Article
Chinese Science Bulletin

Geology

November 2012 Vol.57 No.33: 4356–4362
doi: 10.1007/s11434-012-5465-8

Detrital zircon of 4.1 Ga in South China

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Received June 26, 2012; accepted August 15, 2012; published online September 25, 2012

One hadean zircon from the Cambrian sandstone in the southern part of South China has a U-Pb age of 4107±29 Ma with $\varepsilon_{Hf}(t)$ value similar to that of the homochronous depleted mantle and Hf model age of 4102±21 Ma. This demonstrates the existence of hadean crustal remnant in South China. A close match between the U-Pb age and Hf model age with the highly position $\varepsilon_{Hf}(t)$ value indicates the growth and immediate reworking of juvenile crust from the depleted mantle at ca 4.1 Ga. The prominent "Pan-African" and Grenville zircons derived from the exotic sources were also found in the sample, which indicates a linking between South China and Gondwana in the Cambrian period. The southern part of South China has complex histories of crustal growth and tectonic evolution.

detrital zircon, 4.1 Ga, Cambrian, South China

Citation: Xu Y J, Du Y S, Huang H W, et al. Detrital zircon of 4.1 Ga in South China. Chin Sci Bull, 2012, 57: 4356–4362, doi: 10.1007/s11434-012-5465-8

The formation and evolution of early crust are of great significance to the process and mechanism of continental generation. U-Pb age of zircon combined with its Hf isotope composition has been proved to be a robust tool to understand this process. Up till now, most zircons with age of > 4.0 Ga have been found in the Yilgarn Craton of Western Australia [1–4]. The oldest zircon in the Eurasia is a detrital grain with SHRIMP U-Pb age of 4.1 Ga in quartz schist from Pulan County in Tibet, although depositional time retains unknown [5]. A 4.1 Ga xenocrystal zircon from Ordovician volcanic rocks was found in western part of the North Qinling Orogenic Belt [6]. Detrital zircons and rocks as old as 3.8 Ga were also reported using SHRIMP U-Pb dating in the Anshan area in North China [7,8]. The oldest zircon in South China is preserved in the sandstone from the Liantuo Formation in Yichang, Hubei Province, with a U-Pb age of 3.8 and 4.0 Ga for two-stage Hf model age [9]. Here, a detrital zircon with a U-Pb age of 4.1 Ga in the Cambrian sandstone from the West Daming Mountain in Guangxi Province, South China, is reported. It is the oldest zircon in South China up to now.

1 Location and description of sample

Sample was collected from the West Daming Mountain in the western part of Nanning City, Guangxi Province, where tectonically belong to the Cathaysia Block, the South China Craton (Figure 1a, b). The exposed strata in the West Daming Mountain are the Lower Cambrian Xiaoneichong and Middle-Upper Cambrian Huangdongkou formations. Contact is conformable. The Xiaoneichong Formation is composed mainly of mid-thick pale-green quartz sandstone interbedding with mudstone, with the volume of mudstone increasing upwards. The Huangdongkou Formation consists mainly of pale-green quartz sandstone intercalated with mudstone. The succession is overlain unconformably by the Lower Devonian Lianhuashan Formation. Sample 11FS-3 from the Xiaoneichong Formation is a pale-green quartz sandstone with the angular, variable grain texture. It contains

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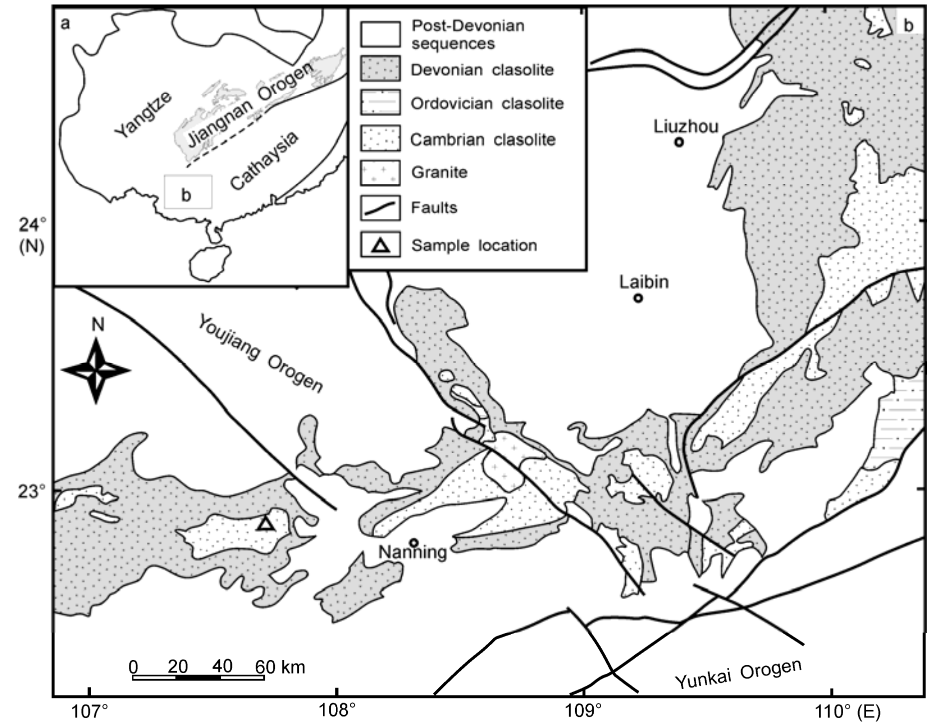

Figure 1 Outcrop distribution of strata and sampling location. Inset shows position of the study area.

85.7% quartz, 5% feldspar and 9.3% lithic fragments.

2 Analytical methods

Zircons were separated by conventional heavy liquid and magnetic techniques. Grains were selected under a binocular microscope and mounted in epoxy resin, sectioned approximately in half, polished. All analyses in this study were conducted at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan. Cathodoluminescence (CL) images, taken on a JXA-8100 with attached Gatan CL, were used to decipher the internal structures and origin of the sectioned grains and to guide U-Pb dating and Hf isotope analysis. Zircon U-Pb dating was conducted by an Agilent 7500a laser inductively coupled plasma mass spectrometer (LA-ICP-MS). Laser sampling was performed using an excimer laser ablation system (GeoLas 2005). Detailed operating conditions follow the documents [10–12]. Zircon 91500 was used as external standard for age calculation and re-analyzed twice after every 5 analyses of the unknowns. Off-line selection and integration of background and analyte signals, and time-drift correction and quantitative calibration for trace element analyses and U-Pb dating were performed by ICPMSDataCal [10,11]. Time-dependent drifts of U-Th-Pb isotopic ratios were corrected using a linear interpolation (with time) according to variations of the standard 91500 [11]. Preferred U-Th-Pb isotopic ratios used for 91500 are from the document [13]. Common Pb correction was not performed as signal of measured ^{204}Pb is low and U-Pb ages are concordant or nearly concordant. Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 [14].

Zircon Hf isotope analysis was carried out *in situ* using a Neptune MC-ICP-MS. The instrumental conditions and data acquisition were described by the documents [15]. The analyses were conducted with a beam diameter of 44 μm, a hit rate of 6 Hz. Analytical spots were located close to or on the top of LA-ICP-MS spots or in the same growth domain as inferred from CL images. The ^{176}Lu and ^{176}Yb interferences on ^{176}Hf were subtracted using the signals of ^{175}Lu and ^{173}Yb and values of 0.02656 for ^{176}Lu/^{175}Lu [16] and 0.7876 for ^{176}Yb/^{173}Yb [17]. To monitor the accuracy of this correction, every 9 sample analyses were followed by analysis of 91500 and GJ-1 as reference zircons. During the analysis, the standard zircons gave 0.282303±8 (n = 15, 1σ) for 91500 with the recommended ^{176}Hf/^{177}Hf ratios of 0.282308 ± 6 [18] and 0.282009±6 (n = 15,1σ) for GJ-1 with ^{176}Hf/^{177}Hf ratios of 0.282015 ± 19 [19], respectively. The decay constant for ^{176}Lu of 1.865×10-11a-1 was adopted [20]. $\varepsilon_{\rm Hf}(t)$ value was calculated relative to the chondritic reservoir with a ^{176}Hf/^{177}Hf ratio of 0.282772 and ^{176}Lu/^{177}Hf of 0.0332 [16]. Single-stage Hf model ages ($T_{\rm DM}$) were calculated by reference to depleted mantle with present-day ^{176}Hf/^{177}Hf ratio of 0.28325 and ^{176}Lu/^{177}Hf ratio of 0.0384 [21]. Two-stage Hf model ages ($T_{\rm DM2}$) were calculated by assuming a mean ^{176}Hf/^{177}Hf value of 0.015 for the average continental crust [22], except that Two-stage Hf model ages of zircon with the age of 4.1 Ga was calculated by assuming a mean ^{176}Hf/^{177}Hf value of 0.022 for the average lower continental crust [23]. The model ages (T_{DM}) were taken for positive $\varepsilon_{Hf}(t)$ values, and two-stage Hf model ages (T_{DM2}) were taken for negative $\varepsilon_{Hf}(t)$ values [24].

3 Zircon origin, U-Pb ages and Hf isotopes

Zircon grains are colorless to purple-red and most are subhedral crystals with prisms partially abraded. CL images show simple oscillatory zoning (Figure 2a, b, g, i), oscillatory zoned grain imposed with igneous sector zoning (Figure 2d, e) and a core with oscillatory zoning enveloped by a metamorphic rim lacking internal structure (Figure 2c, f, h, j). Due to their narrow width of the metamorphic rim, zircons displaying multiple internal structures were analyzed in the core region. Th/U ratios of grains range from 0.2 to 1.2, consistent with a magmatic origin [25].

A total of 48 analyses were undertaken and zircon U-Pb isotopic compositions are presented in Table 1. Uncertainties on individual analyses in the data table and concordia plots are presented at 1σ. All analyses are shown on concordia plots (Figure 3); however, analyses that show greater than 10% discordance were not included in frequency diagrams (Figure 4), and ages less than 1000 Ma are based on the ^{206}Pb/^{238}U ratio whereas older ages are based on the ^{206}Pb/^{207}Pb ratio. The concordant ages demonstrate a wide span, ranging from 4107±29 Ma to 513±8 Ma. Among them, 6 ages range from 2.8 to 2.3 Ga. The rest are grouped into age ranging from 1.8 to 0.5 Ga, with two prominent peaks of ages, namely, between 1.0 and 0.9 Ga, and between 1.3 Ga and 1.0 Ga, respectively. Scattered ages also occur at the two sides of peaks, including 11 grains from 1.7 Ga to 1.3 Ga and 12 grains from 0.8 Ga to 0.5 Ga (Figure 4).

In-situ Lu-Hf isotope analyses were carried out on the zircon with the age of 4.1 Ga and 25 grains with the ages ranging from 1.4 to 0.9 Ga. Zircon Lu-Hf isotope compositions are listed in Table 2 and Figure 5. The single-stage and two-stage Hf model ages of zircon with U-Pb age of 4107±29 Ma are 4102±42 Ma and 4098±63 Ma, respectively. The $\varepsilon_{Hf}(t)$ values of zircons with ages ranging from 1.4 to 0.9 Ga are from −15.6 to +12.2 and their Hf model ages range from 2.9 to 1.1 Ga, suggesting that sources suffered the important episodes of juvenile crust growth and ancient crust reworking in the Mid-Neoproterozoic period.

4 Discussion and conclusions

The South China Craton consists of the Yangtze Block to the northwest and the Cathaysia Block to the southeast. The two blocks were amalgamated during the early Neoproterozoic along the Jiang-Shao suture zone associated with the formation of the Jiangnan orogen (Figure 1a). The previous studies document that the oldest zircon with a U-Pb age of 3.8 Ga and model Hf ages of 3.96 to 4.00 Ga is preserved in the sandstones from the Liantuo Formation in the Yangtze Gorge, suggesting presence of the Eoarchean crustal remnant in the Yangtze Block, with possible crustal growth as early as late Hadean [9]. A lot of detrital zircons with ages from 3.5 to 2.9 Ga are reported in the Yangtze Block [9,26–31]. In addition, Gao et al. [32] and Jiao et al. [33] dated granitoid gneiss from the Kongling area as the oldest rock with U-Pb age of 3.3–3.2 Ga in the Yangtze Block. The magmatic zircons in these rocks have two-stage Hf model ages of 3.7–3.4 Ga, indicating that the rocks were derived from partial melting of Eoarchean crust. These evidences from rocks and detrital sediments jointly suggest that the Eoarchean crust remnants are preserved in the Yangtze Block. The oldest rock in the Cathaysia Block is named as the Badu Group with an age range from 1.9 to 1.8 Ga in southeastern Zhejiang and northwestern Fujian provinces [34–36], prominently younger than that in the Yangtze Block. However, the group contains the detrital zircon with

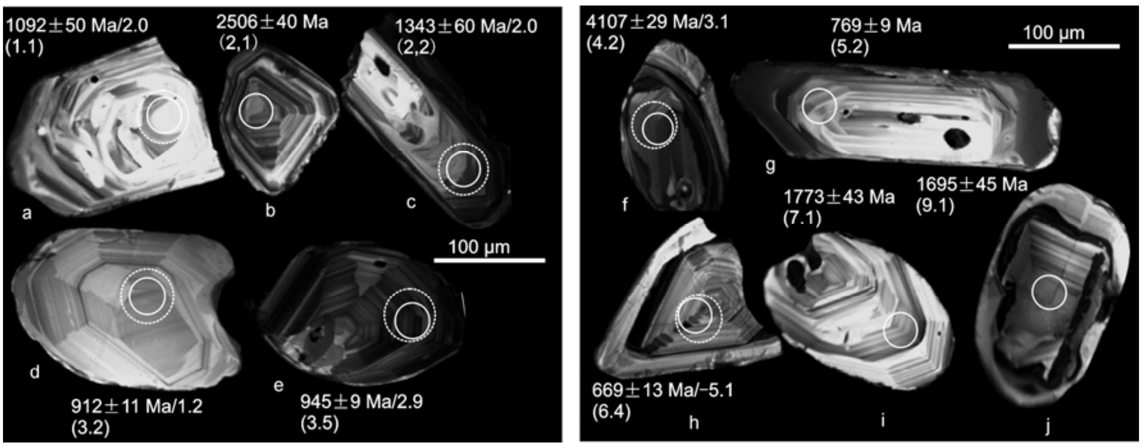

Figure 2 CL images of representative zircons from the Cambrian sandstone in West Daming Mountain, Guangxi, showing main types of internal structures within zircon grains. Solid circles denote U-Pb analysis spot and dashed circles denote Lu-Hf analysis spot. Spot numbers are denoted in brackets.

Table 1 LA-ICP-MS detrital zircon U-Pb isotope data for the Cambrian sandstone (11FS-3) in West Daming Mountain, Guangxi[a)]

Spot	^{207}Pb/^{206}Pb		^{207}Pb/^{235}U		^{206}Pb/^{238}U		^{207}Pb/^{206}Pb		^{207}Pb/^{235}U		^{206}Pb/^{238}U		Concordance
	Ratio	1σ	Ratio	1σ	Ratio	1σ	Age (Ma)	1σ	Age (Ma)	1σ	Age (Ma)	1σ	(%)
1.1	0.0759	0.0019	2.0084	0.0481	0.1899	0.0019	1092	50	1118	16	1121	10	99
1.2	0.0663	0.0013	0.9223	0.0185	0.0994	0.0009	817	42	664	10	611	5	91
1.3	0.0747	0.0020	1.9769	0.0540	0.1895	0.0023	1061	54	1108	18	1119	12	98
1.4	0.1607	0.0032	10.6352	0.2158	0.4729	0.0049	2463	35	2492	19	2496	22	99
2.1	0.1649	0.0039	10.9253	0.2532	0.4748	0.0061	2506	40	2517	22	2505	26	99
2.2	0.0862	0.0027	2.6115	0.0743	0.2175	0.0028	1343	60	1304	21	1269	15	97
2.3	0.0796	0.0034	1.9666	0.0825	0.1827	0.0061	1187	87	1104	28	1082	33	97
2.4	0.2028	0.0052	13.9780	0.3518	0.4963	0.0075	2849	41	2748	24	2598	32	94
2.5	0.0738	0.0017	1.6797	0.0373	0.1630	0.0016	1039	46	1001	14	974	9	97
3.1	0.0641	0.0022	0.8565	0.0307	0.0959	0.0013	746	42	628	17	590	7	93
3.2	0.0763	0.0027	1.6147	0.0569	0.1520	0.0019	1103	70	976	22	912	11	93
3.3	0.0634	0.0037	0.7313	0.0442	0.0828	0.0014	720	126	557	26	513	8	91
3.4	0.0810	0.0022	1.7761	0.0555	0.1568	0.0023	1220	53	1037	20	939	13	90
3.5	0.0755	0.0021	1.6573	0.0447	0.1578	0.0017	1081	60	992	17	945	9	95
4.1	0.1495	0.0037	8.1968	0.2140	0.3954	0.0070	2340	44	2253	24	2148	32	95
4.2	0.4565	0.0090	57.2462	1.1536	0.8964	0.0088	4107	29	4127	20	4125	30	99
5.1	0.0978	0.0038	3.0161	0.1195	0.2212	0.0036	1583	72	1412	30	1288	19	90
5.2	0.0664	0.0022	1.1746	0.0381	0.1267	0.0016	820	69	789	18	769	9	97
5.3	0.0705	0.0028	1.3081	0.0494	0.1340	0.0019	944	86	849	22	811	11	95
5.4	0.1076	0.0098	2.0640	0.1897	0.1489	0.0068	1761	167	1137	63	895	38	76
5.5	0.0745	0.0037	1.8386	0.0935	0.1781	0.0024	1055	100	1059	33	1057	13	99
6.1	0.1039	0.0022	4.1554	0.0817	0.2883	0.0032	1696	71	1665	16	1633	16	98
6.2	0.0796	0.0023	2.4859	0.0714	0.2251	0.0026	1187	57	1268	21	1309	14	96
6.3	0.0770	0.0021	2.0237	0.0542	0.1899	0.0024	1122	21	1124	18	1121	13	99
6.4	0.0688	0.0019	1.0386	0.0321	0.1094	0.0022	900	56	723	16	669	13	92
7.1	0.1084	0.0025	5.2190	0.1210	0.3480	0.0040	1773	43	1856	20	1925	19	96
7.2	0.1050	0.0020	4.8056	0.0958	0.3297	0.0028	1714	36	1786	17	1837	13	97
7.3	0.0884	0.0040	2.5068	0.1298	0.2059	0.0057	1392	87	1274	38	1207	30	94
7.4	0.0678	0.0026	1.4095	0.0516	0.1528	0.0031	865	79	893	22	917	17	97
8.1	0.1735	0.0037	10.6187	0.2769	0.4395	0.0064	2592	36	2490	24	2348	29	94
8.2	0.0682	0.0018	1.5076	0.0394	0.1593	0.0016	876	54	933	16	953	9	97
8.3	0.0721	0.0018	1.6092	0.0400	0.1604	0.0015	989	50	974	16	959	8	98
8.4	0.0921	0.0022	3.3578	0.0803	0.2625	0.0026	1469	41	1495	19	1502	13	99
9.1	0.1039	0.0025	4.2664	0.1005	0.2955	0.0030	1695	45	1687	19	1669	15	98
9.2	0.0747	0.0026	1.8324	0.0599	0.1774	0.0021	1061	69	1057	21	1053	12	99
9.3	0.0612	0.0029	0.7362	0.0328	0.0867	0.0012	656	102	560	19	536	7	95
10.1	0.0883	0.0025	2.3710	0.0643	0.1926	0.0019	1391	21	1234	19	1136	10	91
10.2	0.0699	0.0025	1.3017	0.0473	0.1343	0.0019	924	73	846	21	813	11	95
10.3	0.0819	0.0019	2.2055	0.0537	0.1935	0.0026	1244	45	1183	17	1140	14	96
11.1	0.0706	0.0015	1.2603	0.0301	0.1278	0.0016	946	44	828	14	775	9	93
11.2	0.0819	0.0028	2.1589	0.0700	0.1920	0.0033	1244	67	1168	23	1132	18	96
11.3	0.0910	0.0024	3.0357	0.0900	0.2390	0.0038	1456	50	1417	23	1381	20	97
15.2	0.0701	0.0039	1.3568	0.0725	0.1407	0.0027	931	115	871	31	849	15	97
15.3	0.1923	0.0049	14.0008	0.3631	0.5175	0.0066	2762	42	2750	25	2688	28	97
16.1	0.0706	0.0018	1.4129	0.0366	0.1432	0.0023	946	53	894	15	863	13	96
16.2	0.0759	0.0019	1.9289	0.0465	0.1817	0.0022	1092	50	1091	16	1076	12	98
16.3	0.0871	0.0024	2.2561	0.0629	0.1865	0.0031	1365	54	1199	20	1102	17	91
16.4	0.0786	0.0021	2.0346	0.0542	0.1850	0.0022	1165	53	1127	18	1094	12	97

a) Concordance= (1−abs(^{206}Pb/^{238}U age−^{207}Pb/^{235}U age)/^{206}Pb/^{238}U age) ×100%.

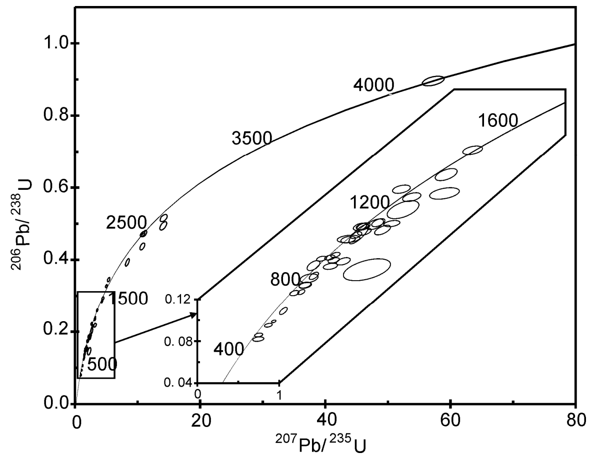

Figure 3 U-Pb concordia diagram of detrital zircon from the Cambrian sandstone in West Daming Mountain, Guangxi Province.

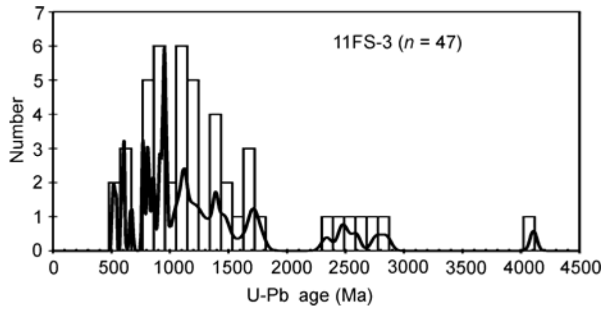

Figure 4 Relative probability density diagram of ages with concordance between 90% and 110% for the analyzed zircons from the Cambrian sandstone in West Daming Mountain, Guangxi.

U-Pb age of 3.6 Ga and Hf model age of 3.99 Ga [35], Integrated with Yu et al's finding of a detrital zircon with U-Pb age of 3.7 Ga and Hf model age of 4.07 Ga in the Tanxi gneiss at Nanxiong, northern Guangdong Province [37], indicating the existence of Eoarchean crustal remnants and continental growth episode in the late Hadean in the Cathaysia Block. Eoarchean ages frequently found in the Yangtze and Cathaysia blocks indicate that Eoarchean crustal remnants are widespread in South China. Hf isotope analyses for some of the Eoarchean zircons indicate the presence of Hadean crustal remnants in South China, which is confirmed by the detrital zircon with the Hadean age in this publication.

The Hadean zircons are located in the core of grains with a core-mantle-rim structure (Figure 2f). U-Pb dating was conducted on the core region and yielded a $^{207}Pb/^{206}Pb$ age of 4107±29 Ma. The core displays oscillatory zoning, combing with a Th/U ratio of 1.09, indicating a magmatic

Table 2 Hf isotope data of detrital zircon in the Cambrian sandstone (11FS-3) in West Daming Mountain, Guangxi[a)]

Spot	$^{176}Hf/^{177}Hf$	1σ	$^{176}Lu/^{177}Hf$	1σ	$^{176}Yb/^{177}Hf$	1σ	Age (Ma)	$\varepsilon_{Hf}(t)$	T_{DM} (Ma)	$\pm(1\sigma)$	T_{DM2} (Ma)	$\pm(1\sigma)$
1.1	0.282163	0.000009	0.000809	0.000006	0.032647	0.000330	1092	2.0	1528	13	1789	21
1.3	0.282238	0.000011	0.000854	0.000010	0.036587	0.000357	1061	4.0	1426	15	1643	24
2.3	0.282163	0.000008	0.000542	0.000015	0.023803	0.000761	1187	4.3	1518	11	1720	17
2.2	0.282000	0.000011	0.000557	0.000014	0.022077	0.000470	1343	2.0	1743	15	1987	24
2.5	0.282248	0.000008	0.000634	0.000007	0.027468	0.000279	974	2.6	1405	11	1666	17
3.4	0.282177	0.000016	0.000546	0.000012	0.027575	0.000601	939	−0.6	1499	22	1841	35
3.2	0.282260	0.000012	0.001319	0.000033	0.049800	0.001178	912	1.2	1412	18	1701	28
3.5	0.282286	0.000011	0.001289	0.000024	0.050757	0.001046	945	2.9	1375	16	1624	26
4.2	0.280407	0.000015	0.002640	0.000054	0.118508	0.002543	4107	2.4	4102	21	4098	32
5.5	0.282427	0.000008	0.000492	0.000002	0.016080	0.000094	1055	10.8	1152	12	1211	19
6.4	0.282221	0.000010	0.000784	0.000036	0.035481	0.001541	669	−5.1	1447	14	1915	23
6.2	0.281992	0.000010	0.000307	0.000003	0.009499	0.000186	1187	−1.5	1742	14	2087	23
7.3	0.282237	0.000013	0.001448	0.000026	0.059613	0.000615	1392	10.7	1450	18	1483	28
7.4	0.281792	0.000013	0.001944	0.000077	0.066143	0.002541	917	−15.6	2103	19	2756	29
8.3	0.282262	0.000013	0.001526	0.000070	0.064658	0.002612	959	2.2	1418	18	1679	29
8.4	0.281567	0.000009	0.001318	0.000011	0.054846	0.000433	1469	−11.3	2380	13	2907	20
8.2	0.282167	0.000008	0.000730	0.000002	0.027580	0.000163	953	−0.8	1520	12	1861	19
9.2	0.281891	0.000010	0.000588	0.000030	0.026017	0.001416	1061	−8.1	1893	13	2400	22
10.1	0.282052	0.000007	0.000204	0.000003	0.009285	0.000078	1391	5.2	1656	10	1821	16
10.3	0.282003	0.000009	0.001262	0.000012	0.046304	0.000568	1244	−0.7	1771	13	2077	21
11.2	0.282085	0.000011	0.000568	0.000021	0.023419	0.001075	1244	2.8	1626	15	1859	24
11.3	0.281716	0.000009	0.001863	0.000030	0.070643	0.001430	1456	−6.9	2205	13	2621	20
16.2	0.281973	0.000010	0.000802	0.000003	0.033298	0.000152	1092	−4.7	1791	14	2210	22
16.3	0.282309	0.000022	0.001889	0.000071	0.071707	0.002666	1365	12.2	1365	32	1365	49
16.4	0.282036	0.000008	0.000722	0.000010	0.027886	0.000529	1165	−0.8	1700	11	2023	17

a) Spots are consistent with those in Table 1.

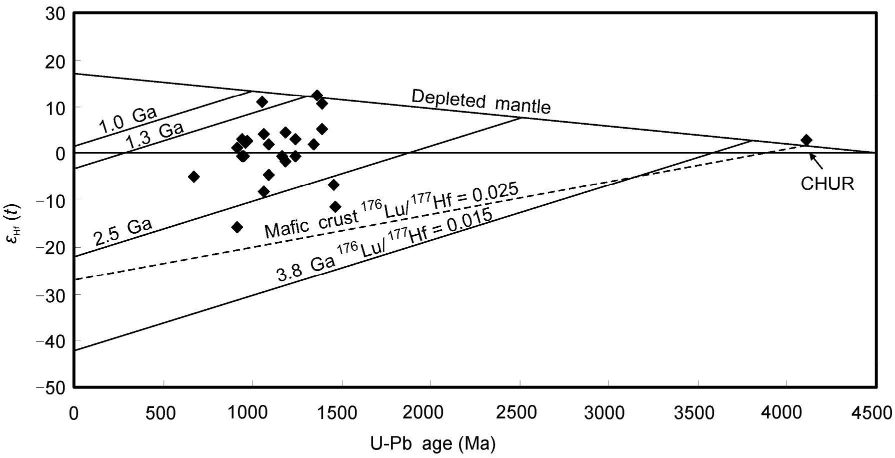

Figure 5 Relationship between $\varepsilon_{Hf}(t)$ and U-Pb ages for zircons from the Cambrian sandstone in West Daming Mountain, Guangxi.

origin. Hf isotope analysis was conducted on the top and slightly upper left of U-Pb dating spot (Figure 2f). ^{176}Hf/^{177}Hf ratios did not change significantly in the 50s data acquisition, which suggests that zircon on the ablation spot has homogeneous Hf isotope composition and is derived from uniform magma. Hf isotope analysis gave highly positive $\varepsilon_{Hf}(t)$ values of +2.4, consistent with the value of homochronous depleted mantle within the uncertainty (Figure 5). Single-stage and two-stage model ages are 4102±42 Ma and 4098±63 Ma, respectively. Two-stage Hf model ages of Hadean zircon was calculated by assuming a mean ^{176}Hf/^{177}Hf value of 0.022 [23] for the average lower continental crust on the basis of Kemp et al's inference that composition of Hadean crust was mafic and similar to that of the lower continental crust [4]. The good agreement between zircon U-Pb and Hf model ages clearly points out the growth and immediate reworking of juvenile crust from the depleted mantle by the ca. 4.1 Ma magmatism, which indicates the existence of depleted mantle and crustal growth at ca. 4.1 Ga.

Vermeesch [38] argued that, within 95% confidence, no fraction ⩾0.05 of the population was missed, and the optimal number of grains that should be dated of a detrital provenance sample is 117. But once these fractions have been found by fewer than 117 grains to be dated, it is enough to prove the presence of one or more specific age fractions in a detrital population. Although only 48 zircons were dated in this study, six grains and eighteen grains yielded "Pan-Africa" (0.6–0.5 Ga) and Grenville (1.3–0.9 Ga) ages (Figure 4), respectively, they differ from the tectonic events of South China, and are consistent with those of Gondwana supercontinent. A number of exotic zircons with "Pan-Africa" and Grenville ages are preserved in the underlying Neoproterozoic strata in the southern part of South China [39–42]. However, available geological evidences in South China—that sag phase prevailed during the late Neoproterozoic period [43], and that the Neoproterozoic strata contacted conformably with the lower Paleozoic strata—suggest that no orogeny happened during the Cambrian. It is impossible that zircons with "Pan-Africa" and Grenville ages derived from the recycling sediments. They must have come from an exotic continent related to Gondwana supercontinent during the Cambrian period, which indicates a connection between South China and Gondwana in the Cambrian period. The southern part of South China may have more complex histories of crustal growth and tectonic evolution than ever known, which needs further study.

This work was supported by the National Natural Science Foundation of China (40972078 and 40921062), "111" Project (B08030) and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan). We thank Prof. Liu Yongsheng and Hu Zhaochu for their help with zircon U-Pb dating and Hf isotope analyses. We also thank Prof. Wu Yuanbao and Ling Wenli for their helpful comments on the manuscript. Two anonymous reviewers are thanked for their constructive and valuable comments.

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