Processes of carbonate precipitation in modern microbial mats

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ABSTRACT

Microbial mats are ecosystems that arguably greatly affected the conditions of the biosphere on Earth through geological time. These laminated organosedimentary systems, which date back to >3.4 Ga bp, are characterized by high metabolic rates, and coupled to this, rapid cycling of major elements on very small (mm-μm) scales. The activity of the mat communities has changed Earth's redox conditions (i.e. oxidation state) through oxygen and hydrogen production. Interpretation of fossil microbial mats and their potential role in alteration of the Earth's geochemical environment is challenging because these mats are generally not well preserved.

Preservation of microbial mats in the fossil record can be enhanced through carbonate precipitation, resulting in the formation of lithified mats, or microbialites. Several types of microbially-mediated mineralization can be distinguished, including biologically-induced and biologically influenced mineralization. Biologically-induced mineralization results from the interaction between biological activity and the environment. Biologically-influenced mineralization is defined as passive mineralization of organic matter (biogenic or abiogenic in origin), whose properties influence crystal morphology and composition. We propose to use the term organomineralization *sensu lato* as an umbrella term encompassing biologically influenced and biologically induced mineralization. Key components of organomineralization *sensu lato* are the "alkalinity" engine (microbial metabolism and environmental conditions impacting the calcium carbonate saturation index) and an organic matrix comprised of extracellular polymeric substances (EPS), which may provide a template for carbonate nucleation. Here we review the specific role of microbes and the EPS matrix in various mineralization processes and discuss examples of modern aquatic (freshwater, marine and hypersaline) and terrestrial microbialites.

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1. Introduction

Microbial mats are widely regarded as the Earth's earliest ecosystem (Tice and Lowe, 2004, 2006; Noffke et al., 2006) and have been present on Earth for over 3 billion years (Hofmann et al., 1999; Schopf, 2006). Through time, microbial mats have influenced planetary evolution, changing the redox conditions (Des Marais, 1995; Farmer, 2000) by "inventing" the process of oxygenic photosynthesis through cyanobacterial activity (Kasting, 1991; Holland, 1994; Des Marais, 2000; Kasting and Howard, 2006), fixing N_2, and producing vast amounts of hydrogen, which was lost to space (Hoehler et al., 2001). Often considered highly resilient ecosystems, microbial mats are important model systems to investigate microbial interactions, biogeochemistry (e.g., element cycling, including carbon, nitrogen and sulfur transformations), and microbe–mineral interactions (precipitation/dissolution of carbonates, silicates and oxides). The properties of microbial mats together with their antiquity, make microbial mats ideal system objects for astrobiological studies of potential biosignatures and extraterrestrial life (Toporsky et al., 2003). Although there is ample evidence for the biogenicity of the 3.5 Ga stromatolites (Hofmann et al., 1999; Allwood et al., 2006, 2007), controversy remains regarding the potential role of abiotic processes in forming these laminated structures (Buick et al., 1981; Lowe, 1994; Grotzinger and Knoll, 1999; Lindsay et al., 2003). Regardless, contemporary microbial mats are believed to hold the key for the past (Krumbein et al., 2003) providing insight into the role of microbes in mineral precipitation. Understanding microbe–mineral interactions is critical for interpretation of the rock record. In this paper, we review principles of carbonate precipitation in modern microbial mats.

Microbially-mediated carbon cycling, especially as related to precipitation and dissolution of carbonate minerals, is one of the fundamental research foci in the rapidly expanding field of Biogeosciences. Microbial communities, particularly microbial mats, have a unique ability to alter the balance between 'more reduced' and 'more oxidized' forms of carbon (i.e. organic matter versus CO_2; Fig. 1). Depending on the pH and carbonate alkalinity, CO_2 can be present in water as carbonate ions, which can bind to cations (e.g., Ca^{2+}, Mg^{2+}) to form carbonate minerals. The process of mineral precipitation as a result of interactions between biological activity and the environment is referred to as *biologically-induced* mineralization (McConnaughey, 1989; Franke and Bazylinski, 2003; Weiner and Dove, 2003; Fig. 2). *Microbially-induced mineralization* is a specific type of the biologically-induced mineralization referring to precipitation that results distinctively from microbial activities. In contrast, *biologically-controlled* mineralization is a radically different process, where cellular activity directs the nucleation, growth, morphology and final location of a mineral, forming an external or internal skeleton, e.g., in calcifying algae, mollusks, echinoderm or mammals (e.g., Addadi and Weiner, 1989; Lowenstam and Weiner, 1989; Weiner and Dove, 2003). In this paper, we also introduce a new term, *biologically-influenced* mineralization, to refer to passive mineralization of organic matter (Fig. 2). In biologically-influenced mineralization, external, environmental

parameters, rather than microbial activities, are responsible for creating the conditions (e.g., increased alkalinity) for mineral precipitation and the presence of living organisms is not required. An organic matrix is, however, involved in biologically influenced precipitation, influencing the morphology and composition of the crystals through interactions between the mineral that forms and the organic matter (serving as template for precipitation).

Improved understanding of controlled, induced, and influenced types of mineral formation may reveal many common chemical and structural characteristics, especially as these relate to the organic matrix in which the mineral is nucleating and growing. Evaluation of carbonate mineral precipitation in microbial mats facilitates understanding the role of the organic matrix of the microbial mat, or extracellular polymeric substances (EPS), in the composition and morphology of the mineral product. The specific purpose of this paper is to review the main processes leading to precipitation of carbonates in modern microbial mats. By focusing on processes rather than specific depositional environments, we emphasize the 'ubiquity' of the main components of this type of mineralization: the *alkalinity engine* responsible for the production of carbonate ions and the *nature of the organic matter* in which the mineral forms.

2. Definitions and the importance of microbial carbonates through time

2.1. Biomineral, organomineral and microbialite

In this paper, we refer to the processes forming biominerals and organominerals as biomineralization and organomineralization, respectively (Fig. 2). However, published definitions of the terms biomineral and organomineral vary widely.

The term 'biomineral' has a range of definitions. In general terms, it refers to a mineral that is produced by living organisms and consists of both mineral and organic components (e.g., Weiner and Dove, 2003; Skinner and Jahren, 2003). In comparison with inorganically produced minerals, biominerals often have their own specific properties of shape, size, crystallinity, isotopic and trace element compositions (Weiner and Dove, 2003). In a more restrictive definition, Mann (2002) and Perry et al. (2007) use biomineral for the product of selective uptake of elements, which are incorporated into functional structures under strict biological control. The latter definition excludes biologically-induced mineral formation. In this paper, biomineral will be strictly referred as the product of biologically-controlled mineralization, as used by Mann (2002), and Perry et al. (2007), and, in this sense, biominerals are considered direct proof of life (e.g., fossils of organisms).

The term 'organomineral' was proposed by Perry et al. (2007) for 'any minerals precipitated by interaction with organopolymers, bioorganic, and/or non-biological organic compounds, without evidence of direct skeletal, intracellular or extracellular biological control'. Organominerals are therefore indirect evidence of life (Perry et al., 2007). In order to confirm the possible biotic origin of
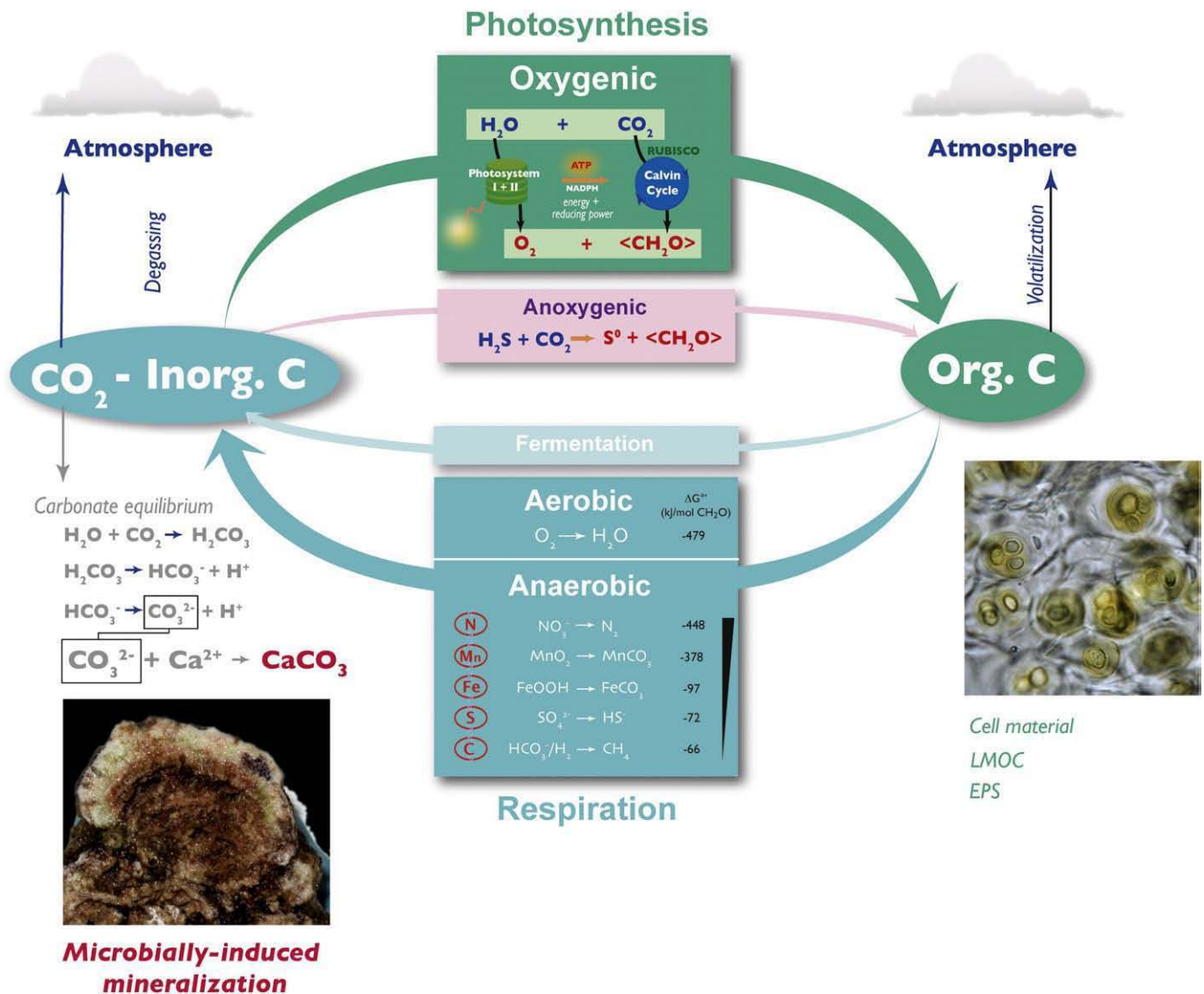
Fig. 1. The microbially-mediated carbon cycle. Through metabolic transformations, microbes influence the balance between "more reduced" (CH_2O) and "more oxidized" (CO_2) forms of carbon. Organic carbon is 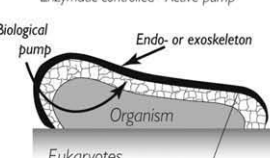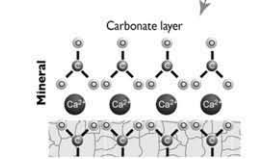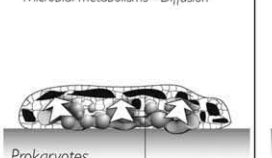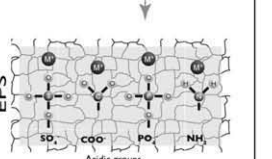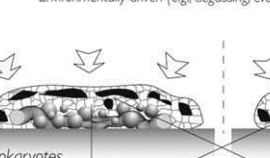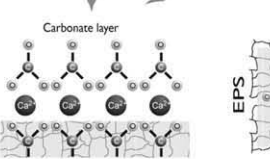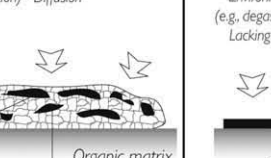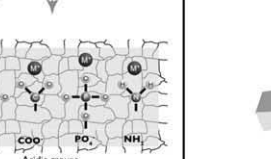formed via photoautotropy. During this process, CO_2 is reduced (fixed) into organic compounds using light energy and water (oxygenic photosynthesis) or sulfur compounds (anoxygenic photosynthesis) as electron donor, producing O_2 and elementary sulfur (or sulfate), respectively. The cell material, EPS, and low-molecular weight organic carbon are efficiently recycled (oxidized) by various groups of heterotrophic bacteria, which perform different types of respiration (the reverse process of photosynthesis). Aerobic respiration uses O_2 as terminal electron acceptor (TEA); electrons are donated by organic matter oxidation, or alternatively from inorganic electron donors, e.g., H_2, HS^-, NH_4^+), whereas anaerobic respiration can use a range of TEA, e.g., Fe(III)/Mn(IV), NO_3^-, SO_4^{2-}. The energy yield ($\Delta G^{\circ\prime}$) is a function of difference in standard potential between the electron donor and acceptor ($\Delta G^{\circ\prime} = -nF\Delta E^{\circ\prime}$). The inorganic carbon produced during respiration can deliver carbonate ions that bind to cations to form carbonate minerals (microbially-induced mineralization). The microbially-mediated carbon cycle is closely coupled with the other element cycles (S, N, Fe, O) that function as electron donors/acceptors.

an organomineral, information is needed regarding the presence and properties of intracrystalline organic matter, the mineralogy, crystal morphology and geochemistry (elemental and isotopic composition) of the mineral, etc. Although Perry et al. (2007) do not specifically use the term organomineralization, their definition of organomineral does not correspond to products of 'organomineralization', as originally described by Trichet and Défarge (1995) based on concepts developed by Mitterer (1968) and Trichet (1968). As used by Trichet and Défarge (1995), the term organomineralization refers to precipitation mediated by non-living organic substrates in soils and sediments (Fig. 2). In contrast to mollusks, which control biomineralization by genetically-directed organization of an acidic mineralizing matrix (e.g., Addadi and Weiner, 1989), Trichet and Défarge's model proposes that the acidic macromolecules in microbial biofilms are randomly distributed throughout the EPS-matrix. Rearrangement of these acidic sites through diagenetic processes provides an organized nucleation template for complete biofilm organomineralization (Reitner, 1993;

Reitner et al., 1995; Trichet and Défarge, 1995). It is important to note that the definition by Trichet and Défarge (1995), which we term organomineralization *sensu stricto*, is restrictive, and does not include biologically-induced mineralization. In this paper, we use the term 'organomineralization *sensu lato*' (Fig. 2) for all processes forming organominerals as defined by Perry et al. (2007), i.e., all mineral precipitation on an organic matrix that is not genetically controlled. The organomineralization process can be intrinsically (microbial metabolisms) or extrinsically driven (e.g., degassing, evaporation). Organomineralization *s.l.* can therefore be either an active (biologically-induced) or passive (biologically-influenced) process.

Mineral deposits resulting from organomineralization *s.l.* (microbially-induced and microbially-influenced mineralization; Fig. 2) are called *microbialites* (Burne and Moore, 1987). Other terms such as microbolite (Riding, 1991), automicrite (e.g, Wolf, 1965; Reitner et al., 1995) or organomicrite (Reitner et al., 1995) are also used. Most microbialites can be classified into one of three main categories based

Fig. 2. Classification of mineralization terms and processes showing the different types of mineralization as they relate to living (biotic) and non-living (abiotic) organic matter. Products (bottom) are some of the examples resulting from biogenic precipitation. See text for details.

on their macroscopic features (Riding, 1991; Dupraz and Strasser, 1999; Fig. 2): *stromatolites,* showing a *laminated* macrofabric (Monty, 1977; Semikhatov et al., 1979), *thrombolite,* displaying a clotted (mesoclots) macrofabric (Aitken, 1967; Kennard and James, 1986; Turner et al., 2000; Shapiro, 2000), and *leiolite,* without well defined macrofabric (structureless; Braga et al., 1995). These three types of microbialites can display a wide range of microstructures including micropeloidal, densely micritic, or agglutinated microfabrics (Riding,

1991; Dupraz and Strasser, 1999). The importance of microbialite in the geologic record has varied through Earth history, as summarized below.

2.2. Microbialites in the Precambrian

Microbially-induced mineralization appears near the beginning of Earth's history, as the microbial communities thriving in the Precambrian ocean orchestrated the precipitation of calcium carbonate to form laminated microbialites called stromatolites. Precambrian stromatolites were formed by iterative accretive growth of microbial communities that precipitated and/or entrapped inorganic materials. (Semikhatov et al., 1979; Dupraz et al., 2006).

The ability of bacteria to 'create' their own geological and biological substrates through microbially-mediated mineralization and recycling of metabolites allows these systems to adapt to the wide range of environmental conditions that prevailed throughout Earth history (e.g., Hofmann, 1976; Grotzinger, 1989; Walter, 1994). As discussed above, microbial mats forming stromatolites had a major impact on the development of the early atmosphere, through photosynthetic consumption of the greenhouse gas CO_2 and production of free oxygen (Kasting, 1991; Holland, 1994; Kasting and Howard, 2006). Microbial mat ecosystems and associated microbialite formation were dominant for over 85% of Earth's history (Grotzinger and Knoll, 1999), regulating most of the global biogeochemical element cycling including components of the carbonate factory (i.e., dissolution and precipitation reactions).

During the Proterozoic, stromatolites diversified morphologically (Hofmann, 1976; Copper, 2001), forming reef ecosystems. These environments supported the development and evolution of the first single-cell eukaryotes and multicellular organisms that developed from synergistic associations of prokaryotes (Margulis, 1993, 1996;

Vellai et al., 1998). These eukaryotes may have inherited parts of the induced microbial precipitation mechanisms to develop biologically-controlled mineralization, which appeared at the beginning of the Cambrian in the fauna of the Burgess Shales (Collins et al., 1983; Briggs, 1991; Conway-Morris, 2000, 2003) and later exploded during the mid-Cambrian diversification and the Paleozoic. In addition, microbial communities possibly preserved soft multi-cellular life of the Ediacarian fauna early in the Cambrian (Gehling, 1999). Experimental evidence suggests that anaerobic bacterial activity enhances tissue preservation (Sagemann et al., 1999), where slower degradation rates and early diagenetic mineralization are usually a prerequisite for preservation (Allison, 1988a,b; Briggs, 2003; Allison et al., 2008).

Despite the fact that organomineralization *s.l.* and biomineralization (Fig. 2) are distinctly different processes, initial control of these two types of mineralization is similar in that an organic matrix shapes the emerging mineral product. Although genetic control is missing in the poorly-organized formation of microbialites, stromatolites can be viewed as the 'first to produce a hard body', and therefore can be symbolically referred to as 'the first shell'. It is unknown how organisms evolved from indirectly mediating precipitation to exercising perfect control over the biomineralization process as present in hard-bodied organisms (Lowenstam and Weiner, 1989).

2.3. Microbialites in the Phanerozoic

Open-marine microbialites (stromatolites and thrombolites) massively declined during the Late Proterozoic as a result of eukaryotic grazing, competition for space, substrate modification or other effects (Fischer, 1965; Garrett, 1970; Awramik, 1971, 1982, 1992; Monty, 1973; Walter and Heys, 1985; Riding, 2006). The role of microbial ecosystems in Earth history does not end with this decline (Pratt, 1982). After the rapid development of hard-bodied organisms,
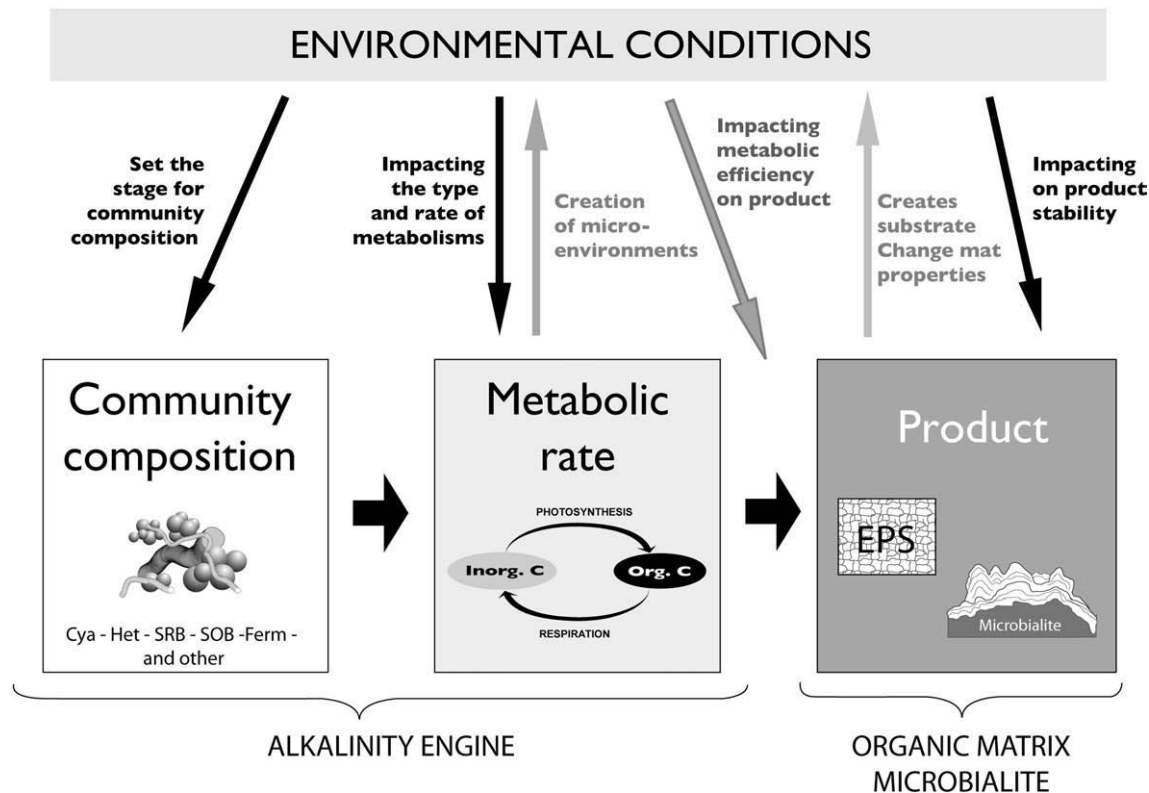
Fig. 3. Environmental control on microbial production of minerals. The mineral product results from complex interactions between bacterial communities, their specific metabolic activities and the environment. The environmental conditions govern microbial community development, influence the type and rate of metabolism, and may control stability and fossilization potential of the mineral product. Metabolic activity is creating microenvironments suitable for mineral production. Once formed, minerals can create a substrate for further microbial colonization and change the mat properties, mechanically stabilizing the ecosystem. Particular environmental conditions (e.g., elevated water alkalinity, high pCO_2) can affect the efficiency of a specific metabolism to produce minerals (see Section 6.1).

organomineralization *s.l.* continued to occur throughout the Phanerozoic time as an active and essential player in most aquatic ecosystems (Ehrlich, 1998). Microbial precipitation is observed in a variety of semi-confined to confined macro- and micro-environments, from the deep sea to shallow platforms and terrestrial environments. Microbial ecosystems strongly impact sedimentation in modern and past carbonate environments by influencing the balance between precipitation and dissolution forming carbonate sediments, e.g., ooids, peloids, and oncoids (Chafetz, 1986; Reitner et al., 1997; Brehm et al., 2004, 2006).

Microbial mats can interact with physical and chemical sedimentary dynamics, which can lead to the formation of microbially-induced sedimentary structure (MISS; see Noffke et al., 2003). For example, microbialites were an important component of most Phanerozoic reefal facies, in which they are crucial to the settlement and edification. Particularly in Mesozoic coral and sponge reefs, microbialites stabilize sedimentary substrates and fill in porosity to form 'physical reefs' (Leinfelder et al., 1996; Dupraz and Strasser 1999, 2002; Olivier et al., 2003). In the absence of macroscopic metazoans, microbes were able to build reef-like structures such as mud mounds in deep oceans (Bosence and Bridges, 1995).

Microbially-induced mineralization is a major structural and ecological player in reefal ecosystems (e.g., Cabioch et al., 1999, 2006; Camoin et al., 1999, 2006; Riding 2002), in beach rock formation (Webb et al., 1999; Neumeier 1999; Hillgärtner et al., 2001; Khadkikar and Rajshekhar, 2003) and in the development of the 'enigmatic' septarian concretions (Hendry et al., 2006). During major crises in Earth history, such as Permo-Triassic extinction and the end of the Triassic, or during local crisis, such as the Messinian crisis, microbialites are generally the last to be affected and the first to recolonize the various niches left by eukaryotes, reminiscent of the time where they dominated the Precambrian world.

2.4. Microbialites in modern environments

Although most of the recent microbial mats lack lithification, several examples of $CaCO_3$ precipitation in modern mats exist: 1) $CaCO_3$ precipitation in travertine platforms of certain hotspring mats in Yellowstone (Farmer, 2000; Fouke et al., 2000), 2) dolomite production in Lagoa Vermelha Brazil (Vasconcelos and McKenzie, 1997; Vasconcelos et al., 2006), and 3) microbialite formation in hypersaline and/or alkaline lakes (Arp et al., 1998, 1999a,b, 2003; Wright, 1999; Dupraz et al., 2004; Wright and Wacey, 2005; Dupraz and Visscher, 2005), freshwater rivers and lakes (Freytet and Verrecchia, 1998, 1999), open marine stromatolites in the Bahamas (Dill et al., 1986; Reid et al., 2000, 2003) and in hypersaline Shark Bay, Australia (Logan, 1961; Logan et al., 1974; Golubic and Hofmann, 1976; Bauld et al., 1979; Golubic, 1985; Reid et al., 2003; Burns et al., 2004).

Organomineralization *s.l.* is a main focus in several emerging investigations, such as studies of life in extreme environments (extreme temperature, salinity and/or pressure; Sassen et al., 1998; Farmer, 2000), the search for traces of extraterrestrial life (Toporski et al., 2002; Kazmierczak and Kempe, 2003; Farmer, 2000), or exploration of new carbon sinks (Braissant et al., 2004), and exploration of unusual types of metabolisms that sustain life in the 'deep biosphere' for thousands or even up to millions of years (Lovley and Coates, 2000; Pedersen, 2000).

3. Components of the organomineralization *s.l.*

Microbial mats can be defined as organosedimentary biofilms, dominated by cyanobacteria, that exhibit tightly-coupled element cycles. Complex interactions between microbial mats and their surrounding environment can result in the production of organominerals (Fig. 3). Specific details of these interactions and the potential role of microbial metabolism on mineral products are not

fully understood. It appears however, that environmental conditions set the stage for various types of precipitation in the mats, particularly by controlling the potential impact of microbial metabolism on mineral products. For example, photosynthesis promotes precipitation. However, this metabolism is relevant for organomineralization only under specific environmental conditions (e.g., low in dissolved inorganic carbon and high in calcium (see Section 3.3.1; Merz-Preiß and Riding, 1999; Arp et al., 2001)). Metabolic activity, in turn, creates micro-environments that promote or inhibit mineral production. The composition and activity of the microbial community can also impact mineral composition and crystallography. In the following sections, we review the current knowledge regarding two closely coupled and fundamental controls of carbonate organomineralization *s.l.*: 1) the alkalinity engine and 2) the exopolymeric organic matrix which ultimately is the location of mineral nucleation (Fig. 4).

4. The alkalinity engine

Carbonate precipitation is a function of carbonate alkalinity and the availability of free calcium, which are combined in the saturation index. The saturation index is defined as:

$$SI = log\left(IAP / K_{sp}\right) \qquad (1)$$

where IAP denotes the ion activity product (i.e., $\{Ca^{2+}\} \times \{CO_3^{2-}\}$) and K_{sp}, the solubility product of the corresponding mineral (Stumm and Morgan, 1996). The solubility products for aragonite and calcite are $10^{-6.19}$ and $10^{-6.37}$, respectively, at 25 °C, 1 bar atmospheric pressure and 35 PSU salinity (Zeebe and Wolf-Gladrow 2001). The solution is supersaturated when IAP>K_{sp}, Furthermore, experimental evidence showed that when SI>0.8, $CaCO_3$ can spontaneously precipitate (Kempe and Kazmierczak, 1994). Arp et al. (2001) use SI>1 (i.e., a 10-fold supersaturation) as a prerequisite for carbonate precipitation. The actual $\{CO_3^{2-}\}$ depends on the carbonate equilibrium:

$$H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-} \qquad (2)$$

which has a pK_a of 5.9 and 8.9, respectively, at 25 °C, at 1 bar atmospheric pressure and 35 PSU salinity (Zeebe and Wolf-Gladrow, 2001), and by extension which depends on the pH. In Eq. (2), H_2CO_3 is formed from CO_2 dissolution in water, which depends of the Henry's Law constant for this gas.

Various processes can increase carbonate alkalinity, indirectly promoting carbonate precipitation (Fig. 4). These processes constitute the 'alkalinity engine', which can be driven by extrinsic or intrinsic factors. When alkalinity changes result from physicochemical processes in the macro-environment, the engine is extrinsically driven. When alkalinity is controlled by microbial communities altering their immediate microenvironment through their metabolism, the engine is intrinsically driven (Fig. 4). These driving factors are discussed below.

4.1. The physicochemical component of the alkalinity engine

All details of physicochemical carbonate precipitation will not be discussed in this paper, since many aspects of this process are not directly related to organomineralization *s.l.* However, microbial communities can serve as an actual substrate for physicochemical carbonate precipitation and, thus, might have a crucial impact on the mineral product. This mineral produced is referred to as an organomineral *s.l.* (see Section 2.1), because it develops in close relationship with microbially derived organic matter or microbial morphological traces.

The two major physicochemical processes that can lead to carbonate precipitation in microbial mats are: 1) evaporation of water, which results in the formation of evaporites, and 2) CO_2 degassing, which is involved in travertine deposition.
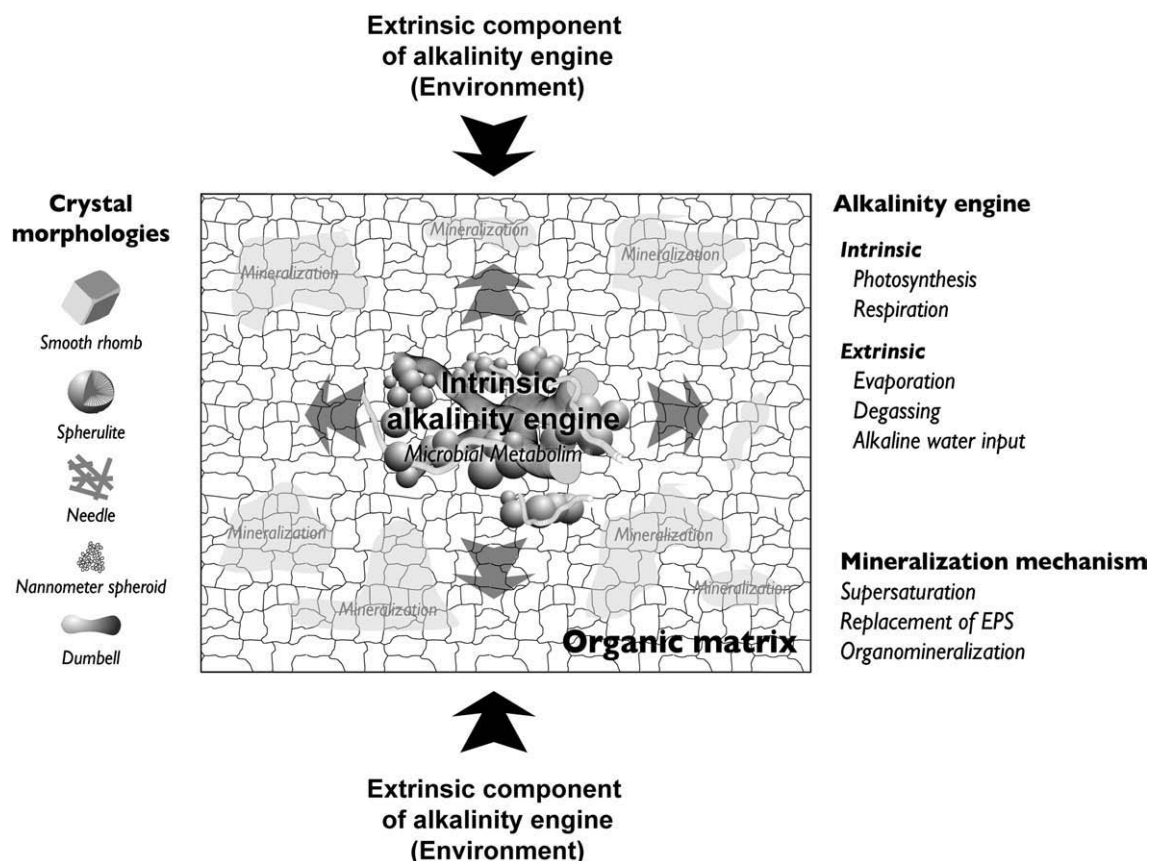
Fig. 4. Factors contributing to the organomineralization *s.l.* The organomineralization *s.l.* can be divided into two closely coupled elements: the alkalinity engine and the organic matrix in which the mineral will nucleate. The alkalinity engine has two components: an intrinsic (microbial metabolism) and extrinsic (the environment) component. The EPS matrix, which is also the result of microbial activity, is not part of the alkalinity engine. This matrix can strongly influence mineral shape and composition, producing an array of crystal morphologies and mineralogies. See Section 5.3.

Evaporites can be defined as salt deposits precipitated from a saturated brine via solar evaporation. They can successively undergo diagenetic alteration and be found as salt rock in the fossil record (Warren, 2006). Although a variety of carbonate minerals (e.g., calcite, ikaite, aragonite, Mg–calcite, dolomite and magnesite) can be produced through this physicochemical mechanism, evaporites largely consist of halite and gypsum. Furthermore, the evaporation process may obscure previously produced microbial signatures. For reviews on evaporites, see Yechieli and Wood (2003) or Warren (2006).

The terms travertine and tufa are often used interchangeably in the literature. However, certain authors are using the term tufa for all near-ambient temperature deposits and travertine for hydrothermal freshwater deposits (Ford and Pedley, 1996). Here we will use the term travertine as reviewed in Pentecost (2005). Travertines represent chemically-mediated continental carbonate deposits that form along streams and lakes. The mineral products are aragonite or calcite deposits with low to average intracrystalline porosity, but high structural and moldic porosity. The precipitation of $CaCO_3$ in travertines is mainly related to the release of CO_2 from the system, resulting in supersaturation with respect to calcium carbonate:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O. \qquad (3)$$

Removal of CO_2 through degassing will shift the equilibrium in Eq. (3) toward the left, favoring precipitation of $CaCO_3$. The nucleation and growth of crystal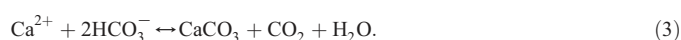s take place underwater or at the air–water interface. Travertines can be classified into two main types depending upon the source of the CO_2 (Pentecost, 2005): meteogene travertine,

when the origin of the CO_2 is atmospheric, and thermogene, when CO_2 originates from hydrothermal sources. Organic and physical structures, such as plant debris and gas bubbles, impact the mesostructure of travertine forming encrusting voids and structural and moldic porosities (Pentecost, 2005). Although the alkalinity engine, responsible for carbonate precipitation, results from an abiotic source, precipitation is initiated on organic substrates, e.g., leaves, woods, algae, or microbial mats. Mineralogy and morphology are therefore strongly influenced by the organic matrix. Even in dendritic formations found in cold-water tufa, nucleation is initiated in an extracellular polymeric matrix (Turner and Jones, 2005). Microbial mats found at hot springs have a profound impact on thermogene travertine by providing substrates for mineralization, even though precipitation is due to vigorous CO_2 degassing (Farmer, 2000; Fouke et al., 2000).

Travertine formation resulting from precipitation within an organic matrix is a good example of biologically-influenced mineralization since the carbonate precipitation is not due to biological activity, but the lithified organisms are indirectly modifying the features of the resulting organomineral.

4.2. The microbial component of the alkalinity engine

Energy and carbon acquisition by microbial communities can have a strong impact on the carbonate alkalinity. Certain types of microbial metabolic activities create carbonate alkalinity, thereby promoting precipitation, whereas other types of metabolism increase the dissolved inorganic carbon (DIC) or produce organic acids, which could lead to a pH decrease and trigger carbonate dissolution. Net accumulation of carbonate minerals results in lithification of microbial

mats, reflecting the balance between the microbial activities (Visscher and Stolz, 2005).

4.2.1. Microbial mat composition and functioning

As outlined by others in this volume, microbial mats are highly organized, laminated communities. The typical arrangement of microbial groups results in a vertically organized structure, where the lamination is determined by the light quantity and quality. The decreasing light regime that occurs with depth results in a cyanobacteria-dominated blue–green layer near the surface, often underlain by a reddish-pink layer of purple sulfur bacteria, and a deeper layer of green sulfur bacteria (Nicholson et al., 1987; Overmann and van Gemerden, 2000). The deepest layers of the mat are typically black, with occasional gray bands. This black layer consists of iron sulfides (e.g., amorphous FeS, greigite and mackinawite; Rickard and Morse, 2005) and sometimes contains pyrite as well (Thamdrup et al., 1993; Visscher and Van Gemerden, 1993; Visscher and van den Ende, 1994; Luther et al., 1992, 2001). Black layers originally contained abundant organic carbon that fuels sulfide production, and the grey layers contain sparse organic matter and more abundant bound and trapped sediments.

Typically, the dominant phototrophic community consists of cyanobacteria, which thrive near the mat surface (Pierson et al., 1992; Bauld et al., 1992; Des Marais, 1995; Stal, 2000,) often at ca. 1–2 mm depth as they are photoinhibited at normal daytime light intensities. These phototrophic organisms are responsible for most of the carbon dioxide fixation and, as a result, their location in the mat is the preferred location for heterotrophic bacteria, which thrive on their organic carbon exudates. Interestingly, the heterotrophic community includes anaerobes, such as sulfate-reducing bacteria (Visscher et al., 1991, 2000) and methanogenic bacteria (Buckley et al., 2008). These supposedly strict anaerobes (organisms that need the exclusion of oxygen from their environment to survive) often are found near the surface as well, despite unfavorable redox conditions. In a typical sedimentary system, the types of microbial metabolism found with depth exhibit a corresponding decrease in thermodynamic yields: aerobic respiration has the highest yield (Fig. 5) and is encountered at surface, while methanogenesis has the lowest energetic yield and occurs the deepest following the redox gradient. However, in microbial mats most, if not all, types of metabolism are found in the oxic surface cyanobacterial layer. Several survival mechanisms have been postulated to explain how organisms deal with the presumably unfavorable conditions. These include the metabolic flexibility of individual species and formation of consortia to limit exposure to oxygen or sulfide (Cypionka et al., 1985; Cypionka, 2000; Hoehler et al., 2001; Baumgartner et al., 2006; Buckley et al., 2008). However, the exact mechanism(s) that allows (strict) anaerobes to survive and even thrive under high oxygen conditions *in situ* are currently unknown. An important consequence is that the redox gradient, which is always thought to be responsible for the characteristic lamination of mats, is not followed.

Molecular investigations indicate that microbial mats contain a plethora of microbial species, with diversity exceeding several thousand species in a few millimeters vertically (Papineau et al., 2005; Ley et al., 2006; Baumgartner et al., 2006; Pringault et al., in press). Nevertheless, the mat community can be described by considering a limited number of functional groups, or guilds, of microorganisms (Ward et al., 1992; Van Gemerden 1993; Ward et al., 1997; Visscher and Stolz, 2005). Depending on the mat type, five to seven key groups of microbes with similar metabolism operate in concert to accomplish complete cycling of key elements, such as O, N, S and C. These include: 1) photolithoautotrophs (i.e., cyanobacteria); 2) aerobic (chemoorgano-) heterotrophs; 3) fermenters; 4) anaerobic heterotrophs (predominantly sulfate-reducing bacteria); 5) sulfide oxidizers; 6) anoxyphototrophs (i.e., purple and green (non) sulfur bacteria); 7) methanogens.

Autotrophs convert inorganic carbon to organic carbon, which functions as an energy source for (chemoorgano)heterotrophs in the mat. Several guilds contribute to inorganic carbon fixation, including both photolithotrophs (that use light energy to fix inorganic carbon) and chemolithotrophs (that use redox reactions, such as oxidation of sulfide, hydrogen and ammonium). As mentioned above, and elsewhere in this volume (Stal, Stolz, this issue), the photolithoautotrophs, notably the cyanobacteria, are the key group responsible for CO_2 fixation: the inorganic carbon fixation rates in the surface layer of the mat exceed 5 g m^{-2} d^{-1} (Jørgensen, 2001). The resulting overabundance of organic carbon fuels aerobic heterotrophs that rapidly deplete oxygen, enabling O_2-sensitive microorganisms to respire in close proximity to the cyanobacteria. Typically aerobic heterotrophs and fermenters degrade large organic molecules to low-molecular weight matter. This low-molecular weight organic matter is then degraded by sulfate reduction, methanogenesis and other "terminal" respiratory processes (e.g., acetogenesis; Fig. 5).

The community composition and the abundance of microorganisms comprising guilds is not the same as diversity. Diversity studies no longer rely on the cultivation of organisms, which is subject to a strong bias caused by the composition of the culture medium. While these culture-dependent studies suggest that the structure of microbial mat communities are relatively simple, the development of culture-independent methods for examining microbial community structure has provided the tools to allow a more complete understanding of microbial mat systems. Many of these culture-independent molecular methods utilize the microbial 16S rRNA gene as a marker to examine the phylogenetic diversity of microbial mat systems. For example, Baumgartner et al., submitted, used 16S rRNA gene cloning and sequencing to determine the microbial diversity of modern Bahamian marine stromatolites. In their molecular study, the three dominant successional types of stromatolites were estimated to contain between 300 and 600 different microbial 'species' (i.e., the number of 16S rRNA sequences with >97% similarity), with each stromatolite mat-type containing unique patterns of microbial diversity.

Using a microbial 16S rRNA gene approach also allows comparisons to be made on similar mat types that are geographically distinct. For example, comparisons of 16s rRNA gene libraries generated from Bahamian and Australian stromatolites shows that Bahamian stromatolites contain a higher percentage of cyanobacteria and an overall higher degree of microbial diversity than the Australian stromatolites (Burns et al., 2004; Papineau et al., 2005; Baumgartner et al., 2006). Similar culture-independent methods have also been used to show that nonlithifying hypersaline microbial mats contain more than 1000 different microbial 'species' and have a higher degree of overall microbial diversity than originally estimated (Baumgartner, 2006). While studies involving the generation of large 16S rRNA gene libraries have increased our knowledge of the overall diversity of different types of microbial mat systems, these studies are often expensive and therefore limited to relatively few samples.

Other techniques that also use the 16S rRNA gene as a microbial phylogenetic marker are denaturing gradient gel electrophoresis (DGGE) and terminal restriction fragment length polymorphism (T-RFLP). DGGE is a polyacrylamide-based electrophoretic method for separation of DNA or RNA that relies on a gradient of chemical denaturants to partially denature nucleic acids based on their sequence composition, resulting in typical banding patterns that can be used to estimate the microbial community species richness. (Muyzer et al., 1993). T-RFLP is a technique in which amplified and fluorescently end-labeled DNA is digested enzymatically, yielding fluorescently labeled DNA fragments of varying length according to the unique positioning of restriction sites for each phylotype. Fragments are subsequently separated and detected based on fragment size using electrophoretic methods and fluorescence detection. The complex T-RFLP patterns for different samples are
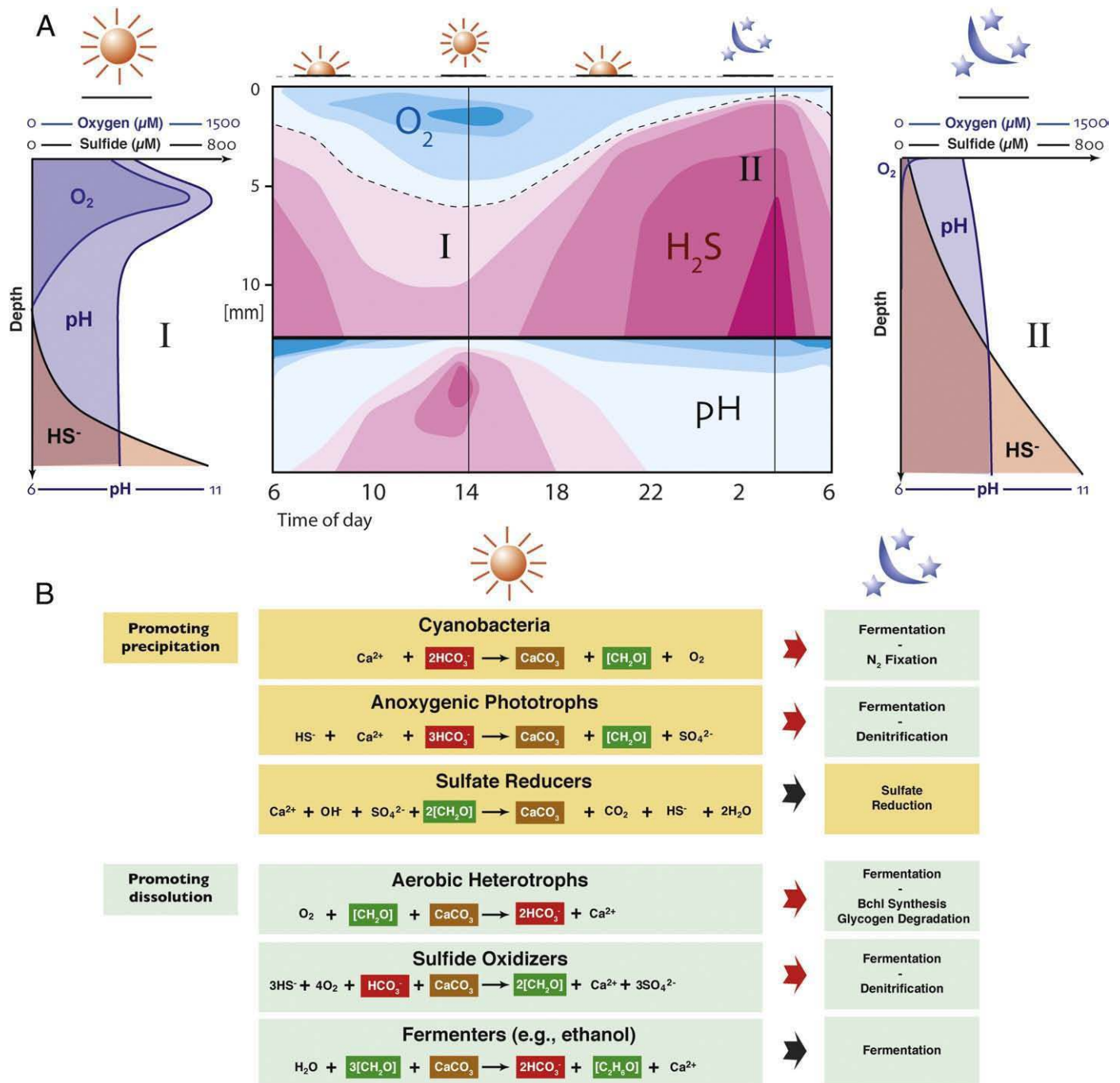
Fig. 5. Diel fluctuations of vertical geochemical gradients in a microbial mat and combined metabolic–geochemical reactions leading to carbonate precipitation and dissolution. Panel (A) shows the variation in oxygen, sulfide and pH within a microbial mat over a 24 h period (redrawn from Visscher et al., 2002). Profiles I and II represent two geochemical "snapshots" taken at 2pm and 3am that show key differences in depth profiles between day and night. As soon as the dark period starts, the photosynthesis ceases and the mat turns completely anoxic because of rapid O_2 consumption by aerobic heterotrophs. (B) The six major guilds of microorganisms that compose a typical microbial mat are arranged by their respective effects on the precipitation process. The equations presented here combine metabolic and geochemical reactions (for details, see Visscher and Stolz, 2005). Photosynthesis and sulfate reduction are known to increase alkalinity (promoting carbonate precipitation), whereas aerobic respiration, sulfide oxidation and fermentation are more likely to induce dissolution. When oxygen-depending metabolisms stop during the night, anaerobic heterotrophy such as sulfate reduction prevails. The net carbonate precipitation depends on the balance between the different metabolic activities as well as their temporal and spatial variations.

then compared to determine changes in microbial community structure (Marsh, 1999). These techniques cannot be used to determine the overall diversity of microbial communities but because of the low cost of analysis, they are very powerful tools to probe for spatial and temporal changes in microbial community composition. For instance, DGGE has been used to compare the microbial community structure of hypersaline mats throughout a vertical profile over a diurnal cycle (Villanueva et al., 2007). This study showed that the overall diversity of the mats depended more on depth-related differences rather than temporal differences. Similarly, T-RFLP has recently been used to investigate the vertical distribution of sulfate-reducing bacteria in hypersaline microbial mats over time (Fourçans et al., 2007). This approach resulted in the discovery of two distinct populations of *Desulfobacter*, one that showed a diurnal vertical migration and one that was always uniformly distributed throughout the mat. While 16S rRNA gene-based approaches have allowed

researchers to couple changes in microbial diversity with changes in microbial mat biogeochemistry, much more information is needed at the functional genomic level in order to completely understand these ecosystems.

Metagenomic techniques use genetic material recovered directly from the environment (reviewed in Handelsman, 2004) and are now routinely applied to many ecosystems. Because metagenomic techniques are not restrained solely to the analysis of the microbial 16S rRNA genes, they provide not only an understanding of microbial diversity but also a relatively unbiased view of the overall metabolic capabilities of the microbial community. These techniques involve the extraction of community DNA followed by either the generation of large insert vector libraries ranging from 30–200 kb in size or by random shotgun sequencing using novel DNA pyrosequencing technology. While both metagenomic approaches are costly and time intensive, they provide a level of genomic resolution that has, up until now, been unavailable. Future research aimed at understanding how the complex network of microbial interactions occurring in microbial mats affects ecosystem function and stability will undoubtedly rely on these newly-emerging molecular techniques.

4.2.2. Impact of metabolic processes on carbonate precipitation

Insight into microbial diversity, abundance and spatial distribution is key in understanding the role the community plays in modifying the geochemical environment, and impacting the precipitation (and dissolution) of minerals, especially that of calcium carbonate. However, diversity and abundance only give a cursory indication of what is metabolically feasible; in order to understand the geochemical processes occurring *in situ*, metabolic rates, or microbial activities need to be determined. Typically, metabolic rates are determined by measuring the rate of change of reactants or products. In microbial mat research, this is accomplished through a number of techniques, including applications of radio- and stable isotopes, and microelectrodes (Revsbech et al., 1983; Megonigal et al., 2003; Hines et al., 2007). The use of microelectrodes and planar optrodes allows one- and two-dimensional mapping of geochemical conditions and the rate of change of key metabolites. For example, oxygen electrodes can be used to assess the depth distribution of oxygenic photosynthesis and aerobic respiration; $^{14}C–HCO_3^-$ is used to measure carbon fixation by phototrophs, lithotrophs and methanogens; ^{13}C stable isotopes indicate which particular mode of CO_2 fixation prevails; and ^{35}S-labelling experiments (especially in combination with silver foil or photographic film) can be used to determine sulfate reduction. Clearly, rate measurements are critical in understanding the role of microbes in modifying the geochemical environment; *in situ* activities are very different than those displayed in laboratory cultures, which can couple certain physiological activities to specific geochemical alterations. Both approaches, however, are useful for understanding community functioning. Often in mat research, the emphasis is on cyanobacterial abundance and activity, as these are predominant primary producers for the community. Environmental characteristics such as light and nutrients are among the key factors that determine rates of photosynthesis (see Stal, this issue), which is critical in determining the flow of carbon through the mat ecosystem, and with that, the individual types of metabolism.

Microbial metabolism can be described as a chemical reaction in which reactants are removed and metabolic products are added to the environment. This alters the geochemical environment, and ultimately impacts mineral precipitation/dissolution reactions. Microbial mats display particularly high metabolic rates that fluctuate on short timescales and as a result, the geochemical environment changes continuously. The dynamics of the overall community metabolism (of all guilds combined) is exemplified by the changing oxygen depth profiles in the microbial mat during a diel cycle (Fig. 5). Oxygen supersaturation of >600% has been reported during the afternoon (Revsbech et al., 1983; Visscher et al., 1991, 1998, 2002; Des Marais,

2003; Wieland and Kühl, 2006) in mat layers that turn anoxic almost immediately after the end of the light period.

In order to better understand the microbial role in carbonate precipitation, the individual metabolic reactions of the guilds outlined above must be considered. One minor caveat of this approach is that organisms within any guild may have variations of the general metabolism for that group. The dynamic character of oxygen outlined above indicates the importance of phototrophs (i.e., cyanobacteria) in the mat. The high rates of oxygenic photosynthesis result in the production of large amounts of metabolic products, notably organic carbon and oxygen. Photosynthetic carbon fixation removes CO_2 from the environment, the rate of which often exceeds the replenishment of CO_2 through diffusion to the layer of maximum photosynthesis. As a result, bicarbonate dissociates into CO_2 and OH^- (Eq. (2)), creating alkalinity that favors $CaCO_3$ precipitation (Fig. 5). The role of photosynthesis in carbonate precipitation through changes in the SI has been well documented (Chafetz, 1986; Chafetz and Buczynski, 1992). The combined net reaction of photosynthesis and the geochemical reaction that results from bicarbonate dissociation is:

$$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CH_2O + O_2. \qquad (4)$$
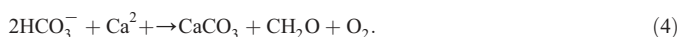
Similarly, the sum of the biotic and abiotic reactions of anoxygenic photosynthesis and sulfate reduction increase the SI, favoring precipitation, whereas aerobic heterotrophy, sulfide oxidation and fermentation decrease the SI (Eq. (1)), resulting in dissolution of $CaCO_3$ (Fig. 5; Visscher and Stolz, 2005).

Photosynthesis and aerobic respiration in a 1:1 ratio result in no net precipitation or dissolution. Ultimately, the balance of all metabolic activities determines whether precipitation or dissolution occurs. In marine and hypersaline microbial mats, the role of sulfate reducers in the overall community metabolism seems to play a key role in the alkalinity change favoring precipitation of $CaCO_3$ (Lyons et al., 1984; Walter et al., 1993; Visscher et al., 2000; Dupraz et al., 2004; Baumgartner et al., 2006). Mapping of the sulfate reduction rate and abundance of SRB in stromatolites and lithifying hypersaline mats indicate that the peak activity and highest abundance occur in the depth horizon of carbonate precipitation (Visscher et al., 2000; Dupraz et al., 2004; Baumgartner et al., 2006). Furthermore, when the relative rates of all key respiration processes in a stromatolite-forming mat are evaluated, (Visscher et al., 1998; Dupraz and Visscher, 2005), the rate of sulfate reduction (increasing the SI) is greater than the rate of aerobic respiration (decreasing the SI). Finally, as long as organic carbon or H_2 are available, SRB operate independently of oxygen and light, and are the only organisms capable of influencing (in this case increasing) the SI throughout the diel cycle (Visscher et al., 1998).

5. The role of organic matrix (EPS)

Microbial metabolism and/or environmental forcing, as described above, can provide macro- or micro-environmental conditions that favor carbonate mineral precipitation in microbial mats. However, organomineralization will only occur if both an appropriate saturation index and nucleation sites are present. The organic EPS matrix, which is an extension of microbial cells (Costerton et al., 1995) and an integral part of the microbial mat (Decho, 1990, 2000), plays a two-fold role, either inhibiting or promoting carbonate formation, depending on the specific intrinsic (i.e., physicochemical) characteristics.

5.1. Nature of the organic exopolymeric matrix (EPS)

The EPS matrix represents an important component of marine biogeochemical processes (Decho, 1990; Bhaskar and Bhosle, 2005). The chemically-reactive EPS matrix is of considerable ecological importance because it is a physical barrier between the cell and

organic and inorganic metabolic substrates, predators, antimicrobial agents, and other bacteria (Costerton et al., 1995). This high molecular-weight (8 to >1000 kDa) polysaccharide matrix, which is produced by bacteria and microalgae, may include protein and peptides, noncarbohydrate acidic moieties, such as pyruvate or succinate, and inorganic compounds, such as sulfates and phosphates, and even extracellular DNA (Sutherland, 2001a,b,c,d). The production and secretion of EPS is controlled by specific sets of genes, which are differentially regulated by chemical signaling (called quorum sensing) among bacteria or groups of bacteria (Miller and Bassler, 2001). Quorum sensing allows groups of bacteria within mats to coordinate activities (e.g. EPS secretion) and increase metabolic efficiencies (e.g. utilization of nutrients).

EPS can be produced by a wide array of microorganisms, both photoautotrophic and heterotrophic bacteria. In microbial mats, cyanobacteria are generally recognized as the most important EPS producers (De Philippis et al., 1998; Stal, 2000; De Philippis et al., 2001; Stal, 2003; Richert et al., 2005). Recently the potential role of heterotrophic bacteria, such as sulfate-reducing bacteria, in the production of the extracellular matrix has been demonstrated (Bosak and Newman, 2005; Braissant et al., 2007). The different microbial sources, in combination with a wide variety of EPS degradation pathways, are expected to result in variations in composition and quantity of exopolymers present in natural microbial mats.

Although some free-living bacteria can produce large amounts of extracellular polymers (Kives et al., 2006), EPS production is a seminal feature of benthic communities, enabling the formation of microbial mats and biofilms. The EPS matrix fulfills many functions within microbial mats (Decho, 1990; Bhaskar and Bhosle, 2005): 1) It allows communities to attach to surfaces and create micro-domains, where various types of metabolism can coexist in microspatial proximity (Decho, 2000); 2) It physically stabilizes microbial cells under variable hydrodynamic regimes (De Winder et al., 1999; De Brouwer et al., 2002; Decho et al., 2005), and 3) it may also help the microbial mat community to resist multiple stress conditions, such as nutrient shortages, UV exposure or desiccation (Potz 1994; Decho, 2000).

EPS within a microbial mat can exist in a continuum of physical states, ranging from particulate to dissolved, or from a 'cohesive gel' to a 'loose slime' to a 'dissolved solute' state. The physical state is largely a function of the EPS concentration (or, the water activity), and the abundance and types of bonds or interactions among individual EPS molecules. These molecular-scale interactions may influence the 'availability' of functional groups to bind ions. For example, EPS may possess abundant functional groups capable of binding Ca^{2+} or Mg^{2+} ions; however, these groups may be 'sterically-inhibited' (i.e. blocked). Thus, binding of ions at a given pH may not occur in proportion to the abundance of functional groups. These molecular-scale interactions then influence the larger scale rigidity, flexibility and potential binding capacity of the EPS matrix, on large or small-spatial scales.

The organization and structure of the EPS matrix may be used in synergetic relationships between various bacteria communities. Examples of this include water channels that are used to manage/enhance nutrient inputs and waste product evacuation (Neu, 1994; Costerton et al., 1995; Decho, 2000). Recent studies even propose that the large amount of extracellular DNA (eDNA) found in biofilms could represent the backbone of EPS, providing a network within the microbial mat that promotes their formation and exchange of genetic material (Whitchurch et al., 2002; Petersen et al., 2005; Vlassov et al., 2007).

From a organomineralization viewpoint, the EPS matrix is the location where the carbonate minerals nucleate and grow. Microscopic techniques, such as low-temperature scanning electron microscopy (SEM), confocal scanning laser microscopy, and Raman confocal microscopy, provide tools to study organomineralization within the exopolymers (Decho and Kawaguchi, 1999; Kawaguchi and Decho, 2002a,b; Petrisor et al., 2004; Dupraz et al., 2004; Dupraz and Visscher, 2005). The EPS matrix is a key player in organomineraliza-
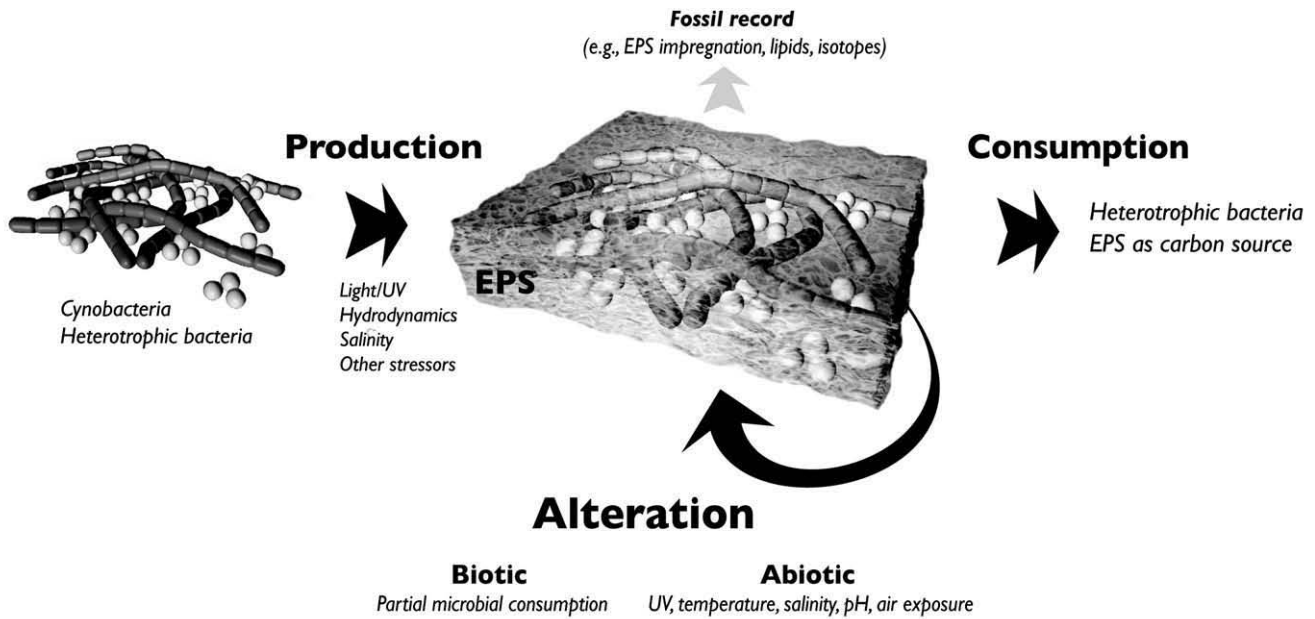
tion, having a distinct impact on the morphology and mineralogy of mineral products (Braissant et al., 2003). The physicochemical properties of the polymer matrix, such as the acidity or functional group composition, are important factors in the metal binding potential (initially inhibiting calcium carbonate mineral formation) and biotic and abiotic degradation or alteration of the EPS (favoring calcium carbonate precipitation) (Dupraz and Visscher, 2005).

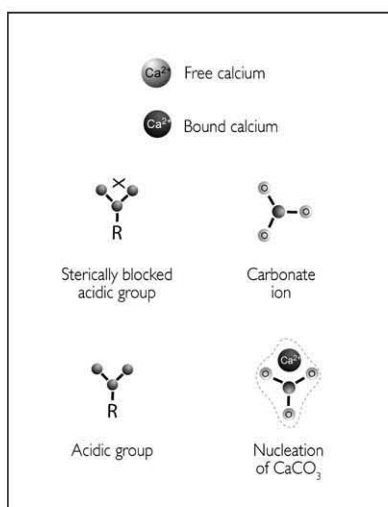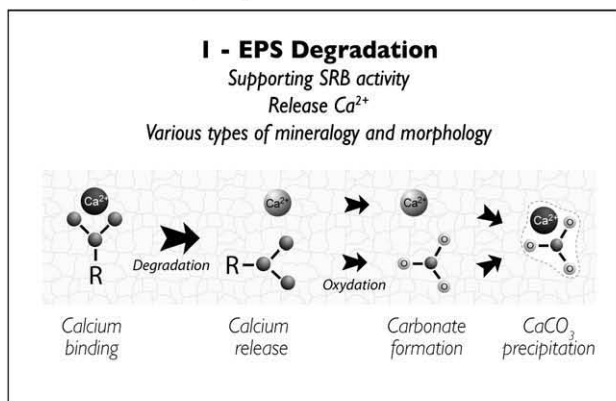### 5.2. EPS inhibition of calcium carbonate precipitation

Negatively-charged acidic groups within the EPS matrix can bind a large amount of mono- and divalent cations, which can help to maintain the structural integrity of EPS by promoting gel formation through bidentate bridge formation (Sutherland, 2001). The cation-binding capacity of EPS removes free Ca^{2+} ions from solution, inhibiting the precipitation of carbonate minerals by depleting them from the proximal surrounding environment. The role of acidic amino acids (e.g., aspartic or glutamic acid) and carboxylated polysaccharides (e.g., uronic acids) as strong inhibitors of calcium carbonate precipitation has been well documented (Ferris et al., 1989; Trichet and Défarge, 1995; Kawaguchi and Decho, 2002a,b; Gautret and Trichet, 2005). The functional group characteristics are therefore key in the mineral formation process.

Determination of EPS properties is facilitated by FT-IR (Fourier Transform Infrared Spectroscopy), which allows identification of the major functional groups responsible for Ca^{2+}-binding (Mao Che et al., 2001; Rougeaux et al., 2001; Kawaguchi and Decho, 2002a,b; Yee et al., 2004a,b; Braissant et al., 2007). Similarly, acid-base titrations of purified EPS provide the degree of protonation of these functional groups within the EPS matrix as a function of the pH (Phoenix et al., 2002; Yee et al., 2004a,b; Braissant et al., 2007). These and other studies (reviewed in De Philippis et al., 2001), which were performed on cultures of cyanobacteria and sulfate-reducing bacteria and on microbial mats, indicate that these functional groups include carboxylic acids (R–COOH), hydroxyl groups (R–OH), amino groups (R–NH$_2$), sulfate- (R–O–SO$_3$H), sulfonate- (R–SO$_3$H) and sulfhydryl groups (–SH), all of which complex strongly with metal ions, including Ca^{2+} and Mg^{2+} (Bianchi, 2007). In aqueous solution, these functional groups deprotonate when the pH increases, resulting in a negative overall charge of the EPS under slightly acidic to alkaline conditions. This is reflected by different pK values (i.e., the pH at which 50% of the functional groups are deprotonated). For example, sulfate groups have a pK<2.5, carboxyl acids a pK between 1 and 5, phosphoryl groups have a pK$_1$ of 4.6–5.4 and a pK$_2$ of 5.6–9.0, sulfonic and sulfinic acids pK values between 6.9 and 7.1, and amino groups have pKs between 8.5 and 12.5 (Stumm and Morgan, 1996; Schiewer, 1999; Sokolov et al., 2001). These pK values indicate that the different functional groups are sequentially activated as a response to the microenvironmental pH, which results in changes in EPS-calcium and -magnesium binding properties. Although several functional groups contribute to the overall negative charge of the EPS and consequently to metal binding, carboxylic acids and sulfate groups are generally considered to be the most important ligands within EPS.

Various methods have been used to estimate the calcium binding capacity of the EPS matrix: Atomic absorption spectrometry using Ca-saturated cyanobacterial EPS showed that 55 mg Ca/g EPS could be bound (Li et al., 2001); Calorimetric analysis revealed a Ca-binding capacity of 53 mg Ca/g EPS of an aerobic heterotroph isolated from a biofilm on a limestone monument (Perry et al., 2005); X-ray photoelectron spectroscopy (XPS) of cyanobacterial EPS showed that 183 mg Ca/g EPS was bound (Ortega-Morales et al., 2006), and chemical titration using CaCl$_2$ and EPS from sulfate-reducing bacteria isolated from lithifying microbial mats revealed calcium binding capacities ranging from 120 to 150 mg Ca/g EPS (Braissant et al., 2007). All the binding capacities are remarkably similar, differing only by a factor of four.

Fossil record
(e.g., EPS impregnation, lipids, isotopes)

Production

Consumption

Light/UV
Hydrodynamics
Salinity
Other stressors

EPS

Cynobacteria
Heterotrophic bacteria

Heterotrophic bacteria
EPS as carbon source

Alteration

Biotic
Partial microbial consumption

Abiotic
UV, temperature, salinity, pH, air exposure

Biologically-induced mineralization

Biologically-influenced mineralization

I - EPS Degradation
Supporting SRB activity
Release Ca²⁺
Various types of mineralogy and morphology

Degradation
Oxydation

Calcium binding
Calcium release
Carbonate formation
CaCO₃ precipitation

2A - Extrinsic Supersaturation of EPS
Forcing of mineralization on the EPS matrix.
Organic matrix and kinetic of precipitation can control mineral morphology.

CO_3^{2-}
carbonate alkalinity

Saturation of binding capability
Precipitation of CaCO₃

2B - Intrinsic Supersaturation of EPS:
Steric Hinderance
Changes in availability of functional groups (steric hinderance).
Cation binding capacity does not reflect abundance of functional groups

CO_3^{2-}
carbonate alkalinity (Intrinsec or extrinsic control)

Steric hinderance
Precipitation of CaCO₃

Ca^{2+} Free calcium

Ca^{2+} Bound calcium

Sterically blocked acidic group

Carbonate ion

Acidic group

Nucleation of CaCO₃

2C - Organomineralization s.s.
Early diagenesis - Creation of a mineralization template

Diagenetic reorganization

Random distribution of acidic groups

Template for CaCO₃ precipitation

As outlined above, the EPS matrix is heterogeneous and most likely varies in composition both from mat to mat and within a mat over small spatial scales. This inherent heterogeneity reflects the large variety of organisms that participate in EPS production, and also rapid post-secretive modification of EPS. As a consequence, the binding capacity of EPS can vary greatly in time and space, resulting in localized precipitation zones. Even in alkaline water, supersaturation with respect to aragonite or calcite precipitation cannot always be achieved because of the lack of free Ca^{2+}. This may explain the lack of carbonate precipitation often observed in microbial mats in alkaline environments (Arp et al., 1999a,b; Dupraz and Visscher, 2005). This biological inhibition of calcium carbonate precipitation has been referred to as "anticalcification" (Westbroek et al., 1994).

5.3. EPS promotion of carbonate precipitation

In order to precipitate calcium carbonate minerals within a microbial mat, the Ca-binding capacity of the EPS matrix has to be greatly reduced. This can be accomplished through biologically-induced mineralization in which EPS is modified by microbes (see Section 5.3.1; Fig. 6) or biologically-influenced mineralization via one of the two following mechanisms (see Section 5.3.2; Fig. 6): 1) super-saturation of the cation-binding sites (see Section 5.3.2), or 2) diagenetic alteration of EPS, i.e., organomineralization *sensu stricto* (Trichet and Défarge, 1995; Section 2.1).

5.3.1. Biologically-induced precipitation (active precipitation)

In addition to providing structural integrity to mats and allowing the physical coexistence of diverse microbial groups in a biofilm, the EPS matrix can also serve as a metabolic substrate (i.e., energy and/or organic carbon source). The consequence is the potentially rapid turnover of the labile fraction of the EPS matrix. A study of EPS turnover in modern marine stromatolites (Decho et al., 2005) reported that 3–4% of the total carbon fixed through photosynthesis was incorporated in newly-produced EPS, and that 40–60% of this new EPS was degraded to CO_2 within 24 h. Net EPS production was low and a dynamic balance existed between production and consumption. In addition, half of the $^{14}C–HCO_3^-$ uptake by cyanobacteria was excreted as low molecular-weight organic carbon (LMWOC; Decho et al., 2005). This LMWOC was rapidly consumed by aerobic and anaerobic heterotrophic bacteria, with the highest microbial activity associated with the surface layer, where $CaCO_3$ precipitates.

In microbial mats, typically half of the organic carbon is oxidized by aerobic pathways and remainder through anaerobic pathways (Troelsen and Jørgensen, 1982). Furthermore, sulfate reduction typically accounts for >90% of the anaerobic respiration. Anaerobic metabolisms may be a key process in the degradation of EPS in mats, because oxygen concentrations rapidly fluctuate between super-saturation and zero when the available light regime changes (Visscher et al., 2002; Paerl et al., 2001).

Experiments with lithifying mat homogenates confirmed this pattern for aerobic and anaerobic respiration when supplied with *Schizothrix* EPS, xanthan, sugars and LMWOC (Visscher et al., 1999, 2002; Decho et al., 2005). SRB are secondary metabolic substrate (LMWOC) users and cannot oxidize the EPS matrix directly. A synergy of fermenters and SRB could be responsible for the anaerobic degradation of EPS (Anderson et al., 1987). In certain cases, UV radiation through browning (Maillard) reactions and other types of weathering mechanisms (e.g., dehydration, pH changes) could facilitate the hydrolysis of EPS and produce LMWOC for sulfate

reduction (Cohen et al., 1984; Stal and Caumette, 1994). Such LMWOC products, called amadori products, have recently been detected in the EPS of hypersaline mats (Decho et al., 2009).

The degradation of the labile fraction of the EPS matrix can liberate calcium bound to the polymers. In addition, depending on the type of metabolism, EPS degradation can also increase the alkalinity (e.g., through SRB metabolism; Fig. 6; Decho, 1990; Visscher et al., 2000; Paerl et al., 2001; Dupraz and Visscher, 2005). This simultaneous increase in the calcium concentration and the alkalinity results in biologically-induced mineralization (Fig. 2) and is important in the formation of open-marine stromatolites (Reid et al., 2000; Visscher et al., 2000) and hypersaline microbialites (Dupraz et al., 2004; Jonkers et al., 2003; Vasconcelos et al., 2006).

5.3.2. Biologically-influenced mineralization (passive precipitation)

The binding capacity of EPS can be saturated when a continuous supply of cations are available. When all the functional groups of the polymer are occupied with bound cations, a combination of local alkaline conditions and the presence of free Ca^{2+} ions can lead to nucleation of calcium carbonate on the EPS matrix (Arp et al., 1999a, b). This can be achieved for example through seasonal upwelling of alkaline water followed by evaporation (Arp et al., 2003). High rates of sulfate reduction in stagnant anoxic water can result in alkaline bottom waters (Kempe, 1990; Kempe and Kazmierczak, 1994; Arp et al., 2003). The basin acts as an alkalinity pump in which SRB oxidize the sinking organic carbon and produce HCO_3^-, thereby increasing carbonate alkalinity. Slow upwelling, diffusion or seasonal turnover of the water column may result in local or regional supersaturation events promoting $CaCO_3$ formation (Kempe and Kazmierczak, 1994). This mechanism is a typical example of biologically-influenced mineralization (Fig. 2). Nucleation, with respect to the precipitating mineral, is controlled by the characteristics of the EPS and the saturation state with respect to the precipitating mineral. Such supersaturation may also occur in hydrated pockets within the EPS matrix of lithifying mats, including stromatolites. Observed with confocal microscopy, these pockets often contain well-developed mineral crystals but lack detectable EPS when stained with lectins (Decho, pers. observ.).

EPS inhibition of carbonate precipitation can also be eliminated though organomineralization *sensu stricto* (Trichet and Défarge, 1995; Section 2.1). This process is defined as a mineral formation mediated by non-living organic substrates in soils and sediments (Fig. 2). The main aspects of this process involve (Neuweiler et al., 1999): (1) enrichment of an organic matrix in acidic amino acids, particularly aspartic and glutamic acid (Mitterer, 1968; Trichet, 1968; Mitterer and Cunningham, 1985); (2) cation-binding to negatively charged carboxylic groups, sulfated glycoproteins and amino sugars (Mitterer and Cunningham, 1985; Addadi and Weiner, 1992); (3) precipitation within a network of reorganized organic matter, which controls the morphology and mineralogy of the precipitate (Defarge et al., 1996). Examples of organomineralization *s.s* have been suggested for the following environments: cryptic marine habitats where the sponge soft-tissue is degraded (Reitner, 1993); microbial crusts from Sahelian soils (Defarge et al., 1999); laminated lithifying mats from atoll lakes in the central Pacific (Defarge et al., 1996; Trichet et al., 2001). Organomineralization *s.s.* is implicated in the formation of some Cretaceous mud mounds (Neuweiler et al., 1999, 2000). A critical aspect of organomineralization is that the acidic macromolecules found in microbial biofilms appear to be randomly distributed throughout the EPS-matrix. These acidic molecules could represent random hot spots of carbonate

Fig. 6. Mechanistic role of the organic EPS matrix in biologically-induced, -influenced and organomineralization *s.s.* The exopolymeric substances are produced by various groups of bacteria (especially cyanobacteria). Newly-produced EPS can bind large amounts of cations (e.g., Ca^{2+}), reducing the calcium carbonate saturation index, inhibiting precipitation. When the EPS matrix is altered, this inhibition may end and carbonate precipitation can commence. This is achieved both through biologically-induced and biologically-influenced mineralization following three main pathways: (1) EPS degradation, (2A) extrinsic, and (2B) intrinsic supersaturation of the EPS binding capacity, and (2C) organomineralization *s.s.* See Section 5 for details.

precipitation within the biofilm. In order to have complete biofilm mineralization through organomineralization, acidic sites have to be rearranged into a template that provides organized nucleation sites (Reitner, 1993; Reitner et al., 1995; Trichet and Défarge, 1995). Défarge et al. (1996) and Trichet et al. (2001) suggest that decaying EPS is reorganized into a 'honeycomb structure' that could promote efficient steric alignment of acidic bonds in EPS. Organomineralization *s.s.* studies are mainly theoretical, often lacking an investigation of the microbial role in producing and consuming the organic matter. It is clear, however, that some abiotic characteristics of the EPS matrix can control the fate of the mineral product.

5.4. EPS control on mineral products

As microbial communities are ubiquitous in basically all environments, bacterial cells and/or their extracellular matrix likely serve as physical substrate for carbonate precipitation and, by extension, to be passively or actively incorporated within the carbonate mineral product. Therefore, the distinction between abiotic and biotic precipitation remains unclear. The definition of biologically-induced mineralization (see Section 1) implies an indirect action of the biota on the surrounding chemical microenvironment that results in carbonate precipitation. Biologically-influenced mineralization (the passive mineralization of an organic substrate) is not a purely abiotic process as the organic matter is biologically produced (see Section 2.1). This issue is even more important considering the search of traces of early life on Earth, which are generally characterized by remnants of organic molecules entrapped within minerals. Abiotic mechanisms that produce organic molecules exist but require special conditions, such as hydrothermal metasomatism (e.g., Fischer–Tropsch type reaction; Anderson et al., 1984; Brasier et al., 2002; Foustoukos and Seyfried, 2004). Additional information, such as the source of alkalinity (which could be physicochemical) is needed to characterize the biogenicity of a carbonate deposit.

Mineral precipitates in microbial mats exhibit a range of morphologies (e.g. micrite, rhombs, dumbbells, needles, spherulites) and mineralogies (e.g., aragonite, calcite, monohydrocalcite, vaterite, high Mg–Calcite to Ca–dolomite). Numerous organomineralization experiments using bacterial cells and/or EPS have shown that the polymer properties (e.g. acidic functional groups abundance, water content) greatly influence the morphology and mineralogy of the calcium carbonate minerals that precipitate (Hardikar and Matijevic, 2001; Braissant et al., 2003; Ben Chekroun et al., 2004; Bosak and Newman, 2005; Ercole et al., 2007; Lian et al., 2007; Rodriguez-Navarro et al., 2007).

Abiotic inorganic experiments using silica gel provide insight in the importance of the gel-like properties of EPS in the precipitation process. Although silica gel differs fundamentally from EPS, this environmentally unusual medium can also produce various types of carbonate minerals (e.g., Given and Wilkinson, 1985; Fernandez-Diaz et al., 1996). Variations in $[Mg^{2+}]$ when supersaturation is reached produce distinct morphologies such as spheres, dumbbell-like, wheat-sheaf-like bundles or rhombs (Fernandez-Diaz et al., 1996). Similar morphologies are also observed in physicochemically-forced precipitation of carbonate minerals within an EPS matrix with (e.g., Ben Chekroun et al., 2004) or without bacterial cells present (e.g., Braissant et al., 2003). Regardless whether organic (EPS) or inorganic (silica gel), the gel properties of the matrix in which precipitation occurs influence diffusion processes, adsorption/complexation of Ca, both of which affect the mineral product.

The experiments with inorganic gel matrices discussed in the previous paragraph, indicate that spherulites or dumbbell shapes in the fossil record do not necessarily represent organomineralization (Ben Chekroun et al., 2004). Therefore, other criteria, such as organic and inorganic biomarkers, have to be considered to conclusively determine a biotic mineral origin. In addition to the extensive use of lipids (Jahnke et al., 2001) and stable isotopic composition (Summons et al., 1999), preserved remnants of EPS matrices (Barbieri et al., 2004; Barbieri and Cavalazzi, 2005; Altermann et al., 2006; Benzerara et al., 2006) and rare Earth elements (REE) fractionation, resulting from preferential sorption of heavy REE on microbial cell walls (Takahashi et al., 2003; Tanaka et al., 2005) have been used in the rock record to determine biotic origin of minerals.

In addition to influencing mm-scale properties of minerals, EPS also affects the nano-scale structure of carbonate precipitates. In natural microbial mats, precipitation often involves replacement of the EPS matrix with small carbonate nanospherulites (e.g., Sprachta et al., 2001; Dupraz et al., 2004). These nanospherulites have sometimes been mistakenly identified as nanobacteria (Kirkland et al., 1999; Schieber and Arnott, 2003; Fratesi et al., 2004). Recent studies of the initial stage of precipitation within the EPS matrix indicate nucleation of ca. 100 nm-amorphous calcium carbonate crystals. Benzerara et al. (2006) used a combination of X-ray and electron microscopy to demonstrate that microbialites from the alkaline Lake Van in Turkey were largely composed of aragonite crystals with a size ranging from 30 to 100 nm in diameter. These crystals are coated by a 10-nm-thick amorphous calcium carbonate layer and are embedded in an organic matrix of EPS. Amorphous calcium carbonate was also found as the initial product in a organomineralization experiment with 12 different *Bacillus* spp., (Hammes et al., 2003). The final morphologies of these minerals, produced during urea hydrolysis varied, possibly as the result of difference in enzyme kinetics. Aloisi et al. (2007) showed that the initial stage of precipitation within SRB EPS consisted of individual amorphous globules (60–200 nm in diameter), clearly forming in the EPS matrix and not as a cell surface process.

The initial precipitation of calcium carbonate in microbial mats (Zavarzin, 2002) can be summarized by the following steps: 1) a local increase in alkalinity and pockets of supersaturation within microdomains of the EPS matrix; 2) formation of an amorphous calcite gel; 3) production of nanospheres from a mixture of amorphous calcite and acidic EPS macromolecules; 4) nanospheres acting as seeds for further carbonate crystallization. The crystals exhibit various shapes, from anhedral to euhedral, as a result of the physicochemical constrains of the organic matrix on the crystal growth. Organic molecules can attach and poison specific crystal faces, thereby inhibiting a part of the crystal growth, which leads to the formation of spherulite, dumbbell or smooth rhombic crystals.

Microbial control of the mineral product is also invoked in the so-called "dolomite problem" (e.g., Land 1998). Dolomite has never been produced in abiotic experiments under Earth surface physicochemical conditions because of kinetic inhibition (Land, 1998). SRB are known to mediate the formation of Ca–dolomite (Vasconcelos et al., 1995; Wright, 1999; van Lith et al., 2003; Wright and Wacey, 2005). However, the exact role of SRB in the dolomite mineralization process remains unclear. It has been suggested that SRB remove SO_4^{2-} inhibition for dolomite formation and that cell walls act as a catalyst for nucleation (e.g., van Lith et al., 2003; Roberts et al., 2004). It is possible that the EPS matrix plays a key role in the dolomite mineralization process, but further studies are needed.

6. Examples of modern microbialites

The purpose of this section is to discuss selected, contrasting examples in various environmental settings rather than reviewing all microbialites that form in natural environments. Theses examples tempt illustrating some of the processes that are described in the previous section of the review.

6.1. Fresh water microbialites

Freshwater microbial deposits often show carbonate precipitation on or impregnation of cyanobacterial sheaths or cells (Freytet and Plet,

1996; Freytet and Verrecchia, 1998). In contrast, precipitation on sheaths is rarely observed in deposits from marine environments (past or present) (Grotzinger and Knoll, 1999) or hypersaline alkaline lakes (Arp et al., 1998, 1999a,b; Dupraz et al., 2004; Dupraz and Visscher, 2005).

Precipitation of $CaCO_3$ associated with the cyanobacterial sheath is believed to be a result of CO_2 uptake during photosynthesis (e.g., Pentecost and Riding, 1986; Thompson et al., 1997; Freytet and Verrecchia, 1998, 1999; Merz-Preisß and Riding, 1999; Riding, 2000). The increase in alkalinity in the cell's microenvironment leading to precipitation is attributed to an exchange of HCO_3^- and OH^- through the cell membrane. Because pH ranges generally from 7 to 10, most of the dissolved inorganic carbon (DIC) is comprised of HCO_3^- ions (Eq. (3)). HCO_3^- is transported into the cyanobacterial cell as a source of inorganic carbon for photosynthesis and converted to CO_2 by the carbonic anhydrase enzyme (Tabita, 1987; Merz, 1992; Verrecchia et al., 1995; Badger, 2001). When cyanobacteria convert HCO_3^- into CO_2, OH^- is released in the exopolymeric sheath environment, which results in an increase of carbonate in solution (see Section 4.2.1). When Ca^{2+} is present, calcium carbonate can nucleate in the cyanobacterial sheath environment, which consists of exopolymeric substances similar to EPS. The same process is invoked for $CaCO_3$ precipitation in the 'S-layer' (exopolymer) of the freshwater cyanobacterium *Synechococcus* sp. during photosynthetic uptake of HCO_3^-, when extracellular OH^- is produced (Thompson and Ferris 1990). Likewise, spherulites (calcitic fibro-radial spherulitic polycrystals) in subaerial calcrete laminar crusts are also a product of photosynthetically induced calcium carbonate precipitation (Verrecchia et al., 1995).

Precipitation within cyanobacterial sheaths through photoautotrophy occurs when a combination of low DIC and a high calcium concentration coexist (Verrecchia et al., 1995; Merz-Preiß and Riding, 1999; Arp et al., 2001). The relatively low DIC is required to allow photosynthesis to effect carbonate alkalinity, enabling precipitation. As a result, in freshwater travertine, impregnation of filaments only occurs in slow-flowing CO_2-poor streams or lakes, whereas high pCO_2 fast-flowing freshwater streams can produce $CaCO_3$-encrusted cyanobacteria through outgassing of CO_2 in resurging groundwater, or in cascades and waterfalls (Merz-Preiß and Riding, 1999). The large DIC pool and pH buffering capacity present under alkaline conditions limit the effect of photosynthetic CO_2 removal, and resulting calcium carbonate precipitation (Arp et al., 2001, 2003). Although the DIC in marine environments is generally lower than in alkaline environments, the presence of complexing ions (e.g., Mg^{2+}, SO_4^{2-}) and acidic organic molecules reduce the concentration of Ca^{2+} and CO_3^{2-} through ion pairing, which results in little change of the saturation index through photosynthesis (Arp et al., 2001). As a consequence, these authors explain the lack of calcified filamentous bacteria in Precambrian stromatolites by the high pCO_2 estimated for this period (Arp et al., 2001).

The *Phormidium encrustatum* travertine from the Sarine River (Fribourg, Switzerland), is an example of precipitation resulting from photosynthetic CO_2 uptake, as demonstrated by SEM pictures (Fig. 7) showing $CaCO_3$ molds of the cyanobacteria (Dupraz, 1999). This simple ecosystem consists only of cyanobacteria, diatoms, and very small crustaceans, lacking significant numbers of other guilds of microbes (e.g., aerobic and anerobic heterotrophs). The travertine also records seasonal growth of vertically- and horizontally-oriented cyanobacterial filaments of *Oscillatoria* and *Phormidium* (Geurts, 1976; Monty, 1976; Freytet and Plet , 1996; Freytet and Verrecchia, 1998).

6.2. Open-marine stromatolites

Open marine stromatolites are found in several locations in the Bahamas (Dravis, 1983; Dill et al., 1986; Reid et al., 1995, 2000, 2003). These microbialites, forming in intert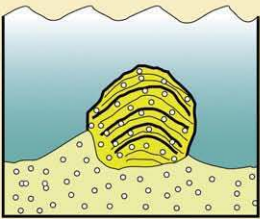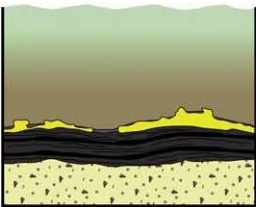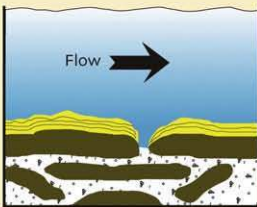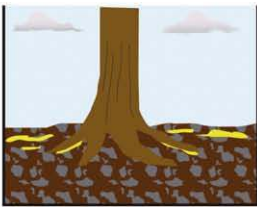idal and subtidal environments, are exposed to high wave energy or strong tidal currents. They are mainly composed of ooids and show an inconstant quality of lamination, from crudely laminated in large build-ups (e.g., Lee Stocking Island; Dill et al., 1986) to very fine, well-developed lamina in small heads (e.g., Highborne Cay; Reid et al., 2000; Fig. 7). Molecular approaches show that the top layers of Bahamian stromatolites are characterized by an unexpectedly high microbial diversity of prokaryotes (Baumgartner et al. submitted). The lamination results from iterative growth at the top of the build-ups of different types of microbial mats, which have distinctive mineral products (Reid et al., 2000). These types include (1) mats dominated by the filamentous cyanobacteria *Schizothrix,* which trap and bind ooids; (2) thin biofilms rich in heterotrophs that rapidly lithify, forming aragonitic micritic laminae, sealing the underlying ooids; and (3) mats periodically colonized by the coccoid cyanobacteria *Solentia*, which bore and fuse ooids together to form well-indurated layers (MacIntyre et al., 2000; Reid and MacIntyre, 2000; Reid et al., 2000).
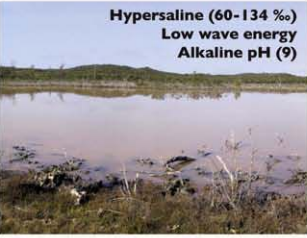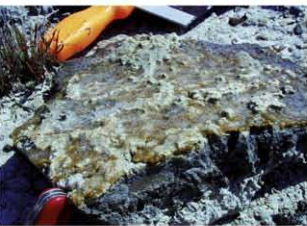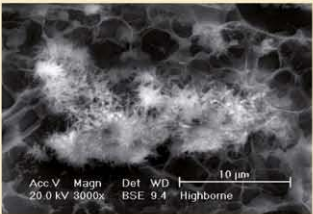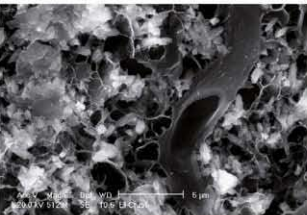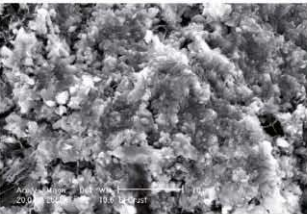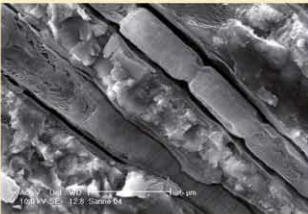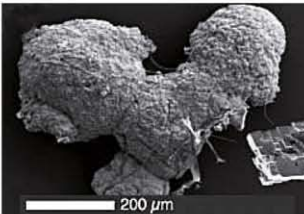
Although eukaryotic microorganisms such as diatoms can participate in the trapping and binding of sediment (Awramik and Riding 1988), the stromatolite-building process that creates lithified, laminated buildups is essentially performed by prokaryotic (microbial) communities (Reid et al., 2000, 2003). Indeed, the environmental selective pressure of periodic heavy burials seems to have favored these bacterial communities, especially cyanobacteria (Andres and Reid, 2006; Kromkamp et al., 2007; Perkins et al., 2007). Changes in sedimentation regime may however allow for macroalgal colonization and laminae destruction. Developing in high energy environments of active sediment transport, these cyanobacterial communities have the ability to survive and recover from deep burial (e.g., by substituting fermentation pathways for oxygenic photosynthesis), a feature that may have contributed to their success in modern and past environments (Kromkamp et al., 2007).

It is important to note that trapping and binding of sediment alone will not produce laminated stromatolites. To generate lamination, the trapping and binding process must be periodically interrupted to allow the formation of micritic lamina and, sometimes, welding of ooids through *Solentia*'s boring activity. The development of the precipitated aragonitic laminae correlates to maximum SRB activity (Visscher et al., 2000) and abundance (Baumgartner et al., 2006). The precipitation of $CaCO_3$ is due to an increase in alkalinity resulting from sulfate reduction and Ca^{2+} release from EPS, when degraded by various heterotrophic bacteria (Visscher et al., 1998, 2000; Reid et al., 2000; Paerl et al., 2001). The result is a thin aragonitic laminar precipitate, with an isotopic signature that confirms the role of SRB (Andres et al., 2005).

The cycling of microbial communities in the modern marine stromatolites, resulting in lamination, is driven by both biological (i.e., intrinsic) and environmental (i.e., extrinsic) factors (Seong-Joo et al., 2000; Reid et al., 2003). It is unknown which specific intrinsic (e.g., ecological interactions, production and consumption of organic and inorganic compounds) and extrinsic (e.g., light, nutrients, space, hydrodynamics and sedimentation) factors are key, and to what extent the intrinsic and extrinsic factors contribute to the community cycling (Andres and Reid, 2006).

Emphasizing the coarse grained, detrital nature of modern marine stromatolites, some authors have proposed that modern marine stromatolites do not represent appropriate analogs for ancient stromatolites, which generally display micritic microstructures. However, the role of the bacterial community in the carbonate precipitation of the micritic laminae has clearly been demonstrated and is an essential feature of most Bahamian stromatolites (Reid et al., 2000; Visscher et al., 2000; Dupraz and Visscher, 2005) as well the Shark Bay stromatolites, especially in subtidal environments (Reid et al., 2003). Also other microbial processes could have played an important role in the Precambrian (e.g., balance between 'trapping and binding' and *in situ* precipitation), based on these geomicrobiological studies, the

MARINE ENVIRONMENTS	HYPERSALINE LAKES	FRESHWATER ENVIRONMENTS	CONTINENTAL ENVIRONMENTS
HIGHBORNE CAY COARSE-GRAINED STROMATOLITES	**ELEUTHERA** MG-CALCITE CRUST AT SURFACE OF MICROBIAL MAT	**SARINE RIVER** CALCITE CRUST ON SURFACE STONES	**IVORY COAST** CALCITE PRECIPITATION IN SOILS

Environments

Open sea (35 ‰) / High wave energy / Neutral to slighty alkaline — Hypersaline (60-134 ‰) / Low wave energy / Alkaline pH (9) — Freshwater / River current — Orthox soils

Dominant microbes

| Schizothrix - Solentia Heterotrophs | Microcoleus - Phormidium Entophysalis - Gleocapsa Heterotrophs | Phormidium - Oscillatoria | Heterotrophs (Oxalotrophic bacteria, Fungi) |

Microbialite

| Open-Marine stromatolites
- Laminated
- Coarse grained | Leiolite to thrombolite
- Carbonate crust at the surface of microbial mat | Travertine
- Laminated
- Micrite | Carbonate crust/blocs
- Micrite - sparite
- Spherulite |

SEM microstructure

Lithification process

| EPS mineralization
Sulfate reduction | EPS mineralization
Sulfate reduction | Sheath and EPS mineralization
Photosynthetic uptake of CO$_2$ | EPS mineralization
Heterotrophic bacteria activity (oxalotrophs) |

ecological model of lamina formation associated with the cycling of bacterial communities at the surface of the build-ups can possibly be transposed in the fossil record and provides an important conceptual model for the fossil counterparts.

6.3. Microbialites in hypersaline lakes

Numerous examples of microbialite formation in hypersaline lakes have been reported (e.g., Neumann et al., 1988; Mann and Nelson, 1989; Gerdes et al., 1994; Reitner et al., 1997; Arp et al., 1999a,b; van Lith et al., 2003; Jonkers et al., 2003; Burns et al., 2004; Wright and Wacey, 2005; Ludwig et al., 2005; Dupraz and Visscher, 2005). Most of these biologically-induced mineralization studies deploy different approaches and often lack a complete characterization of microbial communities and mineral products. It is likely that mechanisms of mineral formation differ from one system to another, as production of alkalinity depends on physicochemical properties and the balance between the various types of metabolic strategies present in the mat (Section 4). Clearly, for a complete understanding of the biologically induced mineralization, a study has to combine both microbiological and geological approaches.

Although some authors invoke the role of photosynthetic uptake of CO_2 by cyanobacteria as a the main process of $CaCO_3$ precipitation in hypersaline lake (Jonkers et al., 2003; Ludwig et al., 2005), an increasing number of studies demonstrate the key role played by heterotrophic communities, such as sulfate-reducing bacteria in the lithification of these mats (Zavarzin, 2002; van Lith et al., 2003; Arp et al., 2003; Dupraz et al., 2004; Lopez-Garcia et al., 2005; Visscher and Stolz, 2005; Dupraz and Visscher, 2005; Vasconcelos et al., 2006). The hypersaline lake of Salt Pan in Eleuthera, Bahamas is an example of lithifying hypersaline microbial mat system in which SRB activity plays a key role (Fig. 7; Dupraz et al., 2004). This closed lake system is approximately 1 km^2 and exhibits a transition from a lithifying (hard continuous crust) to a non-lithifying mat (thick gelatinous mat). The microbialites appear as a thick crust at the top of the mat, the mineralogy of which is a solid solution of high-Mg calcite with 11–17% Mg^{2+} substituting for Ca^{2+}.

Although cyanobacterial CO_2 fixation in the Salt Pan system provides the organic carbon for (an)aerobic respiration and fermentation, no precipitation occurs in or on the sheaths of active cyanobacteria and very little carbonate precipitation occurs where photosynthesis peaks. Alkalinity microgradients within cyanobacterial sheaths, created through photoautotrophic removal of CO_2 and release of OH^-, do not seem to play an important role in carbonate precipitation because of the high DIC content and the strong pH buffering of the hypersaline water, similar to the freshwater scenario described above (Arp et al., 2003; Dupraz et al., 2004). As in the marine stromatolites, two-dimensional mapping of sulfate reduction using $^{35}SO_4^{2-}$ coated Ag-foil, indicates a close spatial relationship between SRB and the precipitated crust (Dupraz et al., 2004). In contrast to the deeper soft mats, the lithifying mats are found in the shallow lake section, where UV radiation might be responsible for alteration of EPS by removing inhibition of precipitation (Fig. 6) producing additional organic carbon. These lithifying mats are characterized by steep geochemical gradients of oxygen, sulfide, pH and organic carbon. The light regime and coupled metabolic activities decrease drastically in the deeper water, producing non-lithifying EPS-rich mats. Observations using low-temperature SEM (with a cryo transfer unit) show that micrite nucleation is initiated within the exopolymer matrix (Fig. 7; Dupraz et al., 2004; Dupraz and Visscher, 2005). The precipitate nucleates on, or replaces, the organic framework, without initially breaking up the three-dimensional structure of the EPS.

6.4. Microbialites in soils

Terrestrial microbialites also form in various terrestrial environments, including soils, caves (Verrecchia and Verrecchia, 1994; Loisy et al., 1999; Canaveras et al., 2006; Barton and Northup, 2007; Belnap and Lange, 2001), and are especially well-studied in desert soils (Verrecchia et al., 1995; Garcia-Pichel, 2002; Garcia-Pichel et al., 2003) and tropical forest soils (Cailleau et al., 2004). In the case of the acidic African forest soils, precipitation is due to the association between plants, fungi and oxalotrophic bacteria (Cailleau et al., 2004, 2005; Verrecchia et al., 2006). These microbial/eukaryotic associations in carbonate-free ferralitic oxisols are responsible for vast $CaCO_3$ deposits around the African iroko tree (*Milicia excelsa*, Moraceae). The formation of these carbonate deposits follows two steps (Braissant et al., 2004): (1) the production of oxalic acid by plants and fungi and (2) bacterially-mediated transformation of oxalate into calcium carbonate.

Two pools of oxalic acid are present in this soil: (1) oxalic acid and calcium oxalate crystals (as whewellite) produced by the tree as a by-product of photosynthetic CO_2 fixation and released during decay, and (2) oxalic acid and calcium oxalate (as weddellite) produced by soil fungi. The first oxalate source is oxidized by endophytic oxalotrophic bacteria inside the tree and the second source in the surrounding soil by free-living oxalototrophic bacteria. The microbial transformation of oxalate into carbonate increases the soil pH (pH 8.9), which makes the immediate iroko tree environment suitable for calcite precipitation and preservation. In contrast, the soil away from the iroko rhizosphere has slightly acidic pH (4.9–6). The oxalate–carbonate pathway creates the "iroko carbon sink", which can store up one metric ton of atmospheric CO_2 during a typical lifespan of the tree (Cailleau et al., 2005). This carbon sink (total 2×10^{-4} Gt for iroko trees in Ivory Coast) is significant because of the long residence time of mineral carbon (10^2–10^6 years), which is 10^5 times longer than soil organic matter. A similar mechanism has been implied in lithification of cacti (Garvie 2003).

7. Conclusions

We present in this paper mechanisms and examples of organomineralization *s.l.* (biologically-induced and biologically-influenced mineralization) forming lithifying microbial mats. The pattern that emerges from a number of studies representing diverse environments is that of microbial mats as "geochemical bioreactors" with two fundamental components: 1) the microbial community, whose metabolism alters the geochemical environment. The combined metabolism of all guilds comprising the microbial community acts as an "alkalinity engine" by changing the $\{Ca^{2+}\}$ and $\{CO_3^{2-}\}$, or SI (Eq. (2)), and 2) the EPS matrix, the properties of which influence the mineral product formation through cation binding/release and by providing mineral nucleation sites. The EPS matrix is influenced by many key players in the microbial community that produce and modify the physicochemical properties of this organic matrix. Additional abiotic processes may alter the EPS matrix as well. The delicate balance of a combination of microbial and physicochemical processes, which is different in different environments, is ultimately responsible for the formation of the emerging microbialite. Clearly, the coordination of microbial metabolism and other physiological properties has been the key to the success of the microbial mat ecosystem throughout Earth's history. This may require chemical communication (through quorum sensing) within and between the various guilds (Decho et al., 2009). All these processes need to be understood in more detail, and currently we are barely touching the

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Fig. 7. Examples of modern microbialites. A. Open-marine stromatolite (Exumas, Bahamas). B. Hypersaline microbialites (Eleuthera, Bahamas). C. Freshwater travertine (Sarine River, Switzerland). D. Carbonate deposits in tropical soils (Ivory Coast, Africa). See Section 6 for details.

tip of the carbonate iceberg. Furthermore, the greatest challenge that remains is the translation of all these processes and products in the fossil record and especially through the filter of the diagenesis. Research in contemporary microbial mat systems has a great potential to link microbial metabolism and properties of the EPS matrix to particular mineral features (e.g., mineralogy, morphology, biomarkers) allowing a better understanding of the past.

Acknowledgements

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