Evolution (Biogenesis)

# Looking for traces of life in minerals

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## Abstract

Traces of life have been extensively looked for in minerals. It is indeed thought that a wide diversity of living organisms can control the formation of mineral phases and thus may leave imprints of their activity in the morphology, chemistry and crystallographic structure of the mineral end-product. Here, we illustrate the bases and limits of this approach by reviewing some studies on biogenic magnetites and carbonates. More than an exhaustive review, we give a personal view on the limitations provided by an empirical approach based on defining so-called biosignatures and suggest developing a more comprehensive mechanistic understanding of how life controls mineral nucleation and growth and induces potential specific features. ***To cite this article: K. Benzerara, N. Menguy, C. R. Palevol 8 (2009).***

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## Résumé

**Recherche de traces de vie dans les minéraux.** Les minéraux ont souvent été utilises dans le cadre de la recherche de traces de vie. Il est en effet couramment admis qu'il existe une grande diversité d'organismes pouvant contrôler la formation de phases minérales et pouvant ainsi y laisser leur empreinte dans la morphologie, la chimie ou encore la structure cristallographique du produit minéral. Ici, nous illustrons les principes et les limites de cette approche à travers quelques études sur les magnétites et les carbonates biogéniques. Plutôt qu'une revue exhaustive de la littérature, ce manuscrit présente une vision personnelle des limites d'une approche empirique consistant à définir des soi-disant biosignatures et suggère d'y préférer une compréhension mécaniste plus poussée de la façon dont la vie contrôle la nucléation et la croissance des minéraux et induit ainsi d'éventuelles caractéristiques spécifiques. ***Pour citer cet article : K. Benzerara, N. Menguy, C. R. Palevol 8 (2009).***

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## 1. Introduction

The search for traces of life in the geological record has stimulated a huge number of studies [79]. For that purpose, the detection of microfossils (e.g. Javaux et al. this issue) or the measurement of chemical parameters,

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such as isotopic compositions, have been particularly important strategies. The morphology, the atomic structure and the texture of minerals have been additional targets in the study of extraterrestrial or ancient terrestrial rocks. Among many examples, we can cite stromatolites as ancient traces of life [5], or magnetites in the Martian meteorite ALH84001 [63]. The basis for these studies relies on the dependency of the chemistry, structure and texture of minerals on the physical and chemical (and possibly biological) conditions prevailing during their formation. Indeed, thinking of the many examples of highly complex skeletal structures in eukaryotes such as the tests of diatoms, of foraminifers, or the skeletons of vertebrates for example suggests that there are mineral assemblages specific of life. Moreover, it has often been assumed that such signatures would be more resistant to diagenesis and metamorphism transformations than organic molecules for example, and thus provide more reliable targets for exobiology and paleobiology studies.

The major question addressed here will be the following: are there peculiar features in minerals that are indicative of a past biological activity? We will review two illustrative types of minerals that have been proposed as possible carriers of biological traces: magnetites and carbonates (e.g. calcite, aragonite). Determining the mineralogy alone of a sample is not constraining: there is no mineral species uniquely related to life [90]. Hence, additional information has to be looked for in minerals, requiring a finer characterization of the chemistry, atomic structures and texture (meaning morphology of minerals and the way they are associated) of a sample. This first, apparently purely methodological, description stage can lead different authors to different conclusions. This is, however, usually difficult for the non-specialist to assess who is right. The interpretation of the data is another source of debates. Our main message is that the naive actualism, consisting in comparing a feature found in a known biomineral with the same feature observed in a sample to conclude that the latter is biogenic, should be completely abandoned. Understanding how minerals nucleate and grow and how life possibly impacts during these processes, the mineralogy of the end-products should be preferred.

As prokaryotes are likely more relevant targets for the search of traces of life in ancient and/or extraterrestrial rocks [67], we will focus on biomineralization by these organisms. However, some recent results on eukaryote biomineralization will also be discussed as our knowledge of those systems is more advanced for the carbonates and provides interesting directions to follow for future studies of microbial systems.

## 2. What is a biomineral?

Biominerals are minerals formed by organisms. Biomineralization is widespread, with more than 60 biologically formed minerals identified [11,90]. There has been a traditional discrimination between biologically induced mineralization (BIM) and biologically controlled mineralization (BCM) with various other terminologies found in the literature, such as passive- and active-biomineralization or organic-matrix mediated [62]. Briefly, in BIM, biominerals are formed subsequently to the modification of the chemistry of the solution by the metabolic activity of bacteria, while in BCM, the microorganisms have a direct (meaning genetically-controlled) role on the formation of the biominerals ([13,41], for a review). This may suggest that minerals formed by BIM can be formed by abiotic processes, while those formed by BCM would be specific of life (although life also uses chemistry). Sometimes, an additional idea is implicitly associated to that categorization: while the mineral products in BIM appear to have no specific recognized functions, biominerals formed by BCM serve some physiological function. As a result, the lack of control over mineral formation in BIM is expected to result in poor mineral specificity. In contrast, the strict biological control over the properties of minerals formed by BCM is reminiscent of many other biomineralization systems, such as diatom silica shells, vertebrate teeth or bones for example and thus a comparable complexity of the mineral end-products should make them valuable for inferring a biological origin.

Some misleading assumptions that are sometimes associated with this general scheme should be corrected here: because of the vague definitions of BIM and BCM, which likely involve similar molecular processes, it is sometimes suggested that BIM refers to extracellular precipitation, while BCM concerns intracellular precipitation processes. This is wrong as many eukaryotes precipitate minerals extracellularly and do have a demonstrated genetically-programmed control on that precipitation (e.g. corals [84]). Extracellular precipitates can hence have very define and specific structures and morphologies. Moreover, *Shewanella putrefaciens* can precipitate magnetites intracellularly [43] in a similar way as Fe-reducers form extracellularly magnetites, the latter being generally considered as BIM products [41]. Finally, inferring whether a biomineral is the product of a BIM or BCM process is usually difficult, and inferring potential physiological functions of biominerals is usually based on arbitrary assumptions. For example, while precipitation of lead phosphate within the periplasm

of some bacteria has been frequently interpreted as a resistance mechanism, the precipitation of calcium phosphates with the same texture and at the same location was considered as a non-specific passive process [19].

In any case, we believe that this discrimination between BIM and BCM is not operational for the purpose discussed here. First, both BIM and BCM biominerals involve a biological activity, which is the only topic here. Although it might be more difficult to assess, some BIM products can certainly be indicative of a past biological activity [31]. Moreover, although eukaryotes do form complex mineral structures through BCM, the complexity of BCM biominerals formed by prokaryotes may *a priori* be very relative and may not provide a more robust signature than minerals formed through BIM. For all those reasons, this classification adds up some complexity to the already uncertain notion of biomineral, which is the major topic of the present discussion. In contrast, it seems more efficient to consider the various steps of mineral formation at which biological activity can be recorded.

The first step consists in the achievement of supersaturation with the biominerals. While biomineralization by prokaryotes usually occurs in solutions that are already supersaturated, the microorganisms can increase this supersaturation by their metabolic activity. If the bulk chemistry of the environment can be assessed, then the presence of some minerals can be indicative of anomalous biologically-mediated chemical changes. We can cite for example, the alkalinization of a solution by photosynthesis or sulfate-reduction leading to the formation of carbonates [33], or the oxidation of iron in the absence of $O_2$ leading to the formation of Fe(III)-phases [51]. The problem is that, in most of these cases, alternative abiotic processes can also lead to these chemical changes and have to be considered attentively [56].

A second step to consider is the nucleation and the growth of biominerals. Biomolecules can impact these processes and modify the size, the morphology, possibly the concentration of defects, and the crystallographic orientations of the minerals that are formed [30]. There are numerous examples in the biomineralization literature of such a role of biomolecules [4,26,39,64,65,80] that may provide indications of a past biological activity.

As a conclusion of this section, it should be noted that understanding the exact role of modern microorganisms in the formation of most of biominerals, and whether the same minerals could be synthesized by purely abiotic processes or not, is certainly one of the major and likely far-reaching goal of geomicrobiology even though a range of sophisticated techniques from molecular biology to condensed matter physics can now be used on

laboratory cultures. Hence, studies concluding a biological origin from few observations performed on ancient and/or extraterrestrial rocks should be regarded cautiously. We detail those ideas further in the next sections.

# 3. The search for traces of life in biogenic magnetites

Magnetite (a mixed valence spinel with chemical formula $Fe_3O_4$) has been an emblematic mineral for the search of traces of life. Particularly because of the finding of magnetites of specific sizes and habits in the Martian meteorite ALH 84001, which have been first interpreted as evidence of past biological activity on Mars [63]. There are already numerous papers detailing the various abiotic [35,89] and biotic [12,15,54] mechanisms of magnetite formation, and the chemistry and mineralogy of the end-products [29]. However, we summarize here the main results to exemplify the way minerals have so far been used as biosignatures and the limits of this approach.

## 3.1. What we know about the formation of biogenic magnetites

The role of prokaryotes in the formation of magnetites has been extensively studied partly to assess their contribution to sediment magnetization [69,70]. Two distinct modes of formation have been discriminated:

- extracellular formation of magnetites by dissimilatory Fe(III)-reducers, such as *Geobacter metallireducens* or *Shewanella putrefaciens*. These bacteria modify the (redox) chemistry of the environment favoring the formation of magnetites by partially reducing Fe(III) to Fe(II) [68,92]. They might also impact the nucleation and growth of the magnetites by producing extracellular organic molecules [88] but this has been only little studied. It should also be noticed that intracellular magnetites have been occasionally evidenced in *Shewanella putrefaciens* CN32 [43];
- intracellular formation of chains of magnetites (in some cases greigite, $Fe_3S_4$) surrounded by a lipid bilayer membrane, forming magnetosomes, by magnetotactic bacteria. The chain is fixed within the cell so that the bacterium can passively align in and navigate along geomagnetic fields [21]. Magnetotactic bacteria are found in the oxic–anoxic transition zone and most of them are chemoheterotrophic and use oxygen as an electron acceptor [14] while some can use $NO_3^-$, $N_2O$ or possibly Fe(III) [82]. The selective advantage of sensing the magnetic field for these bac-

teria might be a more efficient search for low-oxygen environments [54].

Much of what we know on the biochemical processes involved during the formation of magnetites in magnetotactic bacteria is based on the study of cultured strains which represent only a small fraction of the whole diversity of magnetotactic bacteria encountered in the environment [38,50]. The reader will find a detailed and recent review in Komeili [54]. Bacteria have first to import Fe(III) into the periplasm using iron chelators; then they reduce it. Iron is then transferred into the preformed magnetosomes, which have traditionally been described as vesicles but have recently been demonstrated to be evaginations of the periplasm by Komeili et al. [55] at least in *Magnetospirillum magneticum* sp. AMB-1. Fe(II) is then presumably partly re-oxidized leading to the precipitation of magnetite. This step might involve precursor phases such as ferrihydrite [40] but there seems to be no consensus on that point [36,83]. The stability of the magnetosome chain is ensured by a bacterial filament cytoskeleton [55,77]. In addition to a control of the chemical conditions (e.g. pH, Eh, activity of trace elements) necessary to grow pure magnetites, there appears to be involvement of molecules, possibly proteins, controlling the growth, hence the final morphology of the magnetite crystals [6,7,78]. Those last studies offer a promising perspective on the understanding of the origin of the particular morphological features observed in biogenic magnetites by showing how some proteins may control their nucleation and growth.

### 3.2. Biosignatures that have been proposed for biogenic magnetites

Only few studies have been dedicated to the search of signatures of life in extracellular magnetites [24,88]. The idea behind this is that their properties depend strongly on environmental conditions and are thus indistinguishable from minerals formed inorganically under the same conditions. However, the influence of extracellular polymers produced by Fe-reducers, the modifications of the bulk (redox) chemistry of the solution that would not be possible at low temperature without the activity of these bacteria (i.e. reduction of Fe in the presence of organic carbon) should not be ignored. In contrast, it has been proposed that magnetites produced by magnetotactic bacteria have specific physiological functions beneficial for the microbes and are hence the by-products of processes shaped by million years of evolution. Bacteria would thus have a great degree of chemical control over their nucleation and their growth, and such mag-

netites would be biosignatures in the same way as a fossil shell is an unequivocal biosignature. As explained above, we believe that this traditional point of view is somehow misleading regarding the topic exposed here. We agree that finding a mollusc shell on Mars would certainly be a strong evidence for a past biological activity there, but how do we define a complexity parameter for such objects, and are magnetites formed by microbes as complex as a shell? The control by bacteria over the nucleation and growth of magnetites within magnetosomes results from chemical interactions in the same way as extracellular polymers control nucleation and growth of extracellular minerals or as pH and $O_2$ control the chemistry and the morphology of these minerals. Finally, a controlled synthesis may not automatically result in a unique (biological) signature.

Based on the observation of magnetites produced by magnetotactic bacteria, unique features, usually not reproduced by abiotic syntheses, have been noted [27,29,87]:

- crystals in magnetotactic bacteria are of high chemical purity with concentrations of trace elements such as Ti, Al and Cr lower than in most abiotic experiments [13,86];
- they have few crystallographic defects;
- they display a narrow size range in the single domain size range (around 35 to 120 nm approximately) and a narrow distribution of shape factor within a single species. Moreover, the size distribution of magnetites produced by some strains is an asymmetric log–normal function skewed towards smaller sizes while the size distribution in abiotic magnetites generally follows an opposite asymmetry [29,35];
- magnetites produced by magnetotactic bacteria can have various shapes (Fig. 1) depending on the species including equidimensional cubo-octahedra (which can be produced by abiotic syntheses), elongated hexa-octahedral prisms or arrowhead with usually preferential elongation along the [111] axis in elongated magnetites (with exceptions, [50]). Some of those morphologies have been so far observed uniquely in magnetotactic bacteria, for example the truncated hexa-octahedral morphology in MV-1;
- finally, the magnetites in magnetotactic bacteria are aligned in chains.

The possibility of forming chains by abiotic processes has however been discussed by Kopp et al. [58]. All of those features can be seen as an optimization of the system to sense the magnetic field lines. Some variations have been documented within a single species
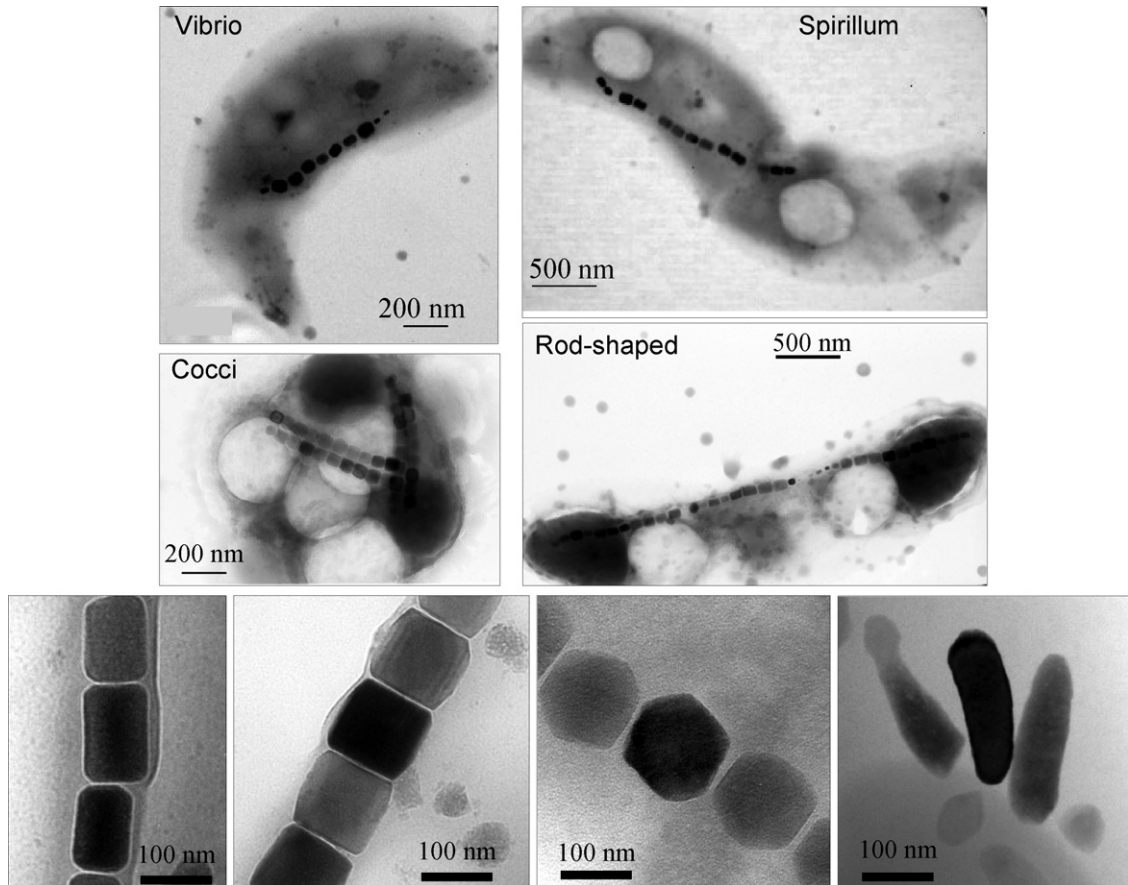
Fig. 1. TEM images showing the morphological diversity of magnetites formed by magnetotactic bacteria in the Seine river [50]. The four upper images show the diversity of bacteria forming chains of magnetosomes. The four lower images show close up on magnetites found within magnetosomes with various shapes.

Fig. 1. Micrographies MET montrant la diversité morphologique des magnétites formées par les bactéries magnétotactiques de la Seine [50]. Les quatre photographies du haut montrent une partie de la diversité des bactéries formant des chaînes de magnétosomes. Les quatre photographies du bas sont des agrandissements des magnétites de formes variées à l'intérieur des magnétosomes.

cultured under different conditions or between different species [8,50,85]. The combination of those features has thus permitted one to look for biogenic magnetites, called magnetofossils, in the geological record. We consider in the next session the magnetites found in the Martian meteorite ALH84001 to show however that looking for such biosignatures can be misleading.

### 3.3. Use and limits of biosignatures: the ALH 84001 example

ALH 84001 is an orthopyroxenite that contains Fe–Mg carbonates of still debated origin, although there is a consensus that they are Martian. It arrived on Earth 13,000 years ago in Antarctica. Different morphological subpopulation of magnetite crystals are associated with the carbonate globules. Based on the criteria mentioned above, some of these magnetites were interpreted as magnetofossils. Thomas-Keprta et al. [86,87] reported that they share the following similitude with magnetites produced by the magnetotactic strain MV-1:

- a narrow size distribution in the single magnetic domain size range;
- the absence of crystalline defects;
- high chemical purity;
- a "truncated hexa-octahedron" morphology with elongation along the [111] axis similar to the strain MV-1.

In addition, Friedmann et al. [42] reported the presence of magnetite chains in ALH84001 using scanning electron microscopy. This observation was, however, mitigated by Weiss et al. [91]. Those different observations thus offer a very good fit to magnetofossils.

However, the whole biogenic interpretation was convincingly contested by Golden et al. [45] and Bell [17] who first revised some of the observations, then proposed an alternative scenario of formation that fits much better to the observations. First, Golden et al. [17] argued that prismatic magnetites elongated along [111] can be formed in inorganic processes such as thermal decomposition of siderite and are no biosignatures. Golden et al. [44] agreed that truncated hexa-octaedron are the most prevalent morphologies in MV-1 but that this morphology was minor in ALH84001 compared to the simple octahedron morphology similarly to what he found in abiotic syntheses. He argued that the ALH84001 magnetites were misinterpreted as truncated prims because of their rounded edges that can be confused with very narrow faces. Regarding the chemical purity of the magnetites in ALH84001, Golden et al. [46] first showed that some are pure (considering the detection limit of energy dispersive X-ray spectrometry available on a TEM), while some can contain up to several percent of magnesium. Moreover, they showed that the chemistry of the ALH84001 magnetites was indistinguishable from the chemical composition of magnetites obtained by thermal decomposition of Mg–Fe carbonates similar to the ones hosting magnetites in the meteorite. Pure abiotic magnetites can be obtained from the thermal decomposition of pure Fe-carbonates which are present in the ALH84001 meteorite, otherwise they incorporate some magnesium. Finally, inorganic magnetites resulting from thermal decomposition of Fe-carbonates were shown to have a size range in the single magnetic domain range and only few defects. To summarize, Golden et al. [45,46] agree with most of the observations made by Thomas Keprta et al. [86], except for the morphology of the magnetites, and show that none of them can be interpreted as a biosignature, as they can be found in abiotic magnetites as well. While finding magnetites with a dominantly truncated hexa-octahedral morphology might be indicative of life, ALH84001 magnetites have dominantly a simple prismatic morphology which can be found in abiotic magnetites. Finally, Barber and Scott [9] showed in ALH 84001 that the magnetite-rich zone is very porous at the nm-scale and that MgO and magnetite crystals showed a topotactical orientation with respect to the host carbonate lattice, suggesting that they formed as solid-state precipitates. All these observations are thus much better accounted for by a scenario where magnetites in the ALH84001 formed during the partial thermal decomposition of the Fe–Mg globules of the meteorite subsequent to a impact heating recorded by the minerals of the meteorite [17,23,49].

Magnetofossils have also been hunted in the terrestrial geological record. For more details, see the review by Kopp and Kirshvink [57]. These authors have set an interesting scheme for rating magnetofossils and include in the criteria an analysis of the context. If a detailed analysis of the context, in particular assessment of the diagenesis conditions encountered by the samples exists, then the report of magnetofossils is more robust. This approach proposing potential indicators of a biological activity but as the same time rating their robustness provides an interesting example to follow.

It is difficult to assess the lessons that can be drawn from such a story: at least, that the use of seemingly robust so-called "signatures" might be misleading. First, the assessment of some features (e.g. the truncated octa-hexaedral morphology) might be difficult. Moreover, although some features are systematically found in biologically-controlled systems, some abiotic processes, including those that may have not even been studied yet, may produce similar features (e.g. narrow size distribution in the single magnetic domain range, pure chemistry, elongated prismatic morphology). More generally, an approach consisting in trying to understand what the conditions of formation of a given object are, considering both abiotic and possibly biotic processes, equally seems safer than the biased approach in which one tries to find which feature in this object might be biogenic. The context has always to be considered. In this case, the observation that the ALH84001 experienced thermal heating consequently to an impact suggests that mineral transformations occurred after the formation of the carbonates and that those mineral transformations can account for the formation of magnetites.

## 4. The search for traces of life in biogenic carbonates

Carbonates as well as phosphates have also been prominent minerals in which traces of life have often been looked for. The traditional view on those minerals is quite different though [41]. They are indeed generally considered as BIM when they are formed by bacteria and thus not good carrier of potential signatures. This view can however be mitigated [25]. First of all, stromatolites are composed of carbonate and are usually considered as one of the oldest trace of life in the geological record. If this is true, there must be some information stored in the texture of the minerals, some biological mechanisms in the build-up of these structures. A second point is the origin of carbonates: are they really biologically induced or not? Their extracellular formation does not provide any definitive answer. Indeed, corals for example form

carbonates extracellularly and there is no question that a genetic control is involved and that as a result, complex and specific architectures can be built [28,84]. Finally, as mentioned above, even if carbonates formed by bacteria are BIM, it does not mean that information on biological processes cannot be stored in these minerals. It seems that only little is actually known of the controls bacteria can have on the formation of carbonate minerals. Here, we will present very general thoughts based on recent observations in eukaryote biomineralization systems and hypothesize about potential mineralogical features that could be looked for in carbonates and could be impacted by a biological activity.

Although it is a fascinating point that could be pertinently reviewed in light of the present topic, it is not the goal of this section to discuss in details whether the macroscopic structure of stromatolites is a biosignature or not. A recent study by Allwood et al. [3] reaffirmed the biogenicity of 3.4 Ga old stromatolites from the Pilbara Craton in Australia simply by describing the diversity of morphotypes at the macroscale. Some numerical models have been developed to simulate various stromatolite morphologies [10,34,47]. Grotzinger and Rothman [47] have suggested that laminations found in stromatolites can be produced by purely abiotic processes. However, a range of morphologies found in modern and Archean stromatolites were only produced in models involving interactions between environmental factors and organic-controlled processes [34]. One interesting point of discussion in Dupraz et al. [34] paper is about the comparison between stromatolite and coral structures. They note that some specific adaptation of some species might be responsible for the building of specific structures. However, they specify that most morphologies are likely to have been initiated by environmental disturbances such as microbial mats, and do not have a genetically-programmed control on the formation of carbonates, on the contrary to corals. It would be very interesting to test this idea further, for example by applying the same kind of models to the growth of corals.

At a smaller scale, it has been however demonstrated by many studies that carbonate microbialites are usually composed of a large amount of small-sized (few tens to few hundreds of nanometers) carbonate (calcite or aragonite) crystals (Fig. 2), producing a micritic texture [20,32,76]. Moreover, it has been shown that amorphous calcium carbonates (ACC), that are usually unstable in solution, can be preserved in modern microbialites [20]. Both of these observations could be the result of nucleation and growth of carbonates within an organic-matrix
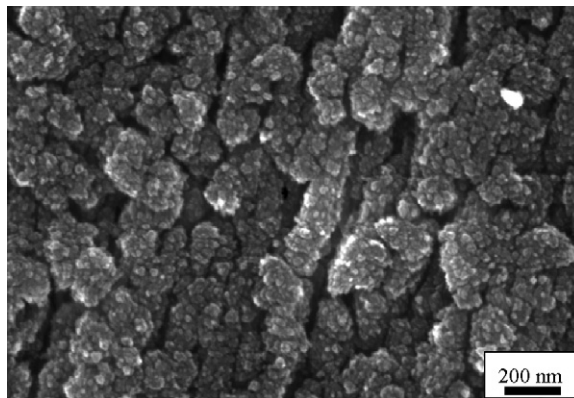


Fig. 2. SEM image of aragonite nanocrystals in a modern stromatolite from Satonda (Indonesia). Particles of few hundreds of nanometers can be observed. They seem to be clusters of few tens of nanometeres nanoaragonite crystals. Organic molecules such as polysaccharides have been shown to be intimately associated down to the nm-scale with these nanocrystals [20].
Fig. 2. Micrographie MEB de nanocristaux d'aragonite dans un stromatolite récent de Satonda (Indonésie). Des particules de quelques centaines de nanomètres peuvent être observées. Il a été montré que des molécules organiques telles que les polysaccharides sont associées intimement jusqu'à l'échelle nanométrique avec ces nanocristaux [20].

that is pervasive in modern stromatolites [22,52,53]. These features (small size and/or presence of ACC) are definitely not biosignatures as they can be produced by abiotic processes [18,59,61,74]. But their presence in biological systems can be explained by the impact of organics on their nucleation and growth. As an example, we recently reported the presence of aragonite crystals associated with organic globules with a baterial-like morphology in 2.7 Ga old stromatolites from Pilbara [60]. We mentioned the similarity of these objects with what can be observed in modern stromatolites and from that proposed that they might represent fossils of microorganisms and of the aragonitic micrite.

The global chemistry and structure (e.g. whether they precipitate as aragonite or calcite) of the precipitated minerals in microbialites seem to be mostly controlled by the chemistry of the environment. However, it is known that some organic molecules in eukaryotes can control which polymorph is precipitated, i.e. calcite or aragonite [16,37]. Whether such molecules exist in bacteria is unknown yet and will be very interesting to evidence in future studies. However, finding aragonite or calcite in a geological sample cannot be used as a biosignature as both polymorphs can form in low-T abiotic processes depending on the chemistry of the environment (e.g. aragonite preferentially forms when the solution is rich in Mg) and moreover, the solid-state transformation from aragonite to calcite can occur during metamorphism.
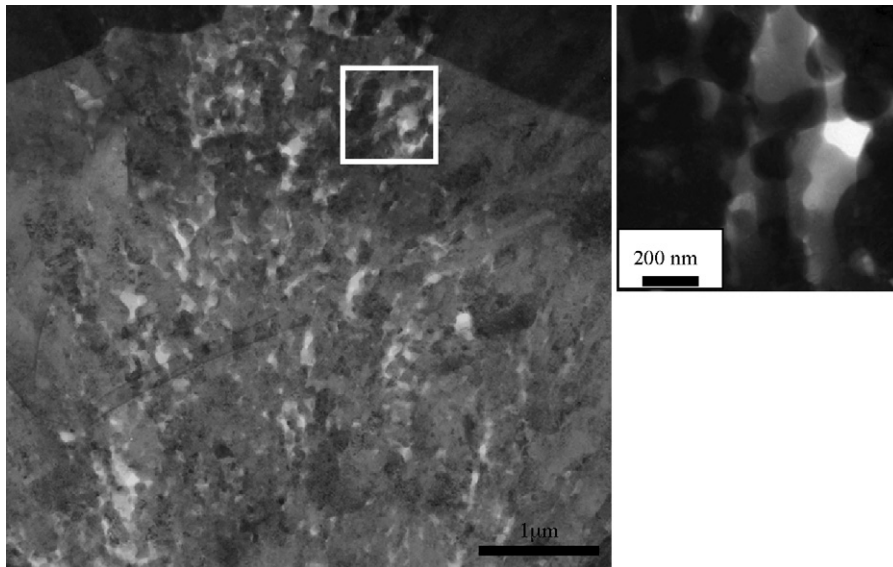
Fig. 3. TEM image of a center of calcification of the coral *Porites sp.* showing a porous texture resulting from the clustering of 100-nm sized aragonite nanocrystals. On the right hand corner, close-up on few aragonite nanocrystals. Electron diffraction analyses show that the aragonite nanocrystals share a common crystallographic orientation and that they all form a mesocrystal (*Benzerara et al., manuscript in preparation*).

Fig. 3. Micrographie MET d'un centre de calcification du corail *Porites sp.* montrant une texture poreuse résultant d'une agrégation de nanocristaux d'aragonite d'une centaine de nanomètres. À droite, agrandissement montrant quelques nanocristaux d'aragonite. La diffraction électronique montre que les nanocristaux d'aragonite partagent une orientation cristallographique commune et qu'ils forment de manière collective un mésocristal (Benzerara et al., manuscript en préparation).

Regarding the textures of the minerals composing stromatolite laminae and whether they contain information on the nucleation and growth processes, only little is known. Recent observations on eukaryote biomineralization, however, show that organisms can impact the crystallography and the texture of carbonates even though they are precipitated extracellularly. Eukaryotes can produce carbonate crystals (calcite or aragonite) with very particular morphologies. For example, sea urchin spicules behave microscopically as single crystals of calcite despite their unusual morphology and nearly isotropic fracture behaviour. It has been shown that these single crystals were actually clusters of crystallographically well-aligned nanocrystals forming what was called a mesocrystal [1,81]. Such mesocrystals have been increasingly identified in biominerals [28,66]. The precipitation of carbonate nanocrystals in an organic matrix might be responsible for the eventual formation of a mesocrystal. Observation of crystallographically aligned nanodomains in carbonates (Fig. 3) could thus result from a biological control, although again the specificity of life in the formation of such structures will have to be further tested. No such structures have been detected up to now in microbial precipitates. Whether it results from inaccurate observations or from an intrinsic difference between the organic matrixes produced by eukaryotic cells and by prokaryotes will be important to assess in the future. Directly related to this, a last feature that might be a potential indication of biogenicity is the entombment of organic molecules within the crystalline structures of minerals [2,72,73]. Whether organic molecules can really be part of the structure of minerals remains very elusive but deserves further studies as finding such molecules would be a major key to infer a biogenic origin of a crystal.

## 5. Preservation of traces left by life in minerals

Taphonomy is an important field in paleontology dealing with processes affecting and transforming fossils during diagenesis and metamorphism. Many mechanisms have been identified, such as recrystallization of small crystals into bigger ones, dissolution of aragonite that can reprecipitate as calcite, or silicification of carbonated structures. Diagenesis and metamorphism have affected all the rocks found in the geological record and extraterrestrial rocks to some extent (e.g. shock-induced transformation, then possible terrestrial contamination of the ALH84001 meteorite). Hence, identifying mineralogical features that are possibly formed by biology is not sufficient; their possible preservation during diagenesis and metamorphism should also be studied. Only

few studies have been dedicated to issue. A discussion of the preservation of signatures in magnetofossils with the issues of secondary oxidation of magnetites, or the breakup of magnetite chains can be found in Kopp and Kirshvink [57]. Regarding carbonates, the modifications in the chemistry and the structures of minerals due to diagenesis have been studied in corals [71] and more generally in carbonates from shallow marine environments [48,75]. Testing more systematically the evolution of any feature that could be proposed as a potential indicator of a biological impact under relevant diagenetically conditions would certainly be of importance for this purpose.

## 6. Conclusions

Based on this review of some current work in biomineralization, which is far from being exhaustive, here are some conclusions that can be made regarding the possibility to infer the presence of life in ancient and/or extraterrestrial samples from the study of minerals.

Biological activity can impact the formation of minerals. Resulting variations can be evidenced in the chemistry, the crystallography, the texture of the minerals. Minerals, as non-labile recorders of the environmental conditions in which they formed, should definitely be systematically prime targets in studies searching for past traces of life and trying to detail the conditions that existed in a paleoenvironment.

Biosignatures, if they exist, should not be simply based on an empirical observation of features occurring in biologically mediated mineralizations. A deeper understanding of the processes leading to these features during nucleation and growth and hence a better assessment of how unique to biological systems those features are, is definitely mandatory. Current research on magnetites produced by magnetotactic bacteria, including genomic and proteomic studies, which intend to infer the biochemical processes controlling the nucleation and the growth of magnetites certainly offers an exemplary approach. Much progress is expected on our understanding of the impact of biology on nucleation and growth of such important phases as carbonates. The fact that they are possibly BIM, produced extracellularly, does not seem to be an appropriate concern.

The approach consisting in listing biosignatures, i.e. features that would be unambiguous indications of a past activity of life in any sample and that would be systematically and exclusively looked for in minerals is misleading. The connection of a given feature to a biological process seems very relative to the conditions existing in the environment. For example, magnetites can form from thermal decomposition of a Fe-carbonate,

but this process is very unlikely if the sample has never experienced high temperatures. Hence determining the conditions prevailing in the environment where the mineral formed (e.g. anoxic or oxic, temperature, pH) is certainly as important as looking for particular features in a mineral. This non-biased approach will allow considering equally abiotic and biotic processes as possible drivers and hopefully prevents erroneous announcement of new forms of life on Earth or elsewhere.

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