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Research paper

Aerobic biomineralization of Mg-rich carbonates: Implications for natural environments

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ABSTRACT

We studied the formation of Mg-rich carbonate in culture experiments using different aerobic bacterial strains and aqueous Mg/Ca ratios (2 to 11.5) at Earth surface conditions. These bacteria promoted the formation of microenvironments that facilitate the precipitation of mineral phases (dolomite, huntite, high Mg-calcite and hydromagnesite) that were undersaturated in the bulk solution or kinetically inhibited. Dolomite, huntite, high Mg-calcite, hydromagnesite and struvite precipitated in different proportions and at different times, depending on the composition of the medium. The Mg content of dolomite and calcite decreased with an increasing Ca concentration in the medium. The stable carbon isotope composition of the Mg-rich carbonate precipitates reflected the isotope composition of the organic compounds present in the media, suggesting that microbial metabolism strongly influenced the carbon isotope composition of biomediated carbonates. We observed that Ca-enriched carbonate precipitates have relatively low carbon isotope composition. These results provide insights into the mechanism(s) of carbonate formation in natural systems, and they are of fundamental importance for understanding modern environments in which carbonate minerals form as a window into the geologic past.

1. Introduction

Bacterially induced precipitation of carbonates (Le Mètayer-Levrel et al., 1999; Castanier et al., 2000) has drawn much attention in recent decades because of its numerous implications. These include: (1) atmospheric CO_2 fixation through carbonate sediment formation and lithification (Krumbein, 1979; Chafetz and Buczynski, 1992; Folk, 1993) and dolomite precipitation (Vasconcelos et al., 1995; Warthmann et al., 2000; Meister et al., 2007, 2008; Sánchez-Román et al., 2008), (2) solid-phase capture of inorganic contaminants (Warren et al., 2001), (3) the production of pathological concretions such as gallstones and kidney stones in humans (Keefe, 1976; Kajander and Ciftcioglu, 1998), and (4) understanding the origin of carbonates found in Martian meteorites (McKay et al., 1996; Thomas-Keprta et al., 1998) and those detected remotely on the surface of Mars (Palomba et al., 2009; Morris et al., 2010).

Calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] are the two most important and abundant carbonate minerals on Earth. This is consistent with equilibrium thermodynamic considerations for the environmental conditions under which most sedimentary carbonates form and persist (Morse and Mackenzie, 1990). The origins of extensive sedimentary dolomite strata and their mechanisms of formation have long been debated because dolomite is very rarely found in modern sedimentary environments even though it is highly supersaturated in the present ocean (Ingerson, 1962). This observation constitutes the heart of the Dolomite Problem (McKenzie, 1991). Furthermore, attempts to synthesize dolomite under the Earth's surface conditions (25 °C 1 atm) have, without exception, been unsuccessful to date (e.g. Land, 1998). Recently, researches have suggested a link between dolomite formation and bacterial activity (e.g., Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Sánchez-Román et al., 2008, 2009a; Bontognali et al., 2008, 2010) although the exact physico-chemical mechanism(s) for the formation of dolomite in this manner have yet to be fully explored. As a result of numerous works focusing on microbial dolomite precipitation, several mechanisms have been proposed based on the metabolic pathway (e.g., sulfate reduction, methanogenesis, aerobic and/or anaerobic oxidation of organic matter) of the microorganism involved (Vasconcelos and McKenzie, 1997; Warthmann et al., 2000; Roberts et al., 2004; Sánchez-Román et al., 2008). However, the exact role of microbes in the mineralization process, as well as their ecological significance, remains unclear. Indeed, the optimal conditions for microbial dolomite

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precipitation are not exactly known in many cases, despite the well-known abiotic factors (e.g. ionic composition of the medium, Mg/Ca ratio, salt concentration) that surely must influence dolomite formation at low temperature.

Moderately halophilic bacteria are highly useful in the determination of how the ionic composition of the environment affects the bacterial precipitation of minerals because they grow under widely changing salinity conditions. Thus, controlled mineral precipitation experiments using these microbes can help to further clarify the biomineralization mechanisms of carbonate minerals in natural environments. In an attempt to better understand microbial dolomite formation we have undertaken a suite of culture experiments to simulate Earth's surface conditions where the precipitation of dolomite and/or Mg-rich carbonates occurred. In the present report, we describe the results from studies of: (1) the influence of Ca, Mg and Mg/Ca ratio on Mg-rich carbonate precipitation at low temperature (30 °C) from solutions of normal marine salinity (3.5% NaCl); (2) the mineralogy, morphology and texture of the precipitates; (3) the stable carbon isotope composition of the carbonate mineral precipitates and the organic carbon sources used in the culture experiments, and (4) the mineral saturation indices in all the culture experiments using the geochemical program PHREEQC (Parkhust and Appelo, 1999). Finally, we discuss the contribution of moderately halophilic aerobic bacteria to carbonate mineral precipitation and its possible implications in natural environments.

2. Materials and methods

2.1. Microorganisms

Twenty one different bacterial strains of moderately halophilic bacteria were used in this study: sixteen species of the genus *Halomonas* (*H. aquamarina* ATCC 14400, *H. canadiensis* ATCC 43984, *H. cupida* ATCC 27124, *H. elongata* ATCC 33173, *H. eurihalina* ATCC 49509, *H. halmophila* ATCC 19717, *H. halodenitrificans* ATCC 1 3511, *H. halodurans* ATCC 29686, *H. halophila* CCM 3662, *H. marina* ATCC 25374, *H. pacifica* ATCC 27122, *H. pantelleriensis* DSM 9661, *H. salina* ATCC 49509, *H. subglaciescola* ACAM 12, *H. variabilis* DSM 3051 and *H. venusta* ATCC 27125); two species of the genus *Marinomonas (M. vaga* ATCC 271119 and *M. communis* DSM 5604); one species of the genus *Marinobacter* (*Marinobacter hydrocarbonoclasticus* ATCC 49840); one species of the genus *Chromohalobacter* (*Chr. marismortui* ATCC 17056) and one species of the genus *Salibacillus (S. salexigens* DSM 11483).

All these bacteria are Gram-negative, chemoorganotrophic, and strictly aerobic bacteria that metabolize organic matter (e.g., proteins, amino acids and nucleic acids) with the subsequent production of CO_2, NH_3 and PO_4^{3-}.

2.2. Culture media

The culture media used are designated C1 through C12, with the following composition (wt/vol): 1% yeast extract, 0.5% proteose peptone, 0.1% glucose, and supplemented with NaCl to provide a final concentration of 3.5% (wt/vol). The media were amended with different concentrations of Ca and Mg (Table 1), and the pH was adjusted to 7.2 with 0.1 M KOH. To obtain a solid medium, 20 g/l Bacto-Agar was added.

The experimental design took into consideration the fact that sediments rich in organic matter and mats contain exopolymeric substances (EPS), which are similar to a gel media where effective diffusion coefficients of organic and inorganic substances are reduced in comparison to those in a liquid media. This difference significantly affects ion concentration and other physico-chemical properties relevant to solid phase formation at the microbial–medium interface during cell growth. Considering this phenomenon all experiments were performed in media gelled with agar.

Table 1
Chemical composition of the culture media before and after mineral precipitation.

Media	[a]Ca (mM)	[a]Mg (mM)	[a]Mg:Ca	[a]pH	[b]Ca (mM)	[b]Mg (mM)	[b]Mg:Ca	[b]pH
C1	5.7	18.7	3.3	7.2	0	1.7	–	9.0
C2	5.7	28	5	7.2	0	2.6	–	9.0
C3	5.7	65	11.5	7.2	0	6.1	–	9.0
C4	11	37	3.3	7.2	2.7	3.5	1.3	9.0
C5	11	65	5.7	7.2	3	6.1	2	8.5
C6	11	92	8.2	7.2	2.5	8.6	3.4	8.5
C7	17	46.7	2.7	7.2	3.6	4.4	1.2	9.0
C8	17	73.8	4.4	7.2	4.5	6.9	1.5	8.5
C9	17	93	5.5	7.2	4	8.7	2.2	8.5
C10	22	46	2	7.2	3.7	4.3	1.2	9.0
C11	22	93	4	7.2	4.5	8.7	1.9	8.5
C12	22	187	8.2	7.2	5.9	17	2.9	9.0

[a] Starting conditions of the medium.
[b] Final conditions of the medium.

2.3. Mineral precipitation

Each strain was surface-inoculated onto a different solid medium, incubated aerobically at 30 °C, and examined periodically with an optical microscope for up to 30 days after inoculation for detection of the presence of minerals. Controls consisting of uninoculated cultures and cultures inoculated with dead bacterial cells were included in all experiments. The pH measurements were performed at the end of the bacterial growth and mineral formation using pH-indicator paper applied directly to the surface of the gel.

After the incubation period, mineral precipitates were isolated, purified and identified. Solids were recovered by scraping the colony from the agar surface. This material was washed several times with distilled water to remove dissolved nutrients, adsorbed ions, remaining agar and cellular debris and dried at 37 °C. Microscopic observation before and after washing demonstrated that this treatment did not alter the crystal morphology.

2.4. XRD and SEM analyses

A Bruker AXS D8 Advance Bragg–Brentano X-ray diffractometer (XRD) with Cu-Kα radiation was used to identify the mineral composition of the precipitates. The samples were scanned continuously at 1° 2θ min^{-1} from 5° to 70° 2θ.

The Mg:Ca ratio of the carbonate minerals was calculated from the d_{104} peak of the diffraction spectra after Lumsden (1979). A LEO 1530 scanning electron microscope (SEM), equipped with a detector for X-ray energy dispersion analysis (EDX), was used for imaging and elemental analysis of single crystals. Secondary electron micrographs and elemental analyses were made with gold-coated samples.

2.5. Stable carbon isotope analysis

Mineral specimens were prepared from the solid retrieved from each experiment. Crystals of struvite were collected using a binocular microscope and a brush to separate them from carbonate minerals, as they are easily distinguisher by shape, colour and size. The remaining solid [hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4(H_2O)$), dolomite, Mg-calcite and/or huntite ($CaMg_3(CO_3)_4$)] was sonicated for one day. As hydromagnesite, high Mg-dolomite and huntite differed greatly in texture and size, these four minerals were separated in the following way. The samples were washed on a 200 μm sieve to retrieve the largest hydromagnesite and high Mg-calcite crystals (diameter: 50–200 μm). Individual hydromagnesite (white crystals) and Mg-calcite (white yellow crystals) were collected with a brush using a binocular microscope. The residue was sequentially washed on 100, 60, 40, 20 and 10 μm sieves until single crystals of dolomite and huntite (diameter: 5–30 μm) remained. Individual dolomite

(colourless) and huntite (lemon-white) crystals were separated by colour and collected with a brush using a binocular microscope.

The stable carbon isotope composition of the carbonate precipitates (hydromagnesite, huntite, Mg-calcite and dolomite) was analyzed by digesting samples using an on-line common acid bath attached to a VG PRISM isotope ratio mass spectrometer (IRMS) (Scientific Instrument services, NJ, USA). The $\delta^{13}C$ value of the carbonates were reported relative to the Vienna Peedee Belemnite Standard (VPDB). Analytical reproducibility based on repeated analyses of internal laboratory standard (MS-2, Carrara Marble) was ±0.1‰ (1σ standard deviation, $n=8$). These analyses were performed in the Stable Isotope Laboratory at the Geological Institute of the ETH-Zürich (Switzerland).

The carbon isotope composition of the media (Ca-acetate, Mg-acetate, glucose, proteose peptone and yeast extract) was determined by combustion using an elemental analyzer (NC 2500, Carlo Erba). The CO_2 produced after combustion was analyzed using a Delta^{PLUS} XL IRMS functioning in continuous flow mode. Multiple in-house standards (DORM, CCHIX and TURK) were analyzed to estimate the analytical precision of the analyses, which was better than ±0.1‰ (1σ standard deviation, $n=9$). The $\delta^{13}C$ values of the organic compounds were reported relative to the Vienna Peedee Belemnite Standard (VPDB). These analyses were conducted at the Savanna River Ecology laboratory, University of Georgia (Aiken, SC, USA).

2.6. Geochemical modeling

The activity of dissolved species and the degree of saturation for specific minerals in the culture media were determined using the geochemical computer program PHREEQC version 2 (Parkhust and Appelo, 1999). These results were presented in terms of the saturation index (SI) for specific minerals. SI is defined by SI = log (IAP/Ksp), where IAP is the ion activity product of the dissolved mineral constituents and Ksp is the solubility product of the mineral. Thus, SI>0 implies oversaturation with respect to the mineral, whereas SI<0 implies undersaturation. All calculations were performed applying the following starting values in the media (g L^{-1}): Mg^{2+} and Ca^{2+} (see Table 1), $Na^{+}=29.58$, $Cl^{-}=45.51$, $P=0.15$ ($PO_4^{3-}=0.46$) and $NH_4^{+}=1.73$. The values of Na^{+}, Cl^{-}, P and NH_4^{+} correspond to the addition of NaCl (35 g L^{-1}), proteose peptone (5 g L^{-1}) and yeast extract (10 g L^{-1}). Total nitrogen in the culture media was determined by the Kjeldahl method, while total phosphorus was determined colorimetrically from the nitrogen digests, using the phosphomolybdate method (Page et al., 1982). The initial pCO_2 value used in these geochemical calculations was 0.004 mg/l assuming that atmospheric CO_2 was in equilibrium with the saline culture media.

3. Results

Table 2 shows the time, in days, required to observe precipitation for each bacterial strains investigated in the different culture media. Carbonate and struvite precipitation was observed in all experimental cultures. The mineralogy of the mineral precipitates is reported in Table 3. In C1 through C6 and C8, C9 and C12 media, carbonate minerals and struvite co-precipitated, whereas in C7, C10 and C11 media only Mg-calcite precipitated. A significant rise in pH occurred in the cultures with living bacteria, from the original pH 7.2 to 9, whereas changes in pH were not detected in control experiments. No precipitates were observed in any of the culture experiments.

In C1, C2 and C3 media, with the lowest Ca concentration (5.7 mM), struvite was the first mineral to precipitate, followed by hydromagnesite, huntite, calcite and dolomite. In C4, C5 and C6 media, with 11 mM of Ca, hydromagnesite precipitated prior to high Mg-calcite, dolomite and struvite. In C8, C9 and C12 media, with higher Ca concentrations (17–22 mM), dolomite precipitated prior to hydromagnesite and struvite. Dolomite was a major constituent in C1, C2, C3, C4, C6, C8, C9 and C12 media, whereas in the remaining media (C5, C7, C10 and C11) dolomite did not precipitate and the only precipitation observed was high Mg-calcite. In all culture experiments, the size and quantity of crystals increased with increasing duration of incubation, and carbonate minerals precipitated preferentially at the expense of struvite.

The Ca and Mg content of the calcite and dolomite precipitates are reported in Table 3. Calcite precipitates from C5, C7, C10 and C11 media contained from 15 to 34 mol% $MgCO_3$, corresponding to high Mg-calcites. Dolomite precipitates from C1, C2 and C3 media were nearly stoichiometric containing from 51 to 53 mol% $CaCO_3$, whereas dolomite precipitates from C4, C6, C8, C9 and C12 media were Ca-rich

Table 2
Time, in days, required to initiate struvite (S) and carbonate (C) precipitation for the bacteria investigated.

Bacterial strain	Medium and type of crystal formed																							
	C1		C2		C3		C4		C5		C6		C7		C8		C9		C10		C11		C12	
	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C
Halomonas pacifica [a]ATCC 27122	8	10	8	11	6	7	14	6	6	6	10	10	12	7	10	6	9	5	12	5	6	4	7	5
H. halophila [b]CCM 3662	9	11	8	11	9	10	14	9	8	6	7	10	12	7	12	6	9	5	12	5	6	4	7	5
H. venusta ATCC 27125	10	11	10	12	7	9	14	7	8	6	11	10	12	7	10	6	9	5	12	5	7	5	7	5
H. pantellerensis [c]DSM 3051	9	10	9	10	7	8	15	8	6	6	9	10	12	7	9	6	9	5	12	5	7	4	8	5
H. halodenitrificans ATCC 13511	9	10	8	11	8	9	15	8	7	5	9	10	10	7	12	6	9	5	10	5	8	4	8	5
H. eurihalina ATCC 49509	10	11	10	12	10	11	15	10	6	5	6	8	10	7	13	6	10	5	10	5	8	4	8	5
H. aquamarina ATCC 14400	9	11	11	12	10	11	16	10	10	5	7	8	10	7	12	6	10	5	9	5	6	4	7	5
H. subglaciescola [d]ACAM 12	10	12	11	12	10	12	16	10	9	5	9	8	10	7	12	6	10	5	9	4	6	4	9	6
H. variabilis DSM 3051	9	10	11	12	10	11	16	10	10	5	12	8	11	7	13	6	11	5	9	4	6	4	7	6
H. cupida ATCC 27124	8	10	9	10	8	9	15	9	9	6	12	8	10	7	10	7	9	5	9	4	6	4	8	6
H. salina ATCC 49509	8	10	10	10	8	9	14	9	9	5	12	10	9	8	10	7	9	5	8	4	6	5	8	6
H. marina ATCC 25374	8	10	11	13	10	11	14	10	14	5	11	10	9	8	9	8	9	4	8	4	7	5	8	6
H. meridiana ACAM 246	8	10	11	13	10	11	15	10	10	5	10	10	9	8	10	8	8	4	8	4	7	5	9	5
H. canadiensis ATCC 43984	9	10	11	13	9	10	16	9	10	5	10	10	9	8	10	8	10	4	8	4	7	5	9	5
H. halodurans ATCC 29686	9	11	11	12	7	8	18	9	10	5	11	10	9	8	11	8	10	4	8	5	7	5	7	5
H. elongata ATCC 33173	8	9	11	13	7	8	20	9	10	5	9	10	10	8	10	8	9	4	7	5	7	5	7	5
Marinomonas vaga ATCC27119	9	10	12	14	9	10	20	9	10	5	12	11	10	8	10	8	9	5	8	5	7	4	8	6
M. comunis DSM 5604	9	10	12	14	7	8	21	9	8	6	12	10	10	8	12	6	9	5	8	4	7	5	9	6
Marinobacter hidrocarbonoclasticus ATCC 49840	8	11	12	14	8	9	19	10	10	6	11	11	10	8	12	6	9	5	8	4	8	5	9	6
Chromohalobacter marismortui ATCC 17056	12	14	10	10	8	9	19	9	14	5	9	10	10	8	12	8	10	6	7	5	8	5	7	5
Salibacillus salexigens DSM 11483	10	11	10	10	8	9	22	9	12	5	10	11	11	8	10	8	10	6	7	5	8	4	8	6

[a] ATCC, American Type Culture Collection.
[b] CCM, Czech Collection of Microorganisms.
[c] DSM, Deutsche Sammlung von Mikroorganismen.
[d] ACAM, Australian Collection of Microorganisms.

Table 3
Mineralogy of the precipitates derived from XRD analysis.

Medium	Mineral (%)	d_{104} (Å) for D and HMC	Formula for D and HMC
C1	D(40%), C (30%), HM(25%), S (5%)	2.893	D: $Ca_{1.06}Mg_{0.94}(CO_3)_2$
C2	D(45%), H(23%), C (10%), HM (15%), S(7%)	2.891	D: $Ca_{1.05}Mg_{0.95}(CO_3)_2$
C3	D(45%), H(30%), HM(15%), S(10%)	2.888	D: $Ca_{1.04}Mg_{0.96}(CO_3)_2$
C4	D(75%), HM(20%), S(5%)	2.905	D: $Ca_{1.14}Mg_{0.86}(CO_3)_2$
C5	HMC(70%),HM(25%), S(5%)	2.976	HMC: $Ca_{0.80}Mg_{0.20}CO_3$
C6	D(60%), HM(35%), S(5%)	2.900	D: $Ca_{1.10}Mg_{0.9}(CO_3)_2$
C7	HMC(100%)	2.932	HMC: $Ca_{0.66}Mg_{0.34}CO_3$
C8	D(65%), HM(25%), S(5%)	2.900	D: $Ca_{1.10}Mg_{0.9}(CO_3)_2$
C9	D(65%), HM(30%), S(5%)	2.907	D: $Ca_{1.15}Mg_{0.85}(CO_3)_2$
C10	HMC (100%)	2.992	HMC: $Ca_{0.85}Mg_{0.15}CO_3$
C11	HMC (100%)	2.982	HMC: $Ca_{0.82}Mg_{0.18}CO_3$
C12	D (75%), HM(20%), S(5%)	2.910	D: $Ca_{1.15}Mg_{0.85}(CO_3)_2$

Note: D (dolomite); C (calcite); HMC (high magnesium calcite); H (huntite); HM (hydromagnesite); S (struvite).
The formulas for dolomite and high Mg-calcite were obtained from d_{104} peak of the diffraction spectra according to Lumsden (1979).

dolomites (55–58 mol% $CaCO_3$). With increasing Ca ion concentration: (1) the Mg content in calcite and dolomite generally decreased (see EDX patterns in Fig. 1 and Table 3); (2) the time required for struvite precipitation increased (Table 2) and the amount of precipitate decreased (Table 3); and (3) the time required for carbonate precipitation decreased (Table 2). SEM study and EDX microanalyses of the mineral precipitates supported the XRD results (Fig. 1). The stoichiometry of struvite crystals is well defined by a nearly constant intensity ratio of P and Mg (Fig. 1a). EDS spectra of carbonate precipitates indicated that some contain Ca and/or Mg (Fig. 1b,c,d,e) while others contain only Mg (Fig. 1f). Small amounts of P and Cl^- are usually present together with Ca and Mg in the microanalyses of the precipitates, but their occurrence is interpreted to be derived from the elements in the culture medium as a result of incomplete washing of the solids.

Crystals of struvite were observed having a variety of morphologies, the most common having a tabular form (Fig. 1a). Spherulites were the most frequent morphology for the carbonate minerals, although other morphologies, such as dumbbells were observed (Fig. 1c,d). Smooth and rough surfaces (Fig. 1c,d,f) were observed for the spherulites, as well as some with fibrous internal structures (Fig. 1b).

Potential mineral phases and SI values for the initial conditions of the culture media are reported in Table 4, suggesting the possibility for the inorganic precipitation of some minerals in the media. According to these data, all the media investigated are undersaturated with respect to calcite, dolomite, huntite, hydromagnesite and saturated with respect to struvite and hydroxyapatite. Based on these geochemical calculations, the increase of Ca in the medium slightly favors the formation of aragonite, calcite, dolomite and hydroxyapatite (the SI of these mineral phases became higher with increasing Ca content in the medium).

The $\delta^{13}C$ values for hydromagnesite, huntite, high Mg-calcite and dolomite are presented in Table 5. These values range from −26.8 to −18.2‰ and become more negative with increasing Ca concentration in the medium. The negative values reflect the microbial origin of carbon and indicate the contribution of isotopically light carbonate ions derived from the microbial aerobic degradation of the organic matter in the culture medium. The $\delta^{13}C$ values of the organic C derived from the yeast extract and proteose peptone (−23.8 and −24.1‰, respectively) are of the same order of magnitude as the microbial carbonate precipitates (Table 6).

4. Discussion

4.1. Mineral precipitation by halophilic aerobic bacteria

Bacteria have the capability of locally changing physicochemical parameters (e.g., pH, ionic strength) in their local environment (e.g., Ahimou et al., 2002). In this way, the precipitation of carbonates and phosphates may occur even if the overall system is undersaturated with respect to these phases (Párraga et al., 1998), if supersaturation is reached locally in the surrounding of the bacterial cells. Simple solution chemistry cannot be applied in analysing this microenvironment because there is a fluid solid-interface in which reaction mechanisms may change and thermodynamic activation energies may be altered resulting in mineral precipitation (Thompson and Ferris, 1990). In addition, bacteria can serve as a nucleus for carbonate mineral precipitation by adsorbing Ca, Mg and other metallic cations onto their cell surface: membranes, walls and extracellular polymeric substances or EPS (Beveridge and Fyfe, 1985; Van Lith et al., 2003; Bontognali et al., 2008). Ca ions are actively excluded from the interior of bacterial cells to maintain low concentrations of intracellular Ca, whereas Mg ions are generally taken up into the cells, as demonstrated by Rosen (1987); and Ca is selectively adsorbed onto the negatively charged bacterial cell surfaces (Wolt, 1994; Maier et al., 2000). Whereas purely inorganic chemical precipitation is difficult in natural environments or in sterile laboratory experiments, the presence of bacteria can induce the precipitation of minerals in microenvironments by (1) modifying the conditions of their surrounding environments and/or concentrate ions in the bacterial cell envelope and (2) acting as nucleation sites. As an example, bacteria can precipitate carbonates by lowering the Mg/Ca ratio relative to that of the environment in which they live.

Proposed mechanisms for the microbial precipitation of carbonates in both natural environments (Ehrlich, 2002; Vasconcelos and McKenzie, 1997; Sánchez-Román et al., 2009a) and in laboratory culture experiments (e.g., Warthmann et al., 2000; Sánchez-Román et al., 2007, 2008, 2009b) suggest that microorganisms induce precipitation on the cell walls through the adsorption of Ca and/or Mg ions together with the production of metabolic CO_2 and NH_3 which hydrate to form CO_3^{2-} and NH_4^+, thereby increasing the pH of the bulk fluid and promoting locally supersaturated conditions. This mechanism may occur in our culture experiments because the medium contains Ca and Mg ions, as well as acetate, glucose, peptone and yeast extract as carbon and nitrogen sources. Halophilic aerobic bacterial activity promotes the production of NH_3 and CO_2 by means of oxidative deamination of amino acids and/or the oxidation of other organic compounds. The importance of metabolic activity in the process of biomineralization is supported by the fact that no precipitation was observed in the control experiments without bacteria or with dead bacterial cells. This demonstrates that bacteria are not simply heterogeneous nuclei for mineral precipitation but are active mediators in the process (e.g., Sánchez-Román et al., 2008).

Geochemical modeling suggested that the chemical conditions of the medium should promote only the formation of hydroxyapatite and struvite. In spite of this, hydroxyapatite was not observed in any culture experiment, whereas struvite co-precipitated with other carbonate minerals (hydromagnesite, dolomite, calcite and huntite). These results demonstrate that bacteria exert some control in the precipitation process. Thus, in media with sufficient concentrations of Ca and Mg ions (as well as CO_2, NH_3 and PO_4^{3-}), halophilic bacteria can induce the precipitation of Mg-rich carbonates and/or struvite instead of hydroxyapatite. The

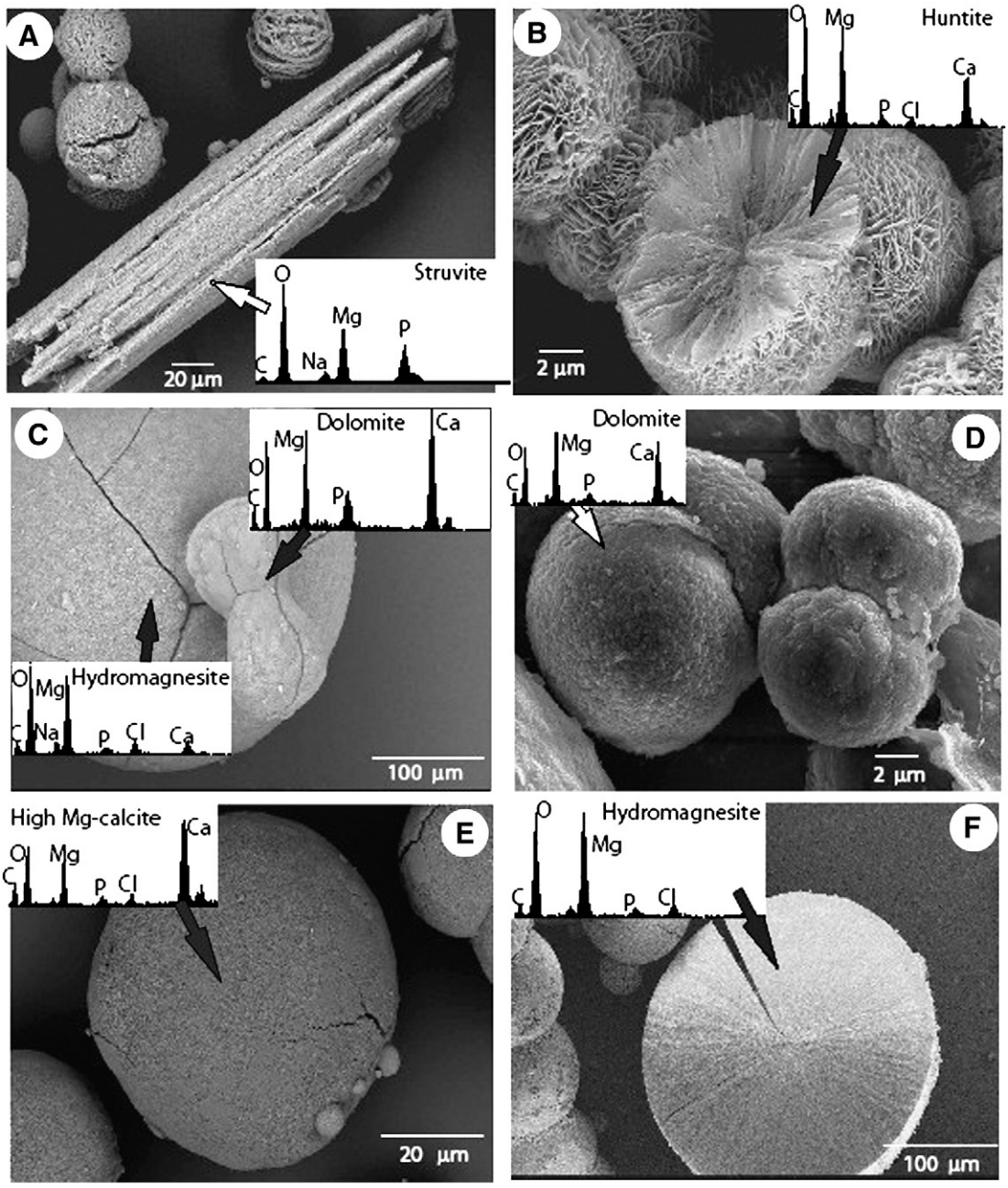

Fig. 1. SEM photomicrographs of some of the mineral precipitates in the aerobic culture experiments. (A) Polyhedral struvite crystal precipitated in C2 medium; (B) spheroidal huntite crystal with fibrous and radial internal structure (C3 medium); (C) dolomite dumbbell resting on a large spherical hydromagnesite crystal (C4 medium); (D) dolomite dumbbells (C6 medium); (E) spherical high Mg-calcite crystal (C7 medium); (F) spherical hydromagnesite crystal with radial internal structure (C12 medium). EDS scans indicate the composition of the selected crystals (arrows). Note: to have a good amount of precipitates for analytical analyses, the length of incubation time was 30 days for all the culture experiments investigated.

Table 4
Saturation index values (SI) for minerals in all media assayed. Results are from the geochemical computer program PHREEQC. These SI values are for initial conditions.

Mineral phase	Media											
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Aragonite, $CaCO_3$	−7.19	−7.18	−7.17	−6.89	−6.88	−6.88	−6.70	−6.70	−6.70	−6.58	−6.58	−6.57
Calcite, $CaCO_3$	−7.05	−7.04	−7.03	−6.75	−6.74	−6.74	−6.56	−6.56	−6.56	−6.44	−6.44	−6.43
Dolomite, $CaMg(CO_3)_2$	−13.35	−13.16	−12.77	−12.73	−12.47	−12.31	−12.45	−12.23	−12.13	−12.33	−12.01	−11.68
Huntite, $CaMg_3(CO_3)_4$	−30.27	−29.70	−28.55	−29.02	−28.25	−27.77	−28.53	−27.88	−27.58	−28.41	−27.46	−26.49
Magnesite, $MgCO_3$	−6.89	−6.71	−6.33	−6.58	−6.32	−6.16	−6.48	−6.26	−6.16	−6.47	−6.16	−5.84
Nesquehonite, $MgCO_3 \cdot 3H_2O$	−9.34	−9.15	−8.77	−9.02	−8.77	−8.61	−8.92	−8.71	−8.61	−8.92	−8.61	−8.29
Hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	−39.00	−38.06	−36.17	−37.43	−36.16	−35.36	−36.92	−35.84	−35.35	−36.91	−35.34	−33.75
Hydroxyapatite, $Ca_5(PO_4)3OH$	7.34	7.14	6.57	8.38	7.98	7.75	9.07	8.73	8.54	9.63	9.12	8.48
Struvite, $MgNH_4PO_4 \cdot 6H_2O$	1.17	1.29	1.47	1.34	1.45	1.54	1.37	1.46	1.50	1.35	1.49	1.60
Halite, NaCl	−2.39	−2.39	−2.40	−2.39	−2.40	−2.40	−2.40	−2.40	−2.40	−2.40	−2.40	−2.40

Table 5
$\delta^{13}C_{V\text{-}PDB}$ (‰) values for hydromagnesite, huntite, dolomite and high Mg-calcite precipitates from culture experiments.

Medium	$\delta^{13}C_{Hydromagnesite}$	$\delta^{13}C_{Huntite}$	$\delta^{13}C_{High\ Mg\text{-}calcite}$	$\delta^{13}C_{Dolomite}$
C1	−18.2	–	–	−20.0
C2	−18.7	−19.95	–	−20.8
C3	−19.3	−21.62	–	−21.9
C4	−22.2	–	–	−22.6
C5	–	–	−22.2	–
C6	−22.7	–	–	−23.0
C7	–	–	−23.0	–
C8	–	–	–	−23.9
C9	−23.7	–	–	−24.1
C10	–	–	−26.5	–
C11	–	–	−26.1	–
C12	−24.0	–	–	−26.8

sequence of metabolic reactions involved in the degradation of the organic compounds in the media may also influence the sequence of microbial precipitates. A high CO_2 concentration is produced, which will lead to carbonate precipitation before a phosphate concentration required for hydroxyapatite and/or struvite precipitation is attained. We must also consider that in media with relatively high Mg content and NH_4^+ ion concentrations, struvite will precipitate before carbonate minerals.

Also, it is well known that Mg and PO_4^{3-} ions hinder the precipitation of calcite (Morse, 1983; Sánchez-Román et al., 2007), while Ca and/or CO_3^{2-} ions hinder the precipitation of struvite (Bouropoulos and Koutsoukos, 2000; Kofina and Koutsoukos, 2005; Sánchez-Román et al., 2007). Our results support these studies; in C1, C2 and C3 media, the precipitation of struvite removes Mg and PO_4^{3-} ions from the media, leading to a major precipitation of carbonates (e.g., dolomite, ± calcite and huntite). At the same time, in the media C4, C5, C6, C8, C9 and C12 the precipitation of Ca and Mg carbonates (e.g., dolomite and high Mg-calcite) removed sufficient CO_3^{2-} and Ca ions (increasing the Mg/Ca ratio) to facilitate the formation of struvite.

All these explanations of our experimental observations could be applied to the differences often found between mineral precipitation induced by different microorganisms in different habitats and in pure inorganic media. Moreover, the mineral precipitation in a given habitat may be influenced by the mineral composition of the habitat and by the amount and kind of existing organic matter.

4.2. Carbon source for precipitation of carbonates

To further understand the relationship between microbial activity and the mineral precipitates in this study, we measured the C-isotope composition of the carbonate crystal precipitates (hydromagnesite, huntite, high Mg-calcite and dolomite, see Table 5). As these culture experiments were aerobically incubated, we assume that the saline medium used in these cultures was in equilibrium with atmospheric CO_2. The biomediated precipitates had relatively low $\delta^{13}C$ values (−26.8 to −18.2‰). The carbon in the solid was derived from the bacterial oxidation of organic compounds in the medium and not from the atmospheric CO_2 [$\delta^{13}C = -8‰$, Jones and Donnelly (2004)]. The $\delta^{13}C$ values of the organic compounds ranged from −38.3 to −11.2‰ (Table 6) which encompasses the range of $\delta^{13}C$ values of the mineral precipitates.

Table 6
$\delta^{13}C_{V\text{-}PDB}$ (‰) values of the organic compounds used in the culture experiments.

Organic compound	$\delta^{13}C_{V\text{-}PDB}$ (‰)
Glucose	−11.2
Yeast extract	−23.8
Proteose peptone	−24.1
Ca-acetate	−36.3
Mg-acetate	−38.3

Based on the known metabolism exploited by microorganisms in this study, the compounds that degraded first in the culture experiments were probably acetate and glucose, which increased CO_2 and decreased pH in the medium (Sánchez-Román et al., 2007). Subsequently, the peptones and yeast extract (nitrogenated organic matter) were degraded, supplying NH_3 that hydrolyzed to NH_4^+ leading to an increase in pH over time as observed in the culture experiments. Furthermore, the bacterial degradation of peptone and yeast extract will also result in the production of CO_2 that will hydrolyze to CO_3^{2-} which is required for the precipitation of carbonate minerals. According to this scenario, $\delta^{13}C$ values show that in our aerobic culture experiments, the carbon in the carbonate precipitates derived from the bacterial degradation of proteose peptone and yeast extract (organic matter), as these organic compounds have nearly the same $\delta^{13}C$ value as the biomediated carbonate minerals. In brief, these bacteria store their metabolic CO_2 in the form of carbonate precipitates avoiding atmospheric pollution. Sequestration of CO_2 as a mineral can have long-term effects.

On the other hand, as the Ca concentration increases in the medium the Mg-rich carbonate precipitates (hydromagnesite, huntite, high Mg-calcite and dolomite) become enriched in Ca and attain slightly more negative $\delta^{13}C$ values, being enriched in ^{12}C (see Table 5 for the $\delta^{13}C$ values and Table 1 for the Ca and Mg content in the medium). Jiménez-López et al. (2006) reported that ^{13}C is preferentially incorporated as the Mg content in solid carbonates increase. In agreement with this explanation, the $\delta^{13}C$ values of the Mg-rich carbonate precipitates were less negative as the Mg content increased in their crystal lattice. Thus, we propose that Ca content in the crystal lattice of biomediated carbonates may favor the preferential incorporation of ^{12}C as what occurred in our culture experiments.

4.3. Precipitation of Mg-rich carbonates in solid media and in natural environments

Using a solid medium in these experiments, which suppressed convective and advective mass transport and favored diffusion, fosters the development of spherulitic instead of polyhedral morphologies; as well as the formation of trigonal Mg-rich carbonates instead of aragonite, which usually precipitates in liquid media (Sánchez-Román et al., 2007; Sánchez-Navas et al., 2009). On the other hand, liquid media supersaturation is uniform through-out the system, whereas the solid media supersaturation gradients must arise from the slow transport properties of the chemical species present in the media. Putnis et al. (1995) reported that the degree of supersaturation driving the crystallization of solids depends on the diffusion gradient in solid porous media. Therefore, a smaller increase in supersaturation is necessary for the precipitation of more soluble mineral phases, as $MgCO_3$, in relation to less soluble minerals, as $CaCO_3$. In solid media higher growth rate is expected for the formation of Mg-rich carbonates than for pure calcite and aragonite because the critical supersaturation for those carbonates is reached more quickly. Consequently, Mg-rich carbonates must be considered as kinetically favored precipitates. Thus, the precipitation of Mg-rich carbonates is favored in solid medium, whereas aragonite preferentially forms in liquid medium under identical conditions. This could explain the absence of aragonite and calcite in shallow marine/lacustrine sediments where precipitation of dolomite and/or Mg-rich carbonates occurs.

The carbonates precipitated in our solid media have spherulitic morphologies (Fig. 1) with smooth and rough external surfaces as a consequence of extremely high growth rates. The large incorporation of Mg into the carbonate structure is related to the development of those crystal features at high crystal growth rate. In addition, the salinity and the initial concentrations of reactants may also affect the crystal growth rate and influence the incorporation of Mg.

4.3.1. Comparisons with natural analogues

The coeval precipitation of dolomite, hydromagnesite and/or huntite in our culture experiments is significant because the same group of mineral precipitates also co-occurs simultaneously in many modern sedimentary environments rich in organic matter and with similar Mg/Ca ratio as those studied in the present work (Kinsman, 1967; Irion and Müller, 1968; Müller and Irion, 1969; Müller et al., 1972; Rosen et al., 1988; Botz and von der Borch, 1984; Renaut, 1990; Warren, 1990; Coshell et al., 1998; Last and Ginn, 2005). However, the presence of hydromagnesite and/or huntite in ancient sedimentary rocks is uncommon, whereas vast deposits of dolomite are present in those same ancient rocks. Hydromagnesite and huntite are metastable carbonate phases which can be altered, dissolved and/or transformed to the more stable carbonate phase, dolomite. For this reason, it is probable that we do not find either hydromagnesite or huntite in the geologic record.

Our results indicate a relationship between aerobic bacterial precipitation of dolomite and other Mg-rich carbonates. These Mg-rich carbonates may be mediated by halophilic aerobic bacteria in a wide range of environments with similar Mg/Ca ratios as the studied in the present work. Bacterial dolomite and/or Mg-rich carbonates formation under certain conditions may even imply an ecological benefit for the microbial community. Most of the environments where dolomite occurs are very rich in aqueous Mg compared to Ca. The precipitation of Mg-rich carbonates may decrease ambient Mg concentration that may be toxic for life.

Due to the scarcity of dolomite in modern environments and the difficulty in precipitating it in the laboratory at Earth's surface conditions, little attention has been paid to the biomediated co-precipitation of dolomite with other Mg-rich carbonates and its geobiochemical implications.

5. Summary

This study shows that microbes can produce microenvironments around their cells in which unusual carbonate minerals (e.g., dolomite, huntite, hydromagnesite), that are undersaturated or kinetically inhibited under other conditions, can precipitate.

We observed that as Ca concentration increases in the medium, the Mg-rich carbonate precipitates become enriched in Ca and in the lightest C isotope, ^{12}C. Based on this, we suggest that halophilic aerobic bacteria may benefit the natural ecosystem where they live because the produced CO_2, as a consequence of their metabolism, is precipitated as carbonate minerals and not emitted to the atmosphere. At the same time, in natural systems where concentration of Mg are very much greater than Ca concentration and may be toxic for life, the bacterial mediation of Mg-rich carbonates could contribute to the maintenance of the bacterial community equilibrium.

Finally, this study provides potential biogeochemical-signatures that may be useful to test the Earth's surface and extraterrestrial habitats for the presence and the biomineralization activity of microbes similar to halophilic aerobic bacteria. Our findings may help interpret the role of microorganisms in diagenetic processes resulting in carbonate and phosphate precipitation in natural systems and may shed new light on the Dolomite Problem.

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