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An experimental approach of the "vital effect" in calcareous biominerals, based on crystallization patterns and process within micron-scale skeleton growth layers.

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In the usual practice, accuracy of the calibration procedure for a potential proxy-bearer is reduced by several causes. It is a long process (in the year range), and growth of mineralizing organisms is far from regular, specifically in countries where important temperature changes occur along the year. Consequently, the correlation between chemical/isotopic measurements at a given point of a calcareous structure and the recorded environmental parameters cannot be precisely established. In addition, as long as resolution of sampling techniques was in the millimetre range, only long term oscillations were visible. Any rapid variation, although possibly recorded in skeletons, was not taken into account because of the low resolution sampling, or was smoothed by bulk measurements. Therefore it is not very surprising that an unexpected variability among values of isotopic or chemical fractionation ratios has been revealed by SIMS measurements. Origin and potential explanation of this variability might be found in a deeper understanding of the bio-crystallization mechanism itself. In most of the mineral structures produced by an epithelial cell layer, the crystal-like units (mollusc prisms, coral fibres etc.) are built by superimposition of a few micron thick growth layers. Chemical and biochemical maps (using microprobe or synchrotron radiation-based methods) have shown that distributions of minor elements and sulfated acidic polysaccharides exhibit a layered pattern that corresponds to the microstructural layering revealed by etching of mineral surfaces. The skeleton growth layer thus appears as the true Environment Recording Unit. Structural observations (from SEM to AFM) and physico-chemical investigations on growth layer compositions support the concept of a biochemically driven crystallization. The hypothesis

can be made that explanation of the long-known “vital effects” might be related to this particular taxonomy-linked crystallization. In addition, recent experiments using fluorochrome molecules have also shown the possibility to include time-marking lines within the growing calcareous units, allowing a new micrometre scaled approach of the chemical or isotopic compositions of skeletons to be developed. A collaborative project has been organized of this basis. This project takes advantage of several biological stations and natural sites* in which various “proxy-bearers” are cultivated in continuously recorded conditions. Fluorochrome time-marks will be made within the growing skeletons. Duration of each experiments will be very short (in the week range), to avoid discontinuity in the biomineralization mechanism. After microstructural analysis, localized chemical and isotopical measurements will be made at the growth layer scale (SIMS and NanoSIMS). In parallel, biochemical characterizations will be carried out. Using mineralizing matrices extracted from the skeleton of studied species, interactions between mineral structures and macromolecular compounds will be studied and molecular forces acting on crystallization will be calculated. This might result in a very precise time-based experimental dataset, allowing both fractionation processes and organo-mineral interactions to be better known and modellised.

* with a worldwide extension, owing to the participation of teams from France (IRD-Paleotropique), Germany (AWI - Bremerhaven)) and UK (Earth Science -Glasgow, each of them involved in long standing cultivation experiments in Atlantic and Pacific Oceans.