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Early Triassic oceanic red beds coupled with deep sea oxidation in South Tethys

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ABSTRACT: Carbonate oceanic red beds (ORBs) are unusual in Phanerozoic shelf settings but can be widespread during discrete intervals. Several scenarios have been invoked to explain the origin of these ORBs but there remains uncertainty about the process by which the red pigmentations of ORB form. Here, we propose that the occurrence of ORBs at intermediate water depths in shelf regions is controlled by fluctuations in the redox state of deeper waters. We have examined Early Triassic Peri-Gondwana shelf sections in South Tibet which show the development of Spathian (late Early Triassic) ORBs at intermediate water depths. The red color of these ORBs is imparted by randomly dispersed hematite crystals that are micrometers in size, showing weak alteration by late burial diagenesis. Widespread anoxia, including in the oceanic realm, was well developed in the Early Triassic. Synchronous occurrence of Spathian ORBs on deep shelf regions is closely related to the improved oxidation in deeper settings,

from anoxia to dysoxia, based on changes in the redox proxy of pyrite framboid sizes. It is, therefore, inferred that prolonged deep-water anoxia might serve as source of Fe (II) to exert control on the formation of ORBs when intensified upwelling develops, and the occurrence of ORBs marks the terminal stage of an oceanic anoxic event.

Key words: oceanic red bed; microfacies; Spathian; deep water oxidation; framboid pyrite

1. Introduction

Oceanic/marine red beds (ORBs or MRBs) are present throughout the geological history especially in deep-water, pelagic settings (Hu et al., 2012; Song et al., 2017). ORBs can be subdivided into three groups in term of their lithology: red shales, red cherts, and red carbonates (Hu et al., 2012). The red color is caused by the presence of small amounts of hematite, goethite, either/or Fe- or Mn-bearing calcite (Cai et al., 2009, 2012; Li et al., 2011). ORBs have occurred sporadically since the beginning of Phanerozoic, and have thicknesses ranging from meters to hundreds of meters, but they are often restricted to short stratigraphic intervals (Hu et al., 2012; Song et al., 2017).

Amongst Phanerozoic ORBs, Cretaceous examples have received the most attention (Wang et al., 2005, 2011; Hu et al., 2006, 2012) due to their global distributions in deep oceans (Wang et al., 2005; Hu et al., 2012). Studies of their red pigmentation, using redox sensitive elements, have generally shown that prevailing conditions were oxic (Li et al., 2011; Wang et al., 2011). It is noteworthy that the deposition of the Cretaceous ORBs typically began soon after ocean anoxic events (Hu et al., 2012). Indeed most Phanerozoic ORBs appear to develop following episodes of widespread ocean anoxia (Song et al., 2017). As a result, several increased oxidation scenarios have been proposed to account for the origin of ORBs: (1) oxidation of anoxic deep oceans caused by enhanced ocean circulation (Wang et al., 2009); (2) oxidation of the ferruginous sea (Song et al., 2017). The former put much emphasis on the redox change and the latter on the inventory of Fe(II), both of which are needed for the formations of ORBs (Song et al., 2017). To understand the dynamics of the oxidation of ferruginous sea during ORBs formation, a detailed temporal and spatial investigation of redox states is needed. We address this little studied issue here.

Early Triassic ORBs have been sporadically recorded (Von Rad et al., 1994; Brühwiler et al., 2009; Takahashi et al., 2009; Sun Y.D. et al., 2015), but they lack constraints on temporal and spatial distributions which obscure the understanding of their origin. We present four Early-Middle Triassic sections from South Tibet, that include two with ORBs. These four sections span a range of water depths from inner shelf to deep basin, thereby allowing us to assess factors controlling the formation of the ORBs at a detailed temporal and spatial scale.

2. Geological setting

2.1. Paleogeography

South Tibet consists of three tectonic units: the Lesser Himalaya (the crystalline Precambrian basement of the High Himalaya), the High Himalaya and the Tethyan Himalaya (Liu and Einsele, 1994) (Fig. 1A). The Tethyan Himalaya unit is separated from the High Himalaya to the south by a series of discontinuous E-W striking thrusts, and is bounded from the Lhasa Block to the north by the Indus-Tsangbo suture. Our study sections are within the middle of the Tethyan Himalaya unit with three sections from the southern part and one section from the northern part (Fig. 1B).

During the Permian-Triassic transitional interval, South Tibet was located on the northern margin of Peri-Gondwana at a paleolatitude of ~40°S (Shen et al., 2003) (Fig. 1C) and experienced at least two rifting events during the late Paleozoic (Liu and Einsele, 1994; Shen et al., 2003). These saw the Qiangtang Block and then the Lhasa Block detach from the North Indian plate and drift northward. The detachment of the Lhasa Block is inferred to have commenced at the end of Permian, and marked the opening of the Neo-Tethys (Liu and Einsele, 1994; Shen et al., 2006). Subsidence rates on the northern margin of Peri-Gondwana during the initial rift-stage were low, resulting in the widespread accumulation of thin, inner shelf deposits during the earliest Early Triassic (Liu and Einsele, 1994). With the opening of the Neo-Tethys, an Early Triassic asymmetrical basin developed in South Tibet, which is characterized by low sedimentation rates of shallow-water sediments in the southern zones and high sedimentation rates of deep-water turbidites in central and northern zones (Liu and Einsele, 1994).

2.2. Stratigraphy and study sections

The Selong section (28°40′15″N, 85°49′36″E) is located near the village of Selong, 77 km NW of old Tingri County where the Lower Triassic Kangshare Formation has a well-established biostratigraphy based on conodonts and ammonoids (Orchard et al., 1994; Wang Z.H. and Wang Y.G., 1995; Shen et al., 2006; Wang et al., 2017; Yuan et al., 2018). It is divided into three units in ascending order: a ~4 m thick limestone yielding the Smithian ammonoid *Nyalamites angustecostatus* and *Owenites carpenteri* (Fig. S1); a middle unit consisting of a 1.2 m thick shale; an upper unit comprising a 2.2 m thick limestone containing the Spathian ammonoid *Procarnites kokeni* (Fig. S1) and conodont *Neospathodus waageni* (Wang Z.H. and Wang Y.G., 1995). The Smithian-Spathian boundary is approximately placed in the lowermost part of a dark gray shale that overlies Smithian carbonates (Fig. 2).

The Tulong section (28°27′11″N，86°09′12″E) is situated near Tulong village, 36 km NW of the capital of Nyalam County. A detailed ammonoid biostratigraphic scheme developed for the Tulong Formation places the Smithian-Spathian boundary at the top of a 9 m thick Smithian limestone bed that is overlain by a 3 m thick shale (Brühwiler et al., 2009). The Spathian succession is conspicuous for the occurrence of a 6 m thick ORB, developed in both shale and limestone (Fig. 2). The red strata span much of the Spathian and are capped by 1 m of gray limestone, above which the presence of ammonoid *Pseudodanubites gymnites* marks the Spathian-Anisian boundary (Brühwiler et al., 2009).

The Xialong section (28°31′21″N，86°41′48″E) is located 1 km west of Xialong village, 32 km SW of the capital of old Tingri county. The Lower Triassic lithological succession belongs to the Tulong Formation and can be divided into three units, which are similar to the Tulong section. The lower unit consists of a ~6 m-thick limestone yielding an ammonoid fauna *Owenites carpenteri*, *Pseudosageceras augustum* and *Subvishnuites posterus* (Fig. S1) that suggests a middle-late Smithian age. The middle unit comprises a

~10 m thick shale (Fig. 2), and here, the Smithian-Spathian boundary is placed at the lowermost part of this unit, based on the lithological correlation with the Tulong section. The upper unit is a ~7 m-thick limestone, with two thin levels of ORB in the lower part (Fig. 2).

The Xiukang section (29°08′05″N，87°59′26″E) is located near the small village of Xiukang, 34 km NE of the capital of Lhaze County and consists of alternations of shale and limestone that belong to the Zhongbei Group. The occurrence of *Eumorphotis multiformis, Claraia* sp. (Li et al., 2018) and ammonoid *Ophiceras* (Shen et al., 2010) in the lower part of the section indicates an Early Triassic age, and the upper part yields the bivalve *Daonella* sp. typical of the Anisian (Li et al., 2018). The Smithian-Spathian boundary is here defined by the organic carbon isotope record (Song H.Y. et al., 2018) as well as by the last occurrence of bivalves *Eumorphotis* and *Claraia* that both suffered a major decline in diversity and abundance during the late Smithian (Komatsu et al., 2008).

3. Methods

Samples from both ORB and non-ORB beds were thin sectioned. Micro-Raman imaging was performed at the State Key Laboratory of Biogeology and Environmental Geology (Wuhan, China) with a WITec 300 Confocal Raman Imaging system. A 532 nm laser was used and focused by a 100X objective (N.A.=0.9) for image scans, with a spatial resolution of 0.36 micron per pixel. The laser power was maintained at 5 mW to avoid sample damage by laser radiation. An optic fibre, 50 microns in diameter, was used to collect a Raman spectrum at a confocal depth of at least 0.5 micron below the polished surface of the thin section. A 600 groves mm^{-1} grating was used to provide spectra with a wavenumber resolution around 4 cm^{-1}. The data was processed with the WITec Project Five Plus software. All Raman spectra were corrected for cosmic rays. The peak intensity for different mineral bonds were mapped and converted into a color-coded hyperspectral Raman map. For all presented average Raman spectra, pixels from Raman images were selected on the basis of their nearly identical point spectra and the resulting average spectra were corrected with background subtraction. For standard Raman spectrum of each mineral in this study refer to http://rruff.info/.

Size analysis of pyrite framboids was also conducted to evaluate redox conditions. Samples were fresh cut and polished and the pyrite petrography was investigated using the scanning electron microscope (Hitachi SU8000) equipped with energy-dispersive X-ray spectroscopy (SEM-EDS) under backscattered electron (BSE) mode at the State Key Laboratory of Biogeology and Environmental Geology (Wuhan, China). Criteria to determine the intensity of anoxia based on size distribution of pyrite framboids follow the protocol of Wilkin et al. (1996) and Bond and Wignall (2010).

4. Results and interpretation

4.1. Microfacies description and interpretation

Macro-sedimentary structures are scarce in the Lower Triassic outcrops of South Tibet, so depositional environment determinations heavily rely on microfacies analysis. A total of nine microfacies were detected and grouped into two associations that correspond to different environments of a middle carbonate ramp and outer ramp. For the detailed microfacies classification see Table 1.

4.1.1. Facies association 1: Oncoid-cortoid dominated middle ramp association

Description: Facies association 1 consists of four microfacies including MF1 to MF4. Oncoid-cortoid grainstone/packstone (MF1) (Fig. S2A, B) and cortoidal floatstone (MF2) (Fig. S2C) only occur within the Olenekian at Selong, and are dominated by oncoids (1 to 3 mm in long axis) that consist of a bioclastic nucleus and successive concentric coatings. Bioclastic packstone with diverse fossils (MF3) (Fig. S2D) is common in the Olenekian at Selong, but is rare elsewhere. Nodular, burrowed bioclastic packstone/wackestone with diverse fossils (MF4) (Fig. S2E, F) is conspicuous for its red color in its only outcrop in the Spathian at Tulong. Abundant burrows, stromatactis and occasional erosional surface are found in MF4.

Interpretation: MF1 to MF4 are interpreted to represent a spectrum of environments from high energy, proximal middle ramp to distal middle ramp. MF1 and MF2 were deposited in the high energy, proximal middle carbonate ramp, a zone that is subject to frequent storm waves. Modern oncoids and cortoids form in the intertidal to shallow subtidal environments and are considered to be representative of shallow subtidal domain (Ratcliffe, 1988; Flügel, 2010). The presence of moderately-sorted oncoids and cortoids in MF1 in a fining upward beds (Fig. S2A), suggests deposition under waning current velocity probably during storm transport (e.g., Pérez-López and Pérez-Valera, 2012). Cortoids, in association with thick-shelled bivalves floating in a micritic matrix, are interpreted as rapidly-emplaced proximal tempestite (e.g., Chatalov, 2016).

MF3 and MF4 were formed in the distal middle ramp, where sediments were occasionally reworked by storm waves (Burchette and Wright, 1992). Packstone of fragmented bioclasts, including bivalves and echinoderms, with abundant burrows indicate an open shelf environment. The red, nodular, bioclastic wackestone contains abundant stromatactis (Fig. S2E), ammonites and occasional erosional surfaces (Fig. S2F), and is strikingly similar to the Devonian 'griotte facies' and Jurassic 'Ammonitico rosso facies' of the Alpine-Mediterranean region. The latter are interpreted as storm-transported sediment in deep shelf environment (Flügel, 2010). The erosional surface in MF4 is represented by a sharp contact between overlying bioclastic wackestone and the underlying lime mudstone (Fig. S2F), probably implying the seafloor was eroded by strong currents induced by storm waves.

4.1.2. Facies association 2: pelagic faunas dominated ramp association

Description: Facies association 2 consists of five microfacies, MF5 to MF9. Bioclastic wackestone containing diverse fossils (MF5) (Fig. S3A) is a common and widespread facies in the Early Triassic of South Tibet. Thin-shelled, filamentous bivalve packstone/wackestone (MF6) (Fig. S3B), consisting of densely packed bivalves, occurs only in the Spathian interval at Xialong and Xiukang. Lime mudstone (MF7) and marly siltstone (MF8) (Fig. S3C) occur as thin intercalations within marly limestone or shales, both of which are predominantly restricted to the Smithian-Spathian transitional interval at Xialong. Radiolaria packstone/wackestone (MF9) (Fig. S3D), consisting of abundant calcified radiolaria, is a major microfacies throughout the Early Triassic at Xiukang, in which erosional surface and floating pebbles were found.

Interpretation: MF5 to MF6 are interpreted to be deposited in deep shelf/basin environments generally below the storm wave base. It is controversial to determine the paleobathymetric position of the thin-shelled bivalves in MF6; many authors regard these filaments as planktonic larval shells living in bathyal deep-water settings, but some argue for a benthic origin (Allison et al., 1995). The parallel arrangement of the shells above a micro-erosional surface (Fig. S3B) suggests current activity. This is supported by the presence of planar bedding and pebbles that are indicative of sediment-gravity flows at Xiukang (Li et al., 2018). Moreover, the coexistence of thin-shelled bivalves and radiolaria further supports the deep shelf/basin environment in which MF6 was deposited.

4.2. Depositional Environments

4.2.1. Selong section

The Smithian and Spathian carbonates at Selong are dominated by middle ramp facies association 1 (Figs. S4, 3A). The Smithian interval is characterized by the presence of oncoid grainstone (MF1) interbedded with bioclastic packstone with diverse fossils (MF3) (Fig. 3B) including echinoderms, thick-shelled bivalves, small gastropods, and foraminifera. Oncoids disappear in the Spathian, and instead, occasional cortoids are found floating in the micritic matrix of this interval (Fig. 3C). These Spathian cortoids show striking similarities with those found in the contemporaneous Virgin Limestone of Nevada (Woods, 2013), although the Tibetan occurrence lacks any associated ooids and oncoids. The floatstone structure of cortoids in the Selong section suggests the re-deposition by storm-induced bottom currents in this middle ramp setting.

4.2.2. Tulong section

The Spathian at Tulong section is conspicuous for its red color and mainly consists of MF4 that formed at the middle/outer ramp transition (Figs. 4A , S5). The ORB beds mainly consist of shale and nodular bioclastic wackestone with diverse fossils (MF4) including echinoderms, bivalves, foraminifera, and ostracods (Fig. 4B). They are characterized by abundant burrows and stromatactis (Fig. 4C), as well as occasional erosional surfaces. The vertical, curved, unbranched burrows are 3 to 12 mm in width and ca. 3 cm in length (Fig. 4C), showing sediment filling within which abundant stromatactis consisting of spar bodies with flat bases and digitate tops are present (Fig. S2E). Erosional surfaces are characterized by sharp truncation surfaces separating the underlying micrite from the echinoderm wackestone (Fig. S2F)

The abundant stromatactis found in burrows in these Tibetan examples supports the burrow network origin of the Spathian stromatactis (e.g., Bathurst, 1980). The presence of erosional surfaces in red nodular bioclastic wackestone that are commonly interpreted as storm-transported sediments (e.g., Devonian 'griotte facies' and Jurassic 'Ammonitico rosso facies' of the Alpine-Mediterranean region, Flügel, 2010), suggests a deep water depositional environment occasionally affected by storm currents.

4.2.3. Xialong section

The Spathian carbonate beds at Xialong mainly consist of bioclastic wackestone with a monotonous composition of thin-shelled bivalves (MF6) (Fig. S6). Two ca. 0.5 m thick, light brown beds are present 3 m above the inferred Smithian-Spathian boundary (Fig. 5A); these are thin-shelled bivalve wackestone with rare ostracods (Fig. 5B) and marly siltstone (Fig. 5C).

The fossil assemblage is suggestive of a deep-water environment (e.g., Lukeneder et al., 2012). The assemblage of small foraminifera, thin-shelled bivalves, juvenile ammonites and occasional calcispheres (interpreted to be calcite-replaced radiolarian in Beds 89, 92) in marly siltstone suggests a deep water setting. The lack of evidence for sediment reworking by bottom currents indicates low energy deposition and further supports the notion of deep-water below the storm wave base.

4.2.4. Xiukang section

The Lower Triassic Xiukang section comprises a 23 m thick succession of dark gray shales intercalated with thin-bedded bioclastic packstone/wackestone (Figs. 6A, S7) containing radiolarians and thin-shelled bivalves (Fig. S3B, D). Thin planar and wavy bedding is seen in the outcrop (Fig. 6B), along with floating pebbles (Fig. 6C). In this section the thin bedding is seen to be interbedded layers of densely packed, thin shelled bivalves (filamentous limestone) (MF6), often with sharp, apparently erosive bases, and micrite or wackestone (Fig. S3B).

Floating pebbles in lenticular limestone, as well as the micro-erosive bases suggest these deposits were transported and deposited as sediment-gravity flows. The existence of densely-packed thin-shelled bivalves and radiolarians suggests a deep basin setting.

4.3. Petrographic observations

Micro-Raman imaging shows that the ORB sample from the Tulong section comprises micritic calcite, quartz and micron-sized hematite (Fig. 7A), which were identified by their diagnostic Raman peaks at 1085 cm^{-1}, 463 cm^{-1} and 1320 cm^{-1} (Fig. 7C). The hematite is closely associated with calcite and is often present as inclusions inside the calcite crystals, indicating that they are primary hematite deposited prior to or coeval with the calcite. SEM imaging and EDS analysis confirm the presence of micrometer to sub-micrometer sized, euhedral or subhedral hematite crystals that are associated with calcite and quartz (Fig. 7D). The age-equivalent carbonate at Selong mainly consists of calcite, quartz, and rare rutile (Fig. 7B) that display a prominent Raman peak at 600-620 cm^{-1} (Fig. 7C), with no hematite detected. Therefore, the red color of the Tulong ORB is attributed to the finely disseminated hematite occurring as inclusions in, or interstitial fillings between, calcite crystals (Fig. 7A).

4.4. Paleo-redox conditions

All samples from Xiukang, a deep basinal section, yield abundant and generally small (mean diameter ~ 6 μm) pyrite framboids, suggesting generally anoxic/euxinic conditions (Figs. 8, S8), but with the larger examples from the Dienerian to the Spathian (Fig. 9). In detail, framboids from Beds 1 to 3 (Induan Stage) are rather small with a mean diameter range from 3.4 to 4.4 μm, but they show an abrupt increase to 5.9 μm at the boundary between Beds 3 and 4 (Dienerian-Smithian boundary), and then remain stable in Beds 4 to 7 (Smithian stage) before an increase to 6.6 μm at the boundary between Beds 7 and 8

(Smithian-Spathian boundary). Framboid diameter declines once again (to 5.5 μm) between Beds 8 to 9 (lower Spathian), and is immediately followed by an increase up to 7.3 μm in Bed 10. The mean framboid diameters in Beds 10, 11 and 20 (middle and upper Spathian) are stable and relatively large with a mean diameter of 7.4 μm, suggesting a stable dysoxic conditions. Finally, framboid diameter drops to 6.0 μm in Bed 24 in the early Anisian age.

Further up slope, at the Tulong section, framboids are generally very rare, especially in the ORB intervals, indicating oxic conditions. Only four beds (Beds 15, 26 to 28) yielded common framboids (mean count of > 110) and they are small (mean diameter of 4.6 μm) (Fig. 8), indicating euxinia.

Stratigraphic and age correlations reveal that the development of ORBs in our deep shelf section (Tulong) coincides with the occurrence of framboid populations indicating stable dysoxia in the deeper basin section (Xiukang) (Fig. 9).

5. Discussion

5.1. Spatial distribution of the Spathian ORBs

The widespread Spathian ORBs are restricted to middle-outer shelf regions, a pattern that is obviously different from that of Cretaceous ORBs. The Spathian ORBs have been described from Thakkhola section in Nepal (Von Rad et al., 1994), Jiarong, Mingtang and Chaohu sections in South China (Sun Y.D., et al., 2015; Song et al., 2017), WHK1 section in New Zealand (Hori et al., 2011) and the Momotaro-jinja section in Japan (Takahashi et al., 2009), confirming their widespread and potentially global distribution. All Spathian

ORBs were deposited in middle shelf to distal outer shelf regions, except the Momotaro-jinja section that belongs to a deep ocean environment. The occurrence of the Spathian ORBs in Momotaro-jinja might represent a local event, since ORBs are absent in most deep basin sections including Xiukang in South Tibet, and Ursula Creek in British Columbia (Henderson, 2011). By contrast, the Cretaceous ORBs are ubiquitous in deep oceans (Wang et al., 2005, 2011; Hu et al., 2012).

5.2. Origin of hematite in ORBs

A few studies of ORBs have confirmed that the morphology and spatial distribution of hematite grains can be used to assess their origin. Hematite that is tens of micrometer in diameter and shows preferential orientation along fracture or layer boundaries is typically interpreted as "secondary" (late diagenetic) in origin, while those, which are smaller (submicrometer to micrometers) in diameter and randomly scattered in the matrix, are interpreted to be of "primary" origin (Sun S. et al., 2015). Hematite grains from the ORBs at Tulong are small (submicrometer to micrometers in diameter) and are randomly scattered (Fig. 7A, D), indicating their "primary" origin.

5.3. Paleoenvironmental implications of the Spathian ORBs

Previous studies have shown that ocean anoxic events are usually followed by development of ORBs and have thus postulated that anoxic deep oceans can serve as the Fe (II) reservoir to supply iron for the formation of ORBs (Song et al., 2017). In some models ORB formation is linked with the oceanic/climatic consequences of prolonged ocean anoxia. Wang et al. (2011) suggested that enhanced burial of organic carbon during oceanic anoxic events would have led to the drawdown of atmospheric pCO_2, with consequent climate cooling (e.g., Damsté et al., 2010). This in turn, would have enhanced the formation of cold, well-oxygenated deep water and lead to the deposition of ORBs in deep oceans, if the preceding anoxic event was sufficiently long lived to allow build up of ferruginous deep waters. However, this model for Cretaceous ORBs does not directly apply to the Spathian ORBs of Tibet which accumulated in an outer shelf setting rather than in deeper waters.

The development of ORBs in shelf regions (Tulong section) is closely related to the improved oxidation of oxygen-poor, deep waters (Xiukang section) indicated by framboidal pyrite evidence (Fig. 9). Thus, the presence of Spathian ORBs marks the terminal stage of the Early Triassic oceanic anoxic event, and turnover of deep water flushing ferruginous waters up slope is a likely scenario for the Tibetan ORBs. Diverse redox proxy evidence has shown that the Early Triassic oceans were generally anoxic at a time of intense global warming (Wignall and Twitchett, 2002; Wignall et al., 2010; Song H.J. et al., 2012; Sun et al., 2012; Song H.Y. et al., 2014; Huang et al., 2017; Zhang et al., 2018). The deep-water anoxia persisted for much of the Early Triassic but was interrupted, in the early to middle Spathian, by an oxidation event that coincided with a significant cooling episode (Sun et al., 2012). The early to middle Spathian oxidation event is supported by evidence from pyrite petrography (this paper; Song et al., 2019), Fe-speciation (Clarkson et al., 2016; Song et al., 2019), carbon and sulfur isotopes (Song et al., 2013, 2014) and uranium isotope (Zhang et al., 2018).

The oxidization of deep waters in the Spathian of South Tibet could relate to strengthening of ocean circulation as a result of global climate cooling. The climate cooling would enhance the sinking of O_2- and nutrition-rich cold water while pole-to-equator thermal gradients strengthened (Kidder and Worsley, 2004). Moreover, intensified wind shear and associated wind-driven upwelling, in return, would enhance the vertical mixing of the stratified ocean, to transfer large amount of Fe (II) from the anoxic deeps to shelf regions where it was oxidized to form precursors of ORBs at intermediate water depths (Fig. 10), which were then dehydrated to form hematites during the early diagenesis. The source of Fe maybe related to a terrigeneous fraction (Neuhuber et al., 2007), but the lack of red beds in shallow-shelf settings indicates that hematite does not have a terrestrial (land-derived) component.

The occurrence of Spathian ORBs is accompanied by a significant rebound in biodiversity, supporting the amelioration of benthic ocean conditions. The Spathian witnessed a rapid increase in diversity of foraminifera (Song et al., 2011), ammonoids (Brayard et al., 2006), and ichnospecies richness (Feng et al., 2018) as well as the first occurrence of calcareous algae (Song et al., 2011) and metazoan reefs sponge (Brayard et al., 2011). A new biodiversity database also shows a significant increase in marine genera numbers in the Spathian (Song H.J. et al., 2018). Abundant burrows that are centimeters in size (Fig. 4C) are found in ORBs in South Tibet, further supporting well-ventilated, benthic conditions. Therefore, the occurrence of Spathian ORBs indicates a significant amelioration of ocean dysoxia, which might be driven by the intense ocean upwelling that provides adequate nutrient and oxygen.

6. Conclusions

The Spathian thick-bedded ORBs are widespread in South Tibet and are restricted to deep shelf to slope depositional environments. These ORBs mainly consist of red nodular limestone with diverse fossils and abundant burrows, indicating well ventilated ocean conditions. The red color of ORBs is attributed to micrometer-sized hematite grains that are randomly scattered in the matrix, without any preferential orientations in fractures and layer boundary, excluding the possibility that they are originated from diagenetic alternations.

Early Triassic deep, basinal waters in South Tibet recorded persistent anoxia/euxinia except in the early-middle Spathian when dysoxia developed. This improved oxygenation coincides with climate cooling and the development of ORBs in deep shelf regions. It is suggested that, upwelling caused by climate cooling flushed large amounts of Fe (II) from anoxic deep water to deep shelf regions where it was oxidized to hematite to form ORBs.

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Figure Captions

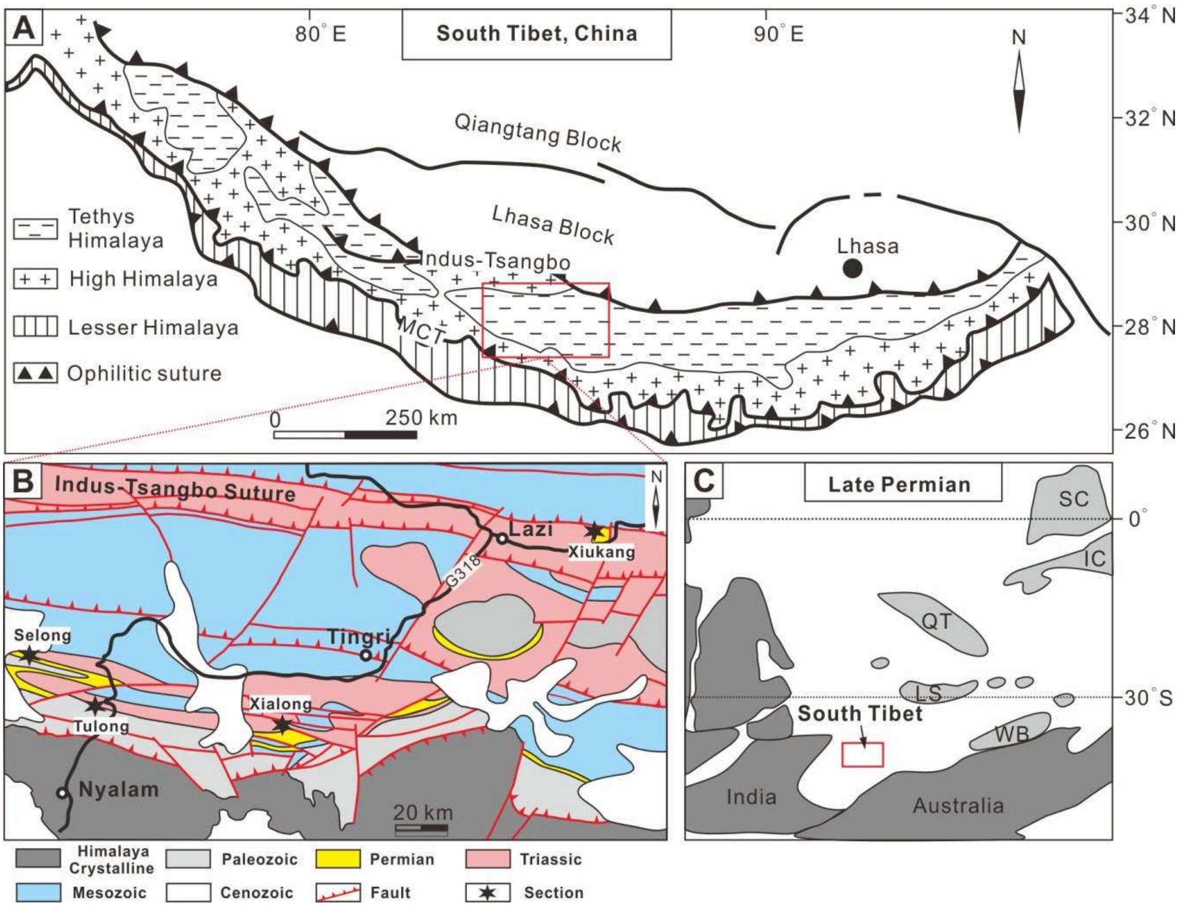

Fig. 1. (A) Major tectonic units of Himalaya region and study area (marked by the red rectangle), Modified from Liu and Einsele (1994). (B) Geological and location map showing the study sections (National Geological Archive, China, http://www.ngac.org.cn/Map/List) (C) Reconstruction map showing the paleo-position of the South Tibet at the end of the Permian (red rectangle) (modified from Shen et al., 2003). WB—Western Burma; LS—Lhasa; QT—Qiangtang; IC—Indochina; SC—South China.

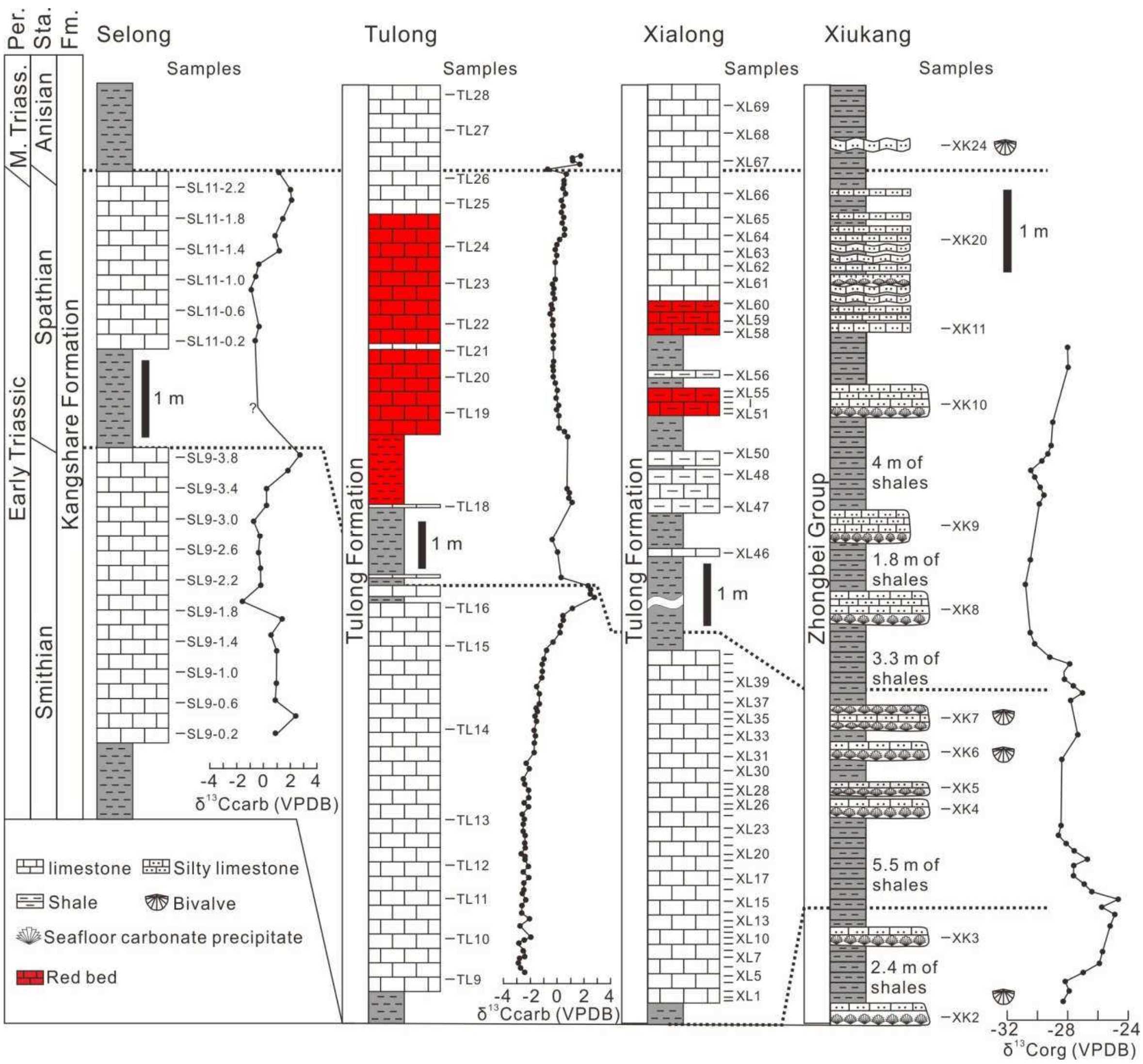

Fig. 2. Correlation of the sections from the South Tibet region. The Smithian-Spathian and Spathian-Anisian boundaries of the Tulong, Selong, and Xiukang sections are defined by ammonoid biozones (Brühwiler et al., 2009), conodont data (Garzanti et al., 1998), bivalve combined with organic carbon isotopes (Li et al., 2018). Only the Smithian-Spathian boundary is recognized at the Xialong section by the occurrence of ammonoid *Pseudosageceras augustum* and *Subvishnuites posterus*. Carbonate carbon isotope data of the Tulong section is after Brühwiler et al. (2009). Organic carbon isotope data of the Xiukang section is from Song H.Y. et al. (2018).

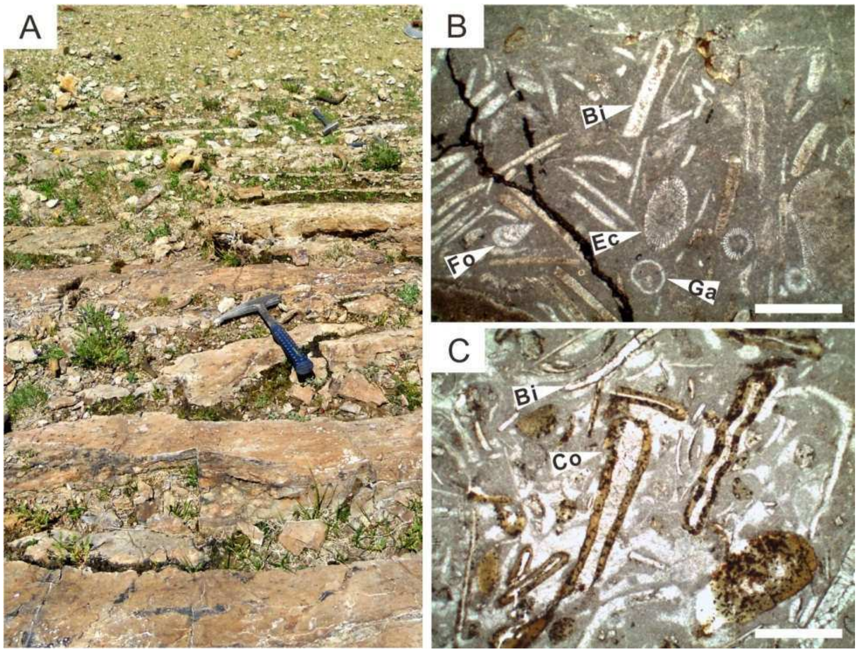

Fig. 3. (A) Field photo of the Spathian carbonate beds at the Selong section, hammer (35 cm in length) for scale. (B) Bioclastic packstone with diverse fossils including bivalve (Bi), echinoid (Ec), foraminifera (Fo), and gastropods (Ga), Sample SL11-2.2, scale bar = 1 mm. (C) Cortoid floatstone showing preferentially oriented cortoids (Co) that consists of bright yellow cortex encrusted on thick-shelled bivalves (Bi), Sample SL11-0.6, scale bar = 1 mm.

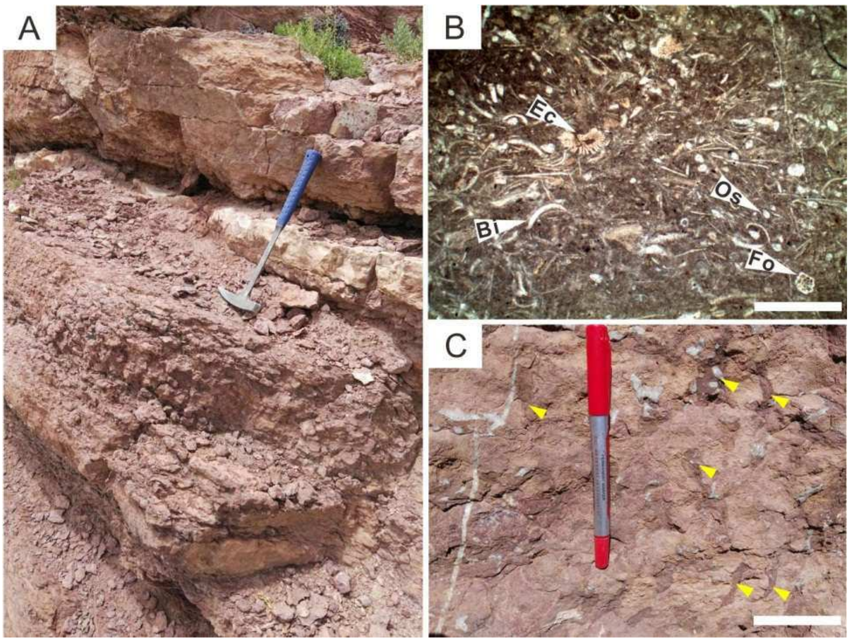

Fig. 4. (A) Field photo of Spathian, red, nodular limestone at Tulong. Hammer (35 cm in length) for scale. (B) Bioclastic packstone with diverse fossils including bivalve (Bi), echinoid (Ec), foraminifera (Fo), and ostracods (Os), Sample TL19-0.2, scale bar = 1 mm. (C) Outcrop photograph showing abundant burrows (yellow arrows) developed in red limestone at the Tulong section, pen (15 cm in length) for scale.

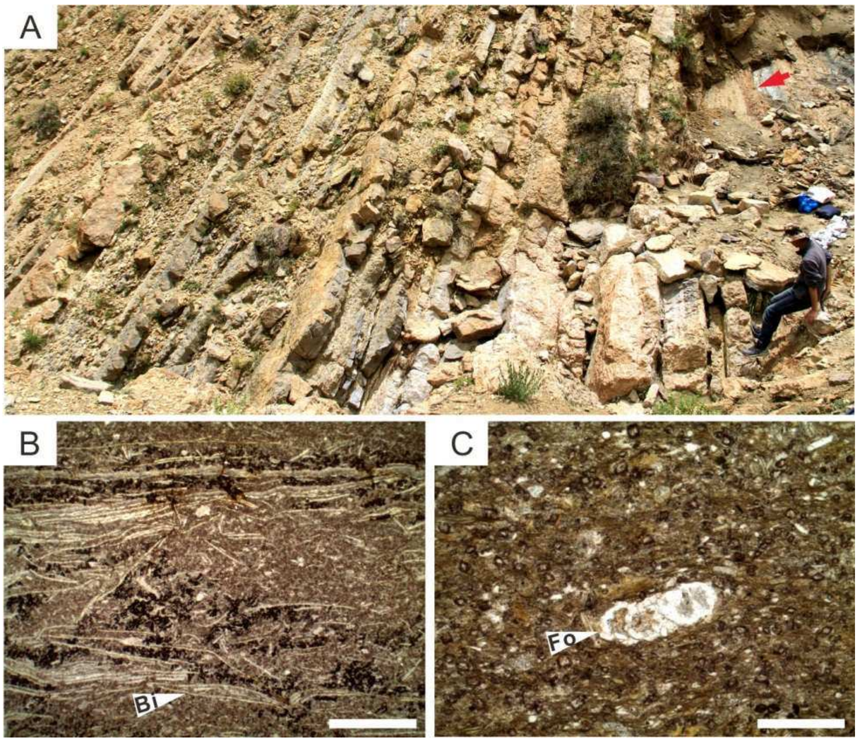

Fig. 5. (A) Field photo of Spathian carbonate beds at Xialong, person (178 cm in height) for scale. (B) Bivalve wackestone consisting of thin-shelled bivalves (Bi) with weak preferential orientation, Sample XL-60, scale bar = 1 mm. (C) Marly siltstone with rare small foraminifera (Fo), Sample XL56, scale bar = 0.5 mm.

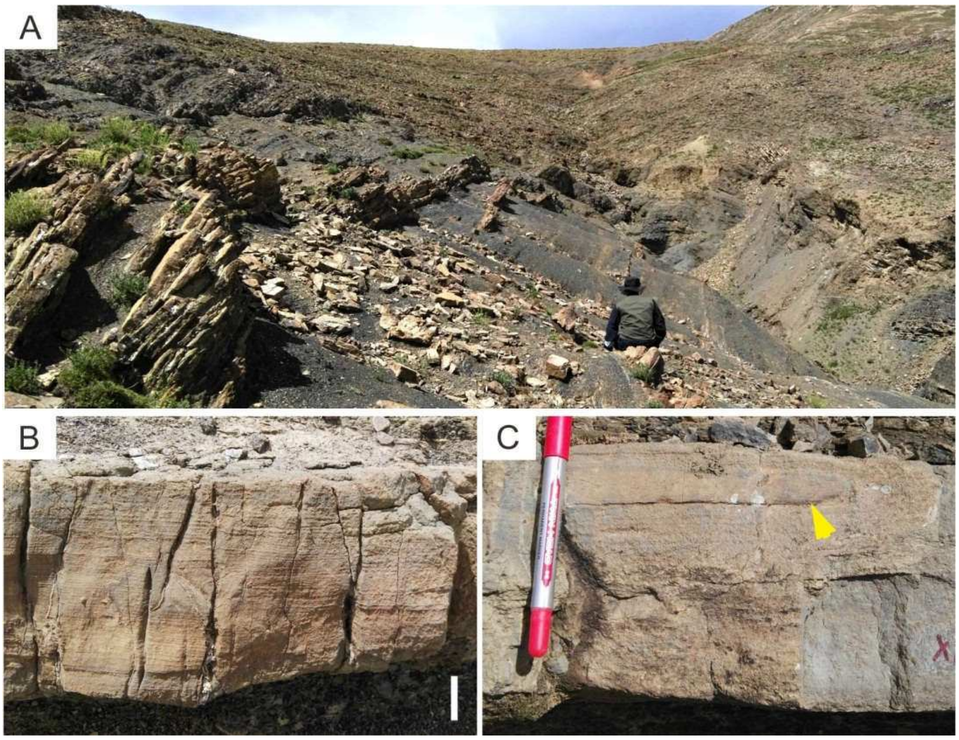

Fig. 6. (A) Field photo of the Lower Triassic sequence at Xiukang, person (178 cm in height) for scale. (B) Silty limestone showing parallel bedding, Bed 10, scale bar = 5 cm. (C) Thin-bedded, silty limestone containing floating pebble (arrow), Bed 6, pen (15 cm in length) for scale.

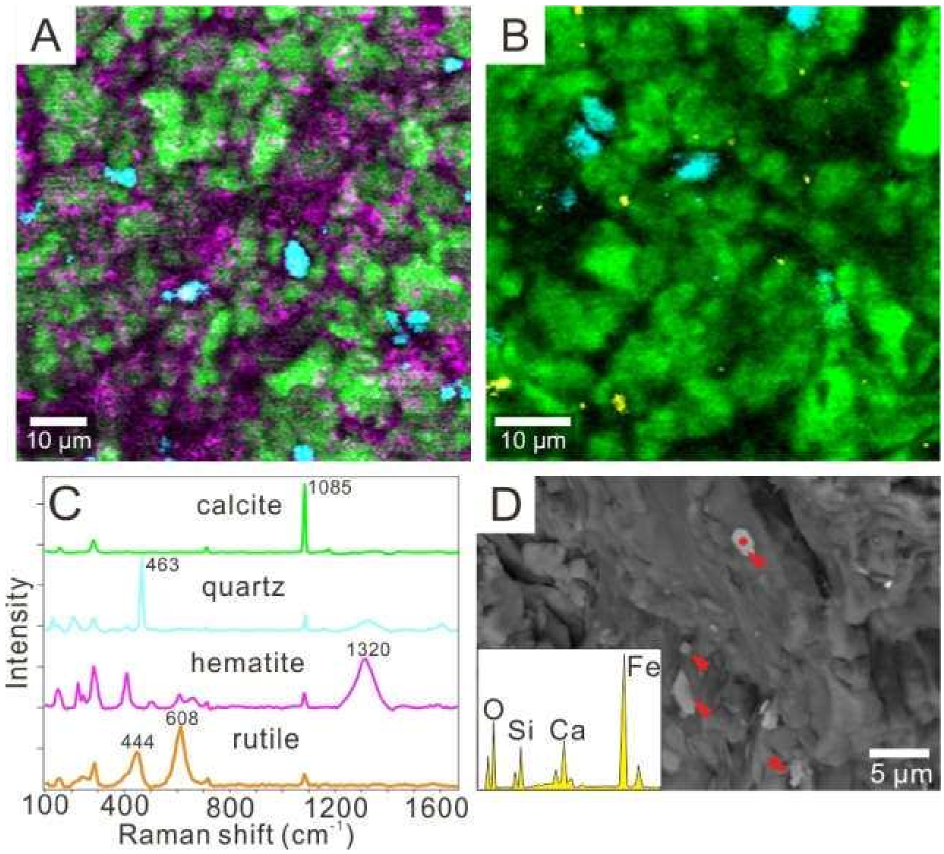

Fig. 7. (A) Raman map of ORB sample from Tulong section showing randomly scattered hematites in matrix, Sample TL19+0.2. Color carmine is for hematite, green for calcite, turquoise for quartz. (B) Raman map of non-ORB sample from Selong section showing the absence of hematite, Sample SL11+100. Colors: light yellow is rutile, green is calcite, turquoise is quartz. (C) Raman spectra of the minerals present in A and B. (D) SEM image of the ORB sample in A showing micrometer-sized, euhedral to subhedral hematite crystals (arrows) that are randomly scattered in matrix. Inset in D, EDS spectrum of the marked hematite.

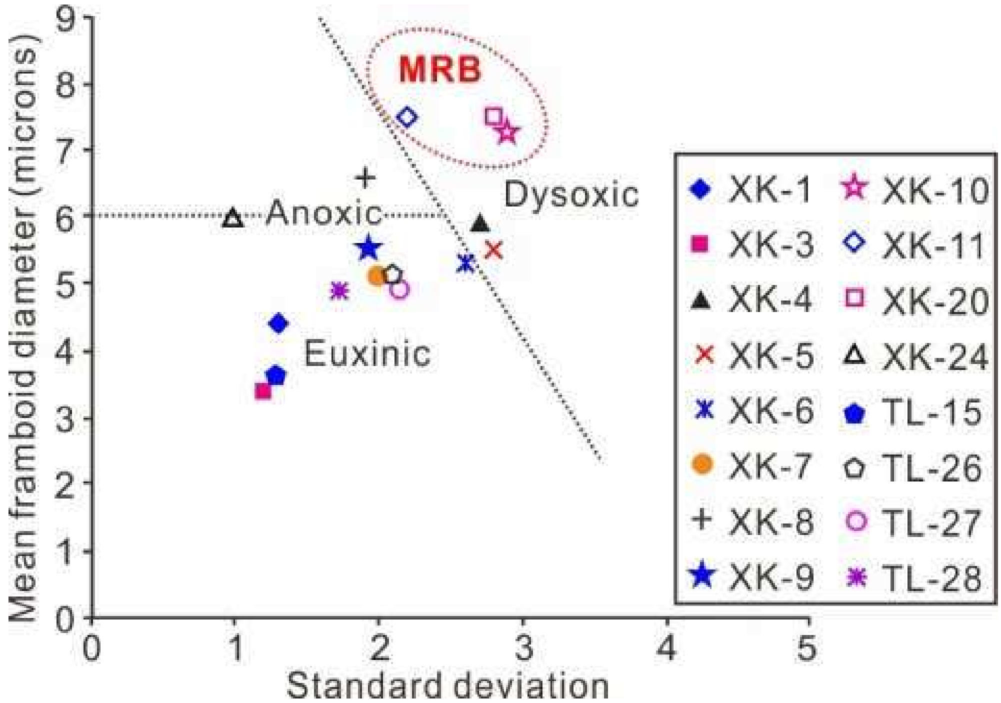

Fig. 8. Cross-plot diagram showing mean diameter vs. standard deviation of framboidal pyrite from Tulong and Xiukang sections. Note that the samples (XK-10, XK-11, XK-20) plotted within the dashed-line ellipse mark the occurrence of ORBs in Tulong section. The boundary separating fields for euxinic and/or anoxic and dysoxic environments follows that of Wilkin et al. (1996) and Bond and Wignall (2010).

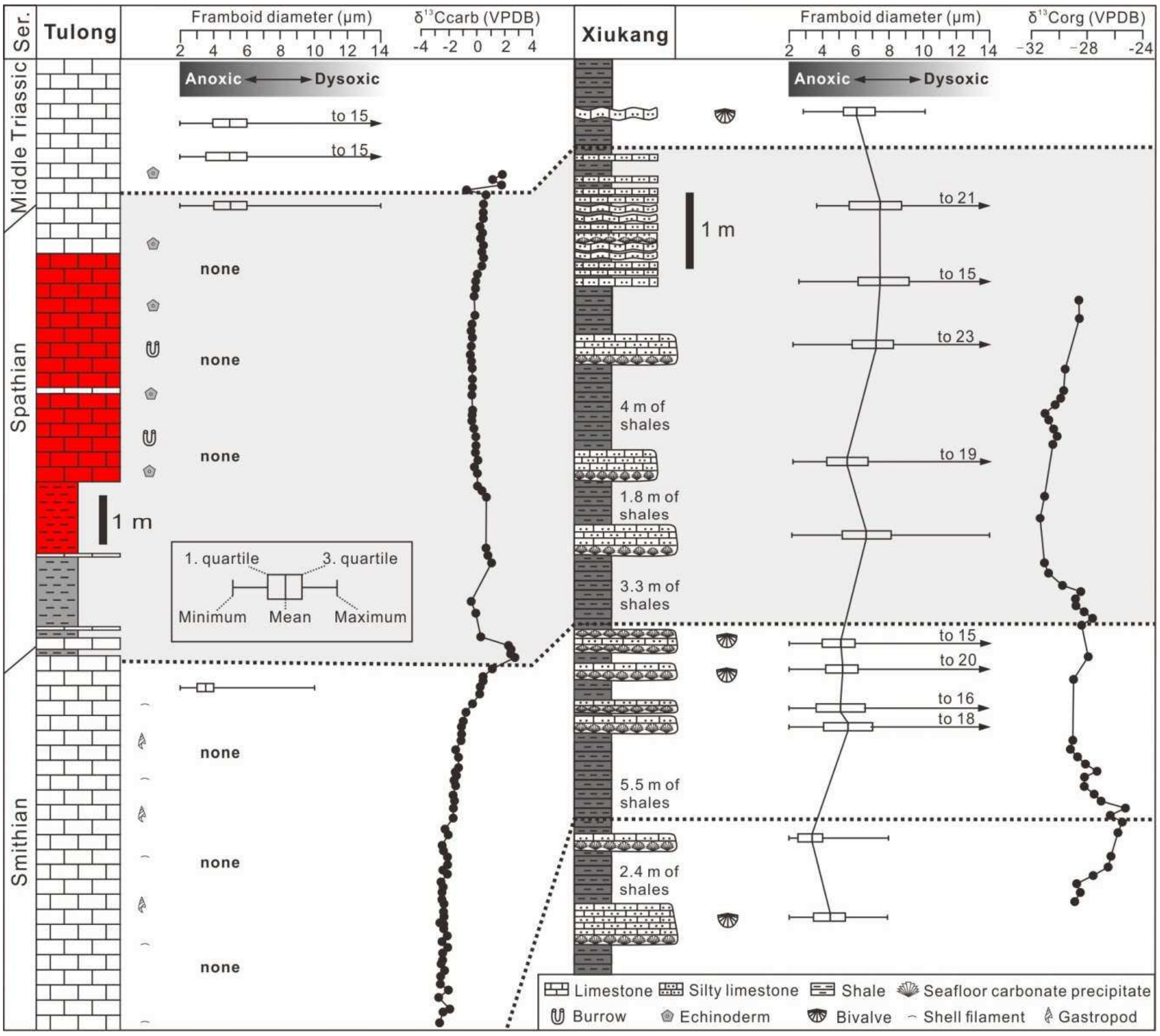

Fig. 9. Logs of the Tulong and Xiukang sections showing framboid pyrite "box-and-whisker" plots. Note the stepwise increase in the diameter of framboid pyrite in Xiukang section, reaching a maximum during the Spathian, which is coincident with the occurrence of ORBs at the Tulong section.

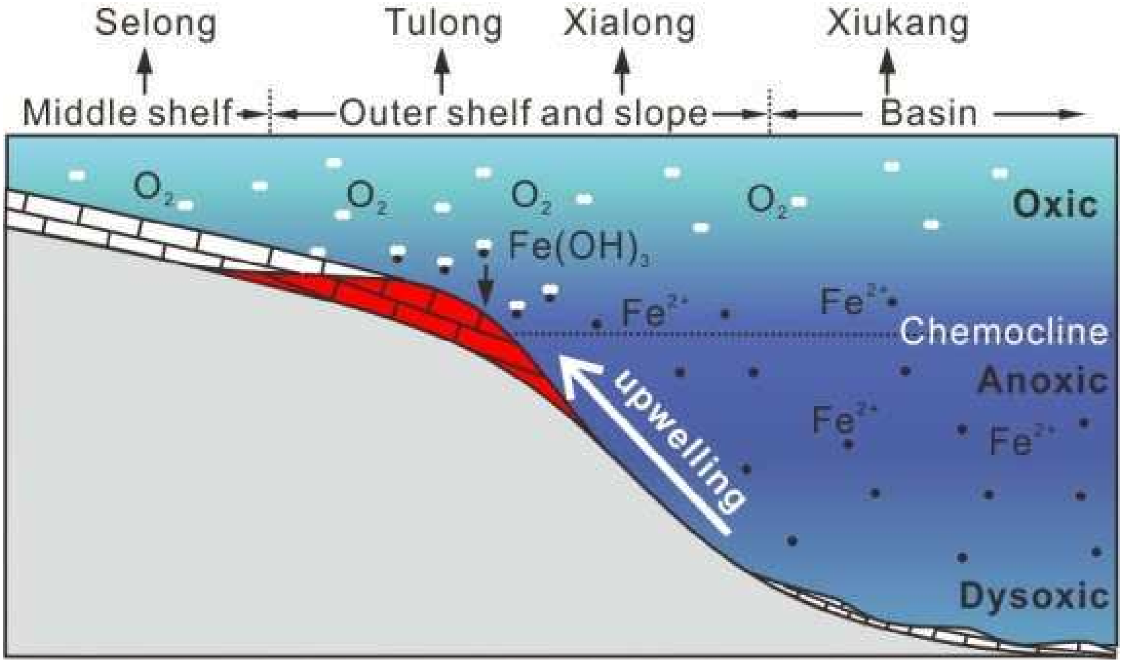

Fig. 10. Schematic model for the Spathian ORBs deposition in South Tibet (modified from Wang et al., 2009). The strengthening of ocean circulation due to climate cooling leads to intense upwelling, transferring large amounts of Fe (II) to shelf regions where it is oxidized and accumulates to form ORBs.

Table 1. Microfacies classification and description.