

Stable isotopic geochemistry of organic carbon and pyrite sulfur from the Early Cambrian black shales in Northwestern Hunan, China^{*}

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Received July 7, 2003; revised August 12, 2003

Abstract The early Cambrian black shale sequence in Northwestern Hunan Province has been investigated for its stable isotopic geochemistry of organic carbon and pyrite sulfur. The relatively low $\delta^{13}\text{C}$ values of organic matter $-29.7\text{‰} \sim -34.2\text{‰}$ are interpreted as caused by the high CO_2 concentration in atmosphere/ocean and an anoxic depositional environment in early Cambrian. Variable, but significantly positive $\delta^{34}\text{S}$ values, $+10.2\text{‰} \sim +28.2\text{‰}$ for sedimentary pyrite reveals bacterial sulfate reduction as the pyrite-forming process but under sulfate-limited conditions. A protected anoxic basin, which had very limited access to open ocean, and its sediments, where metabolizable organic matter was rich and bioturbation was absent, are supposed to be the sulfate-limited environments and might have existed in South China in the early Cambrian.

Keywords: sulfur and carbon isotopes, black shales, early Cambrian, Hunan.

Neoproterozoic-early Cambrian radiations were marked by the mass occurrence of most modern phyla^[1] and by significant changes in physical/chemical environment. The successive discoveries of the early Cambrian metazoan phyla and abundant small shelly fossils from the shallow- to deep-water environments in South China^[2] are of great significance for understanding the Cambrian radiation, and have led to the multidisciplinary studies on the biological and environmental evolution of Precambrian-Cambrian interval in South China. Numerous studies in recent years using carbon and sulfur isotopic methods have been carried out in this region^[3-5] in order to understand the seawater characteristics and its influence on the bio-radiation of this time interval. Most of these studies are focused on the sedimentary sequences deposited on the carbonate platform, whereas only a few represent the deep-water deposition on the continental slope dominated by extensive siliciclastic accumulation. In deep-water environments, syngenetic carbonate and sulfate rocks are absent, thermally unaltered sedimentary organic carbon and syngenetic or diagenetic pyrites are the only carriers of readable carbon and sulfur isotopic signals that may reflect secular palaeo-ocean environmental change. In Northwestern Hunan

Province, the sedimentary sequence of early Cambrian is named Niutitang Formation (Fm.) characterized by a transgressive black shale succession. Carbonate and sulfate rocks are totally absent in this black shale succession, whereas organic carbon and pyrite are rich, with an average concentration close to 7 wt% and 2 wt%, respectively. This study reports the isotopic data of organic carbon and pyrite sulfur from the Niutitang Fm. in Northwestern Hunan (Fig. 1) in an attempt to reveal the paleoenvironmental conditions during Early Cambrian interval.

1 Geological setting

The Niutitang Fm., unconformably overlying on the Neoproterozoic dolostone of Dengying Fm., is about 25 to 85 m thick in total in the study area. Lithologically, it can be divided into three units. The lower unit, with a thickness varying from 0 to 3 m, consists in ascending order of stratiform cherts and nodular/bedded phosphate. The middle unit, embracing the so-called polymetallic sulfide layer, comprises black shale and siliceous shale, with a total thickness varying from 3 to 6 m. The total organic carbon (TOC) and pyrite sulfur in the black shales can be as high as 12.5 wt% and 6.7 wt%, respectively.

* Support by the Major State Basic Research Development Program of China (G1999043210), the National Natural Science Foundation of China (Grant Nos. 40073007 and 40272080) and the Scientific Research Fund of Nanjing University

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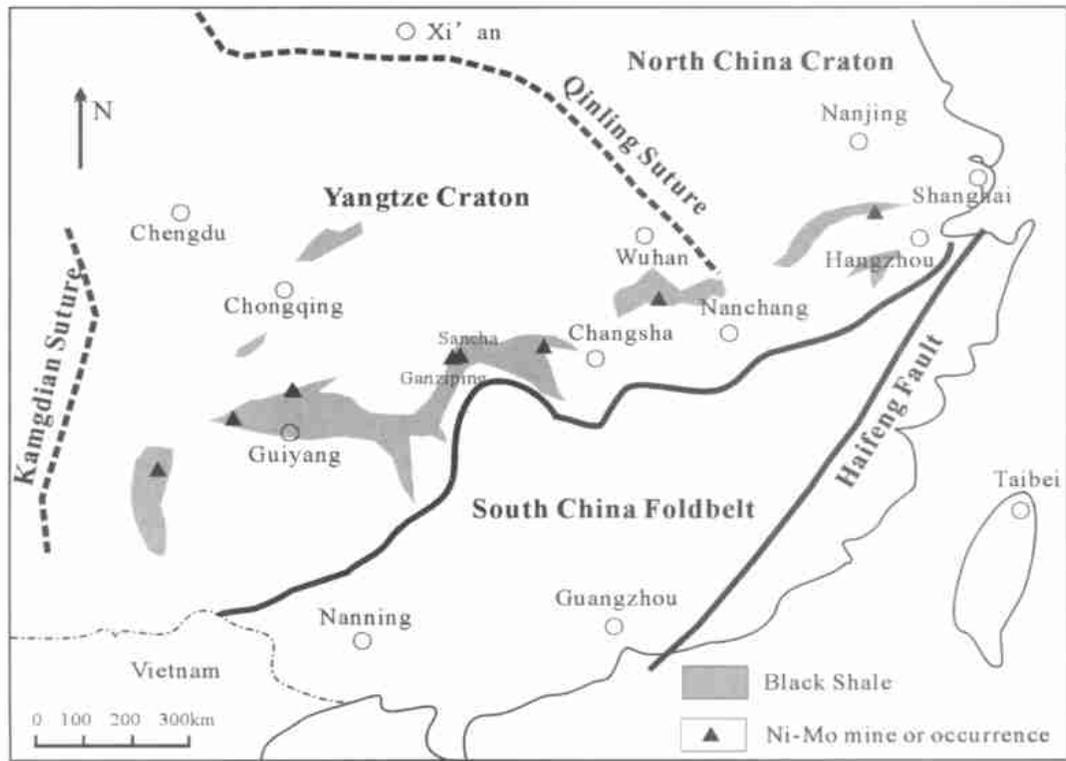


Fig. 1. The geological map showing the locations of sampling section (from Mao et al. [6]).

Trace elements, such as Ni, Mo, V, Cu, Zn, Ba, U and Th, are significantly enriched in comparison with those in both lower and upper units of Niutitang Fm. In particular, Ni and Mo can be of economic value at some locations in the study area. Blocky mudstone and shale intercalations constitute the upper unit with thickness of 20 to 80 m, that is conformably overlain by the Shipai Fm. of Early Cambrian. TOC and pyrite sulfur content in this unit become less than those in the middle unit. Samples for this study were collected from the Ganziping and Sancha sections, respectively located 10 km and 25 km to the south and southeast of Zhangjiajie City, Hunan Province.

2 Analytical methods

Sulfur contents and TOC of the samples were measured with a LECO CS-225 instrument. The detection limit was 0.05%.

Isotopic ratios for organic carbon in the samples were obtained by mass-spectrometer (Finnigan MAT-252 mass spectrometer) measurement of CO₂ liberated from combustion of organic carbon in sealed quartz

tubes. All samples for sealed quartz tube combustion were pretreated with HCl and HF acids. Isotopic results are reported in conventional δ notation as per mil deviation from the PDB standard. The standard deviation for $\delta^{13}\text{C}$ was less than 0.1‰ (PDB) and the reproducibility was better than 0.15‰ (PDB).

Pyrite samples for the measurement of sulfur isotopic compositions were separated from the black shales manually. Great care was taken in extracting and purifying the pyrite crystals under microscope. Pulverized pyrites were mixed with CuO and sealed in a vacuum quartz tube for combustion at 1000 °C. Recovered and purified SO₂ was analyzed for isotopic compositions using a Finnigan MAT-251 mass spectrometer. Sulfur isotopic compositions are given as per mil difference from CDT (Canyon Diabolo trilobite) standard. Reproducibility was better than 0.2‰.

Analytical results for the contents and isotopic compositions of organic carbon and sulfur are listed in Table 1.

Table 1. Contents and isotopic compositions of organic carbon and pyrite sulfur in black shale from Ganziping and Sancha Sections in Zhangjiajie City, Hunan Province

Sample No.	Location (m)	TOC (%)	S (%)	S/C	$\delta^{13}\text{C}_{\text{org}}$ (‰ PDB)	$\delta^{34}\text{S}_{\text{py}}$ (‰ CDT)	Sample No.	Location (m)	TOC (%)	S (%)	S/C	$\delta^{13}\text{C}_{\text{org}}$ (‰ PDB)	$\delta^{34}\text{S}_{\text{py}}$ (‰ CDT)
ZS-4	0.05	1.3	0.15	0.10	-33.2		ZG-14	3.5	9.3	1.70	0.18	-31.8	
ZS-4a	0.1	1.8	0.47	0.26	-33.1	10.2	ZG-15	4	10.8	3.50	0.32	-31.8	16.3
ZS-4b	0.15	1.0	0.19	0.19	-33.0		ZG-16	4.5	6.5	6.70	1.10	-31.8	11.6
ZS-4c	0.18	9.0	5.60	0.62	-32.4		ZG-16b	5	9.7	5.30	0.55	-31.9	
ZS-5	0.33	5.6	5.30	0.95	-33.1		ZG-17	5.46	7.2	4.20	0.58	-31.8	28.2
ZS-6	0.6	9.1	4.80	0.53	-32.5	18.6	ZG-18	7.86	12.5	0.84	0.07	-31.2	
ZS-7	1.45	8.9	1.90	0.21	-31.8		ZG-19	8.44	12.2	1.20	0.10	-30.9	27.4
ZS-8	2.05	9.2	4.10	0.45	-31.8	13.9	ZG-20	8.80	11.9	0.98	0.08	-31.0	
ZS-9a	4.3	9.3	3.30	0.35	-31.7		ZG-21	9.17	8.7	1.35	0.15	-31.0	23.3
ZS-10	6.2	10.4	0.51	0.05	-31.7		ZG-22	9.57	7.37	0.57	0.08	-30.9	16.5
ZS-11	8.95	8.6	0.24	0.03	-31.4	17.2	ZG-23	23.18	3.2	0.12	0.04	-31.8	
ZS-12	11.05	8.9	1.60	0.29	-32.0	20.3	ZG-24	24.77	2.1	0.08	0.04	-32.1	20.3
ZG-1	0.1	10.8	2.30	0.21	-31.7	16.0	ZG-25	32.87	2.0	0.05	0.03	-31.6	
ZG-2	0.2	3.4	0.31	0.10	-34.2		ZG-25b	35.00	1.9	0.03	0.02	-31.3	
ZG-3	0.3	11.9	2.70	0.23	-32.0		ZG-26	47.45	1.7	0.11	0.06	-29.7	
ZG-3b	0.5	12.0	2.50	0.20	-31.8		ZG-27	51.47	2.0	0.11	0.06	-30.0	
ZG-4	1.3	11.6	2.20	0.19	-31.8		ZG-28	61.50	5.4	0.12	0.02	-30.1	
ZG-5	2.1	11.1	2.50	0.23	-31.8	16.6	ZG-29	62.31	4.8	0.23	0.05	-30.1	
ZG-6	2.5	10.0	3.90	0.39	-31.8		ZG-30	66.96	3.1	0.04	0.01	-30.5	
ZG-7	2.55	11.0	2.30	0.21	-31.8	25.7	ZG-31	67.34	2.6	0.54	0.21	-30.1	
ZG-8	2.6	10.6	1.30	0.13	-32.0		ZG-32	69.76	8.2	0.18	0.02	-30.4	
ZG-9	2.65	9.9	2.20	0.22	-31.7	22.6	ZG-33	70.00	4.2	0.59	0.14	-30.5	
ZG-10	2.7	9.3	3.10	0.33	-31.9		ZG-34	73.46	1.5	0.06	0.04	-30.6	
ZG-11	2.8	9.4	1.90	0.20	-31.9		ZG-35	85.84	4.8	0.39	0.08	-31.0	
ZG-12	2.9	9.3	3.90	0.42	-31.8	10.9	ZG-36	94.52		0.09		-30.0	
ZG-13	3	10.4	2.20	0.22	-31.9								

3 Results and discussion

3.1 Isotopic composition of organic carbon

In this study, we analyzed 51 samples from two sections for contents and isotopic compositions of organic carbon.

TOC varies greatly from 1.0 wt% to 13.5%, averaged about 7.0%. A stratigraphic variation of TOC values, especially significant on Ganziping section (Fig. 2), exists from the lower to the upper unit of the Niutitang Fm., with high values in the lower and middle units. Given the lack of remarkable thermal alteration in the study area and the fact that the generally low TOC values mainly occur in the very thick upper unit with coarser detrital grain sizes, sedimentation rate might be the most important factor controlling the organic carbon concentrations in the Niutitang Fm. Nevertheless, we could not exclude the influence of different productivities on the organic carbon concentrations at different time.

The $\delta^{13}\text{C}_{\text{org}}$ values vary from -29.7‰ to -34.2‰ with most values around -31.5‰ showing strong ^{13}C -depletion in comparison with those of most other pre-Devonian organic carbon ($\delta^{13}\text{C}_{\text{org}} \geq -30\text{‰}$)^[7, 8].

Carbon isotopic composition of sedimentary organic matter records both primary and secondary processes within the biogeochemical carbon cycle. Independent studies have revealed that the isotopic ratios of organic carbon in marine sedimentary rocks are largely governed by the isotopic fractionation associated with the primary production^[9, 10]. However, subsequent biological reworking and post-depositional thermal alteration involving additional isotopic fractionation will change the primary signal once the residues of these organisms become incorporated in the sediments. Usually, this secondary process involving biological reworking and post-depositional thermal alteration will lead the organic carbon to a heavier isotopic value relative to its original isotopic ratio^[8, 10]. This would suggest that the primary

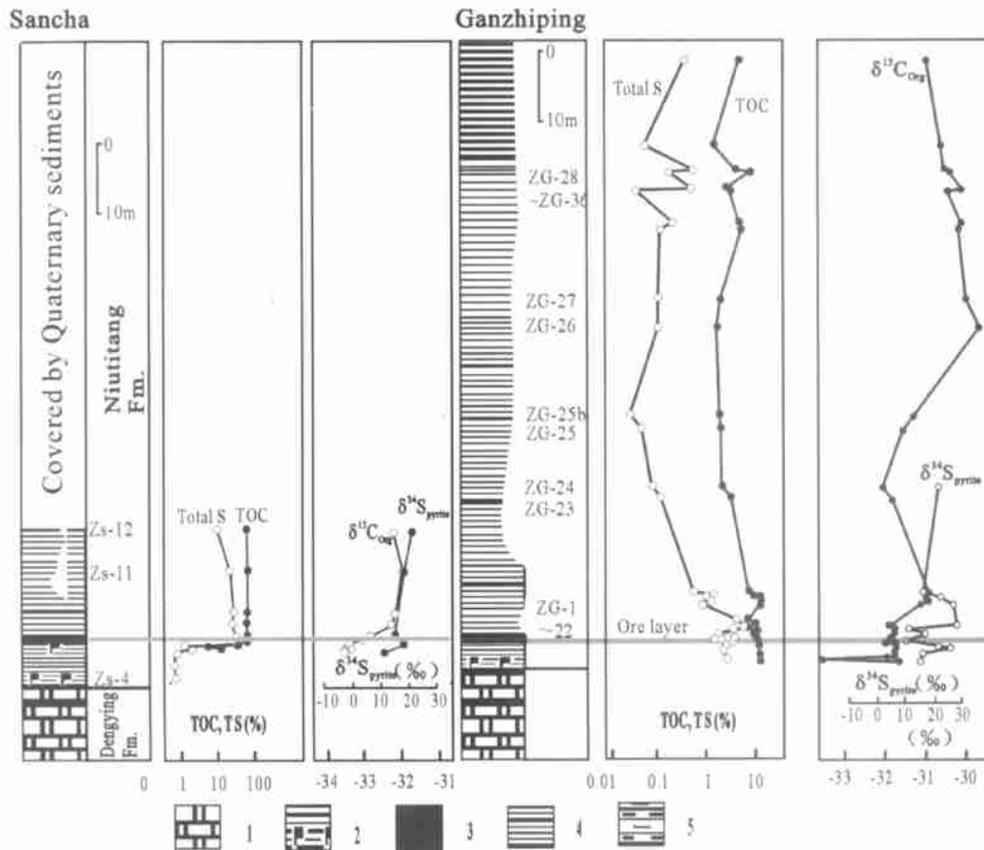


Fig. 2. Diagraph showing the stratigraphic variation of contents and isotopic compositions of organic carbon and sulfur, where 1, 2, 3, 4 and 5 represent dolomite, phosphorite, Ni-Mo sulfide ore, shale and mudstone, respectively.

isotopic composition of the organic matter prior to its incorporation into sediments of Niutitang Fm. in the early Cambrian might have been even more ^{13}C -depleted than the measured isotopic compositions.

For such kind of strong ^{13}C -depletion reflected by organic carbon, a variety of explanations, which involve aqueous CO_2 concentration in seawater, growth rate and cellular size of organism, global temperature variation, etc., have been explored^[7, 11~13]. However, the most promising interpretation continues to be the elevated aqueous CO_2 concentration in seawater which allowed for greater discrimination during algal photosynthesis, resulting in isotopically depleted organic material.

In the Early Cambrian, the CO_2 concentration in the atmosphere is about 20 times higher than today^[14]. The equilibrium of CO_2 between atmosphere and ocean would result in the elevation of dissolved CO_2 concentration in seawater which favored the maximum fractionation during algal photosynthesis. However, the maximum fractionation associated with

the primary production, according to Popp et al.^[12], is 25.3%, which cannot duly interpret the extremely low isotopic values. Therefore, further explanations for the present data are required. A high atmospheric CO_2 content could enhance the global greenhouse effect and the subsequent elevation of global sea level. During the Niutitang interval of Early Cambrian in the Yangtze Platform, high atmospheric CO_2 level, high continental weathering rate, and anoxic environments have been inferred by independent evidence^[3, 15, 16]. Under greenhouse condition, oceanic circulation was dramatically reduced in comparison with those under the icehouse-coldhouse condition. A sluggish ocean circulation would favor the development of a salinity stratification within oceans, and warm, saline, dysaerobic or anoxic waters could be established in deep basins^[17]. Within the dysaerobic or anoxic basins, organic matter degradation in association with sulfate reduction produced isotopically light CO_2 . The ^{13}C -depleted CO_2 accumulated below the redox boundary and, episodically, was mixed into the surface water body, where the photoautotrophic algae and bacteria utilized the CO_2 again during pho-

tosynthesis to produce ^{13}C -depleted organic matter^[18]. With the proceeding of such a recycling process within CO_2 /organism cycle, the organic matter became progressively ^{13}C -depleted. In addition, the nutrients supply might have been insufficient and influenced the growth rate of phytoplankton under anoxic basin condition due to sluggish ocean circulation. Low growth rate could also allow the maximum isotopic fractionation during photosynthesis. Strauss et al.^[19] indicated that some chemical processes, e. g. the fermentation of organic matter, sulfide- and ammonia-oxydation can also enhance the ^{13}C depletion under specific conditions. Given the water column was anoxic in South China in the early Cambrian, these chemical reactions might have influenced the isotopic compositions of organic carbon.

Slightly stratigraphic variation in $\delta^{13}\text{C}_{\text{org}}$ values is discernible from the lower to upper unit of the Niutitang Fm., with the lower unit showing relatively more ^{13}C -depleted. It seems that this variation cannot be explained by growth rate/productivity based on the TOC variations. The most possible interpretation could be the variation of depositional environments. In the late period of Niutitang of the Early Cambrian, the sea level became lowered inferred from the lithological and trace element variations (data was reported in another paper in print), which would cripple the anoxic environments and, consequently led to an isotopic fractionation associated with photosynthesis close to the normal marine condition.

In general, isotopic data of organic carbon reflects the existence of an anoxic basin in South China during the early Cambrian, which agrees with the results of numerous previous studies^[3, 15, 16].

3.2 Isotopic Composition of Pyrite Sulfur

51 samples were measured for total sulfide sulfur contents (TS). The TS varies from 0.03% to 6.7%. Of all samples, 17 were selected for sulfur isotopic analysis, all $\delta^{34}\text{S}$ values for pyrite are positive, ranging from +10.2‰ to +28.2‰.

Sulfur to organic carbon ratios (S/C) are quite variable, but generally less than 1.0 throughout the Niutitang Fm., which is much less than that of the average Cambrian shale (S/C = 2.0)^[19] and was interpreted by Lei et al. as Fe-deficiency in the seawater based on the DOP (degree of pyritization) values^[5]. As shown in Table 1 and Fig. 2, among all

the samples, high total sulfur concentrations are generally associated with high TOC values, but high TOC values do not always correspond to high TS values, reflecting that sulfide production may largely be related to bacterial sulfate reduction (BSR), and organic carbon could not be the main limitation factor for sulfide production.

$\delta^{34}\text{S}$ values are comparable to those of other Neoproterozoic-Early Cambrian sulfides ($\delta^{34}\text{S} = -20\text{‰} \sim +58\text{‰}$) as reported by Strauss^[20, 21], and are in very good agreement with that of the early Cambrian pyrite from Xiuning County in Anhui Province, +10.9‰ ~ +29.2‰^[5]. Assuming BSR as the main process for pyrite formation and a kinetic isotopic fractionation of 20‰ ~ 45‰^[22-25] associated with this process, the average sulfur isotopic composition of 30‰ for the Neoproterozoic and Early Cambrian sulfates^[20, 21] could not explain most of our present isotopic compositions of pyrite sulfur, even if the minimum fractionation of 20‰ was assumed. A plausible explanation for the present data is that most of these pyrites formed in the environment where sulfate reduction and subsequent pyrite formation were exceeding sulfate replenishment. As a consequence of the preferential reduction of ^{32}S , the pyrite would become progressively more ^{34}S -enriched. During the late Proterozoic to early Cambrian period, four distinct facies regions in South China can be distinguished^[16]: carbonate Yangtze Platform, protected basin (back-arc basin), Jiangnan uplift (arc) and deep-ocean basin. The study area was located just in the southeastern margin of Yangtze Platform, a protected basin area behind the Jiangnan uplift, where seawater exchange with the open ocean might have been restricted. In the water column of the basin, due to continuous sinking of organic matter, demands by heterotrophic organisms for oxygen and other electron acceptors in water might be high. Assuming the water column was anoxic as proposed by Li et al.^[3], Steiner et al.^[19], and Yang et al.^[26], production of sulfide by planktonic sulfate-reducing bacteria is likely to have been important^[27]. Continuous consumption of sulfate and preferential reduction of ^{32}S may have resulted in sulfate-depletion and ^{34}S -enriched sulfate in seawater. Canfield^[28] demonstrated that isotopic fractionation associated with BSR is closely related with sulfate concentration, $\Delta \delta^{34}\text{S} \leq 5\text{‰}$ when sulfate concentration of seawater is $\leq 1\text{ mmol/L}$ (about 4% of the present seawater). The sulfate concentration and the isotopic fractionation associating with BSR in

the Early Cambrian seawater is hardly known, but it is highly possible that both the low sulfate concentration and the ^{34}S -enriched sulfate in seawater affected the isotopic compositions of pyrite sulfur on condition of the existence of protected basin and anoxic water. Such a model could well explain most of our present data provided that the $\delta^{34}\text{S}$ values of sulfate in early Cambrian seawater in South China were $+29.0\% \sim +37.0\%$, averaged about $+33\%^{[4]}$. For the several high values (higher than $+25\%$) in this study, a diagenetic origin in a closed system could be an alternative explanation. For diagenetic pyrites formed through BSR within sediments where bioturbation is absent and metabolizable organic matter is rich, sulfate-reducing bacteria would be cut off from supplies beyond those present in pore water and, as consumption of the available sulfate approached completion, the $\delta^{34}\text{S}$ value of sedimentary sulfide would also approach that of the seawater sulfate^[27]. Field and microscopic observations have proved that these samples with extremely high $\delta^{34}\text{S}$ values embody laminar pyrites and framboidal pyrites of diameters larger than $15\mu\text{m}$, which are supposed to be diagenetic instead of syngenetic^[29].

Secular variations of $\delta^{34}\text{S}$ values throughout Niutitang Fm. are not observed due to the lack of sufficient data from the upper unit. However, variations of $\delta^{34}\text{S}$ values between the lower and middle units are still identifiable, with most of the higher values occurring in the middle unit. This might have been related with the elevation of sea level and the formation process of anoxic water column in the very beginning of Niutitang period of the Early Cambrian as it has been discussed above. Remarkable differences in $\delta^{34}\text{S}$ values between the Ganziping and Sancha sections also exist, more high values occurred in the former section, which might have resulted from the geographic and environmental differences. Lithologic properties and geographic locations indicate that the water depth at Ganziping might be larger than that at Sancha in the early Cambrian although both sections are very close and were located on the same marginal area of Yangtze Platform. A deeper water environment would be more favorable for the formations of an anoxic water column and a closed system in sediments and consequently favoured the formation of pyrite with higher $\delta^{34}\text{S}$ values through BSR process.

In summary, we suggest that a protected, anoxic basin and the diagenetic origin in closed systems

were the most important factors controlling the sulfur isotopic compositions of pyrites.

4 Conclusions

The Early Cambrian organic-carbon-rich black shales from Northwestern Hunan Province have been studied for their organic carbon and sulfide sulfur geochemistry. Extremely low $\delta^{13}\text{C}$ values of organic carbon are largely attributed to the high CO_2 concentration in atmosphere/ocean and the anoxic seawater environments in South China in early Cambrian. The correlations between TS and TOC values indicate that sulfides are largely bio-genetic through BSR, and organic carbon was not the limitation factor for pyrite production. Variable, but significantly positive $\delta^{34}\text{S}$ values for sedimentary pyrite, comparable to other early Cambrian sulfur data, are explained by BSR but under sulfate-limited conditions. An anoxic and protected back-arc basin with limited access to open ocean, which might be characterized by sulfate-depleted and ^{34}S -enriched, is proposed for explaining most of the $\delta^{34}\text{S}$ values. Diagenetic process under close-system conditions could produce pyrites with $\delta^{34}\text{S}$ values close to these of the coeval seawater sulfate. In general, stable isotopic geochemistry of the Early Cambrian black shales in Northwestern Hunan reflects, to a large extent, the paleo-oceanic environment, an anoxic basin in South China.

Acknowledgements Sulfur isotope measurement was done at the Yichang Institute of Geology and Mineral Resources, GAGS, Yichang.

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