

# The post-deposition modification of ooids by sulfate-reducing bacteria: Evidence from the Lower Jurassic in the Tethys Himalayas of southern Tibet

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August 23, 2020

## Abstract

Whether ooids are formed through biotic or abiotic progress seems to become increasingly controversial in recent decades. New studies indicate that the microbial effect could make important contributions to the construction, destruction and modification of ooids. Previous studies mainly focused on the organomineralization of carbonate minerals in ooids. This paper investigates the formation process of iron minerals in red oolitic grainstones of the Lower Jurassic Nieniexiongla Formation in the Tethyan Himalaya of southern Tibet. Petrographic studies and electron probe microanalysis revealed that the colorful minerals present in red ooids are hematites. Sulfur was detected in the hematites, which indicates that they were transformed from precursor pyrites. These hematites retain euhedral or framboid shapes of the pyrites. Hematite pseudomorphs distribute randomly in ooids and could not form a whole concentric layer of the ooids. Euhedral crystals usually have larger diameters than amorphous spheres and are scattered mostly in nuclei. Based on the distribution and morphology of hematites, we speculate that precursor pyrites were formed through metabolism of sulfate-reducing bacteria. Moreover, the timing of the pyrite formation was after the deposition but before the lithification. The decomposition of the microorganisms within the ooids by bacterial sulfate-reducing provides the HS<sup>-</sup>, the degradation of organic matters would produce spaces for the intrusion of pore water with sufficient Fe<sup>2+</sup> to facilitate the pyrite deposition. In nuclei, the framboid aggregates of pyrites were transferred to euhedral crystals through continuous growth of the constituent microcrystals. Our study demonstrated organomineralization of sulfate-reducing bacteria mediated pyrites in carbonate ooids.

## Summary statement

This paper investigates the formation process of iron minerals in red oolitic grainstones of the Lower Jurassic Nieniexiongla Formation, demonstrates organomineralization of sulfate-reducing bacteria mediated pyrites in carbonate ooids. We propose that sulfate-reducing bacteria would utilize organic matter within ooids after sedimentation, resulting changes in the mineral composition of ooids.

**Keywords** : Ooidal limestone; Pyrite; Hematitization; Organomineralization; Lower Jurassic Nieniexiongla Formation; Southern Tibet

## 1. Introduction

Ooids are common in the modern and ancient carbonate sediments of both marine and terrigenous environments. They were regarded as chiefly ‘inorganic grains’ in traditional view (Davies, Bubela, & Ferguson, 1978; Morse & Mackenzie, 1990), but recent studies inferred that microbes played important role in ooid construction and destruction (Summons et al., 2013; Diaz et al., 2015; Mariotti, Pruss, Summons, Newman, & Bosak, 2018). Two pathways controlling the organomineralization in ooids are biologically induced and biologically influenced mechanisms (Diaz & Eberli, 2018). Biologically influenced mechanism is passive mineralization, through which mucilaginous material or extracellular polymeric substances (EPS) control

mineral nucleation (Diaz, Piggot, Eberli, & Klaus, 2013; Diaz et al., 2014; Dupraz et al., 2009). Biologically induced mechanism is active mineralization, which generates minerals along metabolic activities (Diaz & Eberli, 2018). Several metabolic processes have been identified throughout molecular techniques. Denitrification oxidizes organic carbon and could produce up to 19g CaCO<sub>3</sub>/g NO<sub>3</sub>-N in 2 days (Erşan, De Belie, & Boon, 2015), which is one of the most significant nitrogen transforming processes in ooids (Diaz, Piggot, Eberli, & Klaus, 2013; Diaz et al., 2015). CO<sub>2</sub> fixation by photoautotrophs has been confirmed through studies on modern (Summons et al., 2013; O'Reilly et al., 2016) and ancient ooids (Pacton et al., 2012; Li et al., 2017). It seems to be the most productive microbes in the formation of ooids (Pacton et al., 2012; Summons et al., 2013). The presence of sulfate reduction, ammonification (Diaz et al., 2014) and sulfate oxidation (Summons et al., 2013; Diaz, Piggot, Eberli, & Klaus, 2013; Diaz et al., 2014; O'Reilly et al., 2016) bacteria in ooids has been detected through biomarker studies. However, their contributions to the formation of ooids were less investigated.

Ooids would be modified by microbes throughout their life cycle (Diaz & Eberli, 2018) as evidenced by isotopic geochemistry studies. The precipitation and/or alteration of ooids by microbial photosynthesis would elevate δ<sup>11</sup>B signal (Zhang et al., 2016). Denitrification may bring positive δ<sup>15</sup>N and δ<sup>18</sup>O of the NO<sub>3</sub><sup>-</sup> in leachates of ooids (Diaz et al., 2015). Weak sulfate reduction is conjectured through leachates of ooids (Diaz et al., 2015). However, the research about the modification of ooids by microbes mainly focuses on geochemical analysis rather than minerals, since carbonate minerals generated biologically (such as amorphous calcium carbonate (ACC), Duguid, Kyser, James, & Rankey, 2010) are thought to be primary minerals during the accretion of ooids. Ooids containing iron minerals are supposed to play a significant role in tracing microbial activities since iron is an important element for the growth and evolution of organisms. For instance, the formation of many banded iron formations (BIFs) has strong connection with bacteria (Posth, Konhauser, & Kappler, 2013; Chi Fru et al., 2013). Reddish pigment of rounded ferruginous oncoidal nucleus in European Phanerozoic red limestones is thought to be caused by iron bacteria mediated hematite (Préat, Mamet, De Ridder, Boulvain, & Gillan, 2000; Mamet & Préat, 2006). However, to date there are very few studies associating iron bacteria mediated organomineralization with carbonate ooids.

The Lower Jurassic Nienixionala Formation in the Tethyan Himalayas of the southern Tibet contains thin- to medium-bedded red oolitic limestones. Although the lithology, microfacies, age and depositional environments were well studied (Han, Hu, Li, & Garzanti, 2016; Han, Hu, Kemp, & Li, 2018), the formation process of the red ooids has not been studied to date. Petrographic analysis shows the identified ferruginous minerals are responsible for the red color of the ooids. Iron minerals in sedimentary rocks are always thought to be related to microorganism activities (pyrites: Berner, De Leeuw, Spiro, Murchison, & Eglinton, 1985; Raiswell & Berner, 1986; Rickard, 2012; Wei, Chen, Wang, Yu, & Tucker, 2012; and hematites: Préat, Mamet, De Ridder, Boulvain, & Gillan, 2000; Mamet & Préat, 2006) and/or ambient redox conditions (e.g., Cornell & Schwertmann, 2003). In this paper, we studied the mineralogy composition and the forming process of the Nienixiongl red ooids in order to identify the metabolic process of sulfate-reducing in these ooids.

## 2. Geological setting

The southern Tibet can be subdivided into five tectonic units, which are Xigaze Forearc Basin, Yarlung-Zangbo Ophiolite, Tethyan Himalaya, Greater Himalaya and Lesser Himalaya from north to south (Fig. 1). Mesozoic strata are well-developed in the Tethyan Himalayan zone, which was divided into the Northern and the Southern subzones (Wang et al., 2005) separated by the Gyirong-Kangmar Thrust. Our study section, the Menqu section (GPS: 28°39'08"N, 86deg02'57"E), is located in the Tethyan Himalayan Southern subzone. During the Mesozoic, the Tethyan Himalaya belongs to the north margin of Indian subcontinent. The Jurassic sediments in Southern subzone are characterized by shallow-water carbonates and terrigenous rocks (Jadoul, Berra, & Garzanti, 1998). The Jurassic sedimentary succession is composed of thick-bedded bioclastic limestones of Pupuga Formation (Fm.), ooidal limestones with sandstone intercalations of Nienixiongl Fm., marls of Lanongla Fm., ooidal ironstones of Dingjie Fm. and clastic rocks of Menkadun Fm. from the bottom to the top (Jadoul, Berra, & Garzanti, 1998; Wang et al., 2005; Li & Wang, 2005; Han, Hu, Li, & Garzanti, 2016).

The Nieniexionglia Formation consists of gray to light-gray, thin- to medium-layered mudstones or oolitic grainstones rhythmically interbedded with sandstones (Li & Wang, 2005) and is Toarcian-Bajocian aged as indicated by ammonites (Yin, 2010). Middle to outer ramp was indicated by microfacies analysis (Han, Hu, Li, & Garzanti, 2016) and foraminiferal ecological research (Wan, 1989). A rapid transgressive and negative carbon isotope excursion initiated at the boundary of the Pupuga and Nieniexionglia formations is recently interpreted as the responses to the Toarcian Oceanic Anoxic Event (T-OAE, Han, Hu, Kemp, & Li, 2018).

### 3. Materials and methods

Polished petrographic thin sections of eighty samples from the Nieniexionglia Formation in Menqu section were investigated by Nikon-LV100POL polarizing microscope. The classification of carbonate rocks we followed is the expanded Dunham (1962) classification proposed by Embry and Klovan (1971). Carbon isotope of bulk carbonate ( $\delta^{13}\text{C}$ ) were measured for forty samples at the Carbonate Reservoir Key Laboratory, of the PetroChina Hangzhou Institute of Geology, using a GasBench II system coupled to a Delta V mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). The instrument was calibrated with Chinese national carbonate standard GBW04405 ( $\delta^{13}\text{C}= 0.57\text{delta}$  notation, relative to VPDB. Eight oolitic grainstone thin sections were selected and studied in the CUGB lab (China University of Geosciences, Beijing) to investigate the mineral and chemical compositions. Geochemical analysis was conducted by electron probe microanalysis (EPMA-1720(1210229S)) on polished and conductively carbon coated thin sections. The oxides of Na, Ti, Si, Co, Mg, Cr, P, Ni, Al, Mn, K, Fe, Ca were determined in this examination. Experimental method relied on general principle for electron probe microanalysis method GB/T15074-2008. A ZEISS Supra 55 field emission scanning electron microscopy (SEM) equipped with an Oxford Electrical Refrigeration Energy Dispersive Spectrometer (EDS) was used to examine the microstructure of ooids in both polished petrographic thin sections and fresh rock fragments by Secondary Electron (SE) and Backscattered Electron (BSE) modes. Prior to SEM examination, samples were washed by deionized water in ultrasonic cleaner for three times and dried to avoid contaminating, then coated by Platinum. The accelerating voltage was 15kV or 20kV and the working distance was 5 to 15 mm.

### 4. Results

#### 4.1 Λιθοστρατιγγραφή ανδ $\delta^{13}\text{C}$ ισοτοπικ στρατιγγραφή

The Menqu section, which has a total thickness of 179.7 m, is located near the Menqu village in the Nyalam area (Fig. 1). In the lower 0-11.7m, the carbonate rocks are composed of medium- to thick-bedded bioclastic grainstones (Fig. 2a), bioclastic wackestones (Fig. 2b) and framestones (coral reef, Fig. 2c). This part is characterized by high content of fossils, e.g., *Lithiotis* (Fig. 2d), corals (Fig. 2c), bivalves, gastropods (Fig. 2a), sponges and echinoderms (Fig. 2a). At the interval of 11.7-179.7m, the section is mainly composed of thin- to medium-bedded mudstones. Besides, texture is frequently interrupted (Fig. 2e) by siltstones, grainstones, wackestones and packstones. This part is characterized by rare fossils and much finer grains. Sedimentary structures include erosive base (Fig. 2f), sand lens (Fig. 2f) and hummocky cross-bedding.

Carbon-isotope data of the Menqu section is shown in Fig. 3. At the interval of 0-12.8m,  $\delta^{13}\text{C}$  values recorded by five samples range between 1.76 and 2.67interval of 12.8-179.7m,  $\delta^{13}\text{C}$  values vary from 0.28 to 2.04

#### 4.2. Geochemical and mineralogical composition of oolitic grainstones

Our materials come from a series of thin- to medium-bedded oolitic grainstones with total thickness of 7.2 m (157.2-164.4 m) near the top of the Menqu section (Fig. 3). These oolitic grainstones of the Nieniexionglia Formation consist mainly of ooids with a few bioclasts and quartz grains. Some grains are surrounded by bladed to dogtooth cement (variously shaped terminations of crystals). The intergranular space is filled by mosaic crystals which may indicate the influence of meteoric water during diagenetic process (Javanbakht, Wanas, Jafarian, Shahsavan, & Sahraeyan, 2018). Additionally, the color, size, shape and type of ooids from the bottom to the top change gradually through the Nieniexionglia Formation. Oolitic grainstones closed to the bottom are mainly composed of gray colored ooids with diameters ranging from 300 to 500  $\mu\text{m}$ . Diverse

nuclei including peloids, quartz grains, bioclasts and preexisting ooids are enclosed by cortices exhibiting indistinct micritic to radial-fibrous structure. Part of the ooids have both micritic and radial-fibrous cortex, which suggests change in sea-water conditions. About 70% of the ooids are broken, compounded and regenerated ooids occurred too, part of these ooids have abraded outline (Fig. 4a). In contrast, oolitic grainstones closed to the top are mainly composed of red colored ooids. Red ooids are 200 to 400  $\mu\text{m}$  in size. The characteristics of their nuclei and cortices are similar with gray ooids. Most ooids are accompanied by circumgranular cement rims. Much fewer broken red ooids were observed than gray ooids (Fig. 4b).

The EPMA backscattered electron images show that the material distribution within ooids is inhomogeneous (Fig. 5), and the EPMA examination reveals the element composition of different minerals (Table 1) in oolitic grainstones. Ooids are mainly composed of calcite (gray color in BSE images, Fig. 5). Mineral displaying average contents of 57.56 wt% CaO (59.58 wt% in total) supposes to be calcite crystal. Minor oxides in calcite are 0.49 wt% MgO, 0.37 wt% SiO<sub>2</sub> and 0.91 wt% FeO, which may come from adjacent quartz grains and ferruginous minerals. The second abundant mineral among ooids is quartz which exhibits dark-gray color in BSE images. Particles contain an average chemical composition of 99.16 wt% SiO<sub>2</sub> and 0.26 wt% CaO belong to quartz particles which occur as the nuclei or in the cortex of some ooids. There are some ferruginous mineral scattered randomly in ooids (white color in Fig. 5). These particles have significantly high contents in FeO (80.61 wt% with 89.00 wt% in total). The minor oxide concentrations in this mineral are 3.53 wt% SiO<sub>2</sub> and 3.46 wt% CaO. From the base (Fig. 5a) to the top (Fig. 5b) of a single oolitic grainstone bed, the rock color becomes more pinkish as the concentration of ferruginous mineral increases.

### 4.3. Morphology and distribution of ferruginous minerals

Ferruginous mineral with diameter ranging from hundreds of nanometers to tens of microns are randomly scattered or gathered in ooids (Figs. 6, 7). Two distinguishing morphologies, euhedral crystals and aggregated spheroids, of these minerals are identified through SEM-EDS examination. Euhedral crystals are generally found in the calcium nuclei of ooids, and usually range from several to tens of microns (Fig. 6a-c). They display regular five to six-sided edges in polished thin sections (Fig. 6d). In several cases, this type of iron oxide depicts concentric zones that differ in thickness, size and possibly in chemical composition (Fig. 6e, 6f). The inner zones have irregular edges in contrast with regular six-sided margin of the outer zones (Fig. 6f). Spheroid aggregates randomly occur in the whole ooids (Fig. 7), and can reach to a high proportion. Every single aggregate consists of fine amorphous ferruginous spheroids with diameters around or lesser than 1  $\mu\text{m}$  (Fig. 7c). The arrangements of the individual ferruginous spheroids are mostly disordered. What is more, at or near spheroid-to-spheroid contacts, there are bridge-like iron oxides exhibiting different brightness with spheroids (Fig. 7c).

The ferruginous minerals occur mostly in ooids and rarely in cements (Figs. 6, 7). Both euhedral crystals and aggregated spheroids distribute randomly in ooids, they can form a whole concentric layer or not (Fig. 7a). The amount and occurrence of them in different ooids are also random. In ooids with quartz nuclei, ferruginous mineral is absent in the nuclei but scatters among the cortex (Fig. 7b, 7d). However, in ooids with calcium nuclei, ferruginous mineral occurs in whole ooids (Fig. 6a, 6b).

Interestingly, in SEM-EDS analysis, ferruginous mineral shows enrichment in S (over 30 cps/0.10 wt%) content relative to surrounding matrix, which contains no more than 30cps/0.05 wt% S (Fig. 8).

## 5. Discussion

### 5.1. Chronostratigraphy of the Menqu section

The Nienixionglia Formation and the overlain Pupuga Formation can be divided by their distinct characteristics of lithology, bioclastics and  $\delta^{13}\text{C}$  values (Han, Hu, Li, & Garzanti, 2016; Han, Hu, Kemp, & Li, 2018).

The *Lithiotis* -rich interval occurs in the top of the Pupuga Formation. This horizon appears extensively in the Lower Jurassic successions in the Tethys realm and can be used as a mark of biostratigraphic correlation (Han, Hu, Li, & Garzanti, 2016). The Pupuga Formation consists mainly of medium- to thick-bedded

(20-50 cm-thick) limestones with abundant bioclastics, e.g., corals, sponges and bivalves. In contrast, the Nieniexionglia Fm. is composed mainly of thin to medium bedded (~10 cm-thick) oolitic grainstones with a few sandstone intercalations (Han, Hu, Li, & Garzanti, 2016). The upper Nieniexionglia Formation reveals an abundance of storm deposits (Han, Hu, Kemp, & Li, 2018). The base of Nieniexionglia Formation is coincided with the onset of negative excursion of the carbon isotope, which was interpreted as the onset of Toarcian Oceanic Anoxic Event (Han, Hu, Kemp, & Li, 2018). A negative carbon isotope excursion of ~2.5 magnitude of about  $\sim -1.5\delta^{13}\text{C}_{\text{carb}}$  (Han, Hu, Kemp, & Li, 2018).

In Menqu section, all the above outlined transitions were found at ~11.7 m. From 0 to 11.7 m of the section, the lithologies are mainly medium- to thick-bedded bioclastic grainstones with a limestone bed yielding rich *Lithiotis* (Fig. 2d). The radiation of the *Lithiotis* fauna is a global sedimentary event during the Pliensbachian (Franceschi et al., 2014), which demonstrates an Early Jurassic age of this interval. From 11.7 m to top of the section, the lithologies change dramatically as thin to medium bedded limestones with sandstone intercalations (Fig. 2). Hummocky cross-beddings were found in these sandstone layers, indicating strong storm wave influences.  $\delta^{13}\text{C}_{\text{carb}}$  values changed significantly at ~12 m to average 2.19 interval below 11.7 m and 1.40 date the Menqu section as Early Jurassic age and reveal that the boundary of Pupuga and Nieniexionglia formations is at ~11.7 m. All the studied oolitic grainstones are from the Lower Jurassic Nieniexionglia Formation.

## 5.2. Pseudomorphic transformation from pyrites to hematites

The red color and chemical composition of the ferruginous minerals indicate that they are iron oxides, i.e. hematites (Franke & Paul, 1980; Pr at, Mamet, De Ridder, Boulvain, & Gillan, 2000; Mamet & Pr at, 2006; Hu, 2013). The significantly viable sizes as well as the euhedral and spheroidal forms of the hematites rule out that the minerals had been transported into the basin to be combined by carbonates to form ooids. Absence of hematite in the matrix of the Nieniexionglia oolitic grainstones further demonstrates that they were not authigenetically formed in the water masses but grew particulate within the ooids.

Sulfur detected from the hematites could indicate that they were transformed from precursor pyrites (Lu et al., 2005; Soliman & El Goresy, 2012). The preservation of framboidal morphology and bridge-like ferruginous minerals at or near spheroid-to-spheroid contacts also indicates complete pseudomorphic transformation from pyrite to hematite (Lougheed & Mancuso, 1973; Mader, 2006; Huang et al., 2019). Framboidal pyrites associated with euhedral pyrite are normally regarded as authigenic pyrites (e.g. Lougheed & Mancuso, 1973; Wilkin & Barnes, 1997; Merinero, Lunar, Somoza, D az-del-R o, & Mart nez-Fr as, 2009; Soliman & El Goresy, 2012; Wang, Huang, Wang, Feng, & Huang, 2013). In many cases, framboidal pyrite aggregates have been observed to completely convert to hematite pseudomorphs (Mader, 2006) or other iron mineral pseudomorphs (Soliman & El Goresy, 2012). Ferruginous minerals at or near spheroid-to-spheroid contacts might be the result of leaching of interstitial hematite, the leaching may exhume the framboidal fabric (Mader, 2006).

The residual sulfur should attribute to leaching and chemical weathering of pyrite which are very common and have been well documented before (Lu et al., 2005; Soliman & El Goresy, 2012). Most of these researches reported that sulfur in pyrite is transferred to sulfuric and sulfate during oxidation and dissolved in pore water (Weber et al., 2004). The low proportion of residual sulfur in our study suggests high conversion ratio of hematite to pyrite, which means intensely leaching and/or chemical weathering. In the last phase of weathering, only a minor part of sulfur remains as sulfate mineral, but the total mass of iron would not be changed considering iron is rather immobile during weathering (Lu et al., 2005).

## 5.3. The formation of pyrite

The formation of pyrite must be under anoxic environments (Berner, 1984; Wilkin & Barnes, 1997; Suits & Wilkin, 1998; Kraal, Burton, & Bush, 2013). However, the Nieniexionglia oolitic grainstones were deposited in mid-ramp environment with periodical influences with storm wave (Han, Hu, Kemp, & Li, 2018). Additionally, a large amount of broken ooids and the sparry calcite cement would recommend highly agitated sea water. Therefore, it can be concluded that the water column was well ventilated and thus hardly to be anoxic

to facilitate the formation of pyrites.

On the other hand, pyrites are thought to have close connection with organic matter (Berner, De Leeuw, Spiro, Murchison, & Eglinton, 1985; Raiswell & Berner, 1986; Rickard, 2012; Wei, Chen, Wang, Yu, & Tucker, 2012). Especially iron-framboids need organic-rich systems suggesting that organics would make a substantial contribution in their formation (Wignall, Newton, & Brookfield, 2005; Cavalazzi et al., 2012). As organic matter decomposition continues after sediment deposition through sulphate-reducing bacteria, it leads to reduction of dissolved interstitial sulphate to  $\text{H}_2\text{S}$ , which compounds with active iron to form pyrites. Meanwhile, intermediate products,  $\text{H}_2\text{S}$  and iron sulphides, also need reduced environment, or they would be oxidatively destroyed (Berner, De Leeuw, Spiro, Murchison, & Eglinton, 1985).

In the case of Menqu, iron minerals are barely found in cements and muds filling in the skeletal chambers, which indicate that the pyrites did not form in the water column. Additionally, the iron minerals are not concentrated around the cracks filled with sparite calcites, which might form during the compaction of the sediments. We suggest that neither the exotic fluids intrusion nor internal remobilized material after lithification of the oolitic grainstones are responsible for the formation of pyrites. Therefore, the timing of the pyrite formation was after the deposition but before the lithification of the rocks. Pore water under reduced condition could provide active iron and  $\text{HS}^-$  (under euxinic condition) to form pyrites. However, the pyrites in Nienixiongla grainstones are not concentrated on the surface of the ooids but randomly distributed in the cortex and nuclei of the ooids, which indicates the materials remobilized from the ooids played more important roles.

Three principal factors that limit the amount of pyrites are organic matter, active iron and dissolved sulphate (Berner, De Leeuw, Spiro, Murchison, & Eglinton, 1985). Organic carbon comes from a variety source of autochthonous or allochthonous. Allochthonous organic carbon is terrestrial origin or detrital form, such as plant debris and animal fragments. Autochthonous organic carbon originates mainly from primary production of the pelagic organisms (Zaborska et al., 2016). Very few fossils of marine microfossils or other kinds of organic matters were observed in the Nienixiongla granistones. However, more studies on ancient and modern cases have revealed that the microorganisms are involved to form ooids (Pacton et al., 2012; Summons et al., 2013; Barale, d’Atri, & Martire, 2013; Li, Yan, Algeo, & Wu, 2013; Li et al., 2017). Therefore, we suggest that the decomposition of the microorganisms within the ooids by bacterial sulfate-reducing (BSR) provides the  $\text{HS}^-$ . Furthermore, the oxygenation of organic matters would produce spaces for the intrusion of pore water with sufficient  $\text{Fe}^{2+}$  to facilitate the pyrite deposition.

#### 5.4. Differences of pyrites in nuclei and cortex

Framboidal pyrites distributed in both cortex and nuclei of the ooids. In contrast, euhedral pyrites were found only in the nuclei composed of carbonate fragments. Euhedral pyrites show concentric fabrics caused by elements concentration indicating multi-stage growth of these minerals, which could lead to significantly larger size of them than framboid pyrites. The early postsedimentary fluids would lead to pyrite overgrowths, and generate chemical zones in pyrites (Agangi, Hofmann, & Wohlgemuth-Ueberwasser, 2013). Previous studies documented that later pyrite often overgrows earlier generations of pyrite resulting in zoned pyrite with different trace elements patterns during hydrothermal fluid-flow processes (Thomas et al., 2011). However, there are not any Jurassic volcanic rocks or other clues of hydrothermal activities recorded in the southern zone of Tibetan Himalayas. Nevertheless, framboid aggregates can transfer to euhedral crystals through continuous growth of the constituent microcrystals (Ostwald & England, 1979; Bailey et al., 2010; Soliman & El Goresy, 2012; Wacey et al., 2015). The Nuclei are also a more open system relative to tightly packed cortex which is more appropriate for the formation of framboids in a close system (Merinero, Lunar, Somoza, Díaz-del-Río, & Martínez-Frías, 2009). This study therefore suggests that in the Nienixiongla grainstones, the euhedral pyrites in the ooid nuclei were transferred from original framboids.

#### 5.5. The modification of ooids by sulfate-reducing bacteria

The biosignature examination of modern Bahamian ooids revealed that there are diverse microbes including photoautotrophs, heterotrophs, and sulfate-reducing bacteria contained in ooids (Summons et al., 2013;

Diaz, Piggot, Eberli, & Klaus, 2013; Diaz et al., 2014; O'Reilly et al., 2016). Although sulfate-reducing bacteria may not contribute significantly in carbonate biomineralization or only play as an unimportant part in cyanobacteria dominated biofilm (Pacton et al., 2012), but we found that sulfate-reducing bacteria would change the mineral composition of ooids after deposition under suitable conditions. However, most ooids would not be modified by sulfate-reducing bacteria without proper environment with sufficient sulfur and active iron influx. Iron ooids are generally red, their cortex may consist of iron minerals (goethite, hematite, chamosite and so on, Sturesson, Dronov, & Saadre, 1999; Mücke, 2006), or iron minerals mixed with other minerals (phosphate-rich layers+Fe-oxide-rich layers; Barale, d'Atri, & Martire, 2013). However, most researches about iron ooid formation indicated that these ooids formed under sufficient iron supplement and agitated hydrodynamic environment (Di Bella et al., 2019), or associated with volcanism activities (basalt extrusions, hydrothermal fluids, volcanic ash) (Sturesson, Dronov, & Saadre, 1999). We speculate that this kind of red ooids are lack of organic matter and sulfate-reducing bacteria, while Bahamian ooids are lack of iron supplement in proper time.

## 6. Conclusion

Ooids in oolitic grainstones of the Nieniexionglia Formation contain significant proportion of hematite which makes ooids reddish. These hematites exhibit mainly two habits: euhedral crystals and aggregated spheroids (framboids). Euhedral crystals are generally found in the calcium nuclei of ooids, and usually range from several to tens of microns. Aggregated spheroids randomly occur in the whole ooids, the diameter of single amorphous spheroid is around or lesser than 1  $\mu\text{m}$ .

EPMA examination revealed that the hematite is pseudomorph after pyrite. According to the analysis of sedimentary and diagenetic environment, pyrite formed after the deposition but before the lithification of the rocks. Under anoxic conditions, the decomposition of the microorganisms within ooids by sulfate-reducing bacteria provides  $\text{HS}^-$  ions. Then  $\text{HS}^-$  ions reacted with  $\text{Fe}^{2+}$  brought by the intrusion of pore water to deposit pyrite.

Larger euhedral pyrites in nuclei may be transferred from framboid aggregates through continuous growth of the constituent microcrystals, since the space of nuclei is an open system and large enough. The research of reddish ooids in oolitic grainstones of the Nieniexionglia Formation demonstrates that sulfate-reducing bacteria would utilize organic matter within ooids after sedimentation, resulting changes in the mineral composition of ooids.

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## Figure and table captions

**Fig. 1.** Simplified tectonic map of the southern Tibet (modified from Pan et al., 2004). Location of the study area is indicated by a red star.

**Fig. 2.** Photos are showing: (a) bioclastic grainstone, (b) bioclastic wackestone, (c) coral framestones, (d) shell bed mainly composed of *Lithiotis*, (e) mudstone and grainstone, (f) sand lens and erosive base. The contact between mudstones and grainstones is erosive.

**Fig. 3.** Correlation of stratigraphic distribution of carbonate carbon isotopes of the Menqu section and distribution of organic carbon isotopes of the Nianduo section (Han, Hu, Kemp, & Li, 2018). The blue dashed line means the boundary between the Pupuga Formation and the Nienixiongla Formation.

**Fig. 4.** Photo of oolitic grainstones from Nienixiongla Formation (plane polarized light microscopy image).

**Fig. 5.** EPMA points of oolitic grainstones (polished thin section, EPMA backscattered electron image, results of green points with numbers could be seen in Table 1). (a) 17MQ56-03:1 and 17MQ56-03:2 are ferruginous mineral, 17MQ56-03:3 is quartz; (b) 17MQ66-02:1, 17MQ66-02:2, 17MQ66-02:3 and 17MQ66-02:4 are all ferruginous mineral.

**Fig. 6.** (a) ooid with euhedral ferruginous minerals in nuclei and ferruginous spheroids in cortex (polished thin section, SEM backscattered electron image), (b) ooid with euhedral ferruginous (polished thin section, SEM backscattered electron image), (c) euhedral ferruginous particles (fresh fragment, SEM image), (d) regular six-sided euhedral ferruginous particles (polished thin section, SEM backscattered electron image), (e, f) euhedral ferruginous minerals show concentric structure (polished thin section, SEM backscattered electron image).

**Fig. 7.** (a) ferruginous particles make up of a concentric layer around the cortex (polished thin section, SEM backscattered electron image), (b) ooids contain ferruginous particles with quartz nuclei (polished thin section, SEM backscattered electron image), (c) ferruginous aggregated spheroids (fresh fragment, SEM backscattered electron image), (d) ooids contain ferruginous particles with different nuclei (polished thin section, SEM backscattered electron image).

**Fig. 8.** Linear scan of sulfur and iron distribution of a ferruginous particle by SEM-EDS. Polished thin section, SEM backscattered electron image.

**Table 1.** Results of EPMA analysis of different minerals in red ooid grainstones (oxide values are given in molar).

| Data(wt%)   | Na <sub>2</sub> O | TiO <sub>2</sub> | SiO <sub>2</sub> | CoO  | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | NiO  | Al <sub>2</sub> O <sub>3</sub> | MnO  | K <sub>2</sub> O | FeO   | CaO   | Tot  |
|-------------|-------------------|------------------|------------------|------|------|--------------------------------|-------------------------------|------|--------------------------------|------|------------------|-------|-------|------|
| 17MQ66-02-2 | 0.17              | 0.03             | 3.89             | 0.15 | 0.36 | 0.02                           | 0.07                          |      | 0.73                           | 0.01 | 0.08             | 80.31 | 3.79  | 89.6 |
| 17MQ66-02-3 | 0.27              |                  | 3.16             | 0.08 | 0.32 | 0.02                           | 0.13                          | 0.01 | 0.32                           | 0.00 | 0.04             | 83.59 | 1.70  | 89.6 |
| 17MQ66-01-1 | 0.09              |                  | 5.21             | 0.13 | 0.34 | 0.01                           | 0.10                          | 0.02 | 0.62                           | 0.03 | 0.01             | 75.98 | 5.62  | 88.3 |
| 17MQ66-04-1 | 0.05              | 0.00             | 2.65             | 0.16 | 0.54 | 0.00                           | 0.14                          |      | 0.22                           | 0.03 | 0.02             | 82.25 | 1.72  | 87.7 |
| 17MQ66-04-2 | 0.16              |                  | 3.52             | 0.15 | 0.34 | 0.02                           | 0.10                          | 0.05 | 0.41                           |      | 0.02             | 81.76 | 1.61  | 88.3 |
| 17MQ66-04-3 | 0.30              |                  | 4.09             | 0.14 | 0.45 | 0.03                           | 0.16                          | 0.02 | 3.08                           | 0.08 | 0.29             | 75.87 | 4.08  | 88.3 |
| 17MQ66-05-1 | 0.08              |                  | 4.16             | 0.07 | 0.28 | 0.03                           | 0.16                          | 0.08 | 0.63                           | 0.06 | 0.03             | 76.14 | 7.18  | 88.3 |
| 17MQ66-05-2 | 0.10              |                  | 4.20             | 0.05 | 0.34 | 0.11                           | 0.04                          | 0.01 | 0.96                           | 0.02 | 0.06             | 79.83 | 3.73  | 89.4 |
| 17MQ66-05-3 | 0.10              | 0.04             | 3.90             | 0.11 | 0.34 | 0.03                           | 0.12                          |      | 0.58                           | 0.04 | 0.03             | 78.59 | 4.98  | 88.3 |
| 17MQ66-03-1 | 0.18              | 0.02             | 3.68             | 0.06 | 0.32 | 0.04                           | 0.17                          | 0.06 | 0.47                           | 0.01 | 0.07             | 82.80 | 1.78  | 89.6 |
| 17MQ66-03-2 | 0.04              |                  | 2.88             | 0.09 | 0.49 | 0.05                           | 0.13                          | 0.05 | 0.22                           |      | 0.03             | 82.66 | 1.78  | 88.4 |
| 17MQ66-03-3 | 0.31              | 0.07             | 5.45             | 0.17 | 0.43 | 0.00                           | 0.16                          |      | 1.90                           | 0.04 | 0.09             | 73.11 | 8.28  | 90.6 |
| 17MQ66-06-1 | 0.07              | 0.04             | 3.27             | 0.09 | 0.47 | 0.03                           | 0.11                          |      | 0.47                           |      | 0.21             | 81.38 | 1.93  | 88.6 |
| 17MQ66-06-2 | 0.07              |                  | 3.50             | 0.10 | 0.28 | 0.01                           | 0.21                          |      | 0.47                           | 0.02 | 0.04             | 79.06 | 4.56  | 88.3 |
| 17MQ66-06-3 | 0.10              |                  | 2.94             | 0.08 | 0.49 | 0.05                           | 0.07                          |      | 0.36                           | 0.02 | 0.05             | 83.60 | 1.64  | 89.4 |
| 17MQ66-06-4 | 0.06              |                  | 3.32             | 0.03 | 0.37 | 0.00                           | 0.14                          |      | 0.39                           | 0.03 | 0.02             | 83.30 | 1.69  | 89.3 |
| 17MQ56-01-1 | 0.01              | 0.01             | 3.06             | 0.13 | 0.20 | 0.02                           | 0.10                          |      | 0.02                           | 0.01 |                  | 84.45 | 1.97  | 89.9 |
| 17MQ56-01-2 | 0.16              |                  | 3.69             | 0.08 | 0.31 | 0.01                           | 0.10                          |      | 0.13                           | 0.09 | 0.03             | 83.32 | 2.29  | 90.2 |
| 17MQ56-01-3 | 0.07              | 0.00             | 3.13             | 0.16 | 0.36 | 0.03                           | 0.15                          | 0.03 | 0.25                           | 0.08 | 0.03             | 83.21 | 2.88  | 90.3 |
| 17MQ56-03-1 | 0.18              | 0.05             | 2.81             | 0.19 | 0.18 |                                | 0.11                          |      | 0.05                           | 0.02 | 0.03             | 77.50 | 7.47  | 88.3 |
| 17MQ56-03-2 | 0.06              | 0.03             | 2.31             | 0.11 | 0.20 | 0.02                           | 0.04                          |      |                                |      | 0.02             | 82.31 | 1.85  | 86.9 |
| 17MQ56-04-1 | 0.07              | 0.05             | 3.64             | 0.15 | 0.31 | 0.03                           | 0.18                          | 0.03 | 0.15                           | 0.00 | 0.01             | 80.98 | 2.75  | 88.3 |
| 17MQ56-04-2 | 0.02              | 0.02             | 2.80             | 0.17 | 0.28 |                                | 0.08                          | 0.16 | 0.22                           | 0.14 | 0.01             | 82.14 | 4.19  | 90.2 |
| maximum     | 0.31              | 0.07             | 5.45             | 0.19 | 0.54 | 0.11                           | 0.21                          | 0.16 | 3.08                           | 0.14 | 0.29             | 84.45 | 8.28  | 90.3 |
| minimum     | 0.01              | 0.00             | 2.31             | 0.03 | 0.18 | 0.00                           | 0.04                          | 0.01 | 0.02                           | 0.00 | 0.01             | 73.11 | 1.61  | 86.9 |
| average     | 0.12              | 0.03             | 3.53             | 0.12 | 0.35 | 0.03                           | 0.12                          | 0.05 | 0.58                           | 0.04 | 0.06             | 80.61 | 3.46  | 89.6 |
| Data(wt%)   | Na <sub>2</sub> O | TiO <sub>2</sub> | SiO <sub>2</sub> | CoO  | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | NiO  | Al <sub>2</sub> O <sub>3</sub> | MnO  | K <sub>2</sub> O | FeO   | CaO   | Tot  |
| 17MQ66-02-1 | 0.02              |                  | 0.85             | 0.04 | 0.44 | 0.04                           | 0.06                          |      | 0.05                           | 0.04 |                  | 1.17  | 57.34 | 60.6 |
| 17MQ56-02-1 | 0.06              |                  | 0.11             | 0.03 | 0.79 | 0.07                           |                               |      | 0.02                           | 0.01 | 0.00             | 0.13  | 58.58 | 59.7 |
| 17MQ56-02-2 | 0.02              |                  | 0.03             |      | 0.22 | 0.05                           | 0.06                          | 0.00 | 0.02                           | 0.06 | 0.02             | 0.10  | 58.53 | 59.3 |
| 17MQ56-02-3 | 0.03              | 0.04             | 0.03             |      | 0.12 |                                | 0.09                          | 0.04 |                                | 0.08 | 0.01             | 0.06  | 59.99 | 60.4 |
| 17MQ56-04-3 | 0.03              | 0.04             | 1.20             | 0.01 | 0.55 | 0.06                           | 0.05                          | 0.07 | 0.01                           | 0.00 | 0.01             | 1.43  | 54.41 | 57.8 |
| 17MQ56-05-3 | 0.07              | 0.11             | 0.12             | 0.02 | 0.60 | 0.01                           | 0.02                          | 0.02 | 0.07                           |      | 0.05             | 0.21  | 58.21 | 59.3 |
| 17MQ56-06-2 | 0.02              | 0.01             | 0.22             |      | 0.64 |                                | 0.03                          |      | 0.10                           | 0.05 | 0.01             | 1.30  | 58.03 | 60.4 |
| 17MQ56-06-3 | 0.02              |                  | 0.42             | 0.05 | 0.57 | 0.01                           |                               | 0.02 | 0.06                           |      | 0.00             | 2.87  | 55.41 | 59.4 |
| maximum     | 0.07              | 0.11             | 1.20             | 0.05 | 0.79 | 0.07                           | 0.09                          | 0.07 | 0.10                           | 0.08 | 0.05             | 2.87  | 59.99 | 60.4 |
| minimum     | 0.02              | 0.01             | 0.03             | 0.01 | 0.12 | 0.01                           | 0.02                          | 0.00 | 0.01                           | 0.00 | 0.00             | 0.06  | 54.41 | 57.8 |
| average     | 0.03              | 0.05             | 0.37             | 0.03 | 0.49 | 0.04                           | 0.05                          | 0.03 | 0.05                           | 0.04 | 0.01             | 0.91  | 57.56 | 59.3 |
| Data(wt%)   | Na <sub>2</sub> O | TiO <sub>2</sub> | SiO <sub>2</sub> | CoO  | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | NiO  | Al <sub>2</sub> O <sub>3</sub> | MnO  | K <sub>2</sub> O | FeO   | CaO   | Tot  |

| Data(wt%)   | Na <sub>2</sub> O | TiO <sub>2</sub> | SiO <sub>2</sub> | CoO  | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | NiO  | Al <sub>2</sub> O <sub>3</sub> | MnO  | K <sub>2</sub> O | FeO   | CaO   | Tot  |
|-------------|-------------------|------------------|------------------|------|------|--------------------------------|-------------------------------|------|--------------------------------|------|------------------|-------|-------|------|
| 17MQ56-03-3 | 0.04              | 0.06             | 99.78            |      | 0.01 | 0.03                           | 0.01                          |      | 0.07                           |      | 0.01             | 0.04  | 0.27  | 100  |
| 17MQ56-05-1 | 0.04              | 0.03             | 98.60            |      | 0.01 | 0.03                           | 0.00                          | 0.03 | 0.07                           | 0.02 | 0.02             |       | 0.40  | 99.2 |
| 17MQ56-05-2 | 0.05              |                  | 99.61            |      | 0.02 |                                |                               | 0.09 | 0.01                           | 0.05 | 0.07             | 0.04  | 0.24  | 100  |
| 17MQ56-05-4 | 0.05              |                  | 98.65            | 0.03 | 0.00 | 0.02                           |                               | 0.08 | 0.05                           | 0.02 | 0.02             |       | 0.14  | 99.0 |
| maximum     | 0.05              | 0.06             | 99.78            | 0.03 | 0.02 | 0.03                           | 0.01                          | 0.09 | 0.07                           | 0.05 | 0.07             | 0.04  | 0.40  | 100  |
| minimum     | 0.04              | 0.03             | 98.60            | 0.03 | 0.00 | 0.02                           | 0.00                          | 0.03 | 0.01                           | 0.02 | 0.01             | 0.04  | 0.14  | 99.0 |
| average     | 0.05              | 0.05             | 99.16            | 0.03 | 0.01 | 0.03                           | 0.01                          | 0.07 | 0.05                           | 0.03 | 0.03             | 0.04  | 0.26  | 99.7 |
| Data(wt%)   | Na <sub>2</sub> O | TiO <sub>2</sub> | SiO <sub>2</sub> | CoO  | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | NiO  | Al <sub>2</sub> O <sub>3</sub> | MnO  | K <sub>2</sub> O | FeO   | CaO   | Tot  |
| 17MQ66-01-2 | 0.12              | 0.07             | 5.37             | 0.08 | 0.43 | 0.06                           | 0.07                          | 0.01 | 1.31                           |      | 0.18             | 59.15 | 16.92 | 83.7 |
| 17MQ66-01-3 | 0.05              |                  | 3.28             | 0.12 | 0.37 | 0.04                           | 0.05                          |      | 0.53                           | 0.06 | 0.03             | 44.42 | 25.57 | 74.3 |
| 17MQ66-05-4 | 0.05              |                  | 2.72             | 0.13 | 0.43 | 0.01                           | 0.06                          |      | 0.43                           |      | 0.02             | 26.89 | 39.91 | 70.0 |
| 17MQ56-06-1 | 0.18              | 0.02             | 3.44             | 0.07 | 0.37 | 0.03                           | 0.11                          | 0.10 | 0.62                           | 0.06 | 0.02             | 33.18 | 33.01 | 71.2 |
| maximum     | 0.18              | 0.07             | 5.37             | 0.13 | 0.43 | 0.06                           | 0.11                          | 0.10 | 1.31                           | 0.06 | 0.18             | 59.15 | 39.91 | 83.7 |
| minimum     | 0.05              | 0.02             | 2.72             | 0.07 | 0.37 | 0.01                           | 0.05                          | 0.01 | 0.43                           | 0.06 | 0.02             | 26.89 | 16.92 | 70.0 |
| average     | 0.10              | 0.05             | 3.70             | 0.10 | 0.40 | 0.04                           | 0.07                          | 0.06 | 0.72                           | 0.06 | 0.06             | 40.91 | 28.85 | 75.0 |











