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PRIMARY MICROBIAL DOLOMITE PRECIPITATION IN CULTURE EXPERIMENTS AND IN STROMATOLITE FORMATIONS: IMPLICATIONS FOR THE DOLOMITE PROBLEM

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Abstract: Dolomite [$CaMg(CO_3)_2$] is abundant in sedimentary rocks throughout the geological record, but it is rarely found in modern sediments. With the recognition that sulfate and magnesium influence primary microbially mediated dolomite, a new geomicrobiological investigation of the Dolomite Problem combining the study of bacterial culture experiments with the study of stromatolites in the geological record is now being used to interpret evidence for the origin of microbes in the dolomite rock record. The sulfate inhibition model may only work in inorganic dolomite at higher temperatures or in the dolomite replacement reaction, but sulfate has not influenced primary dolomite precipitation in the same low-temperature culture experiments. Magnesium that influences primary microbially mediated dolomite may be involved with the limitation of the dolomite lattice on the spatial configuration of CO_3 groups at ambient low temperature conditions, though it was not originally thought that existing cation hydration prevents Mg^{2+} and CO_3^{2-} ions from forming ordered structures. The Dolomite Problem is still not solved, but most of the important organic exopolymers and substrate templates may help dolomite overcome any lattice limitations because of the distributions, arrangements and compositions of specific functional groups. Those methodologies, when applied to the study of dolomite formation, will hold a promising future for the ‘Dolomite Problem

Keywords: Primary microbial dolomite, Culture experiments, Stromatolites

1. INTRODUCTION

The Dolomite Problem is one of the unsolved mysteries in sedimentary geology, as it often stems from the difficulty of precipitating dolomite in abiotic laboratory experiments under Earth’s surface conditions (Lippman, 1973; Land, 1998). In the geologic record, especially during the Precambrian, dolomite [$CaMg(CO_3)_2$] is a common mineral, while dolomite rarely forms in the absence of any high temperature hydrothermal process in modern experiments. In addition, there is a general agreement that the presence of Mg^{2+} ions in a solution has a strong inhibitory effect on the growth of dolomite and favors the formation of Mg-free carbonate (Lippmann, 1973; Berner, 1975; Raz et al., 2000; de Leeuw & Parker, 2001; Higgins & Hu, 2005; Stephenson et al., 2008; Astilleros et al., 2010). In recent years, dolomite formation was observed in zones of microbialsulfate reduction within a black sludge layer directly overlying the water/sediment interface under anoxic hypersaline conditions (Vasconcelos & McKenzie, 1997). Subsequently, the role of microbes in the formation of sedimentary dolomite has been demonstrated in culture experiments: sulfate-reducing bacteria (SRB) (Vasconcelos et al., 1995; Warthmann et al., 2000, 2005; Deng et al., 2010; Bontognali et al., 2012), even under temperatures as low as 21°C (Krause et al., 2012); methanogenic archaea (Kenward et al., 2009); and aerobic bacteria (Sánchez-Román et al., 2008, 2009a, b) are capable of mediating dolomite precipitation at low temperatures

Dolomite that forms early on may experience recrystallisation during diagenesis (Tucker & Wright, 1990), which adds to the difficulty of recognizing microbial signals masked by diagenesis. In recent sediments, a diagenetic trend towards more ordered and stoichiometric dolomite happened with burial depth, which may result in some preservation

(Vasconcelos & McKenzie, 1997; Wright, 2000). In addition, in the geological record, spheroidal-shaped dolomite and fossils identified as bacteria were observed in the Norian Dolomia Principale Formation in southern Italy (Mastandrea et al., 2006; Perri & Tucker, 2007), and microbial dolomite in Cambrian stromatolites in the Tarim Basin, China (You et al., 2013, 2014), which have revealed poorly crystallized dolomite, strongly resemble the morphology and the structures of primary dolomite that precipitated in microbial culture experiments, even preserving mineralized coccoid bacterial remains. However, it remains unclear if and how microbial signatures can be preserved and recognized in ancient rock records. Nevertheless, studies on primary microbial dolomite in culture experiments are now being used to identify the microbial origin of stromatolite formations and to calibrate or interpret microbial evidence derived from the dolomite rock record.

2. INFLUENCE OF SULFATE ON PRIMARY DOLOMITE PRECIPITATION AT LOW TEMPERATURE

During the Deep-Sea Drilling Program (DSDP), dolomite associated with organic carbon-rich hemipelagic sediments was commonly observed on the California Margin and in the Gulf of California (e.g., Murata et al., 1969; Burns & Baker, 1987; Kelts & McKenzie, 1984). Many hypotheses have been developed to explain the formation of deep-sea diagenetic dolomites based on their carbon isotopic compositions (Claypool & Kaplan, 1974). Negative $\delta^{13}C$ values indicate precipitated dolomites in association with bacterial sulfate reduction, whereas positive values indicate methanogenic microbial activity (Meister et al., 2007). The sulfate inhibition model on primary dolomite came from Baker & Kastner's (1981) experiments, in which they demonstrated experimentally that the rate of dolomitisation is increased when the level of sulfate is decreased. Based on observations in natural systems, especially supported by experimental results (Baker & Kastner, 1981), it was inferred that the sulfate concentration of the solutions is the major kinetic factor limiting the low-temperature precipitation of dolomite (Kastner, 1984). Therefore, the sulfate inhibition model has been broadly applied in the study of modern and ancient sedimentary dolomite. Kelts & McKenzie (1984) concluded that the sedimentation rate, limited diffusive transport and the penetration depth of SO_4^{2-} will control dolomite precipitation (methanogenic vs. sulfate reducing). By a reconstruction of past biogeochemical conditions, some dolomite layers (e.g., Moore et al., 2004; Meister et al., 2007; Ussler & Paull, 2008) were proposed to precipitate in the zone of anaerobic methane oxidation (AMO) due to an elevation of pH (cf. Soetaert et al., 2007). However, those experiments were performed at 200°C. At lower temperatures and in most modern dolomite environments, the sulfate concentrations are greater than or equal to those in seawater, but dolomite can still form, meaning it may be a catalyst for dolomite precipitation (Hardie, 1987; Brady et al., 1996; Morse et al., 2007). The first proven experiment to accurately precipitate dolomite at low temperatures in the laboratory involved synthesis in the presence of sulfate-reducing bacteria from the Desulfovibrio Group, in which a ferroan dolomite with a high degree of cation order was directly mediated (Vasconcelos et al., 1995). Subsequently, using the Lagoa Vermelha system, Vasconcelos & McKenzie (1997) proposed a new model called the microbial dolomite model for dolomite formation. In this model, photosynthetically produced organic matter can be microbially recycled by sulfate-reducing bacteria in the anoxic turbid layer at the sediment surface; a continuing supply of sulfate is required as a catalyst to precipitate primary dolomite (Vasconcelos & McKenzie, 1997). Furthermore, Sánchez-Román et al., (2009b) reported that the presence of sulfate does not inhibit dolomite precipitation at low temperatures, as they mediated the direct precipitation of dolomite at 25 and 35°C using variable SO_4^{2-} concentrations (0, 14, 28 and 56 mM) with Virgibacillus marismortui and Halomonas meridian. They hypothesize that Baker & Kastner's (1981) results may only apply to inorganic dolomite formation at higher temperatures; if sedimentary dolomite is a direct precipitate, as in the same low-temperature culture experiments, the kinetic factors involved are quite different from a dolomite replacement reaction.

3. INFLUENCE OF MAGNESIUM ON PRIMARY DOLOMITE PRECIPITATION AT LOW TEMPERATURE

To our knowledge, previous studies have suggested that magnesium ions in an aqueous environment have a stable inner-sphere hydration shell that contains six water molecules in an octahedral arrangement (Jiao et al., 2006, Di Tommaso & de Leeuw, 2010, Yang et al., 2012) and an additional outer shell composed of up to twelve water molecules through hydrogen bonding to the inner shell (Xu et al., 2013). Ca^{2+} has a faster water exchange rate, as much as five orders of magnitude higher than that for Mg^{2+} (Jiao et al., 2006, Di Tommaso & de Leeuw, 2010, Yang et al., 2012), while Ca^{2+} has 60% lower salvation free energy (per water molecule) than Mg^{2+} ions in both the inner and outer shells (Pavlov et al., 1998; Markham et al., 2002). However, in calcite crystals, the cation–C and cation–cation interatomic distances will be altered significantly by substituting Ca with Mg, so maintaining the C–O (within the CO_3^{2-}) and the cation–O bond lengths constant will be local tilt of the CO_3^{2-} groups by computational methods (Elstnerová, et al., 2010). Structural distortions under high lattice-Mg content will stiffen the crystal structure by reducing the equilibrium volume and raising the bulk modulus. Xu et al., (2013) precipitated anhydrous high-Mg carbonate minerals (i.e., magnesite & dolomite) at room temperature in dry formamide, which resembles water in many physical properties; however, because of the stronger steric effect, the hydrogen bonding of formamide molecules is weaker than in water (Pullman et al., 1978). The fundamental barrier for dolomite or magnesite is rooted in the spatial configuration of the CO_3 groups, which is a different lattice limitation than cation hydration (Xu et al., 2013). Nevertheless, suspending the belief of cation-hydration inhibition on dolomite mineralization may provide significant insight into understanding the fundamental chemistry in dolomite biomineralization and mineral processes.

4. MECHANISM IN THE CULTURE EXPERIMENTS AND IN THE STROMATOLITE FORMATIONS: IMPLICATIONS

The first proven synthesis of primary microbial dolomite at low temperature was a ferroan dolomite in the Desulfovibrio group with a fairly high degree of cation order (Vasconcelos et al., 1995). A subsequent study, based on a modern dolomite-forming hypersaline coastal lagoon in Lagoa Vermelha, Brazil, where Ca-dolomite precipitation occurs directly over the water/sediment interface and undergoes an aging process that increases the ordering of the crystal structure, integrated hydrologic, geochemical, and sedimentological approaches to the microbial dolomite model (Vasconcelos & McKenzie, 1997). Many new insights on primary dolomite, including bacterial populations and microbial and mineral-forming processes and their products, came from culture experiments and microbial mats as unique systems in modern precipitated dolomite environments (Vasconcelos et al., 1995; Vasconcelos & McKenzie, 1997; Warthmann et al., 2000; Vasconcelos et al., 2006). Recently, near-edge X-ray adsorption fine-structure spectroscopy (NEXAFS) revealed that a lithified stromatolite dolomite sample from a Lagoa Vermelha core showed similarities with primary microbial dolomite from culture experiments, as both of them contained a single distinctive broad peak centered at 288.2 eV and 288.5 eV (Fig. 1).

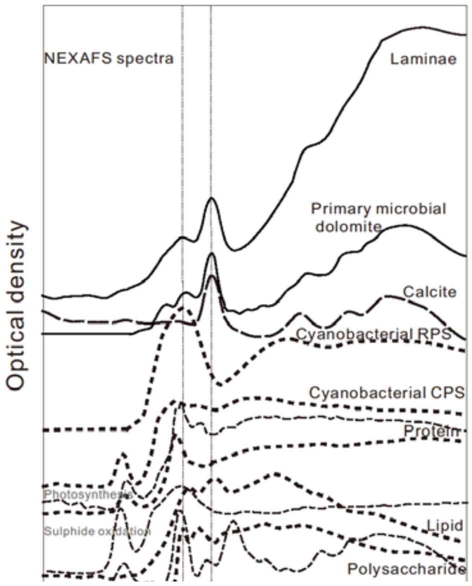

Figure 1. Carbon K-edge spectrum of lithified stromatolite laminae compared with carbon K-edge spectra of cyanobacterial extracellular polymeric substances, relevant inorganic and organic reference materials (Vasconcelos et al., 2014). In figure 1, cyanobacterial capsule polymeric substances (CPS), cyanobacterial released polymeric substances (RPS), reference material proteins (BSA) and lipids (cholesterol) were measured during the experiments, and the spectrum of polysaccharide (chitin) is from Solomon et al.'s (2009) data. Photosynthesis, sulfide oxidation, and sulfate reduction represent three types of microbial activity from a cross-section of the cultured mat: photosynthesis from the uppermost green layer, sulfide oxidation from the intermediate red layer associated with phototropic processes and sulfate reduction from the underlying darker brown zone.

These peaks in the region of 285 to 289 eV are typical for organic matter (Solomon et al., 2009). The spectrum for reagent grade calcite does not contain peaks associated with organic carbon but instead shows peaks centered at 290 and 301 eV (Fig. 1). Reference to the metabolically active microbial mat and reference compounds revealed the possible merging of the two peaks in the dolomite spectrum into a single peak, and lithified laminae contain the bio-molecular signatures of sulfide oxidizers, sulfate reducers, and cyanobacterial extracellular polymeric substances (EPS), which indicated that the metabolic activity of sulfate-reducing bacteria, or their evolutionary precursors, and the degradation of EPS are critical factors in lamina formation (Vasconcelos et al., 2014; Visscher & Stolz, 2005). In fact, SRB, methanogenic archaea (Kenward et al., 2009) and aerobic bacteria (Sánchez-Román et al., 2008, 2009a, b) are all capable of mediating dolomite precipitation, but the mechanisms of sulfate-reducing microbial activity mediation have been widely investigated and are better understood than others (Vasconcelos et al., 1995; Warthmann et al., 2000, 2005; Deng et al., 2010; Bontognali et al., 2012; Krause et al., 2012). SRB form one group of sulfate reducing prokaryotes, and the main genus is Desulfovibrio. Sulfate occurs widely in sediment or water-rich decaying organic material, and in these anaerobic environments, fermenting bacteria extract energy from large organic molecules; the resulting smaller compounds, such as lactate and pyruvate, act as electron donors for SBR (Postgate, 1979). Such reactions can be expressed chemically as follows:

$$2CH_2O(\text{organic material})+SO_4^{2-}\xrightarrow{SRB}HS^-+ +2HCO_3^-+H^+ \qquad (1)$$

The reaction equation shows that sulfate reduction produces dissolved inorganic carbon (DIC) and increases alkalinity, which is commonly suggested to explain the formation of carbonate (calcite and dolomite) buildups such as stromatolites (Visscher et al., 1998, 2000; Vasconcelos et al., 2006), microbial laminates (Camoin et al., 1999; Cabioch et al., 2006; Heindel et al., 2010), cemented layers, and concretions in sediments (Vasconcelos et al., 1995; Raiswell & Fisher, 2004). In addition, this reaction explains the calcification in the Precambrian after the oxygenation of Earth's atmosphere allowed significant sulfur cycling in the oceans (Vasconcelos & McKenzie, 2000). Dupraz et al., (2004) suggested that the carbonate precipitation mechanism needs to resolve whether it is a 'biologically induced' or a 'biologically influenced' mineralization process; in the former, the presence of living microbes is a key factor towards reach the supersaturation of carbonate minerals, which require living, metabolizing microbes, different from the biologically influenced process. Sulfate reduction is unlikely to induce carbonate precipitation in microbial mats through reactive transport modeling (Aloisi, 2008). Meister (2013) also modeled the saturation of carbonates in different environments, which suggested that the net effect of sulfate reduction does not induce carbonate precipitation in near-surface marine and hypersaline microbial mats or in the underlying sediments. This study suggested that sulfate reduction may contribute to mat lithification by lowering the saturation state, causing dissolution and mineral replacement. However, in the alkaline Precambrian ocean, other microbial mechanisms, in combination with the physicochemical conditions, may have been responsible for the early lithification of microbial mats. Actually, the alteration of EPS, even through abiotic processes, yields the reorganization of acidic sites in templates, which allows carbonate precipitation (Dupraz & Visscher, 2005), or the sorption of polysaccharides onto Ca–Mg carbonate surfaces (Zhang et al., 2012). In addition, relatively high aqueous Mg and low Fe (±Ca) concentrations may facilitate the incorporation of Mg in the solid (Romanek et al., 2009). Nevertheless, in culture experiments, organic substrates related to the nucleation of dolomite have been documented to be of crucial importance in experimental investigations (Reid et al., 2000; van Lith et al., 2003; Turner & Jones, 2005; Bontognali et al., 2008, 2010; Dupraz et al., 2009; Vasconcelos et al., 2014). The mode of nucleation process at the nanometer scale in mediated microbial carbonate has been demonstrated in experiments with both aerobic and anaerobic conditions by diverse bacterial strains (Aloisi et al., 2006; Bontognali et al., 2008). In addition, under those experimental conditions, the bulk of carbonate precipitation, including primary dolomite, takes place on globules formed near the microbial cell wall or attached to the surface of the cells, which precipitate only when released by surrounding microbial cells. Bontognali et al., (2014) presented that after EPS was formed in the presence of metabolizing Desulfovibrio brasiliensis and inhibited by an injection of antibiotics, disordered Ca-dolomite can precipitate without the presence of living microbes at the time of the dolomite mineralization process (Fig. 2), which completely confirms that producing an essential organic matrix is required for dolomite formation. The crucial importance of organic exopolymers, other substrate templates and/or living microbes could result from the presence of specific functional groups including carboxylic acids (R–COOH), hydroxyl groups (R–OH), amino groups ($R–NH_2$), and sulfate- ($R–O–SO_3H$), sulfonate- ($R–SO_3H$) and sulfhydrylgroups (–SH), which can bond with metal ions such as Ca^{2+} and Mg^{2+} (Bianchi, 2007), and further influence the spatial configuration to overcome lattice limitations and precipitate dolomite at low temperatures.

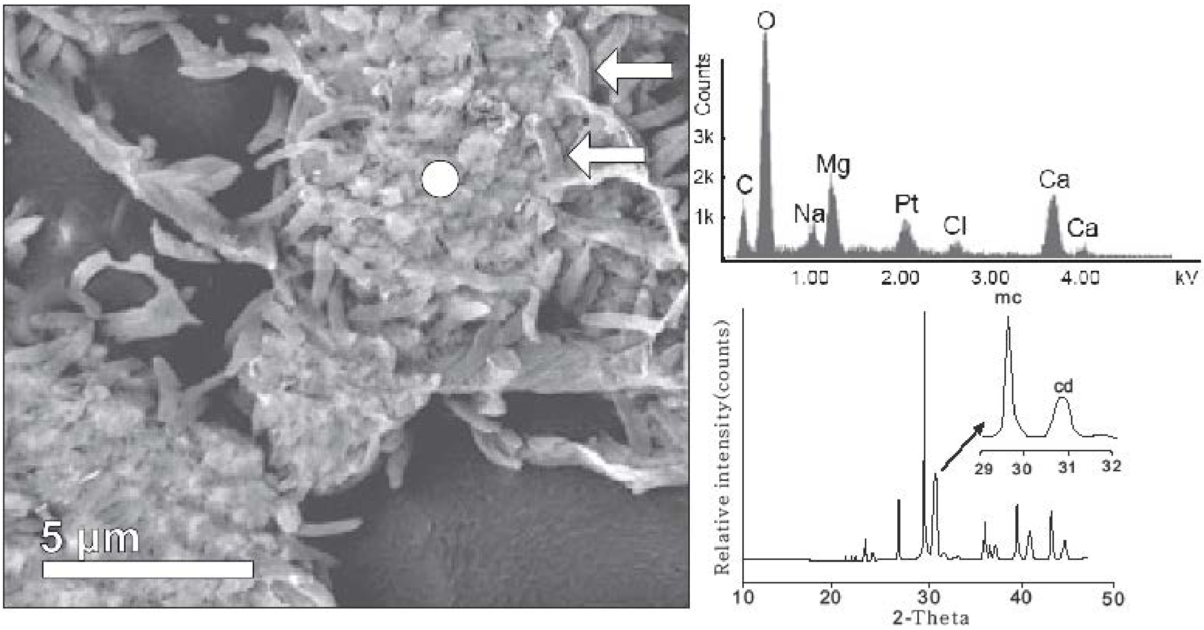

Figure 2. Cryo-SEM imaging of the mineral product formed in the laboratory experiments in the absence of metabolizing bacteria and X-ray diffractograms (Bontognali et al., 2014). A. Photomicrographs showing visualized globules with grainy surfaces within the EPS. In A, SRB activity was inhibited and treated with antibiotics. Dead bacterial cells (oval elongated features indicated by white arrows) are associated with the mineral globules. The EDX spectrum of the mineral (white circle in A) and the elemental analysis is consistent with a Ca-Mg carbonate. The Pt peak corresponds to the coating applied during preparation. The Na and Cl peaks reflect the high salt content of the growth medium. After a longer incubation time, the solid solutions evolved into two distinct mineral phases consisting of Mg-calcite (mc) and Ca-dolomite (cd). Quartz (q) powder was added as an internal standard.

The successful synthesis of primary microbial dolomites at low temperatures has triggered major interest among sedimentologists and geomicrobiologists to decipher the origins of early dolomite formations related with micritic dolomite with fine laminations and stromatolitic structures (McKenzie & Vasconcelos, 2009). Many studies have reported carbonate crystals with spherical and dumbbell morphologies, which are interpreted to be associated with bacteria (Mansfield, 1980; Mastandrea et al., 2006; Lee & Golubic 1999; Kazmierczak & Altermann, 2002), especially dumbbell molds that developed on dolomite enhedral crystals (Feldmann & McKenzie, 1997; Clari & Martire, 2000). Folk (1993, 1999) also observed the remarkable spheroidal growth morphology, which concerned the involvement of microorganisms in mineral nucleation. However, organic exopolymers are important for initial nucleation, as they influence crystal morphology and primary dolomite precipitation. Most importantly, because of the self-preservation behavior of the microbes, the possibility of nanobacteria fossils was excluded, and nanoglobule structures occurred instead. It may be possible that the occurrence of granular-textured dolomites in the above geological samples could be related to microbial mediation by analogy with primary dolomite that precipitated in aerobic (Sánchez-Román et al., 2008) and anaerobic cultures (Bontognali et al., 2008). In the dolomite growth experiments, primary dolomite precipitated with dumbbell morphology, where crystals grew at the polar ends of bacterial cells with close spatial relationships in the initial stages and transformed into a cauliflower-like structure (Warthmann et al., 2000). Currently, for the geological record, most of the primary microbial dolomite that was investigated had evidently developed only in Holocene strata (von der Borch & Lock 1979; Rosen et al., 1988; Deng et al., 2010), especially in some modern hypersaline environments (Vasconcelos & McKenzie, 1997; Wright, 1999). Nevertheless, few instances of primary dolomite have been reported in ancient microbialitic facies found in the carbonate platform (Mastandrea et al., 2006; Perri & Tucker, 2007; You et al., 2013, 2014). Mastandrea et al. (2006) have previously investigated microbialitic facies from the Norian Dolomia Principale Formation of Northern Calabria (Southern Italy), where these peritidal dolomite facies consist of stromatolites, thrombolites and aphanitic dolomites.

Based on scanning electron microscope observations of the organic-rich micritic laminae and clots of the inter-supratidal microbialites, spheroids ranging in size from 70 to 150 nm with aggregated granular texture (Fig. 3A) and much smaller isolated

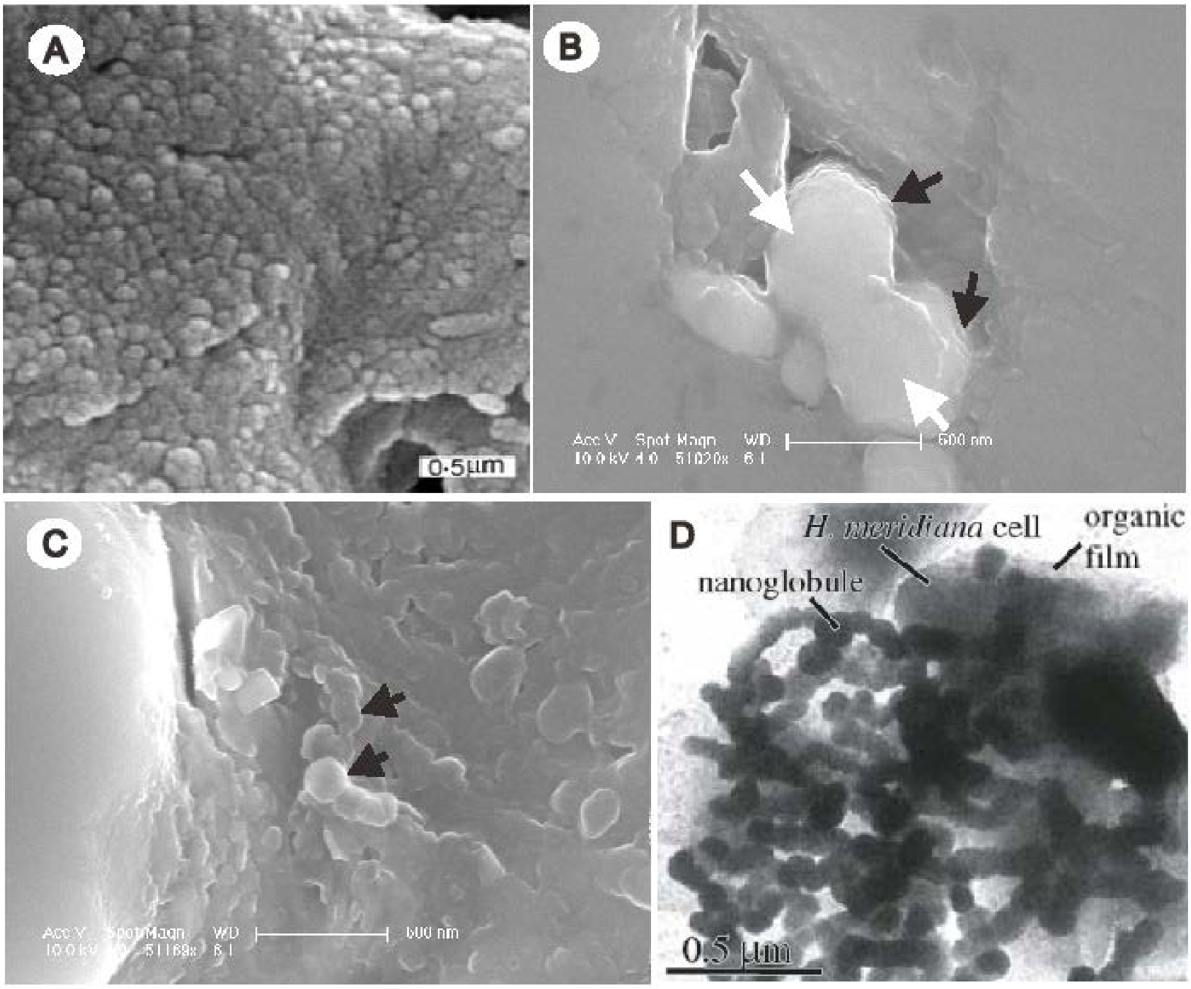

Figure 3. Scanning electron microscope (A, B, C) and atomic force microscopy (D) photomicrographs of dolomite nanoglobule structures in the stromatolite formation and in the Halomonas meridiana culture. A. Granular texture consisting of spheroidal bodies 70–150 nm in size (Mastandrea et al., 2006). B. Two uniform spheroids with a diameter of ~ 550 nm (white arrows), consisting of many nano-particles ranging in size from 50 to 100 nm (black arrows) (You et al., 2013). C. Chain of spheroids with individual spheroid diameters of 50-100 nm that protrude from the spheroid matrix (black arrows) (You et al., 2013). D. Detail of the nanoglobule chain embedded in the thin organic film of H. meridian cells (Sánchez-Román et al., 2008).

spheroidal and ovoidal structures were associated with granular areas, which were interpreted as the fossilization of micron-sized coccoid bacteria. Subsequently, Perri & Tucker (2007) observed the same mineralized bacterial remains, granular-textured surfaces and gently folded sheets, which were 100~200 nm thick and several micrometers long, form a sub-polygonal network reminiscent of EPS in those Triassic stromatolitic dolomites from Italy. Those authors suggested a biological origin for the stromatolites, as in modern microbialmats, and dolomites induced through microbial sulfate-reducing metabolic activities. You et al., (2013) found uniform dumbbell-shaped aggregates composed of smaller nanocrystals ranging from 50 to 100nm (Fig. 3B), chain-like nanometer-sized spheroids (Fig. 3C) and scattered nodules in Cambrian stromatolites from the Tarim basin in northwestern China. Sánchez-Román et al., (2008) showed dolomite that formed attached to the surface of H. meridiana cells or embedded in a thin organic film; the size and distribution are irregular, with the majority being 50~100 nm and the remaining 100~200 nm in size (Fig. 3D). The SEM observations show that the preservation of the morphology and size distributions observed in the microbial culture experiments strongly resembles that in the Cambrian stromatolites (You et al., 2013). The dolomite with nanoglobule structures from stromatolites may have been produced through a similar process as in the culture experiments during the geological past, which could provide a record to trace microbial processes through geologic time.

5. CONCLUSION

Primary dolomite precipitation in low temperatures happened in the culture experiments and in the stromatolite formation. During those processes, sulfate did not influence primary dolomite precipitation in the same low-temperature culture experiments, while the sulfate inhibition model may have only worked in inorganic dolomite at higher temperatures or during the dolomite replacement reaction. The fundamental barrier to magnesium carbonate (dolomite) crystallization at ambient low temperature conditions mainly stems from the limitation of the dolomite lattice on the spatial configuration of CO_3 groups, as it was originally thought that the existing cation hydration prevents Mg^{2+} and CO_3^{2-} ions from forming ordered structures. The Dolomite Problem is still not solved, but the influence of these organic exopolymers and other substrate templates cannot be ignored. The most important factor of the organic exopolymers and substrate templates may be that they can allow dolomite to overcome the lattice limitation because of the distributions, arrangements and compositions of specific functional groups. Although few cases from the geological past existed that confirmed the microbial origin of dolomite formations, the implications from and the comparison between the culture experiments and stromatolite formations may help the search for microbial evidence in ancient dolomite rocks, which will undoubtedly provide new information to better understand the primary precipitation of dolomite and possibly solve the Dolomite Problem.

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