

Global and regional controls on carbon-sulfur isotope cycling during SPICE event in south China

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Abstract The positive S-isotopic excursion of carbonate-associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) is generally in phase with the Steptoean positive carbon isotope excursion (SPICE), which may reflect widespread, global, transient increases in the burial of organic carbon and pyrite sulfate in sediments deposited under large-scale anoxic and sulphidic conditions. However, carbon-sulfur isotope cycling of the global SPICE event, which may be controlled by global and regional events, is still poorly understood, especially in south China. Therefore, the $\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{18}\text{O}_{\text{PDB}}$, $\delta^{34}\text{S}_{\text{CAS}}$, total carbon (TC), total organic carbon (TOC) and total sulfate (TS) of Cambrian carbonate of Waergang section of Hunan Province were analyzed to unravel global and regional controls on carbon-sulfur cycling during SPICE event in south China.

The $\delta^{34}\text{S}_{\text{CAS}}$ values in the onset and rising limb are not obviously higher than that in the preceding SPICE, meanwhile sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope values increase slightly with increasing $\delta^{13}\text{C}_{\text{PDB}}$ in rising limb and near peak of SPICE (130–160 m). The sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope values gradually decrease from 48.6‰ to 18‰ in the peak part of SPICE and even increase from 18‰ to 38.5‰ in the descending limb of SPICE. The abnormal asynchronous C-S isotope excursion during SPICE event in the south China was mainly controlled by the global events including sea level change and marine sulfate reduction, and it was also influenced by regional events such as enhanced siliciclastic provenance input (sulfate), weathering of a carbonate platform and sedimentary environment.

Sedimentary environment and lithology are not the main reason for global SPICE event but influence the $\delta^{13}\text{C}_{\text{PDB}}$ excursion-amplitude of SPICE. Sea level eustasy and carbonate platform weathering probably made a major contribution to the $\delta^{13}\text{C}_{\text{PDB}}$ excursion during the SPICE, in particularly, near peak of SPICE. Besides, the trilobite extinctions, anoxia, organic-matter burial and siliciclastic provenance input also play an important role in the onset, early and late stage of SPICE event.

Keywords sulfate isotope excursion, terrigenous matter, carbonate platform weathering, sea level change, transitional slope environment, Waergang section

1 Introduction

The global Steptoean positive carbon isotope excursion (SPICE) during late Cambrian has been identified around the world, in North America (Laurentia), Kazakhstan, China, Australia (Gondwana) and England (Peng, 1992; Peng and Robison, 2000; Saltzman et al., 2000; Peng et al., 2004a, 2004b; Saltzman et al., 2004; Runnegar et al., 2010; Woods et al., 2011; Dahl et al., 2014). The SPICE is recorded as a 4‰–6‰ excursion in $\delta^{13}\text{C}_{\text{carb}}$ during about 2–4 million years and its onset defines the lower boundary of the Upper Cambrian (Furongian) at about 499 million years ago (Saltzman et al., 2000, 2004; Gill et al., 2011a). The SPICE marks a global oceanographic event and may be related with the global trilobite extinctions, organic-matter burial, sea level change and seawater temperature (Saltzman et al., 2000; Elrick et al., 2011; Dahl et al., 2014), which could be mostly

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confirmed by corresponding widespread positive excursion of sulfur isotope due to the carbon-sulfur cycling (Gill et al., 2011a; Thompson and Kah, 2012; Liu et al., 2016).

The positive S-isotopic excursions of sedimentary pyrite ($\delta^{34}\text{S}_{\text{pyrite}}$) and carbonate-associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) is generally in phase with the SPICE, although the $\delta^{34}\text{S}_{\text{CAS}}$ excursion amplitude varies in different SPICE sections (Hurtgen et al., 2002; Gill et al., 2007; Gill et al., 2011a). These carbon-sulfate isotope synchronous excursions were thought to reflect global transient increases in the burial of organic carbon and pyrite sulfate in sediments deposited under large-scale anoxic and sulphidic (euxinic) conditions (Saltzman et al., 1998, 2000, 2004; Hurtgen et al., 2009; Gill et al., 2011a; Thompson and Kah, 2012). However, controls on the carbon-sulfur cycling during SPICE event, especially the regional factors, was still poorly understood.

The SPICE events were identified in three typical sections of south China including the Waergang Section, Yongshun Section and Yankong Section, which were deposited in different environments (Peng, 1992; Peng and Robison, 2000; Peng et al., 2004a, 2004b; Zuo et al., 2008a, 2008b; Wang et al., 2011). The SPICE event was related to upwelling, the fast burial of organic materials, sea level eustasy, Trilobite extinctions and the weathering of carbonate rocks in Yongshun and Yankong Sections of the south China (Zuo et al., 2008a, 2008b; Wang et al., 2011). However, the carbon-sulfur cycling of SPICE event is still research gap in the south China (Peng, 1992; Peng and Robison, 2000; Peng et al., 2004a, 2004b; Zuo et al., 2008a, 2008b; Wang et al., 2011). As one of typical sections related to SPICE event of south China, the Waergang Section, which was deposited in the transitional slope environment and very close to the Yangtze Platform and deep shale basin, was sensitive to the sea level change, organic carbon burial, regional weathering and siliciclastic provenance input.

To reveal the global and regional controls on the carbon-sulfur cycling during SPICE event, we measured isotopic data ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}_{\text{CAS}}$) and elemental abundance data (TOC, TC, and TS) in samples from the Waergang Section. On the basis of previously published data from Yankong Section of Yangtze Platform and Yongshun Section of slope and the new data of Waergang SPICE Section, we aim to explain the carbon-sulfur cycling mechanism and reveal the controls on the sulfur isotope excursion during the SPICE event.

2 Geological setting

The sedimentary environment of south China mainly comprises the exposed Kangtien old Land, a shallow-water Platform (Yangtze Platform), a slope belt (Xiangxi Basin), deep-water Basin (Jiangnan Basin) and the

Southeast Clastic Platform during the late Cambrian (Peng and Robison, 2000; Feng et al., 2001, 2002; Peng et al., 2004a, 2004b; Zuo et al., 2008a, 2008b) (Fig. 1(b)). The carbonate was mainly deposited in the Yangtze Platform (block) and Slope (Xiangxi Basin) but clastic sediment accumulated in the Jiangnan Basin and Southeast block (Feng et al., 2001, 2002; Peng et al., 2004a, 2004b; Zuo et al., 2008) (Fig. 1(b)). The Kangtien land area, which was a peneplained, only provided limited fine-grained clastic sediment for the Yangtze Platform (block) (Feng et al., 2001). The provenance of clastic rock within Jiangnan Basin and Southeast Clastic Platform mainly comes from the Cathaysia, which was located roughly in the southeast of the southeast Block, provided much fragmentary material (Feng et al., 2001; Feng et al., 2002). The Kangtien Land area expanded in the Late Cambrian (Feng et al., 2001). Compared with the Middle Cambrian, the Yangtze Platform was still a shallow-water carbonate platform evolving to a gypsum-salt lake in the Late Cambrian, suggesting the sea-level rise in the Late Cambrian (Feng et al., 2001). Carbonate deposition increased within Jiangnan Basin in the Late Cambrian (Feng et al., 2001). The gravity flow deposits were more developed within the slope in the Late than Middle Cambrian, indicating the sea-level rise (Feng et al., 2001). The Paibi Stage and Furongian Series are derived from localities and the Global Standard Stratotype-section and Point (GSSP) of south China, and the Furongian Series, which is equal to the Middle-late of Late Cambrian, replaced the old Late Cambrian (Peng et al., 2004a, 2004b, 2004c). Therefore, after larger-scale transgression of the early Wuling Series, the south China area was characterized by sustained regression and sea level fall in the Early Furongian (New Late Cambrian) (Wang et al., 2011).

Both Waergang Section and Yongshun Section are situated within the slope belt, which represents transitional facies between shallow-water carbonate of Yangtze Platform and deep basinal deposits of Jiangnan Basin (Peng, 1992; Wang et al., 2011; Liang et al., 2015; Li, 2017) (Fig. 1(b)). The Yongshun Section was at the Yangtze Platform-Slope boundary, but the Waergang Section was on the boundary of Slope-Jiangnan shale Basin (Fig. 1(b)). The Middle-Upper Cambrian lithological unit mainly consists of Aoxi, Huaqiao, Chefu, Bitiao and Shenjiawan Formations in the Waergang Section of Hunan Province, which mainly comprised carbonate rock, mudstone and argillaceous carbonate rock (Fig. 2) (Peng, 2009; Liang et al., 2015). The Middle-Upper Cambrian lithological unit of Yongshun Section comprises Aoxi Formation, Huaqiao Formation, Chefu Formation, Bitiao Formation and Zhuitun Formation in western Hunan Province (Fig. 2) (Wang et al., 2011; Liang et al., 2015). Besides, the carbonate sediment Yankong Section (Guizhou) was deposited in the Yangtze Platform (Zuo et al., 2008a, 2008b). The lithological unit consist of

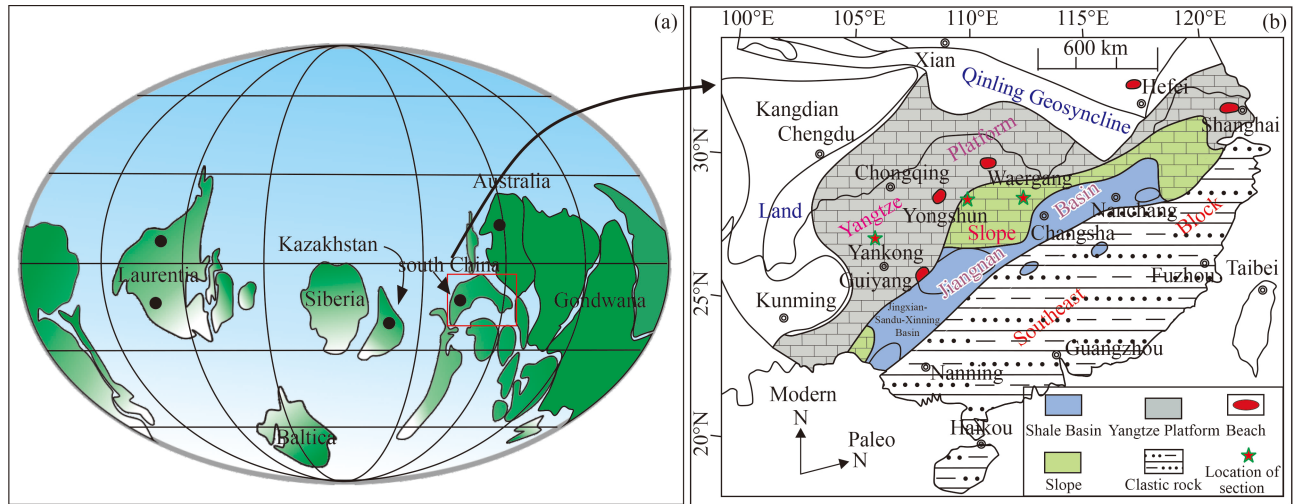


Fig. 1 Paleogeographic map for the Late Cambrian. (a) The global paleogeographic map (Saltzman et al., 2000 and 2004); (b) the lithofacies paleogeography map of the south China (Feng et al., 2001 and 2002).

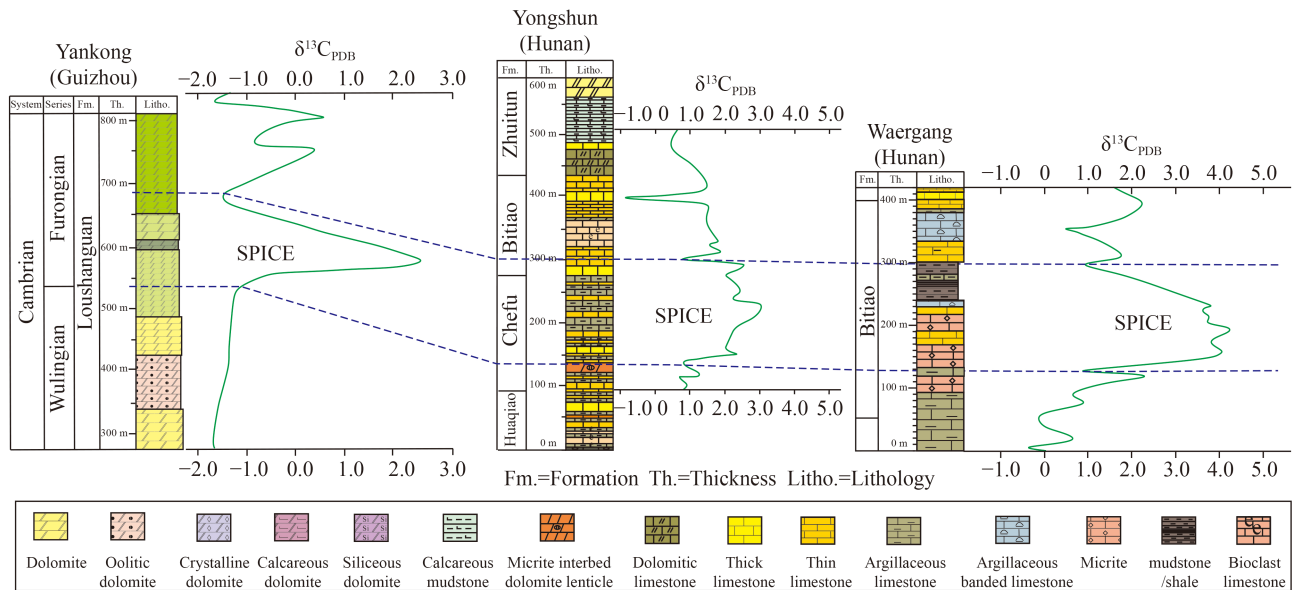


Fig. 2 Stratigraphic correlation and SPICE event of the Yankong Section (data from Zuo et al., 2008a), Yongshun Section (data from Wang et al., 2011) and Waergang Section (data from Peng, 1992) in south China.

Loushanguan Group in the Yankong Section of Guizhou Province (Fig. 2) (Zuo et al., 2008a, 2008b; Liang et al., 2015). Macro fossils are quite rare in the Late Cambrian (Furongian) carbonate in the Yangtze Platform (Zuo et al., 2008a).

The trilobite fauna, which occurred in the slope environment of south-eastern Yangtze Platform during Cambrian, generally contain many global Agnostida trilobites and some Polymerid trilobites that had global ranges (Peng and Robison, 2000; Peng, 2009). The trilobite fauna, which is characterized by the broad distribution in geography, rapid evolution and short stratigraphical age range, contributes to the local and global division of biostratigraphy and chronostratigraphy (Peng, 2009). The Cambrian biostratigraphic succession and

chronostratigraphic system of south China has been summarized by Peng based on the Waergang, Paibi, Yongshun and Luoyixi Sections (Fig. 3) (Peng and Robison, 2000; Peng, 2009).

3 Materials and methods

This study mainly focused on carbonate samples of the Upper Cambrian (Furongian Series) in the Slope, south China, from the Waergang (Fig. 1(b)). Carbon and oxygen isotope data of Yongshun and Yankong Sections were referenced and adopted from the previous results (Zuo et al., 2008a; Wang et al., 2011).

The Waergang Section was sampled (av. 5 m/sample)

System	Global		south China		Lithological unit (Waergang Section)	Lithological unit (Yongshun Section)	Lithological unit (Yankong Section)	Biostratigraphy/Biofossil zone	
Cambrian	Furongian	Stage 10	Furongian	Niucheheian	Shenjiawan Fm.	Zhuitun Fm.	Loushanguan Group	<i>Leioetegium constrictum</i> - <i>Shenjiawania brevis</i>	
		Jiangshanian		Taoyuanian				Bitiao Fm.	<i>Mictosaukia striata</i> - <i>Fatocephalus</i>
		Paibian		Paibian	Bitiao Fm.	Chefu Fm.		<i>Leioagnostus cf. hexelli</i> - <i>Archaeuloma taoyuanense</i>	
	Miaolingian	Guzhangian	Wulingian	Guzhangian	Huaqiao Fm.	Huaqiao Fm.		<i>Lotagnostus americanus</i>	
		Drumian		Wangcunian				Huaqiao Fm.	<i>Probinacmaspis nasalis</i> - <i>Peichianshania humanensis</i>
		Wuliuan		Taijiangian	Aoxi Fm.	Aoxi Fm.		<i>Eolotagnostus decorus</i> - <i>Kaolishaniella</i>	
	Series 2	Stage 4	Qiongdongian	Dunyunian	Qingxudong Fm.	Qingxudong Fm.		<i>Rhaptagnostus citensis</i> - <i>Onchololellus cf. kuruktagensis</i>	
									<i>Agnostotes orientalis</i>
								<i>Agnostus inexpectans</i> - <i>Proceratopyge protracta</i>	
								<i>FAD of Glyptagnostus reticulatus</i>	
								<i>Glyptagnostus stolidotus</i>	
						<i>Linguagnostus reconditus</i>			
						<i>Proagnostus bulbosus</i>			
						<i>Lejopyge laevigata</i>			
						<i>Lejopyge armata</i>			
						<i>Goniagnostus nathorsti</i>			
						<i>Prychagnostus punctuosus</i>			
						<i>Prychagnostus atavus</i>			
						<i>Prychagnostus gibbus</i>			
						<i>Peronopsis taijiangensis</i>			
						<i>Oryctocephalus indicus</i>			
						<i>Ovatoryctocara granulata</i> - <i>Bathynotus holopygus</i>			
						<i>Protoryctocephalus wuxianensis</i>			
						<i>Arthricocephalites taijiangensis</i>			
						<i>Arthricocephalites chauveaui</i>			

Fig. 3 The chronostratigraphy and biostratigraphic system of Middle-Upper Cambrian in south China and global correlation (modified from Peng and Robison, 2000; Qi et al., 2004; Zuo et al., 2008a; Peng, 2009; Liang et al., 2015). Fm. = Formation.

in fresh exposures of Upper Cambrian carbonate rock in the field. Sixty-four large samples (>200 g) were carefully trimmed to remove possible weathered surfaces, post-depositional veins and any visible pyrite nodules or bands, and then cut into small pieces. The freshest pieces were chosen and further crushed to powder (200 mesh) and used for carbon and oxygen isotope, TOC, TC and TS analyses.

Carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotope data of 64 carbonate samples were obtained by using a Finnigan MAT 251 gas source mass spectrometer fitted with an elemental analyzer at the State Key Laboratory of Biogeology and Environmental Geology in China University of Geosciences. The analytic error is less than 0.1‰.

Carbonate associated sulfate (CAS) was extracted using the following method (Gill et al., 2008; Gill et al., 2011a, 2011b). Approximately 3–6 g remaining fine powder from each sample were treated with two deionized water rinses lasting 24 h each. After each rinse, the overlying water was carefully decanted. All samples were then treated with a 4% sodium hypochlorite solution for 48 h to remove any metastable sulfides and organically bound sulfur (for example, ester bound sulfates). Two additional deionized water rinses followed before the samples were dissolved using trace-metal clean 4 N HCl. The resulting sample was then vacuum filtered (45 μm) to remove any insoluble materials. In each case, the insoluble fraction was minor (<0.01 mg), so that concentrations reported for the bulk rocks can be treated as concentrations within the carbonate. We added approximately 25 mL of a saturated BaCl_2 solution (250 g/L) to the remaining solution to precipitate sulfate as BaSO_4 . We let the samples sit for at least 3 days to ensure complete precipitation. The BaSO_4 powders were filtered, dried, and homogenized, and combined with an excess of V_2O_5 and combusted online

for measuring the sulfur isotopic composition of carbonate-associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) then homogenized and loaded into tin capsules with excess V_2O_5 and analyzed for their $^{34}\text{S}/^{32}\text{S}$ isotope ratios at China University of Geosciences using a Thermo Fisher Scientific Delta V Plus isotope ratio mass spectrometer (IRMS) coupled with a Flash elemental analyzer. All sulfur isotope compositions are reported in standard delta notation as per mil (‰) deviations from Vienna Canyon Diablo Troilite (V-CDT) with analytical errors of less than 0.2‰.

The total carbon (TC), total inorganic carbon (TIC) and total sulfur (TS) were obtained at the China University of Geosciences using a Jena multi-EA 4000 carbon-sulfur analyzer through online combustion at 1350°C and acidification with ~30%–40% phosphoric acid, respectively. Analytical errors are better than $\pm 0.2\%$ for TC and TIC based on replicate analyses of Alpha Resources standards AR 4007 and AR 1034. Then total organic carbon (TOC) was calculated by difference between total carbon (TC) and total inorganic carbon (TIC). Total sulfur (TS) was analyzed with the relative standard deviations of 0.15%–3.7% ($n = 3$).

4 Results

4.1 Lithology and sedimentary environment of Waergang Section

The Bitiao Formation of Waergang Section mainly consists of argillaceous limestone, micrite and shale (Fig. 4). The micrite and argillaceous limestone indicate shallow sea and open shelf environment in SPICE rising limb of Waergang Section (Fig. 4). The laminar limestone and argillaceous banded limestone can be interpreted into

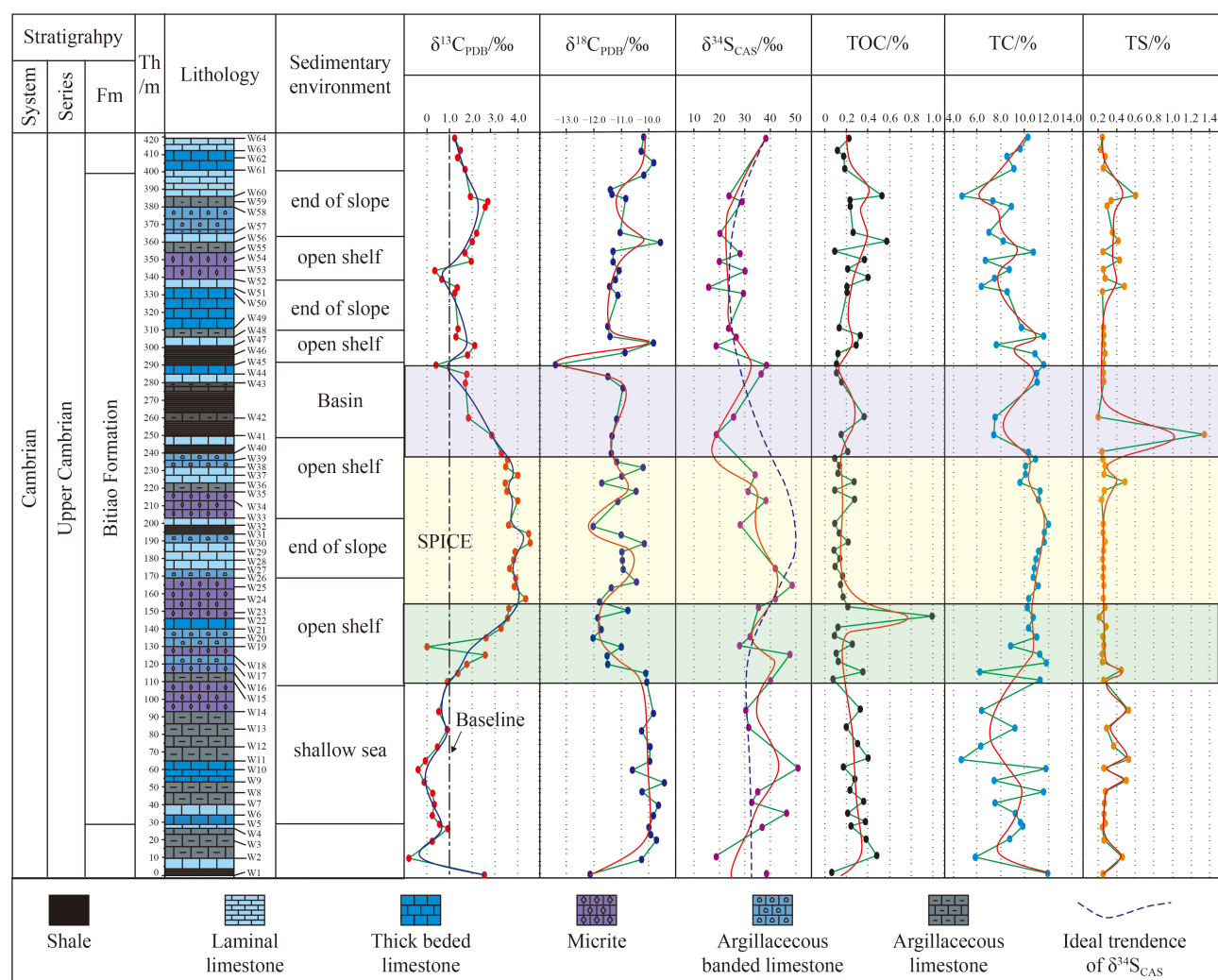


Fig. 4 Geochemical characteristics and sedimentary environment of Waergang section. Color zone showing curve of the different parameters during SPICE event. Blue dashed line indicating the expected response curve of $\delta^{34}\text{S}_{\text{CAS}}$ during SPICE event.

the end of slope in the peak of SPICE section (Fig. 4). The micrite, shale, laminar limestone and some argillaceous limestones suggest the open shelf and basin environment in the descending limb of the SPICE (Fig. 4). The increasing shale indicate that the shelf evolved into the basin environment in the top of SPICE (Fig. 4).

4.2 Carbon isotope and petrology of Waergang Section

The Bitiao Formation calcites at Waergang Section exhibit a total $\delta^{13}\text{C}_{\text{PDB}}$ range from -0.38 to $+4.53$ ‰ with discrete positive anomaly within 180 m thickness (110–290 m), which can be recognized as the carbon isotope excursion (SPICE) (Table 1, Figs. 2 and 4). The SPICE shows maximum $\delta^{13}\text{C}_{\text{PDB}}$ value of 4.53 ‰ with the pre-excursion baseline values of 1 ‰ and excursion amplitude of 3.53 ‰ (Table 1, Fig. 4). The $\delta^{13}\text{C}_{\text{PDB}}$ values of SPICE rising limb vary from baseline values (1 ‰) to peak part (4.34 ‰) over a thickness of about 45 m (110–155 m) (Fig. 4). The $\delta^{13}\text{C}_{\text{PDB}}$ values of SPICE peak part vary

from 3.5 ‰ to 4.53 ‰ with small amplitude variation within 80 m carbonate rock (155–235 m) (Fig. 4). The descending limb of the SPICE displays a more gradual return to baseline $\delta^{13}\text{C}_{\text{PDB}}$ values in the carbonate rocks of 60 m (235–290 m) (Fig. 4).

The strata of pre-SPICE (0–110 m) comprise major argillaceous limestone (~ 45 m) interbedded with thick-layer limestone (10 m and 12 m) and 15 m micrite (Fig. 4). The strata of SPICE rising limb mainly consist of argillaceous banded limestone (interbedded with two layers of micrite) and micrite from bottom to top (Fig. 4). The peak part of the SPICE mainly includes the major laminar limestone, micrite, two thin layers of argillaceous banded limestone and little shale (Fig. 4). The dark shale interbedded with thin-layer limestone mainly constitutes the descending limb strata of the SPICE (Fig. 4).

4.3 Sulfur isotope and total sulfur (TS) of the Waergang section

The sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope values mainly vary from

Table 1 Geochemical data of carbonate rocks in the Waergang section, Hunan Province

Number	Sample No.	Lithology	$\delta^{13}\text{C}_{\text{PDB}}/\text{‰}$	$\delta^{18}\text{O}_{\text{PDB}}/\text{‰}$	$\delta^{34}\text{S}_{\text{CAS}}/(\text{‰ VCDT})$	TOC/wt. %	TC/wt. %	TS/wt. %
1	W-0	Limestone	3.93	−11.54	/			
2	W-1	Limestone	2.55	−12.15	38.7	0.06	11.91	0.25
3	W-2	Limestone	−0.79	−10.29	18.5	0.48	5.82	0.46
4	W-3	Limestone	0.23	−9.68	/	0.39	8.72	0.26
5	W-4	Limestone	0.95	−9.93	37.0	0.24	9.78	0.25
6	W-5	Limestone	0.55	−10	/	0.38	9.65	0.26
7	W-6	Limestone	0.23	−9.83	46.3	0.21	9.24	0.26
8	W-7	Limestone	0.33	−9.65	32.5	0.36	7.48	0.26
9	W-8	Limestone	0.26	−10.25	34.7	0.23	11.61	0.27
10	W-9	Limestone	−0.13	−9.45	/	0.28	7.4	0.50
11	W-10	Limestone	−0.38	−10.61	51.0	0.17	11.69	0.26
12	W-11	Limestone	−0.06	−9.98	/	0.40	4.66	0.52
13	W-12	Limestone	0.47	−9.95	/	0.32	6.24	0.37
14	W-13	Limestone	0.89	−10.28	31.4	0.20	9.21	0.28
15	W-14	Limestone	0.54	−9.85	30.4	0.34	6.37	0.52
16	W-15	Limestone	0.93	−10.08	39.5	0.08	11.28	0.26
17	W-16	Limestone	1.37	−10.11	/	0.35	6.21	0.45
18	W-17	Limestone	1.83	−11.5	/	0.12	11.84	0.24
19	W-18	Limestone	2.57	−11.53	47.7	0.10	11.24	0.24
20	W-19	Limestone	0.01	−11.01	27.7	0.26	8.77	0.26
21	W-20	Limestone	2.6	−12.04	32.0	0.08	11.01	0.25
22	W-21	Limestone	3.26	−11.74	/	0.12	10.32	0.28
23	W-22	Limestone	3.54	−11.87	/	0.99	10.71	0.21
24	W-23	Limestone	3.6	−10.78	35.3	0.21	10.2	0.27
25	W-24	Limestone	4.34	−11.82	41.9	0.17	10.35	0.25
26	W-25	Limestone	3.84	−11.39	48.6	0.15	11.14	0.26
27	W-26	Limestone	3.91	−10.46	/	0.17	10.79	0.26
28	W-27	Limestone	3.64	−10.94	41.9	0.09	10.9	0.26
29	W-28	Limestone	3.81	−10.97	/	0.15	10.94	0.25
30	W-29	Limestone	3.89	−10.99	/	0.08	11.16	0.25
31	W-30	Limestone	4.53	−10.18	/	0.22	11.66	0.26
32	W-31	Limestone	4.48	−11.01	/	0.14	11.67	0.25
33	W-32	Limestone	3.61	−12.04	27.8	0.09	11.93	0.25
34	W-34	Limestone	3.98	−11.14	38.4	0.28	11.17	0.23
35	W-35	Limestone	3.52	−10.47	31.0	0.09	11.32	0.27
36	W-36	Limestone	3.46	−11.73	/	0.28	9.63	0.48
37	W-37	Limestone	3.99	−11	34.1	0.12	10.13	0.26
38	W-38	Limestone	3.45	−10.22	/	0.14	10.11	0.28
39	W-39	Limestone	3.54	−11.19	/	0.09	10.9	0.24
40	W-40	Limestone	3.28	−11.38	/	0.21	10.3	0.23
41	W-41	Limestone	2.79	−11.35	18.2	0.15	7.36	1.34
42	W-42	Limestone	1.84	−11.18	25.4	0.37	7.47	0.20
43	W-43	Limestone	1.7	−10.96	/	0.16	11.06	0.26

(Continued)

Number	Sample No.	Lithology	$\delta^{13}\text{C}_{\text{PDB}}/\text{‰}$	$\delta^{18}\text{O}_{\text{PDB}}/\text{‰}$	$\delta^{34}\text{S}_{\text{CAS}}/(\text{‰ VCDT})$	TOC/wt. %	TC/wt. %	TS/wt. %
44	W-44	Limestone	1.75	-11.51	36.3	0.11	10.95	0.25
45	W-45	Limestone	0.41	-13.44	38.5	0.11	11.64	0.25
46	W-46	Limestone	1.78	-10.88	/	0.12	10.83	0.26
47	W-47	Limestone	2.09	-9.83	18.1	0.29	7.56	0.26
48	W-48	Limestone	1.27	-11.42	26.6	0.33	11.60	0.25
49	W-49	Limestone	1.37	-11.5	23.5	0.13	9.7	0.26
50	W-50	Limestone	1.23	-11.15	29.6	0.21	8.54	0.24
51	W-51	Limestone	1.34	-11.45	15.3	0.21	6.32	0.48
52	W-52	Limestone	0.65	-11.22	/	0.41	7.47	0.27
53	W-53	Limestone	0.35	-11.1	30.4	0.21	8.65	0.25
54	W-54	Limestone	1.96	-11.32	19.8	0.37	6.68	0.43
55	W-55	Limestone	1.67	-11.31	28.0	0.09	10.70	0.24
56	W-56	Limestone	2.02	-9.59	/	0.58	8.20	0.41
57	W-57	Limestone	2.18	-11.06	19.9	0.26	6.94	0.35
58	W-58	Limestone	2.56	-10.84	/	0.24	8.86	0.29
59	W-59	Limestone	2.67	-11.37	29.0	0.24	7.31	0.34
60	W-60	Limestone	1.91	-11.41	23.5	0.54	4.76	0.59
61	W-61	Limestone	1.7	-10.19	/	0.19	9.1	0.25
62	W-62	Limestone	1.36	-9.82	/	0.17	8.48	0.27
63	W-63	Limestone	1.49	-10.29	/	0.12	9.6	0.23
64	W-64	Limestone	1.21	-10.19	38.1	0.22	10.22	0.25

30 ‰ to 50 ‰ with a small amplitude variation in the preceding SPICE (0–110 m) and rising limb of SPICE (110–155 m), but the $\delta^{34}\text{S}_{\text{CAS}}$ values in the onset and rising limb of SPICE are not obviously more than that preceding SPICE (Fig. 4). The $\delta^{34}\text{S}_{\text{CAS}}$ values obviously decrease from 48.6 ‰ (about 160 m) to 18 ‰ (about 240 m) in the peak part of SPICE (Fig. 4). The $\delta^{34}\text{S}_{\text{CAS}}$ values of SPICE peak part are less than that in the pre-SPICE and rising limb of SPICE (Fig. 4). The sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope value just slightly increases with increasing $\delta^{13}\text{C}_{\text{PDB}}$ in rising limb and near peak of SPICE (130–160 m) (Fig. 4). The sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope values gradually decrease from 48.6 ‰ to 18.2 ‰ with stable $\delta^{13}\text{C}_{\text{PDB}}$ values in the peak of SPICE (160–240 m) (Fig. 4). The sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope values gradually increase from 18.2 ‰ to 38.5 ‰ in the descending limb of the SPICE (Fig. 4). Besides, the cross plot of $\delta^{13}\text{C}_{\text{PDB}}$ and $^{34}\text{S}_{\text{CAS}}$ indicates no significant correlation ($R^2 = 0.11$) of carbon and sulfate isotope during SPICE event (Fig. 5(a)). There are just slight positive correlations between Carbon ($\delta^{13}\text{C}_{\text{PDB}}$) and Sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope in the rising limb (Fig. 5(b)) and peak part of SPICE (Fig. 5(c)). However, there is obvious negative correlation between Carbon ($\delta^{13}\text{C}_{\text{PDB}}$) and Sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope in descending limb of SPICE (Fig. 5(d)). The slight sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope excursion was not completely in phase with SPICE (Figs. 4 and 5(a)).

The total sulfur (TS) values mainly range from 0.2% to 0.4% in the Waergang Section (Fig. 4). The total sulfur (TS) values are broadly invariant in the preceding-SPICE, whole SPICE and after-SPICE, but suddenly and abnormally increase in the argillaceous limestone (sample W41) near dark mudstone during descending limb of the SPICE (Fig. 4).

4.4 Oxygen isotope, total carbon (TC) and total organic carbon (TOC) of Waergang Section

The content of total carbon (TC) and the oxygen isotope co-vary with carbon isotope excursion (SPICE) marked in the middle of Bitiao Formation of Wangergang Section (Fig. 4). During the SPICE, the $\delta^{18}\text{O}_{\text{PDB}}$ values ranging from -9.85 ‰ to -13.44 ‰ show a general negative $\delta^{18}\text{O}_{\text{PDB}}$ excursion with several fluctuations, but the total carbon (TC) values varying from 6.21% to 11.93% indicate a positive TC excursion (Fig. 4). The $\delta^{18}\text{O}_{\text{PDB}}$ maintain a steady high value beneath the onset of the SPICE event, but abruptly decrease at the onset of the SPICE (Fig. 4). Besides, the $\delta^{18}\text{O}_{\text{PDB}}$ show negative excursion and low values in the rising limb of SPICE (Fig. 4). The lowest $\delta^{18}\text{O}_{\text{PDB}}$ values and the highest total carbon (TC) values coincide approximately at the peak of the $\delta^{13}\text{C}_{\text{PDB}}$ SPICE (Fig. 4). Total carbon (TC) values at and beneath the onset of the SPICE of SPICE are

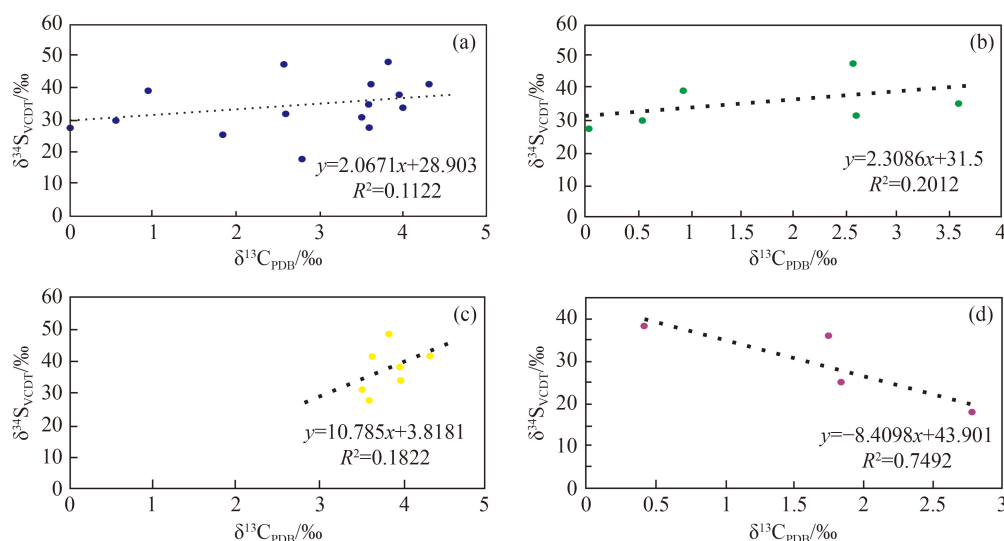


Fig. 5 Cross plot for Carbon and Sulfate isotope during SPICE event in the Waergang Section of south China (Data from Fig. 4 and Table 1). (a) Showing the slight positive correlation between Carbon and Sulfate isotope during the whole SPICE event; (b) showing slight positive correlation between Carbon and Sulfate isotope in the SPICE rising limb; (c) showing slight positive correlation between Carbon and Sulfate isotope in the SPICE peak part; (d) showing obviously negative correlation between Carbon and Sulfate isotope in the SPICE descending limb.

generally lower than that in the rising limb and peak part of SPICE (Fig. 4). The TC values show a general positive excursion coincide with SPICE event (Fig. 4). Besides, the total carbon (TC) shows negative excursion and low values in the descending limb of the SPICE (Fig. 4). Total organic carbon (TOC) is invariant with slight fluctuation beneath SPICE, whole SPICE and upper SPICE (SPICE) (Fig. 4). However, the total organic carbon (TOC) sharply increased to 0.99% and rapidly decreased to the normal value at the rising limb (sample No. w22) of the SPICE (Fig. 4).

5 Discussion

5.1 Evaluation of diagenetic alteration

The diagenetic alteration of marine carbonate generally reduces $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values together and enhances the positive correlation between them (Bathurst, 1975; Knauth and Kennedy, 2009; Derry, 2010; Chen et al., 2014; Peng et al., 2016; Li, 2017). There is only slight correlation between the $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of the Waergang Section (correlation index: 0.15), (Fig. 6(a)). Although many negative $\delta^{18}\text{O}_{\text{PDB}}$ values of the Waergang Section were less than -10‰ (Figs. 4 and 6(a)) suggesting that the carbonate experienced slight diagenetic alteration, the abundant carbon (TC varies 6.21% to 11.93%) might have protected the $\delta^{13}\text{C}_{\text{PDB}}$ values from obvious influence of diagenetic fluids (Figs. 4 and 6(a)). Lithology of Waergang SPICE section mainly consist of micrite and argillaceous limestone (Fig. 4). The argillaceous limestone and micrite were not

susceptible to remineralization by diagenetic fluids because of their extremely low permeability (Poulson and John, 2003; Chen et al., 2014). Therefore, these indicate that the $\delta^{13}\text{C}_{\text{PDB}}$ values of the Waergang Section carbonate, which were slightly altered during diagenesis, may almost represent the original information of seawater during the deposition process (Young et al., 2016). The lithology of the Waergang Section SPICE mainly comprises micrite, argillaceous limestone and mudstone and lacks crystal grain limestone and dolomite (Fig. 4) (Peng, 1990), which indicate limited influence of diagenesis on the carbonate. Therefore, the $\delta^{18}\text{O}_{\text{PDB}}$ values might reflect the main change trend of paleo-seawater to some extent (Elrick et al., 2011). There are many research papers covering the diagenetic effects on $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values in marine carbonates, but few investigations have focused on meteoric influences on $\delta^{34}\text{S}_{\text{CAS}}$ (Gill et al., 2008; Sim et al., 2015). Meteoric diagenesis significantly lowers CAS concentrations but have little to no effect on $\delta^{34}\text{S}_{\text{CAS}}$ values recorded within the strata (Gill et al., 2008; Sim et al., 2015). The absence of $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ correlation of Waergang Section (Fig. 6(b)) suggests that primary marine $\delta^{34}\text{S}_{\text{CAS}}$ values have not been significantly reset during diagenesis.

5.2 Controls on carbon isotope ($\delta^{13}\text{C}_{\text{PDB}}$) excursion during the SPICE event

5.2.1 Sedimentary environment and lithology (regional factor)

The SPICE events of south China mainly occurred in the three typical sections (Figs. 1(b) and 2). Both Waergang

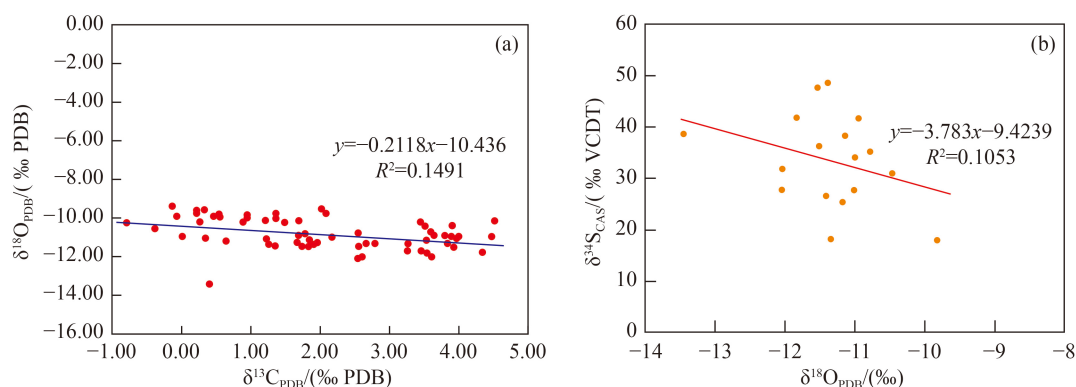


Fig. 6 Plot between the $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of carbonate during the SPICE event. (a) Showing slight correlation between $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values in Waergang Section (Data from Table 1). (b) Showing no significant correlation between $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values in Waergang Section (Data from Table 1).

Section and Yongshun Section were deposited in Jiangnan slope environment but Yankong Section (Guizhou) in the Yangtze Platform (Fig. 1(b)). These indicate that the sedimentary environment and lithology may not be the main reason for the global SPICE event. However, the $\delta^{13}\text{C}_{\text{PDB}}$ excursion amplitude is obviously different in the three sections (Fig. 2). Besides, the global SPICE recorded in the rocks should vary as a function of facies and carbonate platform geometry (Schiffbauer et al., 2017). The water depth of sedimentary environment has an obvious negative correlation with $\delta^{13}\text{C}_{\text{PDB}}$ value of SPICE (Fig. 4). Therefore, the sedimentary facies (Sedimentary environment and lithology) and carbonate platform geometry may influence the $\delta^{13}\text{C}_{\text{PDB}}$ excursion amplitude of SPICE event.

5.2.2 Sea level eustasy (global factor) and carbonate platform weathering (regional factor)

The lithological evidence suggests that sea level fall in the rising limb and peak of SPICE and sea level rise in the descending limb of the SPICE (Fig. 4), which was consistent with the regression and sea level fall in the early Furongian (Wang et al., 2011). The lower TC values of carbonate indicates that lower relative contents of carbonate mineral due to higher contents of argillaceous matter and higher sea level in at and beneath the onset of the SPICE (Fig. 4). The increasing and high TC values supports higher relative contents of carbonate mineral due to lower contents of argillaceous matter and sea level fall in the rising limb of SPICE (Fig. 4). The total carbon (TC) shows negative excursion and low values may be related to the higher content of argillaceous matter and sea level rise in the descending limb of the SPICE (Fig. 4). Besides, the peak of SPICE may coincide with maximum regression (Fig. 4) (Saltzman et al., 2000). Therefore, the general positive excursion of total carbon (TC), which coincide with SPICE, may be related to the sea level eustasy (Fig. 4).

The oxygen isotope of carbonate can nearly reflect the seawater temperature during deposition, because of the slightly diagenetic alteration on the carbon and oxygen isotope values (Fig. 6(a)) (Elrick et al., 2011). Although the limited diagenetic alteration interfered the absolute temperature, the trend of $\delta^{18}\text{O}$ values across the SPICE generally reflects seawater temperature change (Elrick et al., 2011). Besides, the ^{13}C -depleted carbon release operated as positive feedback to temperature (Elrick et al., 2011). The higher $\delta^{18}\text{O}$ values at or beneath the onset of the SPICE suggests seawater cooling and supports earlier hypotheses of upwelling of cool waters and benthic extinction onto the shallow slope at the onset of the SPICE (Fig. 4) (Lochman-Balk, 1970; Stütt, 1975; Taylor, 1977; Palmer, 1984; Saltzman et al., 2000; Elrick et al., 2011), which may be related to a large-scale transgression (Wang et al., 2011).

Negative $\delta^{18}\text{O}_{\text{PDB}}$ excursion in the rising limb of SPICE also suggests that the SPICE event might be related to seawater temperature (Figs. 4 and 5). Descending limb of $\delta^{18}\text{O}$ values suggests seawater warming, which responds to increasing TC values, may be caused by the drop of thermocline due to sea level fall (Saltzman et al., 2000; Wang et al., 2011) (Fig. 4). Yangtze carbonate-platform (Fig. 1(b)), which was susceptible to weathering due to the sea level fall, can result in the positive carbonate isotope excursion (Kump et al., 1999; Kump and Arthur, 1999; Chen et al., 2016). Besides, the facies and carbonate platform geometry, which were mainly controlled by sea level, may influence the $\delta^{13}\text{C}_{\text{PDB}}$ excursion amplitude but not the excursion trend of SPICE event. Therefore, the increasing $\delta^{13}\text{C}_{\text{PDB}}$ of carbonate may be associated with enhanced weathering of carbonate platform (Yangtze Platform) due to regression (sea level fall) in the rising limb and peak of SPICE (Feng et al., 2001, 2002; Peng et al., 2004a, 2004b; Saltzman et al., 2004; Zuo et al., 2008a, 2008b; Wang et al., 2011).

The deeper sea water is generally more ^{13}C -enriched than shallow sea water (Schiffbauer et al., 2017). However, the $\delta^{13}\text{C}$ values of upper SPICE with high sea

level are much less than peak of SPICE, which indicated that transgression was not the critical reason for SPICE. The decreasing carbonate and total carbon (TC), increasing shale deposition, indicate reduced weathering of carbonate platform and enhanced siliciclastic provenance in descending limb of SPICE (Fig. 4). Therefore, the decreasing and low $\delta^{13}\text{C}_{\text{PDB}}$ of upper SPICE limestone may be related to reduce weathering of carbonate platform due to sea level rise and enhanced siliciclastic provenance in the descending limb of the SPICE (Figs. 4 and 7).

5.2.3 Trilobite extinctions, anoxia and organic-matter burial (global factor)

The start of SPICE excursion nearly coincides with a worldwide mass extinction of trilobite species at the base of the *Glyptagnostus Reticulatus* Zone (Palmer, 1965; Öpik, 1966; Saltzman et al., 2000; Ahlberg et al., 2009) (Figs. 3 and 7). The special widespread and rapidly evolving trilobite fauna mainly occurred in the Jiangnan slope environment during the Cambrian (Fig. 3) (Peng, 2009). The abrupted increase and abnormally high value of total organic carbon (TOC), which coincides with the

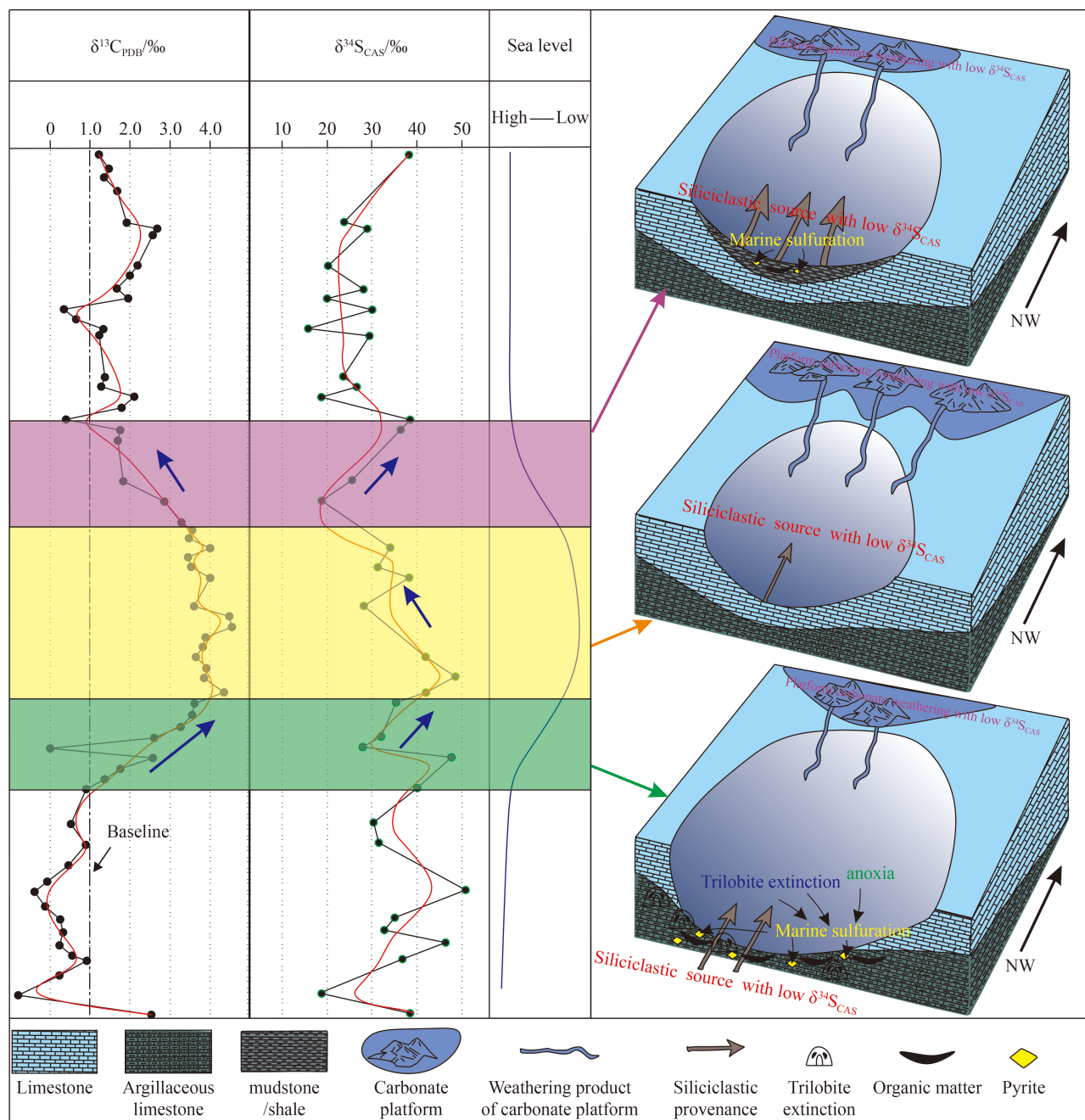


Fig. 7 Conceptual model of Carbon-Sulfate isotope response mechanism during SPICE in the south China.

suddenly remarkable decrease of $\delta^{18}\text{O}$ values at the onset of the SPICE $\delta^{13}\text{C}$ curve (Fig. 4). The mid-depth water transitioned from anoxic condition during Cambrian Age 2 into stable oxic condition during Cambrian Age 4 (Li et al., 2017). These suggest that rapidly enhanced production and mass extinction might have ever existed at the onset or early rising limb of SPICE excursion, and due in part to seawater warming and the drop of thermocline caused by sharp fall of sea level (Saltzman et al., 2000; Wang et al., 2011; Elrick et al., 2011) (Fig. 4). The killing mechanism of extinctions may be attributed to a disruption of food chain that occurred because essential nutrients were depleted by the enhanced production and reduction of dissolved O_2 owing to the seawater warming and sea level fall in the rising limb of SPICE (Paul and Mitchell, 1994; Saltzman et al., 2000; Elrick et al., 2011). Besides, anoxia and organic-matter burial may be caused by reduction in dissolved O_2 and trilobite extinctions due to seawater warming (Arthur et al., 1987; Elrick et al., 2011). Therefore, the increasing $\delta^{13}\text{C}_{\text{PDB}}$ of carbonate may be also related to trilobite extinctions, anoxia and organic-matter burial in the rising limb of SPICE.

5.3 Controls on Sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$) cycling during the SPICE event

The burial of carbon and sulfate as organic matter and pyrite (FeS_2) resulting in the removal of carbon and sulfate from the ocean during SPICE, which generally display the globally parallel excursion behavior between the carbon ($\delta^{13}\text{C}_{\text{PDB}}$) and sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$) during SPICE event (Gill et al., 2011a). The isotopic composition of CAS is an important paleoceanographic proxy, because the primary $\delta^{34}\text{S}$ for carbonates can be strongly preserved during diagenetic alteration (Fig. 6(b)) (Gill et al., 2008). Therefore, the positive excursions of sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$) corresponding to SPICE event may reflect transient increases in the burial of organic carbon and pyrite sulfate in sediment deposited under large-scale anoxic and sulphidic (euxinic) conditions (Saltzman et al., 1998, 2000, 2004; Hurtgen et al., 2009; Gill et al., 2011a; Thompson and Kah, 2012). The $\delta^{34}\text{S}_{\text{CAS}}$ values should have an obvious excursion consistent with the SPICE in the Waergang Section of south China, which can be assumed as the dashed blue line (Fig. 4), although the magnitude of the $\delta^{34}\text{S}_{\text{CAS}}$ excursion of SPICE varies from 0‰ to ~10‰ to 15‰ and even 30‰ (Hurtgen et al., 2002; Gill et al., 2007; Gill et al., 2011a). However, the slight sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) isotope excursion was not in phase with SPICE of Waergang Section in the south China (Figs. 4 and 5).

5.3.1 Sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$) cycling mechanism in the onset and rising limb of SPICE

The $\delta^{13}\text{C}$ positive excursion may be related to trilobite extinctions, anoxia and organic-matter burial in the onset

and rising limb of SPICE. Therefore, the anoxia, abundant sulfate and organic matter provided material basis and environment condition for marine sulfate reduction, which should produce pyrite and result in positive excursion of CAS (Fig. 7) (Johnston et al., 2010; Li et al., 2015). However, the $\delta^{34}\text{S}_{\text{CAS}}$ values in the onset and rising limb of SPICE are similar or just slightly elevated relative to that in preceding SPICE (Figs. 4 and 7).

The major input of sulfur to ocean reservoir from runoff derived from the weathering of continental sulfides and sulfate minerals with sulfur isotope values ($\delta^{34}\text{S}$) between 0 and 10‰ (Holser et al., 1988; Gill et al., 2007). The siliciclastic provenance of clastic rock within Jiangnan Basin and South-east clastic Platform mainly come from the South-eastern Cathaysia (Feng et al., 2001; Feng et al., 2002). The gravity flow deposit was more developed within the slope in the Late rather than Middle Cambrian (Feng et al., 2001). The weathering of continental sulfides and sulfate minerals with low $\delta^{34}\text{S}_{\text{CAS}}$, which mainly derived from weathering product of the Yangtze Platform and south-eastern siliciclastic provenance, was the major input of sulfur to ocean (Holser et al., 1988; Gill et al., 2007). Therefore, the very slight $\delta^{34}\text{S}_{\text{CAS}}$ excursion (130–160 m) may be related to the enhanced input of terrigenous matter (sulfate) with low $\delta^{34}\text{S}_{\text{CAS}}$ in the rising limb of SPICE due to sea level fall, which could significantly reduce the $\delta^{34}\text{S}_{\text{CAS}}$ excursion (Fig. 4).

5.3.2 Sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$) cycling mechanism during peak period of SPICE

The Sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$) started to slightly decrease in early peak period of SPICE and continue to gradually decrease until the descending period of SPICE, which are obviously less than the rising limb of SPICE (Fig. 4). Marine sulfate reduction, which should produce pyrite and result in positive excursion of CAS, was determined by organic matter supply, sulfate availability and the anoxic condition (Johnston et al., 2010; Li et al., 2015). However, the organic matter supply and the anoxic condition could not meet the requirements for strong marine sulfate reduction in the slope (Waergang Section) during peak period of SPICE, because of maximum regression during the peak of SPICE (Fig. 4) (Saltzman et al., 2000). Besides, the weathering of Yangtze Platform carbonate with low $\delta^{34}\text{S}_{\text{CAS}}$, which probably made a major contribution to the $\delta^{13}\text{C}_{\text{PDB}}$ excursion, reduced the $\delta^{34}\text{S}_{\text{CAS}}$ of slope carbonate (Waergang Section) as the important terrigenous matter (sulfate) near the peak of SPICE due to the low sea level (Fig. 7). Therefore, the decreasing and lowest $\delta^{34}\text{S}_{\text{CAS}}$ value during peak period of SPICE may be locally controlled by the absence of marine sulfate reduction, enhanced weathering of Yangtze platform carbonate and low sea level in the slope of south China (Figs. 1, 4, and 7).

5.3.3 Sulfate isotope ($\delta^{34}\text{S}_{\text{CAS}}$) cycling mechanism in descending limb of SPICE

The $\delta^{34}\text{S}_{\text{CAS}}$ decreased to the lowest value (18.2‰) in the bottom and gradually increase to 38.5‰ in the top of SPICE descending limb (Fig. 4). The sulfate leaving the ocean through marine sulfate reduction are enriched in ^{32}S via isotope fractionations, leaving seawater correspondingly enriched in ^{34}S (Gil et al., 2011a, 2011b). Besides, the dark shale with the slight positive excursion of TOC and TS occurred in the descending limb of the SPICE (Fig. 4). Therefore, the gradual increasing $\delta^{34}\text{S}_{\text{CAS}}$ values may be related to marine sulfate reduction due to sea level rise in the descending limb of the SPICE (Figs. 4 and 7). However, the thickness of limestone gradually increased and shale decreased from bottom to top in the descending limb of SPICE (Fig. 4). Consequently, the lowest $\delta^{34}\text{S}_{\text{CAS}}$ value may be related to the enhanced input of siliciclastic provenance with low $\delta^{34}\text{S}_{\text{CAS}}$ in the bottom of SPICE descending limb (Fig. 4).

6 Conclusions

The SPICE event was well discovered in the Waergang Section of the south China. The $\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{18}\text{O}_{\text{PDB}}$, and $\delta^{34}\text{S}_{\text{CAS}}$ values of the Waergang Section carbonates may have ever been altered by the diagenetic alteration, but they can indicate some original information and paleo-temperature change of seawater during the deposition process.

The weathering rate change of carbonate platform due to sea level eustasy probably made a major contribution to the $\delta^{13}\text{C}_{\text{PDB}}$ excursion during the SPICE. Besides, the trilobite extinctions, anoxia, organic-matter burial and siliciclastic provenance input (mudstone deposition) may also play an important role in the onset and rising limb of SPICE event. Sedimentary facies and carbonate platform geometry may influence the $\delta^{13}\text{C}_{\text{PDB}}$ excursion amplitude of SPICE event.

Very slight positive excursion of $\delta^{34}\text{S}_{\text{CAS}}$ in the rising limb of SPICE may be mainly related to enhance terrigenous matter (sulfate) input with low $\delta^{34}\text{S}_{\text{CAS}}$ due to sea level fall, which mainly derived from weathering product of Yangtze Platform and south-eastern siliciclastic provenance.

The decreasing and lowest $\delta^{34}\text{S}_{\text{CAS}}$ value during peak period of SPICE may be locally controlled by the absence of marine sulfate reduction, enhanced weathering of Yangtze platform carbonate and low sea level in the slope of south China. The gradual increasing $\delta^{34}\text{S}_{\text{CAS}}$ values may be related to marine sulfate reduction due to global sea level rise in the descending limb of the SPICE.

The total sulfate (TS) of argillaceous limestone or mudstone content sharply increased due to the enhanced siliciclastic provenance (sulfate) and sea level rise in the

descending limb of SPICE. The obvious lower $\delta^{34}\text{S}_{\text{CAS}}$ values of the descending limb than rising limb of the SPICE may be associated with enhanced siliciclastic provenance input (mudstone deposition), sea level rise, relatively limited organic matter and marine sulfate reduction in the descending limb of the SPICE.

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