

Iron microbial mats in Modern and Phanerozoic environments

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ABSTRACT

The recognition of iron microbial mats in terrestrial environments is of great relevance for the search for extra-terrestrial life, especially on Mars where significant iron minerals were identified in the subsurface.

Most researches focused on very ancient microbial mats (e.g. BIFs) since they formed on Earth at a time where similar conditions are supposed to have prevailed on Mars too. However, environmental proxies are often difficult to use for these deposits on Earth which, in addition, may be heavily transformed due to diagenesis or even metamorphism.

Here we present modern and phanerozoic iron microbial mats occurrences illustrating the wide variety of environments in which they form, including many marine settings, ponds, creeks, caves, volcanoes, etc. Contrarily to their Precambrian counterparts, Modern and Phanerozoic deposits are usually less affected by diagenesis and the environmental conditions likely to be better constrained. Therefore, their investigation may help for the search for morphological and geochemical biosignatures (e.g. iron isotopes) in ancient iron microbial occurrences on Earth but also on other Planets. In particular, many of the case studies presented here show that microstromatolite-like morphologies may be valuable targets for screening potential biosignatures in various rock types.

Keywords: iron microbial mat, Phanerozoic, diagenesis, biosignatures, morphology, Fe isotopes

1. INTRODUCTION

Iron microbial mats have been recognized in a wide variety of Phanerozoic and Modern environments. They are important objects for understanding geochemical cycling of iron on Earth, metal corrosion and they also provide valuable terrestrial analogues for the search of past extra-terrestrial life, especially on Mars.

This paper is not an exhaustive review of iron microbial mats in the Phanerozoic record but a presentation of ongoing researches on deposits in various environments with emphasis on diagenesis as well as morphological and iron isotope biosignatures. The discussion on diagenesis will focus on silica as it is one of the most important host mineral in various fossilized iron biofilms. Case studies are taken from sedimentary (including marine, freshwater and karst environments), low-T hydrothermal and volcanic environments.

2. FOSSIL IRON BIOFILMS: EXAMPLES FROM PHANEROZOIC ENVIRONMENTS

Table 1 summarizes the different case studies of Phanerozoic fossil biofilms that are exposed below.

2.1 Non-cemented fossil iron biofilms

Cryptokarst. Non-cemented filamentous assemblages were found in Late Tertiary cryptokarsts of Ain Khmouda (central Tunisia). Cryptokarsts are not caves but large corrosion pits that are filled with sediments. Karstification proceeds by water percolating *per descensum* through the sediments and dissolution of the limestone bedrock.

Table 1. Field occurrences of fossil iron biofilms and their biofabric. See text for explanation of the biofabrics.

Environment	Age	Location	Host minerals	Biofabric*
Marine pelagic and platform (micritic limestone)	Late Devonian, Jurassic	Tafilat, AntiAtlas (Morocco), NE Italy and Spain	Calcite	μ S, I
Reef (micritic mud mounds)	Devonian (Frasnian)	Diverse locations S Belgium	Calcite	μ S, I
Beach-tidal flats (calcarenite-stromatolithes)	Cretaceous (Cenomanian)	Betrechies (N France)	Calcite	μ S, I, L
Freshwater (fractures and cavities in chert)	Cretaceous – Early Paleogene	Saint-Denis (S Belgium)	Quartz, siderite	μ S, F, L
Subterranean (MVT diapir-type deposit)	Cretaceous?	Djebel Slata (central Tunisia)	Calcite	μ S, F, I
Subterranean (halloysite cryptokarst)	Late Tertiary (Miocene)	Ain Khmouda (central Tunisia)	None	μ S, I
Subterranean (oxidized Cu-Co sulphide ore)	Cretaceous?	Katanga (S Congo)	Quartz	μ S, F, I
Volcanic (basalt vesicles)	Late Tertiary (Miocene)	Mokta El Hadid (N Tunisia)	None	μ S, I
Volcanic (glass veins)	Late Tertiary (Miocene)	Djebel Haddada (N Tunisia)	Amorphous silicates	μ S, I

* μ S : microstromatolitic, I : isolated filaments and other fabrics, L : layered (stromatolithic), F : fenestrate

Cryptokarstification commonly occurs at depth of several meters to tens of meters. A number of mineralogical reactions occur in the sediment and at the interface with the bedrock that may produce differentiation of several mineralogically-distinct horizons [1]. Iron oxides are often observed adjacent to the limestone bedrock. In the Khmouda cryptokarst, the iron layer is ca. 15 cm thick and consists at depth of soft and porous goethite with filamentous and microstromatolitic structures (fig. 1). In shallower parts of the deposits, this horizon resolves in hardened concretionary iron oxides with much less evidence of biogenic structures.

Basalt vesicles. Vesicles in Miocene oxidized basalt piles in the Mokta El Hadid section (northern Tunisia) contain filamentous structures that commonly show an internal μ m-sized hollow (fig. 1).

These examples provide evidences of the preservation of iron microbial mats for a few million years although they are not cemented by stable minerals such as quartz or carbonates. However, their chance of preservation over longer geological times is weak. Basalts are of particular interest since they can readily provide silica through silicate weathering (together with aqueous Fe(II)). Examples of silicified iron biofilms in basalts can be found in e.g. [2].

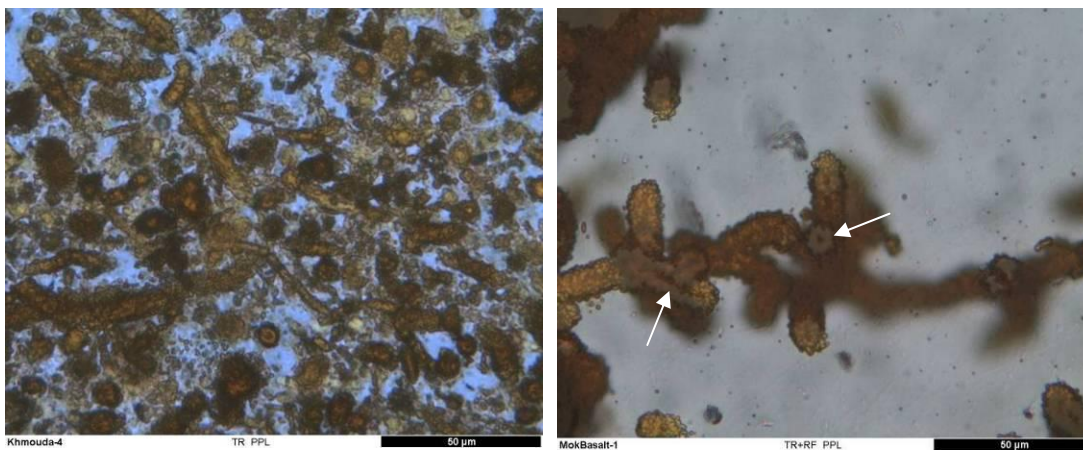


Figure 1. Filamentous structures in resin-impregnated fossil iron biofilms found in cryptokarst (left, scale bar = 50 μ m) and basalt vesicles (right, scale bar = 20 μ m). Arrows point to the central hollow cast of the former organic structure (view in combined transmitted and reflected light).

2.2 Fossil iron biofilms in carbonates

Many microbial structures other than stromatolites have been described in marine and lacustrine carbonates but the biological affinity of some of them still remains uncertain [3]. Fossil iron biofilms in limestones consist of filamentous fabrics and microstromatolitic-like structures found in various environments ranging from the deep sea to supratidal settings. The mineralogy is dominated by goethite and hematite and association with manganese oxihydroxides is common.

Fenestrate filamentous fabric. This fabric has been observed in carbonates from fracture fillings in Djebel Sлата MVT diapir-type ore deposit. It is similar to the fenestrate fabric in iron-silica deposits that will be described in more details later.

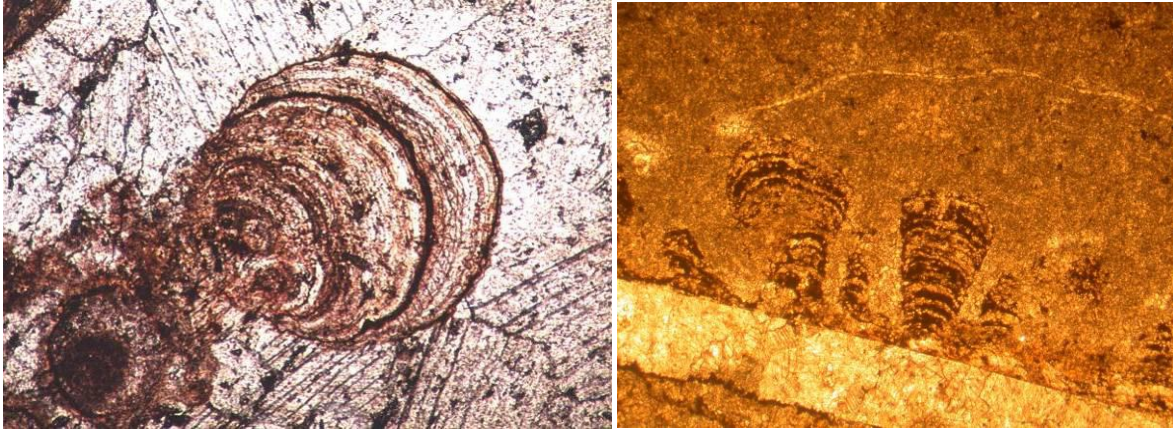


Figure 2. Microstromatolitic structures in Phanerozoic carbonates. Microstromatolites from Devonian carbonates of Belgium (left, field of view is 150 μm wide) and Morocco^[46] (right, field of view is 390 μm wide).

Microstromatolites are small, typically 50 to 500 μm , erect or pendant morphologies ranging from simple asymmetric ooids to more complex multi-lobate, columnar, branching or dendritic structures (fig. 2 and 3). They commonly display growth layering and, less commonly, filamentous radial pattern. Transitional forms are also observed with bundles of filaments resembling shrubs or the *Frutexitis* described in [3]. Variations in morphologies, layering and filamentous pattern may occur in different microstromatolites from the same sample. These variations are also observed in a single microstromatolithe and probably reflect the influence of environmental changes on bacterial growth and iron precipitation.

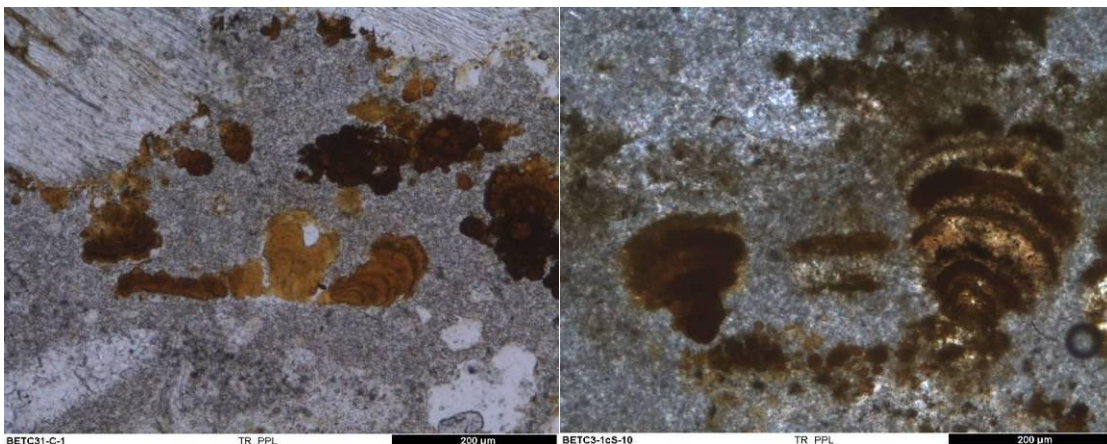


Figure 3. Microstromatolitic structures in a Cretaceous beachrock from Belgium. Left : pendant and erect microstromatolites growing onto bioclasts and micrite, respectively (scale bar = 500 μm). Right : erect microstromatolites with growth zoning (scale bar = 200 μm).

2.3 Fossil iron biofilms in silica

Although fossil iron biofilms preserved in silica have been recognized extensively in the marine hydrothermal environment, records of similar deposits on the continent are quite scarce^[4, 5, 6] and review in^[2]. Numerous biofabrics have been recognized in these deposits (e.g. inventory by^[6]). *Layered fabrics* resemble classical stromatolithes at the macroscopic scale although detailed analysis revealed some extra features. *Pseudostalactitic fabrics* are filamentous or microstromatolitic pendant structures that were further encrusted by minerals (fig. 4). *Fenestrate structures* are generated by sectioning biofabrics that consist of microbial veils connected together and arranged in a typical pattern. It corresponds to the “curtain-like” structure described by Hofmann et al.^[2] and is similar to the pattern described by Sumner^[7] in fenestrate Precambrian microbialites. Each veil is composed of numerous filaments that may no longer be visible due to iron mineralization. Diverse filamentous fabrics may occur in the voids between the veils and onto them. Some mats show gradational transition between the fenestrate and the layered fabric where there are no longer connections between veils that are simply piled up.

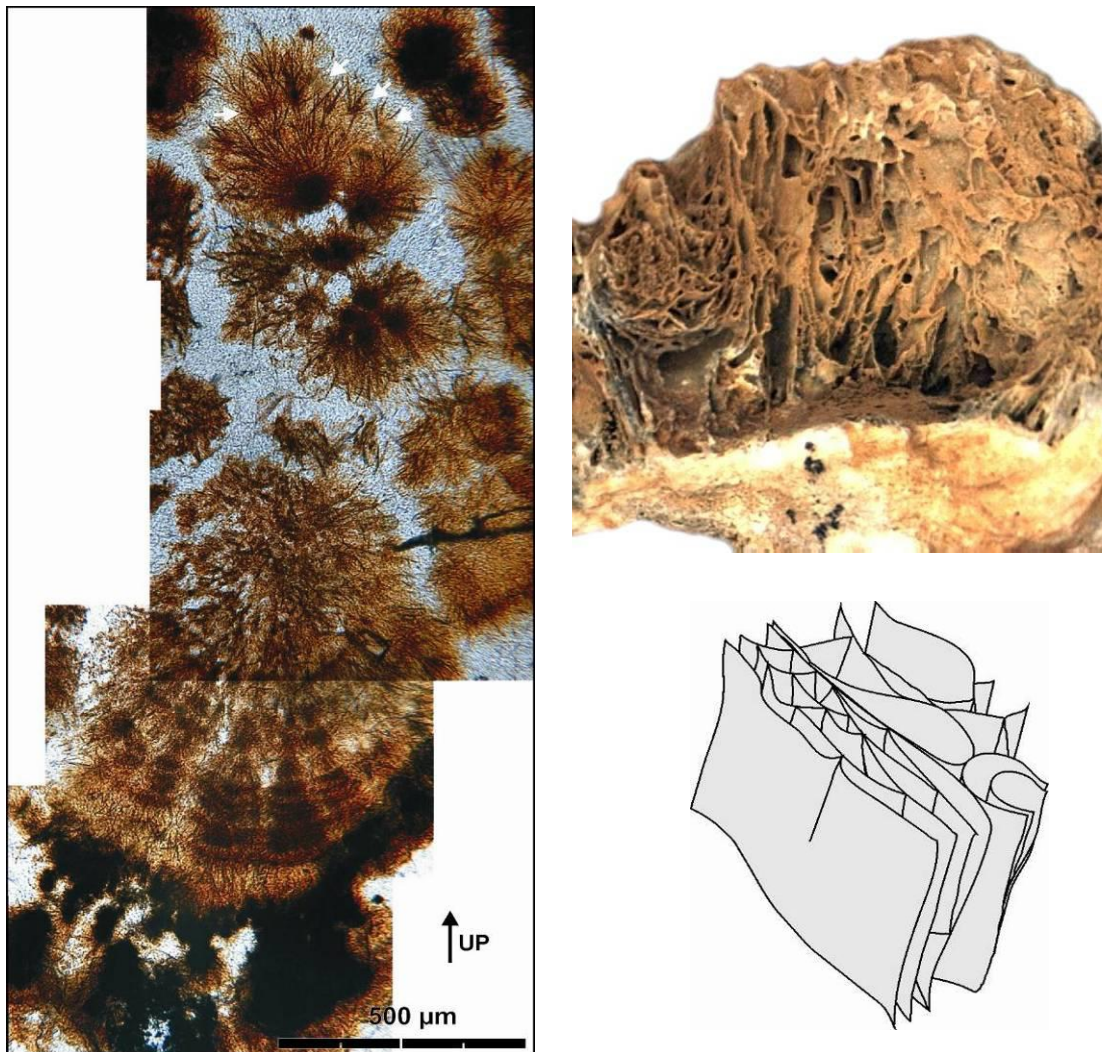


Figure 4. Example biofabrics in the quartz-iron microbialite from Saint-Denis, Belgium. Left : oblique section in pendant microstromatolitic-like structure with filamentous fabric. Arrows point to multiple single-point branchings that induce layering. The groundmass is euhedral quartz. Right: hand specimen (up) and sketch (below) of the fenestrate structure which is here enhanced since quartz encrustation did not fill the voids between the biofilms (the field of view of the hand sample is ca. 10 cm wide).

Iron *microstromatolites* in siliceous deposits are similar to their counterpart in carbonates. However, silica better preserves them over geological times especially when silicification proceeded by the direct precipitation of well-ordered quartz. Striking examples of the wide variety of microstromatolites can be found in the Cretaceous quartz-iron microbialite of Saint-Denis (S Belgium), which formed in low-T sedimentary environment [6]. These allow elucidating some characteristic features such as layering, which may be due to episodes of multiple branching of the filaments that constitute the microstromatolithe (fig. 4).

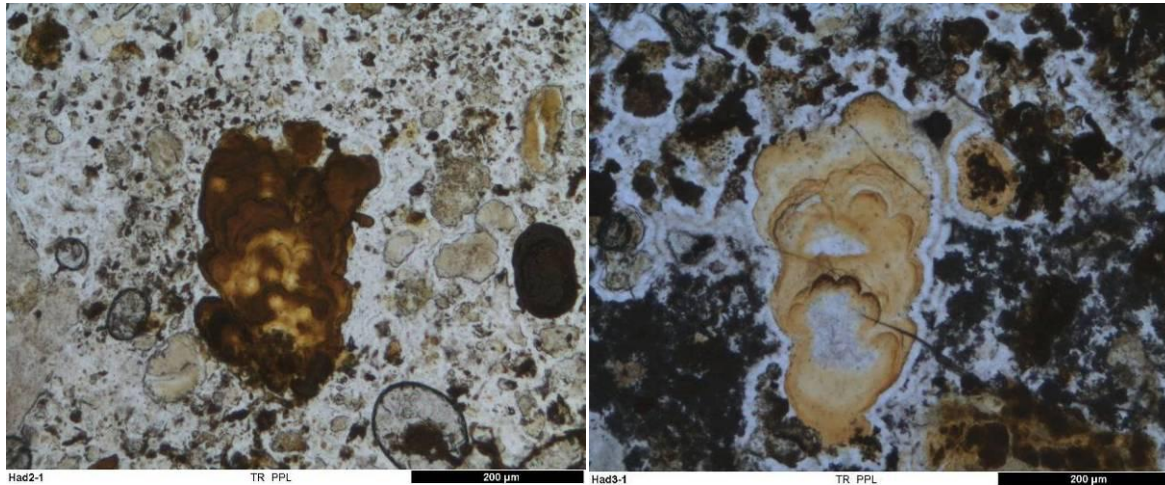


Figure 5. Iron microstromatolitic structures in Mio-Pliocene volcanic glass from N Tunisia (scale bar = 200 µm for all photographs). The groundmass consists of silica minerals ranging from amorphous opal to fibrous quartz.

Iron microstromatolites also occur in volcanic settings as shown by investigations in pechstein-like glass that deposited within fractures in the Miocene granodiorite from Djebel Haddada (N Tunisia). Iron-stained filamentous structures are also found in association. Other nearby deposits, such as the Ragoubet Es Seid red jaspers show no evidence of biofabrics. As inferred from their mineralogy and field relations, these jaspers associated with rhyodacitic rocks probably formed at higher temperature (may be too high for life) than the glass veins of the Djebel Haddada. Large accumulations of iron oxides related to volcanic activity also occur in the area. Iron deposits that formed in small intravolcanic basins further recrystallized and were reconcentrated into massive hematite/goethite duricrusts by pedogenic processes [8]. With the exception of a few pseudostalactites, filamentous and microstromatolitic structures in goethite filling late fractures and cavities [9] there is surprisingly little evidence of fossil microbes in these deposits compared to the vast amount of iron that oxidized. It is likely that in these deposit, biogenic structures were destroyed by the iron enrichment processes that were facilitated due to the absence of early silicification (see further discussion on diagenesis).

3. MODERN IRON MICROBIAL MATS: EXAMPLES FROM CONTINENTAL, NEUTROPHILIC ENVIRONMENTS

Modern and recent iron microbial mats have been documented from various environments (see reviews in [10] and [11]). More recent works include volcanic hot springs (e.g. [12]), oceanic hydrothermal vents (e.g. [13] and [14]), caves (e.g. [15]), marine epibiota [16], acid mine waters (e.g. [17]) and bog iron deposits [18]. Neutrophilic iron microbial mats occur in a number of ground water springs either in natural and anthropic settings such as quarries. Iron-oxidizing bacteria such as the helically stalked *Gallionella ferruginea* and the sheathed *Leptothrix ochracea* form centimetric to decimetric red mats due to ferrihydrite precipitates [19, 20, 21]. Iron oxidation is biologically-driven but inorganic oxidation, which bacteria cannot compete with, also occur depending on oxygen concentration. Variation in microbiota composition is common between mats from different locations but

also within a single deposit. For example, James and Ferris ^[19] observed the change in relative abundance of *Gallionella* and *Leptothrix* as a function of the distance from the spring.

An increasing number of researches, including iron isotopes, are focusing on Modern iron microbial mats mainly because they are potential analogues for past life on Mars (e.g. ^[22]). However, few of them relates about morphology and diagenesis.

Our study focused on neutrophilic iron deposits in Belgium and northern France. Abundant *Gallionella* and/or *Leptothrix* consortia have been found, along with cyanobacteria, diatoms, euglena, etc. In the Trô Maret valley (Liège area, eastern Belgium), iron oxyhydroxides are depositing in the form of centimetric to decimetric stalactites and gelatinous mats on the surface of Paleozoic siliclastics (fig. 6). Water is slowly supplied from an aquifer and it is seen only dripping from the tip of stalactites and flowing as a thin film covering the mats. The stalactites consist of hollow tubes through which water is admitted. Broking the stalactite causes much water to suddenly flow. Obviously, water accumulates in the adjacent rock because it is slowly diffusing through the mat. This ensures optimal exchange between microbes and water together with maintaining microaerophilic conditions that are required for bacterial oxidation of dissolved Fe(II). Although large portions of the mat are exposed to the atmosphere, it seems that microaerophilic conditions are also favored by the (probably inorganic) formation of a tiny protective coating of iron oxides which appears as an oily floating film.



Figure 6. Modern neutrophilic iron microbial mat in the Trô Maret valley (eastern Belgium). Left : view of the mat covering the wallrock. Right : standard 45x35 mm thin section of a resin-impregnated sample from the apical region of a stalactite (original orientation of the stalactite shown by the arrow).

SEM investigation of the Trô Maret mat revealed abundant *Gallionella*-like filamentous structures (fig. 7A, C and D) with varying degrees of encrustation by ferrihydrite. Heavily encrusted filaments commonly show an internal cast of the original *Gallionella* stalks. It is worth noting that organic matter is readily degraded in this kind of deposit, decreasing the chance for biochemical signature preservation. Ferrihydrite encrustation first form an isopachous coating that preserves the helical morphology of bacteria. Further encrustation occurs typically when this coating is thicker than a few micrometers and produces granular and mammillated structures.

The mat fabric, as investigated by the SEM and the light microscope, consist of stacked layers of filamentous assemblages and branching microstromatolithic structures (fig. 7E and F). Filament abundance and/or ferrihydrite encrustation is varying between the layers, either gradually or abruptly, but no general trend was observed. For example, the iron encrustation does not increase with depth in the mat. Filaments are commonly parallel-oriented and they seem to radiate from the center of the stalactite. Layers are separated by thin ferrihydrite films that occasionally connect together to form the fenestrate structures previously described in many fossil microbial mats (fig. 7E). As observed in ancient mats, layers may be disrupted or folded, probably due to localized mass movement or desiccation in the summer. More generally, seasonal changes in water supply induce the observed layering and possibly the variation in microbial morphologies (e.g. filamentous - microstromatolithic).

These iron microbial mats are widespread since they just need water, dissolved Fe(II) and microaerophilic conditions. Water flowing through rocks that contain Fe(II) minerals (e.g. pyrite, siderite, glauconite, olivine, etc.) in “normal” concentration is sufficient for providing nutrient for the iron-oxidizing bacteria. These rocks include

siliclastics (shales, sandstones), limestones, cherts, basalt and other magmatic rocks. Abnormal Fe(II) concentration found, for example, in hydrothermal vents or in water flowing through ore zones is not necessary though iron availability is higher in these environments.

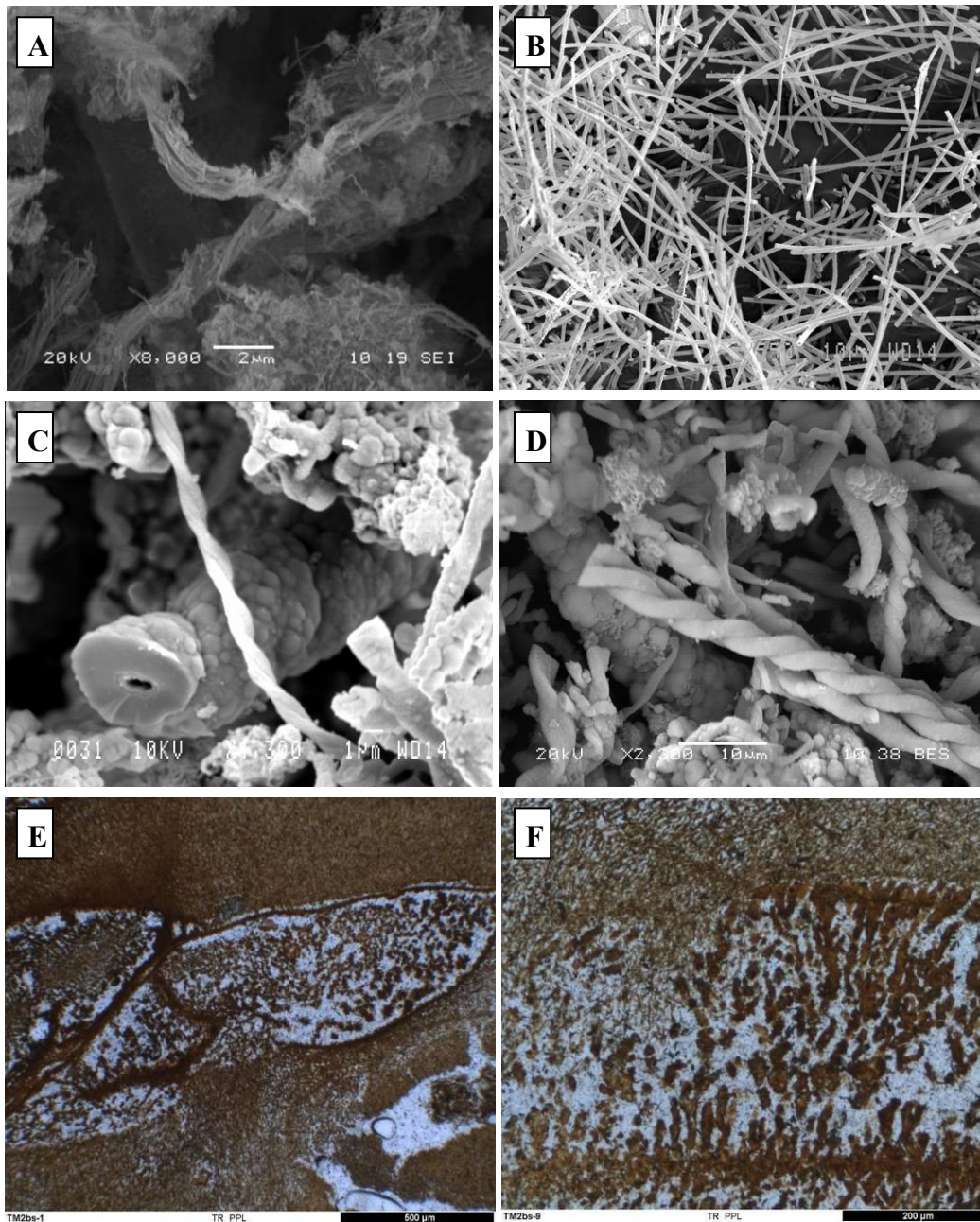


Figure 7. SEM micrographs of Modern neutrophilic iron microbial mats from Belgium. A : *Gallionella* stalks (eastern Belgium). B : *Leptothrix* sheaths. C and D : SEM micrographs of Modern neutrophilic iron microbial mats in the Trô Maret valley (eastern Belgium) showing different stages of encrustation of *Gallionella* stalks by ferrihydrite. E and F : light micrographs of resin-impregnated iron microbial mats from the Trô Maret valley (eastern Belgium) showing the fenestrate structure (E, scale bar = 500 µm) and branching-microstromatolitic morphologies (F, scale bar = 200 µm). In micrographs E and F, the dark groundmass is dense assemblage of *Gallionella* stalks.

4. DIAGENESIS OF IRON MICROBIAL MATS

Microbes are able to produce a wide variety of iron minerals or to be passively encrusted by them^[11]. However, ferrihydrite is the primary mineral precipitating in many Modern microbial mats^[11, 23]. Ferrihydrite is rather poorly ordered and readily, i.e. in a few months or years, transform into more ordered minerals such as goethite or hematite via dissolution-reprecipitation or dehydration processes, respectively^[11, 23]. In natural systems, adsorbed and incorporated compounds such as silica and organic dissolved matter can retard or even inhibit ferrihydrite ordering and its transformation into more stable iron minerals^[24, 25]. In contrast, aqueous Fe(II) fasten mineral transformation of Fe(III) oxyhydroxides, suggesting that the composition of iron minerals is likely to change significantly in environments where redox conditions are variable, such as in soils^[26, 27].

Together with the observed scarcity of microfossils in pure iron deposits, this suggests that morphological biosignatures have greater chance to survive over geological times if microbial mats are rapidly and extensively encrusted by authigenic stable minerals such as silica or carbonates. Many fossil microbial mats are indeed found in such common minerals. Silica is of particular interest since it resists acidic conditions and preserves the detailed microstructure of biofabrics. However, amorphous silica, which is a common precipitate in many hydrothermal and in some diagenetic marine systems, is likely to transform into more stable minerals such as cristobalite, tridymite and finally quartz^[28, 29, 30]. These processes occur by dissolution-reprecipitation and are likely to expose both microfossils and petrofabric to substantial modification.

Since silica does not oxidize nor reduce in natural environments and is therefore not a nutrient for chemoautotrophic bacteria, the question of the possible interaction between microbes, their early precipitates and silica deposition is frequently addressed. Latest findings concerning amorphous silica result from research on hydrothermal vents and sinters and experiments (e.g.^[31, 32]). It appeared from these studies that silica is most of the time inorganically precipitated on the substrate provided by bacteria, with possible enhancement by surface properties of either organic matter or early biogenic mineral.

The precipitation of amorphous silica requires high concentration level, more than 120-140 ppm, which is not usual in sedimentary environments compared to volcanic and hydrothermal settings. However, some fossil mats obviously result from the direct precipitation of well-ordered quartz, such as the quartz-iron microbialite from the Cretaceous chert of Saint-Denis, Belgium^[6]. These mats are less likely to undergo degradation due to diagenesis since quartz is the most stable silica mineral. Heterogeneous quartz precipitation at room temperature requires lower silica concentration, i.e. more than ~10 ppm^[33]. However, a number of physicochemical factors such as dissolved trace elements and surface properties may inhibit quartz nucleation in sedimentary environments^[34].

Silicification of iron microbial mats often occurs early in the diagenesis, as shown, among others, by evidences of flexibility of some organic filaments at the moment the quartz crystals were growing^[35]. This observation suggests that biological activity and silica deposition are not independent but proceed in a continuous sequence. It has been suggested that microbial metabolism inhibits quartz nucleation and possibly decreases the concentration of dissolved free silicic acid due to organic complexing and adsorption of silica onto early biominerals and microbes surfaces^[6]. In addition, researches on quartz corrosion by iron oxides in soil duricrusts showed that Fe(II) oxidation increases the global silica solubility by the formation of an hydrous iron-silica complex^[36]. This suggests that although silica may be initially in sufficient concentration for quartz precipitation, biological activity is able to retard crystal nucleation, especially if iron oxidation occurs. Silicification may then be triggered once biological activity ceases, or more generally, when available surfaces become proper for crystal nucleation. Silica precipitation may also be enhanced by the release of the additional silica deriving from either the destruction of organic complexes or the transformation of ferrihydrite, which usually contains substantial amount of silica. This model needs further research but open new insights for the understanding of the genesis of some ferruginous cherts and jaspers including BIFs (Banded Iron Formations).

Silicified or calcitized iron mats may still undergo diagenetic transformation that obscure significantly biogenicity. For example, iron-encrusted biogenic structures in a Cretaceous quartz-iron microbialite from Belgium were pyritized and then dissolved away^[6], probably by re-oxidation in acid conditions. In some instances, further quartz overgrowth completely occluded the moldic porosity and hence obliterated any biogenic evidence. This was observed in portions of the microbialite where the biogenic structures are just cemented by quartz and not pervasively impregnated. The process was greatly enhanced for the structures that were hollow tubes for which water penetration and chemical exchange were facilitated. However, since silicification initially proceeded by the direct deposition of well-ordered quartz on the biogenic substrate, the biofabric may still be recovered through

analysis of the mineral fabric by using fundamentals of crystals nucleation, growth and geometrical selection ^[37]. This seems to be applicable to other biofabrics, particularly pseudostalactites.

5. MORPHOLOGICAL BIOSIGNATURES

The use of morphological indicators for microbial life is frequently debated, mainly because microorganisms and the structures they produce are rather unfamiliar. At the microscopic scale, cell morphology is quite simple and confusion with inorganic precipitates is therefore facilitated. The fact is that organic (and inorganic) morphogenesis is still unclear in a number of cases and needs further documentation and research ^[38]. Morphology should be used in combination with other bioindicators such as chemistry. However, the latter may not be available, for example due to profound diagenetic modification of the original biochemical composition. In addition, morphology may also undergo significant changes due to fossilization and subsequent geological processes. Many paleontologists have to deal with these situations where morphology is the only remain of past life.

The validity of filamentous, matted and pseudostalactitic fabrics as biosignatures has been discussed by Hofmann et al. ^[2]. Right now, morphological features may be valuable criteria for selecting macroscopic targets for the further search for biosignatures by planetary rovers ^[2, 39]. However, these features, like filamentous and matted fabrics, may not be easily recognized if they experienced complete encrustation by late minerals. In some instances, however, coalescing pseudostalactites due to excessive radial overgrowth yield typical mammillated morphologies that may also constitute interesting targets for the search for past life. These morphologies are for example observed in many goethite or malachite deposits. Contrarily, some filamentous lava deposits and more common boxwork structures are likely to constitute artifacts that may need more detailed analysis. Finally, as discussed earlier, biogenic structures and their original precipitates may be obliterated by diagenesis but can be recovered through the analysis of the petrographic structure providing the latter still reflects the original, direct precipitation of stable minerals. Therefore, biofabrics but also their relations with mineral fabrics on Earth have to be documented as exhaustively as possible.

The fenestrate biofabric appears with its typical pattern by transversal sectioning of some fossil mats. The pattern is observed at different scales in the range of 1 mm to a few cm and is strikingly similar between fossil mats from different environments. It could provide a valuable biosignature if inorganic alternatives such as boxwork structures are ruled out (which is likely to be achieved by analysis of the petrographic and diagenetic context). Morphometric analysis as suggested by Hofmann ^[2] for filamentous fabrics could also be used in this case.

Microstromatolites and related structures are likely to be found sparsely in the bulk of many types of rocks. They may represent more discrete (but perhaps more widespread) bacterial activity compared to stromatolites (in which they are also found) and other microbial mats. Their biogenicity, however, is difficult to assess in a number of cases especially if their filamentous structures is not or no longer visible. Although larger, similar abiotic morphologies have been synthesized ^[40]. However, abiotic theories must be based on experiments that reflect natural conditions (i.e. realistic physical and chemical parameters) and will have to explain the wide range of environments in which microstromatolithic morphologies are found as well as their common association with filamentous fabrics. It is worth noting that none of the 26 samples from ferruginous jaspers collected in the Mio-Pliocene volcanic terrane of Djebel Douharia and Ragoubet es Seid (N Tunisia) showed evidence of biomorphs such as microstromatolithic or filamentous fabrics (likely because temperature was too high for life) but granular and collomorphic iron oxide precipitates.

6. IRON ISOTOPES AS GEOCHEMICAL BIOSIGNATURES

Iron stable isotope has gained intense interest in the last years as a promising technique for geoscientists and others ^[41, 42]. However, significant research is still needed for the application of this technique to biosignatures, especially the understanding of the different fractionation processes that are likely to occur (e. g. ^[43] for the dissolution of minerals). Experiments strongly suggest that isotope fractionation in nature cannot be ascribed to biological processes alone ^[44]. More specifically, Balci *et al.* showed that iron oxidation and reduction is primarily controlled by non-biological factors in microbially stimulated experiments ^[45].

From earlier discussion, it is clear that diagenetic processes, i.e. recrystallisation, may significantly affect the original isotopic composition of iron minerals. Therefore, the search for biosignatures requires careful selection of the material to be analyzed and deciphering its diagenetic history.

The iron isotope composition ($\delta^{56}\text{Fe}$) of 17 Jurassic limestones from the Rosso Ammonitico of Verona (Italy) have recently been analyzed by MC-ICP-MS. Such analysis allowed for the recognition of a clear iron isotope fractionation (mean 0.8 ‰, ranging between -1.52 to -0.06 ‰) on a millimeter–centimeter scale between the red and grey facies of the studied formation ^[46]. After gentle acid leaching, measurements of the Fe isotopic compositions gave $\delta^{56}\text{Fe}$ values that were systematically lower in the red facies residues (median: -0.84 ‰, range: -1.46 to +0.26 ‰) compared to the grey facies residues (median: -0.08 ‰, range: -0.34 to +0.23 ‰). The red facies show clear evidence of iron-bacteria and fungi having passively precipitated iron oxyhydroxides (now hematite) in their sheaths or membranes ^[47]. Lysis of those microbes delivered sub-micrometric iron minerals, which were incorporated into the sediment matrix. Iron was also incorporated in the well-preserved bioconstructions such as microstromatolites and oncoids. The fractionation effects are especially intense in the hardground levels where bacteria and fungi lived and have accumulated. Two hypotheses were considered to explain this strong enrichment in light Fe isotopes ^[48]. Fe isotopic signatures may reflect (1) a possible “vital” effect related to passively adsorbed iron or precipitated iron, or both, within the exopolymeric substances (EPS) in the bacterial sheaths or inside ferruginous microstromatolites, or (2) an effect of assimilation of a $\text{Fe(II)}_{\text{aq}}$ source with a negative Fe isotopic signature followed by a microbially mediated iron precipitation by oxidation characterized by a positive Fe isotopic signature.

These Fe isotope fractionations could therefore be a sensitive fingerprint of a biotic process; systematic isotopic differences between the red and grey facies residues, which consist of hematite and X-ray amorphous iron hydroxides, respectively, are hypothesized to have resulted from the oxidizing activity of iron bacteria and fungi in the red facies ^[48]. This study provides a stepping-stone to further evaluation of the use of Fe isotopes as biogeochemical tracers in old sedimentary records. It also highlights the difficulties involved in the interpretation of iron isotope fractionations in terms of biotic versus abiotic processes. A very important issue is the use of supporting data or direct observations to characterize the biological, (geo)chemical, or physical context in relation to the geological setting. This will become even more pertinent when Fe isotopic studies are expanded to the interplanetary realm, i.e., future studies of real samples from Mars, Jupiter’s moon Europa, or Saturn’s moon Titan ^[48]. The originality of this work has to do with the combination of a sedimentological approach together with a correlative geochemical-isotopic study. Observations of differences in color and petrographic characteristics of the sample matrix, identification of microorganisms, and isotopic “micro-analyses” were integrated from the mm to cm-scale. The results of this study suggest that the Fe isotopes, in combination with complementary data, represent a promising tool when studying biogenic Fe samples formed in the near absence of oxygen or when few preserved fossiliferous traces are obvious (e.g., in Archean-age rocks).

7. CONCLUSIONS

Filamentous, fenestrate and microstromatolithic biofabrics and pseudostalactites can be found in fractures and cavities of virtually all kind of rock on Earth as well as within their matrix. Iron staining makes them easily recognizable under the light microscope and in some cases with the unaided eye. As argued by other authors they provide valuable targets for the search for past life on other planets and meteorites. Comparison between Modern and ancient mats showed some similarities but is still incomplete. Finally, relict organic matter may no longer be present in fossil biofilms and biosignatures based on iron isotopes still need further development, especially the understanding of the diverse fractionation processes and the effect of diagenesis which has to be rigorously documented for each case study.

Acknowledgements

This work is sponsored in part by grant to FB, JDJ, NM and AP by the FNRS (Fond National de la Recherche Scientifique), FRFC N°2.4578.08 « Les isotopes Fe, S, C, traceurs de la médiation microbienne aux interfaces diagénétiques précoces de matrices (carbonatées et siliceuses) rougeâtres phanérozoïques. « Géotraceurs ou biosignatures » de la Vie primitive et en milieu extrême ». We thank Thierry de Putter for providing samples from Congo.

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