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Research on carbon and oxygen isotopes in phosphorus-bearing rock series of the Late Neoproteroic-Early Cambrian Taozichong Formation in Qingzhen City, Guizhou Province, Southwest China

MAO Tie[1], YANG Ruidong[1*], MAO Jiaren[1], YE Chun[2], LIU Kun[1], and GAO Junbo[1]
[1] *College of Resources and Environmental Engineering, Guizhou University, Guiyang 550025, China*
[2] *Guizhou Mining Right Reserve & Trading Bureau, Guiyang 550001, China*
[*] *Corresponding author, E-mail: rdyang@gzu.edu.cn*

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Abstract In the study of the phosphate-bearing stratum at the bottom of the Cambrian system, the authors found that there occurred carbon isotope negative anomalies in the Taozichong section phosphate-bearing stratum in Qingzhen, Guizhou Province; they can be correspondingly compared with other synsedimentary carbon isotope negative anomalies both at home and abroad. The results showed that there occurred three negative anomalies of carbon isotopes in the Neoproterozoic-Early Cambrian Taozichong Formation, indicating that the temporal palaeo-oceanographical environment changed significantly, in which there happened two times of intensive carbon isotope variation, corresponding to creature extinction. Meanwhile, it is believed that the carbon isotope negative anomalies in phosphorites were caused by the ascending water mass of ocean current with the negative carbon isotopic composition of deep-ocean hydrothermal deposits.

Key words carbon-oxygen isotopes; Taozichong Formation; Neoproterozoic-Early Cambrian; Guizhou Province

1 Introduction

In the alternate period between the Neoproterozoic and the Cambrian, a series of significant geologic events had occurred, which have attracted much attention of both domestic and foreign scholars for a long time (Magaritz et al., 1991; Zhu et al., 2006; Li et al., 2009). Additionally, the boundaries between the Precambrian, the Neoproterozoic and the Cambrian is also a controversial problem (Brasiser et al., 1990; Magaritz et al., 1991; Zhu et al., 2006; Li et al., 2009). In the earliest period, the GSSP of the Precambrian-Neoproterozoic-Cambrian boundary in the Newfound land took the first appearance datum (FAD) of trace fossil *Phycodes pedum*. In some regions such as Siberia, India, southern China and so on, the small shell-fossil zones ("*Anabarites trisulcatus*" and "*Protohertzina anabarica*") are taken as the replaceable FAD of bottom boundary (Jiang et al., 1988). The $\delta^{13}C$ characteristics reported from China (Li et al., 2009), Siberia (Magaritz et al., 1986), Iran (Brasiser, 1995) and Canada (Narbonne et al., 1994) have shown that the first negative drift event at the Cambrian bottom occurred slightly earlier than the first occurrence of *Protohertzina anabarica* or trace fossil "*P. pedum*". The $\delta^{13}C$ negative drift age approaching the Cambrian bottom boundary measured in the Khorbusuonka Rvier area of southeastern Siberia is about 543.9±2 Ma (Bowring et al., 1993); the isotope age measured in southern Namibia is about 543±1 Ma to 539.4±1 Ma (Grotzinger et al., 1995); and the isotope age of negative drift volcanic ash measured in the Salt Basin of southern Orman is 542±0.3 Ma (Amthor et al., 2003). These ages are similar to the newly published

"542 Ma age" of the Cambrian bottom boundary (the International Commission of Stratigraphy). The $\delta^{13}C$ negative drift of the Cambrian bottom boundary corresponds to the event of "BACE", i.e., Neoproterozoic Creature Extinction (Zhu et al., 2006). In the 1980s, carbon isotopes were used to divide the boundaries of Cambrian strata (Lamhert et al., 1987). Changes in carbon isotopic composition may be correlated to the creature extinction or radiation (Zhu et al., 2006). In the early Early Cambrian, there was a large quantity of animal fossils. After the flourishing period of animals with small shells at the bottom, mass fossils like Bradoriida also appeared in the black rock series, followed by the rapid reduction of creatures, and this may be equal to point C of the Neoproterozoic-Cambrian boundary (Xu et al., 1986). The reduction of creatures may be related to the sudden change of environment, corresponding to the sharp negative drift of carbon isotope (Xu et al., 1986; Yang et al., 2004). Because of the close relationship between the componential variation of carbon-oxygen isotopes and organic evolution, it recorded the contemporaneous chemical composition of ocean, extinction and anabiosis processes of creatures, and it was also a very good indication to the change of stratigraphic sedimentary environment (Chen et al., 1995). So, these carbon-oxygen isotope compositional characteristics can be considered as a basis for stratigraphic boundary division (Chen et al., 1995). The transitional section between the Neoproterozoic and the Cambrian was discovered in the Ningnan region of western Panzhihua by Yu et al. (2010), its carbon isotope data were comparable with the global carbon isotope data and could be regarded as the geochemical boundary mark between the Neoproterozoic and the Cambrian (Yu et al., 2010). In this stage, the deposits in most Guizhou regions, no matter it was the shallow water shelf or the deep water shelf, are mostly directly contacted in disconformity by the upper Niutitang Formation and lower Dengying Formation, lacking a transition layer between them (Xiao et al., 2006). The Taozichong section in Qingzhen City studied in this paper is the so-called transition layer. It is expected to provide effective isotopic evidence for the Neoproterozoic-Cambrian boundary divisuib through carrying out research on the carbon-oxygen isotopic characteristics of silicious and phosphatic dolomites nearby the Neoproterozoic-Cambrian boundary in the region of Qingzhen, Guizhou Province.

2 Geological background

The Taozichong section at Qingzhen, Guizhou Province, is located at the boundary between Tailong (northern Guizhou) and Taixian (southern Guizhou) on the Yangtze platform, it belongs to the side of Tailong (northern Guizhou). The Paleogeographic position in the Meishucun period of Early Cambrian is located in submerged platform containing phosphorus carbonate on the side of shallow sea extending toward the ocean. This area consists of a set of marine strata dominated by carbonatite, phosphorus carbonate and clasolite. The strata in the study area mainly include the Dengying Formation of the Upper Neoproterozoic Series, the Taozichong Formation of the transition layer and the Niutitang Formation of the Lower Cambrian Series.

The Dengying Formation mainly consists of fine-grained dolostone, including a large amount of algal lamination, and horizontal beddings are well developed. The Taozichong Formation can be roughly divided into two layers: lithologically the lower section is mainly composed of silica bands containing phosphoric dolostone and silt interlayer bands, with stripe algal lamination and well developed horizontal bedding; While the upper section mainly consists of silica and phosphatic dolostone, interbedded by gray black thin breccia-type phosphorite or biodetritus phosphorite, biodetritus mainly consists of small-shell animal debris with horizontal lamination and wart structure developed. The Niutitang Formation mainly consists of a set of compact blocky black shales with horizontal beddings developed.

The sedimentary characteristics of the Taozichong Formation are described as follows:

Upper strata: Cambria Niutitang Formation, constituted by black thin-medium silicalite, black shale interlayering yellow clay stone, containing a little lenticular-type mass of phosphorite at the bottom. The thickness is more than 7.7 meters.

Disconformity

Upper section of the Taozichong Formation of the Lower Cambrian Series

Dark gray laminar silicalite, embedding foliated silica and phosphatic dolostone, as well as phosphoric dolostone. The thickness is about 7.5 m. Dark gray phosphoric silicalite, on the bottom floor is an interlayer containing phosphor siliceous rocks in dark grey. This layer contains compact blocky phosphorite and biodetritus phosphorite, and its thickness is about 0.5 meter. Gray laminar brecciaous phosphoric silicalite, in the supper part is developed compact blocky silicalite and at the top are developed shales, with the thickness being about 0.9 meter. The total thickness of this layer is about 10 m.

Lower section of the Taozichong Formation of the Lower Cambrian Series

Gray yellow thin-medium silica and phosphatic dolostone with horizontal beddings developed. There are stripe-type lamina dolomite and few yellow pelitic bands, with the total thickness being about 25 m.

Disconformity

The Dengying Formation of the Upper Sinian Series

It consistes of gray thick silica phosphoric fine-grained dolostone interbedded by silica stripe, the silica stripe is of black color, and the thickness of silica stripe with biodetritus is about 2−10 cm. Gray medium-bedded silica dolostone appears at the top with horizontal beddings. The thickness of dolomite is about 1 m. The total thickness of this layer is almost greater than 6 m.

3 Experimental method and results

Thirty samples were continuously collected from the phosphoric dolostone at the top of the Sinian Dengying Formation to the black shales at the bottom of the Niutitang Formation after the field observation and description of the Taozichong Formation in Qingzhen, Guizhou Province. All samples collected are fresh rocks with a sign of weak weathering. Firstly, the samples were crashed into 200 meshes; secondly, CO_2 was extracted under 50℃ by using 100％ phosphoric acid; thirdly, the carbon and oxygen isotopes of CO_2 were tested on a MAT252 mass spectrometer. V-PDB standard was adopted for the tested data. The analysis data are given in Table 1. The standard deviation of the tested data is all less than 0.1‰. The isotopic measurement was finished on the MAT252 mass spectrometer at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

Table 1 Measured data of carbon and oxygen isotopes for the Taozichong Formation in Qingzhen City, Guizhou Province

Sample No.	Lithology	$\delta^{13}C$ (‰,V-PDB)	Standard deviation (σ)	$\delta^{18}O$ (‰,V-PDB)	Standard deviation(σ)
QT-1	Dolostone	-0.1	0.021	-8.1	0.010
QT-2-1	Phosphorite	-5.1	0.0014	-10.0	0.024
QT-2-2	Phosphorite	-6.2	0.0027	-9.8	0.017
QT-2	Phosphorite	-7.2	0.016	-11.5	0.021
QT-3	Phosphorite	-0.7	0.016	-9.0	0.040
QT-4	Dolostone	-0.1	0.013	-9.1	0.024
QT-5	Dolostone	1.7	0.012	-3.8	0.024
QT-6	Dolostone	1.1	0.013	-3.1	1.090
QT-7	Dolostone	1.4	0.035	-3.2	0.049
QT-8	Dolostone	1.2	0.028	-2.4	0.033
QT-9	Dolostone	1.1	0.016	-3.9	0.013
QT-10	Dolostone	1.6	0.007	-4.9	0.025
QT-11	Dolostone	1.7	0.022	-5.3	0.016
QT-12	Dolostone	1.1	0.013	-6.6	0.006
QT-13	Silicalite	0.6	0.016	-7.8	0.010
QT-14	Dolostone	0.1	0.016	-8.4	0.012
QT-15	Clay stone	0.5	0.016	-6.3	0.028
QT-16	Silicalite	-0.6	0.020	-7.8	0.017
QT-17	Dolostone	-1.6	0.010	-7.8	0.034
QT-18	Phosphorite	-6.9	0.021	-12.3	0.022
QT-18-1	Phosphorite	-6.1	0.026	-11.5	0.016
QT-18-2	Silicalite	-4.2	0.018	-10.2	0.019
QT-19	Dolostone	-3.3	0.018	-9.9	0.029
QT-20	Silicalite	-1.9	0.002	-4.6	0.008
QT-21	Silicalite	-0.1	0.022	-8.1	0.031
QT-22	Dolostone	0.5	0.026	-5.7	0.025
QT-22-1	Shale	0.4	0.011	-7.2	0.016
QT-23	Silicalite	0.6	0.005	-4.2	0.020
QT-24	Silicalite	-7.2	0.012	-13.3	0.022
QT-25	Silicalite	-5.8	0.018	-10.3	0.008

4 Carbon and oxygen isotopic characteristics of the Neoproterozoic-Early Cambrian Taozichong Formation in Qingzhen City, Guizhou Province

It can be seen from Table 1 that the maximum value of $\delta^{13}C$ for the section is 1.7‰ V-PDB and the minimum value is -7.2‰, with the average value of -1.2‰. The maximum value of $\delta^{18}O$ for the section is -2.4‰ V-PDB and the minimum value is -13.3‰, with the average value of -7.4‰. According to the variation curve of $\delta^{13}C$ values, there are three obvious negative drifts on the section (Fig. 1). The first one appears in the biodetritus phosphorite at the transition part between the top of the Dengying Formation and the Cambrian, with the $\delta^{13}C$ value being -7.2‰; the second one appears in the bioclastic phosphorite in the lower part of the Lower Cambrian Taozichong Formation, with the $\delta^{13}C$ value being -6.9‰; the third one appears in the black silica shale of the Cambrian Niutitang Formation, with the $\delta^{13}C$ value being -7.2‰. In the upper part of the Taozichong Formation, the variation of $\delta^{13}C$ values is quite small, mainly within the range of 0−1‰. The $\delta^{13}C$ values show a regular variation trend: at the bottom of the section, the Dengying Formation displays an obvious negative drift, the variation value is up to about 7.0‰ from sample Nos. QT-1 to QT-5; the average value of $\delta^{13}C$ is 1.1‰ from QT-5 to QT-15; the average value of $\delta^{13}C$ is -3.1‰ from QT-16 to QT-21, showing an obvious negative drift. The variation extent of $\delta^{13}C$ value is up to about 4.0‰; the average value of $\delta^{13}C$ is 0.5‰ from QT-22 to QT-23, $\delta^{13}C$ returns to a positive value again, the average value of $\delta^{13}C$ is -6.5‰ from QT-24 to QT-25, showing again a strong negative drift, and the variation extent of $\delta^{13}C$ value is up to about 7.0‰.

In this section, the $\delta^{13}C$ values from the bottom of the Dengying Formation to the Lower Cambrian Niutitang Formation are comparable with those of the carbonatites of the Dengying Formation of the Xiadong section given by Zhang et al. (2004) and Lamhert et al. (1987). It is also comparable with the Wangjiawan section in Jining County, Yunnan Province (Shen, 2002). Their $\delta^{13}C$ values are comparable to those of carbonatite of the Dengying Formation of the Jiangshan profile in Zhejiang Province reported by Peng (2006). Meanwhile, they have similar characteristics expressed by the $\delta^{13}C$ values of carbonatite made by Yu et al. (2010) in the Ningnan region of Panxi, all showing an obvious negative drift.

The carbon isotopic composition of seawater is mainly controlled by the variation of relative ratio between carbonate sediment and organic carbon (Delaney, 1989). The carbonate deposition in seawater will not cause any carbon isotope fractionation, which can directly react to form the carbon isotopic composition of media. In contrary, the $\delta^{13}C$ value of seawater can be influenced when organic carbon is separated out of seawater (Zhu et al., 2006). The $\delta^{13}C$ value variation of marine carbonate will be influenced by many factors such as exchange between the ocean and the atmosphere, the input of terrigenous matter, production efficiency of creature and so on. The production efficiency of creature and organic carbon burying are the important factors (Kropnick et al., 1974). The activity of creature can cause carbon isotope fractionation. Light carbon in seawater will increase with increasing production efficiency of creature and carbon burial, then the composition of inorganic carbon dissolved in the ocean will become heavier, thus causing an increase in $\delta^{13}C$ value of seawater. In contrary, ^{12}C will be separated out when organic matter is exposed and oxidized, then the inorganic carbon dissolved in the ocean will become lighter, causing a decrease in $\delta^{13}C$ value of marine inorganic carbonate. This is the influence of biological productivity on the $\delta^{13}C$ value of seawater (Zhu et al., 2006).

It can be seen from the measured $\delta^{13}C$ data that the seawater had quite high biological yield and organic carbon burying speed during the early Early Cambrian, which can be proved by the position of negative drift.The negative drifts all took place almost at the time of the first appearance of a large amount of creature fossils with small shells. The biological explosion in the Early Cambrian led to the appearance of a large amount of creatures with small shells, as well as to a very high content of P in seawater, which has provided the background condition for the formation of Meishucun phosphorite. This evidence indicates that seawater in the Early Cambrian period provided good relevant conditions for the reproduction of creature. The strong negative drift of carbon isotopes in seawater indicates that the production efficiency of ocean in that period sharply decreased. The slight isotope fractionation between organic matter and the dissolved carbonate of seawater suggests that the seawater environment changed sharply in that period of time. Because of the seawater environment change, creatures dies in large amounts, meanwhile the isotope fractionation of creature will be stopped, thus causing quite a large negative drift of $\delta^{13}C$ in marine carbonate (Xu et al., 1986). For example, the $\delta^{13}C$ value of the Guangyuan section was normal in the Early and Late Permian (Huang, 1994), but it rapidly decreased near the boundary between the Wujiaping section and the Changxing section, the $\delta^{13}C$ value was reduced from 3.918‰ to -0.718‰ (in the middle period of Dalong). Such an abrupt event indicates that there is a massive death of creature from the late Wujiaping Stage to the Middle Changxing Stage. The minimum value at the bottom of the Feixianguan section is the $\delta^{13}C$ minimum value after the collective extinction event of creature (Magaritz, 1989). In the Ningnan section at Panxi (Yu et al., 2010), the $\delta^{13}C$ value is close to that at the boundary between the Neoproterozoic and the Cambrian, indicating that there also occurred a massive creature death event, thus causinga sharp negative $\delta^{13}C$ drift.

The first $\delta^{13}C$ negative drift of the Taozichong section has been discovered in bioclastic phosphorite at the top of the Neoproterozoic-Sinian Dengying Formation, the $\delta^{13}C$ values decreased from -0.1‰ to -7.2‰, with the decreasing range of 7‰. These characteristics are comparable with those observed in China (Li et al., 2009), Siberia (Magaritz et al., 1986), Iran (Brasiser et al., 1994) and Canada (Narbonne et al., 1994), showing that an obvious global event of $\delta^{13}C$ negative drift occurred during the Neoproterozoic-Cambrian transition stage. The drifting range of $\delta^{13}C$ values is from 5‰ to 10‰, and the negative peak value varies from -3‰ to -12‰. According to the section characteristics, the $\delta^{13}C$ negative drift exists in the marine creature-enriched marine carbonate rocks, it is closely related to creatures (Zhu et al., 2001; Steiner et al., 2007; Yu et al., 2010), it may corresponds to the "BACE" event named by Zhu et al. (2006) on the layer, i.e., the $\delta^{13}C$ negative drift from the top of the Neoproterozoic-Sinian to the bottom of

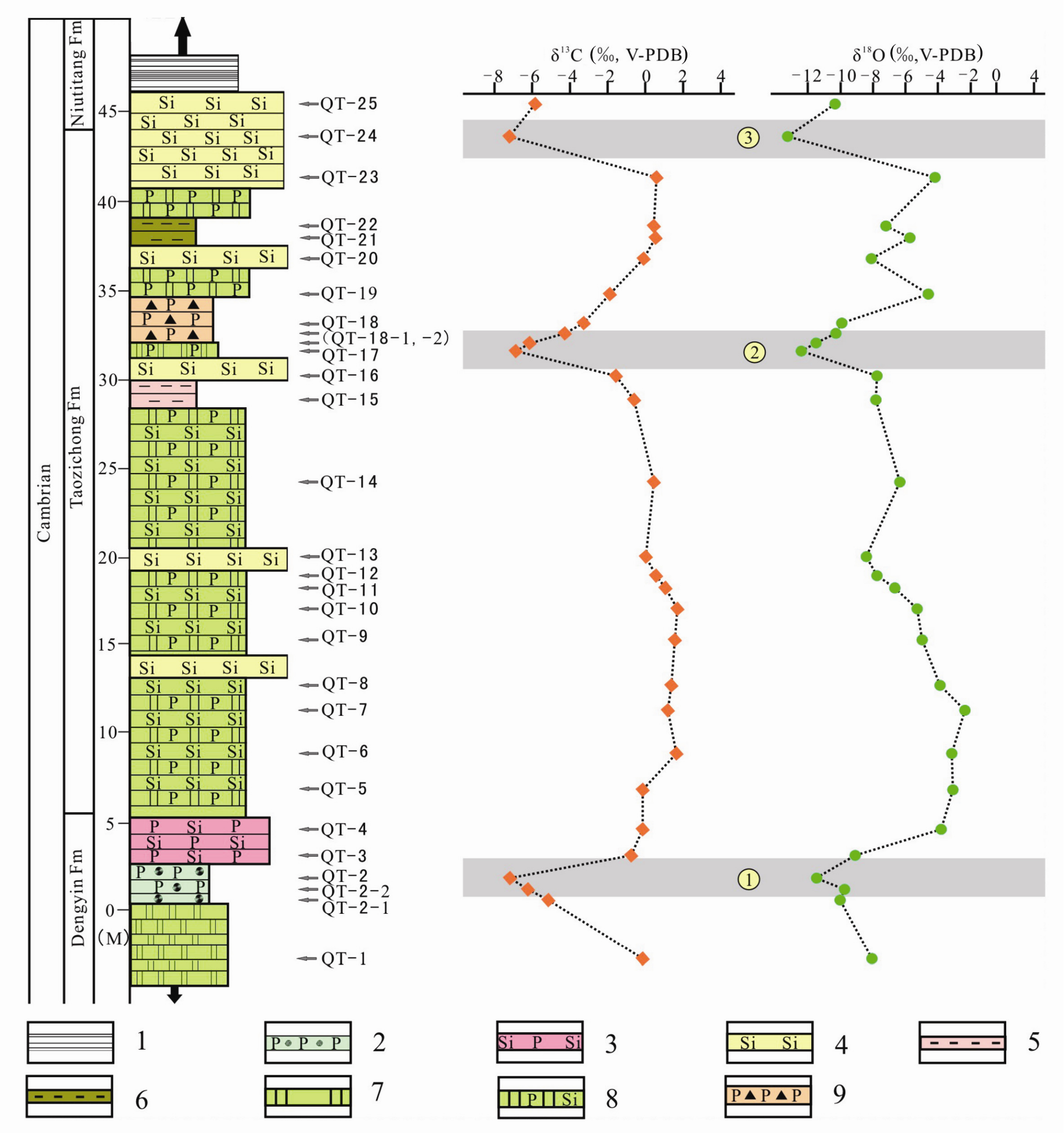

Fig. 1. The curves of carbon and oxygen isotopic compositions for the Taozichong Formation in Qingzhen City, Guizhou Province. 1. Black shale; 2. bioclastic phospholite; 3. siliceous phospholite; 4. silicalite; 5. foliated clay stone; 6. brown weathered crust; 7. dolostone; 8. siliceous dolostone containing phosphorus; 9. brecciaous phosphorite.

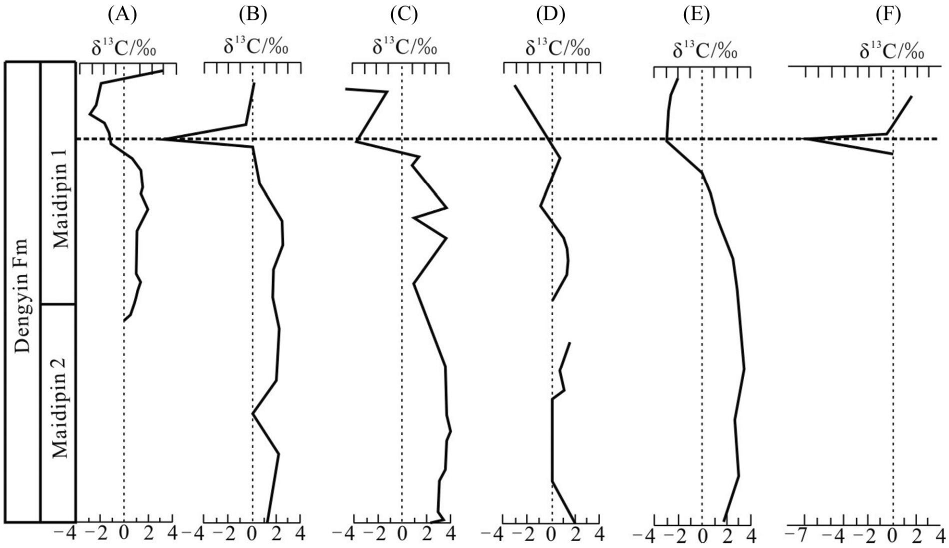

Fig. 2. Comparison of the carbon isotopic compositions of carbonatite in the Dengying Formation of the Yangtze platform (Yu et al., 2010). (A) Section of the Ningnan region of Panxi (Yu et al., 2010); (B) Shibei section in Yichang (Lamhert et al., 1987); (C) Huajipo section in Yichang (Zhang et al., 2004); (D) Wangjiawan section in Jingning (Shen, 2002); (E) Jiangshan section in Zhejiang Province (Peng, 2006); and (F) Taozichong section in Qingzhen City, Guizhou Province.

the Cambrian may responds to the creature extinction event of the Neoproterozoic-Sinian such as acritarchs etc. It is a little earlier than *P. anabarica* or the first discovery of trace fossil "*P. pedum*" (Magaritz et al., 1986; Brasiser et al., 1994; Li et al., 2009). It is possibly caused by the diachroneity of creature boundary (Brasier et al., 1996). Current viewpoint believes that the $\delta^{13}C$ negative drift of the bottom boundary of Cambrian was possibly caused by such an enrivonment in which anoxic event once occurred (Brasier, 1990; Kimura and Watanabe, 2001); or was possibly the result of sharp reduction of ratio (f_{org}) of organic carbon reserve and the total amount of sediment carbon (Kump, 1991), or it was possibly caused by the event of creature extinction (Zhu et al., 2006). It is also possible the result of carbon exhaustion in large amounts, which had been carried by raising ocean current, the sedimentation of phosphorus-enriched materials on the shallow platform, causing the negative drift of carbon isotope (Nie et al., 2006). According to the analysis data on the Taozichong section, the position of first negative drift is the shallow-sea carbonate, therefore it can be eliminated that the first negative drift was caused by the anoxic event. The strong negative drift of $\delta^{13}C$ value reflects the extinction process of creatures. When the surface seawater body was full of nutrition, algae rapidly developed and absorbed CO_2, preferentially ^{12}C, which would relatively inhance ^{13}C of the seawater; Ca-bearing sediments in the water body combined with ^{13}C of the seawater and formed carbonate sediments with rich ^{13}C. So, large ^{13}C values exist in the sediments with rich creatures, showing a positive drift of $\delta^{13}C$. In contrary, because the worsening of seawater environment caused the creature death or even extinction, the biological production capacity decreased, the seawater was characterized as being rich in ^{12}C and poor in ^{13}C. Then, the ^{13}C in sediments relatively decreased, showing a negative drift of $\delta^{13}C$ (Huang, 1994). The Dengying Formation consists of a set of shallow-sea carbonates with great thickness, in which there is a large amount of algae with relatively high phosphor contents, suggesting that the environment of seawater is good for biological reproduction. But the sudden negative drift at the top of the Dengying Formation indicates the strong variation of seawater environment. Such variation is possibly caused by large oxygen consumption in the ocean. Some research suggested that there had occurred anoxic events during this stage (Hiroto, 2002; Wang and Shi, 2010). Large exhaustion of oxygen will cause anoxic condition ($CH_2O+O_2 \rightarrow CO_2+H_2O$) in the ocean, and rich hydrogen sulfide is due to the reducing action of bacterial sulfate ($2CH_2O+SO_4^{2-} \rightarrow H_2S+2HCO^{3-}$) (Wang and Shi, 2010).The abrupt change of such environment will cause the death or extinction of creatures. Phosphor belongs to a biophile element, the organic material of creatures tends to absorb phosphor, which is often in the forms of calcium phosphate, phosphatide, etc. in the skeletons, shells and soft tissues of creatures. Phosphor was deposited at the bottom of sea after dying of creatures, transforming the phosphate dissolved in seawater into sediments at the bottom of the ocean. So, organic matter in creatures has relevant control on the minerals with rich phosphorus. Surface seawater body is the main locus for organic matter or planktons in which there is necessary oxygen for creature's respiration and enough photosynthesis.

Those advanced creatures absorbed phosphor in the water body, causing obviously low phosphor in the upper water body. When creatures died and continuously were precipitated at the bottom of the sea, the dissolved phosphate from seawater would be transformed into the deep-sea sediments.The results of research on the Precambrian phosphorite in central Guizhou Province showed that the formation of Early Cambrian phosphorite is closely associated with the rising current (Dongye et al., 1996; Mou and Wu, 2005; Nie et al., 2006), which is caused by upwelling of water mass characterized as being rich in ^{12}C and P formed under an anaerobic environment (Mazumdar and Banerjee, 1999, 2001). However, in the Precambrian-Cambrian period, in the upper part of the whole ancient ocean water body there appeared an environment rich in oxygen and relaltively rin in ^{13}C, while in the lower part there appeared an anaerobic environment characterized as being poor in ^{13}C (Hus et al., 1985). According to the former studies, the δCe value of the Qingzhen region was less than 0.67, with the lowest value being 0.17 only (Chen et al., 2013), indicating that phosphorite was mainly formed in the anaerobic environment and the obvious ^{13}C negative anomaly of phosphorite was possibly associated with the upwelling water mass characterized as being poor in ^{13}C and rich in P. Nie et al. (2006) also supported this viewpoint through their studies on the carbon isotopic composition of phosphorite in Wengan County and Zhijin County, Guizhou Province. At the same time, deep hydrothermal material had taken part in the mineralization process as revealed by the study on phosphorite and paragenetic siliceous rocks (Chen and Chen, 1993; Zhang et al., 2006; Wang and Sun, 2005; Mou and Wu, 2005; Quan et al., 2007; Shi et al., 2006, 2008). It is possible that the result of research on deep seawater mass has brought about the information about hydrothermal water sedimentation in deep seabeds. So, it can be inferred that the first negative anomaly of the Taozichong section in Qinzhen City, Guizhou Province, is highly associated with the rising ocean current characterized as being rich in phosphor and poor in ^{13}C.

The second δ^{13}C negative drift of the Taozichong section occurred in the transitional layer between the Taozichong Formation and the Niutitang Formation, whose lithology was bioclastic phosphorite with a large amount of fossils of small shell animals. This δ^{13}C value in this location rapidly decreased from 0.5‰ to -6.9‰ PDB, with the decline range of 7.4‰ PDB. This negative drift event corresponds to the negative drift event in central Guizhou Province (Nie et al., 2006). It is found through comparison and analysis, this δ^{13}C negative drift appears in bioclastic phosphorite of animal fossils with abundant small shells, and the explanation of the negative drifts is controversial. Some studies (Nie et al., 2006) hold that the negative drifts of δ^{13}C value are associated with the upwelling of rising current rich in phosphor and poor in ^{13}C caused by a seawater mixing event in the same period. The ^{13}C carried by upwelling ocean current was "exhausted", bringing nutrition materials into the shallow platform and thus causing the deposition of phosphorite with δ^{13}C negative drift (Nie et al., 2006). Research on geological section description and carbon isotope evolution for the classical Meishucun section, for example, the Laolin section (Li et al., 2009) and the Xiaotan section (Zhou et al., 1997) in eastern Yunnan Province, indicated that there was an obvious δ^{13}C negative drift between the top of the Zhongyicun section and the bottom of the Dahai section. This layer basically corresponds to the position of negative anomaly of carbon isotope at the top of upper part of the Taozichong section. In addition, the negative drift was also discovered from section II of the Yanjiahe section in the Three Gorges area (Wang et al., 2012), which is corresponding to the second negative drift of δ^{13}C value of the Taozichong section. Likewise, the lithology of this negative drift position is similar to that exposed during the first negative drift, and also in the bioclastic phosphorite. So, as already noted, this negative drift is still associated with the rising ocean current rich in phosphor and poor in ^{13}C.

The third δ^{13}C negative drift of the Taozichong section occurred at the bottom of the Niutitang Formation, and it lithologically composed of black thin-medium siliceous rocks, black shales intermingled with yellow clay rocks, and a little lenticular phosphorite mass. The δ^{13}C negative drifts of the first two appeared in phosphoric bioclastic phosphorite, implying their coupling relationship with creatures. As for the lithological characteristics of the δ^{13}C negative drift occurring at the bottom of the Cambrian Niutitang Formation, black shales were precipitated at the anoxic event. The formation type distribution of this set of black carbonaceous shales and mudstones is featured by globalization, wide distribution scopee and great deposition thickness, which is the result of extreme reversion of ocean environment. Due to the strong hydrotherm activity at the ocean bottom in this stage, several kinds of black rock deposits were formed in China. even all over the world. These deposits include Mo-Ni, V, PGE, barite deposits, etc. (Wei et al., 2012a), in which the Mo-Ni deposits mainly appeared in the so-called “multiple metal layer”. The appearance of these rare elements and rare-earth elements is closely associated with the hydrothermal activities at the bottom of the sea. The hydrothermal activities also directly effected the carbon isotopic composition. The hydrothermal activities over a wide range were the probable main reason responsible for the rapid change of ocean environment, which controls the composition of creatures and ocean geochemistry. A coarse-grained limestone layer with a thickness of about 15–20 cm originated from hydrotherm activities was discovered at the bottom of Lower Cambrian Mo-Ni deposits, with the lowest $\delta^{13}C$ value being only -8.223‰ PDB (Wei et al., 2012b). So, it is inferred that the negative drift of $\delta^{13}C$ value of the Lower Cambrian Niutitang Formation may be related to the hydrothermal activities at the bottom of sea.

5 The stratigraphic and biological evolution implications of changes in carbon isotopic composition of the Taozichong section in Qingzhen City of Guizhou Province

The Precambrian-Cambrian boundary is always a hot topic in geological research. The trace fossil Tretichnus *Phycodes pedum* Zone discovered in Newfoundland is considered as the Precambrian-Cambrian boundary section spot (Landing, 1994). However, Tretichnus *Phycodes pedum* fossil was found five meters below this section spot. So, new controversy occurred about the Precambrian-Cambrian boundary position.

There are three alternative typical section spots for the Meishucun age in China (Luo et al., 1994). The Xiaowaitoushan section is a typical Precambrian-Cambrian boundary section of the Meishucun age in Huizhe County of Yunnan Province. Our predecessors had executed carbon isotopic research on the Xiaowaitoushan section, and the results were comparable with those obtained from other areas abroad. So, the Xiaowaitoushan section is suitable to be set as the Precambrian-Cambrian boundary section spot (Shen and Schidlowski, 2000), namely the earliest spot of small shell fossils in the Meishucun section. Later, Yang et al. (2005) discovered strong carbon isotopic anomalies at the bottom section of the Cambrian near Yingping of Fuquan City, Guizhou Province. They thought that those carbon isotopic anomalies were comparable with those for other areas abroad, such as the top of the Salarrny Gol section in Siberia (Kaufman et al., 1996), the top of the Tsagaan Oloom section in Mongolia (Brasier et al., 1996), the Mackenzie mountains in Canada (Narbonne and Aitken, 1995) and the Xiaowaitoushan section in Huizhe County, Yunnan Province, China (Shen and Schidlowski, 2000).

In this paper, the carbon isotopic composition and variation trend of the Taozichong section are similar to those in the areas mentioned above (Fig. 3).

In eastern Yunnan Province, there is developed a complete Neoproterozoic-Cambrian boundary section inside the Yangtze block, and the typical sections include the Xiaotang section (Zhou et al., 1997), the Laolin section (Li et al., 2009) and the Meishucun section (Luo et al., 1994). As shown in Fig. 3, the upper strata of the Dengying Formation in Yunnan Province represent the Zhujiaqing section. The Zhujiaqing section was divided into three sections from bottom to top, i.e., the Taibu section, the Zhongyicun section and the Dahai section. The main lithological characteristics are described as follows: the Daibu section is made up of deep grey, gray black phosphoric siliceous rocks and siliceous dolomite; the Zhongyicun section, deep grey psammitic phosphorite, siliceous phosphorite and siliceous dolomite; and the Dahai section, light gray dolomite, and deep grey nodular limestone in the upper part (Qian and He, 1996). Compared with the Taozichong section, the Daibu section is roughly located at the boundary between the Dengying Formation and the Taozichong Formation; the Zhongyicun section is roughly equal to the Taozichong Formation, and the lithological characters of the Dahai section are not observed in the Taozichong section.

Li et al. (2009), Zhou et al. (1997) and Wang et al. (2012) respectively analyzed carbon isotopes of the same layers in the Laolin, Xiaotan and Three Gorges' Yanjiahe sections, acquiring carbon-oxygen isotopic variation curves in the same horizon (Fig. 3). The Taozichong section is comparable with the above-mentioned sections (Fig. 3). There is an obvious negative drift of $\delta^{13}C$ value inside the Daibu layer of the Laolin and Xiaotan sections. Yanjiahe layer I of the Yanjiahe section also has an obvious negative drift, corresponding to the obvious $\delta^{13}C$ value negative drift of the Taozichong section. This negative drift possesses a global comparability, all are the first large-size $\delta^{13}C$ negative drifts after the positive drift of carbon isotopes in the Dengying Formation for a long time (Fig. 3). Based on the previous data, the Neoproterozoic-Cambrian boundary is placed at the transitional part between the Daibu section and the Zhongyicun section (Qian and He, 1996; Zhu et al., 2006), i.e., the top of negative drift of carbon isotopes and the bottom having small shell fossils, which is consistent with the position of bottom small shell animal fossils discovered in this study. The first negative drift position of this study also can well correspond to the negative drift of eastern Yunnan Province and other regions. So, this study agrees with the above views that the position first showing small shell animals (i.e., the Neoproterozoic-Cambrian boundary) is also the position of the first obvious negative drift in this study. The $\delta^{13}C$ value of the first carbon isotopic anomaly of the Taozichong section in Qingzhen of Guizhou is -7‰ V-PDB. But the corresponding carbon isotopic anomaly between sections S1 and S2 in the lower part of the Xiaowaitoushan section of Yunnan Province is -6‰ V-PDB (Shen and Schidlowski, 2000), the carbon isotope value of top "W" of the Tsagaan Oloom section in Mongolia is -6‰V-PDB (Brasier et al., 1996), the carbon isotope below top N of the Salarrny Gol section in Siberia is -5‰ V-PDB (Kaufman et al., 1996), the carbon isotope value of the Ingta section at the bottom of Mackenzie mountain's Cambrian system in Canada (North American) is -10‰ V-PDB (Narbonne and Aitken, 1995). This indicates that this strong carbon isotopic negative anomaly at the bottom of the Cambrian generally exists all over the world. As is the same, the section in this study also affords new supplementary evidence for the determination of the Precambrian-Cambrian boundary.

In addition, a $\delta^{13}C$ negative drift exists in the Zhongyicun part of the Zhujiaqing section of eastern Yunnan Province and Yanjiahe section II of the Three Gorges area (Fig. 3). This negative drift can correspond to the second negative drift of the Taozichong section.

6 Conclusions

(1) Three new carbon isotopic anomalies are discovered at the bottom of the Cambrian Taozichong section in Qingzhen City, Guizhou Province, the first $\delta^{13}C$ negative drift is obvious and it is comparable with the carbon isotopic anomalies in other areas throughout the world.

(2) The first and second $\delta^{13}C$ negative drifts appear in bioclastic phosphorite. It is possible that the rising ocean current characterized by rich phosphor and poor ^{13}C entered the shallow platform and caused the eutrophication of shallow water environment (rich P), as well as flourish creatures and a series of biological-biochemical functions, finally leading to the formation of phosphorite. But the rising ocean current also brings about the geochemical characteristics of hot water sediments in the deep ocean, leading to such a result that the phosphorite possesses the geochemical characteristics of hot water sediments and lithological

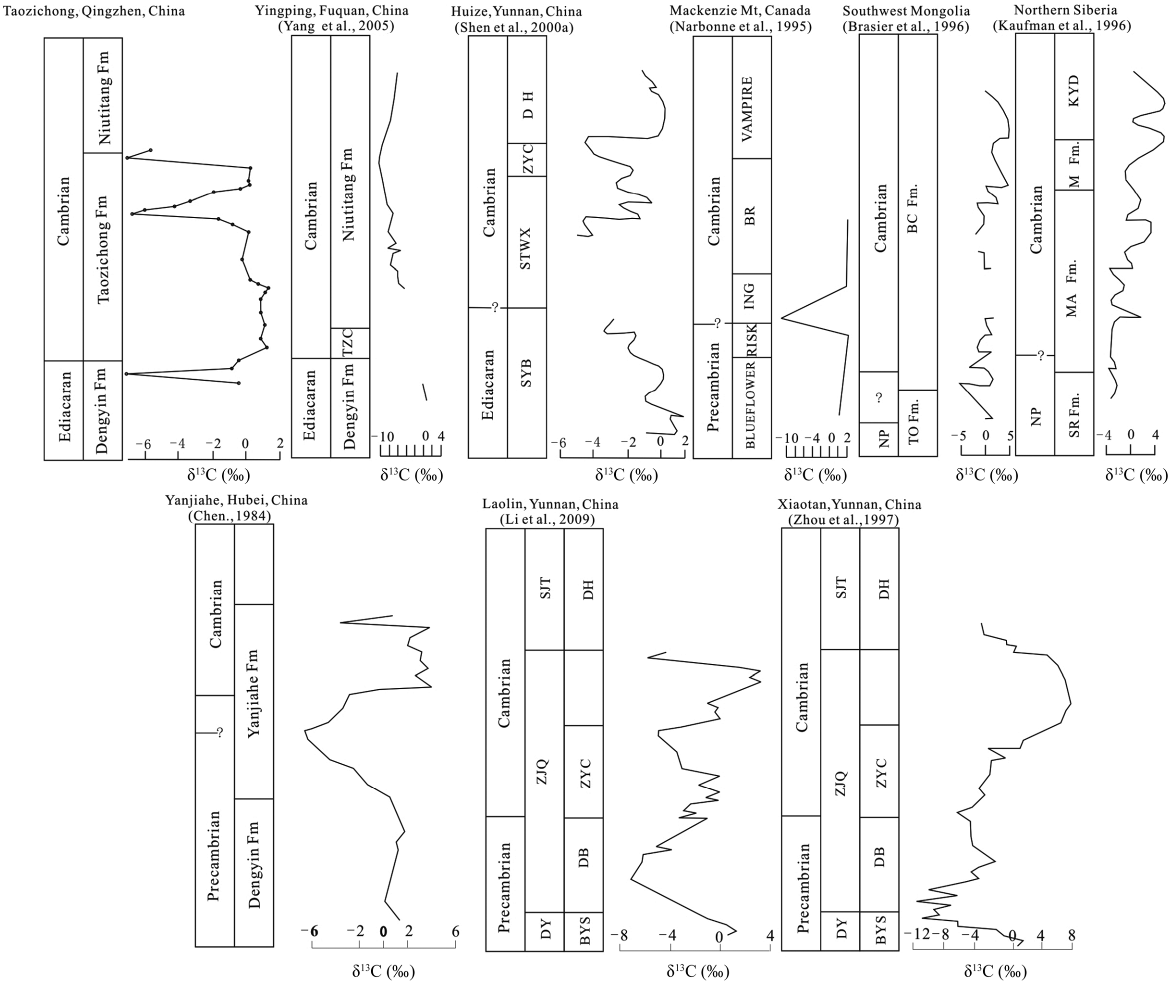

Fig. 3. Comparison of carbon isotope chemical stratigraphy in regions such as the Taozichong section in Qingzhen of Guizhou Province, Fuquan County of Guizhou Province, Huize of Yunnan Province, Laolin of Yunnan Province, Xiaotan of Yunnan Province, Canada, Mongolia and Siberia (modified by Yang et al., 2005). TZC. Taozichong section; BYS. Baiyanshao section; XWTS. Xiaowangtou section; YC. Zhongyicun section; DH. Dahai section; NP. Precambrian; DY. Dengyin section; SJT. Suijintuo section; DB. Daibu section; ZJQ. Zhujiajing section.

association. So, the phosphorites are characterized not only by $\delta^{13}C$ negative drift, but also by the features of hot water sediments. The last negative drift event is also associated with the rising of anoxic ocean current, meanwhile it is also closely related to hydrothermal activities at the bottom of the ocean.

(3) The carbon isotopic characteristics of the strata in this area are similar to the stratigraphic variation trend of other areas both at home and abroad in the same stage. So, there is a global comparability. During the transitional stage between the Precambrian and the Cambrian, this carbon isotopic negative drift of carbonate can be regarded as a geochemical mark for dividing the Precambrian-Cambrian boundary.

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