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Microbial mats as bioreactors: populations, processes, and products

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Abstract

Microbial mats are dynamic and complex ecosystems exhibiting spatial and temporal heterogeneity. The physical/chemical environment is typified by steep gradients and distinct microenvironments. These microenvironments support a great diversity of species with a wide range of metabolic processes. These processes often result in coupled reactions and biogeochemical cycles, and produce important end products such as trace gases and mineral precipitates. The latter can impact the composition and character of the sediment, imparting a "biosignature." These biosignatures can be preserved in the rock record and are useful in the interpretation of fossil record on Earth and possibly as an indication of life on other planetary bodies. The modern marine stromatolites of the Exuma Cays, Bahamas, provide an ideal system for studying the populations, processes, and products in a microbial ecosystem using a multidisciplinary approach. In order to acquire redox energy, microbial populations need to carry out metabolic reactions at rates faster than the equivalent chemical (abiotic) reactions. As such, microbes can be viewed as bioreactors that preferably oxidize carbon to CO_2 to maximize the energy yield. The study of the microbial role in carbonate sedimentation and lithification in these stromatolites provides a picture of microbial mats as bioreactors producing a biosignature.

Keywords: Stromatolite; Microbial mats; Bioreactors; Carbonate precipitation; Lithification

1. Introduction

Microbial mat is a general term that is used to describe a variety of microbial communities, from the cyanobacterial slime that forms in a drainage ditch to the complex, multilayered microbial ecosystems commonly observed in salt marshes and estuaries (Krumbein et al., 1977; Stal et al., 1985; Nicholson et al., 1987). Their propensity for trapping, binding, and precipitating sediments results in the formation of sedimentary structures such as laminated sediments and stromatolites (Riding, 2000). These structures can be preserved in the rock record and it is from these remains that we reconstruct the early history of life on Earth (Schopf, 1983; Des Marais, 1990, 1997;

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Golubic, 1991; Grotzinger and Knoll, 1999). From an ecological perspective, microbial mats are ecosystems even though their geographic extent may be exceedingly small (on the order of a few meters). They contain the essential trophic groups (e.g., primary producers, consumers, and decomposers) and their populations are organized into specific communities interacting with each other and their environment (Stolz et al., 1988). These populations can be further grouped into specific guilds and assemblages, based on their metabolic properties (Visscher et al., 1992, 2002) and taxonomic affiliations (Ward et al., 1998).

The physical/chemical environment is typified by gradients (i.e., oxygen, sulfide, and light) that are often quite steep (i.e., the oxygen concentration may go from supersaturated to immeasurable within a few millimeters), resulting in distinct microenvironments. These microenvironments provide a plethora of habitats resulting in a community structure that exhibits both spatial and temporal heterogeneity. Thus, microbial mats are dynamic ecosystems that support a great diversity of species with a wide range of metabolic processes that take place in close proximity. These processes often result in coupled reactions (e.g., reduction and oxidation of an element such as C, S, N, etc., or, alternatively, stepwise oxidation or reduction of a compound) that support robust biogeochemical cycles. While these processes may be subject to the temporal environmental oscillations (i.e., diurnal and seasonal cycles; Visscher and van den Ende, 1994), the net result can be the formation of important endproducts such as trace gases and mineral precipitates (Fig. 1). As such, microbial mats may be viewed from the materials science perspective as bioreactors. The modern marine stromatolites of Highborne Cay, Bahamas, provide an opportunity to explore this concept. This paper reviews net $CaCO_3$ precipitation from a microbial perspective, exploring the effect of metabolism on geochemical characteristics of Ca^{2+} and $CO_2/HCO_3^-/CO_3^{2-}$ activity.

The classic view of a microbial mat, with a surface community of oxygenic cyanobacteria underlain by subsequent layers of anoxygenic phototrophic bacteria and sulfate-reducing bacteria (SRB) (Krumbein, 1983; Cohen et al., 1984), has been dramatically revised. Instead of a layering that results from a sequence of metabolic reactions determined by gradients of light and redox potential (resulting in the sequence use of O_2, Fe(III)/Mn(IV), NO_3^-, SO_4^{2-}, etc., as electron acceptor), most types of metabolism are found in association with the cyanobacterial layer. For example, populations of SRB have now been found at the surface of mats (Fründ and Cohen, 1992; Visscher et al., 1992), and methanogenesis may peak there as well (Hoehler et al., 2002). Regardless of the vertical structure, marine microbial mats are composed of four major functional groups: oxygenic phototrophs (CYN), aerobic heterotrophic bacteria (HET), sulfate-reducing bacteria (SRB), and sulfide-oxidizing bacteria (SOB). The oxygenic phototrophs, which include primarily cyanobacteria, are the primary producers of the mat system, coupling light energy to CO_2 fixation. They may also provide assimilable nitrogen through nitrogen fixation. The aerobic heterotrophic bacteria oxidize a significant fraction of the fixed organic

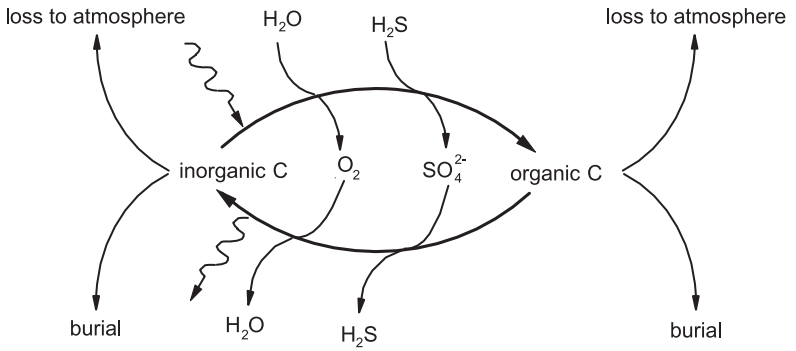


Fig. 1. Coupled cycles of carbon and oxygen and sulfur. Arrows on extreme left and right indicate the potential formation of biogenic signatures; downward arrow on the left is a means by which $CaCO_3$ precipitates.

carbon (e.g., photosynthate) in the system, gaining energy through respiration using O_2 as the terminal electron acceptor. The sulfate-reducing bacteria are the dominant anaerobic respiring organisms, producing sulfide in the process. The sulfide-oxidizing bacteria are chemolithotrophic organisms that oxidize reduced sulfur compounds using either O_2 or nitrate as terminal electron acceptors (Jørgensen et al., 1983; Stal et al., 1985; van Gemerden, 1993; Visscher et al., 1992, 1998). They recycle the reduced sulfur and may provide additional organic carbon through autotrophic CO_2 fixation. However, this outline emphasizes the "metabolic specialty" of the respective functional groups. A significant metabolic diversity and flexibility exists, and in light-driven ecosystems such as microbial mats, it is important to distinguish between daytime and nighttime processes (Table 1).

Microbial mat ecosystems are efficient in element cycling and, once developed, require little more than light to function. As such, they can be viewed as semiclosed systems, making it relatively easy to create mass balances and study element cycling. Compared to other benthic ecosystems, microbial mats have extremely high rates of oxygenic photosynthesis, aerobic respiration, sulfate reduction, and sulfide oxidation (e.g., Revsbech et al., 1986; Canfield and Des Marais, 1993). The metabolic rates of organisms comprising the mats are so high that the community production per unit mass rivals that of rain forests (Krumbein et al., 2003; Jørgensen, 2001).

2. Carbonate sedimentation and lithification in modern marine stromatolites

Highborne Cay is one of many localities in the Exuma Cays where stromatolites are found forming in open ocean waters of normal salinity (Dravis, 1983; Dill et al., 1986; Reid and Brown, 1991; Reid et al., 1995, 2000; Steneck et al., 1996, 1997). The term *stromatolite* is used here for organosedimentary structures formed by trapping and binding of sediment and net carbonate-precipitating activities of microorganisms. These structures, which are characterized by alternating soft and hard layers, may be a few centimeters to over 2 m in height and form within a reef complex lying along the windward east coast of the Exuma Cays (Reid et al., 1995). The stromatolites are composed primarily of fine-grained carbonate sands that range in size from 125 to 250 μm and are stabilized by lithified layers, giving rise to a classic stromatolitic structure (Reid et al., 1995; Fig. 2). The microbial communities involved in the deposition of the Highborne Cay stromatolites have been under investigation for over a decade (Reid et al., 1995, 2000; Visscher et al., 1998, 2000, 2002; Stolz et al., 2001). Three different types of carbonate laminations have been discerned: thick (200 μm to several millimeters) layers composed of unconsolidated carbonate ooids (carbonate grains); thin (10–30 μm) micritic (microcrystalline $CaCO_3$ with diameter smaller than 4 μm) layers; and thicker (100–300

Table 1
Daytime and nighttime metabolic activities of key functional groups of a microbial mat community

Functional group	Daytime metabolic function	Nighttime metabolic function
Cyanobacteria	Carbon fixation (photosynthesis): $CO_2+H_2O \rightarrow CH_2O+O_2$	Fermentation (including H_2 production), N_2 fixation, glycogen degradation
Aerobic heterotrophs	Carbon oxidation (respiration): $CH_2O+O_2 \rightarrow CO_2+H_2O$	Fermentation, denitrification: $5CH_2O+2H_2O \rightarrow HCO_3^-+H^++4CH_3O$ and $5CH_2O+4NO_3^- \rightarrow 5HCO_3^-+H^++2N_2+H_2O$
Sulfide oxidizers	Sulfide oxidation: $H_2S+2O_2 \rightarrow SO_4^{2-}+2H^+$ (sometimes coupled to carbon fixation)	Denitrification, fermentation: $5HS^-+8NO_3^- \rightarrow 5SO_4^{2-}+4N_2+ H_2O+3OH^-$
Phototrophic sulfide oxidizers	Carbon fixation (anoxygenic photosynthesis coupled to sulfide oxidation): $2CO_2+H_2S+2H_2O \rightarrow 2CH_2O+SO_4^{2-}+2H^+$	Fermentation, synthesis of Bchl*a*, degradation of glycogen
Anaerobic heterotrophs-sulfate reducers	Carbon oxidation (sulfate respiration): $2CH_2O+SO_4^{2-} \rightarrow 2HCO_3^-+2H_2S$	Same as daytime
Anaerobic heterotrophs-methanogens	Carbonate respiration: $4H_2+CO_2 \rightarrow CH_4+2H_2O$ and $2CH_2O \rightarrow CH_4+CO_2$	Same as daytime

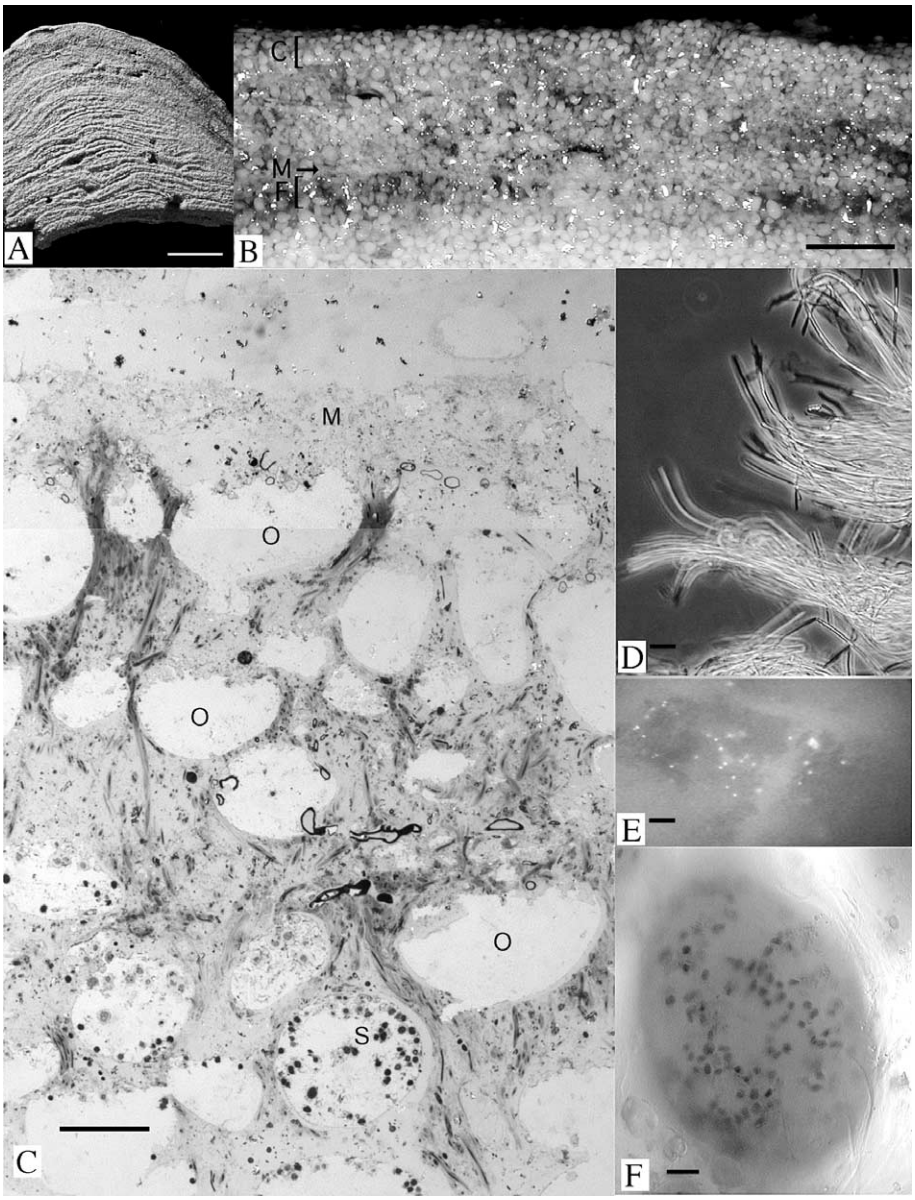


Fig. 2. The surface microbial communities of the modern marine stromatolites of Highborne Cay. (A) Vertical section through a stromatolite revealing the laminations; bar=2 cm. (B) Vertical section of the stromatolite surface showing a caramel-colored stage 1 community at the surface; bar=2 mm. (C) A subsurface micrite crust (arrow) and a subsurface *Solentia* sp.-infested layer (F); bar=100 μm. (C) Bright field light micrograph of an oriented thick section of the top 1.2 mm of stage 3 surface community showing the surface micritic layer (M), ooids (O), and *Solentia* sp.-infested ooids (S); bar=10 μm. (D) Phase contrast light micrograph of *Schizothrix gebeleinii* from the surface of a stage 1 community; bar=10 μm. (E) Fluorescence micrograph of the micritic crust. The bacteria have been stained with acridine orange and are fluorescing (bright spots); bar=10 μm. (F) Bright field light micrograph of an ooid colonized by *Solentia* sp. (the dark spots); bar=10 μm.

μm) hard laminations composed of fused ooid grains. Three different surface microbial communities have been identified, each representing a different growth stage, and each involved in the deposition of a particular form of carbonate (Reid et al., 2000; Fig. 2B and C).

The surface community involved primarily in the trapping of the carbonate ooids is dominated by the filamentous cyanobacterium *Schizothrix gebeleinii* and characterizes the stromatolite surface during periods of rapid sediment accretion (Fig. 2D). This cyanobacterial community, which is clearly visible as a caramel-green layer, provides the stromatolite with organic carbon during photosynthesis. The vertical profile of O_2 varies depending on the time of day, penetrating to less than 2 mm at daybreak and reaching a maximum of 5 mm with concentrations near twice saturation during late afternoon (Visscher et al., 1998, 2002). At depth, the caramel color bleaches with burial, resulting in white unlithified layers of unconsolidated ooids. The community associated with the development of a micritic crust is typified by a stromatolite surface populated by a community of heterotrophic bacteria embedded in amorphous extracellular polymeric secretions (EPS) underlain by filamentous cyanobacteria (Fig. 2E). In situ measurements indicate high rates (approximately 15 μM h^{-1}) of sulfate reduction (Visscher et al., 2000), which are one to three orders of magnitude higher than measured in continental margins (Ferdelman et al., 1999). The micritic crust, which forms during periods of little sediment accretion (i.e., few ooids are trapped), persists at depth in the stromatolite. Prolonged periods of low sedimentation lead to the further development of the community and the colonization of the near subsurface by the endolithic cyanobacterium *Solentia* sp. (Fig. 2F). This mat community shows the greatest species diversity with a variety of filamentous cyanobacteria, anoxyphototrophic bacteria, SRB, and SOB (Visscher et al., 1998, 2000; Stolz et al., 2001, Stolz, 2003). This community is also typified by high rates of sulfate reduction (ca. 20 μM h^{-1}; Visscher et al., 2000). The color of the layer remains for several centimeters below the surface before eventually becoming gray-green. The continued boring activity, characteristic for the endolithic cyanobacteria, and carbonate deposition within the bore holes of the ooids result in a fused-grain layer (Macintyre et al., 2000). In situ observation of the three different surface communities and their characteristic sedimentological products has led to a conceptual model in which the transformation from one type into another occurs in a cyclic fashion (Reid et al., 2000). The cyclical succession and subsequent burial of these surface communities result over time in the growth and laminated structure of the stromatolite. As much as the stromatolites of Highborne Cay are an example of the dynamic nature of microbial ecosystems, their physical structure represents the net result of carbonate precipitation and dissolution.

3. Carbonate precipitation and dissolution

The majority of the carbonates on the Earth's surface is biogenic and results from the precipitation of the CO_2 generated during microbial metabolism (e.g., Castanier et al., 1999, 2000). Due to the low solubility of carbonates, deposits are formed, especially in marine environments. Carbonates can be precipitated intracellularly or extracellularly. Extracellular carbonates (e.g., $CaCO_3$) have been linked to aerobic respiration, which increases the inorganic carbon concentration, resulting in an abiotic reaction with Ca^{2+} ions in the environment (Chafetz and Buczynski, 1992). Locally elevated CO_2 concentrations increase HCO_3^- and CO_3^{2-}, creating favorable conditions for $CaCO_3$ precipitation. Alternatively, HCO_3^- can dissociate under alkaline conditions; the proton can enter the cell while the CO_3^{2-} precipitates with Ca^{2+} (De Vrind-deJong and de Vrind, 1998). A similar scenario has been proposed for intracellular $CaCO_3$ precipitation. HCO_3^- is transported over the cell membrane via a bicarbonate transporter, then is cleaved intracellularly (by carbonic anhydrase type enzymes) to be used in CO_2 fixation (Robbins and Yates, 1998), while the other fraction precipitates with cations like Ca^{2+} and/or Mg^{2+}. It has been hypothesized that microorganisms benefit from $CaCO_3$ precipitation by production of a H^+, which results from the reaction of Ca^{2+} and HCO_3^- (see reaction equations). The precipitation of $CaCO_3$ occurs extracellularly, and the H^+ assists in the generation of a proton motive force (Δp), which provides a mechanism for energy generation, uptake of substrates, discharge of metabolites, and other cellular processes (McConnaughey and Whelan, 1997).

The precipitation depends on the saturation index SI, which is a function of the solubility product constant k_{SP} and the in situ pH and Ca^{2+}, or, SI=log (IAP/k_{SP}), where IAP is the ion activity product in the sample. By default, SI=0 at equilibrium. The solu-

bility product constant $k_{SP}=Ca^{2+}\times CO_3^{2-}/CaCO_3=10^{-8.42}$ for calcite and $10^{-8.22}$ for aragonite. If IAP>k_{SP}, then the solution is oversaturated. Laboratory experimentation has demonstrated that an SI≥0.8 is required before precipitation occurs (Kempe and Kazmierczak, 1994). Interestingly, preliminary investigations have demonstrated that the [Ca^{2+}] in Highborne Cay stromatolites is approximately two to five orders of magnitude higher (24–88 mM) within the surface mats than in the surrounding seawater (P. Visscher, unpublished data). In summary, the requirements for $CaCO_3$ precipitation are: (1) supersaturation with respect to $CaCO_3$ caused by high activities of Ca^{2+} or CO_3^{2-}; and (2) the onset of nucleation, which is the point at which the activation energy is overcome and precipitation of the critical nuclei begins. Calcium carbonates are also formed directly by organisms as surface structures of cells (e.g., calcifying algae) and some protozoan shells (foraminifera and coccolithophorids), as well as mollusks and bryozoa.

Clearly, many factors play a role in net precipitation of $CaCO_3$. The pH of seawater is relatively well-buffered and only a significant shift in the alkalinity (the total concentration of bases in the water) will result in precipitation or dissolution of $CaCO_3$. As is true for all the biochemical reactions below, the observed precipitation of $CaCO_3$ in cultures of aerobic heterotrophs (Castanier et al., 2000; Folk and Chafetz, 2000; Chafetz and Buczynski, 1992; Rivadeneyra et al., 1993, 1999) needs very careful evaluation before extrapolation to the field. Experiments with pure cultures (typically >10^9 cells/ml, or on plates in colonies) are not very relevant for the in situ precipitation, and molecular ecological studies (e.g., fluorescent in situ hybridization) and/or geochemical investigations (e.g., stable isotope ratios) are essential for an appropriate interpretation of laboratory data.

4. Microbes as biochemical reactors

In order to understand the role of microbes in precipitation and dissolution, their metabolic activity and associated biochemical reactions need to be evaluated. The combination of the biotic reactions and their abiotic (geochemical) counterparts determines the net effect that a microbial functional group will have on carbonate precipitation and dissolution.

As outlined above, there are four functional groups that are key players in microbial mats (i.e., CYN, HET, SRB, and SOB; van Gemerden, 1993; Visscher et al., 1998). However, before discussing the specifics of these four groups of microbes on carbonate precipitation in mats, a number of functional groups of general biogeochemical interest will be reviewed. The underlying consideration is the fact that most microbes engage in redox reactions, whether organic or inorganic, in order to generate and conserve energy. In doing so, they must be more efficient in mediating a certain reaction than the abiotic equivalent. Coupling of several redox reactions results in element cycling, which has multiple effects on the environment: (1) physical effects, including dissolution, precipitation, volatilization, and fixation of elements; (2) chemical processes, such as hydrolysis, condensation, biosynthesis, biotransformation, and biodegradation; and (3) spatial translocations, including transport driven by concentration gradients and physical processes. For this review, we will focus on the role microbes play in catalyzing chemical reactions that result in calcium carbonate precipitation or dissolution. Since ecosystems, including microbial ones, maximize the energy yield, we assume here that during respiration, organic carbon is transformed to the most oxidized form, CO_2, and electron donors are reduced to the most reduced forms. It should be noted that under in situ conditions, this may take place in a single metabolic reaction, or more likely in a sequence of aerobic and anaerobic conditions.

5. Coupled biotic–abiotic reactions that precipitate or dissolve $CaCO_3$

5.1. Photoautotrophy

During photosynthesis, microorganisms use light energy to generate ATP and reducing power to support carbon fixation. Oxygenic phototrophs (cyanobacteria) use predominantly H_2O as electron donor for photosynthetic electron transport, while anoxygenic phototrophs (purple and green anoxybacteria) primarily use reduced sulfur compounds as electron donors.

5.1.1. Oxygenic photoautotrophy

Cyanobacterial photosynthetic activity in microbial mats is typically very high (Revsbech, 1984; Jørgensen and Cohen, 1977; Visscher et al., 2002) and, as a result, the pH may increase to values higher than 10 (Visscher and van Gemerden, 1991). This increase in pH is the result of CO_2 production in a bicarbonate-buffered (marine) environment:

$$HCO_3^- \rightarrow CO_2 + OH^- \text{ (chemical)}$$

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \text{ (microbial)}$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \text{ (chemical)}$$

$$H^+ + OH^- \rightarrow H_2O \text{ (chemical)}$$

$$\textit{sum: } 2HCO_3^- + Ca^{2+} \rightarrow CH_2O + O_2 + CaCO_3$$

Thus, carbon fixation by oxygenic photoautotrophs yields 1 mol of $CaCO_3$ per mole of CO_2 consumed.

5.1.2. Anoxygenic photoautotrophy

Purple and green sulfur bacteria are commonly found in microbial mats and stratified water columns. Anoxygenic CO_2 fixation impacts the pH in a similar manner as the oxygenic counterpart, with the difference being that HS^- oxidation decreases alkalinity:

$$2HCO_3^- \rightarrow 2CO_2 + 2OH^- \text{ (chemical)}$$

$$HS^- + 2CO_2 + 2H_2O \rightarrow 2CH_2O + SO_4^{2-} + H^+ \text{ (microbial)}$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \text{ (chemical)}$$

$$2H^+ + 2OH^- \rightarrow 2H_2O \text{ (chemical)}$$

$$\textit{sum: } 3HCO_3^- + Ca^{2+} + HS^- \rightarrow 2CH_2O + CaCO_3 + SO_4^{2-}$$

The overall effect is that during anoxygenic photosynthesis, 0.5 mol of $CaCO_3$ precipitates per mole of CO_2 fixed.

5.2. Aerobic respiration (chemoorganoheterotrophy)

As outline above, heterotrophic microbes can only precipitate $CaCO_3$ if the system is very well-buffered so that CO_2 production results in an increase in $[CO_3^{2-}]$ without a change in pH, and the environment contains sufficiently high $[Ca^{2+}]$. This has been shown in laboratory cultures (e.g., Chafetz and Buczynski, 1992; Rivadeneyra et al., 1993, 1999). Otherwise, the following respiration equations need to be considered:

$$CH_2O + O_2 \rightarrow HCO_3^- + H^+ \text{ (microbial)}$$

$$CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+} \text{ (chemical)}$$

$$\textit{sum: } CH_2O + CaCO_3 + O_2 \rightarrow 2HCO_3^- + Ca^{2+}$$

The overall effect of aerobic heterotrophy is loss of one $CaCO_3$ per CH_2O oxidized.

5.2.1. Fermentation

In the absence of O_2 as terminal electron acceptor, many organisms are capable of fermentation of organic carbon, in which the same compound acts as electron donor and acceptor:

$$3CH_2O + H_2O \rightarrow HCO_3^- + H^+ + C_2H_6O \text{ (microbial)}$$

$$CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+} \text{ (chemical)}$$

$$\textit{sum: } 3CH_2O + CaCO_3 + H_2O \rightarrow 2HCO_3^- + Ca^{2+} + C_2H_6O$$

Fermentation results in the loss of 1 mol of $CaCO_3$ per 5 mol of CH_2O used, and has only a minor impact on the dissolution process. It should be noted that the equation drafted above is derived from ethanol fermentation and that many other potential fermentative pathways may have other effects on the $CaCO_3$ budget.

5.3. Anaerobic respiration (chemoorganoheterotrophy)

In the absence of O_2, alternative terminal electron acceptors (TEAs) can be used in redox reactions. These TEA include: FeOOH, NO_3^-, SO_4^{2-}, and HCO_3^-.

5.3.1. Dissimilatory iron-reducing bacteria

Iron reduction may be important in freshwater and coastal marine environments (Nealson and Stahl, 1997; Lovley and Coates, 2000):

$$CH_2O + 4FeOOH + H_2O \rightarrow HCO_3^- + 4Fe^{2+} + 7OH^- \text{(microbial)}$$

$$7Ca^{2+} + 7HCO_3^- \rightarrow 7CaCO_3 + 7H^+ \text{ (chemical)}$$

$$7H^+ + 7OH^- \rightarrow 7H_2O \text{ (chemical)}$$

$$\textit{sum: } CH_2O + 4FeOOH + 7Ca^{2+} + 6HCO_3^- \rightarrow 7CaCO_3 + 4Fe^{2+} + 6H_2O$$

Iron reduction precipitates $CaCO_3$ with a gain of 7 mol of $CaCO_3$ per mole of CH_2O oxidized.

5.3.2. Dissimilatory nitrate reduction

Denitrification, the dissimilatory reduction of nitrate to dinitrogen, may take place in a variety of sediments. However, in the marine environment, nitrogen is considered to be the limiting element and assimilatory nitrate reduction will compete with the dissimilatory use of NO_3^-:

$$5CH_2O + 4NO_3^- \rightarrow 5HCO_3^- + 2N_2 + 2H_2O + H^+ \text{(microbial)}$$

$$CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+} \text{ (chemical)}$$

$$\textit{sum: } 5CH_2O + 4NO_3^- + CaCO_3 \rightarrow 6HCO_3^- + 2N_2 + 2H_2O + Ca^{2+}$$

The net result is a minor loss (0.2 per CH_2O oxidized) of $CaCO_3$ during nitrate reduction.

5.3.3. Sulfate-reducing bacteria

The reduction of sulfate is a dominant respiratory pathway, especially in marine environments (Canfield et al., 1993): up to 80% of the carbon oxidation may proceed through sulfate reduction. In addition, the sulfide produced as a metabolic by-product is a sink for O_2 (see below):

$$2CH_2O + SO_4^{2-} + OH^- \rightarrow 2HCO_3^- + HS^- + H_2O \text{ (microbial)}$$

$$HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + H^+ \text{ (chemical)}$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \text{ (chemical)}$$

$$\textit{sum: } 2CH_2O + SO_4^{2-} + OH^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + 2H_2O + HS^-$$

Reduction of sulfate results in the precipitation of 1 mol of $CaCO_3$ per 2 mol of CH_2O oxidized. Some sulfate-reducing bacteria are capable of H_2 oxidation while fixing CO_2:

$$4H_2 + SO_4^{2-} \rightarrow HS^- + 3H_2O + OH^- \text{(microbial)}$$

$$2CO_2 + 4H_2 + CoASH \rightarrow CH_3CO - SCoA + 3H_2O \text{ (microbial)}$$

$$2HCO_3^- \rightarrow 2CO_2 + 2OH^- \text{ (chemical)}$$

$$2Ca^{2+} + 2HCO_3^- \rightarrow 2CaCO_3 + 2H^+ \text{ (chemical)}$$

$$2H^+ + 2OH^- \rightarrow 2H_2O \text{ (chemical)}$$

$$\textit{sum: } 8H_2 + SO_4^{2-} + 4HCO_3^- + 2Ca^{2+} \rightarrow HS^- + CH_3CO - SCoA + 3H_2O + 2CaCO_3$$

This lithoautotrophic metabolism deploys the carbon monoxide dehydrogenase pathway for CO_2 fixation and is found in *Desulfobacterium autotrophicum* (Schauder et al., 1989). The net result of this type of sulfate reduction is 2 mol of $CaCO_3$ precipitated per 4 mol of H_2 oxidized or 1 mol of SO_4^{2-} reduced. Other pathways involve a modified TCA cycle (Spormann and Thauer, 1988; not further discussed here). The oxidation of H_2 coupled to CO_2 fixation is much less common than the heterotrophic oxidation of organic carbon.

In addition to the generic equation for heterotrophic sulfate reduction above, it is important to acknowledge the two different metabolic types of sulfate reduction that can be distinguished (Widdel, 1988): sulfate-reducing bacteria can either oxidize organic carbon (e.g., lactate) to CO_2 (complete oxidizers), or to acetate and CO_2 (incomplete oxidizers).

5.3.3.1. Sulfate reduction—complete oxidation

$$2C_2H_5O_3^- + 3SO_4^{2-} \rightarrow 3HS^- + 6HCO_3^- + H^+ \text{ (microbial)}$$

$$3HCO_3^- + 3Ca^{2+} \rightarrow 3CaCO_3 + 3H^+ \text{ (chemical)}$$

$$3HCO_3^- + 3H^+ \rightarrow 3CO_2 + 3H_2O \text{ (chemical)}$$

$$\textit{sum: } 2C_2H_5O_3^- + 3SO_4^{2-} + 3Ca^{2+} \rightarrow 3HS^- + 3CaCO_3 + 3CO_2 + 3H_2O$$

Complete oxidizers precipitate 1.5 mol of $CaCO_3$ per mole of lactate oxidized.

5.3.3.2. Sulfate reduction—incomplete oxidation

$$2C_2H_5O_3^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+ + 2C_2H_3O_2^- \text{ (microbial)}$$

$$HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + H^+ \text{(chemical)}$$

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \text{ (chemical)}$$

$$\textit{sum: } 2C_2H_5O_3^- + SO_4^{2-} + Ca^{2+} \rightarrow HS^- + CaCO_3 + CO_2 + H_2O + H^+ + H_2O$$

Incomplete oxidizers precipitate only 0.5 mol of $CaCO_3$ per mole of lactate oxidized. SRB have also been implicated in the dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) while respiring organic C and liberating CO_2 and Ca^{2+} (Kah et al., 2001).

5.3.4. Methanogenesis

Methanogenesis is energetically the least favorable mode of respiration. However, methane production is prevalent in freshwater and marine environments, and certainly very important in marine microbial mats (Visscher and van Gemerden, 1991; Hoehler et al., 2002). In addition to simple organic molecules, many methanogens use H_2 and CO_2 during respiration:

$$CO_2 + 4H_2 \rightarrow CH_4 + H_2O \text{ (microbial)}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \text{ (chemical)}$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \text{ (chemical)}$$

$$H^+ + OH^- \rightarrow H_2O \text{ (chemical)}$$

$$\textit{sum: } 2HCO_3^- + 4H_2 + Ca^{2+} \rightarrow CaCO_3 + CH_4 + 2H_2O$$

Therefore, methanogens precipitate 0.5 mol of $CaCO_3$ per mole of HCO_3^- reduced. It should be noted that other types of methanogenesis (using methylated compounds and/or acetate) have different effects on the $CaCO_3$ budget.

5.4. Chemolithoautotrophy

The oxidation of H_2, CO, Fe^{2+}, NH_4^+, and HS^- is energetically very favorable. In marine environments, sulfide and ammonium oxidation are the most important modes of chemolithotrophy. The sulfur cycle in microbial mats is quite complicated (van Gemerden, 1993), with many intermediates between sulfate and sulfide. Most of these intermediates can either be oxidized, reduced, or fermented.

5.4.1. Aerobic sulfide oxidation

Oxidation of sulfide can take place with O_2 or NO_3^- as electron acceptor.

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \text{ (microbial)}$$

$$CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+} \text{ (chemical)}$$

$$\textit{sum: } HS^- + 2O_2 + CaCO_3 \rightarrow SO_4^{2-} + Ca^{2+} + HCO_3^-$$

Aerobic sulfide oxidation results in dissolution of 0.5 mol of $CaCO_3$ per mole of HS^- oxidized.

5.4.2. Anaerobic sulfide oxidation

$$5HS^- + 8NO_3^- \rightarrow 5SO_4^{2-} + 4N_2 + H_2O + 3OH^- \text{ (microbial)}$$

$$3HCO_3^- + 3Ca^{2+} \rightarrow 3CaCO_3 + 3H^+ \text{ (chemical)}$$

$$3OH^- + 3H^+ \rightarrow 3H_2O \text{ (chemical)}$$

$$\textit{sum: } 5HS^- + 8NO_3^- + 3HCO_3^- + 3Ca^2 \rightarrow 3CaCO_3 + 4N_2 + 4H_2O + 5SO_4^{2-}$$

Under anaerobic conditions, sulfide oxidation using nitrate produces 3/5 mol of $CaCO_3$ per mole of HS^- oxidized. However, the nitrate (NO_3^-) concentration is typically low in microbial mats, including modern marine stromatolites (Visscher et al., 1998; Paerl et al., 2000). Furthermore, when sulfate reduction is maximal, O_2 availability is typically low. Sulfide-oxidizing bacteria have a preference for HS^- over other reduced sulfur compounds (Kuenen and Beudeker, 1982). Under oxygen limitation, microbial sulfide oxidation yields thiosulfates, polysulfides, and polythionates (van den Ende and van Gemerden, 1993). When oxygen is replenished, these compounds can be further oxidized to sulfate. This results in a two-step sulfide oxidation in which the two individual reactions can be separated in time and/or space.

5.4.3. Two-step sulfide oxidation

$$8HS^- + 6.5O_2 \rightarrow {S_8O_6}^{2-} + 6OH^- + H_2O(\text{microbial})$$

$$6HCO_3^- + 6Ca^{2+} + \rightarrow 6CaCO_3 + 6H^+(\text{chemical})$$

$$6OH^- + 6H^+ \rightarrow 6H_2O(\text{chemical})$$

$$sum: 8HS^- + 6.5O_2 + 6HCO_3^- + 6Ca^{2+} \rightarrow {S_8O_6}^{2-} + 6CaCO_3 + 7H_2O$$

During this first step, 1.75 mol of $CaCO_3$ precipitates per mole of HS^- oxidized. The following reactions:

$${S_8O_6}^{2-} + 9.5O_2 + 7H_2O \rightarrow 8{SO_4}^{2-} + 14H^+(\text{microbial})$$

$$14CaCO_3 + 14H^+ \rightarrow 14HCO_3^- + 14Ca^{2+}(\text{chemical})$$

$$sum: {S_8O_6}^{2-} + 9.5O_2 + 14CaCO_3 + 7H_2O \rightarrow 8{SO_4}^{2-} + 14HCO_3^- + 14Ca^{2+}$$

result in dissolution of 1.75 mol of $CaCO_3$ per mole of S oxidized.

Another example of the potential significance of functional diversity on carbonate minerals can be found among thiobacilli. Two groups of thiobacilli can be distinguished based on the amount of energy required for autotrophic growth (Kelly, 1982, 1988). The first group, which includes *Thiobacillus neapolitanus*, *Thiobacillus thiooxidans*, and *Thiobacillus versutus*, has a low growth yield (i.e., requires significant metabolic energy to fix CO_2) and oxidizes approximately 4 mol of HS^- per mole of CO_2 fixed, resulting in a net loss of 0.5 mol of $CaCO_3$ per mole of HS^- oxidized. The second group (e.g., *Thiobacillus thioparus*, *Thiobacillus aquaesulis*, and *Thiobacillus denitrificans*) has a high growth yield (i.e., needs much less metabolic energy to fix CO_2) and requires ~2 mol of HS^- to be oxidized per mole of CO_2 fixed, resulting in a dissolution potential of 0.5 mol of $CaCO_3$ per mole of HS^- oxidized. As a result, changes in the spatial or temporal distribution of the physiological activities mediated by these two groups could be expected to impact the fate of $CaCO_3$ in sediment communities.

5.4.4. Ammonium oxidation

Ammonium oxidation is another relatively common chemolithotrophic reaction in the marine environment. This oxidation is carried out by two different microbial species: the first is oxidizing ammonium to nitrite; the second species is oxidizing nitrite to nitrate (Capone, 2000):

$${NH_4}^+ + 1.5O_2 \rightarrow {NO_2}^- + H_2O + 2H^+(\text{microbial})$$

$$2CaCO_3 + 2H^+ \rightarrow 2HCO_3^- + 2Ca^{2+}(\text{chemical})$$

$$sum: {NH_4}^+ + 1.5O_2 + 2CaCO_3 \rightarrow {NO_2}^- + 2HCO_3^- + 2Ca^{2+}$$

During this metabolic reaction, 2 mol of $CaCO_3$ are lost per mole of NH_4^+ oxidized. However, these inorganic redox reactions are often coupled to CO_2 fixation. Most sulfide and ammonium oxidizers use the Calvin cycle to fix CO_2:

$$CO_2 + 2NADH + 3ATP \rightarrow CH_2O - P + 2NAD^+ + 3ADP + 2Pi^-(\text{microbial})$$

$$HCO_3^- \rightarrow CO_2 + OH^-(\text{chemical})$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3(\text{chemical})$$

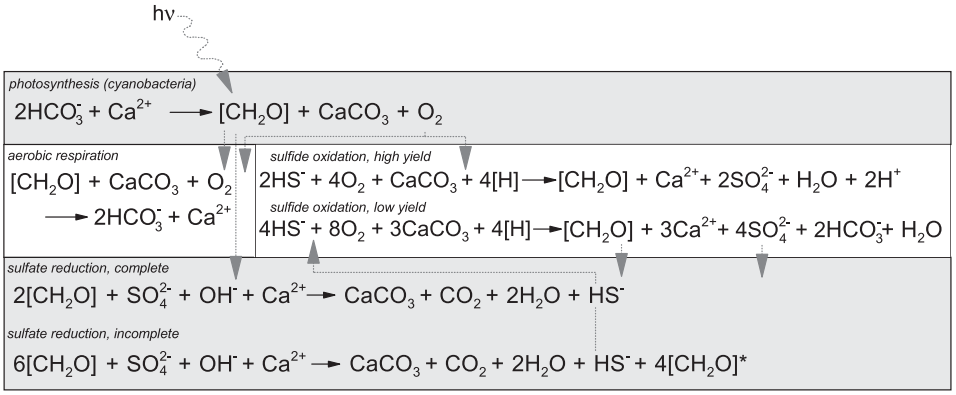
$$H^+ + OH^- \rightarrow H_2O(\text{chemical})$$

$$sum: 2HCO_3^- + Ca^{2+} \rightarrow CH_2O + CaCO_3$$

The net effect of CO_2 fixation is the precipitation of 1 mol of $CaCO_3$ per mole of CO_2 and 9 ATP equivalents needed. Under standard conditions, sulfide oxidation yields $\Delta G'^{\circ}=-798$ kJ/mol and ammonium oxidation $\Delta G'^{\circ}=-287$ kJ/mol. Assuming that CO_2 fixation using the Calvin cycle requires 405 kJ when 100% efficient (1 ATP=45 kJ/mol), and that the actual efficiency of this process is 50% (Kelly, 1982) at best (requiring 810 kJ), the following net effects of chemolithoautotrophy on $CaCO_3$ can be expected: (1) complete aerobic sulfide oxidation coupled to CO_2 fixation produces 0.5 mol of $CaCO_3$ per mole of HS^- oxidized; (2) incomplete aerobic sulfide oxidation to polythionates and CO_2 fixation generate approximately 1.2 mol of $CaCO_3$ per mole of HS^- oxidized; and (3) ammonium oxidation to nitrite coupled to CO_2 fixation yields a loss of ~2.7 mol of $CaCO_3$ per mole of NH_4^+ oxidized.

6. Concluding remarks

We have attempted in this brief review to assess the effects that metabolic processes typically associated



Examples:

Assuming that all C is oxidized through complete SR (SRB(c)) and HS^- is reoxidized by high yield SOB (SOB(hi); see text below), the effect on net $CaCO_3$ precipitation (in parentheses) is:

CYN	$3CO_2 + 3H_2O \rightarrow 3CH_2O + 3O_2$	(+3)
SRB(c)	$4CH_2O + 2SO_4^{2-} \rightarrow 4CO_2 + 2HS^- + 2H_2O + 2OH^-$	(+2)
SOB (hi)	$2HS^- + 4O_2 + CO_2 + 4[H] \rightarrow CH_2O + 2SO_4^{2-} + H_2O + 2H^+$	(-1)
Overall:	*+4 $CaCO_3$ (1.33 per CO_2 fixed by CYN)*	

Assuming that 50% of the C is oxidized through incomplete SR (SRB(i)) and HS^- is reoxidized By low yield SOB (SOB(lo)), the effect on net $CaCO_3$ precipitation (in parentheses) is:

CYN	$47CO_2 + 47H_2O \rightarrow 47CH_2O + 47O_2$	(+47)
HET	$34CH_2O + 24O_2 \rightarrow 24CO_2 + 24H_2O$	(-24)
SRB(i)	$24CH_2O + 4SO_4^{2-} \rightarrow 8CO_2 + 4HS^- + 4H_2O + 4OH^- + 16CH_2O^*$	(+2)
SOB (lo)	$4HS^- + 8O_2 + CO_2 + 4[H] \rightarrow CH_2O + 4SO_4^{2-} + H_2O + 4H^+$	(-3)
Overall:	*+24 $CaCO_3$ (0.51 per CO_2 fixed by CYN)*	

Fig. 3. Metabolic reactions of key functional groups coupled to geochemical precipitation/dissolution reactions in a microbial mat (equations include the effect on $CaCO_3$ balance; reactions assumed in a carbonate-buffered system). Dark boxes designate precipitation and light boxes dissolution. $[CH_2O]$ denotes "generic" organic carbon; $[CH_2O]^*$ is a different C compound (i.e., $[CH_2O]$ is lactate and $[CH_2O]^*$ is acetate in incomplete sulfate reduction). Example calculations show the overall effect on $CaCO_3$ precipitation of two hypothetical C flow scenarios.

with microbial mats have on carbonate deposition and dissolution. The lithifying marine stromatolites at Highborne Cay, Bahamas, were used as our model, but the general principles can be applied to other systems (e.g., organic-rich tidal flat, brackish estuary). We have illustrated that these effects can be chemically predicted in terms of net carbonate precipitation and, therefore, net impact on the geologic record (Visscher et al., 1998; Castanier et al., 1999; Vasconcelos and McKenzie, 1997). Processes such as photosynthesis and sulfate reduction result in net precipitation, while aerobic respiration and sulfide oxidation result in net dissolution (Fig. 3). Many studies have focused on photosynthesis and aerobic respiration as the key processes affecting precipitation (Krumbein et al., 1977; Chafetz and Buczynski, 1992; Pinckney et al., 1995). However, in microbial mats, photosynthesis and aerobic respiration are tightly coupled in space and time, and the coupling of these processes results in no net precipitation. In contrast, sulfate reduction and sulfide oxidation are more likely to be temporally and spatially separated in microbial mats due to the different environmental requirements of these processes (Fig. 3). Their combined activities should therefore result in "hot spots" of precipitation and dissolution (Visscher et al., 1998, 2002). Such a scenario has been observed in the Highborne Cay stromatolites where high rates of sulfate reduction near the surface coincide with microcrystalline $CaCO_3$ precipitation (Visscher et al., 2000) and the greatest abundance of both SRB and SOB (Visscher et al., 1998).

Precipitation outside the cell may contribute to the generation of a proton motive force (see above), but also seems deleterious for the individual cell, since it leads to entombment. As a collective action of a microbial community, however, precipitation of a microcrystalline $CaCO_3$ layer could be advantageous: modern marine stromatolites in Highborne Cay exist in a nutrient-poor environment and a surface $CaCO_3$ crust provides a seal, thereby limiting loss of nutrients to the environment. Furthermore, rather extreme hydrodynamic conditions (high, fluctuating flow in an intertidal/subtidal beach environment) require a significant mechanical strength, and the need to maintain a structure that is minimally impacted by burial due to sand movement requires that the stromatolite mats grow in an upwards direction. The alternating soft layers (bound and trapped ooids in a type 1 community) and hard $CaCO_3$ precipitates (type 2 and type 3 communities) provide exactly that. Finally, the hard surface of the stromatolites somewhat prevents the settlement of eukaryotic organisms.

Overall, our understanding of the effects of metabolic processes upon lithification is limited, and even less is known about how specific metabolic activities (e.g., differences of daytime and nighttime metabolism; see Table 1) and physiological diversity within functional groups can influence the overall metabolism of the community and the formation of mineral products (see Fig. 3; example calculations). Although oxygenic and anoxygenic photoautotrophic bacteria may be considered primary producers, their impact on net carbonate precipitation is different. While the sum total of the sulfate-reducing bacteria populations may be considered a common guild, the predominance of one physiological type over another (i.e., incomplete oxidizers vs. complete oxidizers) can also impact net carbonate precipitation. More information is needed as to the temporal and spatial relationships of metabolic processes and the impact that the coupling of these processes has on mineral production by microbial communities. This may provide insights into carbonate and mineral precipitation processes in general as well as shed light on mechanisms of microbe–mineral interactions.

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