Stratigraphic implications of Sinian-Early Cambrian volcanic ash beds on the Yangtze Platform*

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Abstract Volcanic ash beds from shallow- to deep-water facies strata of the Sinian-Early Cambrian (Meishucunian) on the Yangtze Platform consist of bentonites and tuffites which are readily recognized in the field by their physical features and confirmed by geochemical analyses. Geochemistry suggests that the volcanic ash beds in Meishucunian time are rhyolite and rhyodacite while those in the Qiongzhusian and Sinian are andesite and trachyandesite. The ash beds in the time-equivalent strata, even in different areas display rather similar geochemical features, whereas the ash beds in different strata even in the same areas show large chemical difference. The results suggest that these ash beds can be used for intra- and extra-basinal correlations of the Sinian-Early Cambrian interval on the Yangtze Platform. Additionally, these ash beds suggest high potentials for further U-Pb dating strategies.

Keywords: **bentonite, tuffite, volcanism, geochemistry, Sinian, Cambrian, South China.**

The Sinian and Early Cambrian sequences on the Yangtze Platform are widely exposed and well developed in shallow- to deep-water environments. In general, Sinian sections in the Yangtze Gorges area, Hubei Province, represent the type sequence of the Sinian System. There, they unconformably overlie tillites of the Nantuo Formation and comprise the Doushantuo and Dengying formations[1~3]. The Sinian, in turn, is generally unconformably overlain by Early Cambrian sequences. The best-studied shallow-water Lower Cambrian strata are located in eastern Yunnan[4] where they consist of (base to top) the Zhujiaqing, Shiyantou, and Yu'anshan formations. However, although poorly studied, the most complete and continuous Sinian-Early Cambrian sequences are developed in deep-water environments in eastern Guizhou, in western and central Hunan, in southern Anhui, and in western Zhejiang and Jiangxi provinces. These sequences are composed of largely silicified black shales and cherts of the Liuchapo Formation (Guizhou and Hunan) (known as the Piyuanchun Formation in S Anhui) and subsequent black shales of Jiumenchong Formation (E Guizhou) and its equivalents (Xiaoyanxi Fm., Central Hunan; Hetang Fm. and Huangbailing Fm. in S. Anhui). Because biostratigraphic markers do not exist, correlations between shallow- and deep-water facies are extremely difficult and largely speculative, hindering geochemical, tectonic, and paleoenvironmental studies of this critical time period. Here, we present investigations on volcanic ash beds from several Sinian-Early Cambrian sections both in shallow- and deep-water facies. The results provide a valuable tool for intra- and extra-basinal stratigraphic correlation of the Sinian-Early Cambrian interval on the Yangtze Platform.

1 Distribution of the volcanic ash beds

More than a dozen volcanic ash beds are documented from several horizons of the Sinian- earliest Cambrian interval of the Yangtze Platform. Preserved bed thickness ranges from several millimeters to dozens of centimeters. Ash beds occur in the lower part of the Doushantuo Formation[5], at the top of the Doushantuo Formation (e.g. Maoping section near Zigui, Yichang, Hubei Province), in the middle Dengying Formation (e.g. Nanjiang and Changning counties of Sichuan Province, and Taijiang County of Guizhou Province), in the upper member of the Liuchapo Formation (e.g. Songtao County of Guizhou

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Province, and Yuanling County of Hunan Province), in the Zhujiaqing Formation and at the base of the Shiyantou Formation in eastern Yunnan Province[6,7], and in the lower to middle Yu'anshan Formation (e. g. Haikou, Kunming City, Yunnan Province)(Fig. 1). Moreover, basalt horizon occurs in the upper member of the Liuchapo Formation near Taojiang County, Hunan Province[8]; andesite occurs in the lower part of Lechangxia Group (Sinian) in Lianxian County, Guangdong Province[9].

2 Lithology and mineralogy of the volcanic ash beds

The volcanic ash deposits of the Yangtze Platform can be easily recognized in the field because of their light, greenish-gray color, constant lateral thickness, and sharp basal and upper contacts. They can be grouped into two types. One group has been altered to bentonites, which are soft, generally thin-bedded (from several mm to 10 cm), and free of lamination. They feel sticky and soapy to the touch. Y-ray diffraction analyses of the $< 2\mu$-fraction indicate that the dominant clay minerals are illite, mixed-layer illite-smectite, and kaolinite. Some bentonites from the base of the Shiyantou Formation in the Bajie section, Anning County, Yunnan Province also contain hexagonal bipyramidal quartz phenocrysts. The second group consists of tuffite, which is generally more colorful and harder than bentonite in the field. The tuffites are generally laminated and show vacuoles. Platy and cuspate glass shards are common (Fig. 1.1 ~4). According to XRD analyses, the tuffites contain albite, quartz, sanidine, and illite-montmorillonite mixed-layer clay. Except for an occurrence of sandy tuffite in Nanjiang County (Sichuan Province), they are very fine-grained. Grain size and sorting characteristics of the tuffites suggest that they were deposited at considerable distance from the volcanic center.

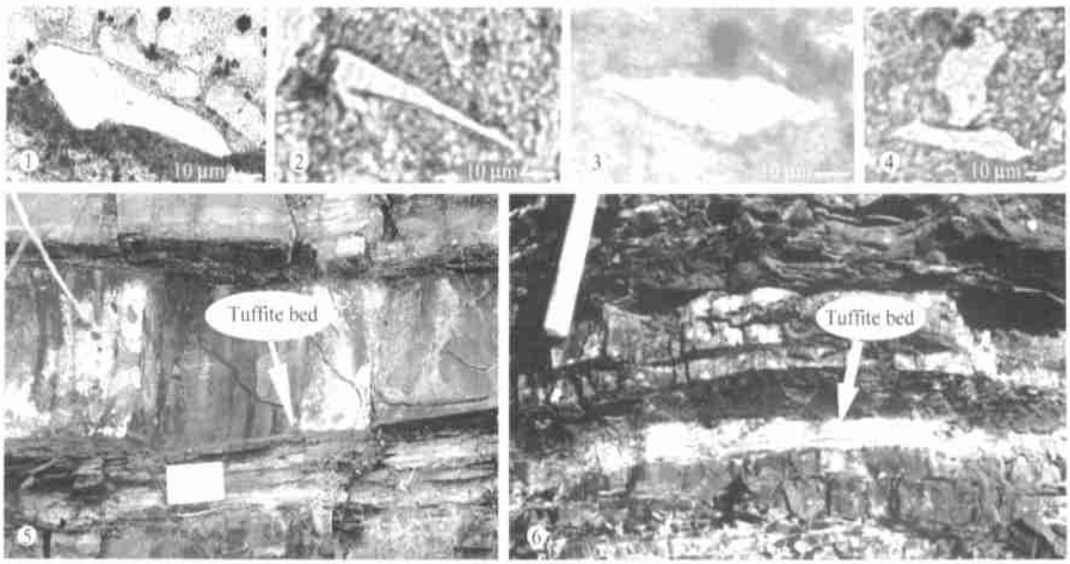

Fig. 1. 1~4. Thin sections (plane light) and outcrop appearance of tuffites of the Pc-C transition, Yangtze Platform. 1, Volcanic glass in sandy tuff of Gaojiashan Mb. of Dengying Formation near Nanjiang County, Sichuan Province; 2, 3, volcanic glass in tuffite-bed at the top of the Doushantuo Formation at Maoping section, Zigui, Hubei Province; 4, volcanic glass in tuffite from upper Mb. of the Liuchapo Formation at Bahuang section, Tongren, Guizhou Province; 5, thin-bedded light grey tuffite at the top of the Doushantuo Formation at Maoping, Zigui County, Hubei Province; 6, light grey, thin-bedded tuffite in upper member of the Liuchapo Formation at Huanglianba section, Songtao County, Guizhou Province.

3 Geochemistry

3.1 Major and trace element geochemistry

In order to confirm the volcanic origin of these ash beds and to distinguish them from surrounding rocks, we selected typical non-volcanic mudstones from adjacent intervals (Yu'anshan Formation; Early Cambrian in eastern Yunnan) as reference samples, because they commonly show lithologic similarity. Surrounding rocks, such as carbonates and cherts, were not analyzed, because of their obvious lithologic differences. Results for major and trace element contents of the volcanic ash layers (analyzed by X-ray fluorescence and ICP-MS methods) as well as the reference non-volcanic mudstones are listed in Table 1. The Al_2O_3 and K_2O contents of most bentonites are higher, while the TiO_2/Al_2O_3 ratio (0.01 ~ 0.009) is lower than that in mudstone (TiO_2/Al_2O_3: 0.04 ~ 0.06%). Trace element concentrations of bentonites and tuffites, particularly ratios of the immobile trace elements (e.g. Zr/Hf), are different from that in the mudstone of the Yu' anshan Formation and argillite[10]. The ratios of Zr/Hf in all bentonites and tuffites are lower than those in the mudstone of the Yu' anshan Formation. As, Sb, Se, and Ba contents from the ash layers are significantly higher than those of the mudstone whereas the contents of siderophile elements (Ni, Co, Fe) from the ash beds are lower than those in the sediments[10].

Table 1. Chemical analyses of Sinian-Earliest Cambrian volcanic ash beds by XRF and ICP-MS

Stratigraphy		Yu	Yu	Shi	Zh	UL	UL	UL	Dy	Dy	Ds	Yu	Yu
Lithology		Bentonites				Tuffites						Mudstone (core)	
Sample		H6	H4	Xi	H1	ST	TR	L14	S	Tn	Mp	M33	M66
Main elements (%)	SiO_2	57.1	58.84	56.5	50.62	54.97	53.83	57	60.16	66.57	67.07	52.4	61
	Al_2O_3	23.1	22.52	19.2	19.72	18.67	22.8	23.8	18.08	16.27	13.61	17.91	15
	CaO	0.07	0.06	0.12	6.81	0.06	0.18	0.03	0.09	0.34	0.22	2.15	1.3
	MgO	1.76	2.01	3.18	3.04	3.43	3.64	3.02	1.74	1.05	2.21	4.84	4.5
	K_2O	4.93	5.64	6.27	5.95	4.89	6	5.46	7.78	3.63	6.46	4.48	4.5
	Na_2O	0.07	0.11		0.06	0.37	0.32	0.1	0.01	0.76	0.06	0.06	1
	P_2O_5	0.09	0.26	0.2	4.25	0.13	0.03	0.08	0.04	0.1	0.18	0.23	0.3
	MnO	0.01	<0.005			<0.005	<0.005	0.005	0.012	0.03	0.008	0.08	0.1
	TiO_2	0.78	0.93	0.25	0.17	0.17	0.24	0.23	0.93	0.95	0.66	0.67	0.9
	Fe_2O_3	3.4	2.66	1.85	1.04	2.38	2.28	0.56	3.56	2.47	3.07	7.98	4.7
	TiO_2/Al_2O_3	0.03	0.04	0.01	0.009	0.009	0.01	0.009	0.05	0.06	0.009	0.04	0.1
Trace elements (pm)	Rb	172	168	118	94	107	162	126	121	108	120	167	136
	Y	33	29	74	86	77	31	30.8	20.7	22	13.9	27	27
	Zr	173	170	335	224	264	155	84	212	239	182	641	435
	Nb	15	15	100	15	44	8	12.3;	15.3	14	13.8	24.6	23
	U	7	11.4	11	23.2	64.8	8	202	1.4	16.5	7.8		
	Th	15	15	27	34	33	18	22.5	5	14	6.4	27	23
	Ba	421	451	1268	972	55550	3405	3553	1005	617	645	445	400
	As	7	19	52	5	188	14	10.2	7.2	8	40.3		
	Se	7.2	2.2		3.6	122.2	2.77	4.3	12.3	5.6	1.4	0.15	1.1
	Hf	5.4	5	16	6	12	14	5.1	6.3	6	4.5	4.4	3.9
	Ni	32	21	25	18	63	22	22.5	6.9	17	3.2	63.3	168
	Co	3	4	6.6	3	3	2	1.7	1.9	3	2.3	22.7	20
	Cr	47	64	43		4		5	110	61	201	111	123
	Zr/Hf	32	34	12.4	37.3	22	11.1	16.5	33.7	39.8	40.4	145.7	112
	Ti/Th	312	371.7	55.5	29.9	30.9	79.9	61.3	1115	406.8	590.6	148.8	236
REE	TREE(ppm)	151	109.7	146	318	452.3	41.6	91.4	111	115.9	19.9	212.2	157
	δCe	0.97	2.57	1.16	1.45	1.22	0.8	1.22	0.65	1.63	0.46	0.87	0.9
	δEu	0.95	1.1	0.22	0.23	0.3	0.63	0.73	0.6	0.84	0.88	0.72	0.7

Ds, Doushantou Formation; Dy, Dengying Formation; UL, Upper Member of the Liuchapo Formation; Zh, Zhongyicun Member of the Zhujiaqing Formation; Ch, Shiyantou Formation; Yu, Yu' anshan Formation. Samples H1, H4, H6: Haikou Town, Kunming City, Yunnan Province; Sample Xi: Xianfeng phosphorite mine, Xundian County, Yunnan Province; Samples ST: Huanglian, Songtao County, Guizhou Province; Samples TR: Bahuang, Tongren County, Guizhou Province; Sample L14: Lijiatou, Yuanling County, Hunan Province; Sample S: Shangliang, Nanjiang County, Sichuan Province; Sample Tn: Nanxiu, Taijiang County, Guizhou Province; Sample Mp: Maoping, Zigui County, Hubei Province.

According to the discrimination diagram of Winchester and Floyd[11,12], except that the non-volcanic mudstone samples is out of diagram, all volcanic ashes from the Sinian to earliest Cambrian on the Yangtze Platform plot in the calc-alkaline suite and range from andesite to rhyodacite and trachyandesite to rhyolite (Fig. 2), indicating their volcanic origins.

Interestingly, the diagram also shows different magmatic sources of these bentonites and turffites (Fig. 2), which seem to be correlated to age. The tuffite from the Dengying Formation and at the top of the Doushantuo Formation appear to be trachyandesitic, the Meishucunian bentonites belong to rhyolites, while tuffites from the upper part of the Liuchapo Formation in Songtao and Yuanling counties

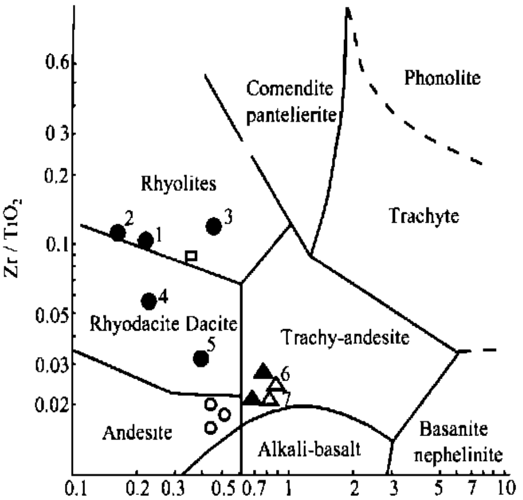

Fig. 2. Samples plotted on the magmatic discrimination diagram (cited from Winchester & Floyd, 1977, Ref. [11]). Open circle, Yu' anshan Fm (Haikou, Kunming); square, Shiyantou Fm (Anning, Kunming); solid circle, Meishucunian (1, Meishucun; 2, Haikou; 3, Songtao; 4, Tongren; 5, Lijiatuo); solid triangle, Dengying Fm (Nanjiang); open triangle, Doushantuo Fm (6, Maoping; 7, Sanhui).

are rhyodacites. But the bentonites in the Lower Cambrian Yu' anshan Formation (Qiongzhusian) are andesites.

3.2 REE geochemistry

The REE contents of the samples were analyzed by ICP-MS, the results are shown in Fig. 3. It can be seen from Fig. 3 that the REE patterns of the ash beds in different intervals differ remarkedly. The REE results suggest that: (1) ΣREE is low with high values of HREE in the tuffites from the Doushantuo Foramtion (Fig. 3(d)), which may indicate existence of zircon grains in these samples that would be used for further U-Pb dating; (2) The chondrite-normalized REE distribution patterns from the bentonites of the lower to middle Yu' anshan Formation (Yunnan) and volcanic ash bed from the Dengying Formation in Taijiang (Guizhou) and Nanjiang (Sichuan) show similar declined curves without Eu anomaly, which may be comparable to Jurassic andesites of China[13] (Fig. 3(a), (b)); (3) Similar high values of ΣREE (452.3 ppm and 318.1 ppm respectively) with pronounced negative Eu anomaly in the ash layers of the upper member of the Liuchapo Formation in Songtao County (Guizhou) and from the middle Zhongyicun Member of Zhujiaqing Formation in Haikou, near Kunming (Yunnan) suggest that these ash beds share similar magmatic origin to bentonite of the Meishucunian[5] (Fig. 3(c)), therefore they can be thought to relate to Meishucunian volcanic events. However, it is noted that the REE distribution pattern of the samples from the upper Liuchapo Formation in Yuanling does not show any negative Eu anomaly (Fig. 3(c)). The results seem against its correlation with Meishucunian ash beds which were suggested by major and trace elements discussed above, and require further investigations.

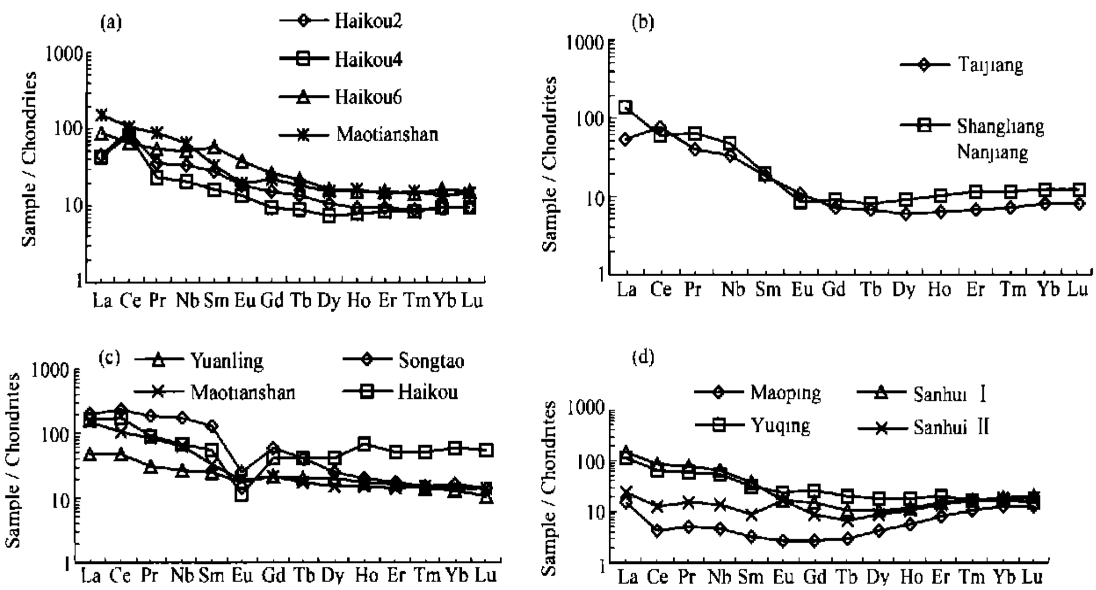

Fig. 3. Chondrite-normalized REE patterns of the volcanic ash beds. (a) Bentonites from the Qiongzhusian at Haikou, Kunming, Yunnan; (b) tuffites from the Gaojiashan Mb. of the Dengying Fm at Nanjiang, Sichuan, and from the Middle Dengying Fm in the section at the west of Taijiang County town; (c) bentonites and tuffites from the Meishucunian in E. Yunnan; (d) tuffites from the Doushantuo Fm at Maoping of Hubei and Sanhui of Guizhou.

In summary, volcanic origin of these Sinian and Early Cambrian ash beds is confirmed by their major, trace element and REE geochemistry. It is likely that the major element characteristics of the volcanic ashes reflect considerable diagenetic and weathering, however, age control on the geochemistry of these ash beds is implied, e.g. similar geochemical features of the Meishucunian bentonite and tuffite in different areas, and different geochemical features of similar bentonite from the Meishucunian and Qiongzhusian strata, suggesting that geochemical variations are closely related with original volcanic sources. Therefore, geochemistry of the ash beds provides a potential tool for extra-basinal stratigraphic correlation. Although geochemistry only provides general nature of these ash beds, the well-preserved volcanic textures, including common preserved outlines of glass shards (Fig. 1) and of lapilli and phenocrysts at Yanwutan and Lijiatou1) suggest that textures can be further used with confidence to constrain their origin.

4 Implications for stratigraphic correlations

Because air-fall volcanic ashes and their altered remnants provide near-ideal chronostratigraphic marker horizons over a wide range of sedimentary environments, they are suitable for stratigraphic refinement and intra- and extra-basinal correlations. In general, the ash beds are powerful markers for intrabasinal correlation. For example, a distinct ash bed which occurs in the Middle part of Dengying Formation and upper part of the Liuchapo Formation is widely recognized in larger area of northeastern Guizhou Province, it can be used as a chronostratigraphic marker for correlation of the Dengying-equivalent strata in this area. Similar correlations using stable and wide distribution of ash beds have been carried out for Meishucunian and Qiongzhusian strata in eastern Yunnan Province[6, 7]. Therefore, our results suggest that more attention on the recognizations of ash beds during field investigation should be addressed for correlations of the Sinian-Cambrian transitional interval on the Yangtze Platform.

Extra-basinal correlation may also be conducted on the basis of geochemistry of these ash beds, such as their chondrite-normalized REE distribution patterns, their Eu anomaly ($\delta Eu = 0.3$), and their comparable trace element concentrations and ratios. Based on all those available data, we propose a correlation for the Sinian-Early Canbrian strata on the Yangtze Platform (Fig. 4). Overall, this correlation suggests that: (1) the volcanic activities are very common during the interval from Sinian to Early Cambrian, particularly the volcanic eruptions occurred widely during the Meishucunian period; (2) the upper part of the Liuchapo Formation in the deep-water facies can be likely correlated to the Meishucunian Zhujiaqing Formation in the shallow-water facies[6, 7], although there may be a slight difference in magmatic sources between the ash beds in the Zhujiaqing (rhyolites) and Liuchapo formations (rhyodacites) (Figs. 2, 3), which would possibly be due to geographic difference; and (3) the lower part of the Liuchapo Formation in Taijiang of Guizhou Province

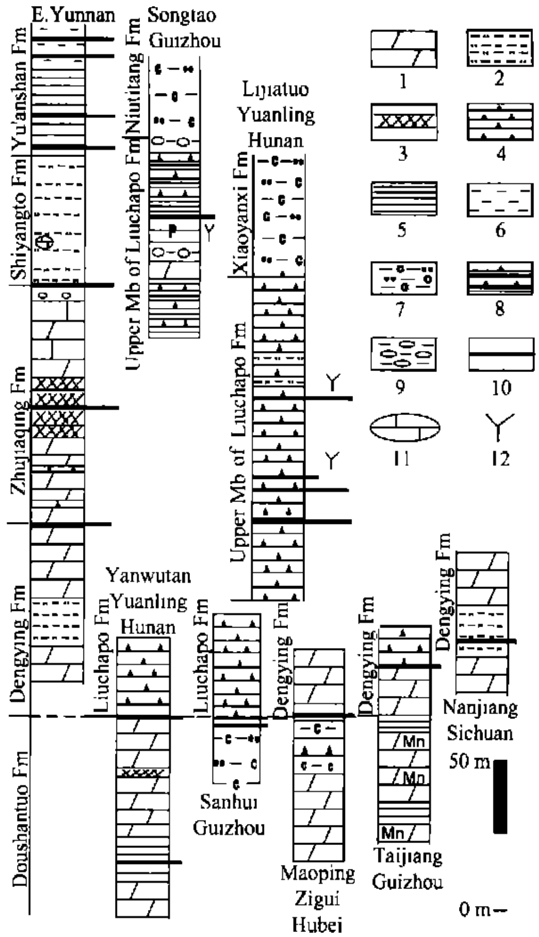

Fig. 4. Stratigraphic correlation of Sinian-Early Cambrian volcanic ash beds of the Yangtze Platform. 1, dolomite; 2, silty mudstone; 3, phosphorite; 4, chert; 5, shale; 6, mudstone; 7, carbonaceous silty mudstone; 8, interbedded thin-bedded chert and carbonaceous shale; 9, nodular phosphorite; 10, volcanic ash beds; 11, lenticular limestone; 12, sponge spicules.

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can also be correlated to the middle part of the Dengying Formation in Nanjiang, Sichuan Province. Mineralogy and stratigraphic occurrence of the ash beds also provide a valuable basis for future U-Pb dating, which can be used to confirm and cross-check the recent Re-Os and Pb-Pb dating of the Sinian-Early Cambrian strata[14, 15]. Precisely geochronological constrains of the strata are very important and can aid palaeotological studies of the Early Cambrian bioradiation.

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