IRON MICROBIAL COMMUNITIES IN BELGIAN FRASNIAN CARBONATE MOUNDS

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SUMMARY

The Belgian Frasnian carbonate mounds occur in three stratigraphic levels in an overall backstepping succession. Petit-Mont and Arche Members form the famous red and grey “marble” exploited for ornamental stone since Roman times. The evolution and distribution of the facies in the mounds is thought to be associated with ecologic evolution and relative sea-level fluctuations. Iron oxides exist in five forms in the Frasnian mounds; four are undoubtedly endobiotic organized structures: (1) microstromatolites and associated forms (blisters, veils...), possibly organized in “endostromatolites”; (2) hematitic coccoids and (3) non dichotomic filaments. The filaments resemble iron bacteria of the *Sphaerotilus-Leptothrix* "group"; (4) networks of dichotomic filaments ascribable to fungi; (5) a red ferruginous pigment dispersed in the calcareous matrix whose distribution is related to the mound facies type. The endobiotic forms developed during the edification of the mounds,

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before cementation by fibrous calcite. The microbial precipitation of iron took place as long as the developing mounds were bathed by water impoverished in oxygen.

1. INTRODUCTION

"Quand sur toi leur scie a grincé,
les tailleurs de pierre ont blessé
quelque Vénus dormant encore,
et la pourpre qui te colore
te vient du sang qu'elle a versé".
Alfred de Musset, Poésies Nouvelles.

For more than one century, geologists have wondered about the origin of the red color responsible for the fame of Belgian Frasnian limestone ("red marble"). These red marbles come from different levels of the carbonate mounds (for instance, the red stromatactis facies, Pl. 1/1). Although the mineralogical nature of the hematitic pigment has been known since Delhaye (1908), its origin remains unclear (extended review in Boulvain, 1993). The various hypotheses can be classified into two groups: a detrital pigment of continental origin (Delhaye 1908, Lecompte 1936) or a pigment formed in situ by the metabolism of microbial communities (Monty *et al.,* 1982, Boulvain, 1989). The influence of microbial communities on sedimentation is now largely taken into account (Riding & Awramik, 2000). This paper investigates the origin of the pigment and illustrates the importance of microbial communities.

2. STRATIGRAPHY

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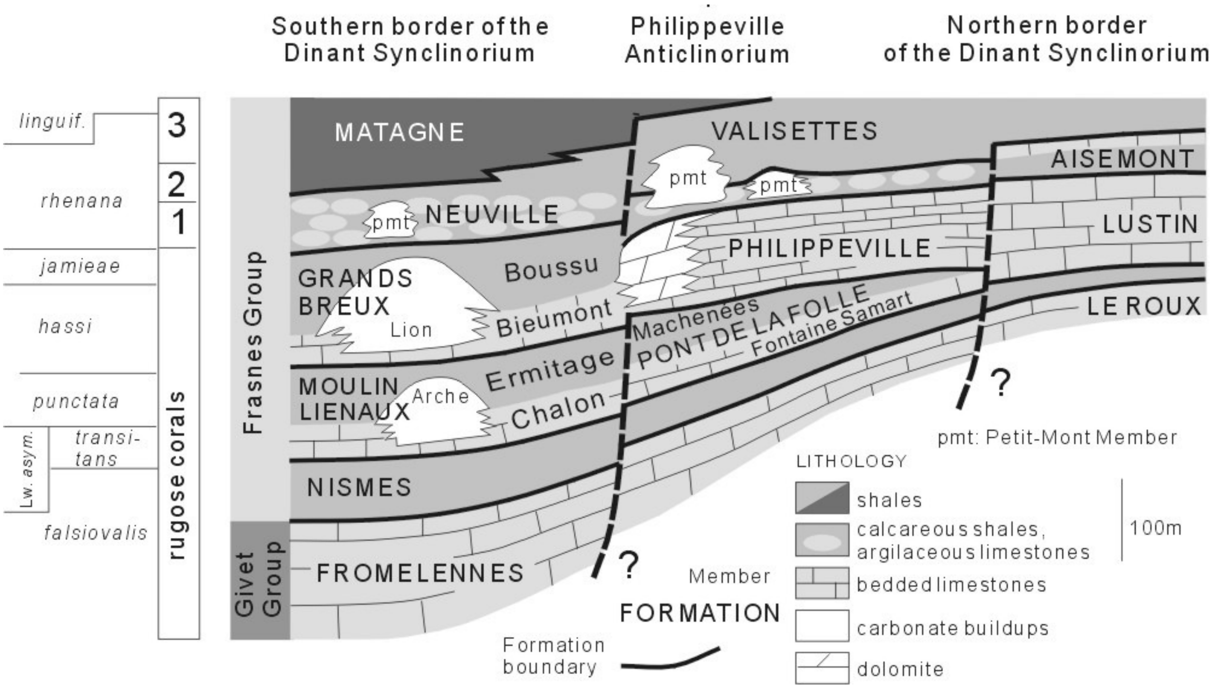
In Belgium, Frasnian carbonate mounds occur at three stratigraphic levels (Fig. 1) : the Arche Member (*transitans-punctata* Zone), Lion Member (*hassi* to *jamieae* Zone) and Petit-Mont Member (*rhenana* Zone) (Boulvain *et al.,* 1999). The Arche mound belongs to the first mound interval, exposed at the southern border of the Dinant Synclinorium (Figs. 1, 2). The Lion mound is the lithostratotype for the middle level, known from the southern border of the Dinant Synclinorium and recently recognized in the southern part of the Philippeville Anticline. The "Les Wayons, "Hautmont", "Les Bulants", and "Beauchâteau" mounds belong to the upper level of mound occurrences (Petit-Mont Member) exposed in the Philippeville Anticline.



- Fig. 1. N-S section in the Frasnian basin, before Variscan structuration.

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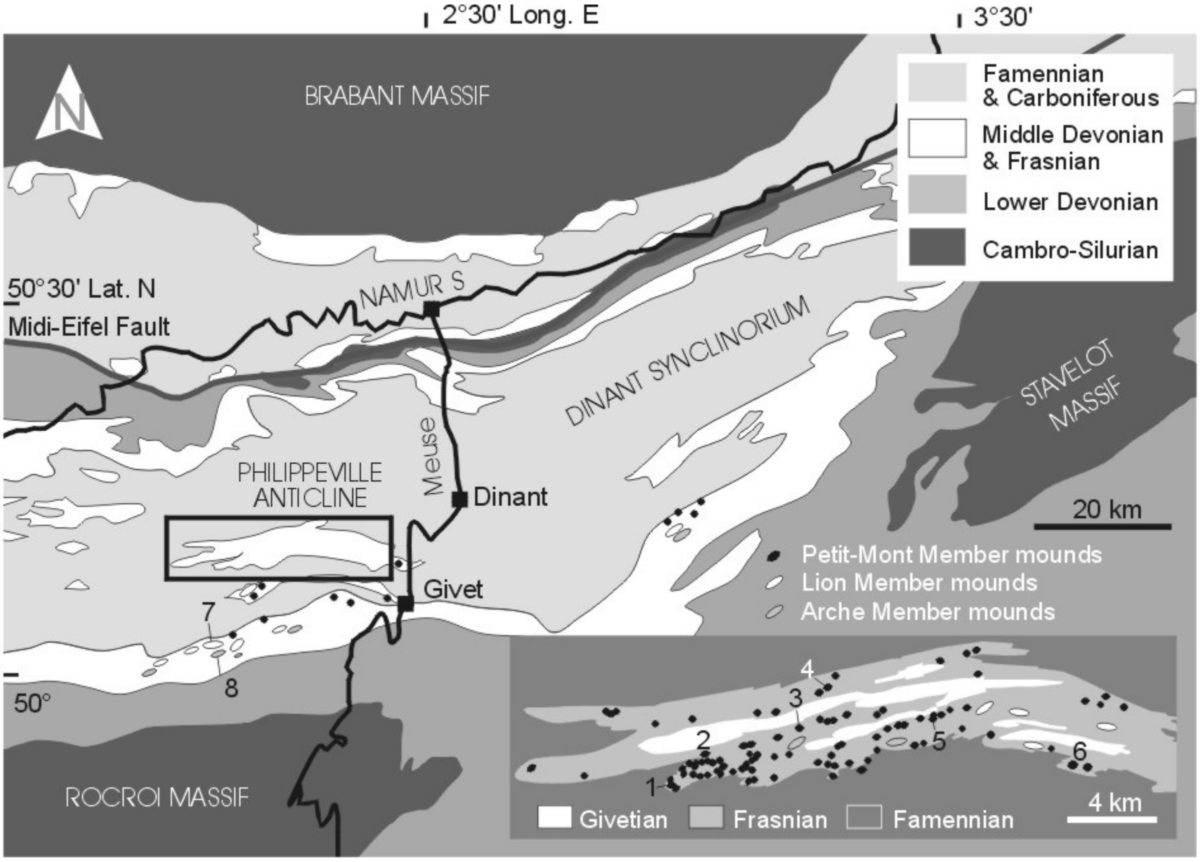


- Fig. 2. Geological map of the Philippeville-Couvin area, with location of Frasnian carbonate mounds. 1: Beauchâteau (Senzeilles); 2: Les Bulants (Neuville); 3: Tienne à l'Gatte (Philippeville) ; 4 : Les Croisettes (Philippeville) ; 5 : Rochefontaine (Franchimont) ; 6 : Hautmont (Vodelée) ; 7 : Nord (Frasnes) ; 8 : Arche (Frasnes).

3. A SHORT VIEW ON SEDIMENTOLOGY

3.1 Petit-Mont Member

3.1.1 Distribution and size of mounds

About fifty "red marble bioherms", are known from the Philippeville area (Fig. 2). Outcrops are of outstanding quality, with quarries exposing large wire-cutted flanks (Pl. 1/2). Mounds of the Philippeville area form an "inner belt", whereas those occurring at the southern border of the Dinant Synclinorium represent an "outer belt". Mound diameters range from 100 m to several hundreds meters with a thickness ranging from 40 to 80 m. The Petit-

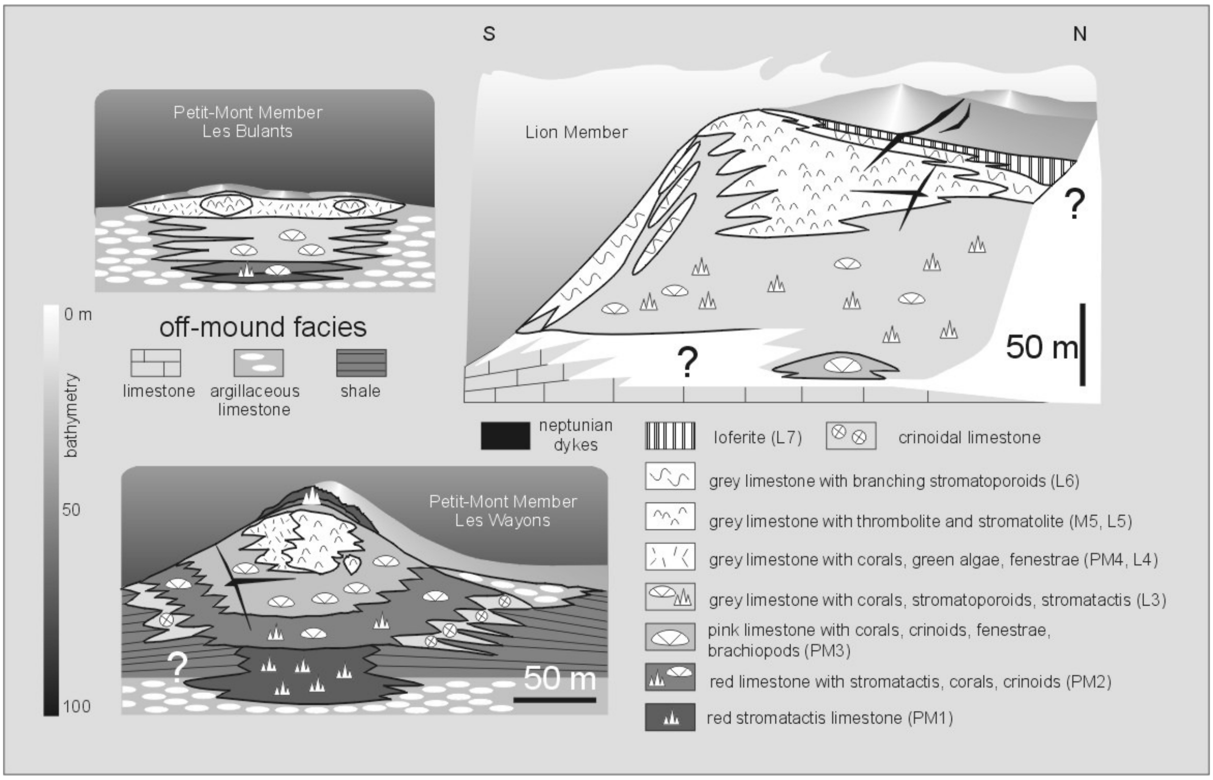
Mont mounds are covered by the Valisettes Formation which is overlain by the Matagne Shale, corresponding to a worldwide drowning phase of Devonian buildups.

3.1.2 Facies

Mounds typically start below the photic zone/storm wave base and build towards shallower water environments. Above an argillaceous limestone substrate, the first mound facies (Fig. 3; Pl. 1/1) consists of spiculitic wackestone with stromatactis (PM1, from Petit-Mont), becoming progressively enriched in crinoids and corals (PM2), then in peloids, stromatoporoids and cyanobacteria (?) dominated deposits, exhibiting fossil structures such as *Sphaerocodium* and *Girvanella* (PM3). PM4 consists of algal-coral-peloid wackestone and packstone with Codiaceae-Udoteaceae and thick algal coatings. A core of algal and cryptalgal bindstone (PM5) sporadically occurs within large mounds. The uppermost part of these mounds may show a recurrence of facies PM2 and PM1. PM1 to PM3 are red colored by hematite; PM4 and PM5 are grey.

The transition from an aphotic to a photic cyanobacterial (?) zone can be drawn along the succession PM2 to PM3; the transition from a cyanobacterial to a green algal photic zone, by PM3 to PM5. The storm wave base is reached within PM3 and fair-weather wave base within PM5. This paleobathymetric interpretation suggests a depth of 100-150 m for the deepest part of PM1.

Based on geometry and facies architecture, three types of mounds can be distinguished: (1) the “Les Bulants” mounds (inner belt) display a continuous vertical facies succession (PM1-2-3-4-5) and virtually no relief (Fig. 3); (2) the “Les Wayons” mounds (inner belt) again show PM1-2-3-4-5 succession, but exhibit a distinct relief with steep flanks and bioclastic talus; and (3) the “St-Rémy” mounds (outer belt) constituted by PM1 and PM2, but bioclastic flank deposits are not observed. The Les Bulants-Les Wayons-St-Rémy succession indicates the deepening of a ramp. PM1 to PM3 seem to correspond to a highstand system tract, while PM4 and PM5 could result from a shelf margin system tract.



- Fig. 3. Sedimentological models of Belgian Frasnian carbonate mounds.

3.1.3 Diagenesis

Spar cementation begins with a radiaxial synsedimentary cement (1) (Pl. 1/4). A fringe of meteoric phreatic cement, at first non luminescent (2), then with a bright orange luminescence (3) occurs in all mounds. It is contemporaneous with a non-luminescent pervasive cement of grainstone deposited closer to the littoral area (N of Namur Syncline). Differentiation between the (reducing) mounds and the (oxidizing) littoral area results from a better aquifer circulation in sedimentary bodies close to the recharge area. Burial cements (4) occlude all the remaining porosity and are contemporaneous with the opening of a Variscan fracture system (Boulvain *et al,* 1992).

3.2 Lion Member

3.2.1 Distribution and size of mounds

Lion Member mounds crop out along the southern border of the Dinant Synclinorium (Fig. 1, 2), from the French border to the Rochefort area and in the south-eastern part of the Philippeville Anticline. Good outcrops of these large buildups are uncommon (Nord and Lion quarries near Frasnes and La Boverie quarry near Rochefort). These mounds extend over a km scale and are 100 to 200 m thick. They are overlain by the Boussu-en-Fagne Shale.

3.2.2 Facies

Lion mounds start above argillaceous limestone including rugose corals and crinoids. The lower mound facies consists of grey to pink wackestone to grainstone with stromatactis, stromatoporoids, brachiopods and corals (L3). Peloids and cyanobacteria (?) are common. This facies is followed by lenses of algal-coral-peloid wackestone/grainstone rich in green algae and thick algal coatings (L4), followed by microbial bindstone and bafflestone (L5). In the back mound area, branching stromatoporoid rudstones occur (L6), with thick algal coatings and discrete green algae. This facies passes into fenestral limestone, rich in calcispheres (L7). Beds of bioclastic limestone prograde in front of the mound. By comparison with the Petit-Mont Member mounds, the initiation of Lion mounds was quite shallow, directly located in the photic zone. Mound growth covered a full TST-HST-LST cycle, possibly related to an oxygenated platform margin setting.

3.3 Arche Member

3.3.1 Distribution and size of mounds

The Arche Member mounds crop out similarly to Lion Member mounds. The best outcrops are in the Arche quarry near Frasnes and in the La Boverie quarry. Arche mounds have dimensions roughly intermediate between Petit-Mont and Lion mounds.

3.3.2 Facies

The facies succession of the Arche mounds shows similarities with the “Les Wayons” type mounds of the Petit-Mont Member. Overlaying a basal level of rugose corals, mound growth started with a pinkish coral-crinoid-brachiopod-zebra coverstone (A3), with peloids, sponges and cyanobacteria (?). However, the main part of the buildups consists of algal-coral-peloid wackestone/packstone (A4) and algal/cryptalgal bindstone (A5).

4. MATERIAL

Nearly 2000 samples coming from all facies of the carbonate mounds were examined. The best samples, showing either the distribution or the morphology of the red pigment were selected. In order to identify the nature, concentration, and major element composition of the pigment, electron microprobe and X-ray fluorescence (Philips PW1404 spectrometer, Rh cathode) analyses were performed.

The red pigment follows two different patterns: (1) dispersed hematite in the matrix and (2) microbial remains (coccoid and filamentous) in cavities and fractures fillings.

5. THE DISPERSED PIGMENT

The intensity of the red pigmentation is a characteristic property of the facies, as is the abundance of stromatoporoids or of cyanobacteria. In the Petit-Mont Member, the intensity of pigmentation decreases from PM1 to PM5. In the Arche Member, the same type of decrease is observed when passing from A3 to A5. In the Lion Member, only some limestone lenses at the base of the mound are red coloured. Surrounding sediments such as argillaceous limestone, shale, nodular shale, are devoid of hematitic pigment.

When the transition between two facies is materialized by a well-defined surface, this discontinuity usually separates two zones of different colour: This contact is particularly spectacular between the grey limestone of the upper part of the Petit-Mont Member mounds (PM5) and the upper "griotte" (PM2-1).

The univocal correspondence between facies and colour has only a few exceptions:
(1) bindstone PM5 are generally grey. Yet, locally, in Beauchâteau, a PM5 facies is red. The corresponding section is, however, located in a peripheral position compared to the usual location of the facies;
(2) PM3, so abundant in the middle part of the mounds is generally pinkish, but in Hautmont, some samples are grey. These "aberrant" examples are systematically located at the edge of the usual distribution zone of the corresponding facies.

Let us now examine the distribution of pigmentation on a smaller scale. How is it distributed within a single sample, homogeneous at the microfacies point of view?
(1) in the red stromatactis limestone (PM1), the pigment distribution is irregular and heavily pigmented zones are often observed around cavities;
(2) sometimes, a thin discolouration on both sides of fractures or, quite the opposite, a more intense red colouring around a fissure is observed;
(3) the colour of internal sediments contrast clearly with the host sediments and are thus easily recognized. Several cases are observed:

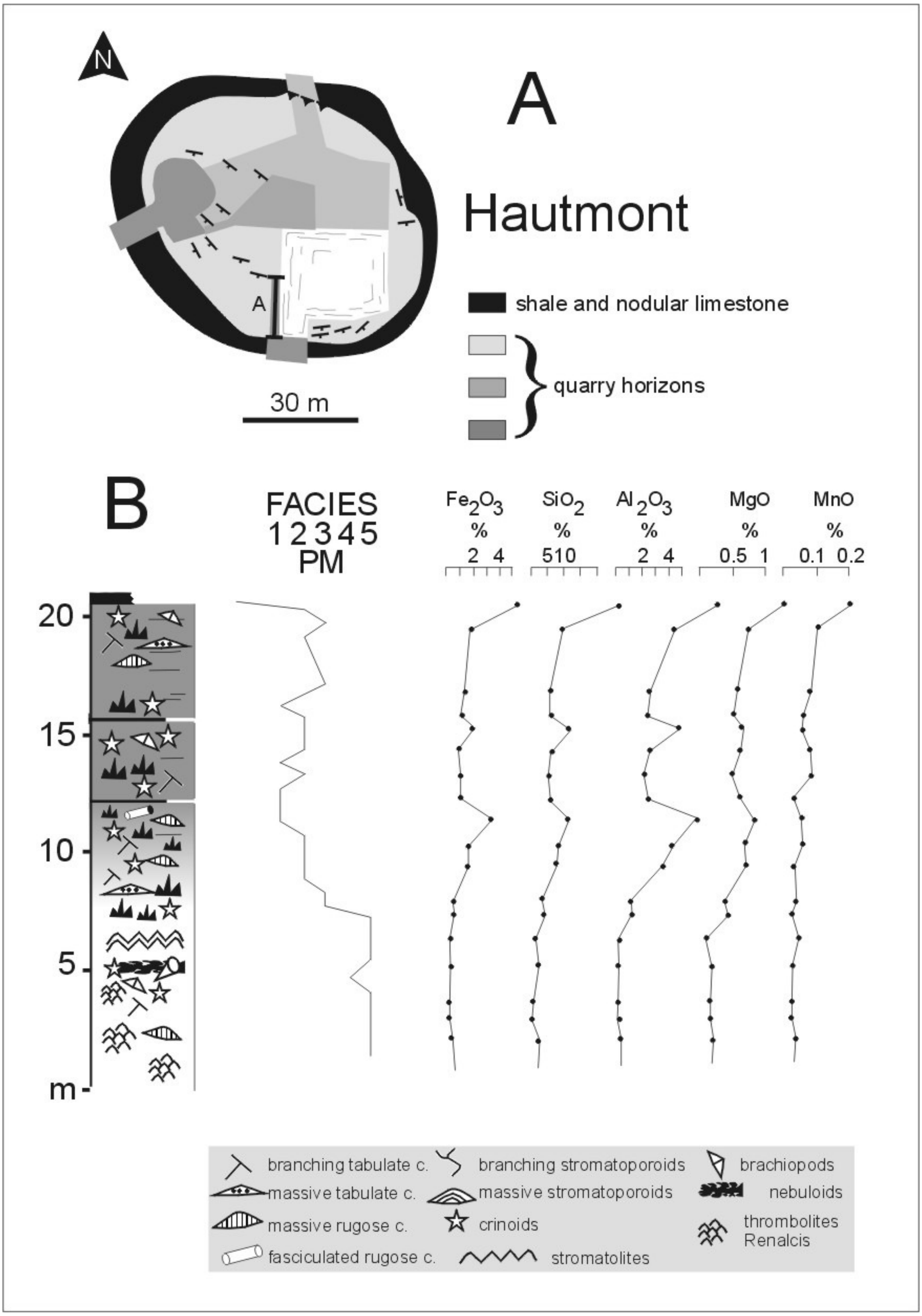
- in the red limestone, the colour of internal sediments is generally slightly lighter than the colour of the primary sediments. This seems related to neomorphism: the intensity of red decreases when neomorphism intensifies;
- in red or grey limestone, internal sediments with an intense red colour, contrasting with the primary sediment, are common (Pl. 2/1). Under the microscope, partially disaggregated hematitic filaments are observed. These filaments are not observed in the primary sediment;

- strongly red coloured peloids occur in microsparitic internal sediments (Pl. 1/5) (also described by Playford, 1984 p. 208 in Devonian buildups of the Canning Basin, Australia);

(4) pressure-solution stylolithes of red limestone frequently show a heavy red colouring. In rare examples, greenish joints are observed but laterally, they pass towards dark red. Grey limestone of the upper part of the mounds exhibits stylolithes without particular colouring.

(5) some particles, and in particular crinoid articles are frequently pigmented in red, even in the grey facies; the pigment concentrates in the intraparticular porosity.

The results of x-ray fluorescence analyses of a range of facies for section A from Hautmont mound (Petit-Mont Member) are presented in Fig. 4. Grey limestones (PM4 and 5) contain very little iron, contrary to red limestone (PM1 and 2) which have contents as high as 5% Fe_2O_3, with an average of about 1,8%. The analysis of magnesium, aluminium and silicon shows that the iron content varies in the same way as the clay content, as was mentioned already by Delhaye (1908).



- Fig. 4. A: horizontal sketch of the Hautmont quarry, with location of section A. B: X-ray fluorescence analyses of samples from section A, Hautmont mound, Petit-Mont Member, Vodelée. Facies 1, 2, 3, 4, 5: see text.

6. MICROBIAL COMMUNITIES

Microbial morphologies are observed in internal sediments and fillings of (1) fenestrae, stromatactis, organisms tests and (2) neptunian dykes and sills.

Three types of microbial associations are observed:

- veils, hematitic blisters and millimetre-length microstromatolites (Mamet & Boulvain, 1988) (Pl. 2/2, 2/8);
- straight non-dichotomic hematitic filaments and coccoids (Boulvain, 1989) (Pl. 2/4);
- networks of dichotomic filaments of variable diameter (Pl. 2/5, 2/6).

Blisters and non dichotomic filaments can be associated, as veils with microstromatolites and networks of dichotomic filaments or microstromatolites with coccoids. Nevertheless, the three associations are generally observed separately.

6.1 Veils, blisters and hematitic microstromatolites

In the Petit-Mont Member, these forms are recognized mainly in the largest cavities: neptunian dykes and sills (Mamet & Boulvain, 1988). These cracks generally cut into red limestone, are of metre- to decametre-scale length and decimetre-scale opening (Pl. 1/6). In the Lion Member, the same structures are also recognizable in zebra with pluricentimetric openings (Pl. 1/3). The bulk of the cements in these structures consists of radiaxial cement (stage 1, Boulvain *et al,* 1992).

6.1.1 Morphology and chronology

The various structures observed seem chronologically related: by order of succession:

- pinkish veils of centimetric extension and approximately 100 µm thick, cross the cavities and delimit coarse spheric “voids” with centimetre-scale diameter (Pl. 2/2). In cathodoluminescence, cementation is centripetal, starts from the veil and progresses towards the center of the voids (Mamet & Boulvain, 1988);

- blisters grow from these veils or are observed as isolated colonies; their diameter is 10 to 50 µm, with a thickness of 10 µm. Walls are pinkish like the veils, and completely or partially hematitic, or greyish and nearly devoid of iron oxide. Their internal filling is made of centripetal calcite with the diagenetic sequence 2-3-4. Very occasionally, lamellar hematite is observed;
- microstromatolithic colonies are (1) isolated colonies, (2) grow from a veil, or (3) from the wall of a cavity. These small colonies were described under various names in the Belgian Frasnian carbonate mounds: "New gen. 3" (Tsien, 1979), "endostromatolite" (Monty, 1982), "épiphytale" (Biron *et al.,* 1983). They are columnar structures reaching a few mm height (Pl. 2/8), show a thin internal lamination, often crenulated, with an individual thickness oscillating between 4 and 10 µm. Laminae are individualized by a thin hematitic layer and form an alternation of several hundreds of µm wide clear and dark bands (Pl. 2/8).

In the largest cavities (plurimetric fractures), microstromatolites can form superstructures called "endostromatolites" by Monty (1982). This is a radiating arrangement of decimetre-scale mammillated masses. Each individual microstromatolite is separated from its neighbour by 1 to 5 mm of sparite. When these “endostromatolites” are covered by internal sediments, their hemispherical outer surface is clearly defined.

6.1.2 Mineralogy

Under the lenses, on polished surface, the microstromatolites appear generally red. In thin section, they consist of an alternation of pinkish and transparent laminae (Pl. 2/8). Under the scanning electron microscope (after diluted HCl attack), concentric zones with variable amounts of submicronic hematite hexagonal plates are recognized in the sparitic cement. Locally, mineralization is pervasive. The veils and blisters are similarly constituted.

Under cathodoluminescence, the transparent laminae are composed of tiny sparite crystals, with orange low and bright luminescence. The darker ones have a weak luminescence. The tiny crystals seems to belong to stages 2 and 3 of the diagenetic sequence of Frasnian mud mounds (Boulvain *et al,* 1992).

To check if the bright luminescence of transparent laminae was produced by the same activator (Amieux, 1982) as the luminescence of the automorphic sparitic calcites, microprobe analyses were performed on a microstromatolite (Les Croisettes quarry, Petit-Mont Member). These analyses show that the main activator is manganese.
FeO: undetected; MnO: 0.85%; MgO: 0.6%; CaO: 95.6%; SrO: 0.05%.

This corresponds rather well to the average analysis of "stage 3" calcites, with a slightly lower MnO content. Two analyses performed on a dark lamina show the absence of manganese and the presence of small quantities of FeO, close to the detection limit of 0.05% (confidence interval of 3 σ).

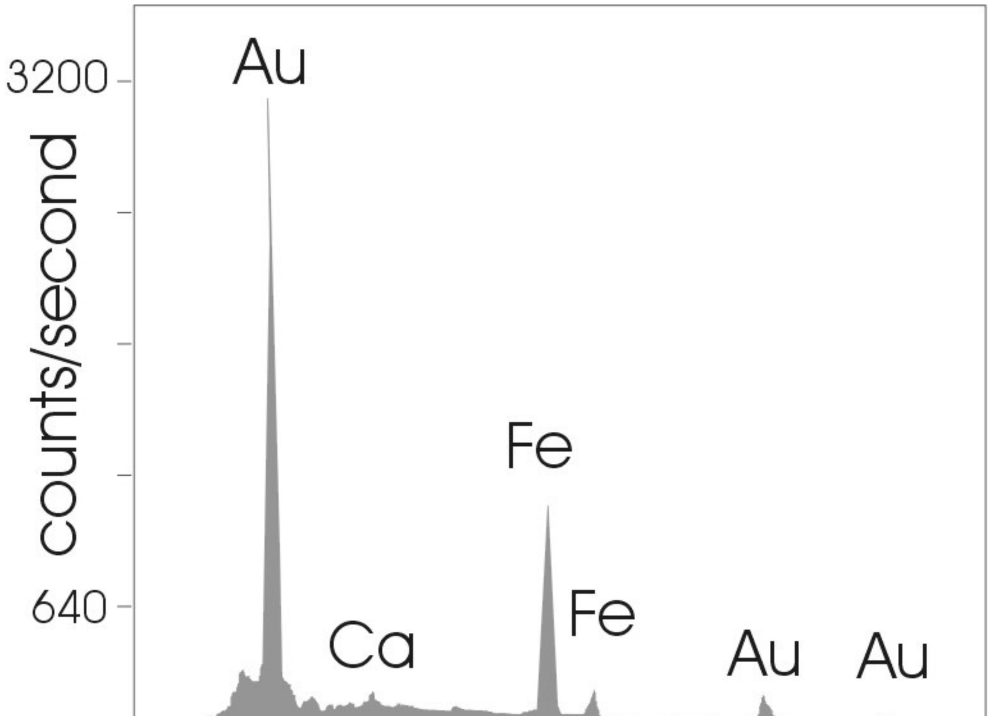
6.2 Hematitic non-dichotomic filaments and coccoids

These forms are rather uncommon in the mounds. They were observed only in the Petit-Mont Member, in the internal filling of a *Receptaculites*, in facies PM3 (Rochefontaine quarry) (Pl. 1/5).

Macroscopically, the internal sediments consist of deep red mm-length peloids, pinkish or grey microspar and sparite. A thin section shows several types of peloids: fecal pellets 0.3 to 1.0 mm in diameter, with an internal structure, close to *Favreina* pellets (Herbig, 1993); 60 µm rods (probably also fecal pellets); peloids without internal structure with a diameter of 150 µm; and finally peloids with diffuse external borders of 60 µm; all these peloids are partially or completely hematitized. Irregular diffuse aggregates, from 2 to 4 mm in diameter, with a red colour are also observed (Pl. 2/3). These aggregates consist of a loose felt of reddish filaments, rather rectilinear, not dichotomic, from 1 to 3 µm in diameter and several tens of µm in length, accompanied by 5 to 10 µm spheres (Pl. 2/4). These filaments and coccoids are cemented by fibrous (1) and granular sparite (2). Some embryonic blisters are locally observed (see above).

Various tests were tried to visualize the three-dimensional structure of the felt: polished samples were attacked by diluted acid solutions (HCl 0,05 M, acetic acid 1 M), then dried, metal coated and observed under scanning electron microscope. Broken samples without any acid attack were also studied. Unfortunately, no filamentous structures or coccoids could be detected; at most, loose arrangements of hexagonal hematite plates, delimiting a circular structure on the surface of the sample were observed. It thus seems that the hematite crystals are not welded together and that by dissolving the calcite, the support maintaining their cohesion in the form of filaments or coccoids is loosened.

A microprobe analysis (Fig. 2) of a filament showed that it contains only iron and no detectable manganese.



- Fig. 5. Microprobe analysis of a filament from sample RFX, Rochefontaine quarry, Petit-Mont Member, Franchimont. Metal coating with gold.

6.3 Networks of dichotomic filaments

These forms were observed in neptunian dykes and sills of carbonate mounds from the Petit-Mont Member (Hautmont, Les Croisettes), in internal sediments of stromatactis (Tienne à l'Gatte, Pl. 2/1), and in zebra from a mound of the Lion Member (Nord quarry, Pl. 1/3).

These networks of several millimetres resemble spider webs. They are often associated with microstromatolites, passing from one to the other, sometimes surrounding each columnar structure (Pl. 2/5). They also encrust the walls of the cavities, even on a first generation of radiaxial cement. They can form isolated structures, without any microstromatolites. The dichotomic filaments, of variable diameter, 3 to 15 µm, have many protuberances and irregularities (Pl. 2/6). Their mineralization is usually intense. In the internal sediments of stromatactis, the networks are dismantled: only loose fragments of dichotomic filaments are recognizable.

7. UBIQUITY AND DIVERSITY OF IRON MICROBES

Iron microbes are microorganisms that are able to oxidize and/or deposit iron (or manganese) oxides extracellularly or, sometimes, intracellularly (Staley, 1989). These microbes are widespread in nature (Pringsheim, 1952, Ghiorse, 1984b, Konhauser, 1998). They occur in environments such as sea beds (Cowen & Silver, 1984; Jannasch & Nelson, 1984; Karl *et al,* 1988), the pelagic aggregates and pellets of the oceans (Cowen & Silver, op. cit.), the marshes, lakes, rivers (Ghiorse, 1984 a), industrial effluents, grounds (Nealson, 1983), wells, systems of water conveyance and drainage (Harder, 1919; Van Veen *et al,* 1978), ferruginous springs (Pringsheim, 1952), deserts, and even as symbionts of invertebrates (Gillan & De Ridder, 1997).

This ubiquity is matched by a large taxonomic diversity, since the “group” of iron microbes encompasses some cyanobacteria (Knoll & Awramik, 1983: cf. stromatolithes of Gunflint Iron Formation, Proterozoic of Ontario; Knoll, 1986), protists (cf. recent examples: euglenidae, chlamydomonadaceae; Pringsheim, 1952), fungi (cf. Jurassic iron oolites from the iron ore of Lorraine; Dahanayake & Krumbein, 1986, in the desert varnish, in partnership with lichens, cyanobacteria, etc...; Krumbein & Jens, 1981) and of course, several types of bacteria (Staley, 1989; Konhauser, 1998).

8. TAXONOMY AND ENVIRONMENTAL IMPLICATIONS

First, it should be noted that the majority of bacteria (as well as many other microorganisms) cannot be identified only on the basis of their morphology (Brock *et al.,* 1994). Despite this inconvenience, the simple observation of microorganisms in ancient environments, regardless of their taxonomy, may nevertheless bring important environmental informations. For example, the Frasnian microorganisms must have produced anionic exopolymeric substances (EPS), like the present-day microbes (EPS are also called sheaths or capsules). These EPS are known to readily bind a variety of metals such as iron and manganese (Mc Lean *et al.,* 1996). So, an abundance of EPS-producing microbes in an iron-rich environment will inevitably lead to the deposition of iron minerals (under appropriate redox conditions).

Although morphology alone is not sufficient to identify most of the microorganisms, some filamentous microbes may be recognized and differentiated on a morphological basis (Strohl 1989). But it should be remembered that such identifications remain tentative because many microbes are still to be discovered and because the cultured species of bacteria represent only a minor fraction of the existing diversity (Service, 1997). In this study, the non-dichotomic filaments of the association filaments/coccoids (Pl. 2/4) resemble the bacteria of the *Sphaerotilus-Leptothrix* group (iron-oxidizing bacteria). The Frasnian hematitized filaments show sheaths comparable to these organisms. *Sphaerotilus* precipitates only iron, whereas *Leptothrix* precipitates both iron and manganese (Van Veen *et al,* 1978). The iron oxide precipitation takes place on the sheath, within the EPS.

Bacteria of the *Sphaerotilus-Leptothrix* "group" grow at pH 6.5 - 8.1 (Van Veen *et al,* 1978), and at temperatures between 15 and 40° C (ibid). These bacteria are microaerophilic (Van Veen *et al*, ibid; Ghiorse, 1984 b). They live in environments where iron and manganese are available in reduced forms, but where the redox potential is sufficiently high so that oxidation can occur. These environments can be interfaces within sediments or water bodies impoverished in O_2 (Nealson, 1983), possibly as a consequence of strong organic matter concentration (Pringsheim, 1952). It can also be microenvironnements (macroparticules or pellets in the water column: Cowen & Silver, 1984), where the iron bacteria are associated with other micro-organisms which maintain a relatively low O_2 concentration (Cowen & Silver, 1984).

Coccoids (Pl. 2/4) resemble the Siderocapsaceae. These iron bacteria are usually not observed in marine environments, except by Cowen & Silver (1984), who described coccoid bacteria in macroparticules within the water column, at 120 m of depth and by Karl *et al.* (1988), in bacterial mats near hydrothermal vents.

Microstromatolites do not have (as far as we know) known Recent equivalents in the marine environment. These organisms can be associated with coccoids or with webs of dichotomic filaments. The Frasnian microstromatolites are morphologically close to the Tertiary structures illustrated by Kretzschmar (1982) and identified as fungi.

The networks of dichotomic filaments show cell diameters that are comparable to those of Recent aquatic filamentous fungi (chytridiomycota and deuteromycota) and Chromista (oomycota) (Cavalier-Smith, 1998). Verrechia (2000) as well as Krumbein (1969) noted that in desert environments, as in soils, fungi play a major role in the precipitation of

Mn and Fe. Filamentous fungi and Chromista are known to be present in marine environments (Kohlmeyer & Kohlmeyer, 1979).

9. SEDIMENTOLOGICAL IMPLICATIONS FOR FRASNIAN MOUNDS

The iron microbes are preserved in two types of contexts:

- within internal sediments in fenestrae and stromatactis: iron-bacteria, less commonly fragments of fungi, often associated with peloids. In this case, the development of bacteria can be related to the existence of microenvironnements rich in organic matter, as described in recent seawater (Cowen & Silver, 1984), leading to a local modification of Eh and a solubilization of iron;
- within later large fractures: fungi, associated or not with microstromatolites;

What were then the environmental conditions occurring in the mound cavities at the time of development of iron microbes, and what were their relations with the microstromatolites?

9.1 When did the iron microbes develop?

Several arguments are in accordance with an early growth of microbes in the fractures and cavities of the mounds:

- in fenestrae, they are included in internal sediment (microspar, pseudospar) coeval with the growth of the mound (before crinoidal sands, deposited during the development of the upper part of the mounds);
- they are cemented in some fractures by early fibrous cement (Boulvain *et al.,* 1992);
- A fracture from the Hautmont mound contains microstromatolites and fungi, cemented by fibrous calcite, overlain by microsparitic sediments with branching tabulate corals, derived from a bed located a few tens of cm above, at the level of opening of the fissure.

9.2. What were the environmental conditions in the cavities?

The smallest cavities could certainly be suboxic and be colonized by microaerophilic iron bacteria. The colonization of the largest cavities by fungi probably indicates more oxygenated conditions. These fissures were the place of precipitation of significant quantities of fibrous calcite, requiring circulation of large volumes of seawater. It is however not proven that microbial growth played an active role in calcite cementation.

The lamination of microstromatolites cannot be produced by an alternation of microbial growth and detrital sedimentation, as is often the case for tidal stromatolites. These organisms are not phototropic. However, other rhythmic mechanisms can be considered (Monty, 1976):

- alternate growth of two types of micro-organisms;
- periodic calcification;
- periodic enrichment of the environment in nutrients (organic or mineral, for example, iron, manganese, and/or oxygen).

10. ORIGIN OF THE DISPERSED FERRUGINOUS PIGMENT

The two principal hypotheses formulated to account for the origin of this ferruginous pigmentation are the following :

(1) the pigment is of detrital origin, it was brought in suspension with clays; it settles in the zones where the water agitation is weak (lower level and top of the mounds). In the peripheral shale, the environment was reducing, iron is in the ferrous state; in the mound, forming a relief on the seafloor, the environment is oxidizing and iron is in the ferric state;

(2) the pigment is of microbial origin; it was precipitated in-situ by micro-organisms. The distribution of the pigment reflects the particular ecology of the microbial communities.

10.1. The detrital origin cannot explain many aspects of the distribution of the ferruginous pigment

The principal argument of authors supporting the first hypothesis is the positive correlation between clay content and ferruginous pigment. This argument, though based on a relevant observation, is not peremptory, since there is also a strong correlation between clay content and presence of sponge spicules for example. However, no one thinks of a simultaneous input of clay and spicules by decantation.

In summary**,** the detrital hypothesis cannot explain the small scale distribution of the ferruginous pigment, its connection with facies repartition and also its presence within peloids and cavity fillings.

10.2. Arguments in favour of a microbial in situ precipitation

The presence of microbial communities in cavities of the mounds from Petit-Mont and Lion Members has been highlighted. When these microbes occur in internal sediments, they confer a very accentuated red color to them (Pl. 2/1, 1/5). By analogy, we suggest that most of the pigment could have been precipitated by iron microbes and that the bulk of these microbes has not been preserved.

Polished thin sections of red limestone under high magnification show that the distribution of the microcrystals of hematite(µm-size) is not homogeneous on a small scale, but concentrates in small elongated clusters (Pl. 2/7). In certain zones relics of filaments appear. The suggested hypothesis is that microbial structures were present in the sediment, but that various processes, including bioturbation, ingestion by mud-feeders and matrix neomorphism disaggregated them; on the other hand, in cavities, the structures were preserved, in particular by early cement and by the absence of bioturbation. It should be noted that bacterial sheaths preserve their capacity of fixing iron post-mortem, even after digestion (Konhauser, 1998).

The correlation between colour intensity and the type of facies is an excellent argument for a biologic origin of the pigment. The abundance of the pigment is thus put on the same level as that of all other organic elements of the community. The distribution corresponds to the ecology of the microbes. The few shifts between facies and colour indicate an environmental tolerance of the pigment producing micro-organisms slightly different from that of the majority of the organisms of the community.

Another fundamental question is to know if micro-organisms grew in the sediment or on its surface. We do not have any argument that brings a decisive answer. Nevertheless, a microbial growth close to the water-sediment interface is probable because:

- Recent iron bacterial and fungal mats develop at the water-sediment interface (Karl *et al.,* 1988);
- the iron microbes able to actively oxidize ferrous iron usually need oxygen to perform this type of metabolism, so they will be more abundant at the sediment-water interface;
- other mechanisms of microbial iron deposition than enzymatic ferrous iron oxydation may exist simultaneously in a microbial community (Gillan *et al.,* 2000); some of these pathways require Fe(III) organic complexes that might be more abundant on the surface of the sediment which is rich in decaying organic matter; another explanation may be (terrigenous) humic Fe-rich substances;
- much of the ferruginous micro-organisms are (micro)aerophilic; they cannot live within a reducing sediment; however one notes occasionally a development of framboids or pyrite crystals within the sediment, in spite of the abundance of oxidized iron. This corresponds with recent observations on micro-aerophilic sulphate reduction.

10.3 Ecological implications

The presence of iron precipitating micro-organisms at certain levels of the Frasnian carbonate mounds has ecological implications. These micro-organisms were present mainly in the lower and the uppermost part of the mounds ("griottes") and to a lesser extent in their middle part (Petit-Mont Member), or exclusively at their base (Arche and Lion Members). Their appearance is generally sudden and they are not observed outside the mounds. They thus seem restricted to zones where an abundant carbonate production existed (in some cases, laterally to the mounds of the Petit-Mont Member, the ferruginous pigment could be observed in carbonate nodules).

The few data that can be deduced from the particular ecology of Recent iron micro-organisms suggest a low level of O_2 and available iron at the time of development of the red facies. The passage of the mounds into a more oxygenated zone caused the progressive disappearance of the micro-organisms and the development of the grey facies.

Lastly, one should not exclude, during the diagenetic history of the mounds, a remobilisation of the ferruginous pigment, even the reduction of the ferric iron during the percolation of strongly reducing fluids. This would explain the discolouration of limestone around fractures cemented by iron-bearing calcite.

11. CONCLUSIONS

Iron oxides exist in five forms in the Frasnian mounds; four are undoubtedly organized structures of biological origin:

- microstromatolites and associated forms (blisters, veils...), possibly organized in “endostromatolites”; these endobiotic organisms consist of alternations of microlaminae of calcite and calcite with microcrystals of hematite;
- hematitic coccoids and filaments, also endobiotic. The filaments resemble iron bacteria of the *Sphaerotilus-Leptothrix* "group". These microorganisms formed felts in cavities. The coccoids can also be associated with the microstromatolites;

- networks of dichotomic filaments ascribable to fungi. These forms may be associated with microstromatolites;
- a red ferruginous pigment dispersed in the calcareous matrix whose distribution is related to the mound facies type.

The endobiotic forms developed during the edification of the mounds, before cementation by fibrous calcite. In the smallest cavities, local conditions favourable to the growth of iron bacteria and fungi could be related to the presence of decaying organic matter. The microbial precipitation of iron took place as long as the developing mounds were bathed by water impoverished in oxygen. Similar conclusions were also drawn for some Devonian carbonate rock sections studied in the Montagne Noire, the red colour of the micritic matrix being also related to bacterial activity (Préat *et al.* 1999a, 1999b).

Due to bioturbation and diagenesis, iron-encrusted microorganisms were destroyed, initially by crystallization of hydroxides to hematite, then by neomorphism of the sediment. Some relics are still observed. In cavities, however, early cementation preserves these delicate structures.

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FIGURES AND PLATES

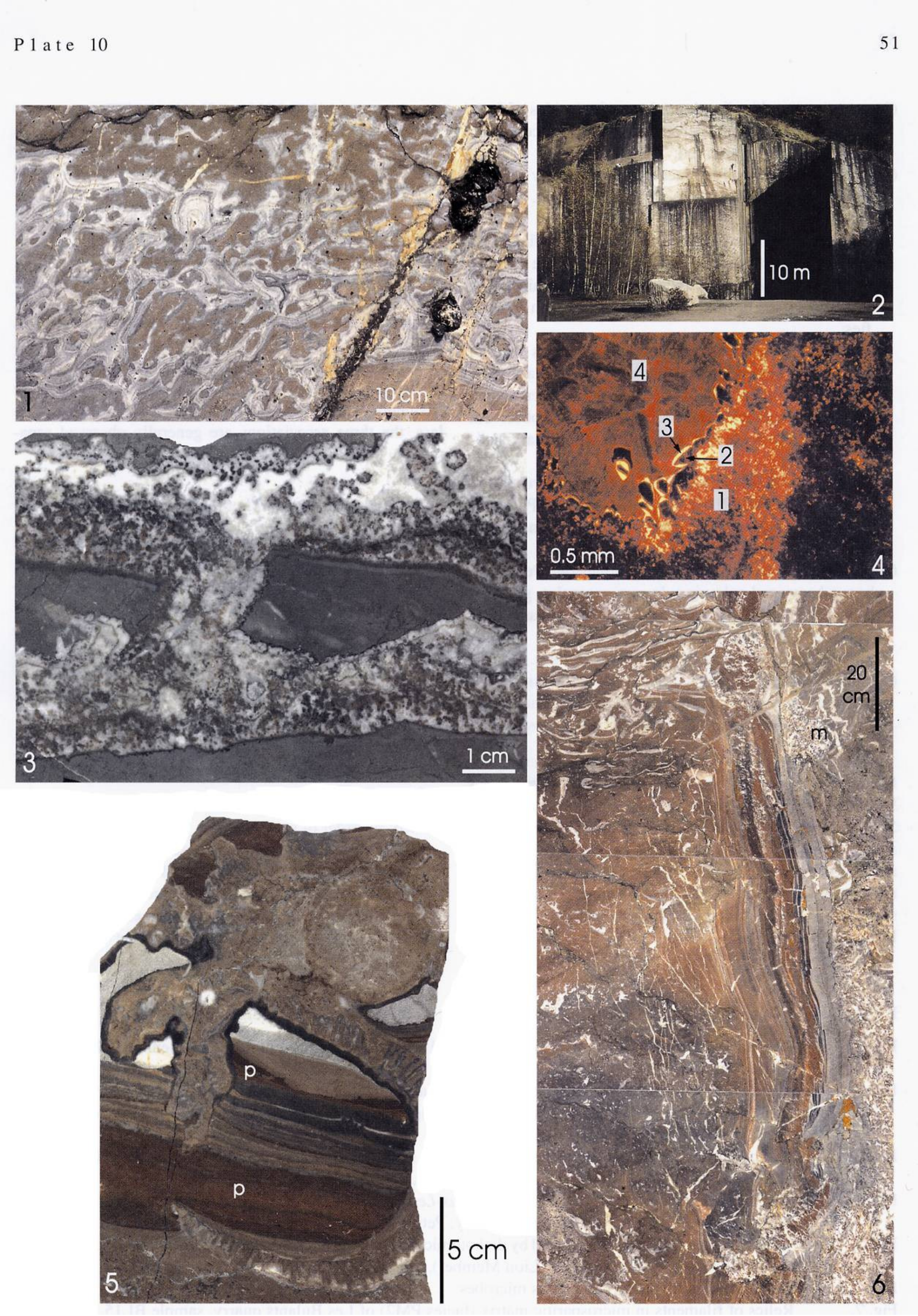

Plate 10

51

PLATE 1

- Fig. 1. Red stromatactis limestone, facies PM1, Les Croisettes quarry, Petit-Mont Member, Vodecée.

- Fig. 2. Beauchâteau quarry, Petit-Mont Member, Senzeilles.

- Fig. 3. Zebra from the lower part of the Nord mound, Lion Member, Frasnes. Microstromatolites are red or black coloured.

- Fig. 4. Diagenetic sequence in Belgian Frasnian carbonate mounds. Stromatactis from Les Bulants quarry (sample BL15), Petit-Mont Member, Neuville. 1, 2, 3, 4 : cementation stages (see text). Cathodoluminescence.

- Fig. 5. Red coloured peloids (p) in internal sediments of *Receptaculites*, facies PM3, sample RFX, Rochefontaine quarry, Petit-Mont Member, Franchimont.

- Fig. 6. Neptunian dyke in the upper part (facies PM2) of the Hautmont mound (Petit-Mont Member), Vodelée; (m): microstromatolites.

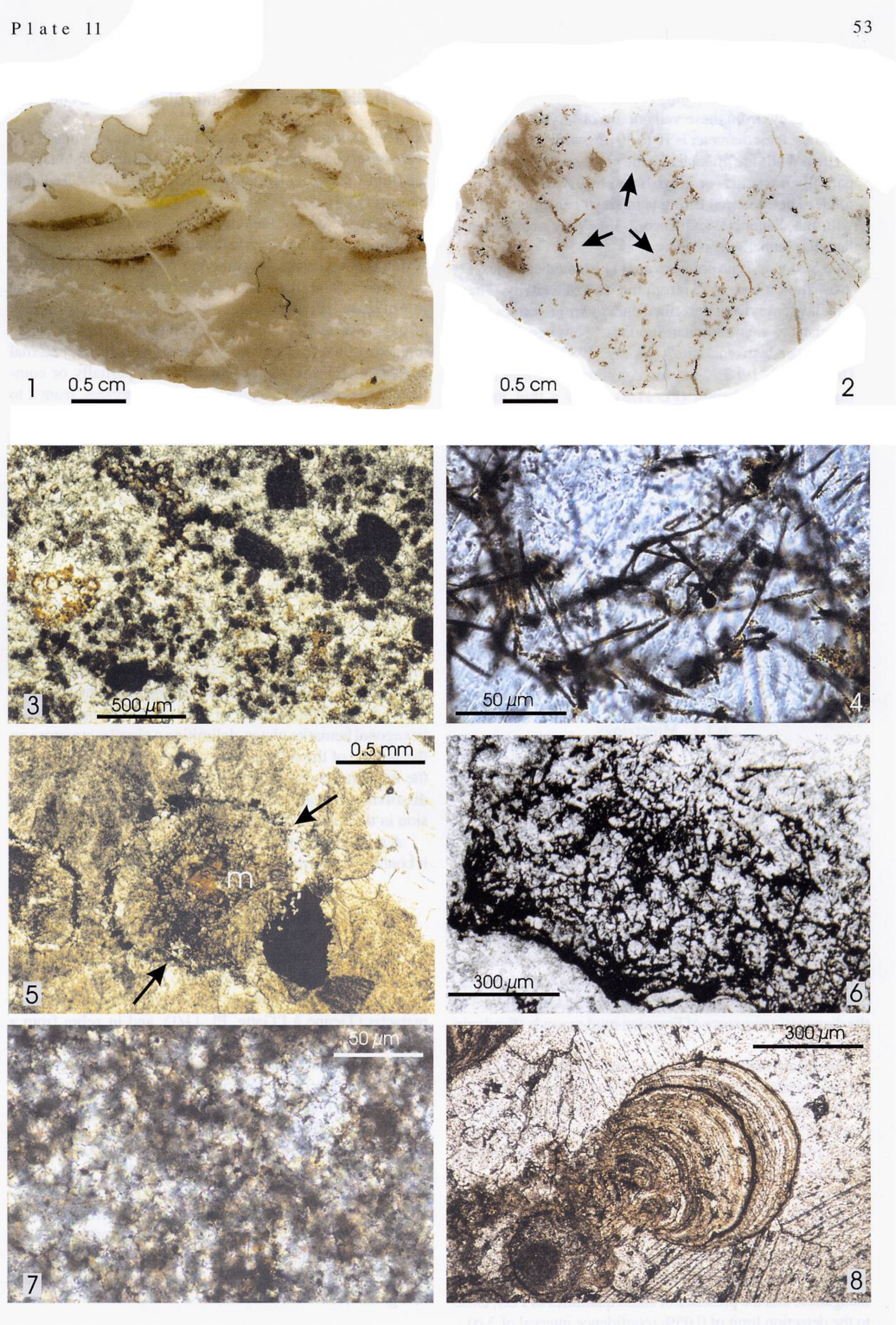
Plate 11
53
1
0.5 cm
0.5 cm
2
3
500 μm
50 μm
4
0.5 mm
m
5
300 μm
6
50 μm
7
300 μm
8

PLATE 2

- Fig. 1. Red limestone with stromatactis; fenestrae with red internal sediments, sample TG21, Tienne à l'Gatte quarry, Petit-Mont Member, Philippeville.
- Fig. 2. Veils, blisters and microstromatolites in the neptunian dyke from Pl. 1/6; sample HMC9b (Hautmont quarry, Petit-Mont Member), Vodelée. Veils are delimiting nearly spherical cavities (arrows). These cavities are centripetically cemented by sparite.
- Fig. 3. Red-coloured peloids and aggregates in the internal sediments of *Receptaculites* (sample RFX, Pl. 1/5); b: blisters. Rochefontaine quarry, Petit-Mont Member, Franchimont.
- Fig. 4: Iron-bacteria (*Siderocapsa*-like and *Sphaerotilus-Leptothrix*-like) in the internal sediments of *Receptaculites* (sample RFX, Pl. 1/5). Rochefontaine quarry, Petit-Mont Member, Franchimont.

-,Fig. 5. Microstromatolites (m), surrounded by dichotomic filamentous microbes (arrows) in a zebra (Pl. 1/3) from the lower part of the Nord quarry (Lion Member), Frasnes.

- Fig. 6. Close up of dichotomic filamentous microbes.
- Fig. 7. Relics of filaments in microsparitic matrix (facies PM2) of Les Bulants quarry, sample BL15, Petit-Mont Member, Neuville.
- Fig. 8. Close-up of a microstromatolite from the neptunian dyke illustrated in Pl. 1/6, sample HMC, Hautmont quarry (Petit-Mont Member), Vodelée.