Organomineralization in Mesoproterozoic giant ooids

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A B S T R A C T

Ooids are common carbonate particles that are traditionally considered as abiotically formed by physical and chemical processes in highly agitated environments. Recent studies point to the importance of microbial activities in ooid formation, but more case studies are required to confirm and clarify the roles of microbes and their organomineralization processes. Here we report an integrated petrographic, element geochemical, and isotopic study of Mesoproterozoic giant ooids from the Wumishan Formation (ca. 1.50–1.45 Ga) of North China. The Wumishan giant ooids (2.0–14.4 mm) are composed of small micritic nuclei and thick radial fibrous cortices. Abundant organic relics, including putative bacterial filaments and mucus-like extracellular polymeric substances (EPS), are present in ooid cortices, Organominerals (e.g., nanoparticles and polyhedrons) are concentrated and lined with the axes of radial fibers, suggesting in situ mineralization of bacterial filaments. The abundance of organic relics and fiber-aligned organominerals confirms the constructive roles of microbes in the formation of the Wumishan giant ooids. The preservation of bacterial filaments/filament bundles in their growth orientation requires fast mineralization in CaCO3-supersaturated environments, which may have been controlled by the shallow chemocline in redox-stratified Mesoproterozoic basins.

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1. Introduction

Ooids are common carbonate particles that are distinguished from oncoids by their smaller (<2 mm) size, smooth surface, and evenly spaced concentric cortical laminae (e.g., Peryt, 1983; Flügel, 2004; Zhang et al., 2014). Unlike oncoids, whose microbial origin has been generally accepted, ooids are traditionally considered to be of abiotic origin, mainly controlled by alkalinity, availability of nuclei, and water-column agitation (e.g., Davies et al., 1978; Tucker and Wright, 1990).

“Giant ooids” refer to marine coated grains that are larger than 2 mm in diameter but virtually have the same interior textures as normal-sized ooids (e.g., Sumner and Grotzinger, 1993; Trower and Grotzinger, 2010; Li et al., 2013). Although the term “pisoids” has been used for coated grains larger than 2 mm in size, many have suggested that “pisoids” be used for large coated grains formed in freshwater or terrestrial environments (Tucker and Wright, 1990; Flügel, 2004), particularly those related to pedogenic carbonates (Peryt, 1983; Flügel, 2004).

Giant ooids are mostly reported from Neoarchean and Neoproterozoic successions (e.g., Simonson et al., 1993; Sumner and Grotzinger, 1993; Trower and Grotzinger, 2010); their paucity in Mesoproterozoic and Phanerozoic carbonates remains an intriguing question (Grotzinger and James, 2000). Based on numerical modeling, Sumner and Grotzinger (1993) concluded that low nuclei supply, high cortical growth rate, and high water agitation are required conditions for ooid formation, particularly for large (giant) ooids. As agitated water-column conditions are not uniquely attached to any particular geological time period, the abundance of giant ooids in Neoarchean and Neoproterozoic successions may have been related to special biogeochemical and/or environmental conditions (Grotzinger and James, 2000; Trower and Grotzinger, 2010).

Recent studies emphasize the role that microbes play in the formation of ooids. Laboratory experiments have successfully synthesized oolitic coatings at the presence of microbial communities, during which carbonate precipitation is seen to closely follow the arrangement of microbial cells (Brehm et al., 2004, 2006). In situ experiments in western Lake Geneva, Switzerland, demonstrate that photosynthetic microbial community mediates carbonate
precipitation in the early stages of freshwater ooid formation (Plée et al., 2008, 2010). Subsequent study from the same lake shows that ooid cortex formation involves a microbially induced amorphous Mg-Si phase prior to the phase transformation to low-Mg calcite (Pacton et al., 2012). Lipid biomarker study of modern marine ooids from Highborne Cay, Bahamas, reveals the presence of highly diversified microbes (Diaz et al., 2013; Edgcomb et al., 2013; Summons et al., 2013) and a variety of functional genes (Diaz et al., 2014) in ooid cortices. Microscopic study of Early Triassic ooids suggests that their finely laminated, cloudy micritic mineralization of degraded biofilms (Kahle, 2007).

In spite of increasing evidence for microbial involvement in ooid formation, some researchers have argued that existing evidence are insufficient to confirm the biogenic origin of ooids, particularly for ancient ooids (e.g., Duguid et al., 2010). Major uncertainties include: (1) laboratory conditions may not be representative of those from natural environments and (2) biomarkers detected from ooids may record organic molecules in the environment and not necessarily from ooid-forming microbes. Based on stable isotopes and trace element analyses coupled with SEM observation, Duguid et al. (2010) conclude that, instead of constructive roles in ooid formation, microbes may have altered the texture and chemistry of ooids through boring during early diagenesis.

Reconciliation of contrasting views on the role of microbes in ooid formation requires more case studies of modern and ancient ooids. In this paper, we report an integrated petrographic, elemental, and isotopic study of giant ooids from the Mesoproterozoic Wumishan Formation of the North China Platform. These giant ooids are closely associated with seafloor crystal fans and form the incipient nuclei of microdigitate stromatolites (MDS), which demonstrates, for the first time, the growth path from giant ooids to MDS. We provide evidence for intensive organomineralization during the formation of giant ooids.

2. Geological setting and occurrence of giant ooids

2.1. Stratigraphy and age constraints of the Wumishan Formation

The Wumishan Formation (ca. 1.50–1.45 Ga) is one of the most widespread Mesoproterozoic carbonate units in the North China platform. It is dominated by peritidal carbonates and is rich in various microbialites including stromatolites (Tang et al., 2013a), thrombolites (Tang et al., 2013b,c), and biolaminates (Tang et al., 2014). The lithological content, paleogeographic reconstruction, and age constraints of the Wumishan Formation have been discussed in detail elsewhere (Tang et al., 2013b).

2.2. Occurrences of giant ooids

Giant ooids studied in this paper are mainly from the upper part of the Second Member of the Wumishan Formation at Yesanpo, Hebei Province, and Shidu, suburb of Beijing (Fig. 1). In these areas, ooid-hosting strata are dominated by dolostones that form numerous meter-scale shallowing-upward parasequences (Tang et al., 2013b; Fig. 2). Common lithofacies in these parasequences include tabular thrombolites, oolites (Fig. 3A), dolarenites, dark biolaminates (Fig. 3B and C), cherty and mat-rich dolostones, and argillaceous dolostone (Table 1). The general features of these facies and their depositional environments are briefly summarized in Table 1. Giant ooids, tabular thrombolites and dark biolaminates commonly form the lower parts of parasequences, and they are interpreted as subtidal shelf lagoon deposits. Normal-sized ooids, dolarenites to dolorudites, cherty and mat-rich dolostones constitute the middle parts of parasequences, likely deposited in upper subtidal to intertidal environments. Argillaceous dolostone commonly occurs in the uppermost part of parasequences, and is interpreted to have formed in upper intertidal to supratidal environments (Table 1).

Ooids in the Wumishan Formation are of different sizes and occur in varying depositional environments. Normal-sized ooids (<2 mm) form medium layer with clear cross-bedding (Fig. 3A) in highly agitated environments of the upper subtidal to lower intertidal zones. Slightly larger ooids (<3.8 mm) are found in lenses (Fig. 3C) or as thin interbeds (Fig. 3D) in dark biolaminites of the shelf lagoon environment (Tang et al., 2014). Giant ooids (<14.4 mm) occur within medium to thick (0.6–1.8 m) beds (Fig. 3E and F) that were most likely deposited within the lower part of the upper subtidal zone.

The growth pattern of ooids and their relationship with MDS are best exemplified in well-preserved centimeter-scale interbeds (Fig. 3D). Small ooids are overlaid on mm-thick isopachous fibrous aragonite (pseudomorph) crusts (Fig. 3G) and some ooids form the nuclei of small MDS (Fig. 3H). Overlying the small ooids and MDS are giant ooids and small MDS that grade upward into small ooids and fibrous crusts (Fig. 3D). This cycle likely reflects the controls from hydrodynamics on the development of fibrous crusts, ooids and MDS. MDS are possibly formed when ooids cannot be rolled and then ooids serve as nuclei for the subsequent growth of the MDS (Fig. 3H). The close association of normal-sized ooids, giant ooids, MDS, and fibrous crusts suggests environments that were highly supersaturated with carbonate and possibly rich in microbes.

2.3. Facies associated with giant ooids

Giant ooids are interbedded or inter-fingering with millimeter- to centimeter-scale fibrous aragonite crusts. Microscopic observation shows that the crusts are predominantly composed of vertically arranged fibrous aragonite (pseudomorph) (Fig. 4A). Similar crystal fans are also seen in thin crusts within dark biolaminites (Fig. 4B and C). The fibrous fans associated with giant ooids are morphologically similar to those observed in late Archean–early Paleoproterozoic carbonates (e.g., Sumner and...
but they are much smaller in size. In addition, flat-pebble conglomerates are also observed in cherty and mat-rich dolostone layers (Fig. 4D). The thickness of individual pebbles in flat-pebble conglomerate is 0.5–3 mm, much thinner than those reported from lowermost Triassic sediments (Wignall and Twitchett, 1999; Myrow et al., 2004; Woods and Baud, 2008).

Fig. 2. Parasequences of giant ooid-hosting strata and their depositional environments from the upper part of the Second Member of the Wumishan Formation at Yesanpo, Hebei Province.
3. Materials and methods

Most samples were collected from the Yesanpo area, Hebei Province (GPS: 39°39'45"N, 115°27'40"E, 215 ± 15 m; Fig. 1). Some samples were collected from Shidu, suburb of Beijing (GPS: 39°38'21"N, 115°32'43"E, 179 ± 12 m; Fig. 1). For comparison purposes, some giant ooids from Middle Cambrian strata in Northwestern China and from Lower Triassic strata in South China were also investigated. A 72-m-thick interval that contains several layers of giant ooids at Yesanpo was logged and systematically sampled (Fig. 2). A total of 100 samples were collected and 50 of them were thoroughly studied using light microscopy, FESEM, Raman spectrometry, ICP-MS, and isotope analyses.

Macroscopic features of the giant ooids were observed in both outcrops and on polished slabs. Microfabrics were examined in thin sections using a Zeiss Axio Scope A1 microscope and fluorescent microscope. Thin sections used for ultra-fabric analysis were cleaned in deionized water for 3 min using an ultrasonic cleaner to remove potential contaminants on sample surfaces. The ultra-fabrics were analyzed using a Zeiss SUPRA 55 FESEM, and micro-zone elemental composition was analyzed by EDS at the China University of Geosciences (Beijing). In order to get better
results, both thin sections and freshly broken sample fragments were used, and they were coated with platinum prior to FESEM analysis.

Non-skeletal carbonates may potentially record seawater REE + Y patterns (e.g., Webb and Kamber, 2000; Kamber and Webb, 2001; Nothdurft et al., 2004), but they are vulnerable to contamination from terrigenous sediments, particularly clay minerals (e.g., Van Kranendonk et al., 2003; Olivier and Boyet, 2006; Ling et al., 2013). In order to avoid the influence of terrigenous sediments on REE + Y, we dissolved the carbonates using acetic acid. In preparation for REE + Y analyses, each sample was cut into two chips to avoid weathered surfaces; polished chips were drilled for powders, avoiding recrystallized areas. About 0.05 g of powdered sample was placed in a 50 ml centrifuge tube, followed by the addition of ~40 ml water and 500 ng Rh internal standard. Next, 2.5 ml acetic acid (98%, purified by sub-boiling) was added to dissolve the carbonate. The solution was diluted to 50 ml. The sealed tube was vibrated for about 1 h and then centrifuged for 3 min at 3000 rpm. The upper layer of solution was used to measure trace elements in a Bruker Aurora M90 ICP-MS at the Institute of Geochemistry, Chinese Academy of Sciences. The accuracy of the ICP-MS analyses was better than ±5–10% (relative) for most analyzed elements.

Well preserved samples were chosen for Raman spectrum analyses. Putative biogenic filaments and abiogenic microspars (for comparison) in thin section were examined by a LabRAM HR800 Raman spectrometer at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The Raman microscope operated confocally at laser wavelength of 532 nm, giving a spectral resolution better than 1.5 cm\(^{-1}\). High-magnification (100×) objective lenses were used; the spectral spot is 1 \(\mu\text{m}\). Each spectrum had about 1 min of total scan time.

Sample powders for carbonate carbon isotope analyses were drilled from clean and polished slabs. Isotopic results are expressed

### Table 1

<table>
<thead>
<tr>
<th>Lithological facies</th>
<th>General features</th>
<th>Position in a parasequence</th>
<th>Depositional environment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tabular thrombolites</td>
<td>0.3–3.0 m in thickness, tabular in morphology with irregular mesoclots, but no disturbed sedimentary structures</td>
<td>Lower</td>
<td>Deep subtidal environment with low energy</td>
<td>Tang et al. (2011, 2013b,c)</td>
</tr>
<tr>
<td>Dark biolaminites</td>
<td>0.4–1.8 m in thickness, characterized by alternating dark fibrous and light micritic laminae, without recognizable disturbed sedimentary structures</td>
<td>Lower</td>
<td>Submarine lagoon behind oolitic shoals</td>
<td>Tang et al. (2014)</td>
</tr>
<tr>
<td>Giant ooids</td>
<td>0.6–1.8 m in thickness, ooids commonly ~0.4 cm in diameter, matrix mainly micrites with some microspar, occasionally with some intraclasts</td>
<td>Lower</td>
<td>Moderately agitated subtidal environments, occasionally influenced by storms</td>
<td>This paper</td>
</tr>
<tr>
<td>Normal-sized ooids</td>
<td></td>
<td>Middle</td>
<td>Agitated upper subtidal to lower intertidal environments</td>
<td>Tang et al. (2013c)</td>
</tr>
<tr>
<td>Dolarenites to dolorudites</td>
<td>0.2–0.4 m in thickness, ooids commonly 0.1 cm in diameter, matrix with some intraclasts, herringbone and low-angle cross-bedding</td>
<td>Middle</td>
<td>Upper subtidal to lower intertidal</td>
<td>This paper</td>
</tr>
<tr>
<td>Dolostone locally rich in chert-bands and microbial mats</td>
<td>0.5–3.0 m thick-bedded micritic dolostone, rich in mat layers, with small domal stromatolites and flat-pebble-like intraclasts</td>
<td>Middle</td>
<td>Intertidal</td>
<td>Tang et al. (2011, 2013b,c)</td>
</tr>
<tr>
<td>Argillaceous dolostone</td>
<td>0.1–0.4 m in thickness, halite pseudomorphs, mud-cracks and mat shrinkage visible</td>
<td>Upper</td>
<td>Upper intertidal to supratidal setting</td>
<td>Shi and Jiang (2011) and Tang et al. (2011, 2013b,c)</td>
</tr>
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</table>

**Fig. 4.** Facies associated with the Wumishan giant ooids. (A) Microscopic texture of the fibrous crust, showing aragonite (pseudomorph) microfabrics. (B) A 7-cm-thick layer of seafloor aragonite fans in dark biolaminite. (C) A 3-cm-thick layer of seafloor aragonite fans arranged in a row in dark biolaminite. (D) Suberect flat pebbles in a flat pebble conglomerate layer.
in the standard notation as per mil (‰) deviation from VPDB. All the analyses were performed at the China University of Geosciences, Beijing. For δ^{13}C_{carb} and δ^{18}O_{carb} analyses, approximately 200 μg carbonate powder was reacted with orthophosphoric acid for 10 min at 70°C in a Gilson 222 autosampler automatically connected to an Isoprime mass spectrometer. Analytical uncertainties determined by duplicate measurements of NBS-19 and an internal standard are better than 0.15‰ for both δ^{13}C and δ^{18}O.

4. Results

4.1. Macroscopic features of giant ooids

Giant ooids from the study area are generally spherical to elliptical in shape, varying from 2.0 mm to 14.4 mm in size (Fig. 3D and E), with a mean diameter of 4.0 mm. The ooids have smooth surfaces, and are typically composed of a small micritic nucleus (0.4–2.7 mm) and a thick cortex (1.7–5.0 mm) characterized by radial fibrous aragonite (pseudomorph) with faint concentric laminae (Fig. 3F). Compared with the Middle Cambrian giant ooids from Ningxia, northwestern China and those from the Lower Triassic of South China (Mei and Gao, 2012; Li et al., 2013), the Wumishan giant ooids are obviously larger in average size, with a much higher ratio of cortical thickness to nucleus diameter (~4.0). In addition, cortices in the Wumishan giant ooids show more distinctive radial fibrous features (Fig. 3F).

Two distinct growth patterns have been observed in the giant ooids: (1) in moderately agitated environments, ooids are commonly larger in size, but retain a spherical morphology (Fig. 3E; growth path I in Fig. 5A); (2) in less agitated environments, ooids tend to change from spherical to ellipsoidal shapes (Fig. 3D; growth path II in Fig. 5A). In the latter case, many ooids show a successive development from normal-sized spherical (Fig. 5B) to giant spherical (Fig. 5C), then to ellipsoidal shapes (Fig. 5D–G), and finally to minute columnar morphology (Fig. 5H and I). These features indicate that some giant ooids served as nuclei for the subsequent growth of MDS (Fig. 5J).

4.2. Microscopic textures of giant ooids

Texturally, individual giant ooids commonly consist of a micritic nucleus and a fibrous cortex (Fig. 6A and B). Occasionally a giant ooid can have multiple nuclei surrounded by a common cortex (Fig. 6C).

4.2.1. Nuclei of giant ooids

The nuclei are commonly small, composed mainly of micrite, and devoid of terrestrial detritus. In well-preserved samples, abundant organic relics can be identified in the nuclei (Fig. 6D), and show strong orange-red autofluorescence under UV excitation (Fig. 6E); in less well-preserved samples, micritic nuclei are often recrystallized to microspar, so that organic relics were difficult to identify (Fig. 6C and F).

In silicified giant ooids, abundant organic relics are observed in the nuclei, including dispersed filaments with constant diameter (relics of putative bacterial filaments) and closely associated mucus-like films or stripes of organic matter. The filaments are commonly 0.4–0.9 μm in diameter, and can be up to 20 μm in length (Fig. 6G). They vary little in terms of width, are often bent to a large degree, displaying frequent directional changes and large variability with respect to tortuosity. These features are similar to biogenic rather than abiotic filaments/fibers (Hofmann et al., 2008; Tang et al., 2013a). FESEM observation reveals that these organic relics have been partially replaced or covered by nanoparticles (Fig. 6H and I). A short distance (a few to tens of μm) from the putative bacterial filaments, nanoparticles coalesce into sub-micron sized polyhedrons (Fig. 6J).

4.2.2. Cortices of giant ooids

Cortices are commonly thick and constitute the major portion of giant ooids, with a cortex-nucleus thickness ratio up to 4.0 (Fig. 6A and B). Two types of fabrics, evenly spaced concentric laminae and radial fibers, co-exist in most ooid cortices, which obviously differ from the uneven laminae observed in the cortices of oncoids (e.g., Shi and Chen, 2006; Shi and Jiang, 2011; Zhang et al., 2014).

Alternation of dark and light laminae is recognizable in the ooid cortex (Fig. 6A and B), and the boundary between laminae is transitional and in some cases, blurry (Fig. 7A–C). Light laminae are comparatively thinner, commonly 20–80 μm, and contain fewer organic relics, with weak orange-red autofluorescence under UV excitation. In contrast, dark laminae are generally 25–300 μm thick and bear more organic relics, with strong orange-red autofluorescence (Fig. 7A). Organic materials in cortices commonly appear as relics of filaments with relatively constant diameter (Fig. 7C and D) and are morphologically identical to those observed in nuclei (Fig. 6G). In addition, they demonstrate a complex interweaving pattern (Fig. 7D).

Fibrous fabrics are distinct in the cortices, and they are commonly perpendicularly to the concentric laminae, especially in the outer parts of the cortices (Figs. 6A–C and 7). They are commonly preserved as evenly spaced fibers and are surrounded by amorphous to microsparitic materials (Fig. 7B). In some samples, fibers in light laminae appear to be interrupted (Fig. 7B and C). Under high magnification, however, it can be seen that the visual interruption is actually caused by the change in abundance of organic relics between dark and light laminae. Some filaments in light laminae can extend into the overlying dark laminae (Fig. 7C). In some samples, fibers are seen to be continuous across different laminae. They are 20–70 μm wide and can be up to 310 μm long (Fig. 7E). In the center of each fiber, organic-rich filaments (or their bundles) and coccolith forms are enriched; whereas in the interstices between the fibers these features are much less common (Fig. 7E–I).

FESEM observation reveals that organic relics in radial fibers are identical to those in the nuclei. These organic relics, including filaments with constant diameter (relics of putative bacterial filaments) and closely associated mucus-like films and stripes with variable width (purported EPS relics), are either partially or entirely replaced or covered by nanoparticles and/or polyhedrons (organominerals) on their surfaces (Fig. 8). These organominerals show distinctive growth patterns. Nanoparticles are commonly 10–50 nm in the fibers but away from the fibers they become larger (50–350 nm) or coalesce into sub-micron polyhedrons (Fig. 8). When the organic substrate is completely replaced by nanoparticles or polyhedrons, no recognizable organic relics can be observed (e.g., lower right corner of Fig. 8B).

EDS point analyses on the mucus-like films and polyhedrons confirm that both of them are dominated by Mg, Ca, Si, C and O in elemental composition. However, the mucus-like films and stripes show higher C concentrations than polyhedrons (Fig. 9A–D). Raman spectrometry analyses of the filaments in ooids show Raman bands at 178, 299, 1348, 1591, and ~2700 cm⁻¹ (Fig. 9E), whereas micromorphs only have Raman bands at 178, 299, and 1088 cm⁻¹ (Fig. 9F).

4.2.3. Matrix surrounding giant ooids

Matrix surrounding giant ooids contains micritic particles and microsparitic cements (Fig. 6A–C). Occasionally, small micritic
intraclasts can also be recognized in the matrix (Fig. 6F). Individual micritic particles commonly have an organic-rich core and an organic-poor outer rim (Fig. 10A), texturally similar to micropeloids identified in some modern marine microbialites (Chafetz, 1986; Pacton et al., 2010; Spadafora et al., 2010; Perri et al., 2012), and to the micropeloids recognized from the contemporaneous thrombolites and stromatolites of the study area (Tang et al., 2013a,b). Organic relics observed in the cores of micritic particles are comprised of putative bacterial filaments and closely associated mucus-like films (Fig. 10B), both of which have been partially

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**Fig. 5.** Growth paths from giant ooids to MDS. (A) Schematic diagram showing possible development from ooids to MDS. (B–I) Photographs showing successive development from normal-sized spherical ooids (NSO in figure (B)) to giant spherical ooids (GSO in figure (C)), then to ellipsoidal ooids (EO in figure (D)–(G)), and finally to minute columnar MDS (in figure (H)–(I)). (J) Field photo showing MDS developed from giant ooids (GO).
Fig. 6. Nucleus features of giant ooids. (A) Plane-polarized and (B) cross-polarized light photomicrographs showing textures of a giant ooid, which consists of a small micritic nucleus and a thick fibrous cortex. Ooid is surrounded by micritic matrix (Mm) and spar-filled voids (Sv). (C) A giant ooid (an aggregate grain) with multiple nuclei (micrite and microspar) wrapped by a common cortex. (D) Organic relics (OR) in micritic nucleus. (E) Fluorescent photomicrograph of figure (D), showing orange-red autofluorescence stimulated from organic relics (UV excitation). (F) Micritic intraclasts (Ic) associated with giant ooids. (G) Filaments (Fi) in an ooid nucleus. (H) Enlargement of the arrowed filaments in figure (G), showing degraded filament (Fi). (I) Enlargement of the boxed area in figure (H), showing the replacement of degraded filament by numerous nanoparticles (Np) of 30–200 nm in diameter (FESEM image). (J) Mucus-like filaments with variable diameter (purported EPS) in an ooid nucleus, and closely associated polyhedrons (Po), which are formed by aggregated nanoparticles (Np) (FESEM image). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Fig. 7. Microscopic features of giant ooid cortices. (A) Fluorescent photomicrographs showing cortex composed of alternating thin light and thick dark laminae. (B) Enlargement of the boxed area in figure (A), showing radial fibers that contain organic relics, and dark and light laminae (DL and LL) (cross-polarized light). (C) Enlargement of the boxed area in figure (B), showing organic relics in dark and light laminae (DL and LL), and the blurry boundary between the laminae, with some filaments (arrows) extending across the boundary. (D) Enlargement of the boxed area in figure (C), showing interwoven filaments. (E) Co-occurrence of concentric laminae and radial fibers in the cortex of an ooid. (F) Fluorescent photomicrograph of figure (E), showing orange-red autofluorescence stimulated from organic remains in concentric laminae and radial fibers. (G) Enlargement of a fiber in figure (E), showing interwoven filaments (arrows) lined with the axes of radial fibers. (H) Radial fibers (arrow) in the cortex of an ooid. (I) Enlargement of the arrowed fiber in figure (H), showing abundant filaments and coccolid forms (possible cross-cutting of filaments) concentrated in the fiber.
replaced by nanoparticles. The nanoparticles are similar to those in the ooid cortices both in morphology and growth pattern; some nanoparticles (10–50 nm) aggregated into sub-micron polyhedrons (Fig. 10C). EDS point analysis shows that the major chemical compositions of nanoparticles are of Mg, Ca, Si, C and O (Fig. 10D).

4.3. REE + Y of oolites

The REE results of the oolite samples are listed in Table S.1 and shown in Fig. 11A. Oolites have REE + Y concentrations of 0.003–0.633 ppm, which are similar to those reported from other non-skeletal carbonates with minimum detrital influence (e.g., Webb and Kamber, 2000; Kamber and Webb, 2001; Nothdurft et al., 2004; Ling et al., 2013).

PAAS (Post-Archean Australian Shale)-normalized REE distribution patterns (REE$_{SN}$) of oolites are virtually flat, with light-to-heavy REE ratios (calculated as Pr$_{SN}$/Yb$_{SN}$; Table S.1) close to 1 (Fig. 11A). The average Y/Ho ratio in our samples is 65, markedly higher than the PAAS composite ratio of 27. All samples show a negative Eu anomaly [calculated as Eu/Eu’ = Eu$_{SN}$/(0.66Sm$_{SN}$ + 0.33Tb$_{SN}$)]. The Ce/Ce’ ratios [Ce/Ce’ = Ce$_{SN}$/(0.5Pr$_{SN}$ + 0.5La$_{SN}$)] are in the range of 0.93–1.05, which is higher than the 0.65–0.8 ratios of Holocene reefal microbialites (Webb and Kamber, 2000). In the Ce/Ce’ vs. Pr/Pr’* [Pr/Pr’* = Pr$_{SN}$/0.5Ce$_{SN}$ + 0.5Nd$_{SN}$] plot (Fig. 11B), the oolites fall in the same field as Archean iron formations, ca. 2.9 Ga Steep Rock carbonates, and the ca. 2.5 Ga Campbellrand carbonates (Planavsky et al., 2010), but apparently differ from those observed in modern (e.g., Webb and Kamber, 2000) and early
Phanerozoic (e.g., Nothdurft et al., 2004) non-skeletal and microbial carbonates.

4.4. C–O isotopes of oolites

Sixteen samples were selected for carbon and oxygen isotope analysis. Among these, 9 samples were from ooid cortices, 6 from the ooid matrix surrounding the ooids, and 1 sample from aragonite crust. As shown in Table S.2 and Fig. 11C, $\delta^{18}O$ values are higher than $+10^\circ$, and the C and O isotopes do not show co-variation ($r^2 = 0.01$). The $\delta^{13}C$ values of ooid cortices and matrix vary from $+0.71^\circ$ to $+0.15^\circ$ (mean $+0.28^\circ$) and from $-0.64^\circ$ to $0.29^\circ$ (mean $-0.12^\circ$), respectively. The $\delta^{18}O$ values vary from $-8.64^\circ$ to $-6.51^\circ$ (mean $-7.74^\circ$) for ooid cortices and from $-8.54^\circ$ to $-7.23^\circ$ (mean $-7.81^\circ$) for matrix. The $\delta^{13}C$ and $\delta^{18}O$ values of the aragonite crust are $0.04^\circ$ and $-7.68^\circ$, respectively. Most ooid cortex and matrix samples have slightly more negative $\delta^{13}C$ values than the aragonite crust sample (Fig. 11C).

5. Discussion

5.1. Redox conditions of ooid-forming environments

The high Y/Ho ratios (average of 65; compared to modern seawater values of 44–74; Bau and Dulski, 1996), and the lack of petrographic evidence for substantial recrystallization of the oolites, suggest that the REE + Y patterns from oolites may record a seawater signature. Particularly, the high Ce/Ce′ values (0.93–1.05) and the flat REE + Y distribution patterns suggest that the ooid-forming environments may have been anoxic–suboxic. In an oxic water column, Ce$^{3+}$ is oxidized to less soluble Ce$^{4+}$ and is preferentially removed by Mn–Fe oxyhydroxides, organic matter, and clay particles (Byrne and Sholkovitz, 1996). Therefore, carbonates precipitated from modern oxygenated marine environments show a negative Ce/Ce′ anomaly (e.g., Webb and Kamber, 2000; Kamber and Webb, 2001). In contrast, sediments deposited from suboxic and anoxic water column do not
Fig. 10. Matrix surrounding giant ooids. (A) Some of the micritic particles display as micropeloids, with organic-rich nuclei (Nu) and organic-poor rims (Ri). (B) Enlargement of part of the organic-rich nucleus indicated in figure (A), showing filaments (Fi) and closely associated mucus-like films (purported EPS), which have been partially to totally replaced by nanoparticles (Np). (C) FESEM image of a part of micropeloid nucleus, showing mucus-like films (purported EPS) replaced by nanoparticles, and polyhedrons (Po) formed by aggregation of nanoparticles. (D) EDS analysis of the spot marked by “+” in figure (C), indicating Mg, Ca, Si, C and O compositions of the polyhedron. Pt is derived from coatings.

Fig. 11. REE + Y and C–O isotope composition of giant ooids. (A) REE + Y patterns of ooid cortex, matrix and aragonite crystal fans in oolites, showing flat REE patterns and negative Eu anomalies. (B) Crossplot of Ce/Ce* and Pr/Pr* of the Wumishan oolites, microbialite-containing carbonates of the ca. 2.8 Ga Steep Rock Group (Planavsky et al., 2010), ca. 2.52 Ga Campbellrand Subgroup (Kamber and Webb, 2001), Devonian Canning Basin (Nothdurft et al., 2004) and Holocene Herron Island (Webb and Kamber, 2000) are plotted for comparison. The Ce/Ce* values of the Wumishan giant ooids are higher than those of the Devonian and Holocene carbonates but are similar to those of Archean carbonates. (C) Crossplot of δ¹⁸O and δ¹³C of the Wumishan giant ooids, matrix and aragonite crust. The δ¹³C values of giant ooids are slightly more negative than those of the matrix and aragonite crusts.
show a negative Ce/Ce* anomaly due to reductive dissolution of settling Mn–Fe–rich particles and release of more soluble Ce*
(13C-depleted CO2 (German and Elderfield, 1990; German et al., 1991; Byrne and Sholkovitz, 1996). Similarly, in oxygenated waters, light REEs are preferentially removed by Mn–Fe oxyhydroxides and other reactive particle surfaces, resulting in low LREE/HREE ratios in oxidized sediments and high LREE/HREE ratios in anoxic sediments (German et al., 1991; Sholkovitz et al., 1992; Byrne and Sholkovitz, 1996).

The lack of a negative Ce/Ce* anomaly (Fig. 11B) and flat REE pattern (Fig. 11A) in the Wumishan oolites likely indicate that the giant ooids may have been formed in suboxic to anoxic environments. This is consistent with the negative Eu anomalies from the same rocks. In reducing and alkaline environments, Eu* could be reduced to more soluble Eu** that may be removed from oolites during deposition or early diagenesis.

5.2. Possible microbial fossil relics in giant ooids

Identification of microbial fossils in ancient rocks, particularly Precambrian carbonates, is difficult due to the general lack of in vivo sheath calcification of microbes (e.g., Riding, 2006; Altermann, 2008; Shi and Jiang, 2011). Most microbes that were active in depositional environments are degraded during diagenesis and/or metamorphism (Grotzinger and James, 2000; de Wet and Davis, 2010). In the last decade, much progress has been made in using microbial relics, organominerals, and associated microtextures to identify microbial activities in ancient sediments (e.g., Dupraz, 2004, 2009; Hofmann et al., 2008; de Wet and Davis, 2010; Spadafora et al., 2010; Perri et al., 2012; Tang et al., 2013a). In this practice, mineralized morphological features are the most important information (Guidry and Chafetz, 2003) and they often provide better evidence than geochemistry for the prior existence of organisms (Hofmann et al., 2008; Tang et al., 2013a, 2014). Morphologically, the filaments in giant ooids (Figs. 6G–I & 7D, G and I) are similar to the biogenic filaments preserved in aragonite fibers of the Wumishan MDS (Tang et al., 2013a), carbonate biominerites (Tang et al., 2014), and many modern microbial mats (e.g., Pacton et al., 2010) or recent tufa (e.g., Perri et al., 2012), suggesting a biogenic origin.

Under UV excitation, the filaments recognized in ooid cortices show clear orange-red autofluorescence (Figs. 6E and 7F), which is thought to be caused by kerogen remains in carbonates (Bezouska et al., 1998; Neuweiler et al., 2003; Tang et al., 2013a, 2014).

Under Raman spectroscopy, filaments show a first-order dispersed Raman band at 1348 cm\(^{-1}\) and a second-order band around ~2700 cm\(^{-1}\) (Fig. 9E). Co-occurrence of these bands is generally taken as the signature of biogenic kerogen (Kudryavtsev et al., 2001; Schopf et al., 2002, 2007; Villar and Edwards, 2006). In contrast, the microspars in giant ooids do not show any kerogen signature (Fig. 9F). All analyzed microspar spots show vibration bands at 178, 299 and 1098 cm\(^{-1}\), which are commonly regarded as corroboration bands of dolomite (Kudryavtsev et al., 2001; Villar and Edwards, 2006).

Based on the morphological, auto-fluorescence and Raman spectral features, most filaments in giant ooids are likely of biogenic origin and may represent the relics of bacterial filaments. Micritized EPS relics in ancient microbialites are commonly identified by their mucus-like morphology and enrichments in organic carbon (Dupraz et al., 2009; Spadafora et al., 2010; Perri et al., 2012; Tang et al., 2013a,b,c). The purported EPS in giant ooids share these attributes, with mucus-like morphology (Fig. 8) and a high carbon content (Fig. 9A–D) that suggests an additional source of organic carbon.

5.3. Formation of radial fibers in giant ooid cortices

In comparison with the vague concentric lamination, radial fibrous fabric is more distinct in giant ooids. Mineralogically, these fibers are similar to those in Archean to Paleoproterozoic seafloor carbonate precipitates (e.g., Sumner and Grotzinger, 2004), MDS (e.g., Grotzinger and Knoll, 1999) and the outer layers of mesoclots in Paleoproterozoic thrombolites (Kah and Grotzinger, 1992). Most of the aragonite fibers in giant ooid cortices, however, are closely associated with abundant organic relics that are lined with the fiber axes. Such preferential alignments suggest that the filament relics may have served as templates for carbonate nucleation and organomineralization during the formation of giant ooids. Similar features have been reported from modern microbialites and calcifying microbial mats (Aloisi et al., 2006; Perri et al., 2012). Morphologically the filaments observed in giant ooids are very similar to the microbial relics identified in modern (Dupraz et al., 2004; Benzerara et al., 2006; Spadafora et al., 2010; Perri et al., 2012) and ancient microbialites (Perri and Tucker, 2007; Tang et al., 2013a,b,c), as well as microbially induced carbonate precipitates formed in laboratory experiments (Aloisi et al., 2006; Bontognali et al., 2008). Comparable organominerals (e.g., nanoparticles and polyhedrons) associated with the filaments in ooid cortices are also identical to those microbial filaments documented from modern and ancient microbialites (Dupraz et al., 2009; Spadafora et al., 2010; Perri et al., 2012; Tang et al., 2013b). Thus, we believe that the organic-rich fibers in giant ooids are most likely the result of mineralization of degraded bacterial filaments.

Since degradation of organic matter via heterotrophic processes would result in addition of 13C-depleted CO2 to microenvironments, carbonate precipitated involving this process may record a negative carbon isotope signature (Guo et al., 1996; Thompson et al., 1997; Sumner, 2001; Andres and Reid, 2006; Breitbarth et al., 2009; Brady et al., 2010, 2014). The δ13C values of giant ooids are only slightly lower than those of the matrix and aragonite crust (Fig. 11C). This suggests that during organomineralization, the majority of DIC was from seawater or pore-water. Bicarbonate from degraded filaments and EPS may have served as a trigger for carbonate precipitation.

An interesting observation from the Wumishan giant ooids is their close association with MDS. Many giant ooids serve as incipient nuclei of some MDS (Figs. 3H and 5). Fibers in giant ooids and MDS share the same mineralogy and filament relics, suggesting similar biogenic origin (Tang et al., 2013a).

Although some filaments in ooid cortices appear to be randomly dispersed, their bundles show an overall orientation perpendicular to the growth laminae and are lined with radial fibers (Fig. 7). These features are likely indicative of their primary outward growth (Fig. 7E–I), possibly through in situ mineralization of bacterial filaments. The preservation of bacterial filament bundles invokes a fast mineralization process, probably within a few days after the death of the filamentous bacteria (Bartley et al., 2000), and high carbonate saturation in the ambient water. Organomineralization possibly started through the replacement of degraded EPS and microbial remains by nanoparticles (Figs. 8 & 9A and B). Similar to that in biogenic MDS (Tang et al., 2013a), fast mineralization may have been one of the prerequisites for the filaments to be preserved in their growth orientation and thus for the formation of giant ooids.

5.4. Depositional model for giant ooids

Sumner and Grotzinger (1993) proposed that low nuclei supply, high seawater carbonate saturation, and high water agitation are
the likely required conditions for the formation of Precambrian giant ooids. Study of early Triassic giant ooids, however, suggested that the supply of potential nuclei may not be an important factor for the growth of large ooids. Instead, high-energy and abnormally high seawater CaCO₃ saturation controlled the formation of giant ooids (Lehrmann et al., 2012; Li et al., 2013, 2015).

Skeletal fragments and fecal pellets are the most common sources of nuclei for Phanerzoic ooids (e.g., Tucker and Wright, 1990). In the Mesoproterozoic ocean, these particles were absent, but many microbial groups including some eukaryotes (e.g., acritarchs and red algae; Butterfield, 2000; Javau et al., 2001) were already evolved (Knoll et al., 2006). These microbes and their fragments could provide sufficient sources for ooid nuclei, given that no metazoans were present to consume microbes at that time. Therefore, there must be some other factors responsible for the formation of the Wumishan giant ooids.

Facies analysis shows that the giant ooids were largely concentrated in a relatively deeper environment close to shoals separating the submarine shelf lagoon from the open sea, and were under the intermittent influence of agitated waters (Fig. 12A). Ooids show varied growth paths (Fig. 5A) in different hydrodynamic conditions, suggesting environmental controls on the development of giant ooids. In the lee-side of the shoal and toward the restricted lagoon, ooids seemed to have less chance to grow into larger size (≤3.8 mm), but a high proportion of them grow into MDS (Figs. 5H, 5J and 12A). In contrast, in the open-water side of the shoal, normal-sized ooids grow in highly agitated shallow waters, while giant ooids (up to 14.4 mm; Fig. 3E and F) occur in deeper and less agitated waters (Fig. 12A).

Study of modern oolitic sands indicates that they are extremely rare in many shallow-water carbonate-producing systems, but are notably concentrated in environments with the highest levels of pH, alkalinity, and carbonate supersaturation (Ranker and Reeder, 2009). In comparison with the modern oolitic sands (Ranker and Reeder, 2009) and the giant ooids from lower Triassic strata in south China (Lehrmann et al., 2012; Mei and Gao, 2012; Li et al., 2013, 2015), the Wumishan giant ooids commonly have much smaller nuclei, thicker cortices, and therefore a markedly higher cortex-nucleus thickness ratio (Fig. 6A and B). Thus, a high accretion rate in cortical growth is inferred for the Wumishan giant ooids, which invokes a highly carbonate-supersaturated environment for ooid formation (cf., Lehrmann et al., 2012; Woods, 2013; Li et al., 2015).

Highly supersaturated seawater conditions during the formation of giant ooids can be deduced from other independent evidence. Fibrous aragonite crusts and seafloor aragonite fans are often interpreted as inorganic seafloor carbonate precipitates indicative of highly CaCO₃ supersaturated seawater (e.g., Kah and Grotzinger, 1992; Grotzinger and James, 2000; Grotzinger and Knoll, 1995; Sumner and Grotzinger, 1996, 2004; Pruss et al., 2008; Woods, 2014). Although the fibrous aragonite crusts (Fig. 4A) and seafloor radial aragonite fans (Fig. 4B and C) from the ooid-hosting Wumishan Formation are thin and relatively small in size (<10 cm high), respectively, they are morphologically and mineralogically similar to late Archean–early Paleoproterozoic crystal fans (e.g., Sumner and Grotzinger, 1996, 2004). The formation of flat-pebble conglomerates is commonly interpreted as resulting from destruction of rapidly cemented carbonate layers by storms (e.g., Wignall and Twitchett, 1999), whereby high seawater CaCO₃ saturation is the prerequisite for rapid cementation (e.g., Wignall and Twitchett, 1999; Myrow et al., 2004; Pruss et al., 2005; Woods, 2014). The common occurrence of flat-pebble conglomerates in the host strata of giant ooids (Fig. 4D) is consistent with highly CaCO₃ supersaturated seawater.

In the modern oceans, locally high CaCO₃ supersaturation could be caused by a number of microbial groups and their metabolisms (Visscher and Stolz, 2005; Dupraz et al., 2009). In early Mesoproterozoic, given a stratified and anoxic ocean (Canfield, 1998; Planavsky et al., 2011, 2014), active bacterial sulfate reduction (BSR, CH₂O + SO₄²⁻ → HCO₃⁻ + HS⁻ + H₂O) under suboxic to anoxic conditions would lead to high CaCO₃ supersaturation in shallow seawater (Bartley and Kah, 2004; Tang et al., 2013c). Previous study on mineralogy and redox sensitive elements suggested that the Mesoproterozoic North China epicontinental sea might have a shallow chemocline around fair-weather wave base (Tang et al., 2011), and the deep subtidal zone was likely suboxic to anoxic (Tang et al., 2013b). This is in good agreement with the REE + Y results. In such redox-stratified conditions, active BSR in the anoxic deep subtidal zone would produce high HCO₃⁻, thus elevating the seawater alkalinity (Visscher et al., 2000; Dupraz et al., 2004, 2009; Baumgartner et al., 2006; Braissant et al., 2007). Concomitant heterotrophic processes in deep subtidal waters...

Fig. 12. Suggested depositional model for giant ooids in the Wumishan Formation. (A) Suggested depositional model for the giant ooids and related sedimentary structures. Aragonite fans are largely developed on the deep seafloor of shelf lagoon, well below the chemocline. MDS are concentrated on the lee-side of the shoal, close to the chemocline. Giant ooids tend to form mainly on windward side of the shoal with a depositional water depth similar to that of the MDS. Normal-sized ooids (<2 mm in size) more commonly occur in the shallower, agitated waters around the shoal. The development of both MDS and giant ooids was facilitated by the bicarbonate and high alkalinity resulted from active BSR in deep waters below the chemocline. (B) Possible changes of calcium carbonate saturation and oxygen concentration across the chemocline in the North China epeiric sea.
may also release CO₂, causing a drop in pH and lower saturation index (SI) relative to the oxic shallower water (Goyet et al., 1991; Hiscock and Millero, 2006). Thus we suspect that the highly supersaturated conditions would have been close to but fluctuated around the chemoclone. Ooids within environments around the chemocline (or the oxygen minimum zone) would have had a greater chance to grow into large sizes with thick cortices (Fig. 12).

6. Conclusions

Giant ooids (2.0–14.4 mm) with thick fibrous aragonite cortices are found in the Mesoproterozoic Wumishan Formation (ca. 1.50–1.45 Ga). Abundant organic relics and closely associated organominerals are identified in cortical coatings, especially concentrated in the center of individual aragonite fibers, suggesting that microbes played constructive roles in the formation of giant ooids. Rapid mineralization seems to be a prerequisite for the preservation of bacterial filaments/filament bundles at their cell entombment. Geology 36, 633–666.


