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Diversity in early crustal evolution: 4100 Ma zircons in the Cathaysia Block of southern China

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Zircons are crucial to understanding the first 500 Myr of crustal evolution of Earth. Very few zircons of this age (>4050 Ma) have been found other than from a ~300 km diameter domain of the Yilgarn Craton, Western Australia. Here we report SIMS U-Pb and O isotope ratios and trace element analyses for two ~4100 Ma detrital zircons from a Paleozoic quartzite at the Longquan area of the Cathaysia Block. One zircon (^{207}Pb/^{206}Pb age of 4127 ± 4 Ma) shows normal oscillatory zonation and constant oxygen isotope ratios (δ^{18}O = 5.8 to 6.0‰). The other zircon grain has a ~4100 Ma magmatic core surrounded by a ~4070 Ma metamorphic mantle. The magmatic core has elevated δ^{18}O (7.2 ± 0.2‰), high titanium concentration (53 ± 3.4 ppm) and a positive cerium anomaly, yielding anomalously high calculated oxygen fugacity (FMQ + 5) and a high crystallization temperature (910°C). These results are unique among Hadean zircons and suggest a granitoid source generated from dry remelting of partly oxidizing supracrustal sediments altered by surface waters. The ~4100 Ma dry melting and subsequent ~4070 Ma metamorphism provide new evidence for the diversity of the Earth's earliest crust.

The Earth's earliest history is poorly known because of the lack of rocks from its first 500 m.y. (i.e., >4050 Ma). The mafic rocks from the Nuvvuagittuq greenstone belt of the Superior Craton, Canada, produced a short-decay Nd isotope isochron age of ~4300 Ma[1]. However, the ^{146}Sm-^{142}Nd values might represent early mantle inheritance and the rock age may be as young as ~3800 Ma[2]. Zircon ($ZrSiO_4$), due to its robust chemical and physical features, may be the only common accessory mineral in continental rocks that could survive the extreme conditions of Earth's early evolution. Rare Hadean-Early Archean zircons are important for understanding the formation of Earth's protocrust and ocean[3,4], the characteristics of primordial mantle[5], and continental weathering[6]. Although still debated[7–9], a number of isotopic observations have suggested that the Hadean Earth may have had a relatively stable, basaltic crustal lid, without plate recycling analogous to modern-style plate tectonics[5,10–13].

It should be noted that our knowledge of early earth crustal evolution has mostly been based on studies of zircons found in Archean metasedimentary rocks in Western Australia (dominantly the Jack Hills)[3,4,14–17]. Is this an accident of preservation or was this area unique in the Hadean eon? We are aware of only four > 4050 Ma zircons analyzed by SIMS (secondary ion mass spectrometer) that have been reported as detritus and xenocrysts outside Western Australia: one in the Itsaq Gneiss complex of West Greenland (4079 ± 18 Ma)[18], one in the Acasta Gneiss of Northwest Territories, Canada (4189 ± 46 Ma)[19] and two in China (one in western Tibet, 4103 ± 4 Ma; and one in the North Qinling Belt, 4080 ± 9 Ma)[20,21]. There is only one *in situ* ion microprobe analysis for each of these four zircons and, although they show concordant U-Th-Pb isotopic ages (concordance > 90%), these ages have not been reproduced. These rare survivors from outside Western Australia need careful and comprehensive investigations by a wide range of methods to establish their origins and to help understand the diversity of the earliest crustal evolution of the Earth. In this work, we report SIMS analyses of two > 4050 Ma zircon xenocrysts from one quartzite sample in the Cathaysia Block of southern China. Their oxygen isotope ratios and trace elements (especially Ti concentrations) provide new evidence for the diversity of earliest continental crust.

Geological setting. Southern China (*i.e.*, the South China Block) is composed of the Yangtze Block to the northwest and the Cathaysia Block to the southeast (Fig. 1a). The Cathaysia Block is dominated by Early Paleozoic metamorphic rocks and Mesozoic granitoids, and volcanic-sedimentary rocks, with minor Precambrian rocks (including Neoproterozoic 970–750 Myr volcanic-sedimentary rocks and rare Paleoproterozoic gneissic metamorphic rocks). Zircon crystals of this study were separated from a quartzite within the Longquan Group paragneiss that was originally deposited after 700 Ma and metamorphosed at ~450 Ma at the Longquan area of southwestern Zhejiang Province in the Cathaysia Block (Fig. 1b, Supplementary Figs. DR1–2).

Results

Two zircon grains (#8 and #123) with $^{207}Pb/^{206}Pb$ ages older than 4050 Ma were found among 235 U-Pb analyses on 214 zircons from the quartzite sample. Grain #8 shows complicated zoning in CL with an oscillatory-zoned magmatic core surrounded by an intermediate CL-intensity unzoned metamorphic mantle (Th/U ≤ 0.05) and two main outermost unzoned overgrowths (one dark and one bright in CL; Fig. 2a; Supplementary Fig. DR3). In addition, there is a bright unzoned domain in the lower right of the core, showing crosscutting relations with other domains of the core in CL (Fig. 2a; Fig. DR3), possibly representing an altered domain. This is supported by the low Th/U (0.06) and high $\delta^{18}O$ (see below). In contrast, grain #123 shows a simple texture in CL, with dark and bright oscillatory zones surrounding an unzoned (possibly radiation damaged) core (Fig. 2b; Fig. DR3).

The results of the two dating sessions are consistent, suggesting the core (pit #s U8.1, U8.8, U8.10) and metamorphic mantle (#s U8.3, U8.7) of grain #8 are nearly concordant (≥95% concordance except #U8.10; Table 1) and formed in the ranges 4150–4100 Ma and 4070–4060 Ma respectively (Fig. 2a). The altered domain of grain #8 core

gives a $^{207}Pb/^{206}Pb$ age of 4121 ± 7 Ma (1σ; 98% concordance), indistinguishable from other core analyses. In addition, the two outermost pits in the overgrowths of this grain were dated at 3843 ± 7 Ma (1σ) and 3679 ± 6 Ma (1σ) respectively (#U8.6 and #U8.9 in Fig. 2a; Fig. DR3m). For grain #123, nine analyses (5 of 9 with concordance > 89%) from the oscillatory region show $^{207}Pb/^{206}Pb$ ages in the range 4130–4030 Ma (Table 1; Fig. 2b), and the unzoned core gives a younger $^{207}Pb/^{206}Pb$ age of 3956 ± 8 Ma (1σ) (82% concordance; #U123.7; Table 1; Fig. 2b; Fig. DR3n).

Four oxygen isotope analyses in the concordant domain of the core of grain #8 give identical results (Fig. DR3g; Supplementary Table S1), yielding an average $\delta^{18}O$ of 7.2 ± 0.2‰ ($n = 4$, 2SD). The metamorphic mantle of grain #8 yielded an average $\delta^{18}O$ of 8.0 ± 0.7‰ ($n = 4$, 2SD), which is similar to the altered domain in the core ($\delta^{18}O = 7.9 ± 0.2$‰, #O8.3; Table S1). The ca. 3840 and 3780 Ma outermost overgrowths yield similar $\delta^{18}O$ values (7.6‰ *vs.* 7.4‰; Table S1; #O8.9, #O8.11 in Fig. DR3g). In contrast, grain #123 shows consistent and mantle-like oxygen isotope ratios in its magmatic zones ($\delta^{18}O = 5.9 ± 0.2$‰, 2SD, $n = 6$), and the unzoned damaged core gives similar $\delta^{18}O$ of 5.6 ± 0.2‰ (#O123.1; Table S1; Fig. DR3h).

The magmatic areas (including the core of #8 and zoned domains of #123) of both grains show a positive slope for chondrite-normalized rare earth element (REE) profiles with significant positive Ce anomalies and negative Eu anomalies (Supplementary Table S2; Fig. 3). They are geochemically similar to pristine continental zircons on Earth in their high $(Sm/La)_N$ and U/Yb ratios (Fig. 4). Two analyses from the core of grain #8 showed the highest [Ti] (Ti concentration) (51.5 and 54.0 ppm). The zoned domains of #123 gave relatively low [Ti] (19.8 ppm for dark zonation and 14.7 ppm for light zonation in CL; Table S2). The altered domain and the metamorphic mantle/rim of grain #8 show similar REE patterns, with relatively low REE abundances and weakly negative Eu anomalies
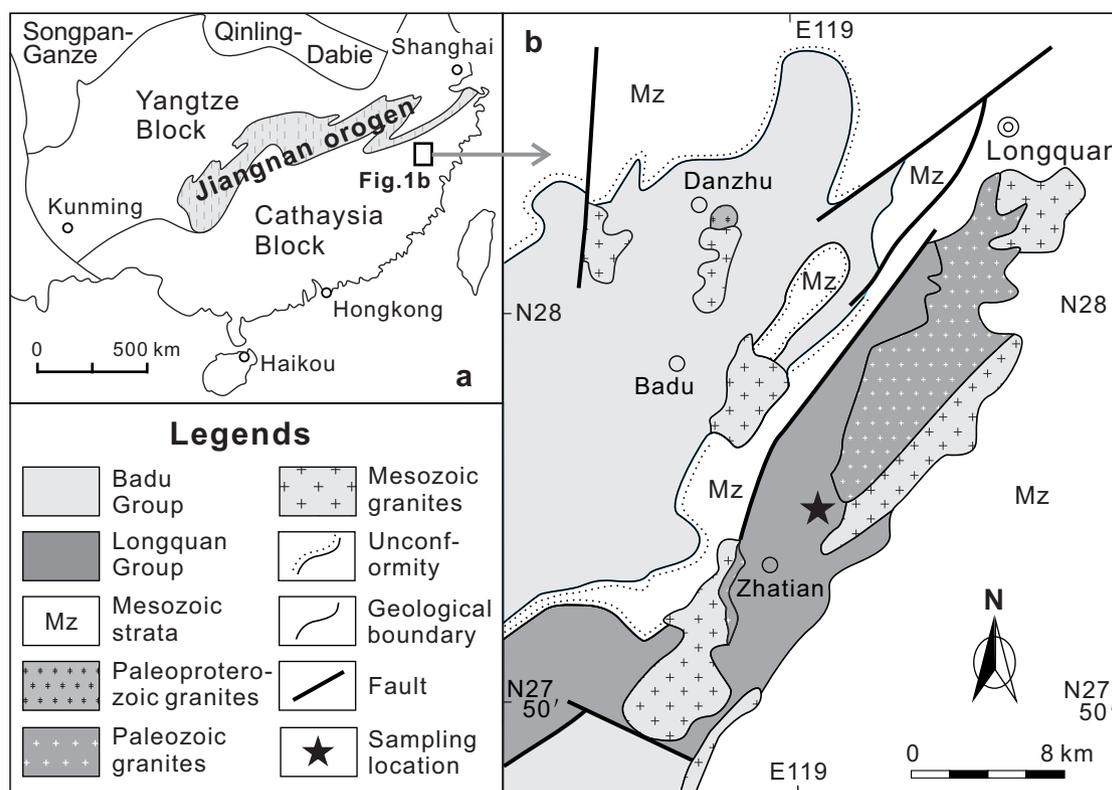
Figure 1 | Geological sketch map showing the sampling location of the two ancient zircon grains. (a) Southern China composed of the Yangtze and Cathaysia blocks and the Jiangnan orogen between them; (b) Longquan area, southwestern Zhejiang Province. This map image was made by the co-authors Jiang Yang and Xing Guangfu according to their geological survey work, using the software Mapgis and CorelDraw.
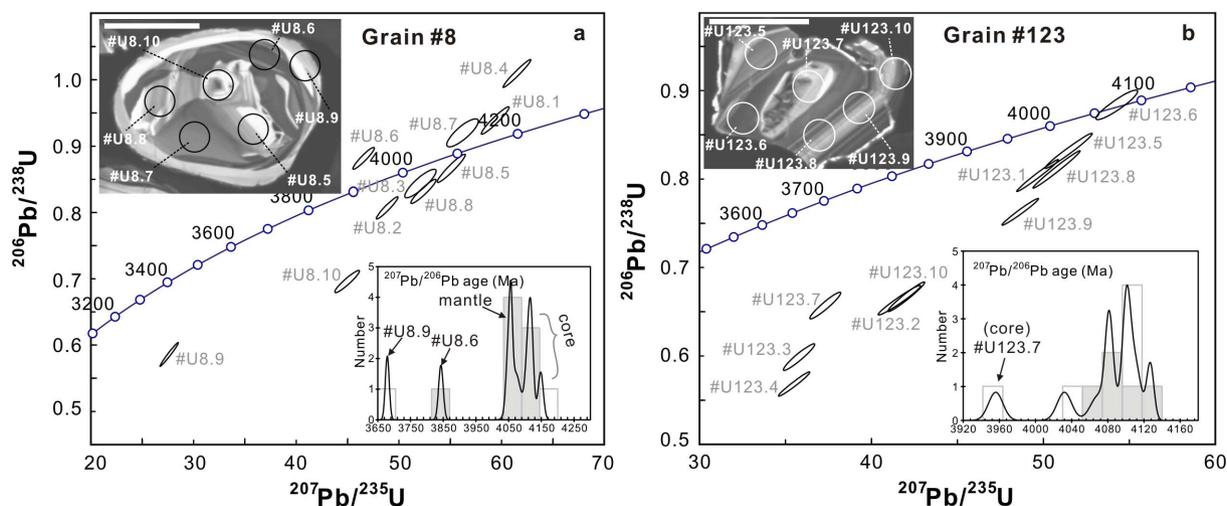
Figure 2 | U-Pb Concordia plots for the two ancient zircons. The CL image (before the second session of U-Pb dating) and age histogram for each grain is also indicated for each grain as insets. The gray filled columns in the lower right insets represent the analyses with concordance > 88%, while the open ones are <88% concordance analyses. Error ellipses are shown in 1σ.

(Fig. 3). They also show similar [Ti] (15.3 ppm versus 23.0–18.8 ppm; Table S2).

Discussion

All of the analyses ($n = 18$) of the two U-Pb sessions show $^{207}Pb/^{206}Pb$ ages older than 3950 Ma, with the exception of the above-mentioned two outermost overgrowths of grain #8 (#U8.6 and #U8.9 in Fig. 2a). Twelve of the eighteen > 3950 Ma analyses show concordance better than 89% (Table 1). Thus the $^{207}Pb/^{206}Pb$ ages are not significantly affected by Pb mobilization[22] that might lead to anomalously lower or elevated $^{207}Pb/^{206}Pb$ ages in some parts of a zircon at the expense of other domains. Four analyses (#s U8.1, U8.4, U8.6 and 8.7) show reverse discordance (Fig. 2a). Most of these analyses are from or overlap the low-Th/U metamorphic mantle of grain #8. The reverse discordance may have resulted from localized Pb mobility within partly radiation damaged zircons. The consistency of $^{207}Pb/^{206}Pb$ ages and good concordance of the analyses suggest that $^{207}Pb/^{206}Pb$ ages with uncertainties lower than 15 m.y. (1σ) give reliable ages that are the oldest known for zircons from southern China.

High-grade regional metamorphism likely accompanied the formation of the earliest granitic rocks on Earth due to heating from the underplating mantle magmas and high geothermal gradient at that time, although radiogenic heat production is also suggested as a mechanism for crustal melting[11]. However, such metamorphic rocks have not been identified and may not have survived. Metamorphic zircon can potentially provide a record of the early Earth metamorphism and help understand the crustal evolution of Earth.

Metamorphic zircons can commonly be distinguished from igneous zircons by their low Th/U ratios (generally <0.07[23]), the absence of oscillatory zonation in CL[24], and weak to absent negative Eu anomalies[23]. The magmatic core of grain #8 is surrounded by a mantle with intermediate CL-intensity that is unzoned (Fig. DR3). Four analyses (trace elements #TE8.3, #TE8.4 and #U8.3, #U8.7) in the mantle all gave Th/U ratios ≤ 0.05 (Table 1 and Table S2), suggesting that the unzoned layer (i.e. the mantle of grain #8) is metamorphic in origin. Hadean to Early Archean analyses with low Th/U (<0.07) ratios have been sporadically reported in detrital zircons from Jack Hills. Cavosie et al.[25] reported one analysis ($^{207}Pb/^{206}Pb$ age of 4062 ± 10 Ma, #22-2 of sample 01JH65) with Th/U ratio of 0.04. Unfortunately, this grain was removed during later polishing. Similarly, Harrison et al.[9] showed one low Th/U (0.05) analysis ($^{207}Pb/^{206}Pb$ age of 4046 ± 12 Ma, #RSES43-5.7) without detailed oxygen isotopes and CL images. The 4070–4060 Ma metamorphic

mantle surrounding the magmatic core of grain #8 shows low Th/U ratio (average 0.04; #U8.7, #TE8.3, #TE8.4; Table 1 and Table S2). Four oxygen isotope analyses (#s O8.1, O8.5, O8.6 and O8.8) in this metamorphic zone gave $\delta^{18}O$ ranging from 7.6‰ to 8.3‰ (Table S1), with a mean value of 8.0 ± 0.7‰, which is a little higher than that (7.2 ± 0.2‰) of the magmatic core. The slightly elevated oxygen isotope ratios suggest the existence of ^{18}O-enriched fluids that sourced from low-temperature supracrustal processes. It possibly represents the oldest known metamorphic event on Earth documented by zircon accompanied by reliable CL images, oxygen isotope and trace element analyses.

The titanium-in-zircon thermometer[26,27] (also see the equation (1) in the supplementary files) has been widely applied to magmatic zircons. Although the meaning of calculated temperatures and the mechanism of Ti in zircon are still unclear[28–32], comparison based on same assumptions can be an effective way to evaluate early crustal evolution[33]. Most of the Jack Hills analyses (free of cracks) contain less than 20 ppm titanium based on published data (Fig. 5), yielding an average calculated temperature of 697 ± 47°C (1SD, n = 50; Table S3) assuming unit activities of TiO_2 and SiO_2 and applying no pressure correction (same assumption below). The mean value is consistent with the result (696 ± 33°C) by Watson and Harrison[26] and their updated value (682 ± 26°C)[4]. A few Jack Hills zircons also show temperatures higher than 800°C due to their high [Ti][34], but no detailed CL and/or BSE images were provided along with [Ti] to help evaluate whether the [Ti] analyses had been affected by the existences of micro- cracks and/or inclusions[8,34–36].

The calculated low temperature for Jack Hills zircons was suggested to correspond to the temperature of wet minimum melting in present-day crust[26,34]. However, two analyses (#TE8.1 and #TE8.5) of the magmatic core of grain #8 give consistent [Ti], with a mean value of 53 ± 3.4 ppm, corresponding to a temperature of 910°C by titanium-in-zircon thermometer. This is the highest reported value for a Hadean zircon from Earth (Fig. 5) with detailed CL and oxygen isotopes, and it may also represent one of the highest values of [Ti] in terrestrial zircons from any time period[29,32,35,37]. Interestingly, the metamorphic mantle of grain #8 and the analyses in grain #123 show uncorrected Ti-in-zircon temperatures (776–820°C; Table S2) higher than many of the published Hadean zircons from Jack Hills. Further imaging has shown that no tiny cracks occur in the analyzing pits to provide additional [Ti] and the consistency of [Ti] of different pits in the core of grain #8 precludes the result of non-Henry's law behavior in the incorporation of Ti in zircon. Therefore, the high-

Table 1 | SHRIMP U-Th-Pb isotopic data for two old zircon grains of southern China

Spot	% $^{206}Pb_c$	U (ppm)	Th (ppm)	Th/U	$^{206}Pb*$ (ppm)	$^{207}Pb*/^{206}Pb*$	$^{207}Pb*/^{235}U$	$^{206}Pb*/^{238}U$	Con.%	$^{207}Pb*/^{206}Pb*$ Age (Ma)	$^{207}Pb*/^{235}U$ Age (Ma)	$^{206}Pb*/^{238}U$ Age (Ma)
Session 1												
#U8.1	0.03	286	146	0.53	230	0.4591 ± 22	59.4 ± 0.9	0.939 ± 14	104	4115 ± 7	4164 ± 15	4267 ± 46
#U8.2	0.04	364	66	0.19	253	0.4392 ± 20	48.9 ± 0.7	0.807 ± 11	94	4049 ± 7	3970 ± 15	3815 ± 41
#U8.3	0.02	635	33	0.05	460	0.4477 ± 41	52.1 ± 1.0	0.844 ± 14	97	4077 ± 14	4033 ± 9	3945 ± 48
#U8.4	0.01	350	50	0.15	303	0.4415 ± 15	61.5 ± 0.9	1.010 ± 14	111	4057 ± 5	4199 ± 15	4501 ± 46
#U123.1	0.07	534	100	0.19	369	0.4486 ± 13	49.7 ± 0.8	0.804 ± 12	93	4081 ± 4	3987 ± 16	3802 ± 44
#U123.2	0.03	495	148	0.31	284	0.4581 ± 19	42.1 ± 0.7	0.667 ± 11	80	4112 ± 6	3822 ± 17	3294 ± 42
#U123.3	0.07	678	154	0.23	350	0.4342 ± 23	35.9 ± 0.6	0.599 ± 10	75	4032 ± 8	3663 ± 17	3026 ± 40
#U123.4	0.05	926	136	0.15	452	0.4543 ± 16	35.6 ± 0.6	0.5684 ± 9	71	4099 ± 5	3656 ± 16	2901 ± 36
Session 2												
#U8.5	0.01	273	17	0.06	203	0.4611 ± 23	55.1 ± 0.9	0.867 ± 14	98	4121 ± 7	4089 ± 16	4023 ± 47
#U8.6	0.00	604	29	0.05	458	0.3829 ± 18	46.6 ± 0.7	0.882 ± 11	106	3843 ± 7	3921 ± 14	4075 ± 40
#U8.7	0.02	417	22	0.05	329	0.4432 ± 44	56.2 ± 1.0	0.920 ± 14	103	4063 ± 15	4109 ± 18	4204 ± 46
#U8.8	0.00	274	134	0.51	196	0.4568 ± 25	52.4 ± 0.8	0.832 ± 12	95	4107 ± 8	4038 ± 16	3901 ± 43
#U8.9	0.01	393	42	0.11	198	0.3435 ± 14	27.7 ± 0.6	0.586 ± 12	81	3679 ± 6	3410 ± 20	2972 ± 47
#U8.10	0.00	225	136	0.62	134	0.4694 ± 26	45.0 ± 0.8	0.696 ± 11	82	4148 ± 8	3888 ± 17	3404 ± 41
#U123.5	0.01	388	79	0.21	278	0.4492 ± 15	51.5 ± 0.9	0.832 ± 13	96	4083 ± 5	4022 ± 17	3903 ± 48
#U123.6	0.02	601	103	0.18	457	0.4454 ± 26	54.3 ± 0.8	0.884 ± 11	100	4070 ± 9	4075 ± 15	4084 ± 40
#U123.7	0.04	327	144	0.45	184	0.4127 ± 22	37.4 ± 0.6	0.657 ± 10	82	3956 ± 8	3703 ± 16	3255 ± 39
#U123.8	0.01	427	107	0.26	297	0.4547 ± 12	50.8 ± 0.9	0.811 ± 14	93	4101 ± 4	4009 ± 17	3828 ± 49
#U123.9	0.01	461	130	0.29	303	0.4628 ± 13	48.7 ± 0.7	0.763 ± 10	89	4127 ± 4	3966 ± 14	3656 ± 38
#U123.10	0.14	317	100	0.33	181	0.4559 ± 20	41.7 ± 0.8	0.663 ± 11	80	4105 ± 6	3812 ± 18	3280 ± 44

*common lead corrected by ^{204}Pb.
% $^{206}Pb_c$ is (common ^{206}Pb/total ^{206}Pb) × 100. $^{206}Pb*$ means the concentration of radiogenic lead. Con.% is percentage concordance of defined as ($^{206}Pb/^{238}U$ age)/($^{207}Pb/^{206}Pb$ age) × 100. All errors are quoted as 1σ level.
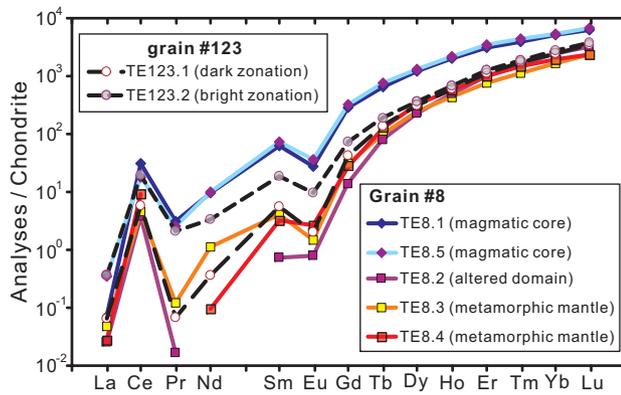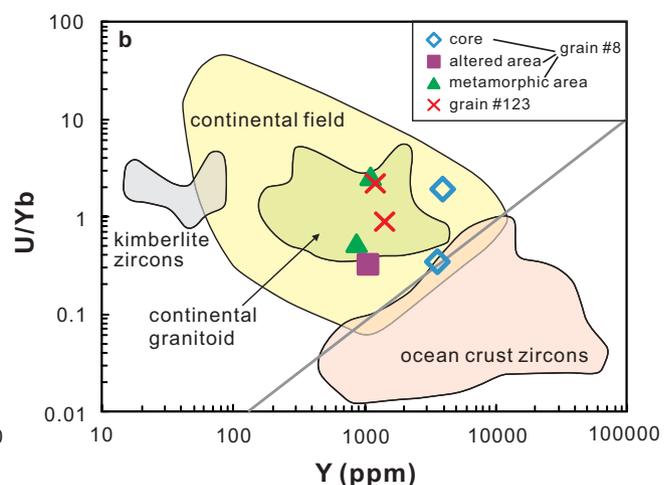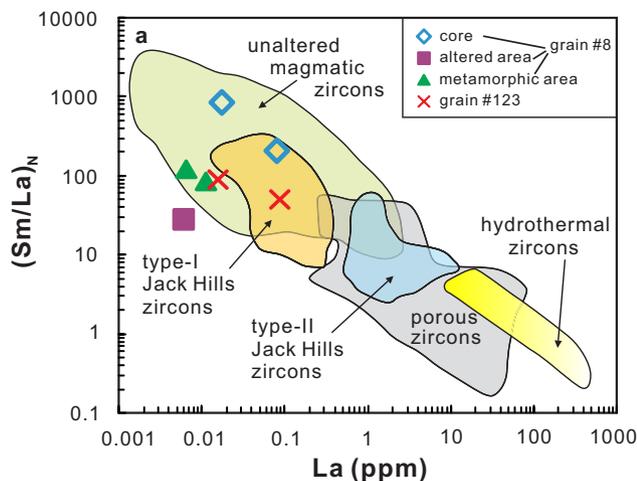
Figure 3 | Rare earth element distribution patterns for the two zircons. Chondrite values are from McDonough and Sun[55].

Figure 5 | Oxygen fugacity (fO₂) versus Ti concentration and calculated temperature by the titanium in zircon thermometer[26,40]. This plot is made based on a compilation (Table S5) of seventy-three >3800 Ma zircons. The temperatures were calculated assuming unit activities of TiO_2 and SiO_2 and no pressure correction. Reaction curves of fO_2 buffer assemblages (HM, hematite–magnetite; NNO, Ni–NiO; FMQ, quartz–fayalite–magnetite) and the boundary between SO_4^{2-} and S^{2-} predominance in silicate magmas (dashed line) are from Chou[42] and Wallace and Carmichael[56] respectively. The black dashed curve represents the oxygen fugacity shown by the two average analyses from the magmatic zonation of the two grains.
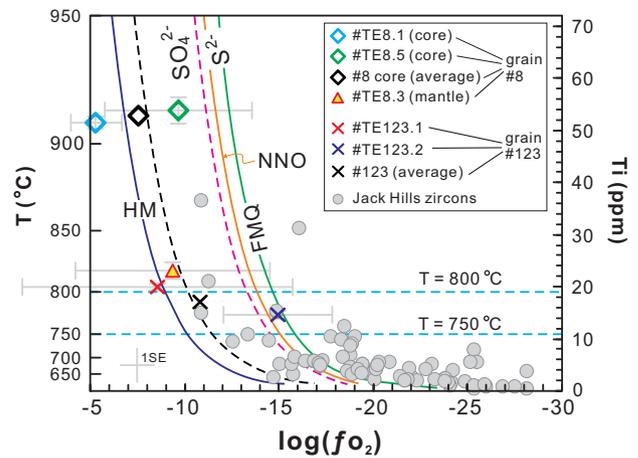
[Ti] grains (especially grain #8) suggest a crystallization condition different from the common Jack Hills zircons.

The $\delta^{18}O$ value (7.2‰) of the core of grain #8 is similar to the highest values for the Jack Hills magmatic zircons (Fig. 6; Table S4), and is higher than the mantle-like magmatic zircon range (5.3 ± 0.6‰, 2SD)[38]. This implies that incorporation of altered crustal material into the magma source, or isotopic exchange of the proto-liths with surface water occurred at 4150 Ma ago, which is consistent with previous conclusions[4,9,15,38–40]. The core of grain #8 may have been formed in a granitoid from the melting of supracrustal sediments as Jack Hills zircons, and its high temperature from high-[Ti] indicates a water-free (dry) melting condition that has not been found from Jack Hills zircons.

Oxygen fugacity calculations based on Ce/Ce* anomalies (see equation (2) in the supplementary files) have been used to constrain the oxidation state of early continental crust[33,40,41]. Note the calculations are mainly controlled by [Ti], [La], [Ce], [Pr] and Ti-in-zircon thermometer, and thus the uncertainty of $\log fO_2$ is constrained by the uncertainties of these factors. The two studied grains show large positive Ce/Ce* anomalies (Table S5; Fig. 3). Two analyses (#TE8.1 and #TE8.5) of the grain #8 core give Ce/Ce* of 65 and 19, respectively, corresponding to $\log fO_2$ of −5.3 (ΔFMQ + 7.3) and −9.7 (ΔFMQ + 2.8) at 910°C (Table S2). The two $\log fO_2$ estimates overlap within uncertainty (Fig. 5) and their mean value (ΔFMQ + 5) is higher than most of published crust-derived Jack Hills zircons (Fig. 5). Although the oxygen fugacity estimates are based on many
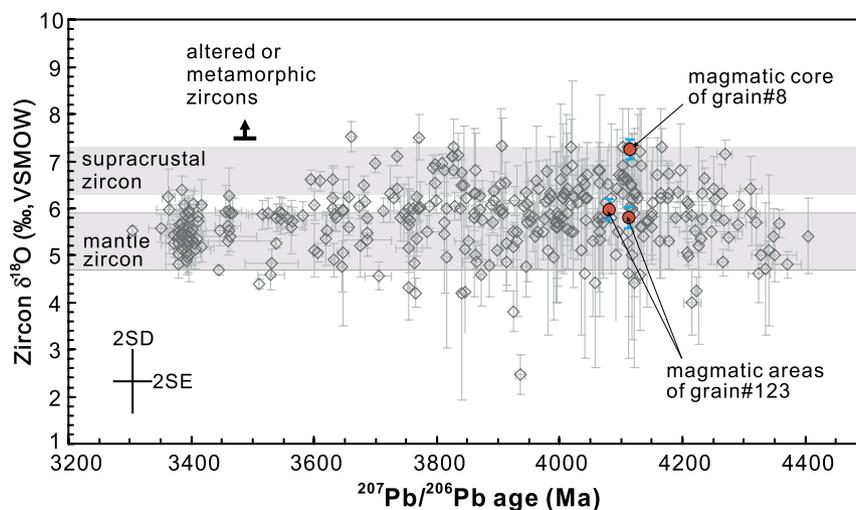
assumptions[41,42], comparisons at same assumptions are still meaningful in particular for the rare Hadean zircons. The Ce/Ce* anomalies of the two core analyses of grain #8 are just within the range of published Hadean zircon data[33] (Table S5), suggesting that the high T is the major cause for the high $\log fO_2$ according to the equations of Ti-in-zircon thermometry[26,27] and oxygen fugacity[41,42]. Earth's earliest atmosphere had no significant free oxygen because of the absence of photosynthetic prokaryotic organisms, although the early mantle had similar oxygen fugacity as Archean and modern times[40]. The high-$\log fO_2$ melt for the grain #8 should generate from melting of crustal rocks which originally formed from locally mantle-derived high-$\log fO_2$ melt which has not been found in Jack Hills zircons yet. This suggests that the oxygen fugacity of early mantle may be heterogeneous.

Figure 4 | (Sm/La)$_N$ versus La (a) and U/Yb versus Y (b) plots for the analyses from the two old zircons of southern China. The areas for continental zircons, modern ocean crust zircons, continental granitoid zircons, kimberlite zircons, porous zircons, Jack Hills zircons and hydrothermal zircons are recited from Bouvier et al.[52].

Figure 6 | A compilation showing the distribution of $^{207}Pb/^{206}Pb$ age versus $\delta^{18}O$ for the published analyses on >3300 Ma zircons and the magmatic areas of the two grains of this study. The value for mantle-like zircon (5.3 ± 0.6‰, 2SD) is from the ref. 19. This plot is made on a compilation (Table S4) of 339 magmatic zircons. Only con% between 80% and 120% are included when multiple isotopic ages were provided. The analyses with $\delta^{18}O$ errors (2SD) bigger than 1.8 were rejected. Detailed rules in data filtration can be seen in the notes of Supplementary Table S3.

The early earth crust may be heterogeneous as revealed by the variations in Hf, Li and O isotopes in Jack Hills Hadean zircons[3,5,9,15,36,43], multiple age domains within single zircon grains[44], and possible heavy bombardment epoch or early earth[45]. Based on the aforementioned discussion, the two 4100 Ma zircon grains (especially grain #8) from southern China are distinct from the published Jack Hills zircons in their high [Ti] and log$f$O$_2$. Although a few published Jack Hills zircons showed complexity in CL texture, the pre-3.6 Ga multiple (possibly three episodes according to CL and U-Pb dating results) overgrowths of grain #8 and the 4070–4060 Ma metamorphic mantle are unusual in comparison to Jack Hills zircons. Two possibilities can be addressed for the origins of the two 4100 Ma zircon grains from southern China. Perhaps they were derived from a source area in Western Australia that differed from that of the Jack Hills zircons, or alternatively they could be from a different landmass never attached to the Yilgarn Craton of Western Australia. Further U-Pb dating on other detrital zircons of the studied sample and comparisons with the U-Pb age patterns of Western Australia will be useful way to distinguish them. If the second possibility is correct, Hadean landmasses may have been more widespread than previously known. Either way, the existence of high-[Ti]-$\delta^{18}O$-[Ce] zircon and the possible dry melting at *ca.* 4100 Ma and its 4070–4060 Ma metamorphism suggest diverse tectonic regimes of the Hadean crust.

It should be noted that all four known > 4050 Ma zircons dated by SIMS from China (including this work and the two xenocrysts from Tibet and North Qinling Belt[20,21]) are from Phanerozoic sedimentary/volcanic rocks, which is different from the Australia, Greenland and Canada localities where ancient zircons were found in Archean rocks. In addition, rare 3900–4020 Ma detrital zircons were also found in Neoproterozoic and Paleozoic sediments in southern China[46,47] and in Late Devonian sediments in Hexi Corridor of northwestern China[48] using laser ablation-ICP-MS method. The sporadic occurrence of Hadean to Early Archean zircons in young sediments in China shows that the Hadean zircons can survive multi-stage crustal recycling. Compared to the other reported >4050 Ma zircons outside Australia, finding two old grains out of 214 zircons of one sample represents a high proportion (nearly 1%) and suggests that more >4100 Ma zircons can be found. Additional U-Pb dating on the detrital zircons in the Longquan area of the Cathaysia Block is necessary to evaluate whether the unusual geochemistry of Hadean zircons in this study is representative and to help constrain the earliest crustal evolution.

Conclusions

Two ~4100 Ma detrital zircons were found in a Paleozoic quartzite from the Longquan area of southern China. One zircon shows normal magmatic oscillatory zonation in CL and constant mantle-like oxygen isotopes ($\delta^{18}O$ = 5.8–6.0‰). The other zircon grain has a ~4100 Ma magmatic core surrounded by three >3600 Ma overgrowths, especially a 4070–4060 Ma metamorphic rim. The magmatic core is distinct in its elevated $\delta^{18}O$ (7.2‰), high titanium concentration (53 ppm) and a calculated high oxygen fugacity (ΔFMQ + 5) and crystallization temperature (910°C), suggesting a granitoid-like source generated from dry remelting of partly oxidizing supracrustal sediments altered by surface waters. The unusual melting condition and the immediately following ~4070 Ma metamorphism recorded in zircon possibly provide new evidence for diversity of the Earth's earliest continental crust and more ancient zircons other than Western Australia as well as other isotopic and geochemical investigations are necessary to understand the earliest crustal evolution of the Earth.

Methods

After crushing and grinding, zircons were separated by heavy liquid and magnetic techniques. They were mounted in epoxy with the standard TEMORA 1 ($^{206}Pb/^{238}U$ age = 417 Ma[49]) and polished to mid-section. Detailed cathodoluminescence (CL) images were made for each surface of analysis (Supplementary Fig. DR3). U-Th-Pb zircon analyses were performed on the SHRIMP II ion microprobe at the Beijing SHRIMP center, Chinese Academy of Geological Sciences, following standard operating techniques[14,50]. There are two dating sessions. Four U-Th-Pb isotope analyses (session-1; Table 1) were initially made for each grain (ion beam ~ 30 μm dia.) on surface-1 (Fig. DR3a–d).

After the session-1 dating, the mount was ground lightly and repolished to remove the SIMS pits. Further CL and SEM imaging (surface-2; Fig. DR3e–j) were performed for oxygen isotope and trace element analyses. Oxygen isotope ratios and trace element compositions were analyzed on surface-2 using the CAMECA IMS-1280 ion microprobe in the WiscSIMS Laboratory, UW-Madison, with detailed analytical conditions and data reduction procedures reported elsewhere[51,52]. Oxygen isotopes were analyzed (ion beam ~8 × 9 μm) with a zircon KIM-5 ($\delta^{18}O$ = 5.09‰ VSMOW)[53] as standard. A $^{133}Cs^+$ primary ion beam (20 kV total impact voltage, 1.9–2.2 nA) was focused to an area of 8 × 9 μm on the sample surface. Total analytical time per spot was about 4 minutes: including pre-sputtering (10 s), automatic retuning of the secondary beam (120 s), and analysis (80 s). Trace element analyses were performed directly on the same pits as $\delta^{18}O$ (beam size ~10 × 12 μm) at WiscSIMS in single collector mode by axial electron multiplier using magnetic peak switching. Zircon 91500 and NBS610 glass were used as standards following the

method of Page et al.[32] and Fu et al.[54]. A primary $^{16}O^-$ beam with a current of 2.5 nA and a total impact energy of 23 kV was defocused to a 10×12 μm spot. An energy offset of 40 eV was applied and the mass resolving power was set at 5000. All analyses consisted of 100 s pre-sputtering, 80 s for centering ions to the field aperture using the $^{30}Si^+$ signal followed by seven mass scan cycles for detection of trace element signals, with total analytical time about 24 minutes. Only the last 5 cycles were integrated; the first two cycles were used to stabilize the magnet. After analysis, each pit was imaged by SEM (Scanning electron microscope). No oxygen or trace element analyses have unusual pits and no cracks or inclusions were found in the pits.

The session 2 (Table 1) U-Pb dating analyses were made after oxygen isotope and trace element analysis at the Beijing SHRIMP center. Zircons were reground and repolished to remove all previous analytical pits; the grains were then re-imaged by CL (surface-3; Fig. DR3k–n). Care was taken to locate new analytical sites away from identifiable cracks and the primary ion beam size was adjusted to about 15–20 μm to avoid overlapping of different zones seen by CL. This proved partially successful, with four of six analyses obtained from each grain showing better than 89% concordance (Table 1).

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Acknowledgments

Author contributions

G.-F.X. and X.-L.W. contributed equally to idea development and data compilation. X.-L.W. and G.-F.X. wrote the main text. G.-F.X. organized the field work, sample preparation and the session-1 SHRIMP zircon U-Pb dating. Y.-S.W., Z.-H.C., Y.-J., K.K., U.T. and G.P. carried out part of analyses and discussed the manuscript.

Additional information