Paleoproterozoic glaciation: Evidence from carbon isotope record of the Hutuo Group, Wutai Mountain area of Shanxi Province, China

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Palaeoproterozoic global glaciation (~2.3 Ga) may have been the first “snowball” Earth event in Earth history. North China has well-exposed sedimentary deposits of this time period with minimal postdepositional alteration. Sedimentary evidence of a glaciation event has been lacking, however. Here we analyzed carbon isotope composition of the Paleoproterozoic Hutuo Group (2.5–2.2 Ga) in the Wutai Mountain area, Shanxi Province, North China. Our data show, in an older to younger chronostratigraphic order, (1) positive $\delta^{13}\text{C}_{\text{carb}}$ values in the Dashiling Formation of the Doucun Subgroup (3.2‰ to 1.0‰, VPDB); (2) a decrease in $\delta^{13}\text{C}_{\text{carb}}$ values from the Wenshan Formation to the middle Daguandong Formation (from 2.0‰ to –1.2‰), during which time the occurrence of stromatolites declined; (3) a pronounced negative excursion in the upper Daguandong Formation, at the boundary of the Daguandong and Huaiyincun formations (from 1.4‰ to –3.3‰), where stromatolites disappeared; and (4) a gradual increase of $\delta^{13}\text{C}_{\text{carb}}$ values in the Beidaxing and Tianpengnao formations (from –1.2‰ to 1.4‰), during which time stromatolites returned. We argue that the negative carbon isotope excursion recorded from the Jian’ancun Formation to the middle Daguandong Formation of the Hutuo Group may have been North China’s response to the Palaeoproterozoic global glaciation.

ice age, carbon isotopes, Hutuo Group, Paleoproterozoic, Wutai Mountain, Shanxi Province

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Stable isotope data have been used widely in reconstructing paleoenvironmental and paleoclimatic changes, especially in the early Earth, where fossil evidence is lacking. Much research progress has been made for this time period, including evaluation of the early Earth’s atmosphere and ocean through studies of the changes in sulfur, carbon and oxygen isotopic compositions [1,2].

Paleoproterozoic (~2.3 Ga) low latitude glacial deposits are well preserved in South Africa (e.g. the Makganyene diamictite) [3], North America (e.g. the Huronian diamictite) [4], and Fennoscandia (Finland, Norway, Sweden and Denmark), suggesting a global glaciation event [2,3]. The cause of this “snowball” Earth event has been linked to the Great Oxidation event [5]. It is believed that the methane-rich

Paleoproterozoic atmosphere may have kept the Earth surface temperature above the freezing point [6], and subsequent increasing in atmospheric oxygen may have reduced methane concentrations, ultimately triggering the Paleoproterozoic global glaciation [4,7].

A Paleoproterozoic succession, spanning from 2.5 to 2.2 Ga, is well exposed in the Wutai Mountain area, Shanxi Province. No diamictite or any distinct glacial sedimentological feature has been reported in the succession, however. If the Paleoproterozoic glaciation was truly global, the Wutai Mountain area in North China should have recorded its signal. Carbon and oxygen isotope measurements have been carried out on Hutuo Group carbonates previously [8,9], interpretation of the data in the context of global glaciation is missing. To look for the stable isotope imprint of a global glaciation event in the Hutuo Group, we collected 205

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carbonate samples from the Hutuo Group and conducted carbon and oxygen isotopic analysis.

1 Geological setting

The Wutai Metamorphic Complex is located between the Fuping and Hengshan metamorphic complexes. Together they constitute the Hengshan-Wutai-Fuping orogen that makes up the middle segment of the Trans-North China Orogen. The Trans-North China Orogen is a narrow, north-east-southwest extending zone, which separates the North China Craton into eastern and western blocks (Figure 1).

The Wutai Metamorphic Complex is a greenstone terrane that consists of tonalitic-trondhjemitic-granodioritic gneisses, granitoids, mafic to felsic volcanic rocks, and metamorphosed volcanic-sedimentary rocks [10]. The Wutai granite-greenstone terrane is mainly composed of the Neoproterozoic Wutai Group and Paleoproterozoic Hutuo Group which comprise subgreenschist facies metasediments and minor mafic volcanics, including quartzites, slates, and metabasalts.

The Hutuo Group is considered the youngest unit in the Hengshan-Wutai-Fuping orogen. It unconformably overlies the Wutai Group, the latter of which interfingers with the Hutuo Group in some areas [10]. The Hutuo Group is distributed in an area of about 1500 km², from northernmost Taihuai-Sijizhuang on the south slope of Wutai Mountain to southernmost Shizui-Dingxiang, and from the upper Taishan River to the east, to Yuanpingqi village in the west. The Hutuo Group also crops out from Daixian to Yuanping and Baishi on the northern slope of Wutai Mountain, as well as in Zhongtai in Fanshi [11].

The Hutuo Group is composed of metamorphic-conglomerate and quartzite at its base, dolostone and marble in central portions, and phyllite and slate interbedded with dolostone in its upper part, representing a complete sedimentary cycle [11]. Although the Hutuo Group succession has locally undergone intense folding and faulting during the younger Lüliang orogeny, many primary structures are well preserved, such as rhythmic bedding, ripple marks and cross bedding, as well as stromatolites in carbonate.

The Hutuo Group is subdivided into the Doucun, Dongye

Figure 1 Geological map of the Wutai Mountain area (modified from Bai [11]).

and Guojiashai subgroups. The Doucun and Dongye subgroups are composed of 11 formations; in ascending order they are: Sijizhuang, Nantai, Dashiling, Qingshicun, Wenshan, Hebiancun, Jian'ancun, Daguandong, Huaiyincun, Beidaxing and Tianpengnao. The Sijizhuang Formation consists mainly of conglomerate, and minor metamorphosed sandstone and mudstone, representing fluvial deposits. The Nantai Formation is characterized by conglomerate, sandstone and limestone, indicating a transition from restricted lagoon to open shelf. The Dashiling Formation is mainly composed of sandstone, shale and limestone, reflecting environmental change from tidal flats to subtidal shallow water conditions. The Qingshicun Formation consists mainly of mudstone, with siltstone and dolomitic limestone interbeds, and basalt at the top of the formation. The Qingshicun Formation is inferred to have been deposited in shoreline or shore delta environments [11]. The Wenshan Formation constitutes sandstone overlain by shale and limestone; whereas, the Hebiancun Formation is characterized by sandstone and limestone, with basalt interbeds at the top. Both the Wenshan and Hebiancun formations were deposited in the tidal zone [11]. The Jian'ancun Formation is mainly composed of thick-bedded dolomitic limestone, which was deposited in tidal zone environments. The Daguandong Formation consists of pink dolomitic limestone interbedded with grayish green slate, representing an open shallow marine environment. The Huaiyincun Formation is characterized by dolomitic limestone with a few stromatolites, indicating a low energy subtidal environment. The Beidaxing Formation is composed of thick-bedded, pink dolomitic limestone, which was deposited in a high energy shallow marine environment. The Tianpengnao Formation is characterized by interbedded, pink calcareous dolostone and shale, with lensoidal dolostone at the top, indicating an intertidal depositional setting.

A basic metavolcanite from the base of the Hutuo Group yields a zircon SHRIMP U-Pb age of 2517 ± 13 Ma. SHRIMP U-Pb zircon ages of 2529 ± 10 Ma and 2553 ± 17 Ma were obtained from two granitic gravels in the Sijizhuang Formation conglomerate. This age range is also confirmed with a SHRIMP zircon age of 2523 Ma from arkose of the Sijizhuang Formation. Therefore, the maximum age of the Hutuo Group is conservatively about 2500 Ma [12].

Meta-basalts from the Qingshicun Formation at the top of the Doucun Subgroup and those from the Hebiancun Formation at the base of the Dongye Subgroup are the best rocks for dating the Hutuo Group. Wu et al. [13] reported a conventional U-Pb zircon age of 2366 ± 94 Ma for Liudingsi basic metavolcanics of the Qingshicun Formation. Wang et al. [14,15] reported SHRIMP U-Pb zircon ages of 2450 ± 10 Ma and 2400 ± 20 Ma for the basic metavolcanics of the Qingshicun and Hebiancun formations, respectively. Therefore, the boundary age of the Dongye Subgroup is about 2350 Ma [12].

In 2003, Wilde et al. [16] reported SHRIMP U-Pb zircon

ages of 2180 ± 5 Ma and 2087 ± 9 Ma for felsic tuffaceous rocks in the Tianpengnao Formation of Dongye Subgroup, near Taihuai in Wutai County. They suggested that the Hutuo Group should be older than 2180 Ma. Therefore, it can be inferred that the minimum age of the Dongye Subgroup is about 2.2 Ga [12].

In summary, the Hutuo Group (excluding the Guojiashai Subgroup) belongs to the early Paleoproterozoic (2.5 to 2.2 Ga). The minimum age of the Doucun Subgroup is about 2350 Ma, and the minimum age of Dongye Subgroup is about 2200 Ma.

Columnar stromatolites occur in carbonate interbeds at the base of the phyllite of the Guquanshan Member, Dashiling Formation, which is considered as the lowermost stromatolite horizon of the Hutuo Group. Stromatolites are abundant in the Wenshan and Hebiancun formations, but decline rapidly in the Jian'ancun Formation, stay at low levels in the Daguandong Formation, and are absent in the Huaiyincun Formation [11]. Upward in the Beidaxing and Tianpengnao formations, stromatolites occur abundantly.

The oldest red beds—grayish red phyllite and slate—appear in the Nantai Formation of the Doucun Subgroup. Red beds also occur in the Beidaxing Formation, and carbonates in the Hutuo Group are mainly red in color. Several meters of a basaltic paleo-weathering crust with clear zonation occurs at the top of the Qingshicun Formation. The $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios in ascending order rise from 0.4 to 15.48 [17]. The occurrence of red beds, stromatolites and weathering crusts suggest that sediments were becoming oxidized during that time period.

2 Methods

We collected samples of micritic limestone, dolomitic limestone, calcareous dolostone and a small quantity of marble from the Doucun and Dongye subgroups at several sections (Table 1). The carbonate-dominated sections were measured and samples of fresh microcrystalline limestone or microcrystalline dolostone without late veins were collected with a sampling interval of 5 to 8 m. In this study, carbon and oxygen isotopic measurements were conducted for 205 samples. CO_2 was extracted using standard offline techniques, where samples were reacted with concentrated H_3PO_4 at 50°C for 12 h [18]. Carbon and oxygen isotopic ratios were determined on a Finnigan MAT 253 mass spectrometer at Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences. Analytical precision is better than 0.1‰ for $\delta^{13}\text{C}$ and 0.1‰ for $\delta^{18}\text{O}$. Isotopic data are reported in ‰ VPDB (Table 2).

3 Results and data evaluation

The carbon isotopic composition of marine carbonate can

Table 1 Sampling horizon and profile position of the Paleoproterozoic Hutuo Group

Sampling horizon			Profile position
Group	Subgroup	Formation	
Hutuo	Dongye	Tianpengnao	Geziling-Luojianao section east of Wutai County
		Beidaxing	Luojianao section, southeast of Wutai
		Huaiyincun	Ma'anshan section near Huaiyin village in Wutai County
		The top of Daguandong	
		Daguandong (excluding the top of it)	Wenshan-Daguanshan section in Dingxiang and Wutai Counties
		Jian'ancun	
		Hebiancun	
		Wenshan	
	Doucun	Dashiling	Xilangshan section in Wutai County
		Pandaoling Member	Guquanshan-Shenxiannao section in Wutai County
Wutai	Taihuai	Baizhiyan	Baizhiyancun section near Taipinggou village, Fanshi County

Table 2 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data of the Paleoproterozoic Hutuo Group

Number	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	Thickness (m)	Number	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	Thickness (m)
H ^{tpn} -27	1.0	-12.4	12979	H ^{bdx} -17	-1.2	-8.7	11446
H ^{tpn} -26	0.8	-12.3	12976	H ^{bdx} -16	-0.9	-6.1	11444
H ^{tpn} -25	1.4	-11.9	12961	H ^{bdx} -15	-0.3	-7.2	11436
H ^{tpn} -24	1.2	-11.1	12944	H ^{bdx} -14	-0.3	-6.3	11425
H ^{tpn} -23	1.2	-10.8	12941	H ^{bdx} -13	-0.3	-7.1	11415
H ^{tpn} -22	1.0	-10.6	12936	H ^{bdx} -12	-0.7	-8.0	11406
H ^{tpn} -21	0.9	-10.7	12933	H ^{bdx} -11	-0.4	-13.3	11399
H ^{tpn} -20	0.9	-10.7	12928	H ^{bdx} -10	-0.0	-6.7	11374
H ^{tpn} -19	0.4	-10.8	12921	H ^{bdx} -9	-0.0	-6.4	11367
H ^{tpn} -18	0.4	-10.7	12911	H ^{bdx} -8	0.1	-7.1	11363
H ^{tpn} -17	0.1	-10.5	12901	H ^{bdx} -7	0.0	-7.1	11357
H ^{tpn} -16	0.7	-10.8	12889	H ^{bdx} -6	-0.3	-7.1	11356
H ^{tpn} -15	0.5	-10.6	12871	H ^{bdx} -5	-0.4	-7.1	11352
H ^{tpn} -14	1.1	-10.6	12861	H ^{bdx} -4	-0.4	-6.5	11316
H ^{tpn} -13	1.0	-10.4	12846	H ^{bdx} -3	-0.3	-7.4	11308
H ^{tpn} -12	1.2	-10.3	12839	H ^{bdx} -2	-0.3	-7.2	11298
H ^{tpn} -11	1.2	-10.5	12835	H ^{bdx} -1	-0.2	-7.1	11275
H ^{tpn} -10	1.1	-10.4	12834	H ^{hyc} -21	-2.5	-8.9	10551
H ^{tpn} -9	1.2	-10.4	12829	H ^{hyc} -20	-2.5	-8.9	10548
H ^{tpn} -8	1.1	-10.6	12777	H ^{hyc} -19	-2.4	-8.2	10539
H ^{tpn} -7	0.3	-10.8	12772	H ^{hyc} -18	-2.3	-8.2	10527
H ^{tpn} -6	0.0	-11.3	12767	H ^{hyc} -17	-2.0	-8.7	10510
H ^{tpn} -5	0.1	-11.7	12760	H ^{hyc} -16	-2.0	-10.4	10499
H ^{tpn} -4	1.0	-9.7	12742	H ^{hyc} -15	-0.8	-5.9	10484
H ^{tpn} -3	0.8	-9.7	12733	H ^{hyc} -14	-0.7	-7.7	10477
H ^{tpn} -2	-0.9	-9.3	12694	H ^{hyc} -13	-0.8	-5.9	10460
H ^{tpn} -1	-0.6	-11.4	12688	H ^{hyc} -12	-1.2	-7.6	10448
H ^{bdx} -30	-0.9	-8.0	12464	H ^{hyc} -11	-0.8	-6.5	10433
H ^{bdx} -29	-0.7	-7.6	12461	H ^{hyc} -10	-1.6	-6.1	10424
H ^{bdx} -28	-0.6	-6.4	12458	H ^{hyc} -9	-1.7	-9.3	10416
H ^{bdx} -27	-0.6	-6.4	12455	H ^{hyc} -8	-2.0	-7.9	10404

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Number	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	Thickness (m)	Number	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	Thickness (m)
H ^{bdx} -26	-0.5	-6.9	12452	H ^{hyc} -7	-2.0	-8.2	10396
H ^{bdx} -25	-0.3	-7.0	12449	H ^{hyc} -6	-2.2	-8.8	10371
H ^{bdx} -24	-0.3	-6.0	12446	H ^{hyc} -5	-3.3	-9.4	10347
H ^{bdx} -23	-0.4	-6.3	11486	H ^{hyc} -4	-3.2	-9.4	10345
H ^{bdx} -22	-0.9	-7.1	11478	H ^{hyc} -3	-3.3	-10.2	10342
H ^{bdx} -21	-0.7	-6.5	11470	H ^{hyc} -2	-3.1	-9.7	10335
H ^{bdx} -20	-0.8	-6.7	11466	H ^{hyc} -1	-2.1	-9.3	10327
H ^{bdx} -19	-0.2	-6.3	11456	H ^{dgd} -53	-0.2	-6.9	10318
H ^{bdx} -18	-1.1	-6.7	11451	H ^{dgd} -52	1.3	-9.5	10307
H ^{dgd} -51	1.2	-9.8	10291	H ^{dgd} -9	-0.8	-7.6	9367
H ^{dgd} -50	0.9	-9.7	10265	H ^{dgd} -8	-0.9	-7.8	9358
H ^{dgd} -49	-2.7	-6.6	10252	H ^{dgd} -7	-0.9	-7.8	9295
H ^{dgd} -48	-2.0	-7.0	10246	H ^{dgd} -6	-0.2	-9.1	9277
H ^{dgd} -47	-3.3	-10.5	10220	H ^{dgd} -5	-0.2	-6.6	9266
H ^{dgd} -46	-3.3	-7.1	10208	H ^{dgd} -4	-0.3	-7.5	9252
H ^{dgd} -45	0.4	-11.3	10189	H ^{dgd} -3	0.9	-10.2	9247
H ^{dgd} -44	0.2	-11.0	10173	H ^{dgd} -2	0.6	-9.6	9235
H ^{dgd} -43	-1.2	-13.2	10152	H ^{dgd} -1	-0.1	-7.7	9228
H ^{dgd} -42	0.4	-10.6	10139	H ^{jac} -28	-0.9	-9.3	8148
H ^{dgd} -41	0.5	-10.2	10138	H ^{jac} -27	-1.3	-7.7	8145
H ^{dgd} -40	1.4	-9.8	10124	H ^{jac} -26	-1.2	-8.4	8134
H ^{dgd} -39	0.3	-9.8	10118	H ^{jac} -25	1.1	-7.9	8122
H ^{dgd} -38	0.1	-9.8	10106	H ^{jac} -24	-0.5	-7.5	8115
H ^{dgd} -37	0.3	-10.2	10097	H ^{jac} -23	-0.5	-6.6	8114
H ^{dgd} -36	0.2	-10.6	10084	H ^{jac} -22	-0.4	-6.7	8111
H ^{dgd} -35	0.2	-10.6	10070	H ^{jac} -21	-0.6	-6.6	8105
H ^{dgd} -34	0.2	-11.2	10061	H ^{jac} -20	-0.4	-6.2	8101
H ^{dgd} -33	0.1	-11.1	10055	H ^{jac} -19	-0.8	-8.1	8097
H ^{dgd} -32	-0.3	-9.1	10046	H ^{jac} -18	0.2	-8.1	8095
H ^{dgd} -31	-0.2	-7.1	10029	H ^{jac} -17	0.4	-7.2	8094
H ^{dgd} -30	-0.1	-6.9	10025	H ^{jac} -16	0.4	-7.3	8093
H ^{dgd} -29	1.4	-10.0	10018	H ^{jac} -15	0.8	-7.2	8091
H ^{dgd} -28	0.8	-9.3	10014	H ^{jac} -14	0.0	-6.4	8089
H ^{dgd} -27	0.4	-9.9	9741	H ^{jac} -13	1.1	-7.7	8086
H ^{dgd} -26	1.5	-7.4	9724	H ^{jac} -12	0.1	-6.8	8078
H ^{dgd} -25	0.0	-6.6	9708	H ^{jac} -11	0.1	-9.9	8075
H ^{dgd} -24	1.1	-8.7	9700	H ^{jac} -10	0.2	-10.7	8072
H ^{dgd} -23	1.1	-7.2	9692	H ^{jac} -9	0.0	-10.3	8055
H ^{dgd} -22	1.0	-8.3	9685	H ^{jac} -8	0.0	-10.0	8052
H ^{dgd} -21	1.0	-8.4	9672	H ^{jac} -7	0.0	-9.7	8051
H ^{dgd} -20	1.1	-8.4	9660	H ^{jac} -6	0.0	-10.4	8040
H ^{dgd} -19	1.2	-8.0	9649	H ^{jac} -5	0.1	-10.2	8039
H ^{dgd} -18	0.5	-8.0	9460	H ^{jac} -4	0.4	-8.0	8035
H ^{dgd} -17	0.2	-6.8	9454	H ^{jac} -3	0.4	-8.1	8030
H ^{dgd} -16	0.4	-7.8	9442	H ^{jac} -2	0.4	-7.4	8025
H ^{dgd} -15	0.3	-9.5	9433	H ^{jac} -1	0.2	-10.1	8020

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Number	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	Thickness (m)	Number	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	Thickness (m)
H ^{dgd} -14	-0.5	-7.4	9426	H ^{ndx} -7	2.8	-7.1	5771
H ^{dgd} -13	0.4	-7.7	9410	H ^{ndx} -6	2.5	-6.7	5762
H ^{dgd} -12	-0.9	-7.4	9392	H ^{ndx} -5	2.5	-6.9	5753
H ^{dgd} -11	-0.8	-8.1	9384	H ^{ndx} -4	1.7	-8.2	5741
H ^{dgd} -10	-0.9	-8.1	9373	H ^{ndx} -3	1.5	-8.9	5721
H ^{hbc} -1	-0.2	-6.9	7813	H ^{ndx} -2	2.0	-9.7	5709
H ^{ws} -7	0.1	-9.3	7365	H ^{ndx} -1	1.0	-10.7	5708
H ^{ws} -6	0.3	-9.2	7356	H ^{pdl} -5	2.2	-13.0	5016
H ^{ws} -5	1.1	-9.2	7344	H ^{pdl} -4	1.3	-13.3	4957
H ^{ws} -4	1.4	-10.7	7336	H ^{pdl} -3	1.8	-13.1	4954
H ^{ws} -3	0.7	-9.8	7320	H ^{pdl} -2	2.9	-13.0	4876
H ^{ws} -2	1.1	-9.7	7307	H ^{pdl} -1	3.2	-13.0	4873
H ^{ws} -1	2.0	-9.5	7292	W ^{bzy} -8	0.9	-19.0	559
H ^{ndx} -20	2.0	-8.9	5848	W ^{bzy} -7	-0.9	-18.4	542
H ^{ndx} -19	2.4	-7.7	5840	W ^{bzy} -6	0.3	-24.0	541
H ^{ndx} -18	2.0	-8.9	5835	W ^{bzy} -5	-2.7	-22.0	514
H ^{ndx} -17	2.7	-7.6	5827	W ^{bzy} -4	-2.8	-20.2	463
H ^{ndx} -16	2.5	-7.1	5821	W ^{bzy} -3	-3.3	-21.2	328
H ^{ndx} -15	2.6	-7.4	5819	W ^{bzy} -2	-2.8	-19.8	325
H ^{ndx} -14	2.3	-8.4	5811	H ^{hbc} -6	1.0	-9.2	7955
H ^{ndx} -13	2.6	-6.9	5805	H ^{hbc} -5	1.7	-7.8	7928
H ^{ndx} -12	2.6	-6.4	5798	H ^{hbc} -4	0.1	-9.4	7909
H ^{ndx} -11	2.4	-7.2	5794	H ^{hbc} -3	0.8	-8.1	7885
H ^{ndx} -10	2.7	-5.6	5789	H ^{hbc} -2	0.9	-6.6	7859
H ^{ndx} -9	2.4	-8.8	5785	W ^{bzy} -1	-4.1	-28.7	306
H ^{ndx} -8	2.9	-6.6	5779				

undergo alteration during post-depositional processes, including early diagenesis, late diagenetic rock-fluid exchange, hydrothermal activities, and metamorphism. The extent of carbon isotopic post-depositional changes [19] may be estimated by evaluating degree of crystallization, with finer grained microcrystalline limestone indicating minimal alteration. Similarly, weathered samples with later veins or diagenetic cementation are not suitable for isotopic measurement. Furthermore, samples with $\delta^{18}\text{O}$ values $< -10\text{‰}$

have likely experienced considerable diagenetic alteration. Samples with no correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values probably did not experience significant diagenetic alteration. The samples utilized in this study were fresh microcrystalline limestone or microcrystalline dolostone without later veins. Most samples yielded $\delta^{18}\text{O}$ values more positive than -10‰ (Table 2) and showed no apparent correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Figure 2), suggesting that $\delta^{13}\text{C}$ values may not have undergone significant post-

Figure 2 $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot of carbonate samples of the Paleoproterozoic Hutuo Group.

depositional alteration.

The variation of carbon isotope composition in the Paleoproterozoic Hutuo Group (2.5 to 2.2 Ga) can be divided into four parts from older to younger ages (Figure 3): (1) positive $\delta^{13}\text{C}_{\text{carb}}$ values in the Dashiling Formation carbonates of the Doucun Subgroup (3.2‰–1.0‰, VPDB); (2) a decrease in $\delta^{13}\text{C}_{\text{carb}}$ values from the Wenshan Formation to the middle of the Daguan Dong Formation (from 2.0‰ to –1.2‰); (3) a pronounced negative $\delta^{13}\text{C}$ excursion in the upper Daguan Dong Formation and at the boundary of the Daguan Dong and Huaiyincun formations (from 1.4‰ to –3.3‰); and (4) a gradual increase of $\delta^{13}\text{C}_{\text{carb}}$ values in the Beidaxing and Tianpengnao formations (from –1.2‰ to 1.4‰).

4 Discussion and conclusions

Both the Paleoproterozoic and Neoproterozoic witnessed the assembly and breakup of supercontinents [5], as well as extensive glaciations [4], which were associated with extreme carbon isotope variations [20]. Before glaciation, the marine carbonates have been shown to be enriched in ^{13}C , and after glaciation, depleted ^{13}C [20]. A large numbers of work on Neoproterozoic glaciation may serve as an analog for the study of the Paleoproterozoic one.

Changes of carbon isotope compositions of marine carbonate and paleoclimate are believed to have been associated with plate tectonic and mantle plume events [21]. A Paleoproterozoic superplume was active between 2.51 to 2.45 Ga [5], during which time the upper mantle and lithosphere were heated up from beneath. Many basaltic eruptions produced oceanic plateaus, and thereby elevated sea level [21]. Volcanic eruptions and associated extensive hydrothermal activity released both CO_2 and reductive gases into the atmosphere-ocean system. The greenhouse effect of increased atmospheric CO_2 thus intensified continental weathering rates. Enhanced weathering and hydrothermal activity brought a large amount of nutrients into the ocean, which combined with the warm ocean water, evidently increased the ocean productivity initially. In general, organic matter burial is enhanced by sea-level rise and the expansion of anoxic waters [21]. Thus it can be seen that the Paleoproterozoic superplume event may have promoted the formation and deposition of organic carbon. An increase in burial rate of organic matter thus resulted in positive carbon isotope values in pre-glacial carbonates, corresponding to the high positive carbon isotope value in the Dashiling Formation ($\delta^{13}\text{C}_{\text{carb}}$ values range from 3.2‰ to 1.0‰) (Figure 3).

Concentration of atmospheric O_2 increased and probably reached $\sim 10^{-5}$ PAL (present atmosphere level) at around 2.4 Ga [5]. The rise of atmospheric oxygen decreased atmospheric methane concentration [4]. Meanwhile, increasing fixation of atmospheric CO_2 into rock (carbonates) via

Figure 3 $\delta^{13}\text{C}$ profile of the Paleoproterozoic Hutuo Group (zircon ages from Wu et al. [12,13] and Wilde et al. [16]). 1, Quartzite; 2, metaconglomerate; 3, breccia; 4, schist; 5, greenschist; 6, shale; 7, marble; 8, dolomite; 9, metavolcanics; 10, samples with $\delta^{18}\text{O} > -10\text{‰}$; 11, samples with $\delta^{18}\text{O} < -10\text{‰}$.

growth of stromatolites may also have helped the drawdown of greenhouse gas, an important trigger for global glaciation. A global cold climate depressed oceanic primary productivity and burial of organic matter [22], and accordingly resulted in the negative carbon isotope excursion seen in marine carbonates of this time period. A negative carbon isotopic excursion occurs from the Wenshan Formation upward ($\delta^{13}\text{C}_{\text{carb}}$ values shift from 2.0‰ to -1.2‰), and $\delta^{13}\text{C}_{\text{carb}}$ values fluctuate around 0‰ from the Jian'ancun Formation to the middle of the Daguan Dong Formation.

During the glaciation and transition to an interglacial period, massive release of CO_2 from oceanic ridges [23] and methane release from shelf and slope settings [22] into atmosphere-ocean system finally triggered the termination of the glaciation. Organic matter in the deep oceans was oxidized via bacterial sulfate reduction to ^{13}C -depleted HCO_3^- , possibly driven by post-glacial invigoration of deep circulation. The ^{13}C -depleted, dissolved inorganic carbon was incorporated into the surface ocean, contributing to the negative $\delta^{13}\text{C}_{\text{carb}}$ values recorded in the micritic carbonates [22]. The pronounced negative carbon isotope excursion at the boundary of the Daguan Dong and Huaiyincun formations (2.35 to 2.2 Ga) ($\delta^{13}\text{C}_{\text{carb}}$ values shift from 1.4‰ to -3.3‰) is here considered to record this process. The negative carbon isotope shift resembles that of cap carbonates in the aftermath of the Neoproterozoic glaciation [22]. Thus, the Paleoproterozoic global glaciation occurred right before this negative excursion.

Negative $\delta^{13}\text{C}_{\text{carb}}$ values range from -3‰ to -1‰ at the boundary of the Daguan Dong and Huaiyincun formations, which is consistent with previously reported data by Zhong and Ma [8] and the data from the Huronian Supergroup ($\delta^{13}\text{C}_{\text{carb}}$ -1.3±0.5‰) [24]. The present data show less pronounced negative values than those from carbonate cements of the Makganyene Formation diamictite in South Africa ($\delta^{13}\text{C}_{\text{carb}}$ values: -15‰ to -3‰) [25]. Although no diamictite occurs in the Wutai Mountain area, North China, the present study suggests that the negative carbon isotope excursion at the boundary of the Jian'ancun and Daguan Dong formations, Hutuo Group, may be a response to the Paleoproterozoic worldwide glaciation.

A later positive carbon isotope shift (2.2 to 2.06 Ga) may be related to post-glacial warm conditions and the breakup of the supercontinent Kenorland [26]. A post-glacial greenhouse condition would have been favorable to planktonic blooms, resulting in increase of oceanic primary productivity and burial of organic matter. The breakup of the supercontinent Kenorland at 2.1 to 2.0 Ga [27] produced many epicontinental shallow sea environments, which provided more living space for organisms. As discussed above, the increase of oceanic primary productivity and burial rate of organic matter may have resulted in the positive shift of carbonate carbon isotope values, i.e. the positive shift of $\delta^{13}\text{C}_{\text{carb}}$ values from the Beidaxing to Tianpengnao for-

mations (from -1.2‰ to 1.4‰).

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