Zircon U/Pb dating and Hf-O isotopes of the Zhouan ultramafic intrusion in the northern margin of the Yangtze Block, SW China: Constraints on the nature of mantle source and timing of the supercontinent Rodinia breakup

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The Zhouan ultramafic intrusion in the northern margin of the Yangtze Block is mainly composed of lherzolite. Zircon grains selected from lherzolite are irregular in shape with distinct oscillatory and sector zoning and have Th/U ratios ranging from 0.8 to 10.6, indicating a magmatic origin. The weighted average $^{206}\text{Pb}/^{238}\text{U}$ age is 637 ± 4 Ma (2σ , $n=15$), which can be considered as the crystallization age of the Zhouan intrusion. Zircon grains have $\delta^{18}\text{O}$ values ranging from 5.2‰ to 7.0‰, with an averaged value of 5.8 ± 0.4 ‰ (1σ , $n=33$), similar to the mantle $\delta^{18}\text{O}$ value of zircon. Their $^{176}\text{Hf}/^{177}\text{Hf}_0$ ratios range from 0.282410 to 0.282594 with $\varepsilon_{\text{Hf}}(t)$ values ranging from 1.3 to 7.6, lower than the corresponding value of the depleted mantle (~ 15), indicating an enriched mantle source. The enriched mantle source may have generated from a metasomatized lithospheric mantle with subducted slab. A number of ~ 635 Ma mafic-ultramafic intrusions in the Suizao basin are associated with coeval bimodal volcanics of the Yaolinghe Formation, indicating a continental rift setting. The ~ 635 Ma magmatic event in this region may represent the product of the last breakup of the Rodinia supercontinent in the northern margin of the Yangtze Block at Neoproterozoic.

zircon Hf-O isotopes, Zhouan ultramafic intrusion, northern margin of the Yangtze Block, Neoproterozoic

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Neoproterozoic (850–630 Ma) magmatic rocks are widely distributed in the northern, western and southeastern margins of the Yangtze Block, which is considered to be part of the Rodinia supercontinent [1–3]. 850–630 Ma magmatic rocks are mainly composed of granitoid plutons and associated mafic-ultramafic intrusions and coeval volcanic rocks [4–16]. These intrusive bodies have arc-like characters in geochemistry, indicating that the margins of the Yangtze Block may have undergone subduction of oceanic slab in early stage (1160–930 Ma) and large-scaled extension in late stage [6,7,17–21]. However, it remains debated in the

timing and mechanism of such a transformation. Three hypotheses have been proposed for the mechanism of the transformation, including mantle plume, lithospheric extension-rifting and subduction in a continental margin. Some workers suggested that <850 Ma magmatic rocks in the margins of the Yangtze Block may have formed by partial melting of the lithospheric mantle and lower crust triggered by a mantle plume [6,7,22]. Others argued that 830–820 Ma magmatic events were related to post-collisional extension and 780–740 Ma magmatic events were related to continental rifting [23]. Also some workers proposed that most of Neoproterozoic magmatic events along the margins of the Yangtze Block were related to subduction in an active

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continental margin [4,24].

Previous studies indicate that the mechanism and timing of the transformation from subduction to extension at Neoproterozoic in the western and northern margins are different from the southeastern margin of the Yangtze Block. Amalgamation of the Yangtze and Cathaysia Blocks at Neoproterozoic along the southeastern margin of the Yangtze Block formed the South China and led to the formation of the Jiangnan folded belt and deformation and metamorphism of the Sibao Formation [25]. Subsequent intracontinental breakup of the South China resulted in intensive magmatism and the formation of the Nanhua basin composed mainly of the Banxi Formation [26]. New zircon U-Pb age data indicated that the Grenvillian Jiangnan folded belt formed at ~ 830 Ma [27] and subsequent breakup may have lasted from 814 ± 12 Ma to 725 ± 10 Ma [26,28].

The mechanism and timing of the transformation from subduction to extension at Neoproterozoic in the western and northern margins of the Yangtze Block are debated. They are supposed to be the same as the southeastern margin in terms of timing and mechanism according to the models of mantle plume and lithospheric extension-rifting [6,7,22,23]. However, it is argued that the western and northern margins of the Yangtze Block had been active continental margins until 735 Ma [4,5,9–13]. But it remains unknown when the final breakup occurred in the western and northern margins of the Yangtze Block.

A number of 640–630 Ma mafic-ultramafic intrusions in the northern margin of the Yangtze Block are distributed in the Suizao basin in the south Qinling area [14–16]. Among them, the Zhouan ultramafic intrusion hosts Ni-Cu-(PGE) sulfide mineralization [29]. In general, mafic-ultramafic intrusions with sulfide mineralization are related to intensive magmatic events in a rift setting [30]. In this study, we present zircon U-Pb age data and Hf-O isotopes for the Zhouan intrusion. The data set enables us to discuss the formation age and the nature of mantle source for the Zhouan intrusion. Together with available Sr-Nd isotopic data of the Neoproterozoic mafic-ultramafic intrusions and basaltic lavas in the northern margin of the Yangtze Block, we discuss the evolution of the mantle sources of these Neoproterozoic mafic-ultramafic intrusions and the final breakup time of the Rodinian supercontinent in the northern margin of the Yangtze Block.

1 Geological background

The Yangtze Block amalgamated with the Cathaysia Block by the Jiangnan folded belt in its southeastern margin during Meso- to Neoproterozoic [31]. It is separated from the North China Block by the Qinling-Dabie-Sulu orogenic belt to the north and bounded by the Tibetan Plateau to the west (Figure 1).

The Yangtze Block consists of a Precambrian basement

overlain by a sedimentary sequence of the late Mesoproterozoic to upper Jurassic. The basement consists of Archean amphibolite (i.e. the 3.2 Ga Kongling Terrane), Mesoproterozoic meta-sedimentary rocks [32–36], Neoproterozoic strata and numerous magmatic plutons [4,5,37,38]. The sedimentary sequence (>9 km) is mainly composed of clastic, carbonate, meta-volcanic rocks and glacial deposits [39].

Neoproterozoic magmatism in the Yangtze Block yielded voluminous 820–630 Ma mafic-ultramafic intrusions which are distributed in the Guibei area in the southeastern margin [22,40], in the Panxi area in the western margin [9,37,41], and in the Hannan and Suizao areas in the northern margin of the Yangtze Block [13–16].

In the Hannan area, 819 ± 10 Ma Wangjiangshan layered gabbroic intrusion with Cu-Ni sulfide mineralization [4] and 782 ± 10 Ma Bijigou gabbroic-dioritic intrusion with V-Ti magnetite mineralization [4] intruded the Paleoproterozoic Houhe Formation, Meso-Neoproterozoic Huodiya Formation and Neoproterozoic Xixiang Formation. The Houhe Formation (2081 ± 9 Ma [42]) experienced high amphibolite facies metamorphism and migmatization and mainly consists of tonalitic gneiss, with small amounts of amphibolite and marble [43,44]. The Houhe Formation is unconformably overlain by the Huodiya Formation which is composed of meta-sedimentary rocks in the lower part and meta-volcanic rocks in the upper part [11]. The Xixiang Formation (950 ± 4 Ma– 895 ± 3 Ma [44]) mainly consists of a sequence of volcanic and sedimentary rocks, possibly of back-arc basin origin [10]. Moreover, numerous coeval granitic plutons occur in the Hannan area, such as the adakite-like 735 ± 8 Ma Wudumen and 730 ± 6 Ma Erliba plutons [11] and the 762 ± 4 Ma arc-like Tianpinghe granite [12].

A number of 640–630 Ma mafic-ultramafic intrusions occur in the Suizao basin, including the 641 ± 5 Ma Zhouan intrusion [16], 638 ± 10 Ma Changling intrusion, 636 ± 11 Ma Shoushan intrusion [14], 632 ± 6 Ma Duchongshan intrusion [15] and 631 ± 11 Ma Bashan intrusion [14]. These intrusions intruded the Meso-Neoproterozoic Zhujiashan Formation and the Neoproterozoic Suixian Formation. The Daqueshan unit of the Zhujiashan Formation is composed of interlayered marble and schist [29]. The Suixian Formation consists of bimodal meta-volcanic rocks with minor interlayers of meta-sedimentary rock in the lower part, meta-sedimentary rocks with interlayers of meta-rhyolitic pyroclastic rock and metamorphosed intermedium-basic lavas in the middle part, and meta-sedimentary rocks in the upper part with meta-trachyandesite or alkaline rhyolite in local places [15]. Coeval Yaolinghe Formation in the Wudang Terrane is a suite of bimodal assemblage composed mainly of metabasaltic volcanic lava, tephra or tuff and small amounts of meta-felsic lava and argillaceous rocks, which is interpreted as the product in a continental rift setting [45–47]. Several different ages were reported for the Yaolinghe Formation, the whole-rock Sm-Nd isochron age is reported to be

Figure 1 Simplified geologic map showing the distribution of Neoproterozoic mafic-ultramafic intrusions, volcanic rocks and granitic plutons in the northern margin of the Yangtze Block, SW China.

780–1000 Ma [48,49], whereas a zircon U-Pb age is 685 ± 5 Ma for the metamorphic rhyolitic lavas and crystal-lithic tuffaceous pyroclastic rocks [46] and is 632 ± 1 Ma for the metamorphic spilite-keratophyre-tuff [50]. The latter is identical with the ages of the mafic-ultramafic intrusions in the Suizao basin.

2 Analytical method

The Zhouan intrusion mainly consists of lherzolite. Lherzolite is composed of olivine (65%–70%), clinopyroxene (10%–15%) and orthopyroxene (10%–15%). Zircon grains were separated from ~20 kg lherzolite using conventional heavy liquid and magnetic technique in uncontaminated condition and handpicked with binocular microscope. Zircon separates were mounted on adhesive tape, enclosed in epoxy resin with zircon standard (Qinghu, Plésovice and 91500), polished down to expose the centers of zircon grains and finally coated with gold. Zircon grains were photographed in transmitted, reflected light and cathodoluminescence (CL) to select the appropriate analytical location. CL images were taken using a scanning electron microscope at the State Key Laboratory of Continental Dy-

namics, Northwest University, Xi'an. Zircon *in-situ* oxygen isotopes were analyzed firstly, and then U/Pb dating and Hf isotope were analyzed successively in the same location.

2.1 Zircon oxygen isotope

Zircon *in-situ* oxygen isotopes were measured using the Cameca IMS 1280 large-radius SIMS at Ion Microprobe Laboratory in the Institute of Geology and Geophysics (IGG), Chinese Academy of Sciences (CAS) in Beijing. Analytical procedures are the same as those described by Li et al. [51–54]. The Cs^+ primary ion beam with an intensity of ~2 nA was accelerated at 10 kV and bombarded the surface of zircon grains. The spot is about 20 μm in diameter, including 10 μm beam diameter and 10 μm raster. The normal-incidence electron flood gun was used to compensate for sample charging during analysis with homogeneous electron density over 100 μm oval area. Negative secondary ions were extracted with a -10 kV potential. The field aperture was set to 5000 μm and energy window was 30 eV, together with a mass resolution of ~2500. Oxygen isotopes were measured using multi-collector mode on two off-axis Faraday cups. One analysis takes ~5 min including pre-sputtering (2 min), automatic beam centering (~60 s) and

integration of oxygen isotopes (20 cycles $\times$ 4 s). Uncertainties on individual analyses are usually better than 0.2‰–0.3‰ (1 σ) and the external accuracy of zircon standard is 0.5‰ (2SD). The instrumental mass fractionation factor (IMF) is corrected using zircon Penglai standard [55]. Measured $^{18}\text{O}/^{16}\text{O}$ ratios were normalized by using Vienna Standard Mean Ocean Water compositions (VSMOW, $^{18}\text{O}/^{16}\text{O}=0.0020052$), then corrected for the IMF as follows: $(\delta^{18}\text{O})_{\text{M}}=((^{18}\text{O}/^{16}\text{O})_{\text{M}}/0.0020052-1)\times 1000$ (‰), $\text{IMF}=(\delta^{18}\text{O})_{\text{M(standard)}}-(\delta^{18}\text{O})_{\text{VSMOW}}$, $\delta^{18}\text{O}_{\text{sample}}=(\delta^{18}\text{O})_{\text{M}}+\text{IMF}$ [54].

2.2 Zircon U-Pb age dating

Zircon U-Pb dating were measured using the same Cameca IMS 1280 SIMS at the Ion Microprobe Laboratory in IGG CAS. Analytical procedures are the same as those described by Li et al. [51–54]. The O_2^- primary ion beam was accelerated at –13 kV, with an intensity of ~10 nA. The ellipsoidal spot is about 20 $\mu\text{m} \times 30 \mu\text{m}$ in size [54]. A 60 eV energy window was used in the secondary ion beam optical, together with a mass resolution of ~5400 to separate Pb^+ peaks from isobaric interferences. In the secondary ion optics, rectangular lenses were used to increase the transmission at high mass resolution. Pb^+ sensitivity for zircon enhanced by the oxygen flooding which was used to increase the O_2 pressure to $\sim 5 \times 10^{-6}$ Torr in the sample chamber. Secondary ion beam intensities were measured by peak jumping with a single electron multiplier. Each measurement includes seven cycles, and the total analytical time is about 10 min. Zircon U-Th-Pb isotopic ratios were corrected using zircon Plésovice standard [56]. Single point errors were gained via propagation of long-term monitoring standard deviation 1.5% (1 σ) [57] for zircon standard and individual internal accuracy. Calibration of Pb/U ratios is relative to the zircon 91500 (1065 Ma) standard. Th and U concentrations were determined relative to zircon 91500 standard (Th=29 ppm; U=81 ppm) [58]. Correction of common Pb was made by using non-radiogenic ^{204}Pb . Although the low abundance of ^{204}Pb makes the correction relatively imprecise, it can provide the direct measure of common Pb [51]. Uncertainties on individual analyses are reported at 1 σ level.

2.3 Zircon Lu-Hf isotopes

Zircon *in situ* Lu-Hf isotopes were measured on a Neptune multi-collector ICP-MS equipped with a Geolas-193 laser-ablation system (LA-MC-ICP-MS) at MC-ICPMS Laboratory in IGG CAS. Analytical procedures are the same as those described by Wu et al. [59]. Typical ablation time for each analysis is 26 s, with a 10 Hz repetition rate, 100 mJ/pulse laser power and ablation pit of ~60 μm in diameter. Isobaric interference of ^{176}Lu and ^{176}Yb on ^{176}Hf signal were subtracted by monitoring the intensity of ^{175}Lu and ^{172}Yb

signals, using $^{176}\text{Lu}/^{175}\text{Lu}$ (0.02655) [60] and $^{176}\text{Yb}/^{172}\text{Yb}$ (0.5886) [61]. External monitor of instrument drift was done by using cross analysis of zircon 91500 standard and samples. The $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of zircon 91500 standard were 0.282294 ± 15 (2 σ , $n=20$) and 0.00031 during the analyses, respectively, approximately similar to the results measured by solution method. ε_{Hf} values were calculated using $1.867 \times 10^{-11} \text{ a}^{-1}$ [62] as ^{176}Lu decay constant, and present-day $^{176}\text{Hf}/^{177}\text{Hf}=0.282772$, $^{176}\text{Lu}/^{177}\text{Hf}=0.0332$ [63] for chondrite. The depleted mantle array was calculated by assuming its present-day $^{176}\text{Hf}/^{177}\text{Hf}=0.28325$ and $^{176}\text{Lu}/^{177}\text{Hf}=0.0384$ [64].

3 Analytical results

3.1 Zircon morphology

Zircons are colorless and transparent, and irregular in shape. They range in size from 50 to 120 μm in length with length/width ratios of about 1:1 to 3:1. CL images of the zircons show that most zircon grains have distinct oscillatory and sector zoning without core-rim structure, typical of the origin from mafic magmas (Figure 2).

3.2 Zircon U-Pb ages

A total of 33 spots on 33 zircon grains were analyzed for U-Pb ages. Zircons have U concentrations ranging from 40 to 1024 ppm and Th from 127 to 2342 ppm. Zircons have Th/U ratios varying from 0.8 to 10.6 (Table 1), consistent with zircons (Th/U >0.5 [65]) crystallized from mafic magmas. On the plot of $^{206}\text{Pb}/^{238}\text{U}$ versus $^{207}\text{Pb}/^{235}\text{U}$, lead loss line intersects with concordia at zero, indicating that a present-day Pb loss due to exposure to the open air and weathering of samples. However, $^{207}\text{Pb}/^{206}\text{Pb}$ ages of all the grains are concordant (Figure 3(a)), with a weighted mean age of 635 ± 8 Ma (2 σ). Fifteen analyses, with greater than 95% confidence, yield a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 637 ± 4 Ma (2 σ) (Figure 3(b)), which is considered to be the crystallization age of the intrusion.

3.3 Zircon oxygen isotope

$\delta^{18}\text{O}$ values of 33 zircon spots range from 5.2‰ to 7.0‰ with an averaged value of 5.8 ± 0.4 ‰ (1 σ , $n=33$) (Table 1). The $\delta^{18}\text{O}$ values show a Gaussian distribution (Figure 4(a)), indicating that the zircons have homogeneous O isotopic compositions. Twenty-six zircon grains have $\delta^{18}\text{O}$ values similar to the mantle value (5.3 ± 0.3 ‰) [66], whereas the other seven grains have $\delta^{18}\text{O}$ values slightly higher than the mantle value (Figure 4(b)). Zircons with >95% confidence for U-Pb age dating have $\delta^{18}\text{O}$ values ranging from 5.2‰ to 7.0‰ and those with <95% confidence from 5.3‰ to 6.4‰, generally identical within the uncertainties (Table 1, Figure 4(b)).

Figure 2 Cathodoluminescence (CL) images of zircons selected from lherzolite of the Zhouan intrusion. Analytical spots for U-Pb dating and Hf-O isotopes are illustrated with ellipses on the grains and the numbers near ellipses are U-Pb ages, $\delta^{18}\text{O}$ and $\epsilon_{\text{Hf}}(t)$ values.

3.4 Zircon Lu-Hf isotopes

Zircons with >95% confidence for U-Pb age dating have present-day $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranging from 0.0002 to 0.0016 and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios from 0.282421 to 0.282608. They have initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios varying from 0.282410 to 0.282589 and $\epsilon_{\text{Hf}}(t)$ values between 1.3 and 7.6 when calculated by $t=637$ Ma (Table 2, Figure 5(a)). Zircons with <95% confidence have present-day $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranging from 0.0003 to 0.0023 and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios from 0.282453 to 0.282620. They have initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranging from 0.282450 to 0.282594 and $\epsilon_{\text{Hf}}(t)$ ($t=637$ Ma) values between 2.1 and 6.9 (Table 2, Figure 5(a)).

4 Discussion

4.1 Enriched mantle source

The greater affinity for Hf than Lu in zircon means that Lu/Hf ratio in zircon is invariably very low (~ 0.002) and the $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of zircon are usually <0.0005 . Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of zircons crystallized from mafic magmas

are often very similar to the present-day value because time-integrated changes to the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio as a result of in situ decay of ^{176}Lu proceed at negligible rates [67]. When the primitive mantle differentiated to form the depleted mantle and continental crust, the depleted mantle acquired a Lu/Hf ratio several times greater than the continental crust [68]. Therefore, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of the depleted mantle increased faster than the continental crust so that ϵ_{Hf} values of the depleted mantle became more and more positive with time, whereas ϵ_{Hf} values of the continental crust more and more negative with time [68]. Zircons that crystallized from a mixing magma of two end-members, the depleted mantle and a continental crust, are supposed to have ϵ_{Hf} values between these two end members. On the other hand, zircons from mafic magmas that have no assimilation of crustal component and have ϵ_{Hf} values positive but lower than the coeval depleted mantle, may indicate that the mafic magmas were derived from an enriched mantle source [68]. Zircons from the Zhouan intrusion have $\epsilon_{\text{Hf}}(t)$ values ranging from 1.3 to 7.6, distinctly lower than coeval depleted mantle (15)(Figure 5(a)). The rocks from the Zhouan intrusion have nearly constant Zr/Nb (13–17) and La/Nb

Table 1 Zircon U-Pb age and oxygen isotopic compositions for the Zhouan intrusion

Spot number	Concentrations				Isotopic ratios						Ages (Ma)						Oxygen isotope
	U (ppm)	Th (ppm)	Pb (ppm)	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm(1\sigma)$ (%)	$^{207}\text{Pb}/^{235}\text{U}$	$\pm(1\sigma)$ (%)	$^{206}\text{Pb}/^{238}\text{U}$	$\pm(1\sigma)$ (%)	$^{207}\text{Pb}/^{206}\text{Pb} \pm(1\sigma)$	$^{207}\text{Pb}/^{235}\text{U} \pm(1\sigma)$	$^{206}\text{Pb}/^{238}\text{U} \pm(1\sigma)$	$\delta^{18}\text{O}(\text{‰})$			
Zazr@1	212	584	42	2.76	0.0604	1.25	0.8842	1.97	0.1061	1.52	619	27	643	9	650	9	5.8
Zazr@2	269	1561	79	5.81	0.0616	1.07	0.8735	1.87	0.1029	1.53	659	23	638	9	631	9	5.5
Zazr@3	103	190	16	1.85	0.0618	2.47	0.8335	2.89	0.0978	1.50	667	52	616	13	602	9	5.4
Zazr@4	512	878	83	1.71	0.0610	1.23	0.8651	1.94	0.1029	1.50	638	26	633	9	632	9	6.2
Zazr@5	154	448	30	2.90	0.0607	1.54	0.8439	2.15	0.1008	1.51	630	33	621	10	619	9	5.5
Zazr@6	194	339	29	1.75	0.0612	1.84	0.8070	2.38	0.0956	1.50	647	39	601	11	589	8	5.6
Zazr@7	213	1469	70	6.88	0.0591	1.41	0.8315	2.06	0.1021	1.50	570	31	615	10	627	9	5.7
Zazr@8	266	2342	102	8.79	0.0612	1.24	0.8764	1.95	0.1038	1.50	647	26	639	9	637	9	5.2
Zazr@9	40	425	15	10.55	0.0658	3.31	0.8852	3.65	0.0975	1.54	800	68	644	18	600	9	5.9
Zazr@10	239	1785	80	7.47	0.0601	1.65	0.8683	2.23	0.1048	1.50	606	35	635	11	643	9	5.4
Zazr@11	142	606	32	4.27	0.0599	1.70	0.8138	2.36	0.0986	1.64	599	37	605	11	606	10	5.3
Zazr@12	223	614	41	2.75	0.0616	1.43	0.8425	2.11	0.0993	1.55	659	30	621	10	610	9	5.4
Zazr@13	210	466	34	2.22	0.0611	2.10	0.8167	2.58	0.0969	1.50	643	45	606	12	596	9	5.6
Zazr@14	146	238	23	1.62	0.0611	2.42	0.8516	2.85	0.1010	1.51	644	51	626	13	620	9	5.8
Zazr@15	289	1285	71	4.45	0.0609	1.18	0.8742	1.94	0.1041	1.53	635	25	638	9	639	9	5.8
Zazr@16	300	615	52	2.05	0.0614	1.19	0.8783	1.92	0.1037	1.50	654	25	640	9	636	9	5.6
Zazr@17	560	627	78	1.12	0.0612	0.69	0.8294	1.65	0.0984	1.50	645	15	613	8	605	9	5.9
Zazr@18	293	930	63	3.17	0.0606	0.96	0.8685	1.78	0.1039	1.50	626	21	635	8	637	9	5.7
Zazr@19	268	378	42	1.41	0.0610	1.11	0.8660	1.87	0.1030	1.50	639	24	633	9	632	9	6.1
Zazr@20	126	913	43	7.23	0.0621	1.78	0.8511	2.32	0.0994	1.50	677	38	625	11	611	9	5.5
Zazr@21	278	686	53	2.47	0.0604	0.93	0.8657	1.77	0.1040	1.50	616	20	633	8	638	9	5.5
Zazr@22	261	824	56	3.15	0.0605	1.25	0.8696	1.96	0.1043	1.51	620	27	635	9	640	9	6.0
Zazr@23	48	127	9	2.63	0.0606	3.67	0.8418	3.97	0.1007	1.51	626	77	620	19	619	9	5.6
Zazr@24	209	277	32	1.32	0.0610	1.50	0.8582	2.18	0.1020	1.58	639	32	629	10	626	9	5.8
Zazr@25	387	676	58	1.75	0.0604	0.98	0.7753	1.79	0.0931	1.50	617	21	583	8	574	8	5.8
Zazr@26	407	475	59	1.17	0.0607	0.84	0.8619	1.72	0.1030	1.50	628	18	631	8	632	9	5.3
Zazr@27	1024	1284	148	1.25	0.0610	0.59	0.8358	1.62	0.0994	1.51	639	13	617	8	611	9	6.4
Zazr@28	76	165	13	2.18	0.0596	1.96	0.8461	2.47	0.1030	1.50	588	42	623	12	632	9	5.6
Zazr@29	406	1012	76	2.49	0.0610	0.88	0.8624	1.76	0.1025	1.52	641	19	631	8	629	9	7.0
Zazr@30	103	229	19	2.21	0.0610	1.65	0.8784	2.23	0.1045	1.50	639	35	640	11	641	9	6.2
Zazr@31	520	394	71	0.76	0.0611	0.74	0.8913	1.73	0.1058	1.56	643	16	647	8	648	10	5.8
Zazr@32	456	860	78	1.89	0.0610	0.87	0.8839	1.76	0.1050	1.53	640	19	643	8	644	9	6.1
Zazr@33	238	1182	65	4.96	0.0607	1.10	0.8871	1.86	0.1060	1.50	629	24	645	9	649	9	5.9

Figure 3 Concordia of zircon U-Pb ages.

Figure 4 Histogram of O isotopic compositions (a) and distribution diagram of O isotopic compositions (b) of zircons. Data source: The $\delta^{18}\text{O}$ value of mantle zircon is from [66].

(1.4–1.6) ratios and high La/Sm (2.3–3.0) and Sm/Yb (2.1–2.6) ratios. They show weak negative Nb-Ta anomalies, positive Ti anomaly and do not have Zr-Hf anomalies in the primitive mantle-normalized trace element patterns (e.g. [16]; our unpublished data), indicating a derivation from an enriched mantle source [69], rather than crustal contamination. Moreover, most zircons of the Zhouan intrusion have $\delta^{18}\text{O}$ values same as the mantle values, indicating that only minor amounts of crustal components may have been incorporated in the mantle source. We therefore consider that the positive $\varepsilon_{\text{Hf}}(t)$ values of the zircons from the Zhouan intrusion are signature of an enriched mantle source.

The rocks from the Zhouan intrusion have nearly constant initial $^{87}\text{Sr}/^{86}\text{Sr}(t)$ ratios (I_{Sr}) (0.7046–0.7055) and $\varepsilon_{\text{Nd}}(t)$ values (–4.4–1.1). They plot in the field near the enriched mantle (EM1) source (Figure 5(b); our unpublished data and Yan et al. [16]). In addition, troctolites from the Duchongshan intrusion (632±6 Ma) in the Suizao basin have very fractionated LREE/HREE and without Nb, Ta, Zr and Hf anomalies, also consistent with a derivation from an enriched mantle source [15]. We therefore conclude that voluminous 640–630 Ma mafic-ultramafic intrusions in the Suizao basin were likely derived from an enriched mantle source.

4.2 Metasomatism of the mantle source

Magmas derived from either mantle wedge in an island arc setting or from mantle plume can have prints of an enriched mantle source. In subduction zone, partial melts of pelagic

sediments and oceanic slab could be enriched in Sr, Nd and Hf [70], the lithospheric mantle that had been metasomatized by the Sr-Nd-Hf-enriched melts may also become enriched [71]. Likewise, plume-derived magmas that had incorporated with recycled ancient pelagic sediments or the lower crust could be also identical to the geochemical features of an enriched mantle source [71].

Slab-derived fluids are generally enriched in LREE and large-ion lithophile elements (LILE), and depleted in high field strength elements (HFSE, e.g. Nb, Ta, Zr and Hf) [72]. Mafic magmas that were generated in an active continental margin setting usually inherited the geochemical characteristics of a metasomatized, enriched mantle source with slab-derived fluid [73]. Neoproterozoic mafic-ultramafic intrusions in the Hannan area show arc-like rocks in geochemistry, which was interpreted as a result of the mantle source modified by subducting slab [13]. The rocks from the Zhouan intrusion have low Nb/Y (0.27–0.40), Nb/Zr (0.06–0.08) ratios and high Rb/Y (0.48–1.64) ratios (e.g. [16]; our unpublished data), indicating that the mantle source may have modified by slab-derived fluids/melts (e.g. [9]).

Available whole-rock Sr-Nd isotopic compositions and zircon Hf isotopic data indicate that the nature of the mantle sources of Neoproterozoic mafic-ultramafic intrusions and mafic volcanic rocks may have evolved eventually from depletion to enrichment with time (Figure 5(a),(b)). The ~820 Ma Wangjiangshan intrusion has high $\varepsilon_{\text{Nd}}(t)$ values (3.4–3.8), low I_{Sr} values (0.7033–0.7037) and high zircon $\varepsilon_{\text{Hf}}(t)$ values (6.0–11.5), indicating a depleted mantle source [13]. The 815–800 Ma Beiba intrusion has lower $\varepsilon_{\text{Nd}}(t)$ values (0.2–2.0), higher I_{Sr} values (0.7038–0.7061) and lower zircon $\varepsilon_{\text{Hf}}(t)$ values (4.5–11.4), features of an enriched mantle source [13]. The 780–735 Ma maficultramafic intrusions have $\varepsilon_{\text{Nd}}(t)$ values (0.9–3.9), lower I_{Sr} values (0.7033–0.7039) and lower zircon $\varepsilon_{\text{Hf}}(t)$ values (2.9–10.0), also indicating an enriched mantle source [13]. The ~637 Ma Zhouan intrusion has much low $\varepsilon_{\text{Nd}}(t)$ values (–4.4–1.1), high I_{Sr} values (0.7046–0.7062) (e.g. [16]; our unpublished data) and low zircon $\varepsilon_{\text{Hf}}(t)$ values (1.3–7.6), indicating a highly enriched mantle source. Likewise, the Neoproterozoic mafic volcanic rocks in the northern margin of the Yangtze Block show similarly compositional variation in the mantle sources. The 950–895 Ma basalts of the Xixiang Formation have whole-rock $\varepsilon_{\text{Nd}}(t)$ values ranging from 8.8 to 4.6 with an arc-like geochemistry, indicating a derivation from a depleted mantle with crustal contamination and formation in a transitional setting from early fore-arc to late back-arc basin [20]. The 840–776 Ma basalts and basaltic andesite from the Bikou Formation have $\varepsilon_{\text{Nd}}(t)$ values from 7.9 to 3.4, indicating signatures of both depleted and enriched mantle sources [74]. The 778–667 Ma mafic volcanic rocks from the Baishuijiang Formation have 4.6 to 1.1 $\varepsilon_{\text{Nd}}(t)$ values [75], similar to $\varepsilon_{\text{Nd}}(t)$ values (4.6–2.0) of the ~755 Ma mafic volcanic rocks from the Wudang Formation, indicating an enriched mantle source [76]. Mafic volcanic rocks from

Table 2 Zircon Hf isotopic compositions for the Zhouan intrusion

Spot number	$^{176}\text{Yb}/^{177}\text{Hf}$	2σ	$^{176}\text{Lu}/^{177}\text{Hf}$	2σ	$^{176}\text{Hf}/^{177}\text{Hf}$	2σ	$^{176}\text{Hf}/^{177}\text{Hf}_{(t)}$	$\varepsilon_{\text{Hf}}(t)$
Zazr@1	0.0306	0.0003	0.0010	0.0000	0.282527	0.000028	0.282515	5.3
Zazr@2	0.0351	0.0003	0.0012	0.0000	0.282480	0.000022	0.282466	3.1
Zazr@3	0.0200	0.0002	0.0006	0.0000	0.282484	0.000027	0.282477	2.8
Zazr@4	0.0415	0.0004	0.0013	0.0000	0.282559	0.000037	0.282544	5.9
Zazr@5	0.0418	0.0008	0.0014	0.0000	0.282571	0.000028	0.282555	6.0
Zazr@6	0.0325	0.0004	0.0009	0.0000	0.282475	0.000033	0.282465	2.1
Zazr@7	0.0538	0.0006	0.0017	0.0000	0.282507	0.000035	0.282486	3.7
Zazr@8	0.0527	0.0007	0.0016	0.0000	0.282570	0.000030	0.282551	6.2
Zazr@9	0.0243	0.0002	0.0008	0.0000	0.282473	0.000023	0.282463	2.3
Zazr@10	0.0651	0.0025	0.0020	0.0001	0.282549	0.000031	0.282525	5.4
Zazr@11	0.0337	0.0005	0.0011	0.0000	0.282500	0.000021	0.282488	3.3
Zazr@12	0.0346	0.0001	0.0011	0.0000	0.282496	0.000024	0.282483	3.2
Zazr@13	0.0737	0.0017	0.0023	0.0001	0.282620	0.000028	0.282594	6.9
Zazr@14	0.0288	0.0003	0.0009	0.0000	0.282484	0.000028	0.282474	3.1
Zazr@15	0.0261	0.0004	0.0008	0.0000	0.282536	0.000029	0.282526	5.4
Zazr@16	0.0529	0.0013	0.0016	0.0000	0.282608	0.000029	0.282589	7.6
Zazr@17	0.0149	0.0005	0.0003	0.0000	0.282471	0.000027	0.282467	2.6
Zazr@18	0.0213	0.0000	0.0006	0.0000	0.282505	0.000020	0.282498	4.4
Zazr@19	0.0153	0.0001	0.0005	0.0000	0.282465	0.000025	0.282460	2.9
Zazr@20	0.0271	0.0007	0.0009	0.0000	0.282491	0.000029	0.282481	3.2
Zazr@21	0.0313	0.0001	0.0009	0.0000	0.282421	0.000022	0.282410	1.3
Zazr@22	0.0242	0.0002	0.0007	0.0000	0.282457	0.000023	0.282448	2.7
Zazr@23	0.0137	0.0002	0.0004	0.0000	0.282488	0.000022	0.282483	3.4
Zazr@24	0.0178	0.0001	0.0005	0.0000	0.282454	0.000025	0.282448	2.4
Zazr@25	0.0201	0.0001	0.0006	0.0000	0.282473	0.000025	0.282466	1.8
Zazr@26	0.0223	0.0003	0.0007	0.0000	0.282454	0.000021	0.282446	2.4
Zazr@27	0.0400	0.0005	0.0012	0.0000	0.282596	0.000046	0.282583	6.8
Zazr@28	0.0184	0.0001	0.0006	0.0000	0.282554	0.000028	0.282547	6.0
Zazr@29	0.0070	0.0001	0.0002	0.0000	0.282484	0.000020	0.282482	3.6
Zazr@30	0.0081	0.0002	0.0003	0.0000	0.282453	0.000019	0.282450	2.8
Zazr@31	0.0200	0.0001	0.0006	0.0000	0.282500	0.000023	0.282492	4.4
Zazr@32	0.0279	0.0001	0.0008	0.0000	0.282501	0.000020	0.282492	4.3
Zazr@33	0.0311	0.0008	0.0009	0.0000	0.282502	0.000021	0.282490	4.4

Figure 5 Plots of zircon $\varepsilon_{\text{Hf}}(t)$ values versus U-Pb ages (a) and whole-rock Sr-Nd isotopic compositions (b) of Neoproterozoic mafic-ultramafic intrusions and mafic volcanic rocks. Data source: Zircon Hf isotopic compositions and whole-rock Sr-Nd isotopic compositions of the 820 Ma Wangjiangshan intrusion, 815–800 Ma Beiba intrusion, 780–735 Ma Bijigou and Luojiaba intrusions are from [13]; Sr-Nd isotopic compositions of basalts of the 950–895 Ma Xixiang Formation are from [20]; those of the 840–776 Ma Bikou Formation are from [74]; those of the 778–667 Ma Baishuijiang Formation are from [75]; those of the 632 Ma Yaolinghe Formation are from [77,78].

the Yaolinghe Formation have $\varepsilon_{\text{Nd}}(t)$ ($t=632$ Ma) values ranging from 3.0 to -0.6 [77,78], indicating a highly enriched mantle source. Therefore, we suppose that the mantle source of Neoproterozoic mafic-ultramafic intrusions in the northern margin of the Yangtze Block eventually became enriched from ~ 820 Ma to ~ 630 Ma. The trigger for such transformation is likely to be the metasomatism of the lithospheric mantle with slab-derived fluids/melts [13].

4.3 Timing of final breakup of the Rodinia supercontinent in the northern margin of the Yangtze Block

Zhao et al. [27] proposed that the Nanhua basin in the southeastern margin of the Yangtze Block was a back-arc basin formed by a long-term subduction of Hannan-Panxi Andean-type continental marginal arc beneath the western and northern margins of the Yangtze Block. The subduction is supposed to have started at <950 Ma and lasted until ~ 735 Ma [9,13,37]. The Zhouan intrusion and other mafic-ultramafic intrusions in the Suizao Basin and the coeval Yaolinghe Formation are considered to have formed in a continental extension setting [45–47], indicating the continental breakup event at ~ 635 Ma. It is therefore suggested that the transformation from subduction to extension in the northern margin of the Yangtze Block may have happened sometime between <735 Ma and ~ 635 Ma. However, it remains uncertain the exact time of the subduction cease in this period as there was no record of magmatism related to the subduction events in the northern margin of the Yangtze Block.

Intracontinental rifting in the Yangtze Block at Neoproterozoic is proposed to be concurrent with the Nantuo glaciation, the last glaciation at Neoproterozoic [79] based on available age data of the late Neoproterozoic-Sinian Nanhua System and Sinian tillite in the southeastern margin of the Yangtze Block and a comparison of strata between the Nanhua and Kangdian basins. The interlayers of volcanic ash in dolomite at the bottom of the Doushantuo Formation that is underlain by the Nantuo Formation was dated to be 635.2 ± 0.6 Ma [80], which referred to the end of the Nantuo glaciation [80,81] and is identical to the age of the global Morinoan glaciation and the mafic-ultramafic intrusions and volcanic rocks in the Suizao basin. Therefore, the volcanic ash layers in the Doushantuo Formation may have been generated by ~ 635 Ma intracontinental rifting of the Yangtze Block. Hoffman [82] suggested that degassing of volcanism resulted in rapid increase of amounts of CO_2 in atmosphere, triggering an abrupt change from Snowball to extreme greenhouse on earth. We therefore assume that the Nantuo glaciation may be ended due to ~ 635 Ma, voluminous magmatism in the Suizao basin.

Paleomagnetic data used for the reconstruction of the Rodinian supercontinent show that an 40° clockwise rotation of the South and West Australian cratons relative to the North Australian craton around a vertical axis in Central

changed the trace of the Australian apparent polar wander path (APWP), indicating that the breakup of major continental blocks of the Rodinia supercontinent occurred at ~ 650 Ma [83]. The 650 – 630 Ma magmatism are also reported in many places, such as those 650 – 630 Ma mafic dykes in the northern margin of the Tarim Block [84] and those 650 – 630 Ma alkaline complexes in the southern margin of the Siberian craton [85]. These intrusions may characterize the last magmatism related to the breakup of the Rodinian supercontinent [86,87]. Therefore, we propose that the ~ 635 Ma mafic-ultramafic intrusions and coeval bimodal volcanic lavas in the Suizao basin recorded the last magmatism related to the breakup of the Rodinian supercontinent in the northern margin of the Yangtze Block.

5 Conclusions

The Zhouan ultramafic intrusion in the Suizao basin is dated at 637 ± 4 Ma and was derived from an enriched mantle source, which was evolved from the lithospheric mantle metasomatized with slab-derived fluids/melts. A number of ~ 635 Ma mafic-ultramafic intrusions in the Suizao basin and the coeval bimodal volcanics of the Yaolinghe Formation indicate a continental rifting setting. They may represent the last magmatism related to the breakup of the Rodinian supercontinent at Neoproterozoic in the northern margin of the Yangtze Block.

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