% $MgCO_3$mole) should be the only stable forms of $CaCO_3$ polymorph to precipitate in the ocean. Nonetheless, it is far from being the case as many marine organisms precipitate pure calcite. Bryozoan are organisms even able to produce polycrystalline carbonate skeleton (with a mix of calcite, Mg calcite and aragonite). It is worth noticing that among the Bryozoa phylum the mineralogical assemblage is specific to each species, but the polymorphs proportion can change within the colonies and at the individual scale (zoecium) ([1], [2]). Several factors such as temperature, Mg/Ca water ratio or atmospheric CO_2 pressure have been proposed to explain the evolution of $CaCO_3$ polymorphs in bryozoan skeleton through geological time. However, the mineralization mechanisms and environmental forcing implicated in the formation of polymorphic zoecium are still poorly understood.

In this contribution, we provide the first mineralogical characterization at the nanometric scale of bryozoan zoecium using synchrotron 2D X-Ray diffraction on natural living samples collected from the Western Mediterranean and North Atlantic coasts. We were able to precisely localized the transition between the different $CaCO_3$ polymorphs within bryozoan skeleton structure. The mineralogical in situ characterization was matched to $d^{18}O$, $d^{13}C$ and clumped isotope (D_{47}) bulk measurements from apical (most recent) parts of the colonies, as well as high resolution $d^{18}O$ profile across bryozoan zoecium using SIMS. Using environmental data (T, pH, S, $d^{18}O_w$ and $d^{13}C_{DIC}$) collected *in situ*, the measured isotopic signatures were compared to their respective expected values (assuming pseudo-equilibrium carbonate precipitation). These results allow to discuss the origin of apparent isotopic disequilibrium (i.e "isotopic vital effect") observed in both $d^{18}O$, $d^{13}C$ and D_{47} and their potential link to bryozoan skeleton polymorph nature.

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[2] Taylor. P. D., Lombardi. C., Cocito. S., (**2015**), Biomineralization in bryozoans: present, past and future, *Biol. Rev* 90, 1118-1150. DOI : 10.1111/brv.12148