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# Significance of fossilized microbes from the Cambrian stromatolites in the Tarim Basin, Northwest China

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Samples of the Cambrian microbial dolomites were collected from Penglaiba section, a well-exposed stratigraphic section in the northwestern area of the Tarim Basin. This study provides an analogue for mediated dolomites that can precipitate in microbial mats and biofilms. The Cambrian stromatolitic dolomites were studied using high-resolution scanning electron microscopy. The results are as follows: (1) dolomites with 50 nm to 100 nm spherical nanostructures are aggregated into minerals of larger sphericities; (2) nanospherical dolomites of 50 nm to 170 nm diameter are densely arranged as dumbbell-shaped or chained aggregates; (3) silicified filaments, as well as dumbbell-shaped and chain arrangements, are preserved as important microstructures. On the basis of sedimentological, compositional, geochemical, and petrographic data, the microstructures were interpreted as nanoglobules that function as bacteria in the nucleation and filament mineralization stages. The microstructures function as such because they are wrapped in extracellular polymeric substance (EPS) or mucus and mineralized fossils. Silicification accounts for the exceptional preservation of microbial mat structures, including biofilms, as well as filamentous and coccoid microbes. In addition, EPS process is capable of binding different elements, with preference for Si, Mg, and Ca. Such suitable composition favors microbe mineralization and dolomite nucleation on organic substrates. These microscopic structures suggest bacterial mineralization and provide visual evidence for the origin of microbial dolomites.

#### Cambrian, stromatolite, fossilized microbe, mediated dolomite

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Sedimentologists have long focused on the link between microorganisms and carbonates. In ancient and modern sedimentary environments, as well as in microbial culture experiments, microorganisms (especially bacteria) have been found highly related to the carbonate deposition process (Buczynski and Chafetz, 1991; Schultze-Lam et al., 1996; Douglas and Beveridge, 1998; Castanier et al., 1999; Bosak and Newman, 2003; Duprza and Visscher, 2005; Visscher and Stolz, 2005). New research possibilities for the study of the "Dolomite Problem" enigma (Fairbridge, 1957; Lippmann, 1973; McKenzie and Vasconcelos, 2009; Sun, 2005) have arisen because of the introduction of microbial factors into such investigations (Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Warthmann et al., 2000). Microbial mediated dolomites can form in some modern hypersaline depositional environments, such as the coastal lagoon Lagoa Vermelha in Rio de Janeiro, Brazil (Vasconcelos and McKenzie, 1997), lakes of the Coorong region in South Australia (Wright, 1999), and the Qinghai Lake in the Tibetan Plateau, Northwest China (Deng et al., 2010). Culture experiments have shown that sulfate-reducing bacteria, methanogens, and moderately halophilic aerobic bacteria

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can mediate the formation of primary dolomites under the Earth's surface (Vasconcelos et al. 1995; Vasconcelos and McKenzie 1997; van Lith et al. 2003a, 2003b; Roberts et al. 2004; Wright and Wacey, 2005; Sánchez-Román et al., 2008, 2009, 2011; Kenward et al., 2009). The Desulfobulbus mediterraneus strain mediated primary dolomite formation at very low temperatures (21°C) in seawater conditions (Krause et al., 2012). Experiments on modern environments and laboratory studies have documented the important role of microorganisms in mediating dolomite formation; such studies support the hypothesis that dolomite formation in geological periods is characterized by recrystallization during diagenesis (Tucker and Wright, 1990). Therefore, the traces or biosignatures of microbes from ancient dolomites are difficult to determine. Nevertheless, similar to stoichiometric dolomites and the dolomites that formed in the Coorong Lake, South Australia (Wright, 1999), some dolomites exhibit a diagenetic trend in terms of burial depth (Vasconcelos and McKenzie, 1997). Based on observations of the microstructure characteristics in ancient dolomite by high-resolution scanning electron microscopy to determine the link among microbial dolomites in geological record, the formation of dolomite in modern environments, and culture experiments, it maybe is a significant approach for elucidating the origin of dolomites (You et al., 2011).

In this study, the well-exposed stratigraphic Penglaiba section (Kalpin areas) in the northwestern region of the Tarim Basin was investigated. The region is composed of the Cambrian strata. Previous studies have been conducted on the microfacies (Liu et al., 2012), as well as the geochemical and isotopic (carbon, oxygen, and strontium) compositions of the Cambrian Series 2 and 3 in the Penglaiba section (Wang et al., 2011). Geochemical data on the Upper Cambrian stromatolites have also been reported (Xie et al., 2009). The current work aimed to determine the microbial origin of the dolomites that formed in the Cambrian stromatolites of the Penglaiba section by high-resolution scanning electron microscopy and other techniques. We also identified the mechanism and process of dolomite formation in this region.

# 1 Geological setting

The Tarim Basin developed from a continental crust composed of the Proterozoic metamorphic rocks into a Mesozoic and Cenozoic foreland basin (Jia, 1997). It is surrounded by the Kunlun and Tianshan tectonic zones to the west, north, and south. The uplifts and depressions in the northwestern area of the basin are shown in Figure 1 (Jia, 1997). As the figure shows, several wells reach the Cambrian strata in the basin: The Awatage Formation (which has a typical red color) can be observed in the Yaha 5 and Yingmai 7 wells of the Tabei area; the Tazhong uplift can be observed in the Tacan 1 well; and the Bachu uplift is evident in the Fang 1 well (Chen et al., 2008). However, typical stromatolites are rarely found in the drilling cores. The outcrops are regarded as appropriate for research on stromatolites, especially those in the Penglaiba section (Figure 1) (Jia, 1997; You et al., 2013; Wang et al., 2011).

We focused on the Middle Cambrian and Upper Cambrian strata as we investigated the stratigraphy and lithology of the Penglaiba section (Figure 2). The Middle Cambrian strata were divided into two formations: The Sayilike ( $\epsilon_2 s$ ) and Awatage formations ( $\epsilon_2 a$ ). The latter is composed primarily of typical stromatolites (Figure 3(a)).

The Awatage Formation is composed of micritic and finegrained dolomites with horizontal bedding and cross-bedding structures. These beds are interlayered with centimeter-thick greenish to reddish mudstones, which contain abundant lenticular anhydrite crystals or moulds. The beds are also associated with layers of stromatolitic dolomites that are deposited in the upper region of the Awatage Formation (Figure 3(a)). This formation is a shallow evaporative environment. The overlying Lower Qiulitage Formation is powder dolomite from sheet to medium-bedding with light to dark gray colors. The thickness of the Formation is over 200 meters, and the bottom of the Lower Qiulitage Formation distributes debris beach and tidal flat in the open platform facies (Liu et al., 2012). The lower part of the Lower Qiulitage Formation continuously is up to a maximum of meter-thick cycles, consisting of four or three microfacies. The cycle comprises, from the bottom upwards, sheet-bedded muddy dolomite with light gray color, sheet-bedded powder dolomite in gray, microbial reef dolomite in dark gray (only developed in four microfacies) and dolomitic stromatolites in brown to light gray (Figure 3(b)). The middle and upper parts of the Lower Qiulitage Formation are continuously distributed up to a maximum of meter-thick cycles, consisting of less microfacies than three, which are transformed from beach- tidal flat to restricted platform facies.

### 2 Methods and sampling

After standard petrographic analyses for the Middle and the Upper Cambrian from Penglaiba section under Olympus BX-51, thin sections were prepared for fluorescence microscopy using a Zeiss Axioskop 40A. Scanning electron microscope (SEM) studies were carried out on polished thin sections or fresh broken surfaces. All samples were ultrasonically cleaned with alcohol. Some samples were first etched with dilute hydrochloric acid before ultrasonic cleaning. To ensure that each sample could be used for microanalysis and textural study, two replicate samples were removed from the same position. One sample was carboncoated and the other was gold-coated. A Gatan Model 682 precision etching and coating system (PECS) was used to spatter the gold coating onto the SEM samples and fresh



Figure 1 Tectonic units of the Tarim Basin and geological units of the study area. Modified after Jia (1997), You et al. (2013) and Wang et al. (2011).

broken surfaces to improve the conductivity. The spattering was carried out by two Penning ion guns trained on a 99.99% pure gold target. The PECS coating system is designed to slowly deposit electron-transparent amorphous gold coating with a built-in thickness monitor, facilitating a controlled deposition of 0.12 nm of gold per second and the ion beam is 300 amps. In this way, a 15 nm-thick gold coating was deposited onto all spattered samples. All microstructures and surface morphologies were observed using JEOL JSM–6490 scanning election microscope and Nova<sup>TM</sup> NanoSEM 230 field emission scanning election microscope (FESEM). At the same time, semi-quantitative analyses of submicron-sized spots were performed with an energy dispersive X-ray (EDX) spectrometer. The SEM/EDX analyses were performed at the State Key Laboratory for Mineral

Deposits Research and the National Laboratory of Solid State Microstructures, Nanjing University.

# **3** Petrological characteristics of stromatolitic dolomites

#### 3.1 Field characteristics and sedimentary microfacies

The stromatolitic dolomites are distributed throughout the Middle Cambrian Awatage Formation and the Upper Cambrian Qiulitage Formation. The Penglaiba section was divided into 227 sequences for the Cambrian strata, and 147 sequences for the Awatage and Qiulitage formations. We obtained 12 stromatolite sequences, which are 8.2% of the total number of sequences in the Middle and Upper Cambrian

Forma-	Bed	Thickness	Lithology	Sedimentary	Description	Sedimentary facies	
tion	No.	(m)	Liulology	structures	Description	Microfacies	Facies
Qiulitage Formation	227- 225	13		Lenticular bedding Cross	Sheet-like beds, 10 to 20 cm thick. The beds are composed of fine-grained dolo- mite showing thrombolitic dolomite.	Bioclastic beach	
	224- 199	70. 5		bedding Cross bedding Horizontal bedding Lenticular bedding Lenticular bedding Mud crack Cross bedding	The beds are composed of micritic dolomite and fine-graineddolomite showing through horizontal-bedding and cross bedding. These beds are interlayered with centimetre-thick mudstones.	Cycles of the beach and tidal flat	Open platform facies
					The beds are composed of fine-grained dolomite showing thrombolitic dolomite. Stromatolitic dolomite is on the top.		
	198	16. 4			Sheet-like beds,10 to 20 cm thick. The beds are composed of fine-grained dolomite showinglenticular-bedding.	beach and tidal flat	
	196	7.8				and tidal flat	
	195- 188	20. 5			Sheet-like beds,10 to 20 cm thick. The beds are composed of fine-grained dolo- mite showing thrombolitic dolomite.	Cycles of bio- clastic beach and tidal flat	
	187- 177	20.5			Sheet-like beds, 10 to 20 cm thick. The beds are composed of fine-grained dolomite .	Clastic bea- ch and tidal flat	
	176- 171	28.8			Sheet-like beds, 10 to 20 cm thick. The beds are composed of fine-grained dolo- mite showing thrombolitic dolomite. Meters thick cycles of microbial beach and tidal flat. Every cycle is composed of fine crystalline dolomite, 10 to 50 cm thick and fine crystal dolomite, 1 to 10 cm thick. These beds are interlayered with stromatolitic dolomite. Sheet-like beds,10 to 20 cm thick, fine- grained dolomite showing thrombolitic dolomite. These beds are interlayered with stromatolitic dolomite. Sheet-like beds, 10 to 20 cm thick. Thrombolitic dolomite is on the top.	Cycles of - bioclastic beach and tidal flat	
	170- 141	48.9					
	140- 138	17. 1				Cycles of bio- clastic beach and tidal flat	
	137- 131	11.2				Cycles of bio- clastic beach and tidal flat	
Awatage Formation	130- 129 128- 80	6.3			Sheet-like beds, 10 to 20 cm thick. Stromatolitic dolomite is on the top. Sheet-like beds, 10 to 20 cm thick, which have locally erosive bases. The beds are composed of micritic dolomite and fine- grained dolomite showing through horizontal-bedding and cross-bedding. These beds are interlayered with centimetre-thick greenish to reddish mudstones which contain abundant lenticular anhydrite crystals or moulds, but also associated with layers of stromatolite dolomite.	Hypersalin- ity lagoons and tidal flat	carbonate platform
0 10 20 m				∽æ∽ Lenticular bedding	Marly dolomite Gypseous micritic dolomite Medium grain dolomite	Thromboli- tic dolomite	Evaporative

Figure 2 Sedimentary log of dolomite succession in the Middle and Upper Cambrian strata in the Penglaiba section.

strata. The thickness of the stromatolites is approximately 22.8 m, accounting for 2.8% of total thickness (826.3 m).

The outcrops are composed of mostly khaki to brick red stromatolitic dolomites and some light gray stromatolitic dolomites. The morphologies of the stromatolites are characterized by low-relief planar-domal laminations, but some exhibit dome-like morphologies. The maximum thickness of the monolayers of the stromatolites is 91 cm. The stromatolite sequences extend in a stable manner.

The stromatolitic dolomites in the Awatage Formation are associated with sheet bedding of 10–50 cm thick. These dolomites are micritic types characterized by frequent subaerial exposure surfaces, anhydrite nodules, or gypsum pseudomorphs. The sheet bedding is composed of anhydrite and single bedding is 5–50 mm thick. Aggregated anhydrite nodules or gypsum pseudomorphs (2–20 mm) are distributed in laminated micritic dolomites. These features indicate that the stromatolitic dolomites in the Awatage Formation are deposited in evaporated tidal flats or Sabkha (Zhu et al., 2008).

In the Qiulitage Formation, the stromatolites are found in the lower portion of the area, particularly around the boundary between the Awatage and Qiulitage formations. These stromatolites are filled with low-relief planar-domal laminations and domes (Figure 3(b)–(d)). In meter-scale cycles, packstone dolomites are from limestones, which were characterized by high energy and were deposited in beach environments (Zhu et al., 2008). Therefore, the stromatolitic dolomites in the Qiulitage Formation were formed by frequent sea-level fluctuations from tidal flats to beach environments (Zhu et al., 2008).

# 3.2 Microscopic characteristics and distribution of organic matter

The crystals in the well-laminated and micritic dolomites in the stromatolites have a diameter of less than 0.03 mm. Dense laminations are stacked as stromatolitic laminae (Figure 4(a)). Laminae are usually isopachous, even and smooth, and varying from 0.1 mm to 0.5 mm in thickness. Stromatolitic laminae consist of alternating layers of dark laminae (d in Figure 4(a)) and light laminae (1 in Figure 4(a)). Light laminae, which have a thickness of 120–440  $\mu$ m, are microspar dominated by large fabric-preserving planar subhedral to euhedral dolomite crystals. Assessment by Alizarin red staining indicates that all the samples are almost dominated by dolomites and minimal calcites, and are macrospar that filled the cavity structures during late-stage formation (Figure 4(b)). X-ray diffraction (XRD) patterns show that dolomite minerals account for more than 96% of sample composition, and calcites account for less than 4%. Further observations show the presence of obvious pustules and dark spherical aggregates in the stromatolitic laminae (white arrows in Figure 4), which are primarily dark laminae. Fabric-preserving dark micrites are uniformly very dull or non-luminescent (Figure 4(c), (d)).

The XRD patterns also indicate that the bright orange luminescent zones in the stromatolitic laminae formed in



Figure 3 Field images of the stromatolitic dolomites. (a) Stromatolites in the Awatage Formation filled with low-relief planar-domal laminations; (b) low-relief planar-domal laminations in the middle part of Qiulitage Formation; (c), (d) low-relief planar-domal laminations and domes in red colour at the bottom of Qiulitage Formation



Figure 4 Photomicrographs illustrating the characteristics of stromatolites. (a) Stromatolitic laminae consist of alternating layers of dark laminae "d" and light laminae "l" and pustules and dark spherical aggregates (white arrows); (b) closed to pustules and dark spherical aggregates (white arrows), and sparry calcite in right formed in late diagenesis; (c), (d) fabric-preserving dark micrites in microscopy and the same area is uniformly very dull or non-luminescent.

late diagenesis. Therefore, dark laminations are rarely altered by late diagenesis. However, the dark laminae are strongly fluorescent (Figure 5(a), (b)), indicating that such laminae are rich in organic matter and well-preserved organic material. The spherical dolomitic aggregates that exhibit strong fluorescence (Figure 5(c), (d)) have morphologies



Figure 5 Microscopic photos of stromatolites visualized under transmitted and epifluorescent light. (a) Thin dark laminae in microscopy; (b) the same area strongly fluorescent and rich in organic matter and well-preserved organic material; (c) the spherical dolomitic aggregates in microscopy; (d) the same area strongly fluorescent (Green fluorescent BP 436/10 nm/LP470 nm).

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similar to the aggregates shown in Figure 4; the latter may be microorganic residues. On the basis of the chromophores in the morphology and size distribution, these aggregates may be categorized as coccoid cells (probably cyanobacteria).

# 4 Microfabrics determined by scanning electron microscopy

Scanning electron microscopy (SEM) observations of the stromatolitic dolomites show numerous microstructures and microfabrics of micron or nanometer size. They are present on the surface of the micritic dolomites in the dark laminae and sometimes extend across dolomite crystals. One of the compositions of these microstructures and microfabrics is dolomites and the others are siliceous minerals.

### 4.1 Dolomitic microstructures

Most of the dolomites are rhombic euhedral crystals in the dark laminae, as determined by SEM. The spherical dolomites in the dolomite crystals or on the surface of the crystals are so poorly crystallized that even part of the crystal surface was modified by those spherical morphology (Figure 6). The EDAX patterns of the poorly crystallized spherical dolomites in the micron, submicron, or nanometer scale show that Mg content is slightly higher than Ca content (Figure 7). The nanoscale spherical dolomites with a 40 nm to 100 nm diameter aggregate into dolomites with diameters of 470 nm to 1020 nm in the micron, submicron, or nanometer scale. In some of the samples, poorly crystallized dolomites are found on the crystal surfaces, thereby modifying surface morphology (Figure 6(a),(b)). In the other samples, spherical dolomites are densely distributed in the crystals; these dolomites remain visible even after the crystals were cut to expose poor crystallization (Figure 6(c), (d)).

The spherical dolomites (diameter, 470–660 nm) on the crystal surface are arranged in chains. Closer observations reveal that all these micron-scale spherical dolomites are aggregated into smaller dolomites with diameters of 50–100 nm; biofilm-like, poorly crystallized dolomites also span the dolomite crystals (Figure 6(a)). Spherical apophysis is observed on the surfaces of the dolomite crystals, a phenomenon that partially changed the morphological characteristics of the dolomite surfaces; these dolomites are distributed in the same manner as the micron-scale dolomites (Figure 6(b)). The poorly spherical nanoscale dolomites (diameter, 50–70 nm) are strongly aggregated into chains, which are



**Figure 6** Photomicrographs (SEM) illustrating the characteristics of spheroidal structure dolomites. (a) The spherical dolomites on the crystal surface arranged in chains; (b) spherical apophysis partially changed the morphological characteristics of the dolomite surfaces; (c) the poorly spherical nanoscale dolomites (diameter, 50 nm to 70 nm) strongly aggregated; (d) these aggregates approximately 1  $\mu$ m in diameter and comprise smaller spherical dolomites of nanometer scale. Red Crosses are spectrum spots.



Figure 7 EDAX spectrum showing the typical composition of the dolomite crystals shown in Figure 6.

visible in the dolomite crystals (Figure 6(c)). In particular, micron-scale aggregates are present. These aggregates are approximately 1  $\mu$ m in diameter and comprise smaller spherical dolomites of nanometer scale. The nanometer-scale spheres are strongly distributed and aggregated around the micron-scale dolomites (Figure 6(d)).

#### 4.2 Siliceous microfabrics

SEM observations reveal not only dolomitic microfabrics, but also unique siliceous microfabrics. The two types of siliceous microstructures are spherical and filamentous microtextures (Figure 8). Such microstructures are composed predominantly of Si, with variable Al concentrations and a small amount of Ca and Mg (Figure 9).

A substantial amount of siliceous microfabrics resemble coccoid remains; in particular, these microfabrics show clusters of spherical pustules in the dark laminae (Figure 4(b)). The SEM results indicate dumbbell-shaped or chain-like spherical fabrics. The dumbbell-shaped spherical fabrics comprise uniform siliceous spheres with a diameter of approximately 3.7  $\mu$ m. Other extra small siliceous spheres with a diameter of 1.2  $\mu$ m are connected to the dumbbell-shaped fabrics, but not in a linear manner. They are instead arranged at a certain angle (Figure 8(a)). Meanwhile, some uniform spheres (diameter, 4  $\mu$ m) are chained in a line and an extra sphere (diameter, 6  $\mu$ m) is incorporated into the chain (Figure 8(b)).

Filamentous remains are always of micron scale, but they differ in length and diameter. Some have diameters that range from 10 to 20  $\mu$ m, and are independent of the size of crystals, which have smooth surfaces and rarely complicat-

ed structures (Figure 8(c)). Some filaments are wrapped by the same siliceous sheets (Figure 8(d)).

With regard to siliceous spherical aggregates and the arrangement of surrounding filamentous remains, which can be related to biomineralization, all the microfabrics show unique mineralized microstructures in microbial mats or biofilms. The compositions of these microfabrics also represent mineralized mucus or extracellular polymeric substances (EPS).

# 5 Discussion

The Penglaiba section was chosen for this study because it is composed of the Cambrian strata that are suitable for this type of research; the Cambrian stromatolites have wellpreserved original geochemical signals (Xie et al., 2009; Wang et al., 2011) and stromatolitic laminae (Figure 4). The strong fluorescences of dark laminae in the stromatolites (Figure 5) represent the presence of residual organic substances (Reitner and Neuweiler, 1995; Russo et al., 1997, 2000). This feature also reveals the distribution and concentration of biological and fluorescent chromophore macromolecules; examples include aromatic compounds, humic acid, and fulvic acid (vandenbroucke et al., 1985; Bertrand et al., 1986; Ramseyer et al., 1997). SEM observations show unusual microstructures in the dolomitic or silicified filamentous and bacterial remains. The distributions are dense in some regions, which is consistent with the finding that microorganisms tend to accumulate at nutrient-rich areas. These results indicate a relationship between special microfabrics and biological origins.



**Figure 8** Photomicrographs (SEM) illustrating the characteristics of silica filaments and coccoid cells. (a) The dumbbell-shaped spherical fabrics with extra small siliceous spheres; (b) uniform spheres (diameter,  $4 \mu m$ ) chained in a line and an extra sphere; (c) filamentous remains independent of the size of crystals; (d) some filaments wrapped by the same siliceous sheets. Red Crosses are spectrum spots.



Figure 9 EDAX spectrum showing the typical composition of the dolomite crystals shown in Figure 8.

#### 5.1 EPS bonding and silicification in mineralization

Previous studies have documented that EPS plays an important role in biogeochemical processes (Decho, 1990; Bhaskar and Bhosle, 2005). EPS is the first biofilm structure to come into contact with potential organic and inorganic metabolic substrates, predators, and antimicrobial agents/ antibiotics (Costerton et al., 1995). These substances are produced extensively by many types of bacteria, either photosynthetic autotrophic bacteria or heterotrophic bacteria. Among these, cyanobacteria are the most important producers in modern microbial mats (De Philippis, 1998, De Philippis et al., 2001; Stal, 2003; Richert et al., 2005). Many studies indicate that the EPS from cyanobacteria can bind ions from ambient water; such ions include calcium, magnesium, carbonate, and silica (Konhauser, 1998; Sánchez-Navas et al., 1998; Léveillé et al., 2000; Arp et al., 2003; Decho et al., 2005). These findings echo the silification microstructures revealed by our results (Figure 9). The EPS from many bacterial strains comprise functional groups, such as carboxylic acids (R-COOH), hydroxyl groups (R-OH), amino groups (R-NH2), sulfate (R-O-SO3H), sulfonate (R-SO<sub>3</sub>H), and sulfhydryl groups (-SH), all of which can induce strong complexation between metal ions and other ions (Bianchi, 2007). However, the role of EPS in the nucleation of Si results from hydrogen bonding between the external residue charges of organic compounds and silicic acid (Westall et al., 1995), or form the absorption of the negative charges of Si ions by the external positive charges of functional groups (Urrutia and Beveridge, 1993). Dupraz et al. (2004) summarized the interactions between microorganisms and minerals in the hypersaline environments of the Bahamas; highly ordered EPS macromolecules facilitate the precipitation of carbonates. Some studies also suggest that certain cyanobacteria can form external layers of subcrystal proteins (Schultze-Lam et al., 1992; Schultze-Lam and Beveridge, 1994); these layers serve as nucleation centers for calcite and other minerals (Schultze-Lam and Beveridge, 1994).

A generally accepted finding is that after cell death in modern microbial mats, cells are rapidly degraded by anaerobic bacteria (Kempe and Kazmierczak, 1993; Kazmierczak et al., 1996; Kazmierczak and Iryu, 1999), but many studies have shown that even after degradation by heterotrophic bacteria, the degraded cells or EPS continue to have the capacity of constraining various ions as nucleation centers (Konhauser et al., 1994; Urrutia and Beveridge, 1994; Tazaki, 1997; Barker and Banfield, 1998; Douglas and Beveridge, 1998).

A typical hypothesis is that when bacteria are involved in carbonate precipitation, the carbonates undergo recrystallization, but the resultant products cannot clearly reveal the presence of bacterial fossils or macromolecule structures in the carbonates. Nevertheless, if silicification in microbial mats occurs at an early stage, the Miocene samples can substantially preserve cell membranes and EPS ultrastructures (Renaut et al., 1998; Konhauser et al., 2001). For example, in the modern microbial environments of the Lake Van Turkey, the Miocene lacustrine stromatolites in the Duro Basin in Spain, and the Archean formations in South Africa, EPS was partially silicified and bound with calcium and magnesium (Kazmierczak et al., 2009; Sanz-Montero et al., 2008). This result indicates that silicification can prevent carbonates from recrystallizing, thereby enabling the preservation of original signals. The silicified spheroids and filaments in our study have compositions and morphologies that are similar to those of the filaments in the stromatolites found in Lagoa Vermelha, Brazil (Spadafora et al., 2010). They are also similar to the mineralized EPS preserved in geological history (Kazmierczak et al., 2009; Sanz-Montero et al., 2008). Therefore, the silicified spheroids and filaments in the current work were preserved because EPS or mucus surrounded the produced metabolites (Westall et al., 2000).

#### 5.2 Origin of microbial dolomites

Under the Earth's surface, dolomites cannot precipitate from abiotic solution, even at 1000-fold oversaturation, because of kinetic barriers (Hartman, 1982; Machel and Mountjoy, 1986; Hardie, 1987; Sibley and Gregg, 1987; Land, 1998). However, sulfate-reducing bacteria, methanogens, and moderately halophilic aerobic bacteria can mediate primary dolomite formation (Vasconcelos et al. 1995; Van Lith et al. 2003a, 2003b; Roberts et al. 2004; Sánchez-Román et al. 2009, 2011; Kenward et al. 2009; Krause et al., 2012). EPS is crucial to the nucleation process (Sánchez-Román et al. 2008; Bontognali et al., 2008, 2010). The Lake Mono in California is characterized by enhanced cyanobacterial mineralization because cyanobacteria and other types of microorganisms have a certain affinity for magnesium ions (Souza-Egipsy et al., 2005); the outer membranes of some bacteria can complex only with calcium and magnesium irons (Coughlin et al., 1983). Such features created a microenvironment favorable to dolomite formation. These characteristics may also be the drivers of spherical dolomite formation in the current study.

Microbial mats are characterized by micritic, rhombic, dumbbell-shaped, needle-shaped, and spherical fabric morphologies; these minerals are carbonates, such as aragonite, calcite, monohydrocalcite, vaterite, magnesium-calcite, and calcium-dolomite. Many studies indicate that polymeric properties (such as the abundance of acidic functional groups, water content) considerably influence the morphology and mineralogy of carbonates (Hardikar and Matijevic, 2001; Braissant et al., 2003; Chekroun et al., 2004; Bosak and Newman, 2005; Dupraz and Visscher, 2005; Ercole et al., 2007; Lian et al., 2007; Rodriguez-Navarro et al., 2007). The electrostatic binding and geometry that occurs during intermolecular interactions at inorganic-organic interfaces can control the nucleation and growth of inorganic crystals (Mann et al., 1993). Generally, these effects can reduce energy, thereby promoting nucleation on organic substances. Culture experiments have shown similar effects on the precipitation of primary dolomites (van Lith et al. 2003b; Sánchez-Román et al. 2009; Bontognali et al., 2008, 2010; Krause et al., 2012). In the present work, the poorly crystallized internal or external dolomite crystals in dark laminae of micron and submicron scales consist of nanoscale spherical dolomites with diameters of 50 nm to 100 nm. Dolomites (e.g., dumbbell-shaped, linearly arranged, or irregularly aggregated dolomites) with diameters of 50 nm to 170 nm are also freely arranged (Figure 6). Nevertheless, the morphology, size, and arrangement of the dolomites are similar to those reported by Bontognali (2008), Sánchez-Román et al. (2008), and Krause (2012). Bontognali (2008) reported that under anaerobic conditions, bacteria produce granular dolomites around ambient cells during the metabolic process; the dolomites are produced in this manner for self-protection. Sánchez-Román (2008) reported that two moderately halophilic aerobic bacteria, Halomonas meridiana and Virgibacillus marismortui, can produce a large number of aggregates of nanometer scale to form granular textures (nanoglobule structures); most of these aggregates have diameters of 50 nm to 100 nm, and a few have diameters of 100 nm to 200 nm. Therefore, the morphology, size, and distribution determined in this study and the primary dolomite precipitation revealed by culture experiments in previous studies may indicate the bacteria involved in the formation of stromatolitic dolomites. Some of these dolomites are primary dolomites and others are microbially mediated dolomites.

## 6 Conclusions

The Cambrian stromatolites in the dark laminae studied in this work are characterized by uniquely preserved attributes: (1) dolomites with 50–100 nm spherical nanostructures are aggregated into minerals of larger sphericities; (2) nanospherical dolomites of 50–170 nm diameter are densely arranged as dumbbell-shaped or chained aggregates; (3) silicified filaments, as well as dumbbell-shaped and chain arrangements, are preserved as important microstructures. The sedimentological, petrological, and geochemical data indicate that organic functional groups bond to ions, thereby ensuring high Mg: Ca ratios; organic substrates favor dolomite precipitation given changes in pH, redox potential, elemental ratio, and alkalinity and saturation indices.

Silicification is a unique preservation mechanism for filaments, as well as spherical and biofilm microstructures.

The results provide evidence for the origin of the dolomites found in the stromatolites of the Tarim Basin, and elucidate the formation of ancient microbial dolomites.

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