Occurrence of Organic Matter in Calcimicrobialites across Permian–Triassic Boundary in Huayingshan Region, Sichuan, South China

Yang Hao (杨浩)
Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, China University of Geosciences, Wuhan 430074, China; Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, China
Wang Yongbiao* (王永标), Chen Lin (陈林)
Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, China University of Geosciences, Wuhan 430074, China

ABSTRACT: Calcimicrobialites across the Permian–Triassic boundary in Huayingshan region were investigated using the fluorescence microscopic measurements to understand the occurrence of organic matter. The microbialites are composed of micrite matrix and coarse spar cement. Abundant rhombic or magnetic needle-like carbonate minerals were observed adrift within the cement. The fluorescence microscopic measurement indicates the micrite matrix in microbialites shows the most abundant organic matter, with the rhombic or magnetic needle-like carbonate minerals and coarse spar cement coming to the 2nd and the 3rd, respectively. Organic matter is mainly preserved in the space between the grains of the micrite minerals but almost evenly distributed in the rhombic or magnetic needle-like carbonate minerals. As one of the common diagenesis types, dolomitization is observed to occur in the microbialites in Huayingshan. However, the carbonate cement in microbialites still has high content of element Sr as shown by the microprobe analysis, reflecting that the dolomitization might have happened in a restricted environment. Observation under the fluorescence microscope shows that dolomitization just led to the redistribution of organic matter in the grain space of dolomite minerals, inferring that the diagenesis has a slight effect on the preservation, and thus on the content of organic matter in the microbialites.

KEY WORDS: organic matter, calcimicrobialite, Permian–Triassic, fluorescence, Huayingshan.

INTRODUCTION
As early as 1983, Zhou et al. (1983) had proposed the importance of the organic matter trapped in the carbonate crystal, which was believed to be one of the potential hydrocarbon sources on the basis of the pyrolysis experiments. In the simulation experiments, they found the release of these trapped organic matter at high temperature and named these organics as the enclosed organic matter to discriminate...
from the absorbed organic matter in sedimentary rocks. Later on, many scholars (Xie et al., 2000, 1999; Zeng, 1998; Fan et al., 1996; Shi and Yu, 1996; Tuo, 1994; Zhang and Tong, 1992; Zhou et al., 1991) conducted a series of work related to the enclosed organic matter. Investigated regions include North China, Tarim, and South China, spanning a variety of geological periods ranging from Precambrian, Cambrian, Ordovician, Permian, Triassic to Tertiary. The involved carbonate rocks include algal dolomite, marl, and bioclastic limestone. All these studies provide an important reference to the further research on the enclosed organic matter found in different kinds of carbonate rocks, as well as a theoretical guidance for the study and exploration of petroleum in marine carbonate rocks.

There exist many kinds of carbonate rocks in the earth’s history. The formation of the enclosed organic matter is related to the sedimentary environments, the diversity and abundance of organisms, as well as the types and processes of diagenesis. Compared with ordinary carbonate rocks, microbialites show somewhat particularity in the high microbial productivity and the sedimentation in an anoxic marine environment, which is favorable to the preservation of organic matter and decreases diagenetic influence. The microbialite, proposed to be one of potential hydrocarbon source rocks, has received more and more attention (Teng et al., 2007; Yang et al., 2007).

Fluorescence is a form of luminescence that expresses the characteristics of materials under the visible light or ultraviolet radiation (Rost, 1992). Fluorescence microscopy is an authoritative technology used in the study of sediments or sediments with abundant organics such as hydrocarbon source rocks. The fluorescence in carbonate rocks may be caused by the organic compounds (Machel et al., 1991). The characteristics of the occurrence of organic matter in microbialites could be identified through the observation under fluorescence microscopy.

GEOLOGICAL SETTING

Microbial carbonates, formed on the top of shallow carbonate platforms immediately after the end-Permian mass extinction in lower latitude Tethys, were recently regarded as microbialites (Baud et al., 2005; Wang et al., 2005; Kershaw et al., 1999). As a part of Tethys, South China was found to be one of the most important regions where the microbialites were widely deposited at that time. Outcrops of microbialites in South China include Huayingshan region (Huayingshan in East Sichuan and Laolongdong in Chongqing) (Fig. 1), Lower-Middle Reaches of the Yangtze River, and Nanpanjiang area (Yang et al., 2006; Wang et al., 2005; Kershaw et al., 1999; Lehrmann, 1999).

The Changxingian reefs universally existed in Huayingshan region (Wang and Qiang, 1992; Fan et al., 1990). During and after the end-Permian mass extinction, the reef ecosystem was destroyed entirely and replaced by the calcimicrobialites. The thickness of the microbialites in Huayingshan region is about 2.5 m. The base of microbialites is indicative of the boundary of faunal mass extinction in the study area. The conodont fossil Hindeodus parvus, the index fossil of the Permian–Triassic boundary, was found within the microbialites (Kershaw et al., 2002). Overlying the microbialites was the laminated limestone of Early Triassic.

The microbialites in Huayingshan region show some special structures in comparison with those found in the other places. The digitate or domal structures could be found in the outcrops of the microbialites in the study region (Fig. 2). However, microbialites with different structures are usually composed of micrite matrix and coarse spar carbonate minerals. Wang et al. (1994) considered these special sediment buildups as calcareous crusts, and Kershaw et al. (1999) named it as “microbialites carbonate crust”.

OCCURRENCE OF ORGANIC MATTER PRESERVED IN MICROBIALITES

The microbialites are composed of micrite matrix and coarse spar cement. The coarse spar cement was found adrift with abundant rhombic or magnetic needle-like carbonate minerals. Under the fluorescence microscopy, the micrite matrix of the calcimicrobialites from both the Huayingshan and Laolongdong sections show strong fluorescence (Figs.
Figure 1. Sketch map showing the locality of the studied sections (denoted as the black stars).

Figure 2. Images showing the digitate (a) or domal (b) structures of the microbialites in Huayingshan (a) and Laolongdong (b) (the diameter of the coin is 2.1 cm).

3A-2, 3B-2 and 3D-2). It appears that the micrite matrix has the most abundant organic matter in comparison with the cement or other minerals.

**Organic Matter Preserved in the Micrite Matrix**

The micrite carbonate minerals in Huayingshan and Laolongdong sections are in the form of grains with the size being about 8–10 μm. However, the surface of the micrite is turbid, making the micrite look darker. The presence of abundant pyrite grains in the micrite suggests an anoxic sedimentary condition. Several gastropod or ostracod fossils could be found in the micrite matrix in Laolongdong Section, although fewer fossils were found in the micrite matrix in Huayingshan Section.

Under the fluorescence microscopy, the micrite matrix fluoresces brightly (Figs. 3A-2, 3B-2 and 3D-2) wherever the calcimicrobialites are from Huayingshan or Laolongdong sections. This shows that organic matter is abundant in the micrite matrix. Organic matter was found to be mainly preserved in the space between the micrite grains, and the grains themselves display relatively weak fluorescence. Sometimes strong fluorescence is observed inside the micrite
Figure 3. Photographs showing microbialites from Huayingshan and their fluorescence characteristics. A-1, B-1, C-1, D-1. thin sections, single polar microscope; A-2, B-2, C-2, D-2. thin sections, fluorescence. Ms. micrite matrix; Ls. limpid spar cement; Ts. turbid spar cement.
minerals (Fig. 3B-2), implying that some small organic grains were preserved inside the crystals during the formation of microbialites.

**Organic Matter Preserved in the Spar Cement**

The coarse spar cement of microbialites can be divided into two parts, the limpid calcite and the carbonate minerals with turbid surface (Figs. 3A-1 and 3C-1). The latter takes the rhombic or magnetic needle-like shape. The large size of calcite spars makes the minerals with turbid surface look like being enchased. The limpid calcite spars are bright under the single polar microscope but dark under the fluorescence microscope, inferring the low content of organic matter in the calcite spars.

The carbonate minerals with the turbid surface show some differences in shapes. Some take a rhombic shape with the size ranging from 40 to 60 μm. Some take a magnetic needle-like shape with the width of 16 μm and the length from 32 to 48 μm. These minerals show the fluorescence in an intensity between the micrite matrix and limpid calcite spars. Unlike the micrite matrix, these minerals do not show any fluorescence in the space between the grains, showing less organic matter being preserved in these spaces. However, the fluorescence within a mineral displays a comparable intensity, indicating the equal distribution of organic matter within a mineral. Thus, the micrite matrix, magnetic needle-like minerals, and limpid calcite spars obviously exhibit three different intensities in fluorescence (Fig. 3A-2).

**PRIMARY PRODUCTIVITY AS THE IMPORTANT BASE FOR THE ORGANIC PRESERVATION**

The micrite matrix shows the strongest fluorescence in microbialites, suggesting the appearance of the most abundant organic matter in the micrite. In contrast, organic matter in the limpid spars is comparatively lower in content. There are always abundant gastropod and ostracod fossils identified in microbialites in Laolongdong Section (Fig. 3D-1). These faunal fossils became the top customers in the food chain of the ecosystem after the faunal mass extinction, and the appearance of these faunas suggests the existence of the abundant primary producers, such as cyanobacteria. The micrite of Huayingshan Section also displays strong fluorescence but with much less faunal fossils being found. Noticeably, however, many minigastropods were found in the outcrops in Huayingshan Section. After the end-Permian mass extinction, all the calcareous algae disappeared, leaving cryptalgal such as cyanobacteria survived. This kind of microbes became the important base for the food chain of the marine ecosystem. Cyanobacteria blooms after the end-Permina mass extinction were recently reported in Meishan Section in South China (Xie et al., 2007, 2005), which is proposed to be an important ecological characteristic in the critical period in the earth’s history. The cyanobacteria not only provided nutrition for the ecosystem but also produced organic matter to be preserved in the microbialites. Therefore, the abundant organics found in the micrite may be directly related to the high primary productivity of cyanobacteria.

**DIAGENETIC INFLUENCE ON THE ORGANIC PRESERVATION**

Under normal conditions, the lower absorptive ability and the complex diagenetic processes of carbonate rocks would result in severe discharge of the organics. As a result, a small proportion of sedimentary organics will be preserved in these rocks. Strong diagenesis will also destroy the calcareous faunal fossils. However, the presence of well-preserved minifossils in microbialites in Huayingshan and the abundant organics found in the space of the micrite are suggestive of the slight influence of the post-depositional diagenesis on the micrite.

The turbid spars in the limpid spars are similar to the micrite minerals in surface but different in both the size and the shape. Because the turbid spars and the micrite share the similarity in brown color and in the fluorescence and cathodoluminescence characteristics, they are considered to be the contemporary products precipitating from the same aqueous solution. The different sizes between the micrite and the brownish crystals in the cement may relate to the space available for their growth. That is to say, some of the minerals in the cement may precipitate in the early
sedimentation stage of the microbialites.

The limpid calcite spars in the cement with comparative cleanness show that the pore water was clean with less mineral contamination during the formation of the limpid spars. The limpid spars have carbon and oxygen isotope data comparable with those of the micrite (Wang et al., 2005). These results suggest that the clean limpid spars grow in the marine environment and are less affected by later freshwater diagenesis.

Some annular dolomite minerals can be seen in the microbialites of Huayingshan Section under the cathodoluminescence examination (Fig. 4a). The microprobe measurement shows that the Sr content is about 600 ppm in the micrite and 1481 ppm in some spar cement (Fig. 4b). This characteristic of Sr abundance is similar to those of carbonate rocks in Feixianguan Formation of Early Triassic in East Sichuan (Huang et al., 2007). Huang et al. (2007) proposed that high content of Sr element probably resulted from the diagenesis occurred in a restricted environment. Under common circumstances, dolomitization will increase the porosity of carbonate rocks and the decrease of organic matter. Dolomitization in the microbialites happened in a relatively restricted environment, which was further demonstrated to be an anoxic condition (Yang et al., 2007). The restricted and anoxic environment favors the preservation of organic matter. Observation under fluorescence microscope also reveals the appearance of the strong fluorescence among the dolomites, implying that dolomitization did not lead to decrease, but only the redistribution of organic matter among the space of dolomite minerals.

![Figure 4](image-url) **Figure 4. Images showing (a) the characteristics of cathodoluminescence examination of the microbialites in Huayingshan and (b) the locations for the microprobe analysis of the carbonate minerals with the Sr content being 610 ppm, 601 ppm, 1481 ppm, 332 ppm, 1035 ppm, 604 ppm, and 1047 ppm for dots 1 to 7, respectively.**

**CONCLUSIONS**

In the microbialites, the micrite shows the most abundant organic matter with the mid-coarse spars cement coming to the next. Organic matter in the micrite can be preserved not only in the space between the mineral grains but also within the crystals, whereas organic matter in the cement is mostly preserved in the brown spars and remains little in the grain spaces. Least organic matter is found in the limpid spars.

Microbialites are proposed to be a special carbonate buildup related to the microbial contribution immediately after the end-Permian faunal mass extinction during the great geological transition. Microbial bloom, such as cyanobacteria expansion, could be the important precondition for the accumulation of a huge quantity of organic matter. The great sedimentary rate ensured less degradation during deposition and the quick preservation of these organic matters. Most importantly, the diagenesis
which occurred in microbialites was found to play less influence on the organics in comparison with that in normal carbonate rocks.

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Abstract


