

Microorganisms Linked to Neoproterozoic Microspar Carbonate Sedimentation in the Jilin-Liaoning Area

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Abstract Molar-tooth carbonate refers to a sort of rock that has pygmatical folded structure comparable to the ivory. This kind of carbonate exists in a special time range (from Middle to Neoproterozoic). Its origin and the possibility to use it in stratigraphic correlation of the paleocontinent is the key task of the IGCP447, a project on Proterozoic molar tooth carbonates and the evolution of the earth (2001–2005). The importance lies in that the molar-tooth structure is the key to solving problems related to Precambrian biological and global geochemical events. The molar-tooth structure is associated with microorganisms. Development and recession of such carbonates have relations with the evolution process of early lives and abrupt changes in sea carbonate geochemistry. In recent years, based on researches on petrology, geochemistry and Sr isotope of molar-tooth carbonate in the Jilin-Liaoning and Xuzhou-Huaiyang area, the authors hold that it can be used as a marker for stratigraphic sequence and sedimentary facies analyses.

Key word: molar tooth carbonate, Neoproterozoic, sedimentary environment, microorganisms, origin

1 Introduction

Along with the progress in the research on Precambrian, especially the further study of global events, stratigraphy and paleo-continental reconstruction, molar tooth (MT in short) carbonate formed in the Mid-Late Proterozoic has become a recent focus among geologists (Meng Xinghua and Ge Ming, 2002). In more than 40 regions and countries, such as Canada, America, Europe, Africa, Australia and China, MT carbonates were found (James et al., 1998). In China, such as Hunjiang of Jilin Prov., Dalian and Benxi of Liaoning Prov. and the Xuzhou-Huaiyang area, MT carbonates are developed in many different stratigraphic horizons, distributed over large areas and have complex types. Since the MT structure is made of microspars, the MT carbonate is also called microsparite carbonate.

2 Sediment Environment of Microsparite Carbonates

Encouraged by the research of predecessors, the authors studied the Neoproterozoic sedimentology and stratigraphy of the MT structure in the Jilin-Liaoning area, and identified a series of MF1-MF10 MT microfacies types. Our work proved that the MT structure is developed in such a sedimentary environment as gentle slopes on the margin of a craton platform (Meng et al., 2002). Figure 1 shows the distribution pattern of MF1-MF10 over gentle-slope

carbonates in a paleo-environment (Meng and Ge, 2002).

Shapes of the MT suggest their relationships with sedimentary environments. In the study area, there are filamentous (MF1), banded, tubercle (MF9) and heterochthonous MT. There may be relationships between shape features, material components and grain sizes of the enclosing sediments.

2.1 Sedimentary facies and environment of the Wanlong Formation in the Jinan area

The Wanlong Formation in the Jinan area is divided into three members. The lowest one is MT limestone and can be used as the marker for regional correlation. The middle member is tubercle and/or lamellar limestone and the upper one is micritic limestone, lamellar micritic limestone, marl and calcarenite. The Wanlong Formation has a gentle-slope sedimentary environment as the sedimentary background at the edge of the craton platform. As a result of sea-level changes, subsidence and supply condition of land-source material and periodic changes of climate, a set of carbonate gentle slope-platform supercyclic sequences were formed. The MT structure is the most striking correlation marker and assume diversified patterns in the cyclic sequences, mainly microcyclic sequences related to storm beds.

In the Laoling section, the Wanlong Formation clearly has three layers. The lower part is mainly shallow-middle gentle slope sediments. The middle part is deep gentle slope sediments made up of tubercle limestone. After a period of

three formations: the lowest Nanguanling Formation, middle Yingchengzi Formation and Gandaozi limestone in the Xingmuncun Formation. Although they are all gentle slope sediments interpreted to have formed at the margin of a craton, the MT structures and material compositions are varied greatly. When sediments of the Nanguanling Formation were formed, water was relatively shallow and the sediments consisted of MT-bearing micritic limestone, calcarenite, lime-dolostone and stromatolite limestone. At the bottom of the Yingchengzi Formation, the shallow gentle slope sediments are composed of calcarenite and stromatolite limestone that has a small amount of MT. In the middle part, there occur mainly medium-shallow gentle slope sediments composed of limestone with MT structure. Upwards, the sediments show a deep gentle slope environment with mainly lamellar micritic limestone. In the middle Yingchengzi Formation that contains MT limestone, sedimentary sequences are composed of several units: the upper gentle slope, the middle gentle slope and the upper deep gentle slope.

According to the new research of Meng Xianghua and Ge Ming (2002a, 2002b, 2003) based on the genetic sequence concept, stratigraphic sequence study, Rb/Sr age measurement and $^{87}\text{Sr}/^{86}\text{Sr}$ change curves, it was proved that the Wanlong Formation in Jilin, Nanfen Formation (include Xingmuncun Formation which was formed at the same time), Nanguanling Formation, Ganjingzi Formation and Yingzhengzi Formation in the Dalian area all belong to the upper Qingbaikou strata. This set of strata is a supercyclic sequence from 850 Ma to 810 Ma in the Jilin-Liaoning area and made up of 9–10 cyclic sequences. The micro Milankovitch sequence in these cycle sequences are similar to the Milankovitch period (0.1–0.4 Ma).

3 Microspar Carbonate Linked to Organic Origin

Till now there has been no commonly accepted MT origin theory (e.g. Ge Ming et al., 2003). However, the following information related to the MT origin may give us inspiration.

3.1 Biologic markers in microspar limestone

Some researchers including Shi et al. (2000), Zhao et al., (1997) have studied the biomarkers of the Proterozoic carbonates in North China. In this paper, the authors mainly studied biomarkers of microspar MT carbonates. Bulk-rock analysis of biomarkers from microcalcsparticle of the Wanlong Formation and Xingmuncun Formation in the Jilin-Liaoning area of northeastern China shows abundant such biomarkers as normal alkane, isoprenoid, hopane, sterane, alkylmethylcyclohexane and alkylcyclohexane.

They show a great diversity of biological sources. Long-chain isoprenoids, the major component of chlorophyll, such as C_{19} , C_{20} , are major biomarkers synthesized early by isoprenoid monomer; hopane is a type of characteristic biomarker from prokaryote, such as archaeobacteria and cyanobacteria; sterane is a biomarker for eukaryote. Moreover, there are two kinds of alkane distribution with C_{17} and C_{18} as the main peak representing water bacteria and C_{23} and C_{24} as the main peak representing fungi. Biomarker analysis shows that there are plenty of biomarkers in microsparite. Almost all these biomarkers indicate microorganisms ranging between aerobic and anaerobic bacteria, reproducing well in normal or saline seawater in weak oxidation/reduction conditions. Calcite is deposited quickly to become microspar due to a certain mechanism. The structural background, climate and sediment environment suitable for MT carbonates are favorable for the existence of multiple microorganisms.

MT carbonates are developed in a gentle-slope environment with a steady structural background, especially a slightly oxidizing and slightly reducing environment in the middle gentle slope-upper deep gentle slope below the tide level. In low-latitude areas with humid climate, MT carbonates are distributed over stages of marine transgression and early highstand systems tract. The sedimentary environment is suitable for populations of both photosynthesis microorganism and anaerobic bacterium.

3.2 Direct evidence for the existence of organisms in microspar limestone: framboidal pyrite

In strata with MT developed, there is a small amount of pyrite in general. Its crystals have complete forms and cubic and pentagonal dodecahedron pyrite druses and crystals are very common. Framboidal (strawberry-like) pyrite can be often see in the Wanlong Formation, especially at its bottom. The major feature of the organic pyrite is that it occurs as framboidal (50 μm) or spherule (10 μm) aggregates. The appearance of this kind of pyrite has a relationship with organic segregation under reducing conditions. Its formation is related to sulphide metabolism of thiopneutes, such as *Desulfovibrio* (Dai, 1994). These, on one hand, demonstrate the existence of thiopneutes in MT limestone and, on the other hand, it shows that the microspar MT structure was formed in a syngenetic environment having reduction bacteria.

3.3 Enrichment of Sn in microspar belts is related with the action of organic matter

Based on the energy spectrum analysis of MT components we found a small amount of Sn, 2.8%–0.5% in general. According to Bao (1996a, 1996b), at a normal (temperature and pressure) condition, Sn is inactive and

persistent on earth's surface. Organisms play an important role in migration and enrichment of Sn. We propose the following two mechanisms for the migration of Sn into sedimentary basins. (1) Transfer through organic complexes, that is, migration of Sn is realized through connection of Sn with organic acids to form Sn-organic complex or chelate. (2) Transfer through organic absorption. Sn is a necessary element for organisms, so it can be transferred and enriched in sediments when organisms enter sedimentary basins. In the first case, when physical and/or chemical conditions, such as salinity, Ph and EH, have some changes, there will be decomposition of Sn-chelate or gelatin. Then Sn will be enriched in sediments. The existence of Sn in MT might show that in the forming process of MT microspar, organic matter and microorganisms were involved.

3.4 Analyses of C and O isotopes

According to Tucker et al., (1991), characteristics of C and O isotopes in shallow carbonate sediments depend mainly on their compositions and temperature. As for marine sediments, O isotope will be heavier than sea water and the range is from -0.5% to $+3\%$; but the $\delta^{18}\text{O}$ value of inorganic carbonate sediment is almost the average value (0%). The $\delta^{13}\text{C}$ value, such as oolitic limestone on the Bahama beach and prehnite in Behtles, ranges from $+2\%$ to $+5\%$, normally $+4\%$. Negative $\delta^{13}\text{C}$ values are seldom seen. This may reflect that organisms are related to fermentation of most anaerobic bacteria, and the production and oxidation of methane. The $\delta^{13}\text{C}$ values of carbonates of organic origin can be far from the average value. Placing the C-O isotope values that we have measured in Tucker's map, we can observe that the values are located at the top left corner (Fig. 2). This suggests that the carbonate sediments we have measured are formed in association with bacterial organisms, as described by Tucker.

4 Discussion of MT origin

4.1 MT serves as a lithofacies marker

Such a marker can be used in the correlation of paleoenvironment and stratigraphic sequence. In their research, Meng and Ge (2003) used the cosmos-earth system sequence events and an integrated study of geological events to do classification and correlation of MT sequences in the Sino-Korean plate and Yangtze plate, and further conducted studies for cycles at different levels: supercycles at a 40 Ma level, cycles at a 4 Ma level and micro cycle from 0.1 to 0.4 Ma. Observations proved that MT carbonates are an important indicator for paleo environments, and evidence for sequence correlation over large areas. The origin of MT is mainly controlled by paleo

environments and is probably not related to earthquake events.

4.2 MT carbonate may have organic-geochemical origin

4.2.1 Compared with stromatolite, MT (Microspar) may be the result of another microbial.

Gillison (1929) believed that MT had an algal origin. Ross (1959) wrote that "Perhaps some (molar tooth) structures have direct or indirect relations to the life processes of primitive organisms in the original lime mud from which the present limestone is derived". O'Connor (1965, 1972) also described the algal origin of MT. Smith (1968) argued that the MT structure was formed as algae were precipitated initially in water-bearing silts and silty limestone and mudstone, which then became curved due to penecontemporaneous compaction in the layer that is 0–1.3 m below the surface of sea-bottom sediments. Pflug (1968) discovered that "MT and their surrounding limestone contain organic residues" and he furthermore observed that the border of MT structure shows the original form of algae.

In the field, MT structure and stromatolites never appear in the same stratum. Usually, MT structure developed in water areas deeper than cohesive algae zones. Krumbain noted that the research by Andrew H. K. and Stanley M. A. divided the microorganism (blue algae) ecosystem into a stromatolite ecosystem and a non-stromatolite ecosystem. The stromatolite ecosystem was produced when blue bacteria of sheet-forming organisms formed cohesive surfaces which captured and cemented sediments, while

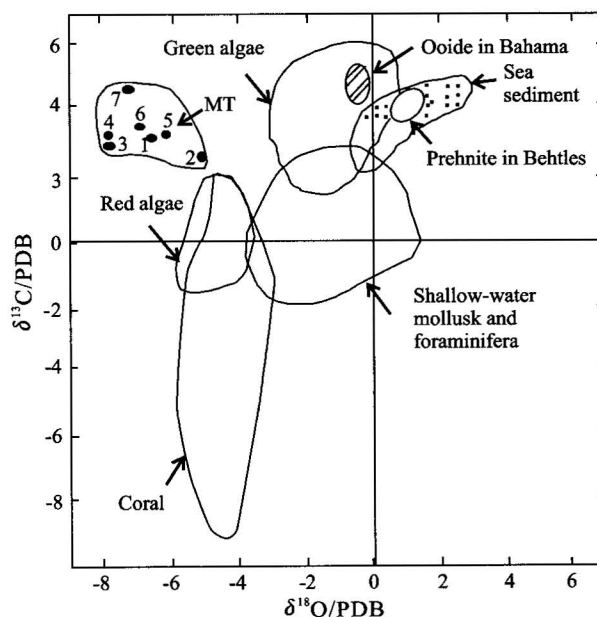


Fig. 2. Distribution features of C and O isotopes from MT carbonate (after Tucker, 1991).

1. TD08 matrix; 2–3. TD08 microspar; 4. TE01W10.1 matrix; 5. TE01W10.1 microspar; 6. TE01W10.8 microspar; 7. Gore and Shields.

the non-stromatolite ecosystem refers to single-cell blue bacteria that do not form sheets, and occur ubiquitously in Precambrian rocks. The non-stromatolite ecosystem is predominant among early-stage marine organisms. Benthos are often densely distributed along sedimentary layers, while zooplanktons are distributed over the seabed randomly. Is the MT structure the result of single-cell blue bacteria that do not form sheets as in stromatolite?

4.2.2 Are MT carbonates associated with phototrophic microorganisms?

MT carbonates were formed in steady paleo-tectonic environments. Warm climate and shallow slope environments are favorable for the existence of phototrophic microorganisms. Yet MT carbonates seem different from cohesive algae stromatolite carbonates. Furniss et al. (1998) and Winston et al. (1999) found a possible Acritarch in MT microspar, which often form spheroidal nepheline (often related with organism). And Furniss et al. found sheath bacteria (Fig. 3). Besides, the authors also found uncertain organic calcicolous protonema in microspar. This is probably a calcicolous organism, which is to be further studied. This may provide direct evidence for the origin of organisms with MT structure. Obviously, decay of the organic components in the sediments would have provided an environment for anaerobic activity.

4.3 Significance of the geologic event of MT carbonates

It has been commonly accepted by the geological community that the formation of MT carbonates is an

important historic event in the early period (the Precambrian) of earth's evolution. MT carbonates are a geochemical product of particular Proterozoic organisms in a paleo-sea environment. Along with the accretion of continental margin in the early Neoproterozoic, which lowered the concentration of CO_2 in the atmosphere, weakened the greenhouse effect, and at last lead to the advent of an ice age, i.e. global radiation disaster, bringing about the global snowball event (Hoffman, 1988, 1998). This ice age event may have directly resulted in extinction of bacteria responsible for the development of the MT.

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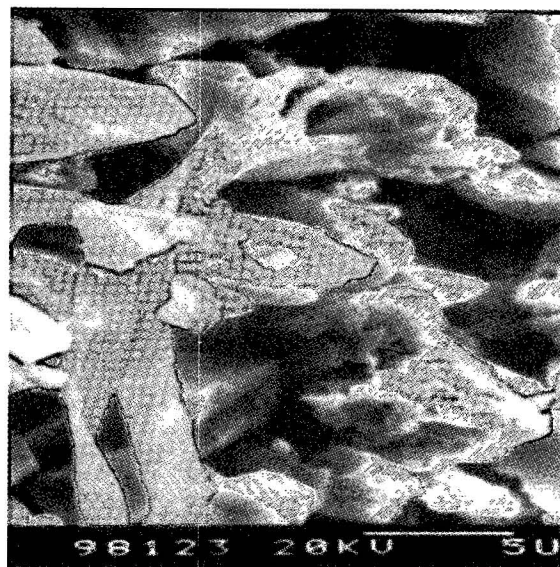
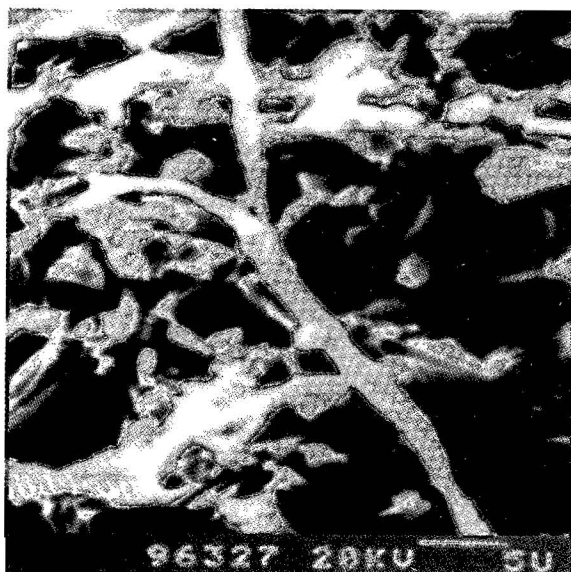


Fig. 3. (a) Sheath bacteria in MT carbonates of thin sections (Furniss et al, 1998, scale bar: 10 μm); (b) possible calcicolous filamentous bacterium in MT of the Wanlong Formation, Qinggouzi, Jinlin, China (SEM image, scale bar: 5 μm).

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