Science Bulletin 63 (2018) 1431–1438

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Science Bulletin
www.scibull.com

Article

Timing the termination of the Doushantuo negative carbon isotope excursion: evidence from U-Pb ages from the Dengying and Liuchapo formations, South China

Mingzhong Zhou [a,*], Taiyi Luo [b], Warren D. Huff [c], Zhiqing Yang [d], Guanghong Zhou [e], Tian Gan [b,f], Hua Yang [a], Di Zhang [a]

[a] School of Geographical and Environmental Sciences, Guizhou Normal University, Guiyang 550001, China
[b] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[c] Department of Geology, University of Cincinnati, Cincinnati, OH 45221, USA
[d] Beijing SHRIMP Center, Chinese Academy of Geological Sciences, Beijing 100037, China
[e] School of Geography and Tourism, Guizhou Education University, Guiyang 550018, China
[f] College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 13 August 2018
Received in revised form 27 September 2018
Accepted 28 September 2018
Available online 10 October 2018

Keywords:
Doushantuo formation
Dengying formation
Shuram carbon isotope excursion
South China

ABSTRACT

The Doushantuo negative carbon isotope excursion (DOUNCE) is the largest known marine inorganic carbon isotope anomaly. The origin of this pronounced negative excursion is still an enigmatic issue that attracts geologists. Time constraints on the excursion are the critical information that would provide insight into its genesis. In previous decades, the timing of its termination has been constrained by the widely cited zircon U-Pb age of 550.5 ± 0.8 Ma for the tuff at the top of the Miaohe Member at the Jiuqunao section in the Yangtze Gorges area, South China. However, results of recent studies indicate that the reliability of this time constraint needs to be re-evaluated. Here, a geochronological study was carried out using two K-bentonites from Fanglong in South China. A K-bentonite in the lower Dengying Formation yielded a U-Pb age of 557 ± 3 Ma, while a K-bentonite in the basal Liuchapo Formation yielded an age of 550 ± 3 Ma. Based on regional correlations between the Ediacaran successions in South China, the age (557 ± 3 Ma) for the K-bentonite in the lower Dengying Formation may serve as a second critical timing constraint for the ending of the DOUNCE. Combined with available estimates of the DOUNCE duration, our new data indicate that the DOUNCE has a maximum onset age ∼570 Ma.
© 2018 Science China Press. Published by Elsevier B.V. and Science China Press. All rights reserved.

1. Introduction

The Doushantuo negative carbon isotope excursion (DOUNCE) recorded in Ediacaran sequences around the world is the largest-amplitude marine inorganic carbon isotope anomaly known to date [1–7]. However, its origin is obscure. Over the past two decades, numerous studies have examined the excursion, and various models regarding the excursion's origin have been proposed, which can be summarized into two groups: (1) the excursion is a primary depositional carbon isotope anomaly related to a globally synchronous ocean oxygenation event [4,8–10]; or (2) the excursion is the result of diagenetic alteration [11–13]. Bristow and Kennedy [14] suggested that oxidants in the paleo-ocean were insufficient to cause the oxidation of a large dissolved organic carbon (DOC) pool if the DOUNCE lasted between 25 and 50 Ma. Based on an estimation of a long-duration (25–50 Ma) excursion, they concluded that the excursion is unlikely to represent a global ocean signal. However, the duration of the excursion is uncertain due to a lack of robust radiometric ages [15–21]. Therefore, the key to understanding the origin of the DOUNCE relies on improved time constraints for the excursion.

Until now, the sole radiometric age (550.5 ± 0.8 Ma) constraining the termination of the excursion comes from a tuff in the top of a black shale interval at the Jiuqunao section (also named the Jijiawan section) in the Yangtze Gorges area, China [22–25]. However, the likelihood of this tuff deposit providing a reliable constraint on the timing of termination was doubted by An et al. [26]. Traditionally, the Miaohe Member was thought to be the equivalent of Member IV of the Doushantuo Formation in the Jiulongwan section from the Yangtze Gorges area [5,6,22]. However, An et al. [26] proposed that the Miaohe Member is

* Corresponding author.
E-mail address: mingzhongzhou@126.com (M. Zhou).

https://doi.org/10.1016/j.scib.2018.10.002
2095-9273/© 2018 Science China Press. Published by Elsevier B.V. and Science China Press. All rights reserved.

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

younger than Member IV of the Doushantuo Formation and is instead correlated with the lower Shibantan Member of the Dengying Formation, overlying the Doushantuo Formation. If the regional correlation scheme of An et al. [26] is correct, then the age of the tuff from the top of the Miaohe Member at the Jiuqunao section would not be suitable for constraining the timing of termination of the DOUNCE.

The result of a recent geochronological study of the Dengying Formation at the Xiaolantian section in the eastern Yunnan Province of China also implied that it is necessary to re-evaluate the reliability of the age of the tuff in the top of the Miaohe Member, Jiuqunao section, for constraining the end of the DOUNCE [27]. Yang et al. [27] obtained a zircon U-Pb age of 553.6 ± 2.7/3.8 Ma for a tuff in the basal Jiucheng Member of the Dengying Formation at the Xiaolantian section in eastern Yunnan Province. Considering the distance (>250 m) between the tuff and the Doushantuo-Dengying boundary in the Xiaolantian section, the age of the boundary in this section would probably be significantly older than 553.6 ± 2.7/3.8 Ma. Given that the Doushantuo-Dengying boundary in the Xiaolantian and Jiulongwan sections is not diachronous, the age of the Doushantuo-Dengying boundary in the Jiulongwan section could be considerably older than 553.6 ± 2.7/3.8 Ma. Thus, when considered with the age (550.5 ± 0.8 Ma) of the tuff at the top of the Miaohe Member [25], the data indicate that the Miaohe Member is younger than Member IV of the Doushantuo Formation in the Jiulongwan section. This also supports the new correlation scheme proposed by An et al. [26]. However, if this is the case, then the U-Pb age of the tuff at the top of the Miaohe Member is not appropriate for estimating the timing of termination of the DOUNCE.

Here, we report zircon U-Pb ages for two K-bentonite layers that were recently discovered at the Fanglong section in Jianhe County, Guizhou Province, South China. The new ages are considered alongside regional correlations of Ediacaran successions in South China and used to re-evaluate the timing of the DOUNCE.

2. Geological settings

During the Ediacaran-Cambrian transition, the Yangtze Platform evolved from a rift basin to a passive continental margin (Fig. 1). The Jiulongwan section in the Yangtze Gorges area is located in the platform interior of the Yangtze Platform. The stratigraphy of this section is well described in the literature [1,5,28]. The Ediacaran strata at Jiulongwan consist of the Doushantuo Formation and the lowermost part of the Dengying Formation (Fig. 2). The Doushantuo Formation is subdivided into four members (Members I–IV). Member I consists of a ~5-m-thick cap carbonate that overlies the tillites deposited during the Nantuo (Marinoan) glaciation and shows a negative carbon isotope anomaly similar to that of the basal Ediacaran cap carbonates globally [1]. Member II is composed of black shales interbedded with dolostones. Member III consists mainly of dolostones and limestones, and Member IV consists of ~13-m-thick black shales [5].

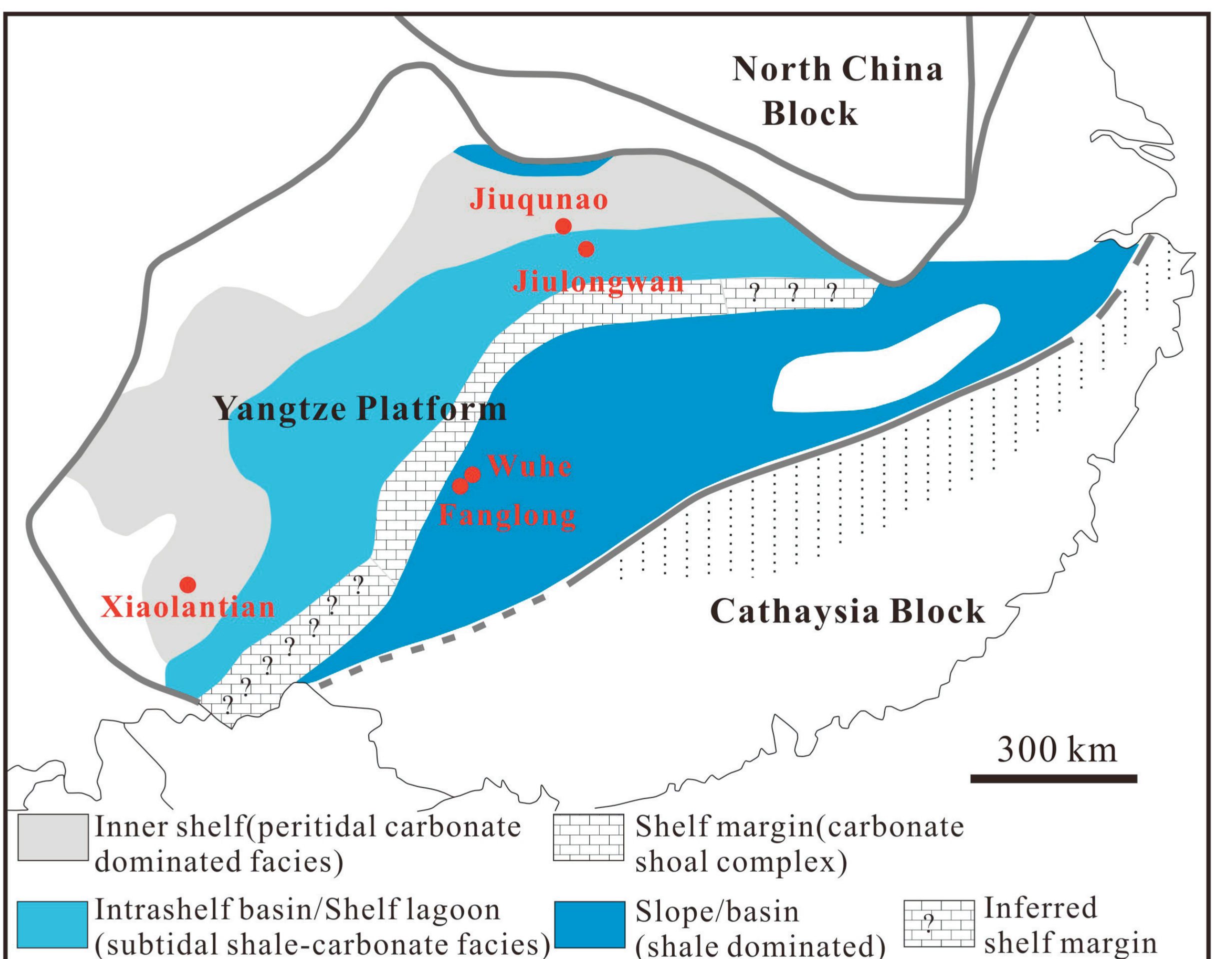

Fig. 1. Sketch-map showing the paleogeography of the Yangtze Platform in South China during the Ediacaran and the locations of the sections included in this study. Red dots represent geological sections.

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

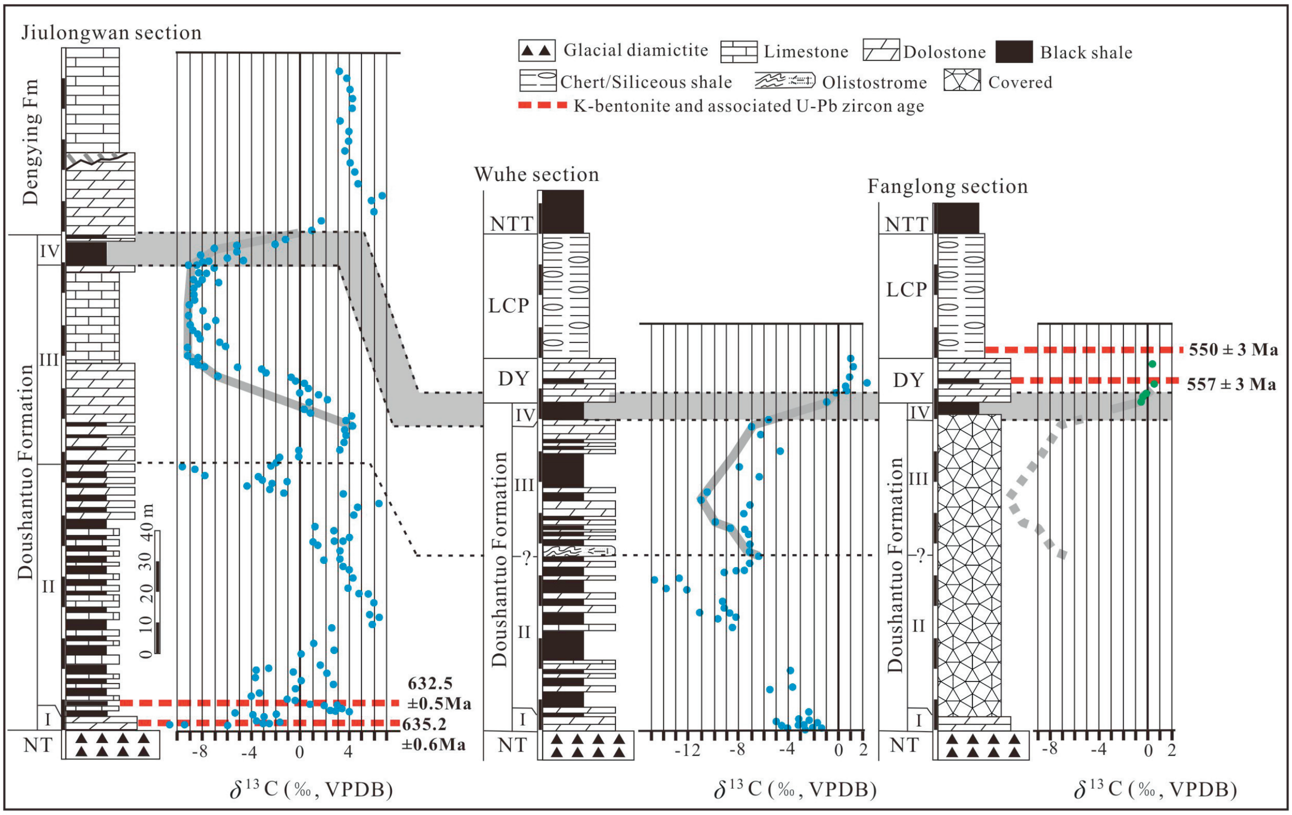

Fig. 2. Correlation of the Ediacaran successions from the Jiulongwan, Wuhe, and Fanglong sections on the Yangtze Platform in South China. Age constraints for the Jiulongwan section are from Condon et al. [22]. Figures of the Jiulongwan and Wuhe sections are adapted from Sahoo et al. [28]. Carbon isotope data of the Jiulongwan and Wuhe sections are from Jiang et al. [1]. NT, Nantuo Formation; DY, Dengying Formation; LCP, Liuchapo Formation; NTT, Niutitang Formation.

In the interval that includes the upper part of Member III and Member IV from the upper Doushantuo Formation, a prominent negative carbon isotope excursion (DOUNCE) has been recognized and correlated with the Shuram carbon isotope anomaly [1,2,29]. The lowermost Dengying Formation is composed mainly of dolostone and limestone, and the dolostone at the bottom of the formation documents the termination of the DOUNCE [1,5,28]. The Jiuqunao section is adjacent to Jiulongwan and the Ediacaran Doushantuo and Dengying formations are also well exposed in this section (Fig. 1). However, the stratigraphic position of a black shale interval (the Miaohe Member), which hosts the Miaohe biota, remains controversial.

The Ediacaran successions at the Wuhe section, in Jianhe County of Guizhou Province, represent the Ediacaran deposits from the slope zone of the Yangtze Platform (Fig. 1). The stratigraphy of this section has been described previously [1,28]. In ascending order, the Ediacaran-Cambrian strata at Wuhe include the Doushantuo, Dengying and Liuchapo formations, and a small portion of the basal Niutitang Formation (Fig. 2). The Doushantuo Formation is subdivided into four intervals (Members I–IV) [28]. Member I is a 2.3-m-thick cap carbonate that overlies glacial diamictite of the Nantuo Formation. Members II and III are composed of carbonaceous shale and subordinate micritic or microcrystalline dolostone. Member IV is a ~5-m-thick black shale interval with phosphatic and pyrite nodules. The Dengying Formation consists mainly of ~12-m-thick bedded dolostone. The Liuchapo Formation is a 40-m-thick chert. The Fanglong section is also located in Jianhe County, near the Wuhe section (Fig. 1). The exposed Ediacaran sequences at Fanglong, which include the uppermost 4 m of black shale of the Doushantuo Formation plus the Dengying and Liuchapo formations, are comparable to those at Wuhe (Fig. 2). We discovered two K-bentonites in the Fanglong section (Fig. 3). The lower K-bentonite is 10 cm thick and interleaved within the dolostone of the lower Dengying Formation (Fig. 3a). This K-bentonite is greenish grey and composed of the minerals illite, mixed-layer illite-smectite, and kaolinite. The upper K-bentonite, which is ~5 cm thick, is located in the basal part of the Liuchapo Formation (4 m above the Dengying-Liuchapo boundary, Fig. 3b). This K-bentonite is blackish grey and has sharp contacts with the Liuchapo chert. It is composed mainly of illite and mixed-layer illite-smectite.

3. Sampling and analytical techniques

K-bentonite samples were collected from the Fanglong section in Jianhe County, Guizhou Province. Sample FL-2 comes from a K-bentonite in the lower part of the Dengying Formation. Another K-bentonite sample (FLA-11) is from the lowermost part of the Liuchapo Formation. Zircon grains were extracted from concentrates of each sample processed by conventional magnetic and density techniques. Considering the characteristic of zircons in K-bentonites (typically, they comprise inherited and/or detrital components) and the advantages of microbeam analytical techniques [30–33], SHRIMP U-Pb dating was used to obtain the ages of the zircons in the two K-bentonite samples. The zircon grains, together with the zircon standard TEMORA (reference age of 417 Ma), were mounted in an epoxy-resin mount, which was then polished until the crystal interiors were exposed. All zircons were documented with transmitted and reflected light micrographs as well as cathodoluminescence (CL) images to reveal their fissures, inclusions, and internal structures, and the mount was vacuum-coated with gold for SHRIMP analysis.

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

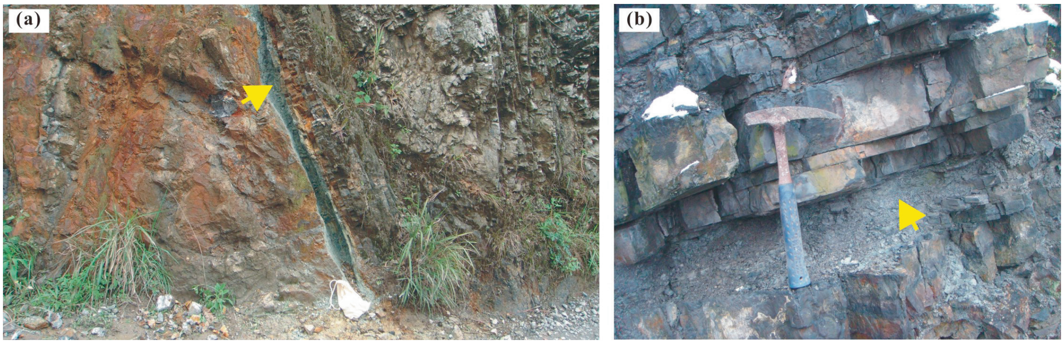

Fig. 3. Field photographs of the two Ediacaran K-bentonites in the Fanglong section in South China. (a) Greenish gray K-bentonite between dolostones of the lower Dengying Formation. The width of the sample bag is 25 cm. (b) Blackish gray K-bentonite intercalated with the cherts of the basal Liuchapo Formation. The length of the hammer handle is 30 cm.

Zircon U-Pb dating of the samples was performed using the SHRIMP II at the Beijing SHRIMP Center, Beijing, China, following procedures described in the Ref. [34]. The data were processed using the Squid v. 1.02 and Isoplot/Ex v. 2.49 programs [35,36], and common Pb was corrected against measured ^{204}Pb.

4. Results

Most of the zircon grains in the two K-bentonite samples are euhedral or subhedral (Fig. 4a-f), but some are rounded (Fig. 4g and h). The zircons are 48–152 μm long and 32–100 μm wide. The length-to-width ratios vary from 1:1 to 4:1, mainly higher than 2:1. Some of the zircons show oscillatory zoning in the CL images, and some show obvious cracks despite their euhedral crystal shape (Fig. 4e and f). SHRIMP U-Pb analyses reveal that the ^{206}Pb/^{238}U ages of the rounded zircons are much older than those from the main population (Fig. 4g and h). We consider these zircons to be detrital. The SHRIMP U-Pb results also show that the zircons with obvious cracks, in spite of their euhedral crystal shape, have ^{206}Pb/^{238}U ages that are distinctly younger than the main population (Fig. 4e and f). We attribute the young ^{206}Pb/^{238}U ages of the zircons to Pb loss.

SHRIMP U-Pb dating was carried out on 41 spots of zircons from sample FL-2 from the lower Dengying Formation at Fanglong (see details in Table 1). During calculations of the weighted mean ^{206}Pb/^{238}U age, 11 analyses were rejected based on the following reasons. (1) The ages of six spots (621.0 ± 7.2 to 1322.6 ± 13.8 Ma) are distinctively older than the main population. The zircons hosting these spots were generally rounded; therefore, we consider them to be detrital and we exclude them from analysis. (2) The ages of four spots range from 423.9 ± 4.9 to 503.1 ± 12.1 Ma, which are much younger than those of the main population. The zircons hosting these spots have obvious cracks. Therefore, we infer that these zircons suffered from loss of radiogenic Pb. (3) The spot FL-2.7 has a discordant age of 562.5 ± 11.4 Ma. To be prudent, we exclude it from the weighted mean age calculation. The ages of the remaining 30 spots yield a weighted mean age of 557 ± 3 Ma (2σ, $n = 30$, MSWD = 0.38). This mean age is interpreted to be the crystallization age of the zircons and it is also the best estimate of the age for the K-bentonite FL-2 (Table 1; Fig. 5).

U-Pb isotopes were measured by SHRIMP on 37 spots of the zircons from sample FLA-11 in the basal Liuchapo Formation (see details in Table 1). During the calculation of the weighted mean

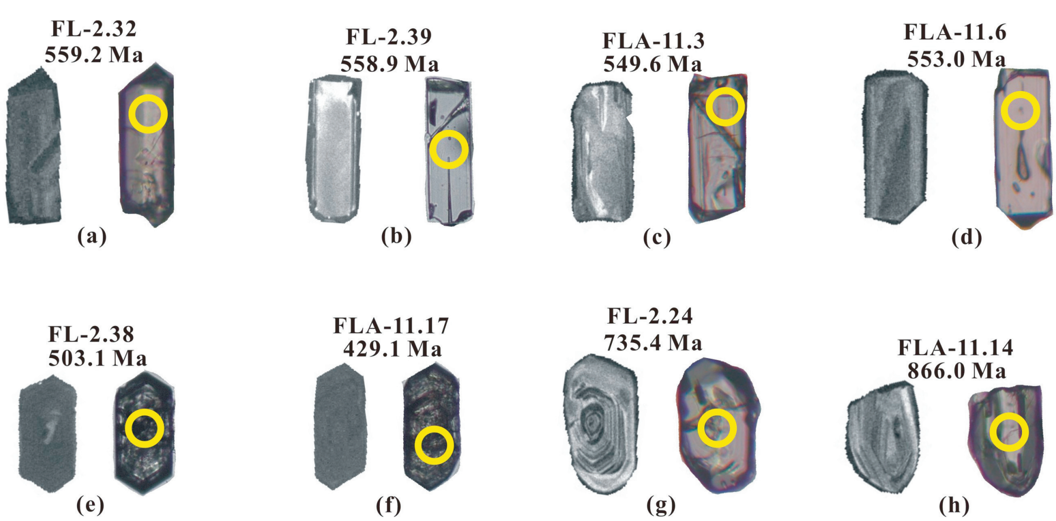

Fig. 4. Cathodoluminescence (CL) images (left-hand image in each pair) and transmitted light photomicrographs (right-hand image in each pair) of representative zircons in the two K-bentonites at Fanglong. (a) and (b) Subhedral prismatic volcanic zircons from sample FL-2 with U-Pb ages that fall into the main population of ca. 557 Ma. (c) and (d) Subhedral prismatic volcanic zircons from sample FLA-11 yield U-Pb ages that fall into the main population at ca. 550 Ma. (e) Euhedral zircon with obvious cracks from sample FL-2, which has a younger U-Pb age than the main population, owing to Pb loss. (f) Euhedral zircon with obvious cracks from sample FLA-11 that yields a U-Pb age that is younger than the main population, owing to Pb loss. (g) Rounded detrital zircon in sample FL-2, which has a U-Pb age that is significantly older than the main population. (h) Rounded detrital zircon in sample FLA-11 that yields a U-Pb age that is significantly older than the main population. The circles on zircons represent the spots of SHRIMP U-Pb isotope analyses and are 30 μm in diameter.

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

Table 1
SHRIMP zircon U-Pb isotope analyses of the Ediacaran K-bentonites at the Fanglong section.

	Spot	U (ppm)	Th (ppm)	$^{206}Pb^{*a}$ (ppm)	Th/U	$^{206}Pb_c{}^{a}$ (%)	$^{207}Pb^{*}/^{206}Pb^{*a}$	±%	$^{207}Pb^{*}/^{235}U^{a}$	±%	$^{206}Pb^{*}/^{238}U^{a}$	±%	$^{206}Pb/^{238}U$ Age (Ma)
FL-2	FL-2.1	177	92	13.9	0.52	1.01	0.0537	6.3	0.670	6.7	0.0905	2.1	558.3±11.3
	FL-2.2	226	138	17.8	0.61	0.93	0.0558	6.2	0.698	6.5	0.0907	2.1	559.7±11.4
	FL-2.3	368	299	28.7	0.81	0.25	0.0577	2.1	0.721	2.9	0.0907	2.1	559.6±11.0
	FL-2.4	227	124	18.1	0.55	0.69	0.0548	4.8	0.696	5.2	0.0922	2.1	568.7±11.5
	FL-2.5	244	105	19.4	0.43	0.48	0.0585	3.6	0.742	4.1	0.0920	2.0	567.1±11.0
	FL-2.6	315	201	25.2	0.64	1.32	0.0517	5.4	0.657	5.8	0.0921	2.3	567.9±12.5
	FL-2.7[b]	247	180	19.8	0.73	2.36	0.0448	12.1	0.564	12.3	0.0912	2.1	562.5±11.4
	FL-2.8	150	88	11.8	0.59	1.69	0.0509	9.1	0.631	9.4	0.0900	2.2	555.4±11.8
	FL-2.9	209	156	16.8	0.75	1.51	0.0525	8.3	0.667	8.5	0.0921	2.1	568.0±11.5
	FL-2.10	275	218	21.3	0.80	1.33	0.0554	5.0	0.681	5.6	0.0891	2.5	550.0±13.4
	FL-2.11	354	150	27.9	0.42	0.74	0.0565	3.4	0.709	4.1	0.0910	2.4	561.5±12.8
	FL-2.12	237	141	18.7	0.60	0.99	0.0543	5.7	0.681	6.1	0.0909	2.1	560.9±11.4
	FL-2.13	275	184	21.9	0.67	1.38	0.0513	6.0	0.645	6.3	0.0912	2.0	562.4±11.0
	FL-2.14[b]	505	238	54.6	0.47	0.16	0.0680	1.2	1.179	1.7	0.1257	1.2	763.2±8.5
	FL-2.15[b]	632	651	124.0	1.03	0.18	0.1473	0.5	4.626	1.3	0.2277	1.2	1322.6±13.8
	FL-2.16	215	103	16.7	0.48	0.92	0.0590	6.0	0.730	6.3	0.0897	1.7	553.5±8.9
	FL-2.17	209	129	16.1	0.62	0.24	0.0587	2.6	0.724	2.9	0.0895	1.4	552.4±7.3
	FL-2.18[b]	454	492	39.8	1.08	1.04	0.0600	5.1	0.836	5.3	0.1011	1.2	621.0±7.2
	FL-2.19	325	263	25.0	0.81	0.00	0.0577	1.6	0.712	2.0	0.0894	1.3	552.0±6.6
	FL-2.20[b]	749	357	50.7	0.48	0.47	0.0597	2.0	0.645	2.3	0.0784	1.1	486.4±5.4
	FL-2.21	233	116	18.4	0.50	0.18	0.0592	2.6	0.750	3.0	0.0918	1.4	566.2±7.6
	FL-2.22	331	253	25.4	0.76	0.19	0.0570	2.0	0.701	2.4	0.0892	1.3	550.6±6.7
	FL-2.23[b]	487	328	28.5	0.67	0.32	0.0592	1.9	0.555	2.2	0.0680	1.2	423.9±4.9
	FL-2.24[b]	247	256	25.9	1.04	1.13	0.0659	3.1	1.097	3.4	0.1209	1.3	735.5±9.0
	FL-2.25	399	300	30.7	0.75	0.15	0.0568	1.8	0.701	2.2	0.0895	1.2	552.5±6.5
	FL-2.26	191	144	14.7	0.76	0.22	0.0601	2.6	0.740	3.0	0.0893	1.5	551.6±7.7
	FL-2.27	253	93	19.4	0.37	0.16	0.0571	2.1	0.705	2.5	0.0895	1.3	552.4±6.9
	FL-2.28	219	133	16.9	0.61	0.16	0.0586	2.7	0.727	3.0	0.0899	1.3	554.8±7.2
	FL-2.29[b]	89	10	11.4	0.11	0.25	0.0669	2.3	1.376	2.8	0.1492	1.6	896.5±13.5
	FL-2.30	276	118	21.7	0.43	0.25	0.0571	2.4	0.718	2.8	0.0913	1.4	562.9±7.4
	FL-2.31	314	202	24.3	0.64	0.18	0.0572	2.4	0.709	2.7	0.0899	1.3	555.1±6.7
	FL-2.32	408	185	31.8	0.45	0.18	0.0569	2.2	0.712	2.5	0.0906	1.2	559.2±6.5
	FL-2.33	185	291	14.6	1.57	1.06	0.0564	5.9	0.706	6.1	0.0909	1.5	560.8±8.1
	FL-2.34[b]	560	274	38.1	0.49	0.54	0.0593	2.1	0.643	2.5	0.0787	1.3	488.1±6.2
	FL-2.35[b]	105	73	12.3	0.69	0.46	0.0649	2.8	1.221	3.2	0.1364	1.5	824.3±11.9
	FL-2.36	446	82	34.2	0.18	0.18	0.0600	2.0	0.737	3.2	0.0891	2.5	550.3±13.2
	FL-2.37	186	82	14.6	0.44	0.00	0.0595	2.4	0.750	3.5	0.0914	2.6	563.6±14.0
	FL-2.38[b]	607	319	42.4	0.53	0.18	0.0588	1.8	0.658	3.1	0.0812	2.5	503.1±12.1
	FL-2.39	111	71	8.7	0.63	0.39	0.0572	3.3	0.714	4.3	0.0906	2.7	558.9±14.3
	FL-2.40	118	73	9.3	0.62	0.97	0.0603	8.1	0.751	8.5	0.0904	2.7	558.0±14.4
	FL-2.41	149	114	11.5	0.76	−0.13	0.0620	3.3	0.766	4.3	0.0896	2.6	553.1±13.9

(Continued on next page)

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

Table 1 (*Continued*)

	Spot	U (ppm)	Th (ppm)	$^{206}Pb^{*a}$ (ppm)	Th/U	$^{206}Pb_c{}^a$ (%)	$^{207}Pb^*/^{206}Pb^{*a}$	±%	$^{207}Pb^*/^{235}U^a$	±%	$^{206}Pb^*/^{238}U^a$	±%	$^{206}Pb/^{238}U$ Age (Ma)
FLA-11	FLA-11.1	314	195	24.0	0.62	0.77	0.0550	6.7	0.67	6.9	0.0881	1.5	544.3±7.7
	FLA-11.2	220	127	17.3	0.57	1.34	0.0520	6.9	0.65	7.1	0.0904	1.6	557.8±8.4
	FLA-11.3	199	60	15.4	0.30	1.08	0.0560	5.2	0.69	5.5	0.0890	1.6	549.6±8.3
	FLA-11.4	447	213	34.1	0.48	0.23	0.0565	2.2	0.69	2.6	0.0886	1.4	547.1±7.1
	FLA-11.5	554	301	42.1	0.54	0.79	0.0574	3.2	0.70	3.5	0.0879	1.3	542.9±7.0
	FLA-11.6	298	187	23.2	0.63	1.14	0.0508	5.4	0.63	5.6	0.0896	1.6	553.0±8.4
	FLA-11.7	289	160	23.0	0.55	2.37	0.0453	10.6	0.57	10.7	0.0905	1.6	558.7±8.6
	FLA-11.8	220	132	17.3	0.60	1.26	0.0565	6.5	0.70	6.7	0.0903	1.7	557.1±9.0
	FLA-11.9	377	242	29.0	0.64	1.05	0.0628	6.1	0.77	6.2	0.0885	1.5	546.5±7.7
	FLA-11.10[b]	191	228	20.9	1.19	0.96	0.0697	4.6	1.21	4.9	0.1256	1.7	762.8±11.9
	FLA-11.11	250	128	19.8	0.51	2.06	0.0608	10.3	0.76	10.4	0.0904	1.7	558.0±9.0
	FLA-11.12	511	139	40.1	0.27	0.86	0.0592	6.3	0.74	6.5	0.0905	1.5	558.5±8.1
	FLA-11.13	362	204	28.3	0.56	1.95	0.0554	6.8	0.68	7.0	0.0894	1.5	551.7±8.1
	FLA-11.14[b]	186	138	23.4	0.74	1.93	0.0712	6.4	1.41	6.6	0.1438	1.7	866.0±13.9
	FLA-11.15	284	88	21.4	0.31	−0.10	0.0619	2.1	0.75	2.4	0.0880	1.3	543.4±6.7
	FLA-11.16	458	276	34.8	0.60	−0.08	0.0611	1.6	0.75	1.9	0.0884	1.1	546.1±5.6
	FLA-11.17[b]	2313	677	136.8	0.29	0.02	0.0654	1.2	0.62	1.6	0.0688	1.0	429.1±4.4
	FLA-11.18	346	209	26.9	0.60	0.20	0.0575	2.4	0.71	2.7	0.0902	1.2	556.5±6.4
	FLA-11.19[b]	788	1007	50.4	1.28	0.22	0.0645	2.7	0.66	2.9	0.0743	1.2	461.9±5.2
	FLA-11.20	276	155	21.1	0.56	0.10	0.0598	2.6	0.73	2.8	0.0889	1.2	549.3±6.5
	FLA-11.21	410	278	31.4	0.68	−0.04	0.0603	1.5	0.74	1.9	0.0890	1.2	549.6±6.3
	FLA-11.22	115	64	8.9	0.56	0.07	0.0602	4.3	0.75	4.8	0.0899	2.1	555.1±11.4
	FLA-11.23	75	34	5.7	0.45	−0.40	0.0596	3.4	0.73	4.1	0.0892	2.3	550.9±12.3
	FLA-11.24	143	49	10.9	0.34	0.35	0.0548	4.3	0.67	4.8	0.0886	2.0	547.3±10.7
	FLA-11.25[b]	417	536	27.5	1.28	7.81	0.0630	10.2	0.61	10.4	0.0708	2.0	441.1±8.6
	FLA-11.26	166	68	12.7	0.41	0.20	0.0564	2.8	0.69	3.5	0.0889	2.1	548.8±11.1
	FLA-11.27	287	127	21.8	0.44	0.08	0.0580	3.0	0.71	3.6	0.0883	1.9	545.4±10.1
	FLA-11.28[b]	135	64	17.0	0.47	0.77	0.0626	4.3	1.25	4.7	0.1451	2.1	873.4±17.0
	FLA-11.29[b]	1562	2201	85.4	1.41	2.72	0.0611	3.6	0.52	4.1	0.0619	1.8	387.1±6.9
	FLA-11.30	357	480	27.1	1.34	0.21	0.0575	2.4	0.70	3.0	0.0881	1.9	544.3±9.9
	FLA-11.31[b]	376	331	47.7	0.88	0.21	0.0682	1.7	1.39	2.5	0.1473	1.9	886.1±15.7
	FLA-11.32	253	135	19.4	0.53	0.52	0.0582	3.5	0.71	4.0	0.0889	2.0	549.1±10.3
	FLA-11.33	566	367	43.2	0.65	0.11	0.0578	1.7	0.71	2.5	0.0889	1.9	548.9±9.8
	FLA-11.34[b]	231	271	21.2	1.17	1.23	0.0561	5.9	0.81	6.3	0.1054	2.1	645.8±13.1
	FLA-11.35	391	235	30.2	0.60	0.20	0.0569	2.0	0.70	2.8	0.0897	2.0	553.8±10.5
	FLA-11.36	177	90	13.8	0.51	0.89	0.0557	5.8	0.69	6.2	0.0902	2.1	556.8±11.1
	FLA-11.37	297	189	23.0	0.64	0.51	0.0563	3.0	0.69	3.6	0.0895	1.9	552.6±10.3

[a] Pb_c and Pb^* indicate the common and radiogenic portions, respectively. [b] Grey shading indicates data rejected from the weighted mean $^{206}Pb/^{238}U$ age calculations.

$^{206}Pb/^{238}U$ age, nine analyses were excluded. Among them, five spots (645.8 ± 13.1 to 886.1 ± 15.7 Ma) were from zircons considered to be detrital, and four spots (387.1 ± 6.9 Ma to 461.9 ± 5.2 Ma) were from zircons considered to have experienced Pb loss. The remaining 28 spots of the main population yield a weighted mean age of 550 ± 3 Ma (2σ, n = 28, MSWD = 0.38), which is interpreted as the best estimate of the age of the K-bentonite FLA-11 (Table 1; Fig. 5).

5. Discussion

The Ediacaran successions at Wuhe are well correlated with those at Jiulongwan (Fig. 2), although they vary laterally in both thickness and facies [1,28,37]. Member I of the Doushantuo Formation at the two sections is the cap carbonate, which serves as the most significant marker bed for the Doushantuo Formation on the Yangtze Platform. Members II and III of the formation at the two sections, which

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

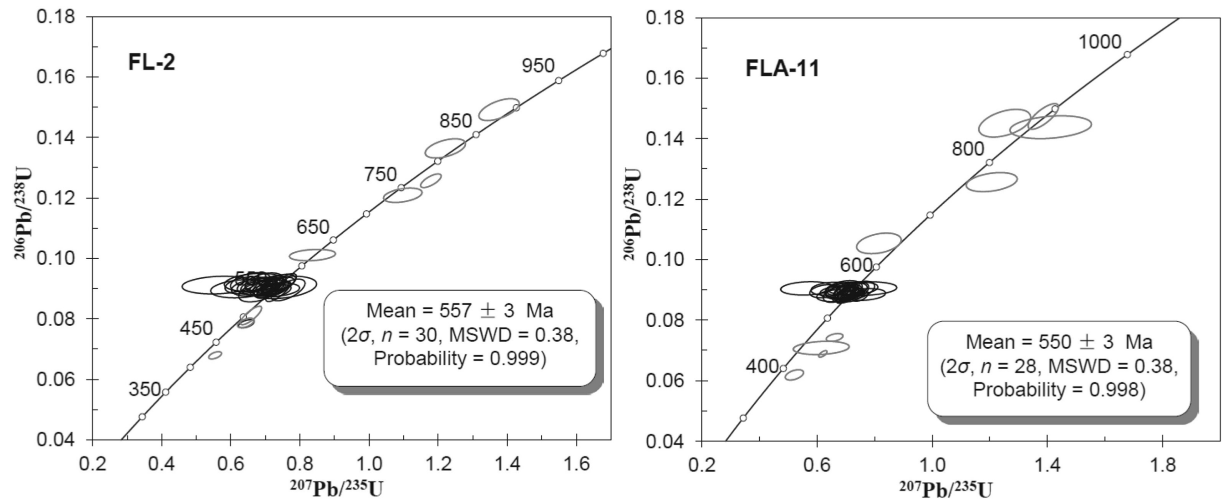

Fig. 5. (Color online) SHRIMP zircon U-Pb concordia diagrams and weighted mean $^{206}Pb/^{238}U$ ages of zircons from the two Ediacaran K-bentonites at the Fanglong section.

are mainly black shale and bedded dolostone, are similar despite a lack of prominent marker beds. Member IV of the Doushantuo Formation at both sections is a black shale layer, and this is the second significant regional marker for the Doushantuo Formation. At the two sections, the lithostratigraphic unit overlying the Doushantuo Formation is the lowermost dolostone of the Dengying Formation.

Chemostratigraphic studies show that the inorganic carbon isotope records in the Ediacaran sequences at Wuhe and Jiulongwan have a similar trend (Fig. 2), which also suggests that the Ediacaran strata from the two sections are well correlated [1,28]. The cap dolostone in Member I of the Doushantuo Formation at the two sections documents a negative carbon isotope anomaly, which can be recognized in the basal Ediacaran cap carbonate globally. A second negative carbon isotope excursion of the Doushantuo Formation has been discovered at the top of Member II at the two sections. In upward succession, the Doushantuo negative carbon isotope excursion (DOUNCE), which is correlated with the Shuram excursion elsewhere, is recorded in Members III and IV of the Doushantuo formation at both Wuhe and Jiulongwan [2,38,39]. The negative values of δ^{13}C in this excursion increase to zero, and then to positive values at the dolostone horizon at the base of the Dengying Formation at both the Wuhe and Jiulongwan sections. In addition, previous geochemical studies have shown that Member IV of the Doushantuo Formation records an oceanic oxygenation event [4,28,37,40,41], which further supports the above-mentioned conclusion that Member IV serves as a significant regional marker for the Doushantuo Formation.

As the exposed Ediacaran successions at Fanglong are entirely similar to those at Wuhe, the Ediacaran strata at Fanglong are also reasonably well correlated with those at Jiulongwan (Fig. 2). The correlation of the Fanglong section and the Jiulongwan section can be summarized as follows: (1) part of Member IV of the Doushantuo Formation at Fanglong can be correlated with the corresponding interval at Jiulongwan; and (2) the Dengying Formation at Fanglong is equivalent to the lowermost part of the Dengying Formation at Jiulongwan.

Based on the above regional stratigraphic correlation, we believe that the timing of the end of the DOUNCE can be constrained by the zircon U-Pb age of the K-bentonite in the lower Dengying Formation at Fanglong. Previously, the absolute age of the termination of the excursion has been constrained only by the zircon U-Pb age of a tuff at the top of the Miaohe Member at Jiuqunao in the Yangtze Gorges area, originally published as 551.1 ± 0.7 Ma [22] and then revised to 550.5 ± 0.8 Ma [25]. An et al. [26] interpreted the Miaohe Member as equivalent to the lower Shibantan Member of the Dengying Formation, rather than Member IV of the Doushantuo Formation at the Jiulongwan section. If this interpretation is correct, the U-Pb age of the tuff at the top of the Miaohe Member may be too young to constrain the end of the DOUNCE. The K-bentonite in the lower Dengying Formation at Fanglong is immediately above the stratigraphic position where the negative δ^{13}C value of the DOUNCE recovers to zero, and then to positive values (from −0.41‰ to 0.67‰, Fig. 2). Thus, the zircon U-Pb age (557 ± 3 Ma) of this K-bentonite could serve as a critical constraint on the timing of termination of the excursion. The date obtained in the present study (557 ± 3 Ma) is older than the tuff at the top of the Miaohe Member at Jiuqunao (550.5 ± 0.8 Ma) [25]. However, we are able to provide only the analytical reproducibility for the date in this study. If both the analytical and external reproducibilities were able to be taken into consideration, as some workers have performed [27], the age of the K-bentonite at Fanglong would possibly be indistinguishable from that obtained for the tuff at Jiuqunao (550.5 ± 0.8 Ma). Therefore, we conclude that the new zircon U-Pb age (557 ± 3 Ma) of the K-bentonite in the lower part of the Dengying Formation at Fanglong is a second important time constraint on the end of the excursion (Fig. 2).

The above evaluation of the timing of the end of the DOUNCE is consistent with some other estimates of the timing of onset of the DOUNCE. An et al. [26] proposed that the top of the DOUNCE is likely to be ≥560 Ma. Following An et al. [26], Sahoo et al. [28] estimated an age of 560 Ma for Member IV and the top of the DOUNCE. Zhu et al. [3] suggested that the DOUNCE ranged from ca. 560 to 551 Ma. If we were to take our age of 557 ± 3 Ma for the termination of the DOUNCE, together with Zhu et al.'s [3] estimate for the duration of the DOUNCE, then we would calculate that the DOUNCE had a maximum onset age of ca. 569 Ma. Gong et al. [42] obtained a duration of 9.1 ± 1.0 Ma for the DOUNCE based on rock magnetic cyclostratigraphy for the Doushantuo Formation. They accepted the age of 551.1 ± 0.7 Ma as the termination age for the DOUNCE and thus estimated the onset age of ca. 560 Ma. If we combine this duration and our estimated age of 557 ± 3 Ma for the termination of the DOUNCE, then the DOUNCE would have had a maximum onset age of ca. 570 Ma. These estimates are essentially consistent with the estimated onset age of ca. 570 Ma for the DOUNCE equivalent in the Wonoka Formation, South Australia, as reported by Williams and Schimdt [43].

6. Conclusions

This geochronological study was based on zircons from two K-bentonites in the lower Dengying Formation and the basal Liu-

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

chapo Formation at Fanglong in South China. These K-bentonites yielded zircon U-Pb ages of 557 ± 3 and 550 ± 3 Ma, respectively. On the basis of intra-basinal stratigraphic correlations, the results in the present study suggest that a zircon U-Pb age of 557 ± 3 Ma for the K-bentonite from the lower Dengying Formation could serve as a second critical time constraint on the end of the Doushantuo negative carbon isotope excursion. Combined with some previous estimates of duration for the DOUNCE, the new data imply that the DOUNCE had a maximum onset age of ca. 570 Ma.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

We are indebted to Senior Engineer Hangqiang Xie of the Beijing SHRIMP Center for technical support, and anonymous reviewers for their constructive comments and valuable suggestions that helped to significantly improve this manuscript. This work was supported by the National Natural Science Foundation of China (41462001, 41072054) and the Project of National Key Research and Development Program of China (2016YFC0502601).

References

[1] Jiang G, Kaufman AJ, Christie-Blick N, et al. Carbon isotope variability across the Ediacaran Yangtze platform in South China: implications for a large surface-to-deep ocean δ^{13}C gradient. Earth Planet Sci Lett 2007;261:303–20.
[2] Zhou C, Xiao S. Ediacaran δ^{13}C chemostratigraphy of South China. Chem Geol 2007;237:89–108.
[3] Zhu M, Zhang J, Yang A. Integrated Ediacaran (Sinian) chronostratigraphy of South China. Palaeogeogr Palaeoclimatol Palaeoecol 2007;254:7–61.
[4] Mcfadden KA, Huang J, Chu X, et al. Pulsed oxidation and biological evolution in the Ediacaran Doushantuo Formation. Proc Natl Acad Sci USA 2008;105:3197–202.
[5] Zhu M, Lu M, Zhang J, et al. Carbon isotope chemostratigraphy and sedimentary facies evolution of the Ediacaran Doushantuo Formation in western Hubei, South China. Precambrian Res 2013;255:7–28.
[6] Lu M, Zhu M, Zhang J, et al. The DOUNCE event at the top of the Ediacaran Doushantuo Formation, South China: broad stratigraphic occurrence and non-diagenetic origin. Precambrian Res 2013;255:86–109.
[7] Zhou C, Xiao S, Wang W, et al. The stratigraphic complexity of the middle Ediacaran carbon isotopic record in the Yangtze Gorges area, South China, and its implications for the age and chemostratigraphic significance of the Shuram excursion. Precambrian Res 2017;288:23–38.
[8] Fike DA, Grotzinger JP, Pratt LM, et al. Oxidation of the Ediacaran ocean. Nature 2006;444:744–7.
[9] Rothman DH, Hayes JM, Summons RE. Dynamics of the neoproterozoic carbon cycle. Proc Natl Acad Sci USA 2003;100:8124–9.
[10] Verdel C, Wernicke BP, Bowring SA. The Shuram and subsequent Ediacaran carbon isotope excursions from southwest Laurentia, and implications for environmental stability during the metazoan radiation. Geol Soc Am Bull 2011;123:1539–59.
[11] Cui H, Kaufman AJ, Xiao S, et al. Was the Ediacaran Shuram Excursion a globally synchronized early diagenetic event? Insights from methane-derived authigenic carbonates in the uppermost Doushantuo formation, South China. Chem Geol 2017;450:59–80.
[12] Derry LA. A burial diagenesis origin for the Ediacaran Shuram-Wonoka carbon isotope anomaly. Earth Planet Sci Lett 2010;294:152–62.
[13] Knauth LP, Kennedy MJ. The late Precambrian greening of the Earth. Nature 2009;460:728–32.
[14] Bristow TF, Kennedy MJ. Carbon isotope excursions and the oxidant budget of the Ediacaran atmosphere and ocean. Geology 2008;36:863–6.
[15] Cui H, Kaufman AJ, Xiao S, et al. Redox architecture of an Ediacaran ocean margin: Integrated chemostratigraphic (δ^{13}C–δ^{34}S–^{87}Sr/^{86}Sr–Ce/Ce*) correlation of the Doushantuo Formation, South China. Chem Geol 2015;405:48–62.
[16] Le Guerroué E. Duration and synchroneity of the largest negative carbon isotope excursion on Earth: the Shuram/Wonoka anomaly. C R Geosci 2010;342:204–14.
[17] Melezhik VA, Pokrovsky BG, Fallick AE, et al. Constraints on ^{87}Sr/^{86}Sr of Late Ediacaran seawater: insight from Siberian high-Sr limestones. J Geol Soc London 2009;166:183–91.
[18] Minguez D, Kodama KP, Hillhouse JW. Paleomagnetic and cyclostratigraphic constraints on the synchroneity and duration of the Shuram carbon isotope excursion, Johnnie Formation, Death Valley Region, CA. Precambrian Res 2015;266:395–408.
[19] Minguez D, Kodama KP. Rock magnetic chronostratigraphy of the Shuram carbon isotope excursion: Wonoka Formation, Australia. Geology 2017;45:567–70.
[20] Wang W, Zhou C, Yuan X, et al. A pronounced negative δ^{13}C excursion in an Ediacaran succession of western Yangtze Platform: a possible equivalent to the Shuram event and its implication for chemostratigraphic correlation in South China. Gondwana Res 2012;22:1091–101.
[21] Zhu B, Becker H, Jiang SY, et al. Re–Os geochronology of black shales from the Neoproterozoic Doushantuo Formation, Yangtze platform, South China. Precambrian Res 2013;225:67–76.
[22] Condon D, Zhu M, Bowring S, et al. U-Pb ages from the Neoproterozoic Doushantuo formation, China. Science 2005;308:95–8.
[23] Zhang S, Jiang G, Zhang J, et al. U-Pb sensitive high-resolution ion microprobe ages from the Doushantuo Formation in South China: constraints on late Neoproterozoic glaciations. Geology 2005;33:473–6.
[24] Yin CY, Tang F, Liu YQ, et al. New U-Pb zircon ages from the Ediacaran (Sinian) System in the Yangtze Gorges: constraint on the age of Miaohe biota and Marinoan glaciation. Geol Bull Chin 2005;24:393–400.
[25] Bowring SA, Grotzinger JP, Condon DJ, et al. Geochronologic constraints on the chronostratigraphic framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman. Am J Sci 2007;307:1097–145.
[26] An Z, Jiang G, Tong J, et al. Stratigraphic position of the Ediacaran Miaohe biota and its constrains on the age of the upper Doushantuo δ^{13}C anomaly in the Yangtze Gorges area, South China. Precambrian Res 2015;271:243–53.
[27] Yang C, Li X, Zhu M, et al. SIMS U-Pb zircon geochronological constraints on upper Ediacaran stratigraphic correlations, South China. Geol Mag 2017;154:1202–16.
[28] Sahoo SK, Planavsky NJ, Jiang G, et al. Oceanic oxygenation events in the anoxic Ediacaran ocean. Geobiology 2016;14:457–68.
[29] Tahata M, Ueno Y, Ishikawa T, et al. Carbon and oxygen isotope chemostratigraphies of the Yangtze platform, South China: decoding temperature and environmental changes through the Ediacaran. Gondwana Res 2013;23:333–53.
[30] Li X, Li Q. Major advances in microbeam analytical techniques and their applications in Earth Science. Sci Bull 2016;61:1785–7.
[31] Pang J, Zheng D, Ma Y, et al. Combined apatite fission-track dating, chlorine and REE content analysis by LA-ICPMS. Sci Bull 2017;62:1497–500.
[32] Zou Y, Chen X, Huang W, et al. Identification of an Early-Middle Jurassic oxidized magmatic belt, south Gangdese, Tibet, and geological implications. Sci Bull 2017;62:888–98.
[33] Wang Y, Zeng L, Gao L, et al. Neoproterozoic magmatism in Eastern Himalayan Terrane. Sci Bull 2017;62:415–24.
[34] Compston W, Williams IS, Kirschvink JL, et al. Zircon U-Pb ages for the early Cambrian time-scale. J Geol Soc London 1992;149:171–84.
[35] Ludwig KR. Users manual for Isoplot/Ex rev. 2.49. Special Publication (1). Berkeley: Berkeley Geochronology Centre; 2001.
[36] Ludwig KR. SQUID version 1.02: A geochronological Toolkit for Microsoft Excel. Special Publication (2). Berkley: Berkley Geochronological Centre; 2001.
[37] Gregory DD, Lyons TW, Large RR, et al. Whole rock and discrete pyrite geochemistry as complementary tracers of ancient ocean chemistry: an example from the Neoproterozoic Doushantuo Formation, China. Geochim Cosmochim Acta 2017;216:201–20.
[38] Jiang G, Shi X, Zhang S. Stratigraphy and paleogeography of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in South China. Gondwana Res 2011;19:831–49.
[39] Sawaki Y, Ohno T, Tahata M, et al. The Ediacaran radiogenic Sr isotope excursion in the Doushantuo Formation in the Three Gorges area South China. Precambrian Res 2010;176:46–64.
[40] Kendall B, Komiya T, Lyons TW, et al. Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late Ediacaran Period. Geochim Cosmochim Acta 2015;156:173–93.
[41] Scott C, Lyons TW, Bekker A, et al. Tracing the stepwise oxygenation of the Proterozoic ocean. Nature 2008;452:159–256.
[42] Gong Z, Kodama KP, Li YX. Rock magnetic cyclostratigraphy of the Doushantuo Formation, South China and its implications for the duration of the Shuram carbon isotope excursion. Precambrian Res 2017;289:62–74.
[43] Williams GE, Schmidt PW. Shuram-Wonoka carbon isotope excursion: Ediacaran revolution in the world ocean's meridional overturning circulation. Geosci Front 2018;9:391–402.

Mingzhong Zhou received his Ph.D. degree at the Institute of Geochemistry, Chinese Academy of Sciences in 2008. He is currently a professor in the School of Geographical and Environmental Sciences, Guizhou Normal University, China. His research interests mainly focus on the discovery and U-Pb zircon geochronology of the K-bentonites in the Ediacaran-Cambrian strata from South China.

(C)1994-2019 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net