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Persistent organic components in heated biogenic aragonites - implications for palaeoenvironmental reconstructions

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Since Urey et al. (1951) have used oxygen isotopic ratio to calculate the sea water temperatures recorded in a Jurassic belemnite, biological Ca-carbonates are frequently involved in the reconstruction of ancient environments. From the very beginning of researches dealing with living organisms (Epstein et al., 1953), cleaning of mineral structures by a complete removal of possible remains of these mineralizing soft tissues was a permanent concern for investigators. Numerous treatments have been proposed, most of them associating physical and/or chemical methods. Recent studies of the biomineralization process in corals and mollusks have shown that the growth of aragonite fibres or calcitic prisms is a stepping process. The crystallization of Ca-carbonate nanograins occurs within a matrix layer made of hydrated proteoglycans or glycoproteins. This new insight in the structure and composition of coral and mollusk skeletons desserves particular interest with respect to the preparative process usually applied to skeleton samples used for the measurements of isotope fractionations in paleoclimate research. Far from being neutral as postulated on the basis of a purely mineral concept of coral fibres, the moderate heating (350°C) that ensure the removal of possible polyp tissue remains generates important chemical changes in the samples. Similar data have been obtained for mollusks. All these results confirm the experiments made by Grégoire (1959-1970) on the nacreous layer of mollusk shells. Owing to the composite structure of the growth layers in coral fibres, mollusk prisms or nacre (organic macromolecules, water and finely dispersed mineral units), complex chemical reactions occur during heating. X-rays diffraction, infrared absorption, HPLC chomatography, electrophoresis and AFM microscopy allow to consistently

assess the importance of changes that occur within the crystal-like units. These various methods show that the organic matrices occluded in the calcitic and aragonitic biocrystals of mollusk shells or coral skeletons are not fully destroyed when heated up to 800°C. Organic components entrapped within the mineral are a common features of biominerals (Lowenstam and Weiner, 1989). They have long been described in Mollusc shells, but there are few studies devoted to coral skeletons. The intimacy of the relationships between mineral and organic components may explain the survival of organic molecules at a heating of 800°C. Attention is drawn on these reactions that should be taken into account to improve the reliability of isotopic ratio measurements. Although heating samples is a common method to clean samples from organic components for isotopic studies, neither the potential biases induced by the aragonite - calcite inversion nor the partial removal of the organic matrices have not been yet investigated.

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