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Lithifying microbial mats in Lagoa Vermelha, Brazil: Modern Precambrian relics?

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Abstract

Bacterial populations, microbial and mineral-forming processes, and their products were analyzed in Lagoa Vermelha, Brazil. The microbial mat and underlying sediment were studied as a unique system to define the boundary conditions responsible for high Mg-calcite and dolomite formation. In the uppermost layers of the microbial mat, oxygenic photosynthesis and aerobic respiration resulted in calcite precipitation, whereas, in the underlying anoxic layers of the mat, sulfide oxidation and sulfate reduction induced formation of a range of carbonate minerals with increasing Mg concentrations.

The chemical, mineralogical, and biological conditions presently found in Lagoa Vermelha may have been more common in the Precambrian. The microorganisms performing the metabolic processes related to carbonate mineral formation within Lagoa Vermelha's hypersaline microbial mat may have already been present in the Precambrian. Thus, microbial carbonate as a biomineral could be a record of metabolism throughout geological time.

1. Introduction

Earth's early history of sedimentary processes remains a subject of debate. For instance, the amount of dolomite relative to limestone varied irregularly throughout geological time and cannot be explained by ongoing dolomitization of limestone (Given and Wilkinson, 1987). A valid explanation may be that the conditions favorable for dolomite formation varied throughout the geologic past (Chilingar and Larsen, 1983; Purser et al., 1994). However, the exact nature of these favorable conditions remains elusive.

Modern Earth surface environments in which primitive Earth characteristics are present provide important insights into the physical and chemical processes operating during its evolution. In addition, biological characteristics must be taken into consideration to provide a better spectrum of the processes, which include biosphere and geosphere interactions. Recent studies consider a microbial factor in addition to the chemical requirements for the formation of carbonates and other authigenic minerals (Krumbein, 1979; Chafetz, 1986; Castanier et al., 1989; Buczynski and Chafetz, 1991; Gerdes et al., 1994; Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Knorre and Krumbein, 2000). Most of these studies are based on field observations and validated by laboratory experiments. The role of microbes in mineral formation has been emphasized because inorganic changes in the conditions, alone, could not induce mineral precipitation. For example,

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the bacterial cell wall can act as nuclei for precipitation and, together with the metabolic activity, triggers precipitation of dolomite (van Lith et al., 2003a,b).

Process oriented research in modern carbonate depositing environments may lead to a better understanding of the formation of large non-fossiliferous carbonate deposits observed in the rock record, such as the Late Proterozoic micritic carbonate, Akademikerbreen Group, Spitsbergen (Knoll and Swett, 1990) and the Middle to Late Proterozoic dolomite (Horodyski and Mankiewicz, 1990). To date, the lack of direct fossil evidence has ruled out a biological involvement in the formation of these large-scale carbonate deposits. Detailed information on early Earth conditions and modern analogues for this ecosystem are missing. Consequently, early carbonate formation processes remain obscure.

Biogeochemical conditions in Lagoa Vermelha, Brazil, indicate that two different mechanisms of carbonate formation are operating at different depths in the sediment. Sulfate reducing bacterial activity and salinity are controlling dolomite precipitation and 'ageing' of unordered into stoichiometric dolomite in the anoxic part of the sediment column (Vasconcelos and McKenzie, 1997; van Lith et al., 2002), whereas sulfide oxidation, and the resulting pH decrease, favors dolomite over Mg-calcite precipitation at the oxic–anoxic boundary in the sediment (Moreira et al., 2004). In this study, we investigate if the Lagoa Vermelha hypersaline lagoon system is a suitable analogue for mineral formation on the shallow-water continental shelves of the early Earth, by considering the complete environment of the microbial mat with its underlying sediment as one unique biogeochemical system. Studying the whole system, we attempted to identify the sum of processes that induce carbonate precipitation. A microscopic and microelectrode study of the microbial mat provided information on the microbial population and the metabolic reactions taking place in different horizons of the microbial mat. Combined with mineralogical and chemical data, we identified zones with favorable biogeochemical conditions for carbonate precipitation.

2. Methods

2.1. Field site

Samples of the microbial mat and underlying sediment were collected from Lagoa Vermelha, a small shallow hypersaline lagoon located on the coast 100 km east of Rio de Janeiro, Brazil (Fig. 1). Lagoa Vermelha is part of a large lagoonal system bordering the South Atlantic. The occurrence of an upwelling zone promotes a particular climatic setting with semi-arid characteristics within an otherwise tropical environment (Barbiére, 1985). Lagoa Vermelha is situated between two parallel dune systems, the youngest of which separates it from the Atlantic Ocean and the older from the much larger Lagoa Araruama, which has a limited connection to the open ocean at its eastern end.

Being approximately 4.5 km long and varying from 250 to 850 m in width, Lagoa Vermelha covers an area of 1.90 km^2 with a mean water depth of 2.0 m. This latter parameter depends ultimately on whether it is the dry or rainy season, as well as on the sea conditions promoting seepage, e.g. spring tides and local storms can considerably increase the lagoon's water volume. Due to its elongated geometry and flat bottom topography, small fluctuations in the water cycle, e.g. variation in the evaporation vs. precipitation ratio, can result in changes in the lagoonal surface area and, therefore, in the water chemistry (van Lith et al., 2002).

Fig. 1. Satellite image of Lagoa Vermelha located between the Atlantic coast and Lagoa Araruama in Rio de Janeiro state, Brazil. Image courtesy of Earth Sciences and Image Analysis Laboratory, NASA Johnson Space Center.

Fig. 2. Cross-section of a microbial mat from Lagoa Vermelha. Stratified layers of carbonate precipitation (white layers) alternate with non-lithified organic layers. The height of the mat section is approximately 3 cm. Note centimeter-scale on left side. Numbers on the right side correspond to the sampled carbonate layers.

Lagoa Vermelha water has a typical seawater Mg/Ca molar ratio of 5 indicating a seawater origin, modified by evaporation and dilution processes (van Lith et al., 2002; Moreira et al., 2004). A decreased Ca/Cl molar ratio in the pore water relative to the seawater ratio indicates carbonate precipitation within the top 10–20 cm of sediment. Dolomite precipitates predominantly in periods of the year with the highest salinities (van Lith et al., 2002). The presence of sulfide in the upper 6 cm of the sediment and sulfur isotopic values of sulfate enriched with respect to seawater sulfate indicates active bacterial sulfate reduction in the lagoon sediment (van Lith et al., 2002). However, the sulfide concentration is not very high and, together with enriched oxygen isotopic compositions of the sulfate, indicates biotic or abiotic sulfide oxidation. The acidifying effect of sulfide oxidation favors dolomite over Mg-calcite formation, as indicated by the saturation states of the two minerals (Moreira et al., 2004). High salinity, sulfate reducing bacterial activity, and sulfide oxidation are proposed to be the controls on dolomite formation in Lagoa Vermelha.

The special mineralogical composition and microbial macrostructures in Lagoa Vermelha sediments are in contrast with the neighboring lagoons where detritic sedimentation predominates. The microbial mat formation in Lagoa Vermelha is mainly located on the edge of the lagoon and in the anaerobic bottom layer (sludge) at the water/sediment interface of the deepest part (Höhn et al., 1986; Vasconcelos, 1994; Vasconcelos and McKenzie, 1997). The activity and structure of the microbial mat community responsible for the formation of the stromatolitic-like structures were measured by means of microelectrodes, stable isotope studies, fluorescence in situ hybridization, and electron microscopy.

2.2. Microbial activity and diversity

Microelectrodes were used for real-time measurement of pH, O_2 and sulfide in the upper 30 mm of the mat, according to Visscher et al. (1991a, 2002). Measurements were carried out every 30–45 min (daytime) to 2–3 h (nighttime) for 26 h. Light intensity was recorded with a quantum sensor recording photosynthetically active radiation (PAR). The community composition of the microbial mats was analyzed by confocal

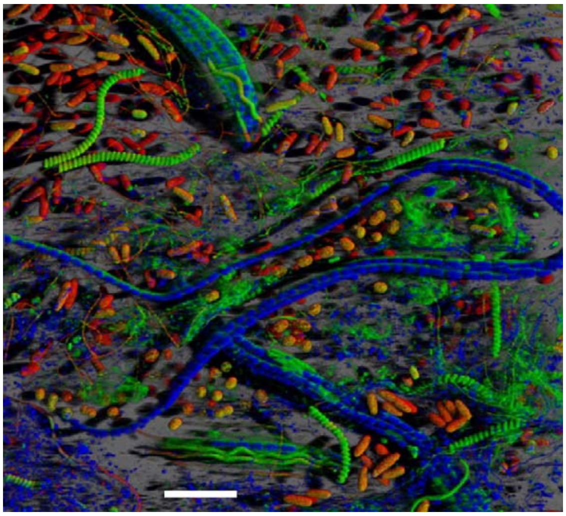

Fig. 3. False-color CLSM picture illustrating the abundance of oxygenic photosynthetic bacteria (cyanobacteria) in a sample of the top layer (1–4 mm) of a Lagoa Vermelha microbial mat. Halotolerant EPS-producing *Gloeocapsa* (red-orange rods), bundles of *Microcoleus* (large blue filament) and *Spirulina* (green spirals), and heterotrophic bacteria (small blue spots) are recognized. Scale bar 30 μm.

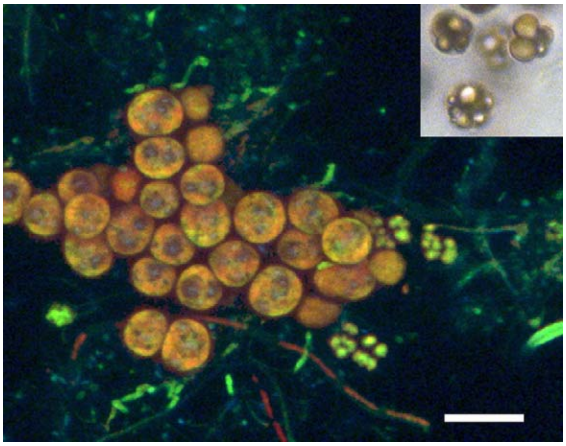

Fig. 4. False-color CLSM image of a sample from 8 to 12 mm depth of a Lagoa Vermelha microbial mat. This layer has a reddish color, indicative of purple sulphur bacteria. These phototrophic sulphur bacteria, such as the *Thiocystis* sp.-cluster, are recognized by the elemental sulphur inclusions inside their cells (violet cell inclusions). The insert illustrates the sulphur inclusions in interference contrast. Scale bar 10 μm.

laser scanning microscopy (CLSM) with DAPI stained sediment samples. Excitation wavelengths were 364, 488, and 633 nm, detection windows maxima were set to 460, 530, and 650 nm.

2.3. Mineralogy

Composition and ordering of carbonates were measured by X-ray diffraction analysis (Scintag). From the d_{104} peak of the diffraction spectra, the Mg : Ca ratio of the carbonate minerals was calculated after Lumsden (1979). A LEO 1530 scanning electron microscope (SEM), equipped with an electron dispersive detector (EDS), was used for imaging and elemental analysis of single crystals.

2.4. Stable isotopes

Stable oxygen and carbon isotopic analyses were made on bleached minerals (5% Na-hypochloric solution, 2 h) from microscopically selected layers of microbial mat precipitates. The stable isotope composition was measured on a Prism mass spectrometer (Bernasconi and Pika-Biolzi, 2000).

3. Results

3.1. Microbial mat structure and population

The microbial mat in Lagoa Vermelha is on average ~3 cm thick and is composed of alternating carbonate and non-lithified organic layers (Fig. 2). The areas of authigenic carbonate precipitation are embedded in a matrix of extracellular polymeric substances (EPS) and microorganisms. The continuous laminae of Ca-Mg carbonates within the microbial mat resemble a stromatolitic-like structure. No obvious trapping and binding of particles by the microbial mat were recognized. The non-lithified organic layers exhibit a stratification of microbial communities visible by the layering of differently colored microbial bands.

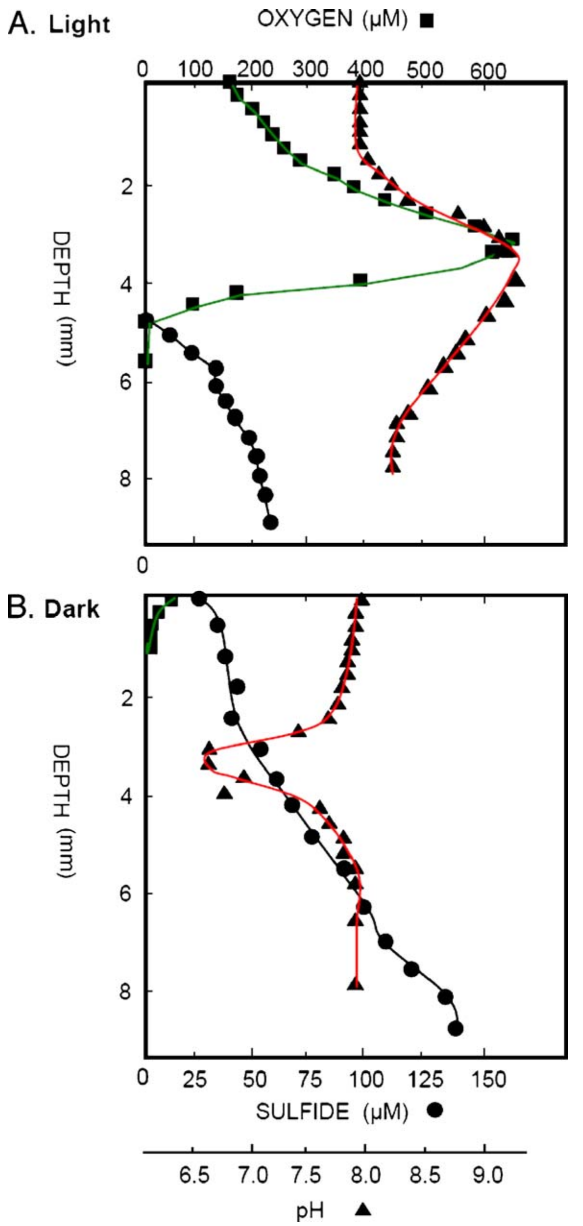

Fig. 5. Microelectrode profiles of O_2 (squares), sulfide (circles), and pH (triangles) measured in situ in the upper 10 mm of a Lagoa Vermelha microbial mat: (A) 14:00 h (Light) and (B) 5:00 h (Dark).

Table 1
$\delta^{13}C$ and $\delta^{18}O$ isotopic values and carbonate mineralogy of Lagoa Vermelha microbial mat

Sample no.	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)	Carbonate mineral
1	−0.312	0.06	Calcite
2	−2.499	−0.01	High Mg-calcite
3	−4.176	−0.84	High Mg-calcite

Sample number corresponds to the discrete layers illustrated in Fig. 2.

The microbial mat exhibits two layers of oxygen-evolving cyanobacteria, as was demonstrated by the different maxima in the chlorophyll spectra (data not shown). The surface layer (0–2 mm) is inhabited by halotolerant cyanobacteria *Gloeocapsa*, *Spirulina*, and *Microcoleus*, whereas the directly underlying layer (2–4 mm) contains mainly filamentous cyanobacteria, such as *Spirulina* and *Microcoleus* (Fig. 3). Large amounts of phototropic sulfide oxidizers were detected below the cyanobacterial layer from ~5 to 12 mm, recognized by the elemental sulfur stored inside their cells (Fig. 4). Eubacteria and Archaea are coexisting in all of the sampled layers, as confirmed by specific FISH cell counting (data not shown). Higher eukaryotic organisms, such as Vertebrates or Crustacea, are nearly absent.

3.2. Microbial activity

Concentration profiles of O_2, sulfide, and pH were monitored in situ in a microbial mat from Lagoa Vermelha over 26 h. The depth distributions of these concentrations show extreme fluctuations between day and night (Fig. 5). pH values fluctuate between <6.5 and >9 in a day–night cycle, with the lowest pH values observed during nighttime. The maximum pH was recorded at 3.5 mm depth during the early afternoon and coincides with a maximum in oxygen concentration (3–4 times air saturation). Oxygen concentrations essentially reduced to zero during the night. Sulfide profiles show a flux out of the sediments at night, indicating that sulfate reduction dominates the mat during nighttime (Fig. 5B). During the day, a sharp transition from oxic to sulfidic sediments occurs at ~5 mm depth (Fig. 5A).

3.3. Mineralogy

The Lagoa Vermelha microbial mat contains discrete layers of calcite and Mg-calcite (Table 1; Figs. 2 and 6). In particular, the Mg-calcite precipitates of layers 2 and 3 are typically round- or oval-shaped, not rhombohedral (Fig. 6B, C). Electron dispersive spectroscopy (EDS) of mineral particles demonstrates Mg concentrations of up to 12 mol%, indicating the presence of high Mg-calcite.

3.4. Stable isotopic analysis

The isotopic composition of samples collected from discrete carbonate layers shows variations with respect to the depth in the microbial mat (Table 1). The near zero oxygen isotopic values of all three samples are

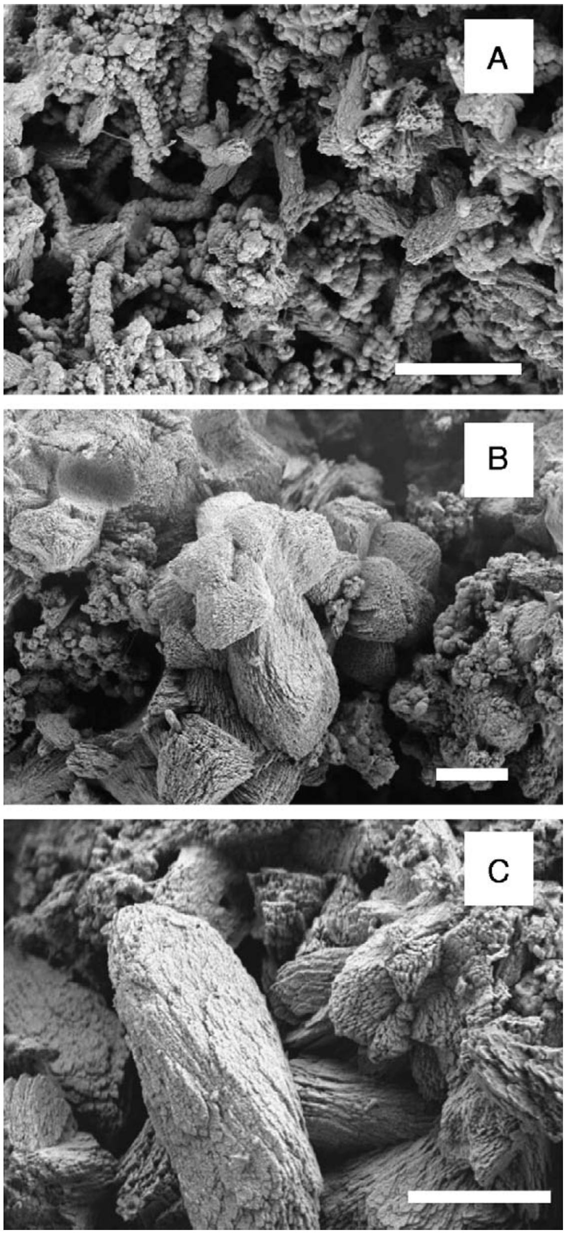

Fig. 6. SEM image of hypochloride-bleached samples of the three uppermost carbonate layers of a Lagoa Vermelha microbial mat showing crystal structures with increasing Mg concentrations: (A) calcite from layer 1; (B) high Mg-calcite from layer 2 and (C) high Mg-calcite from layer 3. Note that the calcite from layer A contains fossilized microbial filaments. Scale bar 5 μm.

indicative of isotopic equilibrium with non-evaporated water. The carbon isotopic values of Samples 1–3 are consistent with an increasing contribution of organic carbon-derived carbonate with depth, which is associated with microbial processes, such as heterotrophic sulfate reduction.

4. Discussion

4.1. Lagoa Vermelha microbial mat

To our knowledge, the lithifying mat found in Lagoa Vermelha is the first reported modern, stromatolite-resembling mat that is associated with Ca–Mg carbonate formation, as well as being associated with the underlying dolomite sediment. The shapes of high Mg-calcite precipitates in the microbial mat (Fig. 6B, C) are similar to those found in the fossil microbial mat of Lagoa Vermelha at 25 cm depth in the sediment column (Calvo et al., 2003). In microscopic dimensions, the minerals have a typical shape which is similar to the precipitates produced in culture experiments by halotolerant sulfate-reducing bacteria (Warthmann et al., 2000, 2005) and by aerobic heterotrophic bacteria (Knorre and Krumbein, 2000).

The decreasing overall microbial activity from the surface to deeper layers of the Lagoa Vermelha mat is typical for microbial mat systems (Visscher et al., 1991a, 1998). The microbial composition of the Lagoa Vermelha mat, with green layers of photosynthetic bacteria on top, followed by intersections of brownish layers, inhabiting heterotrophic bacteria, red layers with purple sulfur bacteria, and an underlying grey layer with sulfate reducers, is often found associated with high saline microbial mats (e.g. Jonkers et al., 2003). The maximum oxygen concentration during the day versus the low oxygen concentration during the night indicates photosynthesis (Fig. 5). The coinciding maxima in photosynthetic activity and pH can be explained by the high CO_2 fixation rate and possibly by the consumption of fermentation products (Visscher et al., 1991b). The low pH values at night may result from aerobic respiration and fermentation, producing organic acids and CO_2. The net reaction of oxygenic photosynthesis results in an alkalinity increase due to the uptake of CO_2. Aerobic respiration at night, however, results in an alkalinity decrease of the pore water.

Immediately below the zone of oxygenic photosynthesis, the sharp transition from the oxic to sulfidic zone during the day indicates that the produced sulfide is readily oxidized within the microbial mat (Fig. 5A). In this zone where light and sulfide are present, phototrophic sulfur bacteria can develop (van Gemerden et al., 1989). The high pH recorded during daytime confirms the microscopic detection of sulfide oxidizing bacteria. Microbial sulfide oxidation to elemental sulfur, which was observed to occur in the mat (Fig. 4), has a positive effect on alkalinity because the pH shifts to alkaline by the removal of 3 protons accordingly to the following reaction:

$$2HS^- + HCO_3^- + 3H^+ \rightarrow 2S^\circ + <CH_2O> + H_2O$$

But, further oxidation of sulfur to sulfate or reduction to sulfide results in an acidification. This shows that the sulfur metabolism has a great impact on carbonate alkalinity and carbonate precipitation.

In deeper layers (>10 mm), microbial sulfate reduction dominates (Fig. 5). The effect of sulfate reduction on carbonate alkalinity depends on the substrate used, but generally it produces alkalinity or shifts the pH to alkaline (Knorre and Krumbein, 2000; van Lith et al., 2003a). For example, if H_2 is used, the pH increases by the reaction:

$$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$$

Because sulfide and bicarbonate are weaker acids than sulfate, the alkalinity increases when acetate is oxidized, following the reaction:

$$C_2H_3O_2^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$$

However, if biomass is used, a slight acidification can occur as follows:

$$2<CH_2O> + SO_4^{2-} \rightarrow HS^- + H^+ + 2HCO_3^-$$

Depending on the type of electron donor used (organic carbon or hydrogen), sulfate reduction can increase the pore water alkalinity. That microbial sulfate reduction, in fact, contributes to alkalinity and carbonate precipitation is confirmed by the increasing shift to negative carbon isotope values with depth (Schidlowski, 2000). The nearer to the sulfate reduction zone, the more expressed is the organic contribution to the isotopic signal in the carbonates (Table 1). The dynamic pH profiles recorded in Lagoa Vermelha are often observed in microbial mats examined by microelectrodes (Visscher et al., 1991a; Canfield and Des Marais, 1994). These ‘snapshots’ in time of combined microbial–geochemical activity demonstrate an extremely dynamic system, similar to observations in other highly productive microbial mats (Jørgensen et al., 1983; Canfield and Des Marais, 1994; Visscher et al., 2002). The extreme fluctuations and steep chemical gradients undoubtedly play an important role in creating conditions that lead to precipitation and dissolution of a range of minerals. To promote carbonate precipitation, the pore water should be saturated with respect to the mineral, i.e. a high calcium and magnesium activity is needed, as well as a high carbonate activity or alkalinity. Sulfate reduction promotes the conversion of unstable high Mg-calcite to Ca-dolomite to stoichiometric dolomite with increasing depth in the sediment (Krumbein et al., 1977; Vasconcelos and McKenzie, 1997) and is undoubtedly responsible for the ageing of metastable Ca-dolomite with depth.

In summary, microbial metabolic processes with the accompanied changes in alkalinity are responsible for carbonate precipitation in the Lagoa Vermelha mat. Oxygenic photosynthesis and aerobic respiration result in calcite precipitation in the uppermost layers of the mat, and sulfide oxidation together with sulfate reduction induces diagenetic processes, which promote high Mg-calcite to Ca-dolomite precipitation.

4.2. Lagoa Vermelha as a Precambrian analogue

From an evolutionary point of view, the anaerobic sulfur cycling organisms in the Lagoa Vermelha mat represent one of the oldest communities, which may have existed already in the Early Archean. Walter (1994) presented a succession of microbial associations responsible for the evolution of calcifying Archean stromatolites, which did not include the genus Archaea. Even archaeo-prokaryotic ecosystems, which have become extinct with evolution, may have been active in the Early Archean (Schidlowski, 2001) and since have been replaced by modern organisms with similar functions. The absence of higher eukaryotic organisms, such as Vertebrates or Crustacea, and the presence of Ca–Mg carbonate laminae contribute to Lagoa Vermelha being a unique natural laboratory in which to study early biochemical processes involved in carbonate formation. This setting may be similar to the shallow-water continental shelves of the early Earth.

Carbonate sedimentation presumably began as a chemical system, being a combination of hydrothermal and biochemical processes. The latter processes probably led to the first formation of low-temperature carbonate sediments in an Archean geological setting marked by the limited area of continental shelf under a high atmospheric CO_2 pressure. In shallow water under reduced conditions, biochemical processes may have formed the first carbonate deposits. Thus, the largest carbon cycle reservoir would have been the atmosphere and to some extent the mantle (Javoy et al., 1982; Keppler et al., 2003), as demonstrated by deep-sea carbonate related serpentinization processes with microbial impact (Früh-Green et al., 2003; Schrenk et al., 2004).

Many of the early biochemical reaction pathways which are basic to life, such as anaerobic sulfur metabolism, can be considered to have been dynamically conserved in the evolutionary process over billions of years (Jensen, 1985; Rothschild and Mancinelli, 1990; Nisbet and Sleep, 2001). The exceedingly conservative nature of the evolutionary process has preserved such “relics” in all living species (Dayhoff and Eck, 1972). Phylogenetically deep-branching microorganisms, such as extreme halophiles (Woese et al., 1991), sulfate-reducing bacteria (Henry et al., 1994) or green photosynthetic bacteria (Xiong et al., 2000) or even some archaeo-prokaryotic organisms, are still important players in contemporary “relic” ecosystems.

Through the study of modern environments that can be considered as an analogue to early Earth, a better evaluation of the microbial ecology and metabolic processes involved in biomineral formation and an estimation of the balance between biological and inorganic processes can be achieved (Des Marais, 1990; Reid et al., 2000; this study). This assumes that microorganisms in these analogue environments played similar biochemical roles in comparable ancient settings. This approach could potentially constrain the boundary conditions predominant on the early Earth, deciphering the relationship between the history of life on Earth and the history of the planet. The process of carbonate formation mediated by the early life forms is conservative because phylogenetically old metabolic pathways are retained and supplemented by newer additions (Dayhoff and Eck, 1972). Modern organisms are more complex, but the basic structure or biochemical functions are similar to those of their ancestors in terms of (bio)mineral precipitation. Thus, biomineral formation might be a record of metabolism throughout geological time. Lagoa Vermelha, therefore, represents an exceptional, small-scale Precambrian analogue that permits the analysis of environmental conditions that may have dominated during certain periods in Earth's history.

5. Conclusion

Biominerals can be a considered as fossils of metabolism and comprise a powerful tool to understand evolutionary processes. The combination of ecological and biogeochemical models results in the geomicrobiological approach which relates population, processes, and geological products. The understanding of biochemical, biological, and geological interactions, as one unique system, can be an important step to better understand the origin of the signals created by early life on Earth. The possible relationship between diverse microbial processes and associated authigenic minerals could provide an important step to trace microbial evolution in the geological record. Moreover, geochemical, mineralogical and microbiological characteristics of Lagoa Vermelha support its classification as an important fossil environment, particularly as an analogue for the Precambrian environments where the metabolic pathways within microbial mats were more related to the formation of Mg-calcite and Ca-dolomite than today.

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