Geochemical and palaeontological evidence for the definition of the Silurian/Devonian boundary in the Changwantang Section, Guangxi Province, China

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Abstract. Southern Guangxi Province is one of the important areas for the study of the Silurian/Devonian boundary (SDB) in South China. Despite attempts to define the exact level of the SDB in the Yulin (Guangxi Province) area using biostratigraphy, no consensus has been reached as the indicator fossils (e.g. graptolite *Monograptus uniformis uniformis*, conodont *Icriodus woschmidti woschmidti* and trilobite *Warburgella rugulosa rugosa*) are not coexistent in South China. Since Mann et al. (2001: Dynamics of the Silurian/Devonian boundary sequence: sedimentary cycles vs. organic matter variation. *Terra Nostra*, **2001**, 44–48) reported the first isotope curve based on organic carbon for the SDB at Klonk in the Czech Republic (GSSP), some comparable variation curves of $\delta^{13}C_{org}$ across the SDB have been obtained at several locations including sections in Turkey and China. This distinct variation curve of the isotopic composition of organic carbon across the SDB provides a chemostratigraphic reference for a worldwide correlation of the SDB. In this study, organic geochemistry together with graptolite biostratigraphy is applied as a tool for identifying the SDB at the Changwantang Section in Yulin (Guangxi Province). The results suggest that the variations in some indexes of organic geochemistry can be correlated to the representative curve of the SDB in the Klonk and Esenyali sections. The exact level of the SDB in the Changwantang Section is positioned within the upper part of the Fangcheng Formation, which is consistent with the available palaeontological data from graptolites (e.g. *Colonograptus colonus*, *Plectograptus* sp., *Monograptus uniformis*, *M.* cf. *M. praehercynicus* and *M. aequabilis*).

Key words: chemostratigraphy, biostratigraphy, Silurian/Devonian boundary, Changwantang Section, Yulin area, Guangxi Province, China.

INTRODUCTION

The well-exposed Silurian/Devonian boundary (SDB) sequences in China are mainly preserved in three areas, i.e. Qujing (Yunnan Province), West Qinling (Sichuang Province) and Yulin (Guangxi Province) areas in the South China Block (Zhao et al. 2010; Zhao & Zhu 2014). Although many attempts have been made to locate the SDB in these areas (Mu et al. 1983, 1988; Luo et al. 1985; Rong et al. 1987, 1990; Cai et al. 1994; Fang et al. 1994; Rong & Chen 2000; Wang 2000), the SDB in South China remains contentious because the indicator fossils in the Klonk Section (e.g. graptolite *Monograptus uniformis uniformis*, conodont *Icriodus woschmidti woschmidti* and trilobite *Warburgella rugulosa rugosa*) are not coexistent nor even found (Rong et al. 1987; Zhao & Zhu 2014). In recent years, we have conducted studies on the chemostratigraphy and biostratigraphy of the SDB sequences in the Xishancun Section (Qujing area in Yunnan Province), Putonggou Section (West Qinling area in Sichuan Province) and Changwantang Section (Yulin area in Guangxi Province) for pinpointing the SDB within different sedimentary facies in the South China Block (Fig. 1). The findings from both the Xishancun Section and the Putonggou Section have proved useful towards obtaining a better definition of the SDB in these two sections and are mainly based on the distinct $\delta^{13}C_{org}$ trend and occurrence of micro-vertebrate remains across the Silurian/Devonian transition (Zhao et al. 2010, 2011, 2012).

In this paper, we provide new geochemical and palaeontological data that will help in resolving the long-standing debates over the position of the SDB in the Changwantang Section exposed in Yulin, Guangxi Province, China, and will be conducive to the worldwide correlation of the SDB in different facies.

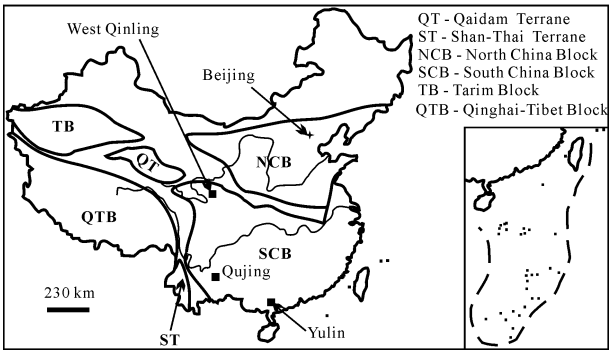

Fig. 1. Sketch map showing the Chinese tectonic units and the location of the Yulin area, Guangxi Province (revised from Zhao & Zhu 2010).

REGIONAL SETTING AND STRATIGRAPHICAL CHARACTERISTICS

Tectonically, the Yulin area in Guangxi was situated at the southern margin of the South China Block during the middle Palaeozoic (Fig. 1). The continuous strata from Upper Silurian to Lower Devonian, including the upper part of the Fangcheng Formation and the lower part of the Beijuntang Formation, are well exposed in the area (Mu et al. 1983; Lin et al. 1984; Hou & Wang 1988). The rich graptolites from the Silurian/Devonian transition sequence dominated by silty shale and shale in the area suggest that the sedimentary environment should be a deep-water trough (Lin 1979; Hou & Wang 1988; Zhong et al. 1992).

Some Siluro-Devonian biostratigraphic works have been conducted since the 1970s in the Yulin area. The Changwantang Section (Figs 2, 3), one of eight measured sections in the area, has long been regarded as the best section for studying the SDB because of the continuous strata ranging in age from Upper Silurian to Lower Devonian rich in graptolites (Mu et al. 1983). The reported graptolites include *Monograptus* cf. *M. aequabilis*, *M. microdon* and *M. microdon silesicus* from the lower part of the Beijuntang Formation and *Pristiograptus* sp. and *Monograptus* sp. from the upper part of the Fangcheng Formation (Lin 1979; Mu et al. 1983, 1988; Hou & Wang 1988). Thus, previously the SDB was usually placed within the section between the Beijuntang Formation and the Fangcheng Formation based on the graptolites and lithostratigraphy (Mu et al. 1983; Hou & Wang 1988). However, the position of the SDB within the section remains contentious because of the absence of the index fossils found in the Klonk Section, the Global Stratotype Section and Point (GSSP) (Zhao & Zhu 2014).

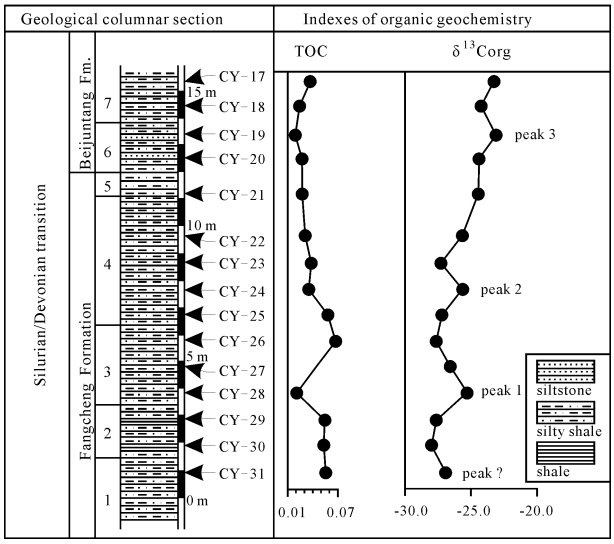

Fig. 2. Stratigraphic succession, total organic carbon content and stable isotopic ratio of organic carbon versus depth in the Changwantang Section.

MATERIAL AND METHODS

Based on previous studies on biostratigraphy (Mu et al. 1983, 1988), we collected 31 samples (about 200 g weight of each rock sample) at about 1.0 m intervals for the geochemical analysis from the Changwantang Section (28 m long). We also collected some well-preserved graptolite material from six layers within the section. Fifteen rock samples (close to the potential SDB location in the section) for geochemical analysis were measured and analysed in the laboratory of the Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences.

We mainly measured the contents of total organic carbon (TOC) and stable isotopic values ($\delta^{13}C_{org}$) of every individual rock powder by means of an elemental analyser (Vario Pyro Cube) connected to a continuous flow system (Isoprime 100), after removal of carbonate with HCl. The average standard deviations of these measurements were ±0.2% for TOC and ±0.2‰ for $\delta^{13}C_{org}$. The values of $\delta^{13}C_{org}$ are expressed in standard delta notation relative to the Vienna Pee Dee Belemnite (VPDB). The new graptolite material collected from the Changwantang Section during field work were identified by Professor Xu Chen from the Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences.

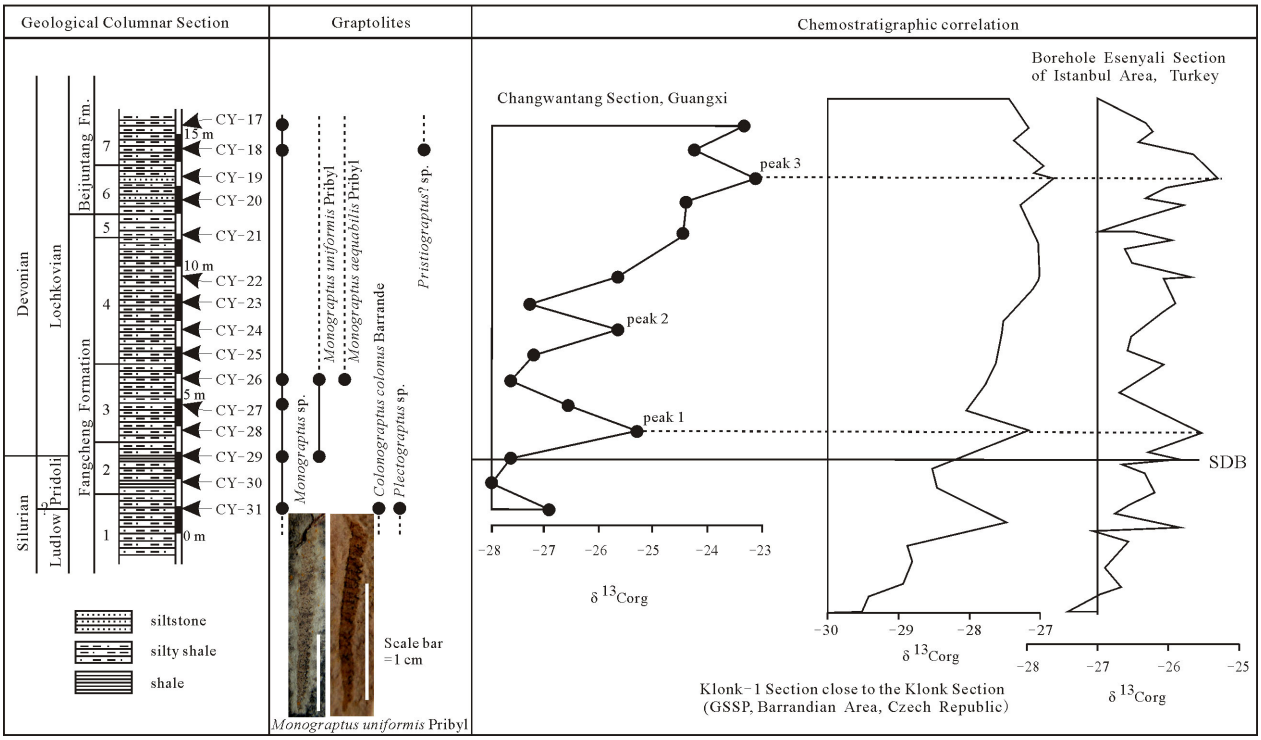

Fig. 3. Chemostratigraphic correlation of the isotopic variation in organic carbon between the Klonk-1 Section close to the GSSP, the Borehole Esenyali Section and the Changwantang Section with new graptolite data.

RESULTS

In the Changwantang Section, the TOC content values are not high, only ranging from 0.01% to 0.07% (Fig. 2). The values of $\delta^{13}C_{org}$ mainly vary between –8‰ and –23‰, and exhibit three reliable peak values at the samples of CY-28 (–25.4‰), CY-24 (–25.8‰) and CY-19 (–23.2‰), respectively, although they are mostly one-sample $\delta^{13}C_{org}$ peaks (Fig. 2).

The lower TOC content values from the Changwantang Section are mainly related to the Silurian/Devonian transition limited primary production (Malkowski & Racki 2009) and the lower depositional rate, which are not suitable for the burial and preservation of organic carbon. Herein we try to fix the SDB within the section mainly based on comparison with the carbon isotopic variation pattern that is present in the Klonk-1 Section close to the GSSP and the Borehole Esenyali Section of Turkey. Based on the correlation of variations in $\delta^{13}C_{org}$ between the Changwantang Section, the Borehole Esenyali Section and the Klonk-1 Section, it is likely that the SDB within the Changwantang Section can be placed below sample CY-29, which is consistent with the new palaeontological data from graptolites (Fig. 3).

Some well-preserved graptolites were collected from six different layers within the Changwantang Section, corresponding to rock samples CY-17, CY-18, CY-26, CY-27, CY-29 and CY-31, respectively (Fig. 3). The Silurian graptolites, including *Colonograptus colonus* and *Plectograptus* sp., were collected from the layer of rock sample CY-31. The Devonian graptolites from the layers of rock samples CY-17, CY-18, CY-26, CY-27 and CY-29 mainly included *Monograptus uniformis* (Fig. 3), *M.* cf. *M. praehercynicus* and *M. aequabilis*, which are the index fossils for the lowermost Devonian. The above-mentioned graptolites indicate that the SDB in the Changwantang Section should be placed below sample CY-29, within the upper part of the Fangcheng Formation (Fig. 3).

DISCUSSION AND CONCLUSION

A distinct positive excursion of $\delta^{13}C_{org}$ from the uppermost Silurian to the lowermost Devonian has been recognized in several sections exposed in the Czech Republic, Ukraine, Turkey, Austria, Morocco, Poland and China (Porębska et al. 1999; Mann et al. 2001; Buggisch & Mann 2004; Herten et al. 2004a, 2004b; Małkowski & Racki 2009; Zhao et al. 2010, 2011; Racki et al. 2012), which seems to provide a consistent chemostratigraphic tool for a worldwide correlation of

the SDB (Buggisch & Mann 2004; Małkowski & Racki 2009; Zhao et al. 2010, 2011). The related chemostratigraphic research together with new graptolite data in the Changwantang Section, Yulin area in South China, provides additional empirical evidence.

Based on the correlation of variations in $\delta^{13}C_{org}$ between the Changwantang Section, the Borehole Esenyali Section of the Istanbul area (Turkey) and the Klonk-1 Section close to the GSSP, and the new palaeontological data from graptolites, here we suggest that the exact level of the SDB within the Changwantang Section should be placed below sample CY-29, within the upper part of the Fangcheng Formation, which does not show any contradiction to a global bioproductivity event taking place shortly above the SDB within the Klonk-1 Section (Mann et al. 2001). The first distinct positive shift in $\delta^{13}C_{org}$ across the SDB in the Changwantang Section provides strong support for the large-scale global biogeochemical perturbation across the SDB (Klonk Isotope Event) (Kaljo et al. 1996; Buggisch & Joachimski 2006; Małkowski & Racki 2009; Racki et al. 2012).

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