Characterization of the Microbial Dolomite of the Upper Sinian Dengying Formation in the Hanyuan Area of Sichuan Province, China

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Abstract: The algal dolostone of the Upper Sinian Dengying Formation (corresponding to the Ediacaran system) in the Upper Yangtze Platform of China possesses a rich diversity of microorganisms and is an ideal site for the study of ancient microbial dolomite. We focused on algal dolostone and its microbial dolomite in the Hanyuan area of Sichuan Province, China. The macroscopic petrological features, microscopic morphology, texture characteristics of the fossil microorganisms and microbial dolomite, and geochemical characteristics were investigated. We found rich fossil microorganisms and microbial dolomites in the laminated, stromatolithic, uniform and clotted (algal) dolostones. The microorganisms present were mainly body fossils of cyanobacteria (including Renalcis, Girvanella, Nanococcus, and Epiphyton) and their trace fossils (including microbial mats (biofilms), algal traces, and spots). In addition, there was evidence of sulfate-reducing bacteria (SRB), moderately halophilic aerobic bacteria, and red algae. The microbial dolomites presented cryptocrystalline textures under polarizing microscope and nanometer-sized granular (including spherulitic and pene-cubical granular) and (sub) micron-sized sheet-like, irregular, spherical and ovoidal morphologies under scanning electron microscope (SEM). The microbial dolomites were formed by microbiologically induced mineralization in the intertidal zone and lagoon environments during the depositional and syntgenic stages and microbially influenced mineralization in the supratidal zone environment during the penecontemporaneous stage. The microbial metabolic activities and extracellular polymeric substances (EPS) determined the morphology and element composition of microbial dolomite. During the depositional and syntgenic stages, the metabolic activities of cyanobacteria and SRB were active and EPS, biofilms and microbial mats were well-developed. EPS provided a large number of nucleation sites. Accordingly, many nanometer-sized pene-cubical granular and (sub) micron-sized sheet-like microbial dolomites were formed. During the penecontemporaneous stage, SBR, cyanobacteria, and moderately halophilic aerobic bacteria were inactive. Furthermore, nucleation sites reduced significantly and were derived from both the EPS of surviving microorganisms and un-hydrolyzed EPS from dead microorganisms. Consequently the microbial dolomites present nanometer-sized spherulitic and micron-sized irregular, spherical, and ovoidal morphologies. Overall, the microbial dolomites evolved from nanometer-sized granular (including spherulitic and pene-cubical granular) dolomites to (sub) micron-sized sheet-like, irregular, spherical and ovoidal dolomites, and then to macroscopic laminated, stromatolithic, uniform and clotted dolostones. These findings reveal the correlation between morphological evolution of microbial dolomite and microbial activities showing the complexity and diversity of mineral (dolomite)-microbe interactions, and providing new insight into microbial biomineralization and microbial dolomite in the Precambrian era.

Key words: microbial dolomite, microbial biomineralization, morphological evolution of dolomite, algal dolostone, Dengying Formation

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1 Introduction

Dolomite has been studied over 200 years, and its research history roughly consists of three phases: (1) the germination phase was from the late 18th Century to the end of the 19th Century (Burns et al., 2000), in which macroscopic and microscopic research and early physical and chemical experiments predominated (e.g. de Dolomieu, 1791; de Saussure, 1792); (2) the development phase included most of the 20th Century (Burns et al., 2000), and mainly focused on early investigations of the Dolomite Problem. The research included the proposal and perfection of the Dolomite problem (e.g. Van Tuyll, 1916; Fairbridge, 1957), which is the apparent paradox posed by the paucity of dolomite in modern marine depositional sediments versus its relative abundance in ancient sedimentary rock. This time period also included the discovery of primary dolomite in the modern environment (e.g. Alderman and Skinner, 1957; Illing et al., 1965), the proposal of dolomitization models (e.g. Sherman et al., 1947; Illing, 1959), and experiments on primary dolomite (e.g. Rosenberg and Holland, 1964; Land, 1998). (3) The bloom and transition phases were from the end of the 20th Century to now. During this phase, there has been further analysis and summary of earlier work on the Dolomite Problem (e.g. Land, 1991; Melim et al., 2004), and microbiology was formally introduced into the study of the Dolomite Problem (e.g. Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997). The formal introduction of microbiology provides new ideas and directions for dolomite research, and resulted in increased study of microbial dolomite, the focus of this work.

The research history of microbial dolomite can be also divided into four phases: (1) the germination phase was from the 1900s to the 1940s. A Former Soviet Union biologist precipitated a small amount of fine-granular dolomites under anaerobic conditions using sediment containing sulfate-reducing bacteria (SRB) from a salt lake (Nadson, 1903). However, the research failed to draw wide attention amidst the ongoing booming research of stromatolites. (2) The development phase was from the 1950s to the 1990s. During this phase, research focused on the discoveries of primary dolomite in modern environments, including Coorong lagoon (Alderman and Skinner, 1957), Persian Gulf (Illing et al., 1965), the coast of Oregon (Russell et al., 1967), submarine canyons of continental shelf (Deuser, 1970), deep Bering Sea (Hein et al., 1979), subtidal zone of hypersaline lagoon (Gunatilaka et al., 1984), and beach rock of the Xiaoachaidan salt lake (Xia Wenjie and Li Xiuhua, 1986). Meanwhile, researchers noticed the significant influences of algae, bacteria and organic matter during the dolomite formation process (e.g. Spotts and Silverman, 1966; Muir, 1974; Xia Wenjie and Li Xiuhua, 1986; Compton, 1988). (3) The bloom phase was from the 1990s to date. It began with the research carried out by Vasconcelos et al. (1995), who experimentally synthesized highly ordered, submicron-sized, and spherically ferroan dolomite using SRB from the Desulfovibrio group extracted from black sludge from the coastal lagoon in Lagoa Vermelha, Brazil under low-temperature and anaerobic conditions. Based on this, Vasconcelos and McKenzie (1997) proposed the generally accepted microbial dolomite model (e.g. Wright et al., 1999, 2005; Warthmann et al., 2000; Visscher et al., 2000; van Lith et al., 2003; Moore et al., 2004; Roberts et al., 2004; Yu Bingsong et al., 2007; Perri and Tucker, 2007; Sánchez-Román et al., 2008, 2009; Bontognali et al., 2008, 2010; McKenzie and Vasconcelos, 2009; García-Cura et al., 2014).

Currently, the microbial dolomite model includes the anaerobic model of SRB and methanogenic archaea (e.g. Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997) and an aerobic model of moderately halophilic aerobic bacteria (e.g. Sánchez-Román et al., 2008, 2009). Microbial dolomite shows particular and recognizable characteristics: (1) The microscopic morphologies of microbial dolomite include (solid, hollow, ovoidal, framboidal and nest-like) spherulites in nanometre and micrometre sizes; cauliflower-like, spindle-like and dumbbell-like shapes in micrometre size; rod-like, filamentous, sheet-like and irregular shapes in submicrometre and micrometre sizes; (2) The microscopic structures include biofilm-like, nanogranular, loose, fibrous, radial, clustered, sheet-like and irregular structures. (3) The geochemical characteristics include carbon ($\delta^{13}$C$_{PDB}$) and oxygen isotopes ($\delta^{18}$O$_{PDB}$) at widely varying levels related to the presence of microorganisms, especially $\delta^{13}$C$_{PDB}$, which shows both negative bias (deficit) and positive bias (enrichment). For example, the $\delta^{13}$C$_{PDB}$ of dolomite generated by the anaerobic oxidation of methane (AOM), SRB, and halophilic aerobic bacteria shows a greater negative bias, but the $\delta^{13}$C$_{PDB}$ of dolomite, generated by methanogenesis with methanogenic archaea, shows a positive bias.

Microbial dolomite research is in a phase of vigorous development. There have been many advances from microbial culture experiments and the additional analyses of microbial dolomite in geological history have been performed. However, there are many remaining questions. For example, determination of the origin and evolution of microbial dolomite in different regions requires correlation between the presence of microorganisms and the types of dolomite, or the process of microbial biomineralization. In
this context, we studied the algal dolostone of the Sinian Dengying Formation (that is, the Neoproterozoic Ediacaran) in the Hanyuan area of Sichuan Province, China. We used this example to describe the microbial biomineralization and morphological evolution of microbial dolomite. Our results contribute to understanding the mechanisms of formation for microbial dolomite.

2 Geological Background

The Sinian Dengying Formation (that is, the Neoproterozoic Ediacaran) in China is characterized by a set of very thick dolostone with complex origins (e.g. Lian Chengbo et al., 2016). It has been well studied due to its rich mineral resources including lead-zinc ore and natural gas (e.g. Xu Fanghao et al., 2016). The study area is located in the Hanyuan area at the southwestern boundary of the Sichuan Basin of Upper Yangtze platform, in Hanyuan County, Ya’an City, Sichuan Province, China (Fig. 1). It is an ideal study area with a large outcropping area of dolostone of the Dengying Formation. The dolostone is about 1 km thick in the study area without unified strata division. The Dengying Formation is divided into four sections from bottom to top in this paper. Typical algal dolostone formed as the marker bed of the Sections II and IV (the second and fourth sections of the Dengying Formation) indicating the depositional environment of a tidal flat-lagoon. The characteristics and origins of the dolostone of the Dengying Formation have been studied extensively, particularly the algal dolostone (e.g. Ye

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![Figure 1](image_url). The location, stratigraphy distribution and structure outline map of the study area.
Zhizheng et al., 1965; Zhang Yinben, 1966; Yang Wanrong et al., 1978; Cao Renguan, 1980; Tang Tianfu et al., 1980; Lei Huaiyan and Zhu Lianfang, 1992; Zhu Tongxing and Luo Anping, 1992; Fang Shaoxian et al., 2003; Yao Genshun et al., 2014; Lin Xiaoxian, 2014; Peng Hanlin et al., 2014). The description of “agal dolostone” is broadly defined, and this algal dolostone was formed by microbial activities of algae and bacteria and/or the dolomitization of microbial limestone. Therefore, this material could better be described as “microbial dolostone”. There has been little systematic study of primary microbial dolomite and our knowledge of the microbial activities related to algal dolostone remains limited. It is this lack of comprehensive information about microbial dolomite and the related processes that we sought to address with this work.

3 Samples and Methods

Samples of algal dolostone were collected from Sections II and IV in the study area, and were analyzed using methods of sedimentology and geochemistry to determine their fossil microorganisms and microbial dolomite. Morphology, structure, mineral content, and optics of fossil microorganisms and microbial dolomite were observed using a polarized light microscope (PLM) (Eclipse LV100POL, Nikon, Japan). Scanning electron microscope (SEM; Quanta250 FEG, FEI Co., US) equipped with an energy dispersive spectrometer (EDS; INCAx-max20, Oxford, UK) was used for characteristic observation of morphology, structure, minerals and crystals and component analysis of the minerals of fossil microorganisms and microbial dolomite. The trace element analysis of microbial dolomite was examined by inductively coupled plasma mass spectrometry (ICP-MS; ELAN DRC-e, Perkin Elmer, US). All analyses were carried out at the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, Chengdu, Sichuan, China.

4 Results

4.1 Macroscopic characteristics

Algal dolostone is the combination of multiple rock types, and can be classified into secondary dolostone types, though this classification remains controversial (e.g. Yang Wanrong et al., 1978; Tang Tianfu et al., 1980; Lei Huaiyan and Zhu Lianfang, 1992). According to macroscopic morphology, primary structure and microbial action, there are algal binding and algal intralastic type of algal dolostone (Lei Huaiyan and Zhu Lianfang, 1992). Using this division, the algal dolostone of the Dengying Formation in the study area can be subdivided into: (1) algal binding dolostone, including laminated (or laminite or biolaminite), stromatolithic (or stromatolite), clotted (or thrombolite), botryoidal (or lump), snowflake-like, oncolite and uniform (or leiolite or structureless) dolostones; and (2) algal intralastic dolostone including algal dolorudite, algal dolarenite, and algal dolositite. The algal dolostones are mainly laminated, stromatolithic, botryoidal and uniform dolostones, followed by clotted dolostone, snowflake-like dolostone, and algal dolarenite (the other forms are rare). The laminated dolostone contains clear, horizontal, bright and intermittent or continuous dark layers, and microbial mats and fenestral pores occur (Fig. 2a). The stromatolithic dolostone is mainly mounded (usually called an algal mound) and rarely columnar and show clear lamination, distinct, bright and dark layers, and highly developed microbial mats (Fig. 2b). The botryoidal dolostone is composed of botryoidal lumps and cements or fillings, in which the lumps contain cores and thick coatings with clear, curved, bright and dark layers (Fig. 2c). The uniform dolostone is structureless dolomite with dark color (e.g. dark grey) due to the presence of organic matters (Fig. 2d), and commonly intergrows with laminated, stromatolithic and clotted dolostones. In addition, most algal dolostone was seen in Section II followed by Section IV, and is the product of high-stand system tracts (HST). Each type of algal dolostone exhibits certain spatial developmental rules. For example, stromatolithic, clotted, uniform and algal pellet dolostones and algal dolarenite were found in the lower position of profile, while laminated and botryoidal dolostones were found in the middle position, and snowflake-like dolostone was seen in the upper position.

4.2 Microscopic characteristics

4.2.1 Fossil microorganisms

The fossil microorganisms of the Dengying Formation are mainly in stromatolithic (Fig. 3a–b), laminated (Fig. 3c), uniform (Fig. 3d–e) and clotted (Fig. 3f) dolostones, followed by botryoidal and snowflake-like dolostones and algal dolarenite in the study area, evidenced in the forms of trace fossils and body fossils (Figs. 3–4).

The microbial trace fossils were present as microbial mats (or biofilms), algal traces, and algal spots. Microbial mats mainly develop in stromatolithic dolostone (Fig. 3a), followed by laminated dolostone (Fig. 3c). In other types of algal dolostone (Fig. 4a–c), microbial mats are less developed or are seen as early biofilms. Microorganisms and dolomite are wrapped by microbial mats (biofilms) that sheeted and mat-like clay minerals (Figs. 3a, 3c, 4a and 4c). Meanwhile, framboidal and sub-cylindrical pyrites are usually present with the microbial mats and
dolomite (Fig. 4b), suggesting the existence of SRB. These results are similar to reports from Teske et al. (1998), McKenzie and Vasconcelos (2009), and Bontognali et al. (2010). The algal traces and algal spots mostly existed in laminated and uniform dolostones (Fig. 3c–e), and are mainly composed of cryptocrystalline dolomite and organic matter with dark color. Moreover, algal spots frequently appear as brown and dark pellets, near which algal traces develop commonly. Many algal spots can form algal aggregates or generate local lamina by directional array.

The microbial body fossils are mainly bacteria and algae. The bacteria (Fig. 3b and Fig. 4c–f) are typically single cells and filaments, and are smaller than 200 μm (mostly in the size range of 1–20 μm). The surface of bacteria is rich in Si and Mg elements, likely cell wall or extracellular polymeric substance (EPS) and the interior is dolomite. The single cells of bacteria were generally (solid and hollow) spherical, ovoidal, nodular, reniform, and dendritic, while the filaments were mainly solid. The bacteria were mainly *Renalcis*, *Girvanella*, *Nanococcus* and *Epiphyton* of *Chroococcophyceae* and *Hormogonophyceae* of *Cyanobacteria* or *Cyanophyta*, important producers of EPS (De Philippis et al., 1998). Most algae present were red algae, with a small amount of green algae. The red algae (Fig. 3d) were mostly nodular, ovoidal and spherical shapes, and most were larger than 200μm, with a filamentous algal community at millimetre scale. The cell walls of red algae showed cryptocrystalline texture, while the dolomite crystals in the cells were larger sizes, possibly tissue structures such as sporangium and conceptacle.

In addition to these bacteria and algae, we also identified moderately halophilic aerobic bacteria based on special dolomite textures such as spherical dolomite with radial internal patterns (Fig. 5c) that are characteristic of microbial action. This finding is similar to the report of Sánchez-Román et al. (2009). Additionally, there were a small amount of small shelly fossils, whose formation is thought to be earlier than the commonly accepted origination time (early Cambrian).

4.2.2 Microbial dolomite

The microscopic characteristics of microbial dolomite
include microscopic morphology and microscopic structural characteristics.

Using the PLM, the microbial dolomites of the Dengying Formation present cryptocrystalline textures with dark color and are rich in organic matters, but their characteristics were not obvious and did not allow identification.

By SEM, the microbial dolomites mainly present as sheet-like, irregular, spherical, ovoidal and nanometer-sized granular morphologies, with obvious characteristics that
Fig. 4. The characteristics of microorganisms in the algal dolostone of the Dengying Formation based on SEM analysis.

(a), The dolomite with nanometre-sized (pene-cubical) granular texture (EDS, marked with red cross) was wrapped by the microbial mats (or biofilms or EPS) (blue arrow) (SEM) in Section IV; (b), The microbial mats (or biofilms or EPS) (yellow arrow) are symbiotic with sub-cylindrical pyrite (EDS, red cross) (SEM) in Section IV; (c), The solid spherical fossil cyanobacteria (Nanococcus) showed enrichment of Si and Mg elements on their surfaces (EDS, red cross), likely cell walls or EPS (blue arrow) (SEM) in Section IV; microbial mats (yellow arrow) were also evident; (d), There are clay minerals or micritizations (EDS, red cross) on the surfaces of hollow spherical fossil cyanobacteria (SEM) in Section II; (e), The dendritic fossil cyanobacteria (Epiphyton) (yellow arrow) were completely dolomitized (EDS, red cross), revealing the internal substances of cells and are symbiotic with sheet-like (red arrow) and irregular (blue arrow) dolomites (SEM) in Section IV; (f), The filamentous fossil cyanobacteria (blue arrow) in the bright layers of the coatings of botryoidal dolostone may be Girvanella (SEM) in Section II.
enable their identification. The sheet-like microbial dolomites (Fig. 4c and Fig. 5a–b) were widely developed and compact, but still showed some internal micro pores. In their fracture section, the sheet-like microbial dolomites lamellately accumulate with a clean surface and without clay mineral development, similar to the lamellation of shale. The irregular microbial dolomites (Figs. 4e and 5b) were intergrown with sheet-like microbial dolomites or alone, with surfaces rich in Si and Mg elements due to the influence of clay minerals. The sheet-like and irregular microbial dolomites are similar to those identified by Perri and Tucker (2007) and Wang Xiaolin et al. (2010). The spherical and ovoidal microbial dolomites (Fig. 5c–f) present similar morphologies with surfaces rich in Si and Mg elements and particle sizes in the 1–20 μm range, with most in the 1–3 μm range. The smaller microbial dolomites (Fig. 5d–f) were either solitary or fasciately, while the larger ones (Fig. 5c) were solitary with internal radial structures and surrounding intergrown clay minerals. Nanometre-sized granular microbial dolomite commonly develop around microbial mats (biofilms) in the form of pene-cubical granular (Fig. 4a) or on the surfaces of irregular, spherical, and ovoidal microbial dolomites as spherical granules (Fig. 5b, 5c–f). These characteristics of spherical, ovoidal and nanometre-sized granular microbial dolomites are similar to those reported by Vasconcelos and McKenzie (1997), Aloisi et al. (2006), Sánchez-Román et al. (2008, 2009), Bontognali et al. (2008, 2010) and McKenzie and Vasconcelos (2009).

As mentioned above, the microbial dolomites mainly exhibited microscopic structures (Figs. 4a, 4c and 5) such as mat or biofilm structure, sheet-like structure, irregular structure, nanometre-sized granular structure, radial structure within spherical dolomite, or cluster structure formed by several spherical and ovoidal dolomites together.

The formation of these morphologies and structures of microbial dolomites is closely related to the development of microbial mat (biofilm) and the organomineralization of EPS. In particular, the nanometre-sized granular dolomite likely represents microbial dolomite in the early nucleation stage, and its presence serves as an important indicator of microbial dolomite.

4.3 Geochemical characteristics
4.3.1 Characteristics of major elements
SEM and EDS analyses were performed on the sheet-like, irregular, spherical and ovoidal microbial dolomites of the Dengying Formation in the study area. The Mg/Ca ratio of the dolomites ranged from 0.76 to 1.53 (1.11 on average) (Table 1), which is very close to the Mg/Ca ratio (1.00) of ideal primary dolomites and characteristic of primary precipitation. However, some Mg contents of samples are higher with Mg/Ca ratios as high as 5.00, which is related to the enrichment effect of microbial EPS on cations such as Mg and Si (Bontognali et al., 2010).

4.3.2 Characteristics of trace elements
Trace element ratio analyses (Table 2) of algal dolostone of the Dengying Formation showed that the Sr/Ba ratios were mainly in the range of 6.66–17.76 (12.32 on average), the U/Th ratios were 12.09–38.83 (31.40 on average), and the Ce/La ratios were 1.64–2.79 (1.96 on average). Based on the paleo-salinity and paleo-oxygenation facies criteria of sedimentary environment analyses (Table 2), these results indicate that the algal dolostone mainly formed in a dysoxic-anoxic marine environment, which is consistent with the geological background of tidal flats and lagoon facies in the Dengying Formation, and is an environment suitable for the growth of microorganisms.

4.3.3 Characteristics of δ¹³C_PDB and δ¹⁸O_PDB
We collected and analyzed the δ¹³C_PDB and δ¹⁸O_PDB of algal dolostone of the Dengying Formation in the study and adjacent areas (Table 3) and found that the δ¹³C_PDB content was mainly in the range of −0.33 to 2.35‰ (0.84% on average) and the δ¹⁸O_PDB content −8.09 to −3.31‰ (6.46‰ on average), consistent with the results obtained by Veizer and Hoefs (1976), Huang Zhicheng et al. (1999) and Luo Beiwei et al. (2013). These data

Table 1 The levels of Mg and Ca atoms in microbial dolomite of the Dengying Formation of the study area.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Position</th>
<th>Descriptions of samples</th>
<th>Mg (%)</th>
<th>Ca (%)</th>
<th>Mg/Ca</th>
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<td>Y001-02</td>
<td>Section IV</td>
<td>Irregular dolomite</td>
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<td>Y002-02</td>
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<td>Sheet-like and irregular dolomites</td>
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<td>1.09</td>
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<td></td>
<td></td>
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<td>1.53</td>
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<td>Dolomite wrapped by microbial mat</td>
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<td>Y009-04</td>
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<td></td>
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<td>Nanometer-sized dolomite</td>
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<td>3.48</td>
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<td></td>
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<td>7.51</td>
<td>5.30</td>
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<td></td>
<td></td>
<td>9.61</td>
<td>7.54</td>
<td>1.27</td>
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Average values of Section II and IV

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<tr>
<td>Y002-02</td>
<td>1.09</td>
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<td>Y004-02</td>
<td>0.91</td>
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<td>Average values</td>
<td>1.12</td>
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Fig. 5. The characteristics of microbial dolomite in the algal dolostone of the Dengying Formation based on SEM analysis.
(a), The sheet-like dolomite (yellow arrow) (EDS, red cross) (SEM) in Section II; (b), The irregular dolomites (blue arrow) (EDS, red cross) were present with sheet-like dolomite (yellow arrow) with nanometre-sized granular dolomites (red arrow) on the surfaces of irregular dolomites (SEM) in Section IV; (c), The inner of micron-sized spherical dolomite (yellow arrow) is radial, similar to the study of Sánchez-Román et al. (2009) and is associated with the effect of moderately halophilic aerobic bacteria, and the surrounding is clay mineral (blue arrow) (SEM) in Section IV; (d), Three micron-sized spherical dolomites (yellow arrow) (EDS, red cross) are symbiotic and showed surface enrichment of Si and Mg elements (SEM) in Section IV; (e and f), There was evident enrichment of Si and Mg elements (EDS, red cross) and nanometre-sized spherical dolomites on the surface of micron-sized ovoidal dolomite (SEM) in Section IV.
Table 2 Trace elements characteristics of algal dolostone of the Dengying Formation

<table>
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<tr>
<th>Samples</th>
<th>Position</th>
<th>Descriptions of samples</th>
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<th>Ba</th>
<th>Sr/Ba</th>
<th>U</th>
<th>Th</th>
<th>U/Th</th>
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<td>Section IV</td>
<td>Uniform dolostone</td>
<td>35.65</td>
<td>2.46</td>
<td>14.49</td>
<td>0.27</td>
<td>0.02</td>
<td>12.09</td>
<td>0.34</td>
<td>0.20</td>
<td>1.66</td>
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<td>Section IV</td>
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<td>0.35</td>
<td>0.02</td>
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<td>Laminated dolostone</td>
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<tr>
<td>Y013-01</td>
<td>Section II</td>
<td>Uniform dolostone</td>
<td>44.27</td>
<td>6.64</td>
<td>6.64</td>
<td>1.06</td>
<td>0.02</td>
<td>66.31</td>
<td>0.32</td>
<td>0.17</td>
<td>1.88</td>
</tr>
<tr>
<td>Y014-03</td>
<td>Section II</td>
<td>Laminated dolostone</td>
<td>46.25</td>
<td>4.11</td>
<td>11.26</td>
<td>0.43</td>
<td>0.03</td>
<td>16.62</td>
<td>0.19</td>
<td>0.12</td>
<td>1.64</td>
</tr>
<tr>
<td>Y028-03</td>
<td>Section II</td>
<td>Laminated dolostone</td>
<td>46.14</td>
<td>2.98</td>
<td>15.48</td>
<td>1.56</td>
<td>0.04</td>
<td>38.00</td>
<td>1.76</td>
<td>0.63</td>
<td>2.79</td>
</tr>
</tbody>
</table>

Average values of Section II and IV

|                  |          |                     | 43.35 | 3.99 | 12.32 | 0.77  | 0.03  | 31.40  | 0.60 | 0.29 | 1.90  |

Paleo-salinity and paleo-oxygenation facies criteria (Jones and Manning, 1994; Sun et al., 1997)

- Fresh water environment: Sr/Ba<0.6; brackish water environment: 0.6<Sr/Ba<1; saline water environment: Sr/Ba>1
- Anaerobic and semi-anaerobic environments: U/Th>1.25; dysoaerobic environment: 0.75≤U/Th≤1.25; aerobic environment: U/Th<0.75
- Anaerobic and semi-anaerobic environments: Ce/La>2.0; dysoaerobic environment: 1.5≤Ce/La≤1.8; aerobic environment: Ce/La<1.5

Note: the unit of element is µg/g.

5.1 Microbial activity and microbial dolomite

The microbial activities related to microbialites and microbial carbonates (Chen Jitao and Lee Jeong-Hyun, 2014) include physical biostabilization, baffling, trapping and binding (e.g. Noffke et al., 2001), and chemical biomineralization and organomineralization (e.g. Trichet and Défarge, 1995; Schlager, 2003). In the traditional view, the term “microbial biomineralization” was used to describe biologically controlled and biologically induced mineralizations (e.g. Heim, 2011). However, recent studies have identified organomineralization (Dupraz et al., 2004) or biologically influenced mineralization (Dupraz et al., 2009) or microbially influenced mineralization (Bontognali et al., 2014) as a third potential process of mineralization, and likely all three pathways can contribute. Based on our analysis of the macroscopic, microscopic and geochemical characteristics of algal dolostone, we conclude that the microbial dolomite was formed by microbially induced and microbially influenced mineralizations during the depositional, syngenetic, and pencontemporaneous stages.

5.1.1 Microbially induced mineralization

Microbially induced mineralization occurs mostly during the depositional and syngenetic stages followed by the pencontemporaneous stage, which is associated with active microbial metabolic activity in the intertidal zone.

Table 3 The carbon and oxygen stable isotopes characteristics of algal dolostone of the Dengying Formation

<table>
<thead>
<tr>
<th>Position</th>
<th>Descriptions of samples</th>
<th>δ¹³C_Cratio (‰)</th>
<th>δ¹⁸O_Cratio (‰)</th>
<th>Z value of paleo-salinity</th>
<th>Z value of paleo-temperature (°C)</th>
<th>Data sources</th>
<th>Study area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section IV *</td>
<td>Laminated dolostone</td>
<td>0.77</td>
<td>-7.71</td>
<td>125.04</td>
<td>56.64</td>
<td>Wang Shifeng and Xiang Fang, 1999</td>
<td>Ziyang, Sichuan Province</td>
</tr>
<tr>
<td>Section II *</td>
<td>Algal dolominitite</td>
<td>-0.33</td>
<td>-8.09</td>
<td>122.60</td>
<td>58.87</td>
<td>Huang Zhicheng et al., 1999</td>
<td>Emei Mountain, Sichuan Province</td>
</tr>
<tr>
<td>Section II *</td>
<td>Algal dolostone</td>
<td>1.66</td>
<td>-3.31</td>
<td>129.05</td>
<td>32.49</td>
<td>Xue Weizhi et al., 2013</td>
<td>Sichuan Province</td>
</tr>
<tr>
<td>Section II *</td>
<td>Algal dolostone</td>
<td>2.35</td>
<td>-4.74</td>
<td>129.75</td>
<td>39.91</td>
<td>Lei Huaiyan and Zhu Lianfeng, 1992</td>
<td>Sichuan Basin</td>
</tr>
<tr>
<td>Section II *</td>
<td>Algal dolostone</td>
<td>0.32</td>
<td>-6.93</td>
<td>124.51</td>
<td>51.94</td>
<td>Xiang Fang et al., 1998</td>
<td>Ziyang, Sichuan Province</td>
</tr>
<tr>
<td>Average values of Section II and IV</td>
<td>0.84</td>
<td>-6.46</td>
<td>125.80</td>
<td>49.36</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: the * symbol indicates that the information is inferred from the original paper; the formulae of Z value and T value: Z=2.048x(δ¹³C_Cratio+50)+0.498x(δ¹⁸O_Cratio+50), T=16.9-5.78x(δ¹³C_Cratio+0.1xδ¹⁸O_Cratio).
and lagoon environments. These microorganisms are mainly cyanobacteria and SRB (Figs. 3b, 4c, 4d, 4e and 4f) and provide a large number of nucleation sites and beneficial microenvironments for the formation of microbial dolomite. In addition to the well developed primary nanometer-sized granular microbial dolomites (Fig. 4a and Fig. 5b, 5e–f), abundant sheet-like microbial dolomites are formed by nanometer-sized pene-cubical granular microbial dolomites (Fig. 4e; Fig. 5a–b). The intergrown and/or accompanying minerals with these nanometer-sized granular and sheet-like microbial dolomites are mainly pyrites (Fig. 4b) and fibrous dolomites (or precursors of high-Mg calcite and aragonite) (Fig. 6a and 6c), while the intergrown and/or accompanying structures include microbially induced sedimentary structure (MISS) associated with microbial mats (Fig. 3a).

5.1.2 Microbially influenced mineralization

Microbially influenced mineralization describes passive microbial action and mostly occurs during the penecontemporaneous stage in the (shallow burial) supralittoral zone environment, where microbial metabolic activity declines and microorganisms die on a large scale. These microorganisms include predominantly SRB followed by cyanobacteria and moderately halophilic aerobic bacteria (Fig. 5c). These microbes can provide some nucleation sites and relatively beneficial microenvironments for the formation of microbial dolomite. However, the nucleation sites are reduced significantly and are provided by EPS of surviving cyanobacteria and un-hydrolyzed EPS from dead cyanobacteria. The alveolar texture of EPS allows Mg and Si ions to be adsorbed, followed by Ca ion (Bontognali et al., 2010), which overcomes the dynamic obstacle of

Fig. 6. The mineral, texture and structure seen in samples of microbial dolomite of the Dengying Formation.
(a) The cores of dolomitized botryoidal lumps are crypto-cristalline precursors of high-Mg calcite and are rich of organic matters, while the coatings are precursors of isopachous fibrous aragonites and show obvious undulous extinction (XPL) in Section II; (b) The bird's eye pores (blue arrow) were partly filled with organic matter and developed in uniform dolostone (PPL) in Section IV; there are also algal traces (red arrow); (c) The fibrous dolomites developed in the bright layers of coatings of botryoidal lumps, whose precursors are aragonites, and the brachyaxes of their fibrous pseudomorphs were in the range of 1–8 μm (SEM) in Section II, and there were clear growth lines of crystals (blue arrow) as well as intercrystal and intracrystal micro pores (red arrow); (d) The granular gypsum (blue arrow) (EDS, red cross) is symbiotic with the microbial mat (red arrow) (SEM) in Section IV.
dolomite formation and explains the enrichment of Mg and Si elements in the EDS analysis of microbial dolomite (Fig. 5b, 5d–f). This triggers the formation of nanometre-sized granular microbial dolomite that can aggregate into micron-sized irregular, spherical and ovoidal microbial dolomites. The microenvironment of microbial dolomite formation is affected by microbial action and strong evaporation in the penecontemporaneous stage, which is indicated by the intergrown and/or accompanying granular, flake and acicular gypsums (Fig. 6d) and bird’s eye structures (Fig. 6b) with microbial dolomite. In addition, fibrous dolomite and MISS continue to develop and fossil microorganisms begin to form frequently (Fig. 3b, 3d; Fig. 4c–f).

5.1.3 Microbially catalyzed mineralization

As mentioned above, secondary fibrous dolomites closely intergrow and/or accompany primary microbial dolomites, which implies a close genetic relationship between fibrous dolomites and microbial dolomites. To interpret this phenomenon, we propose the term “microbially catalyzed mineralization”.

To describe the genesis of the obvious pseudomorphs of high-Mg calcite and aragonite precursors in fibrous dolomites, we use “mimetic dolomitization”. Mimetic dolomitization was first proposed in comparative research of Cenozoic and Paleozoic dolomite textures (Sibley, 1991) that included research into the means of classification for dolomite texture and dolomitization (e.g. Sibley, 1982; Kald and Gidman, 1982; Bullen and Sibley, 1984; Sibley and Gregg, 1987). At present, this term has been accepted by many researchers (e.g. Zempolich and Baker, 1993; Corsetti et al., 2006; Hood and Wallace, 2012; Kaczmarek and Sibley, 2014). Here, we redefine mimetic dolomitization as dolomitization rapidly occurring during or slightly after the time of aragonite and/or high-Mg calcite precipitation and preserving their fine original textures in the (lagoon and tidal flat) environments with high Mg/Ca ratio water, flourishing microbial mats, relatively high temperature and highstand systems tracts during the syngenetic and penecontemporaneous stages. In the study area, the botryoidal dolostone and fossil microorganisms of the Dengying Formation result from mimetic dolomitization. The precipitates of botryoidal dolostone are mainly isopachous fibrous and messy acicular aragonites and fibrous and cryptocrystalline high-Mg calcites (Fig. 6a and 6c), and the precipitates of fossil microorganisms are mainly cryptocrystalline high-Mg calcites (Fig. 3b, 3d; Fig. 4c–f). During mimetic dolomitization, the EPS of alive and recently dead microorganisms can sustainably absorb and aggregate Mg ion and even release Mg ion after hydrolysis and decarboxylation (Dupraz et al., 2004) to promote and maintain a Mg-rich microenvironment. This environment facilitates the entry of Mg ion into the crystal lattices of aragonite and high-Mg calcite where it can catalyze or stimulate aragonite and high-Mg calcite to rapidly transform into dolomites. Here, we call this microbial action microbially catalyzed mineralization, but this term will need to be confirmed by additional studies.

5.2 Morphological evolution of microbial dolomite

As described above, different morphologies of microbial dolomites are formed by different activity status, action modes, and action phases of microorganisms (Fig. 7). Microbial metabolic activity controls the macroscopic morphology of microbial dolostone. For example, flourishing microbial activity promotes the formation of stromatolite and laminate (or biolaminites) with laminated structures, while inactive microbial activity generally results in structureless leiolite. The formation of microbial dolomite is closely related to microbial EPS. EPS is an alveolar organic network, in which the organic macromolecule or functional group can act as an acidic organic template (Bontognali et al., 2010). The acidic organic template can determine structure, balance charge (or adsorbing cations) and influence the elemental composition of precipitate as well as provide nucleation.

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Fig. 7. The morphological evolution of microbial dolomite of the Dengying Formation.
sites for dolomite formation.

During the depositional and syngentic stages, there is active microbial metabolic activity and abundant EPS, biofilms, and microbial mats. The microenvironment is reductive and the EPS allows a large number of nucleation sites. In this context, abundant nanometer-sized pene-cubical granular microbial dolomites are formed mainly by microbially induced mineralization (Fig. 4a) and can further compose (sub) micron-sized, sheet-like microbial dolomites (Fig. 4a, 4c; Fig. 5a–b).

During the penecontemporaneous stage, sea level and microbial metabolic activity decrease, while microbially influenced and microbially induced mineralizations can occur in the near-surface environment of the supratidal zone. In the phreatic zone or pores of this environment, some original seawater remains, and microenvironments are controlled by both microbial mediation and strong evaporation. Moreover, there are a reduced number of nucleation sites due to the death of microorganisms. The smaller number of sites are provided by EPS of the smaller amount of surviving microorganisms and by un-hydrolyzed EPS from dead microorganisms. Therefore, there are fewer microbial dolomites formed in this stage and these dolomites are distributed sporadically. Nevertheless, owing to the relatively stable microenvironment, they often are of relatively larger volume as well as nanometer-sized spherulitic and micron-sized irregular, spherical and ovoidal morphologies (Fig. 5b, 5e and 5f).

Finally, sheet-like, irregular, spherical and ovoidal microbial dolomites and dolomites of different genesis (e.g. microbially catalyzed mineralization) compose laminated, stromatolithic, uniform and cotted microbial dolostones.

6 Conclusions

(1) The algal dolostone of the Dengying Formation was determined to be microbial dolostone composed of primary microbial dolomite and secondary mimetic dolomite in the study area. It can be subdivided as laminated, stromatolithic, botryoidal, uniform, cotted and snowflake-like dolostone as well as algal dolarenite. The first four algal dolostones are rich in microbial dolomites and associated fossil microorganisms, and can be distinguished based on their morphological and geochemical characteristics.

(2) The fossil microorganisms of the Dengying Formation are mainly body fossils and trace fossils. The body fossils are mainly cyanobacteria (include Renalcis, Girvanella, Nanococcus and Epiphyton) and red algae and the trace fossils are mainly microbial mats (biofilms), algal traces, and spots. SRB and moderately halophilic aerobic bacteria were also present, but their body fossils are rarely preserved. Instead, they are recognized through their intergrown and/or accompanying minerals, textures and structures.

(3) The microbial dolomites of the Dengying Formation show cryptocrystalline textures in PLM as well as nanometer-sized (spherulitic and pene-cubical) granular and (sub) micron-sized sheet-like, irregular, spherical and ovoidal morphologies or textures in SEM. Microbial mat and biofilm structures are also present.

(4) The microbial dolomites of the Dengying Formation are mainly formed by microbially induced and microbially influenced mineralizations during the depositional, syngentic, and penecontemporaneous stages. The microbially induced mineralization mostly occurs in intertidal zone and lagoon environments during the depositional and syngentic stages, and this activity is related to active cyanobacteria and SRB and forms microbial dolomites with nanometer-sized pene-cubical granular and (sub) micron-sized sheet-like morphologies. The microbially influenced mineralization mostly occurs in the (shallow burial) supratidal zone environment during the penecontemporaneous stage, which is related to inactive SRB, cyanobacteria, and moderately halophilic aerobic bacteria and forms microbial dolomites with nanometer-sized spherulitic granular and micron-sized irregular, spherical and ovoidal morphologies. Additionally, the microbial activity of fibrous mimetic dolomite is defined as microbially catalyzed mineralization.

(5) The morphologies of microbial dolomites depend on activity status, action modes, and action phases of microorganisms, which are closely related to EPS. In the depositional and syngentic stages, microorganisms are active, and EPS, biofilms, and microbial mats are well developed. EPS provides many nucleation sites. At the same time, abundant nanometer-sized pene-cubical granular microbial dolomites can form and then further compose (sub) micron-sized sheet-like microbial dolomites. In the penecontemporaneous stage, microorganisms are no longer active, but nucleation sites are still provided by EPS of surviving microorganisms as well as un-hydrolyzed EPS from dead microorganisms. In this stage, the formed microbial dolomites have relatively larger volume and are mainly micron-sized, irregular, spherical and ovoidal microbial dolomites composed by nanometer-sized spherulitic ones. Finally, these microbial dolomites and mimetic dolomite compose laminated, stromatolithic, uniform and cotted microbial dolostones.

(6) Understanding the relationship of microbial biominereralization and microbial dolomite is key to elucidation of the formation process and mechanisms of microbial dolomite. Additional comprehensive work with
this focus will be needed to analyze dolomite in other locations.

Acknowledgments

This paper was supported by the open fund of Key Laboratory of Sedimentary Basin and Oil and Gas Resources, Ministry of Land and Resources (China) (NO. zdysys2015002). Thanks are given to the referees for the valuable suggestions; the support of editor, periodical office, and publisher to this study; State Key Laboratory of Oil and Gas Reservoir and Exploitation (China) for the test and analysis provided; the Regional Geological Survey Team of the Sichuan Geology and Mineral Bureau (China) for the field working security provided; all people providing assistance for this paper.

Manuscript received June 28, 2015 accepted Apr. 5, 2016 edited by Fei Hongcai

References


Huang Zhicheng, Chen Zhina, Yang Shouye and Liu Yan, 1999. Primary δ13C and δ18O values in marine carbonates and the sea water temperature of Dengyingxia Age in South China.


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