Microbial Mats in the Mesoproterozoic Carbonates of the North China Platform and Their Potential for Hydrocarbon Generation

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ABSTRACT: The well-preserved Mesoproterozoic succession in the North China platform consists mainly of three lithological associations including peritidal quartz sandstone, shallow marine and lagoonal dark to black shales, and shallow epeiric carbonates, with a total thickness of up to 8 000 m. In addition to well-documented microplants, macroalgae, and microbial buildups, abundant microbially induced sedimentary structures (MISS) and mat-related sediments have been recognized in these rocks. Intensive microbial mat layers and MISS are especially well preserved in the carbonates of the upper Gaoyuzhuang (高于庄) (ca. 1.5 Ga) and lower Wumishan (雾迷山) (ca. 1.45 Ga) formations, indicating diversified microbial activities and a high organic production. In these petrified biomats, putative microbial fossils (both coccoidal and filamentous) and framboidal pyrites have been identified. The abundance of authigenic carbonate minerals in the host rocks, such as, acicular aragonites, rosette barites, radial siderites, ankerites, and botryoidal carbonate cements, suggests authigenic carbonate precipitation from anaerobic oxidation of methane (AOM) under anoxic/euxinic conditions. Warm climate and anoxic/euxinic conditions in the Mesoproterozoic oceans may have facilitated high microbial productivity and organic burial in sediments. Although authigenic carbonate cements may record carbonate precipitation from anaerobic methane oxidation, gas blister (or dome) structures may indicate gas release from active methanogenesis during shallow burial. Bituminous fragments in mat-related carbonates also provide evidence for hydrocarbon generation. Under proper conditions, the Mesoproterozoic mat-rich carbonates will have the potential for hydrocarbon generation and serve as source rocks. On the basis of petrified biomats, a rough estimation suggests that the Mesoproterozoic carbonates of the North China platform might have a hydrocarbon production potential in the
order of $10 \times 10^8$ t.

KEY WORDS: Mesoproterozoic carbonate, microbially induced sedimentary structure, microbial mat, anaerobic oxidation of methane, hydrocarbon-generation potential, North China platform.

INTRODUCTION

Life has evolved on the earth at least since 3.5 Ga (Allwood et al., 2006; Knoll et al., 2006; Schopf, 2006). Before the advent of metazoans (ca. 580 Ma, McFadden et al., 2008; Canfield et al., 2007; Fike et al., 2006), the Proterozoic ocean was dominated by microbes (Eigenbrode and Freeman, 2006), with macroalgae thriving since Mesoproterozoic (Knoll, 2003). As the major product of microbial metabolism (Gerdes, 2007), microbial mats must have been widespread over the seafloor and been an important source for organic matter buried in the sediments, in addition to the coated organic particles falling from the surface of the ocean (Holland, 2006; Kasting and Ono, 2006). In the modern ocean, the majority of organic matters generated by photosynthesis ($H_2O + CO_2 \rightarrow CH_2O + O_2$) is either consumed by grazing organisms or destroyed by aerobic decomposition prior to burial, so that only a small fraction of them are finally buried. The organic burial ratio today is relatively constant, about 0.2% to 1% of the total primary production (Claire et al., 2006; Holland, 2002; Kasting and Siefert, 2002; Field et al., 1998), with an average burial rate of 10 Tmol C/a (1 Tmol = $10^{12}$ mol; Holland, 2006; Catling and Claire, 2005). This rate was thought to be applicable for the Mesoproterozoic oceans on the basis of the carbon isotope fractionation (Pavlov et al., 2003).

It has been argued in recent years that the atmosphere evolved through three major stages in the Precambrian (Holland, 2006; Catling and Claire, 2005; Kasting, 2004). Before the “Great Oxidation Event” at approximately 2.4 Ga (Kump, 2008; Holland, 2006, 2002; Bekker et al., 2004; Brocks et al., 2003), the Archean atmosphere was almost oxygen free, with O$_2$ concentration in the order of $10^{-4}$–$10^{-3}$ PAL (present atmosphere level, PAL = 0.21 atm; Kasting and Siefert, 2002). In the second stage, from approximately 2.45 Ga to approximately 0.85 Ga, the O$_2$ concentration had a significant rise, probably 1%–15% PAL (Kump, 2008; Kerr, 2004; Anbar and Knoll, 2002). The third stage, from approximately 0.85 Ga to 0.54 Ga, witnessed a significant rise in O$_2$ concentration, the late stage of which may have had O$_2$ concentration close to the modern level (Holland, 2006). In response to atmospheric oxygenation, the Precambrian oceans also experienced, perhaps through more complicated processes due to the buffer of ocean seawater, three major oxidation stages (Holland, 2006; Kasting and Ono, 2006; Canfield, 2005, 1998; Anbar and Knoll, 2002). Before 2.45 Ga, which probably lasted to 1.85 Ga, the ocean was entirely anoxic, rich in iron, but extremely low in sulfate concentration ($<200 \mu$M), which was less than 1% of the modern ocean sulfate level (Kasting and Ono, 2006; Anbar and Knoll, 2002; Habicht et al., 2002). From 1.84 Ga to 0.85 Ga, the ocean became permanently stratified, with the upper water column moderately oxygenated, whereas, the lower portion remained anoxic and sulfidic (Arnold et al., 2004; Poulton et al., 2004; Shen et al., 2003, 2002; Anbar and Knoll, 2002). In this stage the ocean was lacking in iron, with a sulfate concentration of 0.5–2.5 mM (Brocks et al., 2005) and somewhat similar to that in the Black Sea (Rouxel et al., 2005; Jorgensen et al., 2004). In the period of 0.85 Ga to 0.54 Ga, the ocean was largely oxidized and might not have been significantly different from the Phanerozoic ocean, where only the deep bottom seawater remained anoxic (Holland, 2006; Anbar and Knoll, 2002). Only in such an oxygenated ocean state did the benthic eukaryotic microbes diversify and bloom noticeably (Cavalier-Smith, 2006). However, it should be noted that recent researches have suggested that the oxygenation of deep oceans and important changes in seawater chemistry occurred much later, probably around 0.58 to 0.55 Ga (McFadden et al., 2008; Scott et al., 2008; Canfield et al., 2007; Fike et al., 2006; Jiang et al., 2006), which may have directly led to the evolution of metazoans and multicellular algae in the Ediacaran period (McFadden et al., 2008; Yin et al., 2007; Yuan et al., 2005; Xiao et al., 1998).

If the Mesoproterozoic ocean experienced long-term anoxic/euxinic conditions, it might be conceivable that the organic matter produced from
Figure 1. Mesoproterozoic subdivisions, stratigraphy, and major fossils in the North China platform.
surface oceans and in microbial mats could have less potential to be oxidized in the water column and at the sediment/seawater contact, leading to proportionally higher burial and preservation than those from the Phanerozoic and modern oceans. Taking the modern Black Sea as an example, the organic burial rate was from 2% to 5% (Jorgensen et al., 2004; Pavlov et al., 2003), much higher than the average burial rate of the modern earth’s surficial environments (0.2% to 1%; Claire et al., 2006; Kasting and Siefert, 2002). If the chemistry of the Mesoproterozoic ocean was somewhat similar to that of the modern Black Sea, a larger organic burial rate (e.g., 2% of the primary production or the minimum burial ratio in the anoxic Black Sea) was to be expected. A larger organic burial, if it existed, could have two important implications. First, high organic burial could lead to a significant rise in atmospheric O$_2$ within a few million years (Berner et al., 2000; Berner and Canfield, 1989). However, as stated earlier, geochemical and biological evidence indicated that substantial oxygen increase did not occur until much later, during the Ediacaran period. One possibility was that the organic carbon entering sediments returned back to the ocean and the atmosphere through anaerobic mineralization and through methanogenesis during shallow burial. A portion of the methane from methanogenesis would be mineralized in seawater through sulfate reduction (CH$_4$ + SO$_4^{2-}$ → HCO$_3^-$ + HS$^- + $H$_2$O), leaving authigenic carbonate cements and other related minerals in the sediments. The other portion of the methane would enter the atmosphere due to low sulfate concentration in Proterozoic oceans in general and consume oxygen (CH$_4$ + 2O$_2$ → CO$_2$ + 2H$_2$O), balancing out the potential O$_2$ rise by increased organic burial. Second, the organic matter formed by microbial mats might have a higher potential to be preserved due to more pervasive anoxic/euxinic bottom water conditions, and could serve as a type of source rock for hydrocarbon generation. In this article, the authors examine the microbial mats and their hosting carbonates from the thick (up to 8 000 m) Mesoproterozoic carbonate-rich succession of the North China platform. The abundance of authigenic carbonate cements and other associated minerals such as siderite, barite, frambooidal pyrite, and ankerite in these carbonates is consistent with anaerobic methane oxidation and carbonate precipitation in the seawater at the bottom or shallow burial. The well-preserved microbial mats within the carbonates suggest their potential as an important hydrocarbon source.

The Mesoproterozoic is well developed and widespread in the North China platform, with a total thickness of up to 8 000 m, and is composed of nine formations (Fig. 1). They are, in ascending order, the Changzhoupou (quartzite), Chuanlinggou (dark shale), Tuanshanzi (dolomite), Dahongyu (quartz sandstone), Gaoyuzhuang (carbonate), Yangzhuang (dolomite), Wumishan (carbonate), Hongshuizhuang (dark shale), and Tieling (dolomite) formations. The first five formations are grouped into the Changcheng Group, with the basal boundary set at 1.8 Ga and top boundary at 1.4 Ga traditionally. The other four formations are assigned to the Jixian Group, with its top boundary set at 1.0 Ga (Chen et al., 1999). A recent SHRIMP dating on zircons from the Xiamaling Formation in the lower Qingbaikou Group, which was taken as the lowermost Neoproterozoic (Xing et al., 1996), yielded a U-Pb age of 1 368 Ma (Gao et al., 2007). This important geochronological constraint has led to a suggestion that the Changcheng and Jixian groups represent only the Early Mesoproterozoic sediments, whereas, the Late Mesoproterozoic sediments from 1.3 Ga to 1.0 Ga are probably absent in the central North China platform (Qiao et al., 2007).

**MAT-RELATED FEATURES IN THE MESOPROTEROZOIC CARBONATES OF THE NORTH CHINA PLATFORM**

Mat-related sedimentary structures are abundant through the Mesoproterozoic over the North China platform both in siliciclastics and carbonates. In general, microbial buildups, such as stromatolite (Figs. 2A, 2G), thrombolite (Fig. 2C), oncolite (Fig. 2E), and biolaminites (Fig. 2D) are mainly developed in carbonates. They are particularly abundant in the Gaoyuzhuang, Wumishan, and Tieling formations. Microbially induced sedimentary structures (MISS) are abundant in the sandstones of the Dahongyu Formation (Shi et al., 2008; Mei et al., 2007; Shi and Chen, 2006); some of them are also found in the dark shales of the Chuanlinggou and Xiamaling formations.
Microbial Buildups in Carbonates

Microbial buildups in the Mesoproterozoic carbonates of the North China platform have been well studied in the past, though in most cases they have been commonly treated as organisms themselves rather than bio-sedimentary structures (Cao and Yuan, 2003). Generally, stromatolites are simple and small in the Tuanshanzi Formation, having fewer branches and rarely forming large reef-like buildups. In the Gaoyuzhuang Formation, the stromatolites became more diversified, and small buildups are well shown in its lower part (Fig. 1, Fig. 2G). Columnar, conical,
and low-relief dome-shaped forms are common. They often occur together and are densely packed into reef-like buildups, tens meters long and a few meters high. On bedding planes, after weathering, these biogenetic structures show concentric circles that are similar to annual growth rings in tree trunks (Fig. 2G). Large scale, reef-like buildups are prominent in the Tieling Formation, where diversified branching and columnar stromatolites form densely packed buildups more than 30 m high (Figs. 2A and 2B). Thrombolites (Figs. 2C) and dendrolites (Figs. 2E and 2F) are mainly recognized in the Wumishan Formation. In some places they also form buildups up to 1 m high and 2 m wide, although these structures have not been properly studied yet. The preliminary statistics on these buildups in outcrops indicates that they account for at least 2%–5% of the total thickness in these carbonate strata. If these buildups were originally composed of microbial mats of about 4%–6%, the potential organic burial would be 0.3% of the total carbonate volume. Microscopic observation on the thin sections of these buildups reveals that the petrified biomat layers or microbially mediated clots in some of these biogenetic sedimentary structures could actually attain up to 15% of the total volume.

**Oncolite-Like Concretions in Carbonates**

Oncolite-like carbonate concretions are found in the upper part of the Gaoyuzhuang Formation (the Huanxiusi Member), and they are densely accumulated in a ~12 m thick interval at the lower Huanxiusi Member. These carbonate concretions, 15–45 mm in diameter, occur in layers up to 1.6 m thick, and are commonly associated with bitumen-rich carbonate layers or blocks. Individual concretions display spheroidal shapes with faint concentric layers in the interior and are coated with 1–4 mm thick shells, but no nuclei in the center. The shells are composed of fibrous aragonites or aggregates of crystal fans.

On the bedding planes, the concretions are often expressed as small domes with 2–6 mm positive relief. The surfaces of these “domes” are either smooth, imprinted with fine radial fissures, or in a compressed donut-shape (Figs. 3A–3G, Fig. 4A), suggesting an origin related to gas domes or gas blisters (MISS; Eriksson et al., 2007; Gerdes, 2007; Noffke et al., 2001). In many cases, aragonite crystal fans occur around or near the concretions, forming isopachous cements at the outer layer of concretions (Figs. 3D and 3E). Abundant acicular aragonites (Fig. 4E), radial barites (Fig. 3B) and frambooidal pyrites are present within the concretions and in host rocks surrounding the concretions. Authigenic carbonate minerals (Pierre and Fouquet, 2007; Reitner et al., 2005a, b), such as rosette siderites (Fig. 4J), dumbbell-shaped aragonites (Fig. 4E) and ankerites (Fig. 4K), and botryoidal carbonate cements (Fig. 4F), are common in the concretions and the host rocks, suggesting carbonate precipitation from the anaerobic oxidation of methane (AOM) (Bahr et al., 2007; Jiang et al., 2006; Mazzini et al., 2006; Peckman and Thiel, 2004; Boetius et al., 2000). An AOM origin seems to be supported by the presence of microbial filaments and coccoids less than 10 μm (possibly sulfate reducing bacteria?) in both concretions and host rocks (Figs. 4H and 4I), as well as by the presence of light-colored micrite veins (Figs. 2F and 2G). The lack of nuclei in concretions and absence of scouring sedimentary structures in the host rocks, along with their large sizes, do not support an origin similar to that of the normal oncolites formed in shallow oscillating environments (Riding, 2000; Shapiro et al., 2000). Instead, the presence of well developed fine laminations and the abundance of organic matter in hosting rocks suggest that the concretions were formed in relatively deep and quiet depositional environments. The concretions are somewhat similar to those occurring in the seep facies in the Black Sea (Reitner et al., 2005a, b; Jorgensen et al., 2004; Michaelis et al., 2002) or the hydrothermal springs in Mexico Bay (Canet et al., 2003).

Dispersed authigenic carbonate minerals in sediments suggest that the concretions may have been originally formed either as gas bubbles on the sediment surface, sealed by mats, or as gas-generated cavities in sediments, which were later filled by microbially mediated carbonate precipitation (MMCP) through anaerobic methane oxidation (CH$_4$ + SO$_4^{2-}$ + Ca$^{2+}$$\rightarrow$CaCO$_3$ + H$_2$S + H$_2$O). Methane may have been generated either from anaerobic decomposition of the buried organic matter (2CH$_2$O$\rightarrow$CH$_4$ + CO$_2$) or from bacterial methanogenesis (CO$_2$ + 4H$_2$$\rightarrow$CH$_4$ + 2H$_2$O) during shallow burial (Catling et al., 2007; Claire et al., 2001).
These biochemical processes suggest that the organic accumulation at the seafloor may have been high enough to release an adequate amount of methane to create these gas bubble structures and form authigenic minerals through anaerobic methane oxidation.

Figure 3. Oncolite-like concretions and some microbial mat-related structures (MISS) from the Mesoproterozoic carbonates of the North China platform. (A) Field photo showing a 25 cm thick layer of oncolite-like concretions. The concretions have clear shells but no nuclei; (B) rosette barites in thin section of an oncolite-like concretion; (C) a 1.6 m thick layer composed of oncolite-like concretions. Faint concentric layers can be seen in these concretions; (D) compressed oncolite-like concretions on a bedding plane. The concretions have clear shells composed of aragonite fibers. The large concretion (right) is covered with aragonite fans on the surface and has marginal aragonite fringes; (E) aragonite crystal fans on the bedding plane associated with the concretions; (F–G) polished slabs showing concretions in vertical section (F) and plane section (G); (H) irregular network pattern on a bedding plane. They are interpreted as mat-protected ripple marks, somewhat similar to “Kinneyia style ripples” in morphology, but much larger in scale; (I) mat-protected ripples in vertical section. A thin mat layer is clearly visible along the upper surface of the ripples and organic-rich micrite fills in the ripple valleys and is covered by horizontal mat-layers; (J) microwrinkles on a bedding plane. (A)–(G) are from the upper part of the Gaoyuzhuang Fm., Jixian, Tianjin, and (H)–(J) are from the Wumishan Fm., West Mountain of Beijing.
Figure 4. Photographs showing mat decay structures, associated minerals, and putative bacterial fossils from the Mesoproterozoic carbonates of the North China platform. (A) Plane view of gas domes (or blisters). Radiating ruptures and central depression are present in some of the domes; (B) gas chambers beneath multi-layered microbial mats. Chambers are partially filled with barite crystal fans. Pinnacles are observable on the mat surface (upper left). Coin for scale is 2.1 cm in diameter; (C) Kinneyia-style microwrinkles. This structure may have resulted from gas-trapping beneath the microbial mats; (D) Kinneyia-style structure has resulted from gas-trapping beneath microbial mats. The irregularly shaped bulges show sharp flattened tops and steep slopes, bitumen visible in the gas pits (lower left); (E) dumbbell-shaped aragonite fiber clusters in thin section; (F) microscopic features of stromatoid micrite cement (center), botryoidal carbonate precipitation (half spheroids), Fe-rich calcite (left) and ferroan dolomite (upper right) minerals; (G) plane view of gas blisters. Most of them have central depressions suggesting collapse after gas release; (H) putative filamentous microbial fossil; (I) putative coccoidal microbial fossil; (J) rosette siderite mineral aggregation; (K) ferroan dolomite crystal with dark, iron-rich rings. (A), (D), (E), (F), (G), (H), and (I) are from the Gaoyuzhuang Fm., Jixian, Tianjin; (B) is from the Wumishan Fm., Laishui, Hebei Province; and (C), (J) and (K) are from the Wumishan Fm., West Mountain of Beijing.
A comprehensive sedimentary study of the upper Gaoyuzhuang Formation has suggested that it was deposited in relatively deep water, below the fair-weather wave base (Mei et al., 2007; Song, 2007). In stratigraphic intervals containing oncolite-like concretions, no sedimentary structures or particles indicative of high-energy water conditions have been observed. Instead, well-developed, fine laminations and relatively rich organic matter and mud suggest deposition from relatively deep and quiet water environments, far from the shore. According to the paleogeographic reconstruction of the Mesoproterozoic in the North China platform (Qiao et al., 2007; Ma et al., 2002), the Gaoyuzhuang Formation and its equivalents have the widest distribution on the platform and were formed during platform-wide transgression. On the basis of regional stratigraphy and facies analysis, the Huanxiusi Member has been considered as a deposition that had formed during the late stage of a transgressive systems tract in the formation (Mei et al., 2007), possibly deposited in a shallow epeiric marine environment with water depth of 30–120 m. The oncolite-like concretions may have been formed close to the maximum flooding surface, in environments below the storm wave base.

It has been argued that the Mesoproterozoic ocean was in a permanent stratified state globally, with only its upper portion moderately oxidized (Holland, 2006; Javaux et al., 2004), and the lower portion remaining anoxic and sulfidic (Rouxel et al., 2005; Anbar and Knoll, 2002; Shen et al., 2002). The oxycline in the ocean at that time was probably less than 20 m below the water surface (Brocks et al., 2005). In the Mesoproterozoic, the ocean had a sulfate concentration of 0.5–2.5 mM (Catling et al., 2007; Kah et al., 2004), higher than that of the Archean to Paleoproterozoic (< 200 μM, Habicht et al., 2002), but 10–50 times lower than that of the present ocean (28 mM, Catling et al., 2007). In the modern ocean, due to the high sulfate concentration, the sulfate-methane transition zone (SMTZ) can reach downwards a depth of 4 m below the sedimentation-water interface (Catling et al., 2007; Claire et al., 2006). In this case, a major part of the burial organic matter will be converted into methane through fermentation and by active bacteria sulfate reduction (BSR), and nearly all the methane (about 99%) generated through methanogenesis will be consumed by AOM (Catling et al., 2007; Zanhle et al., 2006), unless the deposition rate is very high. In the Archean to Paleoproterozoic ocean, due to extremely low sulfate concentration, the SMTZ is narrowed to a depth less than a few centimeters below the sediment surface, so that no significant AOM occurs and most of the methane generated will be released into the atmosphere (Catling et al., 2007), resulting in a very high atmospheric methane concentration of 10^5–10^4 ppmv (Holland, 2006; Kasting, 2004). Considering that the Mesoproterozoic ocean was in a transitional state with sulfate concentration between the Archean and present, it might be reasonable to deduce that only part of the buried organic matter will be converted into methane and half of the latter will be consumed by AOM, with the SMTZ probably around ten centimeters downwards below the sediment surface. This probably implies that the methanotrophs will be much more prolific than those in the modern ocean and the resultant organic burial in the Mesoproterozoic ocean will be considerably high.

The oncolite-like concretions in the Upper Gaoyuzhuang Formation have probably been formed by microbes in a methane-rich shallow sea involved with anaerobic oxidation of methane. The shells coated on the concretions possibly represent microbial mats that have been replaced by the MMCP (Figs. 2A, 2C, 2D), whereas, the interior layers of concretions probably originated from the fills of methane-derived carbonate precipitation into the cavities created by gas expansion (Figs. 2F–2G). The morphology and mineral composition of these concretions are similar to the carbonate concretions found in the seep facies of the Black Sea (Reitner et al., 2005a, b) and other places (Bahr et al., 2007; Gontharet et al., 2007; Pierre and Fouquet, 2007), particularly reminiscent of the carbonate nodules and crusts illustrated by Michaelis et al. (2002), which have been explained as the products of active microbes fueled with methane and authigenic carbonate precipitation. The organic-rich hosting carbonates and the oncolite-like concretion layers in the upper part of the Gaoyuzhuang Formation, therefore, can be taken as one of the most
prospective potential source rocks in the Mesoproterozoic carbonates of the North China platform, and deserve further investigations in detail.

**Microbially Induced Sedimentary Structures (MISS) in Carbonates**

Microbial mats are organic-rich layers formed by microbes and their extracellular polymeric substances (EPS) through binding, trapping, and baffling sediments at the water/sediment interface (Noffke et al., 2003, 2001; Gerdes et al., 2000). In the present world, they can occur in a broad variety of environments, including mid-ocean ridges, hot springs, hypersaline lakes, deserts, ice-sea, and euxinic waters (Gerdes, 2007; Schieber, 2007). The most successful mat-producers are cyanobacteria, due to their high tolerance and wide adaptability. In normal marine environments, the majority of mats will be consumed by metazoan grazing or destroyed by aerobic degradation prior to burial, and can rarely be preserved as direct sedimentary records. In contrast, in anoxic/dysoxic, sulfidic, and super-salinity waters, where metazoans are largely depressed, microbial mats are often well developed and have a great potential to be preserved. In the Phanerozoic, mat-related structures have been reported from the lowermost Triassic (Pruss et al., 2004), Lower Silurian (Pflüger, 1999), and upper Famennian (Michael et al., 2002), and are explained as the consequences of biotic mass extinction and as the indicators for high-stressed environments (Kershaw et al., 2007; Wang et al., 2005).

In the Precambrian, microbial mats must be widespread on the seafloor, but their identification is still a challenge. MISS, as a significant supplement to microbial buildups, has been taken as one of the important biosignatures for ancient microbial communities and mats (Noffke and Paterson, 2008; Noffke et al., 2003, 2001; Gerdes et al., 2000) and has drawn extensive attention in recent years (e.g., Noffke and Paterson, 2008; Porada et al., 2008; Sarkar et al., 2008, 2006; Shi et al., 2008; Eriksson et al., 2007; Gerdes, 2007; Mei et al., 2007; Porada and Hafid, 2007; Schieber, 2007, 1999; Noffke et al., 2006, 2003; Shi and Chen, 2006; Draganits and Noffke, 2004; Noffke et al., 2003, 2001; Gerdes, 2007; Mei et al., 2007; Porada and Hafid, 2007; Schieber, 2007, 1999; Noffke et al., 2006, 2003; Shi and Chen, 2006; Draganits and Noffke, 2004; Pruss et al., 2004; Pflüger, 1999). Most of the reported MISS are from siliciclastics, especially peritidal sandstones, whereas, those in the carbonates have rarely been dealt with, except for microbial buildups and biolaminite. Here the authors report some of the MISS found in the Mesoproterozoic carbonates of the North China platform, following the genetic classification scheme proposed by Schieber (2007, 2004) and Eriksson et al. (2007).

**Mat metabolic structures**

Structures related to the metabolism of the growing mat are mainly derived from the mineral precipitation effects caused by metabolic processes such as photosynthesis, and the floating grains trapped by microbial filaments. Some authigenic carbonate precipitations, such as, botryoidal micritic to cryptic carbonate cement between terrigenous grains, very early diagenetic dolomite, some irregular ooids, stromatactis-like cryptic carbonate cement in organic-rich layers, and organically coated grains, have been taken as indicators for mat metabolisms (Eriksson et al., 2007; Gerdes, 2007; Draganits and Noffke, 2004; Noffke et al., 2003, 2001; Bouougri and Porada, 2002). The highly lamina-conformable distribution of pyrite may also reflect the metabolic activity of sulfate-reducing bacteria beneath the photosynthetic surface layer of the mat (Schieber, 2007). These structures have been widely recognized in carbonates from the Wumishan and Gaoyuzhuang formations. Particularly well-preserved forms are included in petrified mats (Figs. 4E–4F, 4J–4K) and microbial buildups (Figs. 2D, 2F). Some of the fabrics in oncolite-like concretions (Figs. 3F–3G) described in the previous section are also considered as a type of metabolic structures.

**Mat growth structures**

Mat growth-related structures are created by the changes in microbial activity, growth direction, and growth rate, in response to the environmental factors (Gerdes, 2007), and by the interplay between microbes and sedimentation (Eriksson et al., 2007). They often show as minute pustules, tufts, and pinnacles, as well as polygonal growth ridges, on the bed surface. Mat growth structures are well observed in modern microbial mats of tidal flat environments.
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Figure 5. Photographs showing mat growth and destruction structures from the Mesoproterozoic carbonates of the North China platform. (A) Plane view of irregular growth ridges on mat-surface, forming a network pattern; (B) irregular polygonal syneresis cracks with thin, ‘blotting paper’ like laminae on the bedding plane. Pen for scale is 14 cm long; (C) plane view of worm-shaped syneresis cracks with curled margins; (D) silicified mat chips. Sub-vertical arrangement of mat chips that may have resulted from reworking of microbial mats by storms contrasts with the underlying horizontal mat-layers; (E) large round-crested growth ridges (biogenic petees) with cracks visible on the ridge tops; (F) Machuriophycus structure. The sinuous syneresis cracks occur along ripple valleys but rarely on ripple ridges. (A) and (C) are from the Wumishan Fm., West Mountain of Beijing; (B) and (D) are from the Wumishan Fm., Laishui, Hebei; (E) and (F) are from the Tieling Fm., West Mountain of Beijing. Coin for scale is 2 cm in diameter.

(Gerdes, 2007; Noffke et al., 2001; Gerdes et al., 2000), but Precambrian examples have rarely been documented. The identified growth ridges in the Wumishan Formation are about 1–3 mm high and 2–4 mm wide, forming an irregular network with the reticulations less than 1 cm on bedding planes (Fig. 5A). Along the growth ridges, tiny pinnacles or pustules can be observed occasionally. In a vertical
cross section, they may show as irregularly spaced crenulations. In a few cases, due to the localized overgrowth and lateral expansion, large and round-crested petees (not tepees, Eriksson et al., 2007) are formed (Fig. 5E). The round-crested petees recognized in the Tieling Formation are 1–4 cm high and 2–6 cm wide, and can form polygonal patterns (Fig. 5E), which are very similar to those reported by the coastal sabkhar of Tunisia (Gerdes, 2007; Porada and Hafid, 2007). Cracks that develop on the petee ridges (Fig. 5E) suggest that the latter are derived from the folding and protection of mats. Mat-protected ripples (Figs. 3H, 3I) are quite common in the Wumishan and Gaoyuzhuang formations. Due to the protection of mat layers, previously formed ripple marks are protected from wave erosion (Fig. 3I) and are superimposed with subsequent ripple marks, forming irregular network patterns (Fig. 3H). These structures are commonly considered as a type of mat growth structure (Eriksson et al., 2007).

**Mat destruction structures**

Physical destruction of mats creates a broad range of structures that may occur in situ or may be found as redeposited materials (Eriksson et al., 2007). Variably shaped syneresis cracks, curled crack margins, mat chips, mat roll-ups, and some of the microwrinkles are the most commonly recognized destruction structures in the Precambrian strata, especially in siliciclastics. Microwrinkles result from slight movement and deformation of microbial mats. Mat roll-ups and small mat fragments are more often observed in argillaceous sediments of quiet, deep subtidal environments. Whereas, syneresis cracks are commonly found in the upper intertidal to supratidal tidal flat, and larger mat chips and reworked fragments are often found in high-energy environments. In the Wumishan Formation, mat chips (Fig. 5D), syneresis cracks with “blotting paper” like laminae (Fig. 5B) and curled crack margins (Fig. 5C) have been recognized on the bedding planes. Small mat fragments with clear frayed edges are identified in the thin section. The *Manchuriophycus* structure has been recognized from the dolomite of the Tieling Formation (Fig. 5F). This kind of structure is characterized by sinuous ridges waving in ripple valleys, but rarely on ripple ridges. They have been widely reported in Precambrian sandstones (Sarkar et al., 2008, 2006; Eriksson et al., 2007; Pruss et al., 2004), but not known in carbonates. A *Manchuriophycus*-style structure had been interpreted as resulting from thicker mats developed within the troughs, between ripples (Eriksson et al., 2007). In some cases, subcircular or “8-shaped” features are formed in sandstones (Shi et al., 2008; Eriksson et al., 2007; Pflüger, 1999).

**Mat decay structures**

These refer to the structures formed on the sediment surface or within sediments by gas and fluid escapes (Dornbos et al., 2007; Noffke et al., 2001; Gerdes et al., 2000). Gases may be derived from the decay of buried microbial mats or directly from microbial photosynthesis. Due to the sealing of impermeable mats on the sediment surface, the escaping gas will push the mat upward to form various domes or blisters. If the mat is thin or the upward-rising gas pressure is high enough, the sealing mat will break, resulting in “mud-volcano” structure or partially ruptured ‘Astropolithon’ structure (Sarkar et al., 2008; Eriksson et al., 2007; Pflüger, 1999). After compaction, they may express as biscuit-like and donut-shaped structures on the bedding plane. *Kinneyia*-style ripples are explained to result from gas trapping beneath the mats (Porada et al., 2008; Pflüger, 1999). In a broad sense, some of the fabrics caused by the precipitation of anoxic minerals such as pyrite, siderite, and ferroan dolomite may also be included in this category (Eriksson et al., 2007). It has been reported that in modern tidal flats and swamps, microbes can grow on gas bubbles, so that the bubbles are coated with and protected by leathery biomats (Eriksson et al., 2007; Gerdes, 2007). These microbially coated bubbles can be filled later with sediments and therefore have the potential of preservation in sediments. Gas dome structures are abundant in the carbonate of the Gaoyuzhuang Formation (Figs. 4A and 4G); some of them can be observed with radial cracks/ruptures on the top surface (Fig. 4A) and others have central depressions or pits (Fig. 4G). Structures similar to *Kinneyia* ripples have been found in the Gaiyuzhuang Formation (Fig. 4D).
In this structure well-developed bulges have sharp flattened tops and steep slopes, but they differ from the typical Kenneyia structures (e.g., Porada et al., 2008; Bouougri and Porada, 2007; Pflüger, 1999), in that they do not have continuous ridges. The authors interpret this structure as resulting from gas trapping beneath the mat. In the pits around the bulges of the structure, bituminous matter is clearly visible (Fig. 4D). Two kinds of mat decay structures are found from the Wumishan Formation (Fig. 1), one of them resembles the Kinneyia-style microwrinkles (Fig. 4C) and the other apparently represents the gas chambers below the multilayered microbial mats (Fig. 4B). Minute pinnacles can be observed on the mat surface and barite fans are preserved in the gas chambers underneath the mat layers (Fig. 4B).

HYDROCARBON-GENERATION POTENTIAL OF MICROBIAL MATS

In the study of petroleum geology, extensive attention has been focused on hydrocarbon source rocks as they have constituted the basis for oil-gas generation (Zhang et al., 2006; Jin and Wang, 2004). In practice, however, the evaluation of source rocks heavily relies on the remnant organic matter in sediments as indicated by the TOC value, which partly depends on the absorption of clay minerals in the sediments (Qin et al., 2007; Zhang et al., 2006). In carbonates, due to the lower clay content, the TOC is generally lower than that in the argillaceous sediments (Qin et al., 2007; Jin and Wang, 2004), though significant oil-gas reservoirs have been found in the carbonates, such as those in the Triassic of South China (Ma et al., 2005), the Upper Carboniferous of the Tarim basin (Jin and Wang, 2004), and the Proterozoic carbonates of the Siberia platform (Qin et al., 2006). In fact, the TOC may largely indicate the organic carbon left in the rocks after hydrocarbon discharge, and not the organic carbon amount that had been involved in hydrocarbon generation. As a significant supplement to the traditional inverse methodology, a forward analytic method for evaluating hydrocarbon source rocks has recently been suggested, with special emphasis on the geobiological processes (Xie S C et al., 2007; Xie X N et al., 2007). According to the ideas in this forward method, the primary production and potential burial of organic matter, along with the redox state in depositional environments are critical for source rock evaluation.

In the Mesoproterozoic carbonates of the North China platform, the mat-related structures are abundant in addition to the microbial buildups. In the lower-middle parts of the Wumishan Formation, according to the statistics in a stratigraphic interval of 120 m thickness, the mat layers can occupy 5%–15% of the total thickness, with the thickest single mat layer up to 5 cm. If 25% area of the North China platform (approximately $1.2 \times 10^5$ km$^2$, Ma et al., 2002) is covered with this 120 m of mat-rich carbonates (this is a minimum estimation), a rough total mat volume of $3.6 \times 10^{11}$ m$^3$ (calculated from: $120 \times 10^5 \times 25\% \times 1.2 \times 10^5$ m$^2$) will be obtained. It has been estimated that in the Black Sea, the bacterial cells in the microbial mats are as much as $10^{12}$ cell/cm$^3$, which corresponds to about 25 mg/cm$^3$ of the organic carbon (Michaelis et al., 2002). The authors do not have the number of bacterial cells in the Mesoproterozoic microbial mats, but reasonably assume that they will not be significantly less than those in the Black Sea mats (Pavlov et al., 2003). Thus, the authors have a rough amount of $9 \times 10^9$ t of burial organic carbon ($25 (mg/cm^3) \times 3.6 \times 10^{17} (cm^3)$) that would potentially be stored in the carbonates of the calculated 120 m thick strata originally. However, it must be kept in mind that not all of the buried organic carbon will be retained till the late thermolysis stage and will be subsequently converted into hydrocarbon. Instead, a majority will be lost through various processes in the diagenetic and postdiagenetic stages. If a very rough estimation is made that the oil-generation ratio is 1.5 kg/t for the buried organic carbon (this is an average amount for hydrocarbon source rocks dominated by type-I and type-II kerogens, and should be a minimum value for the oil-production ratio of the buried net organic carbon), then a potential oil-generation amount over $13.5 \times 10^6$ t can be obtained for the carbonate of 120 m, in the lower-middle Wumishan Formation. For the whole formation (about 3 500 m), the potential oil-generation amount would be $\sim 4 \times 10^8$ t.

For the Gaoyuzhuang Formation, the lower portion of the Huanxiusi Member in the upper part of the formation is taken as an example. As mentioned
earlier, the lower 12 m of the Huanxiusi Member is characterized by dense oncolite concretions and is highly rich in organic matter. An estimation on the microbial mats and mat-related carbonates accounts for about 25% of the total carbonate by, again, taking the organic carbon content in the biomats of the Black Sea as a reference. Assuming that the other factors are the same as those used for the Wumishan Formation, the amount of buried organic matter in this portion would be \(-0.9 \times 10^{11} \text{ m}^3\) (calculated by 12 m \(\times\) 25% \(\times\) 25% \(\times\) 1.2 \(\times\) 10\(^{11}\) \text{ m}^2) and the total potential amount of burial organic carbon would be \(-2.25 \times 10^9 \text{ t}\) (25 (mg/cm\(^3\)) \(\times\) 0.9 \(\times\) 10\(^{17}\) (cm\(^3\))) in this 12 m thick carbonate strata. Such an amount of burial organic matter would have a potential to generate 3.4 \(\times\) 10\(^6\) t of oil at least. The Gaoyuzhuang Formation is about 1 600 m in thickness, thus the total potential amount of oil-generation would be \(-4.4 \times 10^8\) t.

Apparently, the above estimation on the potential of hydrocarbon generation may not be taken as a precise calculation and a final evaluation, as it involves many uncertain factors. It should be noted, however, that the authors have based this estimation only on the visible mat-related layers, whereas, the scattered organic matter in rocks has not been taken into consideration, and the hydrocarbon-generation ratio for the buried organic carbon may have largely been underestimated. By adding together the Tuanshanzi and Tieling formations, a minimum of 10 \(\times\) 10\(^6\) t of oil could be the total potential hydrocarbon production for the Mesoproterozoic carbonates of the North China platform.

CONCLUDING REMARKS

Microbial mats and microbially induced sedimentary structures (MISS) are abundant in the Mesoproterozoic carbonates of the North China platform. Thriving microbial communities and their active metabolisms imply a high primary production and a large accumulation of organic matter on the sea floor. A general anoxic and sulfidic state in the lower water column of the Mesoproterozoic ocean and absence of metazoan consumption may result in a high burial ratio of organic matter in sediments.

With a low sulfate concentration, less than 10% of the modern ocean, the sulfate-methane transition zone (SMTZ) below the sediment surface in Mesoproterozoic oceans would be considerably thinner than that in the Phanerozoic oceans. This may imply that the methane generated from bacterial methanogenesis on the sedimentary surface and in the sediments would have a greater potential to release, resulting in a methane-rich atmosphere and warm climate. It seems that the widespread, mat-rich Mesoproterozoic carbonates in the North China platform could have a great potential for hydrocarbon generation, if the buried organic matter could partly retain to the post-diagenetic stage and be subjected to kerogen pyrolysis. Based on the petrified microbial mats in the carbonates and their corresponding organic carbon content, a potential hydrocarbon production of 10 \(\times\) 10\(^8\) t has been estimated for the Mesoproterozoic carbonates in the North China platform. Although this is by no means a precise and final evaluation, it may provide a first-order reference from the angle of forward analysis method for future study and exploration. The lower-middle parts of the Wumishan Formation and the upper part of the Gaoyuzhuang Formation are especially rich in petrified mats and organic matter, and may have a greater potential for hydrocarbon-generation. These two formations need to be further studied and explored in more comprehensive ways.

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