Carbon isotope stratigraphy across the Silurian-Devonian transition in Zoige (West Qinling), China

Wen-jin Zhao, Ulrich Herten, Min Zhu, Ulrich Mann & Andreas Lucke

ABSTRACT - Carbon isotope ($^{13}$C$_{org}$) analyses of neritic carbonates and black shales spanning the Silurian-Devonian transition are compared from two richly fossiliferous sequences in Zoige County (West Qinling Region) of Sichuan Province, China. The two sections, Putonggou and Yanglugou sections in West Qinling, reveal positive $^{13}$C$_{org}$ shifts happening in the upper Pridoli and lower Devonian and reaching peak values as heavy as -19.9‰ (Putonggou) and -19.7‰ (Yanglugou) in the lowermost Lochkovian following the first occurrence of the brachiopod fauna and the conodont Icriodus woschmidti woschmidti. These results replicate a globally known positive shift in $^{13}$C$_{org}$ from the uppermost Silurian to the lowermost Devonian. The isotopic trend for organic carbon across the Silurian-Devonian Boundary (SDB) offers an approach to a potential correlation of the SDB from different sedimentary facies. The $^{13}$C$_{org}$ variations across the Silurian-Devonian transition at the two sections in West Qinling exhibit a similar shift in their carbon isotopic composition as the detailed SDB curves from the borehole Klonk-1 drilled at top of the Klonk GSSP in the Prague Basin, Czech Republic. This suggests that the SDB in West Qinling is located at the upper part of the Yanglugou Formation (between ZY-07 and ZY-06) in the Yanglugou Section and the lower part of the Xiaputonggou Formation (between ZP-09 and ZP-10) in the Putonggou Section. More data will help to reveal individual causes for the isotopic shift, such as enhanced carbon burial due to anoxic conditions and/or increased productivity, alternating arid and humid periods, or changes in the composition of primary producers.

INTRODUCTION

The Silurian-Devonian Boundary (SDB) at Klonk near Suchomasty (35 km southwest of Prague, Czech Republic) is the first boundary selected as a Global Stratotype Section and Point (GSSP) by the International Union of Geological Sciences in Montreal in 1972 (McLaren, 1977). The SDB at Klonk is defined at the base of the graptolite Monograptus uniformis uniformis in the upper part of Bed No. 20. The auxiliary indicators of the boundary include the first occurrence of the trilobite Warburgella rugulosa rugosa and the conodont Icriodus woschmidti woschmidti (Chlupac et al., 1972, 1998; McLaren, 1977). However, except I. woschmidti woschmidti (Wang, 1981; Li, 1987), other indicator fossils cannot be found in West Qinling because they are restricted to the typical pelagic facies in general. Furthermore, although the conodont I. woschmidti woschmidti is commonly considered as an index fossil for the lowermost Devonian, it is a little bit lower than the graptolite M. uniformis uniformis in Podolia, Bohemia, and Nevada, conversely, in the Carnic Alps on the border between Austria and Italy, and in Rabat-Tiflet area of Morocco (Rong et al., 1987). Therefore, if only I. woschmidti woschmidti is found in another continent, one cannot know whether its first appearance is coeval
with the base of the zone from the type area in Bohemia. This fact brings a considerable difficulty to the location of the SDB in West Qinling (Rong et al., 1987). Although many biostratigraphic attempts have been made to define the exact level of the SDB in West Qinling (Rong et al., 1987; XIGMR & NIGPAS, 1987a), the SDB in the area remains contentious.

Carbon isotope as well as oxygen and strontium isotopes has been intensely used to study secular isotopic variations of ancient ocean water, and some variations in the carbon isotopic composition of marine carbonate rocks and components (fossils, marine cements) have been used for chemostatigraphic correlations and paleoenvironmental interpretations (Veizer & Hoefs, 1976; Fischer & Arthur, 1977; Scholle & Arthur, 1980; Arthur et al., 1985; Dean et al., 1986; Knoll et al., 1986; Popp et al., 1986; Hayes et al., 1989; Kauffman et al., 1991; Popp et al., 1997; Geldern et al., 2006). An appreciation of the possibilities of variations in carbon isotopes in ancient carbonates was first deduced by Garrels & Perry in 1974, but reliable δ13C curves of bulk carbonate samples were only available for the SDB during the last 12 years (Hladikova et al., 1997; Veizer et al., 1999; Saltzman, 2002; Buggisch & Mann, 2004; Buggisch & Joachimski, 2006; Gill et al., 2007; Malkowski & Racki, 2009), and evidenced also in Podolian well preserved brachiopod shell calcites (Azmy et al., 1998; Veizer et al., 1999; Prokoph et al., 2008). The major positive δ13C excursion, the Klonk Isotope Event at the SDB, is correlated with sea-level changes, the deposition of black shales and in part with bio-events (Jeppsson, 1998; Afanasieva & Amon, 2006; Buggisch & Joachimski, 2006; Malkowski et al., 2009). Although the isotopic composition of both organic and inorganic carbon has been studied extensively, secular trends in inorganic carbon, primarily as measured in carbonate minerals, have received the most attention (Scholle & Arthur, 1980; Shackleton, 1985). However, because reliable δ13C curves are usually based on analyses of brachiopod shells, which are strongly facies-dependent (Buggisch & Mann, 2004), our chemostatigraphic approach concentrates on the isotopic variation of organic carbon. Mann et al. (2001) reported the first isotope curve based on organic carbon for the SDB from a fully cored borehole drilled through the complete sedimentary sequence at the GSSP, and suggested that the distinct positive excursion of δ13Corg from the uppermost Silurian to the lowermost Devonian was related to the high bioproductivity, mass burial of organic carbon and transpression-regression of 3rd order, and represented a global bioproductivity event. Subsequently, the distinct positive shift of δ13Corg across the SDB were confirmed at several locations including the sections from Ukraine, Turkey, USA, Morocco and Poland (Mann et al., 2001; Buggisch & Mann, 2004; Herten et al., 2004). Thus, this distinct δ13Corg trend across the SDB seems to provide a consistent chemostatigraphic tool for a worldwide correlation of the SDB.

The purpose of this paper is to provide additional data for a better definition of the SDB in the Putonggou and Yanlugou sections of West Qinling by means of chemostatigraphy (variation of carbonate and organic carbon as well as the isotopic composition of organic carbon) in order to narrow the depth interval for future detailed studies in paleontology and chemostatigraphy and for a precise position of the SDB in this region.

REGIONAL SETTING AND STRATIGRAPHY

The Silurian-Devonian transition is preserved in many localities in South China, showing non-marine (Qujing Area), neritic (West Qinling Area) and pelagic facies (Yulin Area) (Mu et al., 1983, 1988; Fang et al., 1994; Cai et al., 1994; Wang et al., 1998; Wang, 2000). Tectonically, Qujing and Yulin areas are located in the South China Block (SCB) during the mid-Paleozoic (Zhao & Zhu, 2007). However, there are still many debates on the tectonic evolution of West Qinling (Zhang, 1987; Yin & Huang, 1995; Du, 1995; Yin et al., 1999; Cao & Hu, 2000; Feng et al., 2003). As a part of the Qinling Orogenic Belt, West Qinling has changing tectonic framework during different tectonic evolutionary stages. Cao & Hu (2000) suggested that West Qinling is situated in the northwestern margin of the SCB during the mid-Paleozoic. The Siluro-Devonian biota of West Qinling shows the proximity to that from the Xiangzhou type of South China, confirming West Qinling as a part of the SCB in the mid-Paleozoic (Fig.1; XIGMR & NIGPAS,
Fig. 2 - Biostratigraphy in the Putonggou Section in West Qinling, China. a) geologic columnar section of the Silurian-Devonian transition and biostratigraphic character at Putonggou, West Qinling; b) cross-section of the Silurian-Devonian transition at Putonggou, West Qinling (revised from XIGMR & NIGPAS, 1987a, b).
The study on the SDB sequence in the area will help to understand the history of the SCB during the mid-Paleozoic.

In West Qinling, the strata spanning from upper Pridoli to lower Devonian, including the Yanglugou and Xiaputonggou formations (SDB sequence) with abundant fossils, are well developed in Zoige (Sichuan Province) and Tewo (Gansu Province) areas (Fig. 1; Wang, 1981; XIGMR & NIGPAS, 1987a, b; Wang et al., 1998). The Putonggou and Yanglugou sections represent the best sections for studying the SDB biostratigraphy in West Qinling (Fig. 1).

The SDB sequence in the Putonggou Section includes the upper part of the Yanglugou Formation and the lower part of the Xiaputonggou Formation. Close to the SDB transition, the Yanglugou Formation is composed of grey phylite-like calcareous shale intercalated with thin-bedded weakly metamorphosed fine sandstone. The Xiaputonggou Formation is mainly composed of grey phylite-like calcareous shale intercalated with several beds of metamorphosed limestones (Fig. 2). The fossils in the SDB sequence mainly include conodonts, brachiopods and vertebrate remains (Fig. 2; Wang, 1981; XIGMR & NIGPAS, 1987a, b; Wang et al., 1998), indicating a shallow sea shelf facies.

The SDB sequence in the Yanglugou Section, similar to that in the Putonggou Section, comprises the upper part of the Yanglugou Formation and the lower part of the Xiaputonggou Formation. The upper part of the Yanglugou Formation is composed of thin to thick-bedded limestone intercalated with argillaceous and bioclastic limestones. The lower part of the Xiaputonggou Formation is mainly composed of calcareous silty shale and silty shale intercalated with several partly metamorphosed limestone beds (Fig. 3). The fossils in the SDB sequence are mainly brachiopods, conodonts, spores and corals inhabiting a shallow sea shelf (Fig. 3; XIGMR & NIGPAS, 1987a, b; Wang et al., 1998).

**SAMPLES AND METHODS**

Based on previous studies on biostratigraphy (Wang, 1981; XIGMR & NIGPAS, 1987a, b; Wang et al., 1998), we collected 45 samples at about 1.5 m intervals from a 35 m section (Yanglugou Section - ZY Section) and a 48 m section (Putonggou Section - ZP Section) in West Qinling. All sampling positions were placed near to the potential SDB location in the two sections (Figs. 2-3) and each rock sample for the geochemical analysis was about 200 g in weight. We analysed the contents of organic carbon, carbonate carbon and total sulphur, in order to check the availability of organic carbon for isotopic analyses.

Organic carbon and sulphur contents of individual rock powders were determined by use of a Leco carbon-sulphur analyzer. The values of their contents are presented in percentages of weight [wt%]. The CaCO3 contents, also presented in percentages of weight [wt%], are calibrated by the following formula: (A-B)/Ax100%. A is the total weight of one sample, while B is the weight of the same sample after being processed by hydrochloric acid (5%, or 10% and 32% as necessary).

Whole rock samples for isotopic analyses of organic carbon were first decarbonized by hydrochloric acid (in steps of 5%, 10% and 32% HCl as necessary) at 40°C for several hours to ensure complete removal of inorganic carbonates. The samples were then washed with deionized water and freeze-dried. A sample weight equivalent to ~150 μg total organic carbon was packed into tin capsules and combusted in excess oxygen at 1080°C. The resulting CO2 was analysed online by an Optima (Micromass Ltd.) isotope ratio mass spectrometer. All measurements on stable carbon isotope ratios (δ13C = [(13C/12C)sample - (13C/12C)standard]/(13C/12C)standard) are presented in conventional δ-notation versus the VPDB standard [%e=VPDB]. Determinations were carried out by comparison with internal reference samples, which are calibrated against the VPDB standard. Accuracy and precision was controlled by replicate measurements of laboratory standards and was better than ±0.1‰ (1σ) for carbon isotopes.

**GEOCHEMICAL RESULTS AND CHEMOSTRATIGRAPHY**

Geochemical results

In the Putonggou Section, the values of TOC and TS contents are not high, ranging from 0.03% to 0.17% and from 0% to 0.07% respectively. The CaCO3 contents vary from 0% to 95.54%, apparently relating to the lithological change. The δ13Corg values mainly vary between -26‰ and -23‰, and exhibit five relative maxima in the samples of ZP-07 (-23.2‰), ZP-22 (-24.1‰), ZP-25 (-24.6‰) and ZP-27 (-24.7‰), besides the lowest value in the sample of ZP-01 (-28.1‰) (Fig. 4).

In the Yanglugou Section, the TOC and TS contents are very similar to those in the above-mentioned Putonggou Section, ranging from 0.03% to 0.16% and from 0% to 0.04% respectively. The CaCO3 contents are rather high with more than 92% because limestone is the dominant rock exposed in the section. The δ13Corg values in the Yanglugou section vary between -25‰ and -23‰, and exhibit five relative maxima in the samples of ZY-01 (-19.7‰), ZY-03 (-21.2‰), ZY-06 (-22.7‰), ZY-09 (-22.9‰) and ZY-14 (-22.5‰), and five relative minima in the samples of ZY-05 (-26.3‰), ZY-09 (-25.1‰), ZY-15 (-24.7‰), ZY-22 (-24.1‰), ZY-25 (-24.6‰) and ZY-27 (-24.7‰), besides the lowest value in the sample of ZY-01 (-28.1‰) (Fig. 4).

Chemostratigraphy in the Putonggou and Yanglugou sections

The lower values of TOC and TS contents from two sections in the SCB are mainly related to the type and amount of organic matter, preservation potential and sedimentary rate. Here we try to fix the SDB in two sections, mainly based on the carbon isotopic variation pattern encountered in Morocco and the Prague basin. We did not want to correlate just the three major peaks from three different locations, but we would like to refer to the overall trend line at the individual sections in order to avoid short-time local influences such as short blooms by primary producers.
Fig. 3 - Biostratigraphy in the Yanglugou Section in West Qinling, China. a) geologic columnar section of the Silurian-Devonian transition and biostratigraphic character at Yanglugou, West Qinling; b) cross-section of the Silurian-Devonian transition at Yanglugou, West Qinling (revised from XIGMR & NIGPAS, 1987a, b).
Based on the correlation of δ13Corg variations among the Putonggou Section, the Morocco sections and Klonk-1 Section close to GSSP, it is likely to place the SDB in the Putonggou Section in between the Sample ZP-09 and ZP-10, the lower part of the Xiaputonggou Formation (Fig. 6). This result is based on the correlation with Klonk-1 Section and a combined section from Bled Dfa and Mount Issimour sections in Morocco (after Herten 2004a,b) with some distinct peak levels of δ13Corg. The peaks at the locations of samples of ZP-13 and ZP-10 in the Putonggou Section correspond to the peaks occurring at depth levels of 21.90 m and 22.99 m in Klonk-1 Section and the peaks at depth levels of 11.5 m and 8.8 m in the Bled Dfa-Mount Issimour Section, respectively.

The highest δ13Corg value (-19.7‰) in the Yanglugou Section, measured at the top of the studied section, should be a relative maximum of δ13Corg value, although the δ13Corg values might still increase in the upper part of the section (not studied). If possible, we should enlarge the data set in the section in order to get better arguments or more reliable evidence in the future. Based on the available chemostratigraphic and biostratigraphic data (Figs. 3, 5), together with the overall trend of δ13Corg values, we suggest the correlation of δ13Corg variations between the Yanglugou Section and Klonk-1 Section, and the SDB in the Yanglugou Section is likely to be placed in between the sample ZY-07 and ZY-06, the upper part of the Yanglugou Formation (Fig. 7).

**DISCUSSIONS AND CONCLUSIONS**

Based on the appearance of the conodont *Icriodus woschmidti woschmidti*, the distinctive features of the brachiopod faunas and lithostratigraphical changes, the SDB in the Putonggou Section was mainly placed at three different positions as follows (Fig. 2): the scheme A, at the base of the Xiaputonggou Formation mainly based on lithostratigraphical changes (Cao et al., 1987); the scheme B, at the base of the bed No. 3 of the Xiaputonggou Formation based on the Protathyris-Lanceomyonia fauna (Rong et al., 1987); the scheme C, at the base of the bed No. 4 of the Xiaputonggou Formation based on the appearance of the conodont *I. woschmidti woschmidti* (Figs. 2, 4; Wang, 1981; Li, 1987).

According to the distinctive features of the conodonts, brachiopod faunas, spores, corals, and lithostratigraphical changes, the SDB in the Yanglugou Section was mainly placed at five different positions as follows (Fig. 3): the scheme D, at the base of the bed No. 12 of the Yanglugou Formation.
Formation (about 57 m under the base of the Xiaputonggou Formation) mainly based on *Emmosiella saaminicus-Squameopora sichuanensis-Squameofavosites sokolovi* assemblage (Lin & Huang, 1987); the scheme E, in the upper bed No. 15 of the Yanglugou Formation based on the *Protathyris-Lanceomyonia* fauna (Rong et al., 1987); the scheme G, at the base of the bed No. 16 of the Yanglugou Formation based on the Early Devonian spores (Gao & Ye, 1987); the scheme H, in the lower part of the Xiaputonggou Formation (about 65 m above the base of the Xiaputonggou Formation) based on the occurrence of the conodont *I. woschmidtii* woschmidtii (Figs. 3, 5; Wang, 1981; Li, 1987).

In general, the SDB in the West Qinling area of China remains contentious by now. The present research on the carbon isotope stratigraphy has considerably increased our knowledge of SDB, and may help to clarify the debates on the study of SDB in West Qinling.

In order to test the validity of the carbon isotopic data, we looked for potential parameters indicating the thermal stage of organic matter for West Qinling. Based on conodont alteration indices (CAI) of 4-5 in this area (the conodonts finding in the Putonggou and Yanglugou sections are usually dark grey or black), we expect a burial temperature range of about 190-480°C (Königshof, 2003). Differences in maturity between the two sections investigated at West Qinling remain unknown. Within this temperature range, i.e. below and during low grade and green schist facies metamorphism, source related carbon isotopic signals should still be visible (Des Marais, 2001, and references therein), although thermal alteration of kerogen generally increases δ13C by about 3 permil as H/C is lowered from >1 to 0.1. This agrees with theoretical arguments (Watanabe et al., 1997), measurements of kerogens in sedimentary rocks (Simoneit et al., 1981) and laboratory experiments (Lewan, 1983; Peters et al., 1981). Furthermore, thermal maturation due to overburden or regional tectonism should have affected the entire section equally (Cramer & Saltzman, 2007). Therefore, it seems that thermal maturation cannot be a cause of any excursion in our data. Nevertheless, any secondary bitumen impregnation in addition to the original carbon source may have some influence on the isotopic composition. The off-set of the
absolute carbon isotope values between Klonk-1 and Putonggou sections, confirms the very different thermal stage of Putonggou Section compared to Klonk-1 Section with 0.7-0.8% vitrinite reflectance according to Herten (2000) and Kranendonck (2000) by a difference of about 3 permil in $\delta^{13}C_{org}$. The absolute values of $\delta^{13}C_{org}$ data of the combined sections from Morocco exhibit a relatively slight increase only of about 0.5 permil compared to Klonk-1 which agrees well with a thermal stage of about 1.1% vitrinite reflectance or a Tmax of 455°C from Rock-Eval Pyrolysis (Kranendonck, 2004).

At the present stage of the known isotopic data variation, it is far beyond the scope of this study to evaluate the local mechanism underlying this variation in the West Qinling area. Generally, more effects are combined. Scenarios proposed may include different primary producers (Watanabe et al., 1997), enhanced carbon burial due to anoxic conditions (Cramer & Saltzman, 2005), enhanced productivity (Wenzel & Joachimski, 2006) or arid versus humid periods (Bickert et al., 1997).

The determination of the SDB in two sections of the West Qinling by means of chemostratigraphy agrees well with available palaeontological data and the biostratigraphic zonation. However, there is still the need for a refined biostratigraphical subdivision in the sedimentary sequences of West Qinling, China. Based on the available data, we suggest to place the level of the SDB in West Qinling at the lower part of the Xiaputonggou Formation (between ZP-09 and ZP-10) in the Putonggou Section (Fig. 6) and the upper part of the Yanglugou Formation (between ZY-07 and ZY-06) in the Yanglugou Section (Fig. 7), which correspond to the above-mentioned scheme B and E respectively.

ACKNOWLEDGMENTS

We thank Cao Xuan-duo, Wang Nian-zhong and Jia Lian-tao for the field works and Werner Laumer and Holger Wissel for stable isotope analyses. This work was supported by the Creative Research Project of CAS (KZCX2-YW-156), the Major State Basic Research Projects (2006CB806400) and the Basic Research Projects of Science and Technoloy: Research on standard sections and some GSSPs in China (2006FY120300-6) of MST of China, the National Natural Science Foundation of China (40930208, 40572021), and the CAS/SAFEA International Partnership Program for Creative Research Teams. Jirí Fryda, Bradley D. Cramer and Michael M. Joachimski are thanked for helpful reviews of the manuscript.
REFERENCES


Fig. 7 - Chemostratigraphic correlation of the isotopic variation of organic carbon between the borehole Klonk-1 drilled through the sedimentary rock sequence at the GSSP location (Klonk, Suchomasty, Czech Republic) and the Yanglugou Section in West Qinling, China (in ‰–VPDB).
Hayes J.M. (1993). Factors controlling $^{13}$C contents of sedimentary...


Geldern R.V., Joachimski M.M., Day J., Jansen U., Alvarez F., Yolkin...


