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General Paleontology (Taphonomy and Fossilization)

Decay of skeletal organic matrices and early diagenesis in coral skeletons

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Abstract

Due to its particular mode of growth, the coral skeleton provides a natural model for evaluating the successive stages of diagenesis in a still-living organism. The spatial distribution of skeletal organic matrices and their early diagenesis have been investigated in a scleractinian skeleton with in situ micron-scale analyses by Raman Microspectroscopy. Results indicate that the decay of the organic matrices occurs within a few years. We suggest that the gradual deterioration of the skeletal organic matrices is a key-mechanism driving earliest diagenesis in coral skeletons and represents the starting-point of the process of fossilization. ***To cite this article: C. Perrin, D.C. Smith, C. R. Palevol 6 (2007).***

Résumé

Dégradation des matrices organiques intra-squelettiques et diagenèse précoce. Grâce à son mode particulier de croissance, le squelette corallien, fournit un modèle naturel pour analyser les premiers effets de la diagenèse dans un organisme vivant. La distribution des matrices organiques squelettiques et leur diagenèse ont été étudiées dans un squelette corallien, grâce à des analyses in situ par microspectroscopie Raman. Les résultats montrent la dégradation très rapide du matériel organique intra-squelettique. Nous proposons que la dégradation progressive des matrices squelettiques constitue le mécanisme-clé de la diagenèse précoce de ces squelettes. ***Pour citer cet article : C. Perrin, D.C. Smith, C. R. Palevol 6 (2007).***

Keywords: Diagenesis; Biominerals; Aragonite; Organic matrix; Scleractinian corals; Raman Microspectroscopy

Mots clés : Diagenèse ; Biominéraux ; Aragonite ; Matrices organiques ; Scléractiniaires ; Microspectroscopie Raman

Version française abrégée

La compréhension des processus de fossilisation des tissus minéralisés est fondamentale, aussi bien du point de vue de la paléontologie que de celui de la sédimentologie. Des modifications diagénétiques à fine

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échelle ont été mises en évidence dans des squelettes minéralisés à un stade post-mortem très précoce [3,20,41], ou même au cours de la vie de l'organisme [26,27]. La précocité de ces transformations devrait conduire à renouveler les vues traditionnelles sur la fossilisation et les concepts des modèles diagénétiques, en particulier ceux relatifs à l'intervention post-mortem et à la nature des mécanismes de la diagenèse. Grâce à son mode particulier de croissance, le squelette corallien fournit un modèle naturel pour analyser, dans un organisme vivant, les premiers effets de la diagenèse, notamment les interactions potentielles entre les modifications des matrices squelettiques glycoprotéiques et celles des constituants minéraux.

L'objectif de cet article concerne la précocité de la diagenèse des matrices organiques intra-squelettiques coralliennes, dont la dégradation est démontrée pour la première fois in situ, grâce à des microanalyses par microspectroscopie Raman.

Ultrastructure et diagenèse précoce des squelettes coralliens

La microarchitecture du squelette des scléractiniaires résulte de la répartition spatiale de deux structures élémentaires (Fig. 1A–C) : les « centres de calcification » et les « fibres d'aragonite » [28]. Ces fibres ne sont pas des cristaux homogènes, mais des structures composites, caractérisées par une zonation transverse submicronique (Fig. 1B) [28 (fig. 19, p. 134),8,22,50], témoignant de leur croissance incrémentale au cours de la biominéralisation [29,52].

Les premiers effets de la diagenèse sont perceptibles quelques années après que le squelette a été secrété et se traduisent par des ciments syntaxiques d'aragonite [38,43,51] et par des transformations texturales du squelette lui-même [31]. Ces dernières, directement contrôlées par l'ultrastructure biologique originelle, correspondent à une altération de la zonation incrémentale des fibres et à une dissolution sélective des centres de calcification [30,31].

Matériel et approche méthodologique

La microspectroscopie Raman permet d'effectuer des analyses directement in situ, avec une résolution spatiale compatible avec la taille micronique des biocristaux et, si les conditions analytiques sont efficacement optimisées, l'analyse simultanée des composés organiques et minéraux. Avec l'appareillage utilisé, le point d'analyse (résolution spatiale inframicronique) peut être visuellement positionné sous un microscope et, ainsi, les sources de matériaux organiques et minéraux non squelettiques (microperforations, par exemple, Fig. 1D) peuvent être évitées.

Les microanalyses Raman ont été réalisées avec une source laser vert Ar^+ 514 nm (voir § 3) sur des préparations polies issues des zones sommitales (vivantes) et profondes (anciennes) d'une colonie de *Lobophyllia corymbosa*, récoltée vivante dans le lagon de Mururoa. Les caractéristiques ultrastructurales ont préalablement été étudiées au microscope électronique à balayage [25].

Résultats

Partie sommitale de la colonie corallienne

Tous les spectres Raman obtenus à partir des centres de calcification ou des fibres de la zone sommitale de la colonie (Fig. 1A–C) montrent la présence d'aragonite, sans trace de calcite. La distinction entre les deux polymorphes est effectuée grâce aux bandes exclusives de l'aragonite, vérifiées et affinées par nous-mêmes sur des cristaux de qualité gemme : un doublet 702 + 706 cm^{-1} formant un triplet avec 717 cm^{-1}, 1460 cm^{-1} et 1572 cm^{-1}, ainsi que plusieurs bandes en dessous de 275 cm^{-1} (Fig. 2). Elle se base aussi sur l'absence de la bande de la calcite à 713 cm^{-1}, ainsi que de celle de forte intensité à ∼280 cm^{-1}, la bande principale à ∼1084 cm^{-1} étant commune aux deux minéraux [18,36].

Les matrices organiques ont été identifiées dans plusieurs spectres réalisés dans des centres de calcification et dans des fibres du sommet de la colonie, ceci sur la base de plusieurs bandes typiques de vibrations C–H dans la zone 2847–2960 cm^{-1} (Fig. 2). Des spectres issus de centres de calcification ou de fibres ont montré la présence de carbone semi-amorphe, figuré par un large massif comportant des intensités plus fortes à 1335 et 1580 cm^{-1}, qui pourrait provenir de la détérioration des composés organiques squelettiques sous le faisceau laser (voir § 4.1).

Zones anciennes du squelette

Les bandes C–H n'ont pas été détectées dans les parties anciennes ; les matrices organiques y sont donc beaucoup moins abondantes que dans la zone sommitale du squelette.

Discussion

Quelques études seulement ont concerné l'analyse de carbonates biogéniques par microspectroscopie Raman. Mis à part un pigment caroténoïde détecté dans une perle

d'huître [53], aucune de ces publications ne décrit de matériel organique identifié avec certitude par le biais des bandes Raman [9,45–47]. Grâce à l'optimisation de la méthode d'acquisition spectrale, nos analyses par microspectroscopie Raman du squelette corallien représentent ainsi les premières caractérisations chimiques in situ des matrices organiques squelettiques [32,33] et confirment que celles-ci sont présentes dans les centres de calcification et, de façon plus discrète, dans les fibres. Cette répartition des matrices organiques dans l'ensemble du squelette amplifie encore l'importance de leur rôle potentiel au cours de la diagenèse.

Nos résultats montrent aussi que les matrices organiques se dégradent rapidement dans les centres de calcification et dans les fibres, puisque les bandes C–H ne sont plus enregistrées dans les parties anciennes de la colonie. Dans le spécimen étudié, cette dégradation s'est effectuée en quelques années seulement. Cette dégradation est à mettre en relation avec l'hydrolyse naturelle des matrices organiques solubles, qui favoriserait le développement de ciments diagénétiques [12,13] et pourrait être à l'origine des recristallisations très précoces des carbonates biogènes [26,27,30,41].

Dans les squelettes carbonatés ou phosphatés [4,26,27,30], ce sont les mêmes mécanismes qui interviennent dans l'altération des biocristaux durant la vie de l'organisme et au cours des premiers stades post-mortem. Ainsi, les biominéraux à peine secrétés sont instables et subissent des modifications texturales et chimiques, qui débutent du vivant de l'organisme et se poursuivent à un stade post mortem.

Conclusions

(1) La microspectroscopie Raman est un outil efficace pour l'analyse in situ, simultanée et à fine échelle des composés organiques et minéraux des carbonates biogènes, à condition toutefois que l'ultrastructure du spécimen étudié soit bien connue.

(2) Les matrices organiques sont présentes dans l'ensemble du squelette corallien et plus abondantes dans les centres de calcification.

(3) Elles peuvent être rapidement dégradées en quelques années.

(4) Cette dégradation, qui résulte de l'hydrolyse progressive des matrices organiques, constitue le mécanisme-clé des premières étapes de la diagenèse et, ainsi, le point de départ des processus de fossilisation.

(5) Du carbone semi-amorphe a été détecté dans les centres de calcification et les fibres ; il résulterait de la dégradation des liaisons C–H sous le laser.

1. Introduction

The understanding of patterns and processes involved in the fossilisation of mineralised tissues is of fundamental importance from both palaeontological and sedimentological points of view. The massive use of skeletal remnants for providing geochemical proxies for past environments and climates, together with the organo-mineral duality of these skeletons, which undoubtedly increases the complexity of diagenetic pathways, further enhances the need of integrating our knowledge of biomineralisation processes and patterns into a fine-scale evaluation of diagenetic changes. Some recent works have shown that fine-scale textural modifications (i.e. changes of crystal size or arrangement), including recrystallisation of the original skeletal biominerals, do occur in skeletons at a very early stage after death [3,20,41], or even in a still-living organism [26,27]. A better understanding of the timing of these textural changes and of the alteration of biominerals in living organisms should help in renewing traditional views on fossilisation and classic concepts of diagenetic models.

The skeletal organic matrices are known to be mainly composed of glycoproteins often rich in aspartic acid [25]. The primary structure and the cloning of a major protein composing the skeletal matrix in scleractinian coral have been recently described for the first time [11]. Despite the long-recognised organo-mineral composition of mineralised skeletons and the fashionable development of research in the field of biomineralisation, few studies have concerned the fossilisation of macromolecules forming the skeletal matrices [5,10,12,13]. Hence, potential interactions between diagenetic changes of the organic matrices and contemporaneous textural alteration of the skeletal aragonite are still poorly understood.

This paper reports the early diagenetic alteration of organic matrices in a scleractinian skeleton, which is demonstrated for the first time by in situ Raman Microspectroscopy analyses by means of the recognition of the C–H bonding. Due to its particular mode of growth, the coral skeleton represents a natural model for assessing the stages of diagenesis in a carbonate skeleton of a still-living organism.

2. Ultrastructure and early diagenesis in scleractinian skeleton

Biomineralisation in scleractinian corals occurs extra-cellularly in the subcalicoblastic ectodermal space (see [1] for a review); two basic structural features, the 'calcification centres' and the 'aragonite fibres'

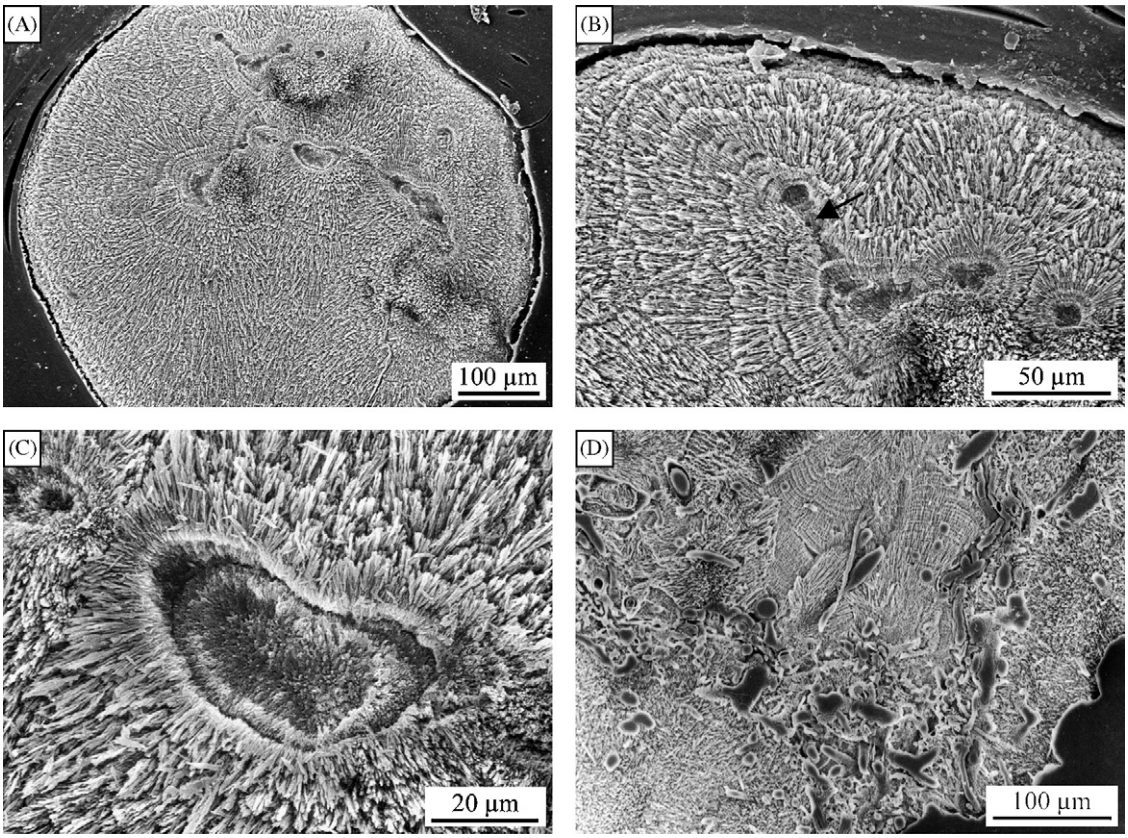

Fig. 1. Ultrastructure of *Lobophyllia corymbosa,* polished slightly etched sections, SEM. (**A**) Transverse section of a spinous tooth at the distal margin of a septum (living zone). (**B**) Detailed view of (**A**) showing the calcification centres (arrow, axis of calcification centres) and the incremental zonation of fibres. (**C**) Detailed view of a calcification centre in (**A**). (**D**) Skeleton in the basal part of the colony with numerous microborings.
Fig. 1. Ultrastructure de *Lobophyllia corymbosa*, sections polies ayant subi une légère attaque acide, MEB.

(Fig. 1A), were already recognised at the end of the 19th century when microstructural patterns began to be used as the basic criteria for coral taxonomy and evolution (e.g., [28]). The three-dimensional micro-architecture of the skeleton results from the distribution of the calcification centres and of the fibrous zones, both formed at pre-defined sites at the distal margin of the skeleton. The coral fibres are not homogenous crystals, but instead are composite structures characterized by a submicronic zonation (Fig. 1B) [8,22,28,50] testifying to their incremental growth during biomineralisation [29,52]. The characteristics of the calcification centres and the aspect of the zonation of fibres (Fig. 1B–C) are taxon-specific and interact with the taxon-dependent three-dimensional skeletal ultrastructure to account for differential diagenetic patterns between taxa [6,7].

At the scale of coral-colony life-time, the first effects of diagenesis occur in a few years in the form of thin fringes of syntaxial aragonite cement developing upon skeletal structures [38,43,51], together with textural changes in the skeleton itself [31]. The latter are directly controlled by the original ultrastructure and lead to an alteration of the fine-scale zonation of fibres and a selective dissolution of calcification centres [30,31].

3. Material and methodological approach

Raman Microspectroscopy allows ultrastructural features to be analysed directly in situ with a spatial resolution compatible with the micronic size of biogenic crystals and, provided that the analytical conditions are adequately optimised, both organic and mineral compounds can be recorded at the same time. This technique has thus a tremendous advantage over the more conventional analyses of organic skeletal matrices extracted through demineralisation of skeleton because (1) it avoids co-extraction of organic material from endolithic boring infillings, since these can be directly observed under the microscope (Fig. 1D), and (2) the analytical spot can be precisely positioned by the eye, allowing the

spatial distribution of organic matrices and diagenetic features to be directly investigated.

Raman microanalyses were performed on polished slabs sampled from the uppermost and the older skeletal parts of a living coral colony of *Lobophyllia corymbosa*. The living colony was sampled from the Lagoon of Mururoa (Polynesia) and immediately cleaned in order to remove soft tissues of polyps. In was then stored and dried for a few weeks before being sampled for analyses. The age of the colony at time of collection was 4–5 years, which hence represents the largest age difference between the living and the older skeletal parts studied. In order to compare results obtained from the centres of calcification and the fibres, previous detailed ultrastructural mappings of the studied slabs were achieved with a Scanning Electron Microscope (SEM). The Au–Pd cover, necessary for observation by SEM, was then removed by a slight polishing using a diamond spray. Analytical conditions were adapted and optimised for simultaneously recording mineral and organic compounds. Raman microanalyses were performed with a DILOR® XY® model with a green Ar^+ 514.5-nm laser, using 300 mW at the source (30–50 mW at the sample) with a 1-μm spatial pseudo-confocal filter and peak position calibrated to standard diamond at 1332 cm^{-1}. The reproducibility of results has been intensively tested and, under fixed conditions, the precision is better than 1 cm^{-1}.

4. Results

4.1. Living zone of skeleton

Several Raman spectra were obtained from both calcification centres and fibres (Fig. 1A–C). All spectra record aragonite, but no calcite. The distinction between the two polymorphs is based on previously published results (e.g., [18,36]), and also on our own reference spectra performed on gem-quality single crystals of aragonite and calcite. The two strong bands at about 155 and 1084 cm^{-1} are common to aragonite and calcite, and distinction between the two minerals is thus based on other bands. In particular, the doublet at 702–706 cm^{-1}, making a triplet with the 717-cm^{-1} band, is typical of aragonite, whereas calcite has a single band at 713 cm^{-1}. Aragonite has also two other bands at 1460 and 1572 cm^{-1} (Fig. 2), whereas calcite has bands at 1435 and 1747 cm^{-1}. Great differences occur also at low wavenumbers, where the strong 280 cm^{-1} band of calcite is replaced by a series of bands at 179, 204, 244 and 257 cm^{-1} in aragonite.

Skeletal organic matrices have been clearly recognized in spectra obtained from both calcification centres and fibres on the basis of several bands typical of C–H vibrations in the region 2847–2960 cm^{-1} (Fig. 2). However, these bands have much weaker intensities, equivalent to the weakest aragonite bands, in part due to the contrasting proportions of mineral and organic material in the coral skeleton, and in part to the different inherent Raman 'cross-section' of each species. Therefore, analytical conditions of spectral acquisition have to be specifically optimised to detect simultaneously low levels of organic substances within a mostly mineral material. This includes a significant increase of the time of analysis and also the measurement over a spectral range much wider than is generally used for recording pure mineral compounds.

Semi-amorphous carbon was detected in some spectra obtained from both calcification centres and skeletal fibres, especially the latter. This carbon is recorded by a very characteristic wide hump with greater intensities around 1335 and 1600 cm^{-1} [respectively the D_1 and $(G + D_2)$ bands of disordered graphite (Fig. 2)]. The well-known doubling of the D_1 band at about 2670 cm^{-1} is recognised by a typically very wide band and the typically very wide D_3 band is shown in the 'col' around 1500 cm^{-1}, which raises the apparent baseline between the two stronger bands (Fig. 2). Although the origin of this carbon is enigmatic and the mechanisms of its formation are still poorly understood, several features indicate that it could result from the deterioration of certain skeletal organic compounds under the laser beam. In particular, it is clear that the probability of recording semi-amorphous carbon increases with the duration of spectral acquisition, and hence the exposure of the specimen to the laser beam, such that this mechanism at least contributes to the presence of elemental carbon.

4.2. Old skeletal parts

Aragonite is the only mineral appearing in our Raman spectra from the ancient parts of the colony. This confirms that, during the first steps of fossilisation, fine-scale textural changes occur without any change of the mineral species. The C–H vibrations were not recorded in the older parts, thus demonstrating that the organic matrices are less abundant than in the living parts. However, some spectra from the calcification centres have shown the presence of semi-amorphous carbon.

5. Discussion

Despite numerous studies on the biomineralisation pattern in carbonate skeletons, the distribution of the organic matrices and their functional relationship with aragonite crystals are poorly known. In scleractinian

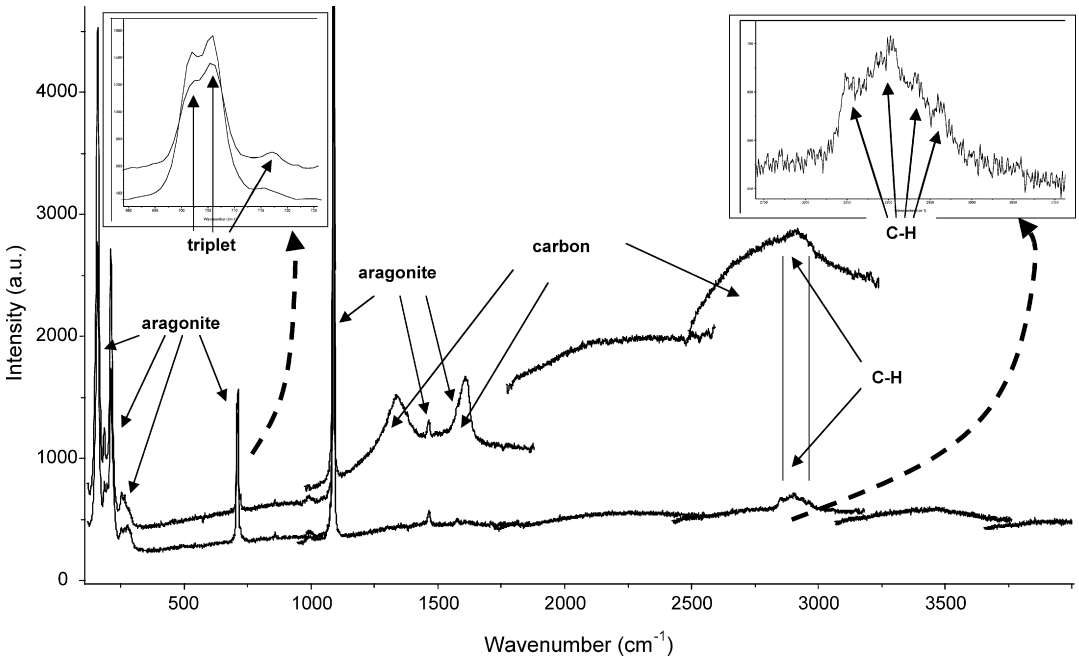

Fig. 2. Raman spectra from a calcification centre (lower spectrum) and a fibre (upper spectrum) in the living part of *Lobophyllia corymbosa*. Raw data except for 3pt smoothing. Inserts display close-ups of the spectral zones of the aragonite triplet and the C–H bonds. Peak positions in text.
Fig. 2. Spectres Raman d'un centre de calcification (haut) et de fibres (bas) de la zone vivante de *Lobophyllia corymbosa*.

corals, it was hypothesised as early as the beginning of the 20th century that the organic material forms thin membranes surrounding groups of crystals [19,24]; later, it was reported that calcification centres are richer in organic compounds than the fibres [2]. The organic envelopes surrounding the groups of fibres were revealed by demineralisation and staining of the skeleton surface [23]. Organic material in both calcification centres and fibres was recorded either by fluorescence microscopy [16,40,52] or by SEM imaging [29]. XANES spectra from living coral skeleton have shown the presence of sulphate, the origin of which has been regarded as organic (chondroitin, [9]) or inorganic (SO_4-CO_3 substitution, [37]), and is still a matter of considerable doubt and debate [48]. A few studies involved Raman spectroscopy on biogenic carbonates, including corals, but with the exception of a carotenoid pigment detected in an oyster pearl, no Raman bands corresponding to C–H bonds in organic phases have previously been reported [9,45–47,53]. Our Raman Microspectroscopy study provides the first in situ-recorded chemical data concerning these C–H-bearing skeletal matrices and confirms that these are present in both skeletal fibres and calcification centres, although they are more abundant in the latter [22,33–35]. This overall occurrence of the organic matrices in the skeleton emphasizes their potential importance in diagenesis.

Our results also indicate the rapid diagenetic decay of the organic matrices both in calcification centres and in coral fibres, as C–H vibrations have not been recorded in the old parts of the colony. In the studied specimen, this occurs only in a few years although the intensity of the organic degradation is not necessarily proportional to time. Further investigations are in progress in order to understand better the variations of the C–H signals in the different parts of the colony. The presence of semi-amorphous carbon detected in a few spectra from the calcification centres in the basal part of the colony suggests that a small amount of organic matrices can be still preserved in some centres, this small quantity of matrices being easily deteriorated under the laser beam during analysis. The decay of skeletal matrices has been demonstrated as a rapid and widespread early diagenetic process in various carbonate skeletons [5,12–14,17,21,44]. In scleractinian corals, some organic remnants can be preserved in fossil skeletons as old as the Cretaceous [49] or the Triassic [15], although the main difficulty in this case is to be sure that the organic components extracted from fossils are relics of the original skeletal matrices [44]. This organic decay results from the hydrolysis of the glycoproteinous matrices due to the rearrangement of the sugar moities through hydrolytic cleavage of the glycosidic bonds [5,44]. During hydrolysis, the C–H

vibrations are decomposed into a series of multiple vibrations, and therefore, this decreases the signal of individual Raman bands. In Recent scleractinians, it has been reported that the extracted acid-soluble organic matrices have a less inhibiting effect on $CaCO_3$ precipitation with age, potentially favouring development of early cement [12,13]. The break-up of skeletal matrices has been considered as a major cause of early recrystallisation of biogenic carbonates [39] in various living and post-mortem organisms [26,27,41]. We suggest that in corals, the hydrolysis of organic matrices can also initiate the early recrystallisation of the biogenic aragonite into secondary aragonite [30,42] and that the total or partial break-up of these matrices can be regarded as a pre-requisite to iso-mineralogical diagenetic changes.

Several examples indicate that the same mechanisms are involved in the alteration of biocrystals in living organisms and during the earliest post-mortem diagenesis, both in carbonates [26,27] and phosphates [4]. This implies that the textural and chemical changes of biominerals that had started during life, continue after death, and hence, that early diagenesis occurs as a continuous process. Furthermore, this also disrupts the strict definition of diagenesis as a set of post-mortem processes.

6. Conclusions

Raman Microspectroscopy performed on the living and ancient skeletal parts of a coral colony has shown that:

(1) Raman Microspectroscopy represents an efficient tool for recording in situ and simultaneously both mineral and organic compounds of biogenic carbonates, provided that the ultrastructural pattern of the studied specimen is already well understood;
(2) skeletal organic matrices are present both in calcification centres and in the skeletal fibres, although more abundant in the former;
(3) organic decay of the skeletal organic matrices does occur very rapidly, in a few years;
(4) this organic decay, which results from the hydrolysis of the organic matrices, is one of the key-mechanisms driving the first steps of diagenesis in coral skeletons. It therefore represents the starting-point of the process of fossilization;
(5) semi-amorphous carbon has frequently been observed in the calcification centres or in the fibres, but its origin remains enigmatic; a strong possibility is the deterioration of C–H bonds under the laser beam.

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