Sedimentary Fabrics for Thrombolite Bioherm in Cambrian Zhangxia Formation in the Western Part of Shandong Province

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\textit{Abstract.} Thrombolite is a non-laminated fabric of microbial carbonate, which is in sharp contrast with stromatolite that is characterized by the laminated fabric. Thrombolite bioherm developed in Cambrian Zhangxia Formation in the Western part of Shandong Province mainly consists of clots that are composed of dense micrite and microspar. Both the remain of calcified extracellular polymers (EPS) and calcified cyanobacteria fossils are observed within the clot that makes up thrombolite. Within the complex microscopic fabrics, it can be observed that the remain of calcified EPS are marked by the spherical structure, the sheet structure, the mat structure, and the honeycomb-like structure, which further indicate that the formation of clots within thrombolite should belong to a complex organic mineralization process. Together with both the dense micrite and the calcified cyanobacteria fossil, the calcified EPS provides an important clue for understanding the enigmatic formation mechanism of thrombolites. Therefore, this study can provide an important clue and thinking approach for further research in the future.

\textit{Key words:} Calcification; Thrombolite; Zhangxia Formation; the western part of Shandong Province.

1. Introduction

Microbialites were first proposed by Burne and Moore (1987), which are organosedimentary deposits formed by benthic microbial community trapping and binding sediment particles and/or microbial mineralization \cite{1}. At present, it mainly researches the microbial carbonates, which can be divided into stromatolite, thrombolite, dendrolite, leiolite, oncoid according to their macroscopic features \cite{2, 3}. As one of the microbial carbonates, thrombolite was first put forward by Aitken (1967), which refers to the cryptophytic fabric related to stromatolites, lacking of laminae, and the macroscopic clot fabric is different from other microbial carbonates with microscopic clot fabric \cite{4}. There is still some confusion for the definition of thrombolite \cite{5, 6}. Thrombolites have been existing from Neoproterozoic \cite{7} to present \cite{8}. With the extensive development of metazoan during Cambrian, a large number of microbial
carbonates with non-laminar fabric appeared, and microbial carbonates gradually increased, which formed the first episode of cyanobacteria calcification event in early Phanerozoic [2, 9, 10]. It made thrombolites wide in Cambrian-Ordovician [11]. The Neoproterozoic thrombolites are interpreted as the products of strong dolomitization of stromatolites [2, 12]. The abundant thrombolites appeared near the basement of Cambrian, which indicates that they may be representative of burrow stromatolites, and also reflects the production of abundant calcified microorganisms, especially Epiphyton, Angusticellaria, and Renalis [13]. It is believed that these calcified microorganisms and micrite are the main reasons for the formation of thrombolites [2]. The clot structure may be a spheroid formed by calcification of coccus glial sheath, which converges with each other to form different macroscopic structure [14].

The Cambrian in the western part of Shandong Province is a set of mixed sedimentary strata consisted of carbonate and clastic rock, which widely developed microbial carbonates, and provides good conditions for the study of microbial carbonates. Zhangxia formation, which belongs to the Miaolingian, Cambrian [15], produces a large number of thrombolite bioherms. The purpose of this research is to reveal the signal of microbial action and activity in the complex formation process of thrombolite by observing the macro and microfeature of thrombolites in Zhangxia formation of Middle Cambrian in western Shandong, in order to provide some important clues and thinking ways for further research in the future.

2. Cambrian Zhangxia Formation
The Miaolingian Zhangxia Formation includes the bottom of Guzhang stage, Gushan stage and the top of the fifth stage (Fig. 1). The lithology of Cambrian Zhangxia formation in the western part of Shandong Province varies considerably. It mainly develops thrombolites, oolitic limestone, micritic limestone, shale and bioclastic limestone, etc., but it generally develops a set of carbonate platform sediments dominated by oolitic shoal [16], which is obviously different from the overlying Gushan formation and the underlying Mantou formation. Some Cambrian strata have been measured (Fig. 1), including the strata of Jiulongshan, Jining, Jiaxiang and Cangshan, Linyi. A large of microbial carbonates developed in the Cambrian, and thrombolites mainly developed in Zhangxia formation, which is the main stratum for studying thrombolites. The Zhangxia formation in Jiulongshan and Laiwu developed 11 layers of thrombolites, which mainly appeared in the upper the lower limestone, with the total thickness of 48.5 m. The Zhangxia formation in Jiaxiang and Jining mainly developed oolitic limestone, thrombolites and bioclastic limestone. And it exposed 7 layers of thrombolites, with a total thickness of 33.6 m. The thickness of every layer is usually 4-10 m, which the thinner is 0.2 m, and the thicker is 18.4 m. There are 5 layers of thrombolites exposed in Zhangxia formation of the Cangshan section, Linyi, with a total thickness of 11.8 m, which mainly exposed in the upper limestone section and lower limestone section (Fig. 1). The thickness of every layer is generally 0.1-4 m. Compared with thrombolites in different sections, it is found that the Cambrian thrombolites in western Shandong are mostly embedded in different surrounding rocks in the form of domes, which conforms to the definition of bioherm [17].
3. Macroscopic Feature of Thrombolite Bioherms

According to the macroscopic feature of microbialites, they can be divided into four types: megastructure (Biostrome and bioherm), macrostructure (tens of centimeters to several meters, such as clot, laminar and dendritic) and microstructure (microscopic microstructure, such as peloids and filamentous microbes in spar) [5]. The thickness of the Cambrian thrombolite in study area (Fig. 2A) ranges from tens of centimeters to several meters. Macroscopically, the internal fabric of thrombolite is composed of non-layer clot formed by dense micrite, which the size of the clot is usually 1~2.5 cm, with the feature of mesostructure (Fig. 2B). Most of the clots are irregular and evenly distributed, including round and oval clots. Those with unclear boundaries between the clots are often distributed in the form of network. Clots account for about 60%-80% of the rock volume in the thrombolite bioherm. Between the clots is filled with micrites, few micr spar, and argillaceous clots. In some of the thrombolites, there are some bioclasts (trilobites, gastropods) bound by dense micrite (Fig. 2C).
4. Microscopic Feature of Thrombolite Bioherms

The observed clots in the thrombolites are mainly composed of binding micrites by polarizing microscope and scanning electron microscope. And cyanobacterial calcified products are also observed, which mainly include Epiphyton, Girvanella, Renalcis, etc. The longitudinal section of Epiphyton is usually dendritic (Fig. 3A), and the transverse section of Epiphyton is like mud ball similar to Renalcis. Some of Epiphyton grows in chamber (Fig. 3B). Renalcis usually has thin micrite wall and is hollow inside, which can form grape-like clot by binding with each other (Fig. 3D). Girvanella is filamentous without branch. The size of single Girvanella filament is generally uniform (Fig. 4A), with the length of 50-200 μm and the diameter of 2-4 μm. There are three kinds of thrombolites: clots formed by micrite binding single Girvanella filaments, clots formed by micrite binding parallel filaments with each other (Fig. 3C), clots formed by micrite adhering to intertwined filaments.

Most of the clots formed by micrite are irregular, and some of them have smooth edges. There are many small clots around the larger clots. Micrite sheath is observed at the edge of some particles (Fig. 3F). Some clots are reticulated due to unclear boundaries (Fig. 3D). And microspar is common in the clots.

Rhombic, brown, subhedral-euhedral dolomite crystals are common in the thrombolite (Fig. 4B). Pyrite is observed in the clots formed by dense micrite and in the spar cement (Fig. 4C and D). In the dense micrite of thrombolite, there are also some bioclasts such as brachiopods, echinoderms, and trilobites (Fig. 3E). Round or oval oolites are also observed, including radial oolites (Fig. 3E). There is generation cement between the clots (Fig. 3F), which the first generation is blade-like, and the second generation is embedded crystal-like. Fibrous rim-cement with equal thickness is also observed. Through scanning electron microscope the intergranular pores in the thrombolite are well-developed, and some of them are filled with quartz particles with good crystal shape. There are also gypsum crystals on the surface of calcite particles, filamentous cyanobacteria polymer (Fig. 4B), spherical microfossils (Fig. 4D), special honeycomb-like structure (Fig. 5B), sheet and mat structure (Fig. 5C and 4D), and spiral cyanobacterial fossils (4C).
5. Discussion

Calcified cyanobacteria are the best-preserved microorganisms in the most of microbial carbonates [2]. Dead and dying bacteria can calcify [18], and calcification is closely related to the mucopolysaccharide sheath of cyanobacteria [19] and the representative form of biomineralization and organic mineralization [20]. Most microorganisms can secrete extracellular polymeric substances (EPS). Microbial cells and EPS are always negatively charged and have the ability to bond Ca2+, which becomes the nucleation field of carbonate crystals to promote the precipitation of CaCO3 [2, 21, 22], and capturing and binding sediments are completed through the production of bacteria in EPS [23, 24]. Girvanella is the calcified sheath of filamentous cyanobacteria [2]. Pratt [25] suggested that the calcification of Girvanella may be induced by the special chemical changes caused by the chemical degradation of heterotrophic bacteria in the sheath. Therefore, Epiphyton, Girvanella, Renalcis may not be original cyanobacteria, but the products of cyanobacterial sheath or cyanobacterial calcification. The existence of these products
indicates traces of cyanobacterial growth during the formation of the thrombolite. Based on the observation of the macro and micro features of thrombolite bioherms, it shows many microbial signals during the formation of thrombolite, which shows that the formation of thrombolite may be closely related to the complex microbial activity.

**Figure 4.** Calcified cyanobacteria microfossils in scanning electron microscope

5.1. *The Ways of Cyanobacterial Sheath Calcification*

Different experiments proved that the calcification of cyanobacteria is related to the absorption of carbon in the environment by photosynthesis [26], so the different forms of cyanobacterial calcification can reflect the changes in chemical properties of the environment. According to the microscopic features of the thrombolite in the study area, it shows that the morphology of Epiphyton, Girvanella, Renalcis is different. The products of calcification reflect the different calcification process of cyanobacteria sheath or cyanobacteria. The thrombolite bioherm of Cambrian Zhangxia formation in the western part of Shandong Province is formed in a relatively low-energy subtidal environment [27]. Cyanobacteria is a kind of autotrophic microorganism, and in this environment it contributes to photosynthesis of cyanobacteria. Photosynthesis reduces CO2 in water and increase pH value of water. With the increase of environmental alkalinity and the increase of CaCO3 saturation in the surrounding environment, it promotes calcification.

According to microscopic features of thrombolite bioherms, there are 3 kinds of filamentous Girvanella in the thrombolite for the study area, and the calcification may be as follows: the clots formed by the micrite adhering to single tubular Girvanella thallus (Fig. 4A), and the calcification sheath of cyanobacteria may be caused by calcification caused by direct CaCO3 precipitation which is induced by the adsorption of Ca2+ by EPS secreted by some cyanobacteria as a direct nucleation point; calcified sheath which is formed by direct precipitation of CaCO3 particles due to adsorption of Ca2+ by EPS as a direct nucleation point bind with each other, and calcification formed by direct precipitation of CaCO3
particles and carbonate particles precipitated in the surrounding environment (Fig. 3C); mutual entangled calcified filaments bound by micrite.

According to the analysis of the calcified products of Girvanella, the cyanobacterial sheath, it is known that the calcification of the cyanobacterial sheath is mainly caused by the direct precipitation of CaCO3 particles caused by EPS capturing Ca2+ in the surrounding environment and the calcification induced by capturing and binding sediments caused by the production of EPS. Epiphyton and Renalcis may also be produced by the calcification of cyanobacterial sheath. The special grape-like Renalcis clot (Fig. 3D) is formed by the calcification of the cyanobacterial sheath and the mutual adhesion.

5.2. EPS calcification residue and calcified cyanobacteria fossils
Via scanning electron microscope, microbial calcification products were observed, including spherical microbial fossils, filamentous cyanobacteria aggregates, sheet and mat structure, honeycomb-like structure and spiral calcified cyanobacteria fossils. Spherical microbial fossils are generally 2-5 μm in diameter, which may be the product of calcification after the death of some spherical microbe. Some of the global structures grow on the surface of mats (Fig. 4D), some grow in the void between grains, some are symbiosis with the mat, and well-preserved, which are not affected by the later sedimentation. It indicates that the globular structure is the product of the contemporaneous period, and also shows that the early diagenesis is more important than cementation for the formation of microbial carbonates.

The sheet and mat structure generally exist on the surface of calcite particles or between the calcite particles, and have no specific crystal morphology. As shown in Fig. 5C, it may be the products of calcification induced by the supersaturation of carbonate in the surrounding environment causing EPS to capture or bind Ca2+ and making carbonate particles precipitate directly. There are irregular combinations and many micropores between different sheets. These discontinuous micropores may be the result of bacterial decay [28], or may be the result of the self-mineralization of EPS or heterotrophic bacteria decomposing organic matter. In addition to the late diagenesis, these microbial pores are also an important source of pores. The sheet structure shown in Fig. 5D is surrounded by the micrite net formed by mutual binding micrites. This sheet structure may be the product of calcification of biofilm, on which observes the attached microcrystalline calcite. It may be caused by the viscosity of EPS itself. It precipitates many fine particles with different sizes on the mat structure of surface in Fig. 4D, which may be bacterial debris [29], or the residue of EPS calcification. It presents saw-toothed combination between different mats, which may be formed by organic mineralization after the death of microorganisms. In Fig. 5A, the clots formed by the binding fine particles are surrounded by sheet structure, which may be the product of EPS calcification after the death of bacteria. The special honeycomb-like structure (Fig. 5B) is likely to be the product of the decomposition of organic matter by anaerobic heterotrophic bacteria, or the mineralization of EPS itself after the bacteria forming biofilm and during the process of continuing to grow upward. The existence of these complex fabrics may explain the complex process of microbial organic mineralization.

The morphology of cyanobacteria is mainly spherical, filamentous, or spiral [30]. Through scanning electron microscope, spiral microfossil is observed (Fig. 4C), which are dextral in shape, with an internal rotation diameter of about 4 μm and an external rotation diameter of about 6 μm. The spiral microfossils may be the calcified fragments of cyanobacteria, Oscillatoriaceae [30]. And it also observes the radial microbial fossils on the surface of calcite crystals (Fig. 4B), and some filaments around them. The radial microbial fossils may be the aggregates of filamentous cyanobacteria, which are produced by the calcification of filamentous cyanobacteria with the cohesive EPS.
5.3. Micrite Fabric

Based on the microscopic fabric in the thrombolite bioherms, whether it is the product of cyanobacterial calcification, clot, or the cement that binds bioclastic, oolitic, and other particles, their component is mainly micrite. It is difficult for the micrite fabric to ensure the exact cause of formation and the specific mechanism of microbial precipitation [2]. Therefore, the genesis of the micrite is inferred as follows: (1) cell residues of calcified bacteria [31]; (2) calcified products of cyanobacterial filaments [36]; (3) response of heterotrophic bacteria community to organic matter enrichment [32]; (4) possibly calcified bacterial cells, microbial whittings and calcified biofilm [2]. In the dense micrites, there are many subhedral or heteromorphic pyrite crystals with 2~10 μm. These pyrite crystals may indirectly represent the important role of anaerobic heterotrophic sulfate-reducing bacteria (SRB) in the formation of thrombolite bioherm [33], and it also suggests that the process of the formation of the thrombolite experienced a weak reduction environment. In addition to pyrite particles, micrite envelope and some microspar are also observed in the micrites. Micrite envelope may be the result of microbial drilling filled with micrites, or calcification of biofilm. Microspar may be the products of micrite recrystallization, or the pores produced by microbial decay filled with microspar in the process of thrombolite formation. The size of micrite is usually between 2 and 5 μm. There are also many bioclasts (Fig. 3E) and clots formed by small particles (Fig. 5A) in dense micrites. This fabric may represent the aggregation behavior during the growth of microorganisms [34] and a strong aggregation process. All these indicate a kind of cohesion of micrite, which may be related to the mucus excreted by bacteria. Therefore, the micrite fabrics in the thrombolite are probably the common result of (1), (2), (3), and (4), which reflects the complex microbial mechanism of micritic fabric.

6. Conclusion

The thrombolite bioherms for Cambrian Zhangxia formation in the western part of Shandong Province developed in relatively deep water environment. The calcification products such as Epiphyton,
Girvanella and Renalcis, together with the common dense micrite and calcified cyanobacteria microfossils, indicate that the growth process of the thrombolite is closely related to the complex microbial activity. The sheet and mat structure, honeycomb-like structure, and globular cluster clots indicate the importance of EPS calcification and organic mineralization during the formation of thrombolite. The complex origin of micrite fabric is difficult to ensure. The micrite fabric containing pyrite indicates the complex metabolic process of sulfate-reducing bacteria during the growth of thrombolite. The micritic fabric with micritic envelope represents biofilm calcification and micritization associated with microbial drilling. Autotrophic cyanobacteria and heterotrophic bacteria play an important role in the formation of thrombolite. In the relatively complex sedimentary fabric, more detailed problems need to be further studied in the future. Therefore, this research also provides important clues and thinking ways for further study of microbial carbonates in the future.

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