

# Carbon and oxygen isotopic composition of Lower to Middle Cambrian sediments at Taijiang, Guizhou Province, China

QING-JUN GUO\*†, HARALD STRAUSS‡, CONG-QIANG LIU\*, YUAN-LONG ZHAO§,  
DAO-HUI PI\*, PING-QING FU\*, LI-JUN ZHU§ & RUI-DONG YANG§

\*State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,  
Chinese Academy of Sciences, Guiyang 550002, China

‡Geologisch-Paläontologisches Institut, Westfälische Wilhelms-Universität Münster,  
Corrensstrasse 24, 48149 Münster, Germany

§Institute of Resource and Environmental Engineering, Guizhou University of Technology, Guiyang 550002, China

(Received 14 October 2004; accepted 16 June 2005)

**Abstract** – Secular variations in the carbon isotopic composition of organic and carbonate carbon characterize the Lower to Middle Cambrian transition that is exposed on the Yangtze Platform at Taijiang, Guizhou Province, southern China.  $\delta^{13}\text{C}$  values for organic matter range between  $-33.4$  and  $-26.5$ ‰. The carbon isotopic composition for carbonate carbon fluctuates between  $-2.7$  and  $+3.1$ ‰. A progressive decrease in the isotopic difference ( $\Delta\delta$ ) between these two isotope records reflects a decrease in the proportional contribution of bacterial biomass to the total sedimentary organic matter. In general, the observed changes are interpreted to reflect primary depositional values, notably variations in the burial rates of organic matter. These, in turn, are linked to biological changes across the Lower to Middle Cambrian transition. No distinct shift in the carbon isotopic composition marks the proposed Lower–Middle Cambrian boundary.

**Keywords:** Lower–Middle Cambrian, carbon and oxygen isotopic composition, sedimentary organic matter, chemostratigraphic correlation, China.

## 1. Introduction

Secular variations in the carbon isotopic composition of carbonate and organic carbon throughout Earth's history (e.g. Veizer *et al.* 1999; Hayes, Strauss & Kaufman, 1999; Jacobsen & Kaufman, 1999; Montañez *et al.* 2000) represent valuable proxy-signals for tectonic, climatic, biological and environmental changes. They offer a qualitative and quantitative way to constrain the biogeochemical cycling of carbon on Earth. Isotope mass balances show that secular variations reflect temporal changes in the fractional burial of organic carbon (e.g. Hayes, Strauss & Kaufman, 1999). A large number of studies, particularly in terminal Neoproterozoic and Early Cambrian successions, have revealed the great chemostratigraphic potential of detailed carbon isotope records (e.g. Brasier *et al.* 1994; Kaufman & Knoll, 1995; Saltzman, Runnegar & Lohmann, 1998; Brasier & Sukhov, 1998; Montañez *et al.* 2000). Furthermore, substantial changes in the carbon isotopic composition of carbonate rocks and organic matter seem to be associated with major faunal boundaries in the Phanerozoic (e.g. Holser & Magaritz, 1987; Magaritz, 1989; Zachos, Arthur & Dean, 1989). Only a few studies have been published to date on carbon isotopes from the Lower to Middle Cambrian (e.g.

Donnelly, Shergold & Southgate, 1988; Brasier, 1993; Brasier & Sukhov, 1998; Montañez *et al.* 2000).

A succession of largely siliciclastic sediments across the Lower to Middle Cambrian transition at Balang village, Taijiang County, Guizhou Province, southern China (Figs 1, 2), has recently been proposed as a potential global stratotype for this transition (Zhao *et al.* 2001a). Palaeontological research at Balang has been performed by Zhao *et al.* (1992, 1993, 1994, 1996), Zhu & Zhao (1996), Yuan *et al.* (1997), Yuan, Zhao & Guo (1999), Sundberg & McCollum (1997), Sundberg *et al.* (1999) and Zhao *et al.* (2001a,b), including work on trilobites and acritarchs. The first appearance datum (FAD) of *Oryctocephalus indicus* has been proposed to define the base of the Middle Cambrian. Subsequently, this has been discussed by Geyer & Shergold (2000). Rare earth element (REE) patterns and abundances of trace elements were determined for sedimentary rocks from this succession by Zhu & Zhao (1996), Guo, Zhao & Yuan (1999) and Guo *et al.* (2001a,b).

Here, we provide data for organic carbon abundances and isotopic compositions and carbonate carbon and oxygen isotope results for 88 samples from the Balang section at Taijiang County, southern China. For selected samples, elemental abundances of Mn and Sr and Mn/Sr and Ca/Sr ratios are given in order to constrain carbonate diagenesis.

† Author for correspondence: gqjowen@163.com

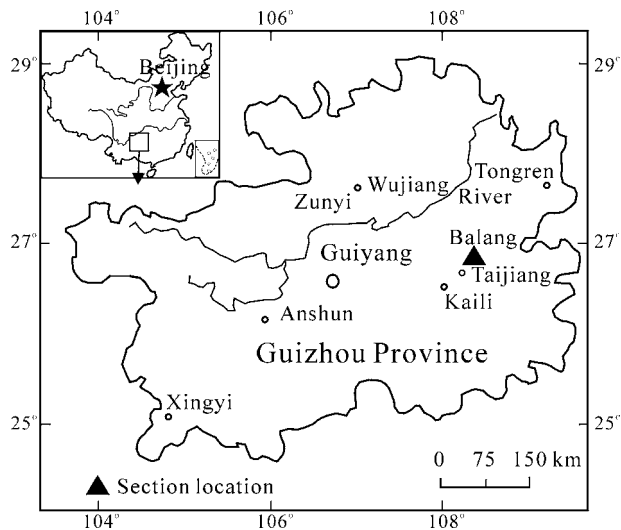


Figure 1. Map showing the location of the Balang section of the Lower–Middle Cambrian at Balang village, Taijiang County, Guizhou Province, southern China.

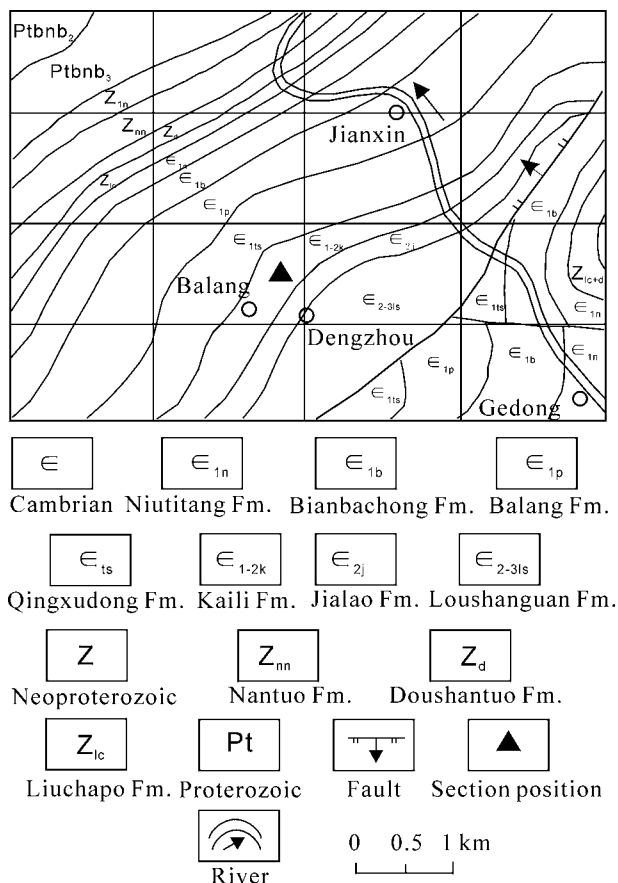


Figure 2. Geological map of Taijiang, Guizhou Province (from Zhao *et al.* 2001a).

## 2. Biostratigraphical control of the Lower–Middle Cambrian boundary

The Kaili Formation at Balang, Taijiang County, encompasses the Lower–Middle Cambrian boundary. The

exposed section has a total thickness of 214.2 m and is divided into 30 strata (GTB1–GTB30). The boundary is tentatively placed between GTB9 and GTB10 (Zhao *et al.* 1993, 1994, 1996; Guo, Zhao & Yuan, 1999; Guo *et al.* 2001a,b), marking the change from the *Bathynotus–Nangaops* ASS. zone to the *Xingrenaspis–Oryctocephalus* zone (Zhao *et al.* 1993, 1996). More precisely, the boundary level is located at the base of bed 15 (at 52.8 m) (Zhao *et al.* 2001a,b). Beds 15 to 19 contain *Oryctocephalus indicus*, an index fossil whose first appearance datum has been used elsewhere to define the Lower–Middle Cambrian boundary (e.g. Yuan *et al.* 1997; Sundberg & McCollum, 1997). This level also marks the last appearance of *Redlichia*-type trilobites at Taijiang (e.g. Sundberg *et al.* 1999). In addition, this position of the boundary level is further supported by acritarch studies (Yin & Yang, 1999; Moczyłowska, 1999; Geyer & Shergold, 2000; Yang & Yin, 2001).

In summary, the Lower–Middle Cambrian boundary level is exposed within the Kaili Formation at Balang. Sundberg *et al.* (1999) and Zhao *et al.* (2001a,b) consider this succession a potential global stratotype and point (GSSP) for this boundary.

## 3. Samples and analytical methods

Eighty-eight unweathered samples were collected from the Lower–Middle Cambrian boundary section at Balang for geochemical and palaeontological studies. The stratigraphic positions for the samples are provided in Figure 3 and Table 1. Fifty samples are mudstones and 38 samples are carbonates. Recovered palynomorphs are scarce and, in most instances, occur together with abundant finely dispersed organic matter. Prior to geochemical analyses, all samples were chipped and pulverized (200 mesh). Subsequently, they were studied for their carbonate and organic carbon isotopic compositions.

### 3.a. Carbonates

CO<sub>2</sub> was liberated from whole rock samples via phosphorylation (McCrea, 1950; Zhen, Zhen & Mo, 1986) with enriched H<sub>3</sub>PO<sub>4</sub> at 25 °C for 24 hours (limestone), 50 °C for 24 hours (dolomite), 75 °C for 16 hours (dolomite), and 75 °C for 24 hours (mudstone) (Wachter & Hayes, 1985; Zhen, Zhen & Mo, 1986). All carbon and oxygen isotopic compositions were measured in the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, using a Finnigan MAT 252 mass spectrometer. Data are reported in the standard delta notation relative to the PDB Standard.

In order to constrain carbonate diagenesis, samples were further studied for their elemental abundances of Mn, Sr, Ca and Mg (Veizer, 1983; Popp, Anderson & Sandberg, 1986; Kaufman, Jacobsen & Knoll, 1993; Veizer *et al.* 1997, 1999). Samples were weighted and

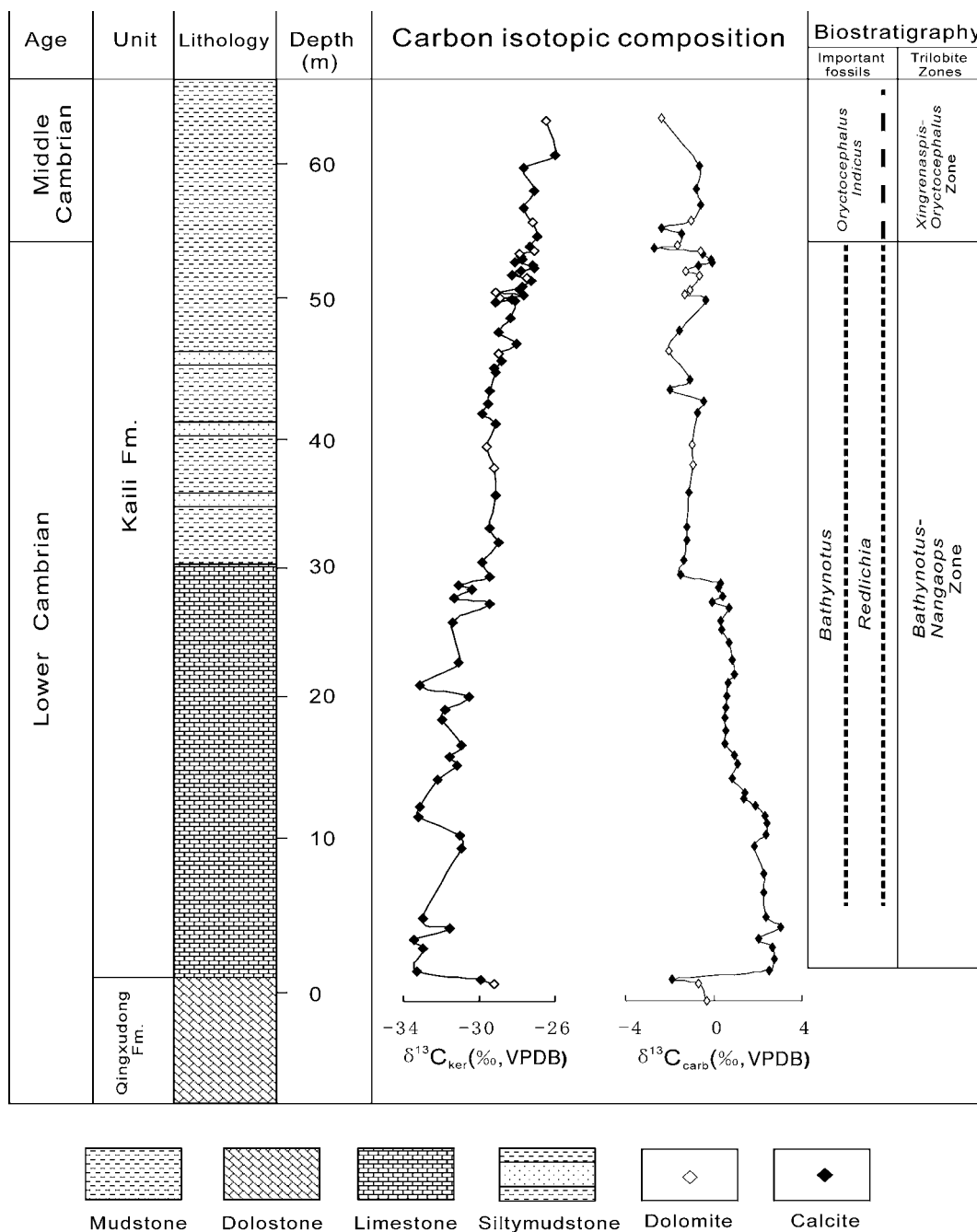


Figure 3. Profiles of  $\delta^{13}C_{ker}$  and  $\delta^{13}C_{carb}$  at the Balang section, Taijiang County, Guizhou Province, southern China.

digested in 3N HCl and elemental concentrations were measured with atomic absorption spectroscopy. Results were corrected for the amount of insoluble residue (soluble (%) = (total weight - weight insoluble residue) / (total weight)).

**3.b. Organic matter**

Total organic carbon (TOC) concentrations were determined gravimetrically, following the removal of carbonate with 15% HCl. Organic carbon isotopic compositions were measured for the kerogen fraction. Kerogen

extraction has been performed according to a procedure modified after Lewan (1986) and Fu & Qin (1995).

Approximately 200–300 ml of HCl (18%) were slowly poured into a 500 ml Teflon-beaker containing 50 g of pulverized rock. The beaker was placed into a water bath (60–70°C) for four hours and the mixture was stirred thoroughly. Following acid digestion, the sample-acid mixture was centrifuged and the HCl carefully decanted. The process was repeated for carbonate samples.

The next step involved 300–400 ml of an HCl (18%)–HF (40%) mixture in order to digest the remaining silicate residue. Again, the mixture was

Table 1. Analytical results for sediments from the Balang section, Taijiang county

Sample Unit name	Lithology	Depth (m)	$\delta^{13}\text{C}_{\text{ker}}$ (‰, PDB)	$\delta^{13}\text{C}_{\text{carb}}$ (‰, PDB)	$\Delta\delta$ (‰, PDB)	$\delta^{18}\text{O}_{\text{carb}}$ (‰, PDB)	TOC (mgC g <sup>-1</sup> )	Insoluble residue (%)	Ca (wt %)	Mg (wt %)	Sr (ppm)	Mn (ppm)	Mn/Sr	Ca/Sr	Mg/Ca		
1	Qingxudong Fm.	Dolostone	0.0		-0.3		-6.1	3.77		0.2	21.78	4.98	169	446	2.6	1285	0.23
2	Qingxudong Fm.	Dolostone	1.3	-29.2	-0.7	28.5	-6.2	0.71		3.0	23.13	5.75	113	402	3.6	2044	0.25
3	Kaili Fm.	Limestone	1.6	-29.9	-1.9	28.0	-6.5	1.33		5.0	38.91	0.61	189	232	1.2	2058	0.02
4	Kaili Fm.	Limestone	2.2	-33.3	2.5	35.8	-6.9	4.29		18.0	39.61	0.55	547	495	0.9	725	0.01
5	Kaili Fm.	Limestone	3.1		2.7		-6.8	2.01		26.5	34.46	0.64	518	1063	2.1	666	0.02
6	Kaili Fm.	Limestone	3.9	-33.0	2.7	35.7	-6.6	4.22									
7	Kaili Fm.	Limestone	4.6	-33.4	2.0	35.5	-7.2	6.06		36.0	40.33	0.71	410	989	2.4	985	0.02
8	Kaili Fm.	Limestone	5.4	-31.6	3.1	34.7	-6.9	4.00									
9	Kaili Fm.	Limestone	6.1	-33.0	2.4	35.3	-7.5	4.10		44.8	40.30	0.94	475	849	1.8	849	0.02
10	Kaili Fm.	Muddy limestone	8.0		2.3		-7.5	4.61									
11	Kaili Fm.	Silty limestone	9.3		2.3		-7.5	9.37		34.0	38.84	0.77	461	710	1.5	842	0.02
12	Kaili Fm.	Limestone	11.3	-31.0	1.9	32.8	-6.1	2.65		12.0	37.42	0.44	544	477	0.9	688	0.01
13	Kaili Fm.	Muddy limestone	12.2	-31.0	2.4	33.4	-7.6	4.77									
14	Kaili Fm.	Muddy limestone	13.0		2.4		-7.8	3.03									
15	Kaili Fm.	Limestone	13.6	-33.2	2.3	35.6	-7.6	8.10		20.0	38.68	1.47	740	596	0.8	523	0.04
16	Kaili Fm.	Muddy limestone	14.3	-33.2	1.9	35.1	-7.7	5.25									
17	Kaili Fm.	Muddy limestone	14.8		1.4		-8.3	3.53		37.0	38.24	1.17	577	831	1.4	663	0.03
18	Kaili Fm.	Muddy limestone	15.3		1.4		-8.2	1.32									
19	Kaili Fm.	Muddy limestone	16.3	-32.2	0.9	33.1	-8.4	6.03		36.0	40.58	0.86	462	928	2.0	878	0.02
20	Kaili Fm.	Muddy limestone	17.4	-31.2	1.1	32.2	-8.3	0.92									
21	Kaili Fm.	Muddy limestone	18.1	-31.6	0.9	32.5	-8.0	4.22									
22	Kaili Fm.	Silty limestone	18.9	-30.9	0.5	31.4	-8.4	3.41									
23	Kaili Fm.	Silty limestone	19.8		0.6		-7.8	0.01		37.5	37.82	0.86	433	888	2.0	874	0.02
24	Kaili Fm.	Silty limestone	20.8	-31.9	0.5	32.5	-8.4	2.42									
25	Kaili Fm.	Silty limestone	21.5	-31.8	0.6	32.4	-8.7	5.42									
26	Kaili Fm.	Silty limestone	22.4	-30.6	0.6	31.2	-8.2	4.91		50.0	40.28	1.04	406	922	2.3	992	0.03
27	Kaili Fm.	Silty limestone	23.3	-33.2	0.6	33.8	-8.4	2.55									
28	Kaili Fm.	Silty limestone	24.0		0.9		-8.6	2.51									
29	Kaili Fm.	Silty limestone	25.0	-31.1	0.8	32.0	-8.6	2.55									
30	Kaili Fm.	Silty limestone	26.3		0.7		-8.1	0.06									
31	Kaili Fm.	Silty limestone	27.2		0.4		-7.8	0.53									
32	Kaili Fm.	Silty limestone	27.9	-31.4	0.3	31.7	-7.8	1.62									
33	Kaili Fm.	Silty limestone	28.8		0.7		-8.2	0.02									
34	Kaili Fm.	Silty limestone	29.3	-29.4	-0.1	29.3	-8.1	3.37		62.0	27.06	2.02	551	1447	2.6	491	0.07
35	Kaili Fm.	Silty limestone	29.7	-31.3	0.4	31.7	-8.3	1.89		43.0	39.76	1.02	475	1110	2.3	838	0.03
36	Kaili Fm.	Muddy limestone	30.3	-30.4	0.2	30.6	-8.6	3.29		52.0	29.80	1.48	416	1229	3.0	717	0.05
37	Kaili Fm.	Silty limestone	30.6	-31.1	0.3	31.4	-7.9	0.09									
38	Kaili Fm.	Mudstone	31.3	-29.5	-1.5	28.0	-8.9	1.74		43.0	6.70	1.80	158	1000	6.3	426	0.27
39	Kaili Fm.	Mudstone	32.3	-29.9	-1.3	28.5	-8.7	4.28									
40	Kaili Fm.	Mudstone	33.8	-29.0	-1.2	27.8	-8.6	3.32									
41	Kaili Fm.	Mudstone	34.8	-29.4	-1.2	28.2	-8.3	3.71		81.0	17.57	5.07	267	3372	12.6	658	0.29
42	Kaili Fm.	Mudstone	37.3	-29.1	-1.1	28.0	-8.7	2.95									
43	Kaili Fm.	Mudstone	39.3	-29.2	-0.9	28.3	-8.8	3.48		85.0	4.21	6.95	532	4600	8.6	79	1.65
44	Kaili Fm.	Mudstone	40.8	-29.6	-1.0	28.6	-8.4	3.35		81.7	9.51	6.71	545	3497	6.4	174	0.71
45	Kaili Fm.	Mudstone	41.8					1.78									
46	Kaili Fm.	Mudstone	42.5					1.52									
47	Kaili Fm.	Mudstone	43.2	-29.9	-0.7	29.1	-9.2	1.60		81.1	16.64	5.987	403	2314	5.7	413	0.36
48	Kaili Fm.	Mudstone	44.0	-29.5	-0.4	29.1	-9.2	2.19									

49	Kaili Fm.	Mudstone	44.9	-29.4	-2.0	27.4	-9.6	2.26									
50	Kaili Fm.	Mudstone	45.6		-1.1		-9.0	1.29	79.8	15.69	5.624	251	2317	9.2	626	0.36	
51	Kaili Fm.	Mudstone	46.3	-29.1				4.63									
52	Kaili Fm.	Mudstone	46.6					1.61									
53	Kaili Fm.	Mudstone	47.1					1.75									
54	Kaili Fm.	Mudstone	47.7	-29.0	-2.0	26.9	-8.3	1.82	83.3	9.508	6.938	406	1970	4.9	234	0.73	
55	Kaili Fm.	Mudstone	48.4					1.58									
56	Kaili Fm.	Mudstone	49.2	-29.0	-1.5	27.4	-8.6	1.78									
57	Kaili Fm.	Mudstone	50.3	-28.4				0.02									
58	Kaili Fm.	Mudstone	51.5	-28.1				2.98									
59	Kaili Fm.	Mudstone	51.4	-29.2	-0.3	28.8	-9.3	3.78	79.0	12.05	4.07	569	2613	4.6	212	0.34	
60	Kaili Fm.	Mudstone	51.6	-28.3				2.63									
61	Kaili Fm.	Mudstone	51.8	-28.9	-1.3	27.6	-7.1	2.92	75.0	8.30	4.86	519	1800	3.5	160	0.59	
62	Kaili Fm.	Mudstone	52.0	-27.6				2.50									
63	Kaili Fm.	Mudstone	52.2	-29.2	-1.1	28.1	-7.5	4.62	80.0	8.70	5.84	549	2400	4.4	159	0.67	
64	Kaili Fm.	Mudstone	52.4	-27.9				2.93									
65	Kaili Fm.	Mudstone	52.6	-27.8				3.02									
66	Kaili Fm.	Mudstone	52.8					3.21									
67	Kaili Fm.	Mudstone	53.0	-27.2				0.02									
68	Kaili Fm.	Mudstone	53.2	-27.5	-0.6	26.9	-9.2	1.27	83.2	9.47	5.45	534	3214	6.0	177	0.58	
69	Kaili Fm.	Mudstone	53.4	-28.3				0.02									
70	Kaili Fm.	Mudstone	53.6	-27.9	-1.3	26.6	-8.4	3.29	83.1	6.51	6.94	649	1834	2.8	100	1.07	
71	Kaili Fm.	Mudstone	53.8	-27.8				2.47									
72	Kaili Fm.	Mudstone	54.0	-27.1	-0.7	26.4	-8.1	2.79	81.5	7.75	1.26	137	2111	15.4	566	0.16	
73	Kaili Fm.	Mudstone	54.2	-27.1	-0.1	27.1	-9.9	2.79									
74	Kaili Fm.	Mudstone	54.4	-28.1	-0.1	28.0	-9.4	2.69	72.0	20.29	0.73	242	2344	3.9	840	0.04	
75	Kaili Fm.	Mudstone	54.6	-27.7				3.40									
76	Kaili Fm.	Mudstone	54.8	-27.8	-0.5	27.3	-9.4	0.04									
77	Kaili Fm.	Mudstone	55.0	-27.9	-0.6	27.3	-9.1	2.72	82.0	9.71	7.02	554	2500	4.5	175	0.72	
78	Kaili Fm.	Mudstone	55.2	-27.1	-2.7	24.4	-8.4	0.02									
79	Kaili Fm.	Mudstone	55.5	-27.3	-1.6	25.7	-8.4	4.60	82.0	6.08	7.05	443	2111	4.8	137	1.16	
80	Kaili Fm.	Mudstone	56.3	-26.9	-1.5	25.5	-8.9	2.70									
81	Kaili Fm.	Mudstone	56.7		-2.4		-8.9	0.94									
82	Kaili Fm.	Mudstone	57.3	-27.2	-1.0	26.2	-9.1	1.07	82.5	10.88	6.127	242	2590	10.7	450	0.56	
83	Kaili Fm.	Mudstone	58.4	-27.6	-0.6	27.0	-8.8	0.94									
84	Kaili Fm.	Mudstone	59.6	-27.1	-0.8	26.3	-9.1	0.52	79.9	17.36	5.475	210	2679	12.7	826	0.32	
85	Kaili Fm.	Mudstone	61.3	-27.7	-0.6	27.0	-9.1	0.82	79.7	18.69	5.027	167	2701	16.2	1119	0.27	
86	Kaili Fm.	Mudstone	62.3					0.71									
87	Kaili Fm.	Mudstone	63.3					0.72									
88	Kaili Fm.	Mudstone	64.8	-26.5	-2.4	24.1	-8.9	0.88	83.6	6.803	7.526	310	2336	7.5	220	1.11	



thoroughly stirred and placed into a warm water bath (60–70 °C) for four hours. Subsequently, the mixture was centrifuged and the process was repeated. Finally, the solution was carefully washed and neutralized to pH 7.

Additional steps involved addition of zinc powder and HCl (18 %) in order to remove pyrite, and heavy liquid in order to separate heavy minerals. The final residue is considered to be kerogen and was dried in a vacuum oven at 60–70 °C for 24 hours.

Organic carbon isotopic compositions ( $\delta^{13}\text{C}_{\text{ker}}$ ) were measured at the Geologisch-Paläontologisches Institut, Westfälische Wilhelms-Universität Münster, Germany, and at the Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, using a Finnigan Delta Plus mass spectrometer, equipped with an elemental analyser. The data are reported in the standard delta notation relative to the PDB standard.

#### 4. Results

The total organic carbon content (TOC) ranges from < 0.1 to 9.4 mg g<sup>-1</sup>. The organic carbon isotopic composition for kerogen samples ( $\delta^{13}\text{C}_{\text{ker}}$ ) displays values between -33.4 and -26.5 ‰, averaging  $-29.5 \pm 1.9$  ‰ (n = 66). Whole-rock  $\delta^{13}\text{C}_{\text{carb}}$  values lie between -2.7 and +3.1 ‰, averaging  $0.1 \pm 1.5$  ‰ (n = 69), and respective  $\delta^{18}\text{O}_{\text{carb}}$  values range from -9.9 to -6.1 ‰, averaging  $-8.2 \pm 0.9$  ‰ (n = 69). The difference between the organic and carbonate carbon isotopic compositions ( $\Delta\delta = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{ker}}$ ) varies between 24.1 and 35.8 ‰, averaging  $29.7 \pm 3.2$  ‰ (n = 55). Despite some variability, a slight decrease in  $\Delta\delta$  up-section can be observed. Elemental abundances of Mn and Sr are highly variable (Mn: 232–4600 ppm; Sr: 113–740 ppm). The lithological change from carbonate to mudstone at c. 30 m is accompanied by a distinct change in elemental abundances and ratios. For example, Mn/Sr ratios are around 2 for the carbonates in the first 30 m of section and higher in the mudstones. Mg/Ca ratios are consistently low in the lower 30 m and increase thereafter. Analytical results are given in Table 1.

#### 5. Preservation of organic matter

In order to utilize the organic carbon isotopic composition of sedimentary organic matter as a proxy-signal for temporal variations in the global carbon cycle, it is crucial to evaluate the preservation of the organic matter. Major processes with the potential of altering the primary isotopic composition of sedimentary organic matter include biological reworking during diagenesis and post-depositional thermal alteration.

Biological reworking of sedimentary organic matter occurs through a sequence of redox-reactions involving aerobic respiration, nitrate, iron and sulphate reduction as well as methanogenesis. Such reactions generally transfer organic into inorganic carbon (such as carbon

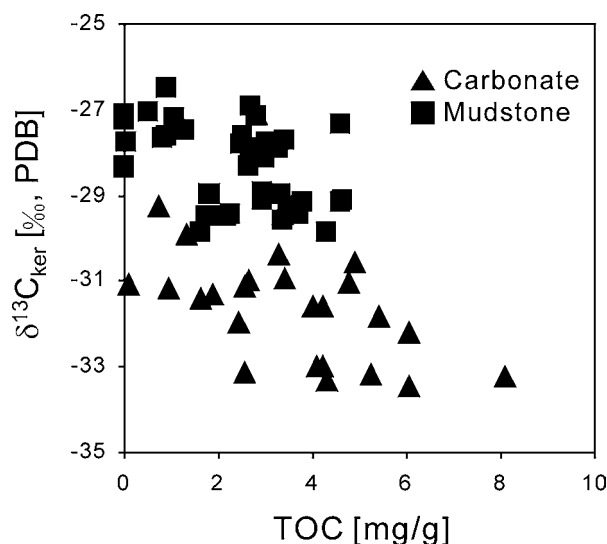


Figure 4. Cross-plot of TOC and  $\delta^{13}\text{C}_{\text{ker}}$ .

dioxide or bicarbonate) which is frequently incorporated into diagenetic carbonates (e.g. Irwin, Curtis & Coleman, 1977). Due to the <sup>13</sup>C-depleted nature of organic carbon, resulting diagenetic carbonates display a shift towards more negative carbon isotope values in comparison to open marine precipitates.

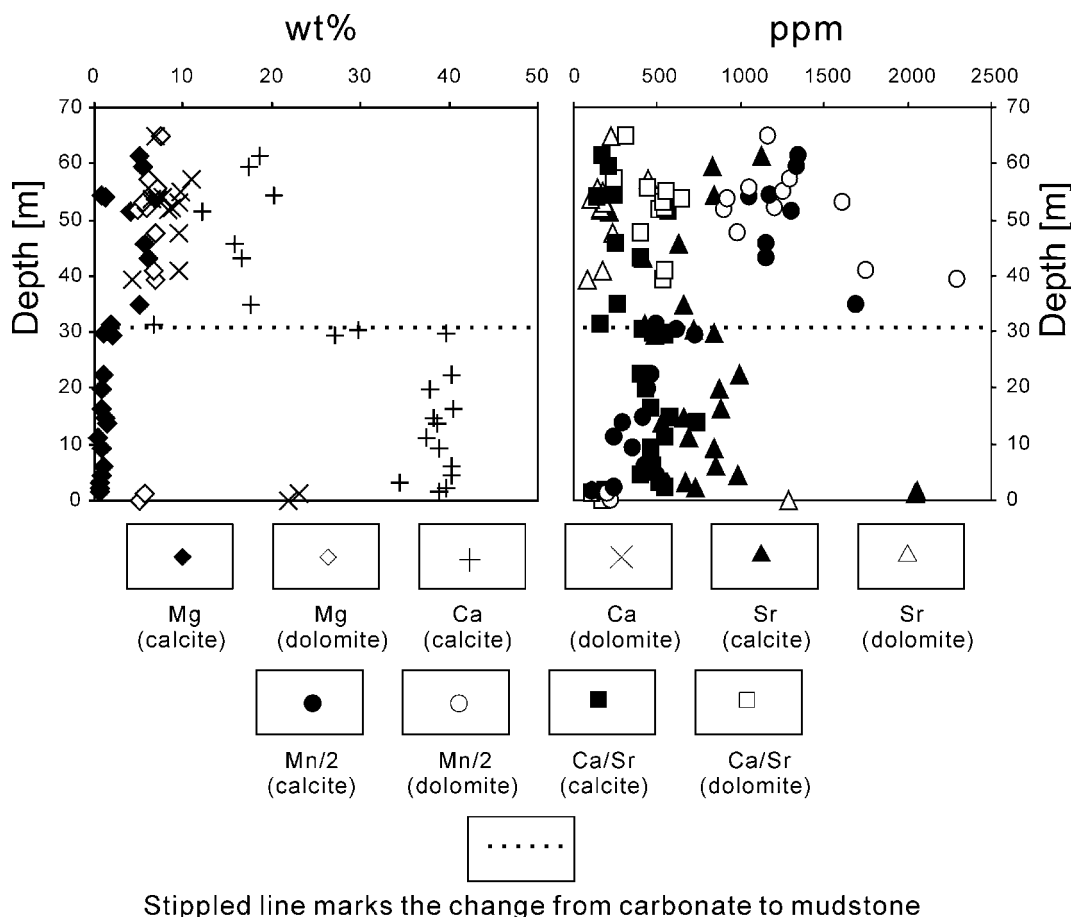
Post-depositional thermal alteration during metamorphism changes not only the structure and chemical composition of sedimentary organic matter but will ultimately result in the loss of (<sup>13</sup>C-depleted) organic compounds, shifting the  $\delta^{13}\text{C}$  of the residual sedimentary organic matter to more positive values (Strauss *et al.* 1992). However, a cross-plot of organic carbon abundance versus isotopic composition for studied samples (Fig. 4) reveals no significant correlation.

A direct indicator for thermal alteration is a colour change in the sedimentary organic matter. Thereby, variations from clear to yellow to light brown to dark brown to black reflect increasing temperatures. This can be quantified through a thermal alteration index (TAI; e.g. Hayes, Kaplan & Wedeking, 1983). Acritarchs from the succession at Balang were studied by Yang & Yin (2001). The colour of the acritarchs is light yellow, which corresponds to a TAI value of 1. This suggests that the organic matter has been exposed only to low temperatures.

In summary, there is no evidence that  $\delta^{13}\text{C}_{\text{ker}}$  values have experienced a substantial shift from their primary values as a consequence of post-depositional, particularly thermal alteration of the sedimentary organic matter.

#### 6. Discussion: organic carbon

Total organic carbon contents vary around an average value of  $2.6 \pm 1.8$  mg g<sup>-1</sup> (n = 88). Despite a change in lithology from carbonates in the lower part of the



Stippled line marks the change from carbonate to mudstone

Figure 5. Elemental abundances and ratios v. depth.

succession to mudstones, no clear difference in TOC is discernible between these lithologies.

Organic carbon isotope values for the entire Lower to Middle Cambrian section at Balang vary between  $-33.4$  and  $-26.5$ ‰. This range in  $\delta^{13}\text{C}$  is quite comparable to values from other Early and Middle Cambrian successions (e.g. Hayes, Strauss & Kaufman, 1999).

The distribution of  $\delta^{13}\text{C}$  (Fig. 3) reveals distinct changes in the organic carbon isotopic composition up-section. A few  $\delta^{13}\text{C}$  values at the base (Qingxudong Formation) of the section decrease from  $-29.0$  to  $-33.4$ ‰, followed by a clear increase in  $^{13}\text{C}$  to values around  $-26.5$ ‰ within the Kaili Formation and across the Lower to Middle Cambrian boundary. A distinct shift in  $\delta^{13}\text{C}_{\text{ker}}$  is visible across the lithological change within the Kaili Formation at 31 m. Despite the lack of a significant difference in preservation, the shift in  $\delta^{13}\text{C}_{\text{ker}}$  at 31 m could still be related in part to the change in lithology. No significant shift in  $\delta^{13}\text{C}_{\text{ker}}$  occurs at the proposed Lower–Middle Cambrian boundary which is situated in mudstones.

## 7. Carbonate diagenesis

Several proxy signals, sensitive to carbonate diagenesis, have been developed as quality criteria in

assessing the degree of post-depositional alteration (e.g. Kaufman, Jacobsen & Knoll, 1993; Kaufman & Knoll, 1995; Jacobsen & Kaufman, 1999). Commonly, Mn/Sr ratios  $< 2$  and  $\delta^{18}\text{O}$  more positive than  $-10$ ‰ are viewed as reflecting a moderate degree of diagenetic alteration (Kaufman & Knoll, 1995), leaving the carbonates still suitable for an interpretation of their carbonate carbon isotopic compositions.

Elemental abundances and selected elemental ratios clearly indicate a correlation with lithology (Fig. 5). Carbonates in the lower part of the succession (below 30 m) display higher abundances of Ca and higher Ca/Sr ratios than in the overlying mudstones. The opposite is true for Mg with lower abundances in the carbonates and higher ones in the mudstones. The Mg/Ca ratio increases clearly in the mudstones. Similarly, Mn abundances show a distinct increase in the mudstones. Associated stratigraphic variations likely reflect a combination of primary differences in elemental abundances due to differences in lithology, which were further enhanced during diagenesis.

Interestingly, the oxygen isotopic composition does not reflect as clearly a systematic shift when the lithology changes (from carbonate to mudstone at 30 m). In fact, all  $\delta^{18}\text{O}$  values are more positive than  $-10$ ‰ (Fig. 6). No correlation exists between  $\delta^{18}\text{O}$  and

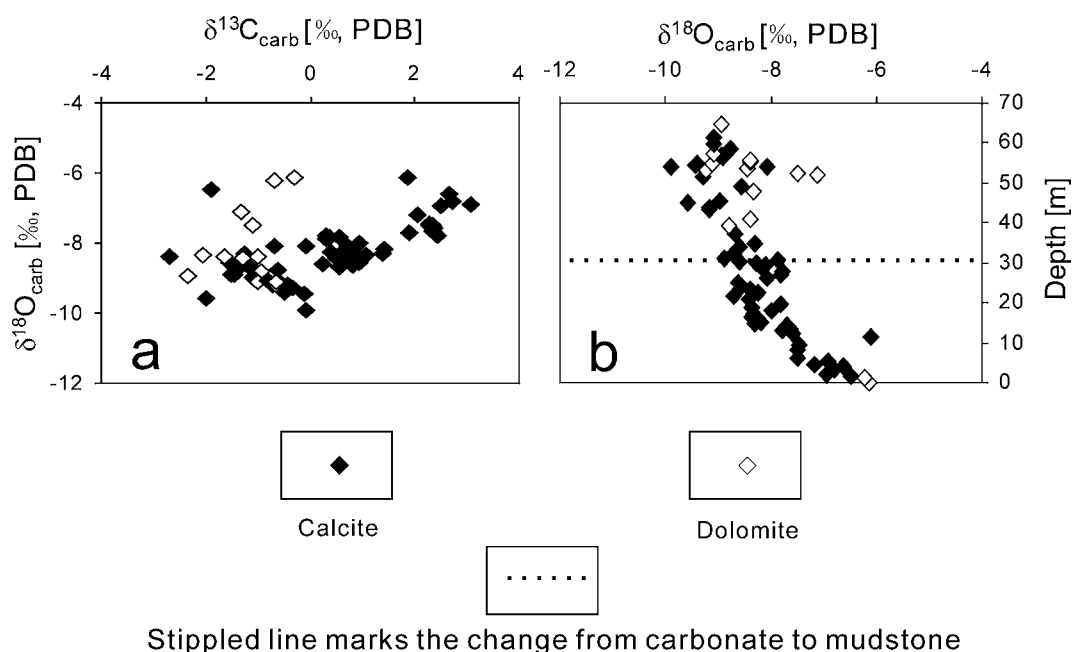


Figure 6. Cross-plot of (a)  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  and (b)  $\delta^{18}\text{O}_{\text{carb}}$  v. depth.

Mg/Ca. Still, mudstones tend to be more depleted in  $^{18}\text{O}$ , displaying  $\delta^{18}\text{O}$  values between  $-10$  and  $-8.5\text{‰}$ . In addition, the absence of a clear correlation between the carbonate carbon and oxygen isotopic compositions (Fig. 6) suggests minor diagenetic post-depositional alteration of the isotope signals.

The carbonate carbon isotopic composition displays a distinct shift in  $\delta^{13}\text{C}$  of almost  $2\text{‰}$  from values between  $0$  and  $+3\text{‰}$  in the lower part of the Kaili Formation (excluding the values from the underlying Qingxudong Formation) to values between  $-2$  and  $0\text{‰}$  in the upper part of this unit (Fig. 3). Figure 7 with  $\delta^{13}\text{C}_{\text{carb}}$  plotted against TOC/%soluble shows that the different natures of these two carbonate types suggest that they will have had different diagenetic evolutions and the lower carbonate-rich part would be more strongly buffered against isotopic alteration than the upper part; in any case, the lower values in the upper section are probably due to diagenetic alteration. The absence of a clear correlation, however, exists between  $\delta^{13}\text{C}_{\text{carb}}$  and the ratio of %soluble/TOC abundances (Fig. 7), excluding intense microbial reworking of sedimentary organic material during diagenesis as the dominant cause for this stratigraphic variation in  $\delta^{13}\text{C}$ .

While we acknowledge some degree of diagenetic alteration as shown by selected elemental abundances and/or ratios, the absence of a clear correlation between the carbon isotopic composition and the abundance of organic carbon, the absence of a distinct correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  and the absence of a clear stratigraphic variation in  $\delta^{18}\text{O}$  as a consequence of either the lithological change and/or diagenesis suggest that the carbonate carbon isotopic composition has not been altered substantially during post-depositional

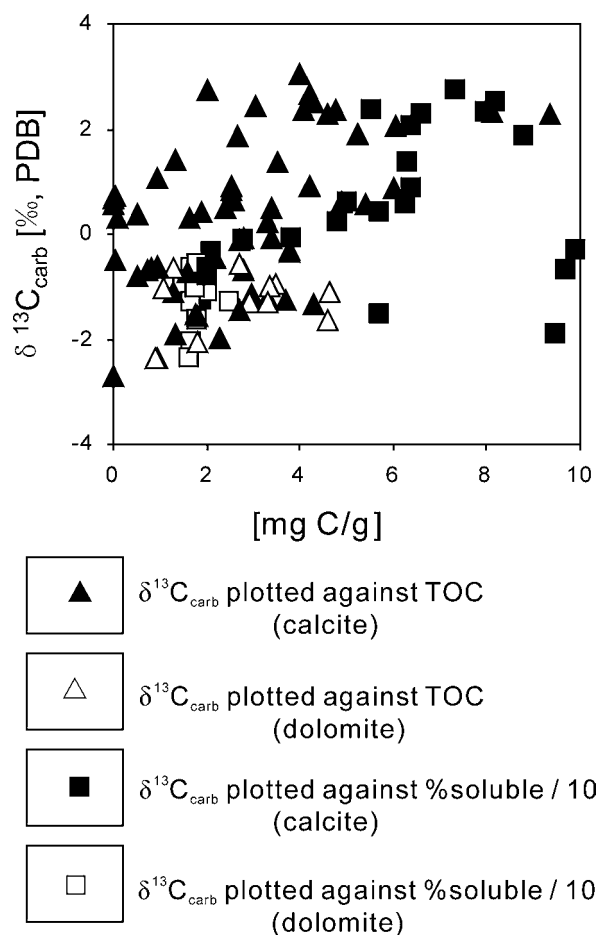


Figure 7. Cross-plot of TOC/% soluble and  $\delta^{13}\text{C}_{\text{carb}}$ .

alteration. As a consequence, the carbonate carbon isotopic composition will be interpreted further with respect to any possible primary variations.



## 8. Discussion: carbonate carbon

The carbonate carbon isotopic composition displays a decreasing trend in  $\delta^{13}\text{C}$  clear variation up-section. With the exception of a few negative values in the Qingxudong Formation, carbonates in the lower part of the Kaili Formation followed by mudstones in the upper part of the Kaili Formation up to the lower Middle Cambrian boundary record a continuous, yet stepwise decrease in the carbonate carbon isotopic composition from  $\delta^{13}\text{C}$  values around +2‰ to values around -2.5‰ (Fig. 3). Such negative values continue across the Lower–Middle Cambrian boundary with no significant carbon isotope excursion marking the proposed boundary level at 52.8 m. This tendency is towards more negative  $\delta^{13}\text{C}$  values.

Interestingly, the carbon isotopic difference between carbonate and organic carbon ( $\Delta\delta$ ) decreases continuously up-section, from values as large as 36‰ to a value of 24‰. Comparable large-scale secular variations in  $\Delta\delta$  have been reported for parts of the Neoproterozoic and the Oligocene to Recent (Hayes, Strauss & Kaufman, 1999). In the absence of any clear evidence for significant thermal alteration and/or diagenetic alteration as the obvious cause for this evolution, we regard this as an original feature. Explanations which have been suggested for the Neoproterozoic and the Late Cenozoic records of  $\Delta\delta$  include large inputs of bacterial biomass into the sediment (high  $\Delta\delta$ ) and small carbon isotopic fractionations during photosynthetic carbon fixation (low  $\Delta\delta$ ) as a consequence of lower atmospheric carbon dioxide abundance. Model calculations generally suggest a high  $p\text{CO}_2$  for the Early Palaeozoic (e.g. Berner & Kothavala, 2001). Hence, we envision that a decrease in the contribution of bacterial biomass to the total sedimentary organic matter is the primary cause for the observed decrease in  $\Delta\delta$  up-section.

The variation in  $\delta^{13}\text{C}_{\text{carb}}$  measured for the Taijiang section is correlated with data of the first carbonate carbon isotope excursion across the Lower–Middle Cambrian interval at the Wangcun section, western Hunan (Zhu *et al.* 2004).

Hence, our results allow chemostratigraphic correlation for this time interval across the Yangtze Platform.

## 9. Conclusions

A sedimentary succession across the Lower–Middle Cambrian transition at Balang village, Taijiang County, Guizhou Province, southern China was studied for its organic and carbonate carbon isotopic composition. Organic carbon isotope values reveal a clear stratigraphic trend up-section, with an increase in  $\delta^{13}\text{C}$  of almost 7‰.  $\delta^{13}\text{C}_{\text{carb}}$  varies from positive  $\delta^{13}\text{C}$  values in the Lower Cambrian to negative  $\delta^{13}\text{C}$  values in the Middle Cambrian. The magnitude of this change across the entire section is 4.5‰. No distinctive carbon isotope excursion marks the actual boundary level, which has

been defined on the basis of trilobite biostratigraphy. Part of the variation in the carbon isotopic composition of carbonate as well as the elemental abundances reflect a change(s) in lithology with some additional effects from diagenesis. The decrease in  $\Delta\delta$  up-section is believed to reflect a decreasing contribution of bacterial biomass to the total sedimentary organic matter, probably relating to increased anoxia and decreased bacterial processing of primary production (Logan *et al.* 1995).

**Acknowledgements.** We wish to sincerely thank Prof. Dr Peng Ping'an, Prof. Dr Zhu Maoyan, Prof. Peng Shanchi, Prof. Dr Yuan Jinliang, Dr Tatiana Goldberg, Dr C. Ostertag-Henning, Mr A. Fugmann, Miss Dong Liming and Mr An Ning for discussion and for assistance and expertise in the field and the laboratory. Constructive suggestions by Dr G. Shields improved an earlier version of this work. Reviews of this manuscript by Dr M. Brasier and an anonymous reviewer are gratefully acknowledged. Financial support by NSFC (No. 40303001) and DFG (No. Str 281/16-1/16-2) is gratefully acknowledged.

## References

- BERNER, R. A. & KOTHAVALA, Z. 2001. GEOCARB III: a revised model of atmospheric  $\text{CO}_2$  over Phanerozoic time. *American Journal of Science* **301**, 182–204.
- BRASIER, M. D. 1993. Towards a carbon isotope stratigraphy of the Cambrian System: potential of the Great Basin succession. In *High resolution stratigraphy* (eds E. A. Hailwood and R. B. Kidd), pp. 41–50. Geological Society of London, Special Publication no. 70.
- BRASIER, M. D., ROZANOV, A. YU., ZHURAVLEV, A. YU., CORFIELD, R. M. & DERRY, L. A. 1994. A carbon isotope reference scale for the Lower Cambrian succession in Siberia: report of IGCP Project 303. *Geological Magazine* **131**, 767–83.
- BRASIER, M. D. & SUKHOV, S. S. 1998. The falling amplitude of carbon isotopic oscillations through the Lower to Middle Cambrian: northern Siberia data. *Canadian Journal of Earth Sciences* **35**, 353–73.
- DONNELLY, T., SHERGOLD, J. H. & SOUTHGATE, P. N. 1988. Anomalous geochemical signals from phosphatic Middle Cambrian rocks in the southern Georgina Basin, Australia. *Sedimentology* **35**, 549–70.
- FU JIANG & QIN KUANGZONG. 1995. *Kerogen geochemistry*. Guangzhou: Guangdong Science and Technology Press, 637 pp. (in Chinese).
- GEYER, G. & SHERGOLD, J. 2000. The quest for internationally recognized divisions of Cambrian time. *Episodes* **23**, 188–95.
- GUO QING-JUN, YANG WEIDONG, ZHAO YUAN-LONG, ZHU LIJUN & YANG RUIDONG. 2001a. Geochemical characteristics of the stratotype preliminary boundary section of the Middle-Lower Cambrian in Taijiang, Guizhou. *Geochimica* **30**, 383–9 (in Chinese with English abstract).
- GUO QING-JUN, YANG WEIDONG, ZHAO YUAN-LONG, ZHU LIJUN, YANG RUIDONG & YUAN JINLIANG. 2001b. The Middle–Lower Cambrian Boundary Division of Danzhai, Guizhou. *Journal of Mineralogy and Petrology* **21**, 11–18 (in Chinese with English abstract).

- GUO QING-JUN, ZHAO YUAN-LONG & YUAN JIN-LIANG. 1999. The restudy of *Redlichia* from the Lower part of the Kaili formation in Kaili area, Guizhou Province. *Acta Palaeontologica Sinica* **38**, 157–64 (in Chinese with English summary).
- HAYES, J. M., KAPLAN, I. R. & WEDEKING, K. M. 1983. Precambrian organic geochemistry, preservation of the record. In *Earth's Earliest Biosphere: its Origin and Evolution* (ed. J. W. Schopf), pp. 93–134. Princeton: Princeton University Press.
- HAYES, J. M., STRAUSS, H. & KAUFMAN, A. J. 1999. The abundance of  $^{13}\text{C}$  in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. *Chemical Geology* **161**, 103–25.
- HOLSER, W. T. & MAGARITZ, M. 1987. Events near the Permian–Triassic boundary. *Modern Geology* **11**, 155–80.
- IRWIN, H., CURTIS, C. & COLEMAN, M. 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature* **269**, 209–13.
- JACOBSEN, S. B. & KAUFMAN, A. J. 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chemical Geology* **161**, 37–57.
- KAUFMAN, A. J., JACOBSEN, S. B. & KNOLL, A. H. 1993. The Vendian record of Sr- and C-isotopic variations in seawater: implications for tectonic and paleoclimate. *Earth and Planetary Science Letters* **120**, 409–30.
- KAUFMAN, A. J. & KNOLL, A. H. 1995. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. *Precambrian Research* **73**, 27–49.
- LEWAN, M. D. 1986. Stable carbon isotopes of amorphous kerogens from Phanerozoic sedimentary rocks. *Geochimica et Cosmochimica Acta* **50**, 1583–91.
- LOGAN, G. A., HAYES, J. M., HIESHIMA, G. B. & SUMMONS, R. E. 1995. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* **376**, 53–6.
- MAGARITZ, M. 1989.  $^{13}\text{C}$  minima follow extinction events: a clue to faunal extinction. *Geology* **17**, 337–40.
- MCCREA, J. M. 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *Journal of Chemical Physics* **18**, 849–57.
- MOCZYDŁOWSKA, M. 1999. The Lower–Middle Cambrian boundary recognized by acritarchs in Baltica and at the margin of Gondwana. *Bollettino della Società Paleontologica Italiana* **38**(2–3), 207–25.
- MONTAÑEZ, I. P., OSLEGER, D. A., BANNER, J. L., MACK, L. E. & MASGROVE, M. L. 2000. Evolution of the Sr and C isotope composition of Cambrian oceans. *GSA Today* **10**, 1–7.
- POPP, B. N., ANDERSON, T. F. & SANDBERG, P. A. 1986. Textural, elemental and isotopic variations among constituents in Middle Devonian limestones, North America. *Journal of Sedimentary Petrology* **56**, 715–27.
- SALTZMAN, M. R., RUNNEGAR, B. & LOHMANN, K. C. 1998. Carbon isotope stratigraphy of Upper Cambrian (Steptoean Stage) sequences of the eastern Great Basin: Record of a global oceanographic event. *Geological Society of America Bulletin* **110**, 285–97.
- STRAUSS, H., DES MARAIS, D. J., HAYES, J. M. & SUMMONS, R. E. 1992. Proterozoic organic carbon – its preservation and isotopic record. In *Early Organic Evolution: Implications for Mineral and Energy Resources* (eds M. Schidlowski, S. Golubic, M. M. Kimberley, D. M. McKirdy and P. A. Trudinger), pp. 203–11. Berlin, Heidelberg: Springer Verlag.
- SUNDBERG, F. A. & MCCOLLUM, L. B. 1997. Oryctocephalids (Corynexochida: Trolobita) of the Lower–Middle Cambrian boundary interval from California and Nevada. *Journal of Paleontology* **71**, 1065–90.
- SUNDBERG, F. A., YUAN JIN-LIANG, MCCOLLUM, L. B. & ZHAO YUAN-LONG. 1999. Correlation of the Lower–Middle Cambrian boundary of South China and Western United States of America. *Acta Palaeontologica Sinica* **38**, 102–7.
- VEIZER, J., ALA, D., AZMY, K., BRUCKSCHEN, P., BUHL, D., BRUHN, F., CARDEN, G. A. F., DIENER, A., EBNETH, S., GODDERIS, Y., JASPER, T., KORTE, C., PAWELLEK, F., PODLAHA, O. G. & STRAUSS, H. 1999.  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  evolution of Phanerozoic seawater. *Chemical Geology* **161**, 59–88.
- VEIZER, J. 1983. Chemical diagenesis of carbonates: theory and application. In *Stable Isotopes in Sedimentary Geology* (eds M. A. Arthur *et al.*), pp. 3–1–3–100. S.E.P.M. Short Course 10.
- VEIZER, J., BRUCKSCHEN, P., PAWELLEK, F., DIENER, A., PODLAHA, O. G., CARDEN, G. A. F., JASPER, T., KORTE, C., STRAUSS, H., AZMY, K. & ALA, D. 1997. Oxygen isotope evolution of Phanerozoic seawater. *Palaeogeography Palaeoclimatology Palaeoecology* **132**, 159–72.
- WACHTER, E. A. & HAYES, J. M. 1985. Exchange of oxygen isotopes and carbon isotopes in carbon dioxide-phosphoric acid systems. *Chemical Geology (Isotope Geosciences)* **52**, 365–74.
- YANG RUI-DONG & YIN LEI-MING. 2001. Acritarch assemblages from the Early–Middle Cambrian Kaili formation of East Guizhou Province and biostratigraphic implication. *Acta Micropalaeontologica Sinica* **18**, 55–69 (in Chinese with English abstract).
- YIN LEI-MING & YANG RUI-DONG. 1999. Early–Middle Cambrian acritarchs in the Kaili formation from Taijiang county, Guizhou, China. *Acta Palaeontologica Sinica* **38**, 66–78 (in Chinese with English summary).
- YUAN JIN-LIANG, ZHAO YUAN-LONG & GUO QING-JUN. 1999. On the Kaili Formation. *Acta Palaeontologica Sinica* **38**, 15–27 (in Chinese with English summary).
- YUAN JIN-LIANG, ZHAO YUAN-LONG, WANG ZONG-ZHE, ZHOU ZHEN & CHEN XIAO-YUAN. 1997. A preliminary study on Lower–Middle Cambrian boundary and trilobite fauna at Balang, Taijiang, Guizhou, South China. *Acta Palaeontologica Sinica* **36**, 494–524 (in Chinese with English summary).
- ZACHOS, J. C., ARTHUR, M. A. & DEAN, W. E. 1989. Geochemical evidence for suppression of pelagic marine productivity at the Cretaceous/Tertiary boundary. *Nature* **337**, 61–4.
- ZHAO YUAN-LONG, HUANG YOU-ZHUANG, MAO JIA-REN, SHEN ZHI-DA & XIE HONG. 1992. Some suggestions of Lower–Middle Cambrian boundary in South China. *Geology of Guizhou* **9**, 241–4 (in Chinese with English summary).
- ZHAO YUAN-LONG, YUAN JIN-LIANG, HUANG YOU-ZHUANG, MAO JIA-REN, QIAN YI, ZHANG ZHENG-HUA & GONG XIAN-YING. 1994. Middle Cambrian Kaili fauna in Taijiang, Guizhou. *Acta Palaeontologica Sinica* **33**, 263–71 (in Chinese with English summary).
- ZHAO YUAN-LONG, YUAN JIN-LIANG, ZHANG ZHEN-HUA, MAO JIA-REN, HUANG YOU-ZHUANG, GONG XIAN-YING & WANG KUN. 1993. Preliminary study of the Cambrian Kaili Formation and its synchronous strata

- in transitional area, South China. *Journal of Stratigraphy* **17**, 171–8 (in Chinese with English abstract).
- ZHAO YUAN-LONG, YUAN JIN-LIANG, MCCOLLUM, L. B., SUNDERBERG, F. A., YANG RUIDOING, GUO QING-JUN, ZHU LIJUN & YANG XING-LIAN. 2001a. A potential GSSP for the Lower and Middle Cambrian boundary near Balang village, Taijiang county, Guizhou Province, China. *Acta Palaeontologica Sinica* **40**, 130–42.
- ZHAO YUAN-LONG, YUAN JIN-LIANG, ZHU LI-JUN, CHEN XIAO-YUAN, ZHOU ZHEN & ZHOU PI-KAN. 1996. The Division of the Lower–Middle Cambrian boundary in China. *Journal of Guizhou University of Technology* **25**, 15–20.
- ZHAO YUAN-LONG, YUAN JIN-LIANG, ZHU LI-JUN, GUO QING-JUN, YANG RUI-DONG & YANG XING-LIAN. 2001b. A progress report on research and prospects of the Lower–Middle Cambrian boundary in China. *Journal of Stratigraphy* **25**, 376–83.
- ZHEN SHUHUI, ZHEN SICHENG & MO ZHICHAO. 1986. Geochemistry analysis of stable isotope. Beijing: Beijing University Press, 486 pp. (in Chinese).
- ZHU LI-JUN & ZHAO YUAN-LONG. 1996. Studies of Trace Element and REE Geochemistry Rocks in Middle–Lower Cambrian Boundary Section of Taijiang, Guizhou. *Acta Palaeontologica Sinica* **35**, 627–29 (in Chinese with English summary).
- ZHU MAO-YAN, ZHANG JUN-MING, LI GUO-XIANG & YANG AI-HUA. 2004. Evolution of C isotopes in the Cambrian of China: implications for Cambrian subdivision and trilobite mass extinctions. *Geobios* **37**, 287–301.