



Age and nature of eclogites in the Huwan shear zone, and the multi-stage evolution of the Qinling–Dabie–Sulu orogen, central China

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ABSTRACT

In situ LA-ICPMS U–Pb, trace element, and Hf isotope data in zircon demonstrate a Carboniferous age for eclogite-facies metamorphism in Siluro-Devonian protoliths in the Huwan shear zone, Dabie Mountains, Central China. This age contrasts with the more prevailing Triassic age for high- to ultrahigh pressure (HP to UHP) metamorphism in the Qinling–Dabie–Sulu orogen. Metamorphic zircon in two eclogite samples from Sujiahe is characterized by low Th/U ratios, small negative Eu anomalies, flat HREE patterns, and low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios. These geochemical signatures suggest that the zircon crystallized in the presence of garnet and in the absence of plagioclase feldspar. Furthermore, temperatures of ~ 655 and ~ 638 °C, calculated using the Ti content of zircon, are consistent with their formation during eclogite-facies metamorphism. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 309 ± 4 Ma (2σ) for this zircon improves previous age estimates for eclogite-facies metamorphism in the Huwan shear zone, ranging from 420 to 220 Ma. Metamorphic zircon from one eclogite sample from Hujiawan, most likely formed during prograde metamorphism, yields an equivalent age estimate of 312 ± 11 Ma. Magmatic zircon cores in the three samples yield ages for the magmatic protoliths of the eclogites ranging from 420 ± 7 to 406 ± 5 Ma, and post-dating the middle Paleozoic collision of the North China and the Qinling terrain. The zircon crystals in the three eclogite samples display a large variation of $\varepsilon_{\text{Hf}}(t)$ values of -4.9 to 21.3 . The metamorphic zircon overgrowths show the same range of $\varepsilon_{\text{Hf}}(t)$ values as those of the inherited magmatic crystal interiors. This suggests that the metamorphic zircon overgrowths may have formed by dissolution-reprecipitation of pre-existing magmatic zircon thereby preserving their original Hf isotopic composition. The high $\varepsilon_{\text{Hf}}(t)$ values suggest that the protoliths were derived from depleted mantle sources, most likely Paleotethyan oceanic crust; while the low $\varepsilon_{\text{Hf}}(t)$ values are attributed to crustal contamination. Some eclogites in the Huwan shear zone have a distinctive signature of continental crust most probably derived from the Yangtze Craton. The coexistence of Paleozoic oceanic crust and Neoproterozoic continental crust with similar metamorphic ages in the Huwan shear zone implies that Paleozoic Paleotethyan oceanic crust was produced within a marginal basin of the northern Yangtze Craton. The opening of the Paleo-Tethyan ocean was slightly younger than the collision of the North China Craton and the Qinling terrain during the Late Paleozoic in the Qinling–Dabie–Sulu orogen. Subduction of the Paleo-Tethyan oceanic crust and associated continental basement resulted in the 309 ± 2 Ma (2σ) eclogite-facies metamorphism in the Huwan shear zone. The subsequent Triassic continent–continent collision led to the final coalescence of the Yangtze and Sino-Korean cratons. Amalgamation of the Yangtze and North China cratons was, therefore, a multistage process extending over at least 200 Ma.

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1. Introduction

The Qinling–Dabie–Sulu orogen marks the suture zone between the North China and Yangtze cratons in Central China (Fig. 1). Despite intensive study for more than 20 years, controversies still exist about the location and number of sutures and the timing of collision. Researchers working in the western part of the orogen, i.e. the Qinling

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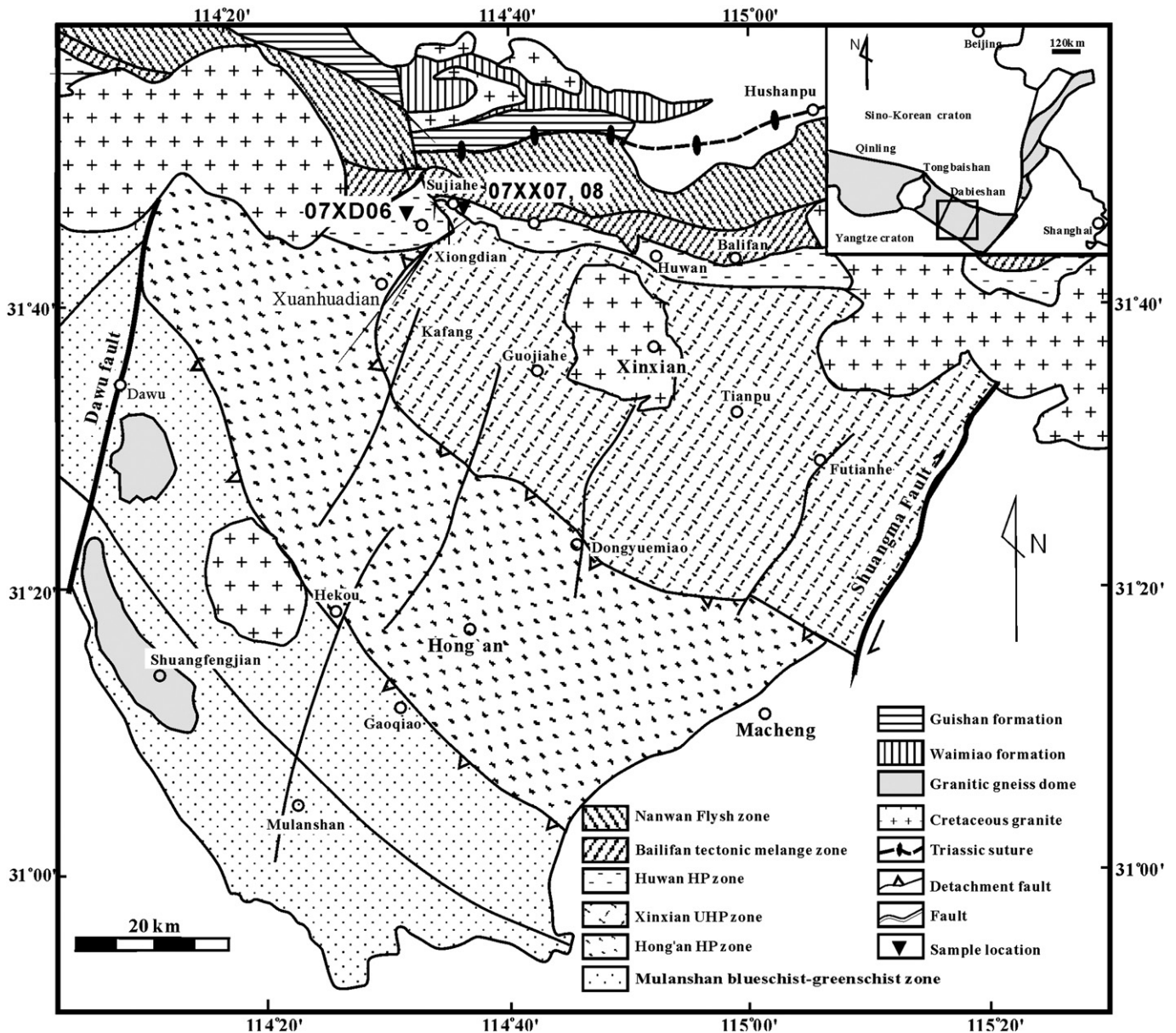


Fig. 1. Sketch geological map of the Huwan shear zone in the Qinling-Dabie-Sulu orogen and sample locations (Modified after Liu et al., 2004b).

and Tongbai mountains, have argued for a Paleozoic amalgamation (Kröner et al., 1993; Yang et al., 2005) or a Paleozoic collision overprinted by Mesozoic intracontinental shortening (Mattauer et al., 1985; Zhai et al., 1998). In contrast, investigations in the eastern part of the orogenic belt, i.e. in the Dabie-Sulu terrane, suggest Triassic subduction (Ames et al., 1996; Hacker et al., 1998; Li et al., 2000; Ayers et al., 2002; Zheng et al., 2003, 2004; Hacker et al., 2006). Multi-stage subduction, and extension and rifting, in relation to the opening of the Paleotethyan ocean floor have been proposed as a model to reconcile these controversies (Meng and Zhang, 1999, 2000; Ratschbacher et al., 2003, 2006). This model, however, has been debated because of the scarcity of precise ages (Sun et al., 2002; Liu et al., 2004a; Jahn et al., 2005; Qiu and Wijbrans, 2006).

The Hong'an Block, that forms part of the western Dabie Mountains, is one area critical to decipher the tectonic evolution of the Qinling-Dabie-Sulu orogenic belt (Fig. 1), as it is located at the junction between the western and eastern sections of the orogenic belt, and forms the transition between zones exposing low-pressure and ultra-high pressure rocks. The east-west trending 5–10 km wide Huwan shear zone defines the tectonic contact between the more

inboard Qinling belt to the northwest and the outboard Dabie-Sulu belt in the southeast (Fig. 1). The timing of eclogite-facies metamorphism and protolith formation of the Huwan shear zone is important for testing multi-stage subduction, and extension and rifting models. However, published $^{40}\text{Ar}/^{39}\text{Ar}$, U/Pb, Rb/Sr, and Sm/Nd ages interpreted to date the eclogite-facies metamorphism from the Huwan shear zone span from ca. 420–220 Ma (Ratschbacher et al., 2006, and references therein). The age and origin of the protoliths of eclogites in this zone have not yet been well documented. In this paper, we present an integrated study of in situ U-Pb, trace element, and Lu-Hf analysis, for zircon crystals from three eclogite samples from the Huwan shear zone. These results not only unravel the eclogite-facies and protolith ages and origin of these eclogites, but also shed light on the multi-stage tectonic evolution of the Qinling-Dabie-Sulu orogen.

2. Geological setting and previous geochronology

The Hong'an Block forms the central section of the Qinling-Dabie-Sulu orogen and is bounded by the Shangma Fault in the east and the Dawu Fault in the west (Fig. 1). The Huwan shear zone is the

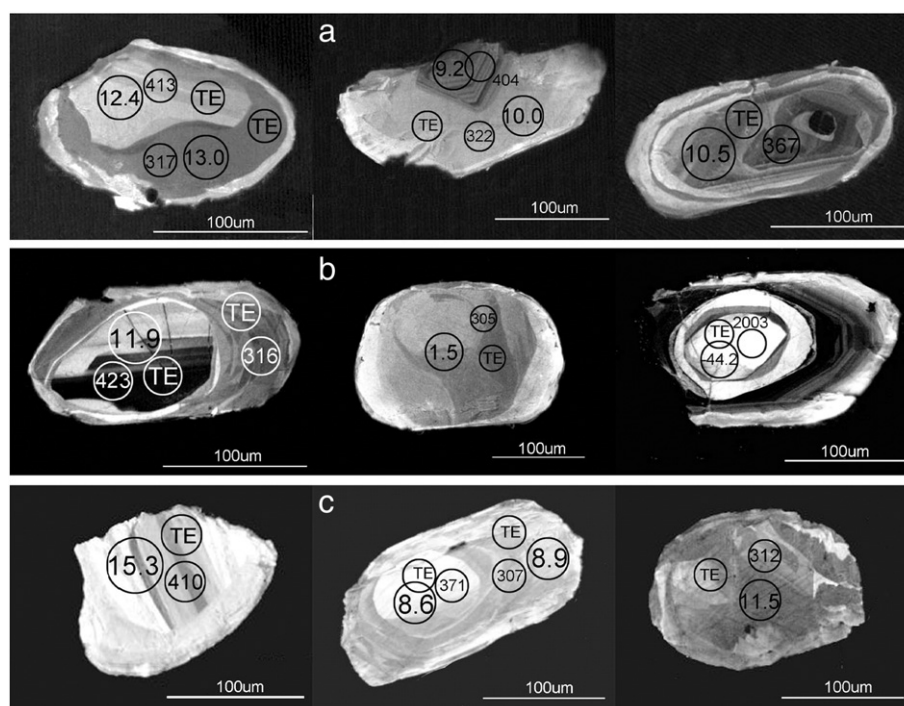


Fig. 2. Typical CL images of zircons in samples 07XD06 (a), 07XX07 (b), and 07XX08 (c). The smaller circles show LA-ICPMS dating spots and corresponding U-Pb ages (in Ma) and LA-ICPMS trace element analysis spots (marked with TE). Bigger circles show locations of Lu-Hf isotope analysis and the corresponding $\epsilon_{\text{Hf}}(t)$ values.

northern bounding eclogite zone of the Hong'an Block (Fig. 1). Eclogites occur as bands, or lenses (Ye et al., 1994; Eide and Liou, 2000; Fu et al., 2002; Liu et al., 2004b). Both eclogites and enclosing lithologies have been subjected to greenschist- to amphibolite-facies metamorphism (Ratschbacher et al., 2006). The eclogites yielded peak metamorphic conditions of 540–730 °C and 1.4–2.1 GPa and retrograde metamorphism at 530–685 °C and ~6 kbar (Fu et al., 2002; Liu et al., 2004b; Ratschbacher et al., 2006). Eclogites with three different types of protolith are identified in this shear zone: eclogites with oceanic crust protoliths (MORB) (Li et al., 2001; Fu et al., 2002; Gao et al., 2002); with probable late Proterozoic island arc basalt protoliths (Li et al., 2001); and with probable Neoproterozoic continental protoliths (Hacker et al., 2000; Liu et al., 2004a; Jahn et al., 2005).

In spite of efforts to establish a geochronologic framework for this shear zone, the timing of the eclogite-facies metamorphism and protolith formation is still inconclusive. Jian et al. (1997, 2000) reported U-Pb ages of ca. 400 and 300 Ma on zircon from an eclogite at Xiongdi, and interpreted a 424 ± 5 Ma sensitive high resolution ion microprobe (SHRIMP) zircon core age as the minimum age of the eclogite-facies metamorphism and the ca. 300 Ma as the time of retrograde metamorphism. Xu et al. (2000) acquired phengite $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 350–420 Ma for eclogites from the same outcrop, and interpreted those dates as recording retrograde metamorphism. Metamorphic zircon from three samples from Xiongdi and Hujiawan gave a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 309 ± 3 Ma by SHRIMP (Sun et al., 2002). That date was interpreted as the time of eclogite-facies metamorphism, although there was a large variation of $^{206}\text{Pb}/^{238}\text{U}$ ages from ca. 200 to 330 Ma, and complex REE compositions of the metamorphic zircon grains (Sun et al., 2002). Zircon cores from the same samples yielded U-Pb ages of 430–350 Ma, and were interpreted as detrital zircon grains. Gao et al. (2002) reported zircon SHRIMP U-Pb ages of 449 ± 14 Ma, and 307 ± 14 Ma, and a 216 ± 4 Ma ($n=6$) cluster for zircon dates from an eclogite at Xiongdi, interpreting these latter ages as a Triassic overprint of the eclogite forming event. Permo-Triassic $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite ages (ca. 210–270 Ma) were reported by Ratschbacher et al. (2006) which were interpreted as cooling ages. In contrast, zircon samples in two

eclogites from the eastern part of the Huwan shear zone have been dated by SHRIMP (Liu et al., 2004a). Magmatic cores in the two samples yielded ages of 716 ± 28 and 733 ± 10 Ma, interpreted as their protolith ages. The metamorphic rims from one sample gave a range of $^{206}\text{Pb}/^{238}\text{U}$ ages from 315 ± 17 to 229 ± 12 Ma. The youngest age was interpreted as the maximum age of the eclogite-facies metamorphism (Liu et al., 2004a). Jahn et al. (2005) obtained Rb-Sr mineral isochron ages of 210 Ma to 225 Ma from this region, which were interpreted as supporting a Triassic eclogite-facies metamorphism of the Huwan shear zone.

For the present study, three eclogite samples (07XD06, 07XX07, 07XX08) from the Huwan shear zone were selected. Two samples (07XX07 and 07XX08) were collected at Sujiahe from outcrops approximately 80 m apart (Fig. 1). The third sample (07XD06) was collected from Hujiawan (Fig. 1). All three samples are foliated quartz eclogite. These eclogites contain garnet + quartz + omphacite + rutile + amphibole \pm phengite \pm epidote, with minor accessory minerals including apatite, zircon, and titanite. Garnet is euhedral and coarse-grained, with mineral inclusions of amphibole, quartz, omphacite, and rutile. Some omphacite rims are completely replaced by amphibole. Amphibole also occurs as fine-grained aggregates in matrix.

3. Analytical methods

Cathodoluminescence images of zircon was acquired using a Quanta 400FEG environmental scanning electron microscope (ESEM) equipped with an Oxford energy dispersive spectroscopy (EDS) system and a Gatan CL3+ CL detector at Northwest University, Xi'an. Zircon U-Pb dating and trace element analysis were done using an Geolas 193 nm ArF Excimer laser ablation (LA) system coupled to an Agilent 7500a inductively coupled plasma mass spectrometer (ICPMS) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences. Two samples 07XD06 and 07XX07 were also dated using a Finnigan ELEMENT XR double focusing magnetic sector field ICP-MS in combination with a Geolas 193 nm ArF Excimer laser located in the Inco Innovation Centre, Memorial University of Newfoundland. In situ zircon Lu-Hf

isotopic measurements were done using the Nu Plasma high-resolution (HR) Multi-Collector (MC) – ICPMS, equipped with a Geolas 193 nm ArF Excimer laser, at Northwest University. Full details of analytical methods are provided in the on line Supplementary Materials.

4. Results

4.1. Zircon morphology and U-Pb ages

Zircon crystals in sample 07XD06 at Hujiawan are subhedral, transparent, and colorless. In CL images, most zircon grains exhibit a clear core-rim structure (Fig. 2a). The cores show igneous growth zoning variably overprinted by bright homogeneous, unzoned, or in some cases sector zoned, domains. These grains are interpreted as magmatic zircons crystals that have experienced different degrees of solid-state recrystallization (Hoskin and Black, 2000; Corfu et al., 2003). The rims are unzoned or weakly zoned and are thought to represent metamorphic overgrowths (Corfu et al., 2003; Hanchar and Hoskin, 2003).

Twenty U-Pb analyses on 17 zircon grains from sample 07XD06 were done by LA-ICPMS at China University of Geosciences are reported in Table S1 and presented in Fig. 3a. Fifteen analyses on zircon cores yield concordant to nearly concordant ages with apparent $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 412 ± 5 to 344 ± 4 Ma (1σ) (Table S1 and Fig. 3a). The five analyses on metamorphic rims yield concordant $^{206}\text{Pb}/^{238}\text{U}$ ages of 307–322 Ma with a weighted mean of 314 ± 7 Ma (2σ , MSWD=1.6), which represents the best estimate of the age of metamorphism preserved in these zircon grains. There are two plausible interpretations of the core data: (1) the spread of ages indicates that the sample contains a heterogeneous population of inherited zircon crystals that formed between 412 and 344 Ma; or, (2) the zircon crystals may have formed at ca. 410 Ma and then lost variable amounts of Pb during an isotopic disturbance event at ca. 310 Ma, which is often observed in magmatic rocks that underwent slow cooling rates or metamorphic re-equilibration after crystallization (Ashwal et al., 1999; Hoskin and Black, 2000; Giacomini et al., 2007). Although we can not completely rule out the possibility that the core-rim interface was sampled for some of the analyses which would also lead to intermediate ages, we prefer the second interpretation for our results because: (1) the young ages were mostly obtained from zircon crystals with complex internal structures (Fig. 2a); (2) the oldest seven analyses define a main peak on a probability density plot (Fig. 3a), while the other younger analyses are dispersed toward the metamorphic zircon age; and (3) detrital magmatic zircon grains from adjacent metasedimentary rock do not yield ages younger than 390 Ma (Wu et al., unpublished data). Therefore, the seven oldest analyses with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 406 ± 5 Ma (2σ , MSWD=1.4) are used to infer the protolith formation age; while the other eight core ages ranging from 385 to 344 Ma most likely represent different degrees of resetting, and thus have no obvious geological significance.

Eighteen zircon crystals in sample 07XD06 were also dated by LA-ICPMS at Memorial University of Newfoundland (Table S2 and Fig. S1a). Twelve analyses on magmatic cores have concordant to nearly concordant ages varying from 346 ± 17 to 412 ± 18 Ma (1σ), and the oldest 6 analyses show similar ages, and give a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 399 ± 9 Ma (2σ , MSWD=0.17) (Fig. S1a). These data suggest that the 399 ± 9 Ma age represents the formation age of the magmatic zircon crystals, while the other younger ages represent different degrees of resetting. Five analyses on metamorphic rims on the zircon grains have $^{206}\text{Pb}/^{238}\text{U}$ ages of 301 ± 11 to 334 ± 26 Ma (1σ) with a weighted mean of 307 ± 10 Ma (2σ , MSWD=1.6). One zircon inner core shows a slightly older $^{206}\text{Pb}/^{238}\text{U}$ age of 556 ± 22 Ma (1σ), which is interpreted as a xenocrystic core.

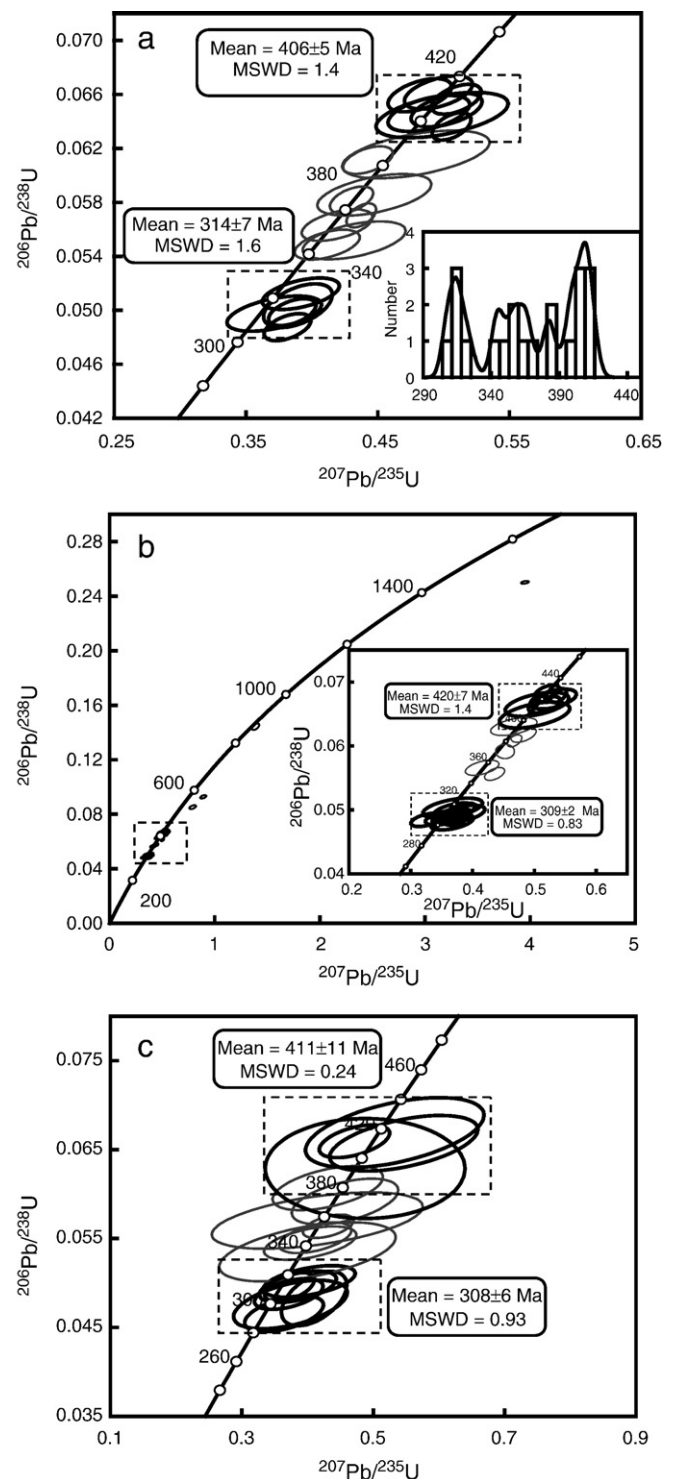


Fig. 3. Concordia diagrams of LA-ICPMS zircon U-Pb dating of eclogite samples at China University of Geosciences. (a) 07XD06 (the inset is a probability density plot of U-Pb ages of the magmatic cores), (b) 07XX07, and (c) 07XX08.

Zircon grains in sample 07XX07 from Sujiahe are colorless and transparent, anhedral to subhedral. Cathodoluminescence imaging reveals that these zircon crystals generally have distinct core-rim structures (Fig. 2b). The cores show igneous growth zoning, whereas the rims are unzoned or only weakly zoned, which are interpreted as igneous cores and metamorphic overgrowths, respectively (Corfu et al., 2003). Some of the zircon crystals have inner irregular shaped cores with a brighter CL emission. These inner cores are either unzoned, or weakly zoned, and mantled by the more common igneous

growth zoned magmatic zircon. The inner cores are interpreted as xenocrystic inherited zircon grains of the protolith with the inner cores recording an earlier geologic event.

A total of 28 LA-ICPMS U-Pb analyses were done on 24 zircon grains from sample 07XX07 at China University of Geosciences (Table S1 and Fig. 3b). Twelve analyses on magmatic zircon cores show a range of concordant to nearly concordant ages between 349 ± 4 and 426 ± 5 Ma (1σ). Similar to the previous sample, the oldest six ages define a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 420 ± 7 Ma (2σ (MSWD=1.4), interpreted as the protolith age. Six younger ages varying from 349 ± 4 to 394 ± 6 Ma (1σ) reflect partial Pb loss due to the subsequent metamorphism. Twelve analyses on metamorphic zircon rims define within analytical uncertainty identical $^{206}\text{Pb}/^{238}\text{U}$ ages at 303 ± 5 to 316 ± 6 Ma with a weighted mean of 309 ± 2 Ma (2σ , MSWD=0.83). The other four analyses on xenocrystic cores show variably discordant ages with $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2003 ± 52 to 770 ± 75 Ma (2σ). This indicates that there may be a range of xenocrystic zircon grains each with a different provenance in this sample.

For comparison, twenty-three LA-ICPMS U-Pb analyses were also done for 22 zircon grains from sample 07XX07 at Memorial University of Newfoundland (Table S2 and Fig. S1b). The data from the two laboratories are consistent. Fifteen analyses on metamorphic zircon rims form a cluster with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 306 ± 7 Ma (2σ , MSWD=1.4). Three analyses on magmatic zircon cores yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 369 ± 22 – 404 ± 15 Ma (1σ). The other five analyses obtained from xenocrystic zircon cores are discordant. Three of them give a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 797 ± 23 Ma (2σ), the other two have $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 675 ± 55 and 1679 ± 16 Ma (1σ). This confirms the observation that the sample contains xenocrystic inner cores with different ages and hence different provenances.

Zircon crystals in sample 07XX08 from Sujiahe are colorless and transparent, and have oval to short prismatic shape. In CL images, most of these zircon grains exhibit clear core-rim structures (Fig. 2c). The cores show weak igneous growth zoning, and in some cases no zoning, with brighter luminescence than the rims, indicating that they are magmatic zircon grains modified by different degrees of solid-state recrystallization (Hoskin and Black, 2000; Corfu et al., 2003). The rims are weakly zoned, and are interpreted as metamorphic overgrowths. Some grains wholly show sector or weak zoning, identical to the metamorphic rims and have no cores.

Sixteen zircon grains from sample 07XX08 were dated by 18 LA-ICPMS U-Pb analyses at China University of Geosciences (Table S1 and Fig. 3c). Except for analysis #4, all of the analyses have very low U contents of 6–49 ppm, resulting in relatively high analytical uncertainties. Eleven analyses on magmatic cores are concordant to nearly concordant with a large variation of $^{206}\text{Pb}/^{238}\text{U}$ ages between 336 ± 13 and 418 ± 16 Ma. The oldest four analyses yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 411 ± 11 Ma (2σ (MSWD=0.24), therefore, represents the protolith formation age; while the other seven younger analyses with $^{206}\text{Pb}/^{238}\text{U}$ ages of 336–380 Ma may be related to subsequent Pb loss. The other seven analyses on metamorphic domains show coherent $^{206}\text{Pb}/^{238}\text{U}$ ages of 293 ± 8 to 316 ± 7 Ma with a weighted mean of 308 ± 6 Ma (2σ) (MSWD=0.93), which is interpreted as the metamorphic age.

4.2. Zircon trace elements

Sixteen trace element analyses were done on 13 zircon grains from sample 07XD06 (Table S3 and Fig. 4a). The magmatic cores have relatively low Th (26.6–87.5 ppm) and average to relatively high U (176–982 ppm) contents with Th/U ratios of 0.05–0.25. The chondrite normalized rare earth element (REE) patterns of the magmatic cores are enriched in heavy REE (HREE) ($\text{Lu}_N/\text{Sm}_N = 443$ – 634 and $\text{Lu}_N = 3651$ – 9943), and have a positive Ce anomaly and a large negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.04$ – 0.12) (Fig. 4a). The titanium contents of the cores vary from 4.26 to 22.9 ppm (Table S3). Using the Ti-in-zircon

thermometer (Watson and Harrison, 2005), the temperatures calculated range from 671 to 820 °C by assuming the activity of $\text{TiO}_2 = 1$ (i.e., zircon crystallized in the presence of rutile), which may estimate the temperatures at the time the zircon cores formed.

In contrast, the metamorphic rims have more variable Th (6.18–67.3 ppm) and U (60.7–1945 ppm) contents, and low Th/U ratios of 0.03–0.11. The chondrite normalized zircon REE patterns (Fig. 4a), for these zircon crystals also display HREE-enriched patterns ($\text{Lu}_N/\text{Sm}_N = 121$ – 460 and $\text{Lu}_N = 315$ – 1205) with a positive Ce anomaly and a relatively insignificant negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.31$ – 1.02). Their HREEs, however, are less enriched than those of the magmatic zircon crystals (Fig. 5a). They have Ti contents of 2.59–5.13 ppm (Table S3), yielding metamorphic temperatures of 635–686 °C at the activity of $\text{TiO}_2 = 1$ (Watson and Harrison, 2005).

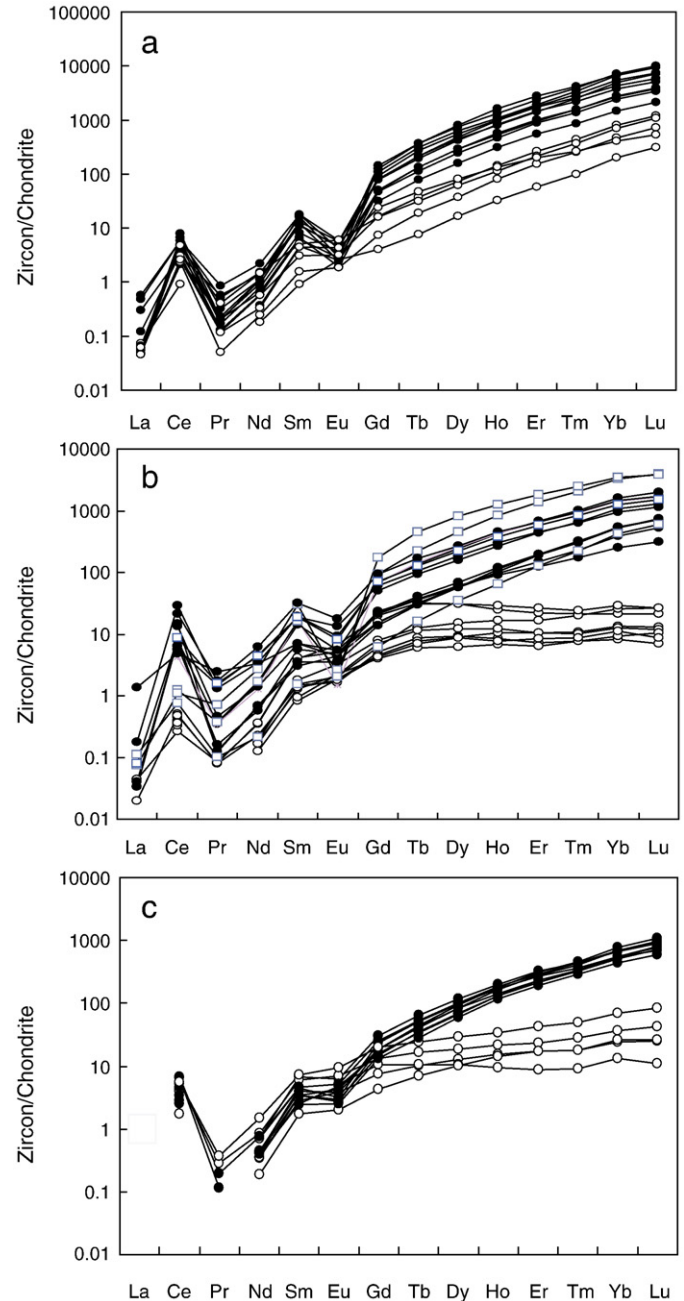


Fig. 4. Chondrite-normalized REE patterns of zircons from samples 07XD06 (a), 07XX07 (b) and 07XX08 (c). Open circles denote metamorphic domains; solid dots represent protolith domains; and open squares represent inherited domains. Chondrite-normalization values are from Sun and McDonough (1989).

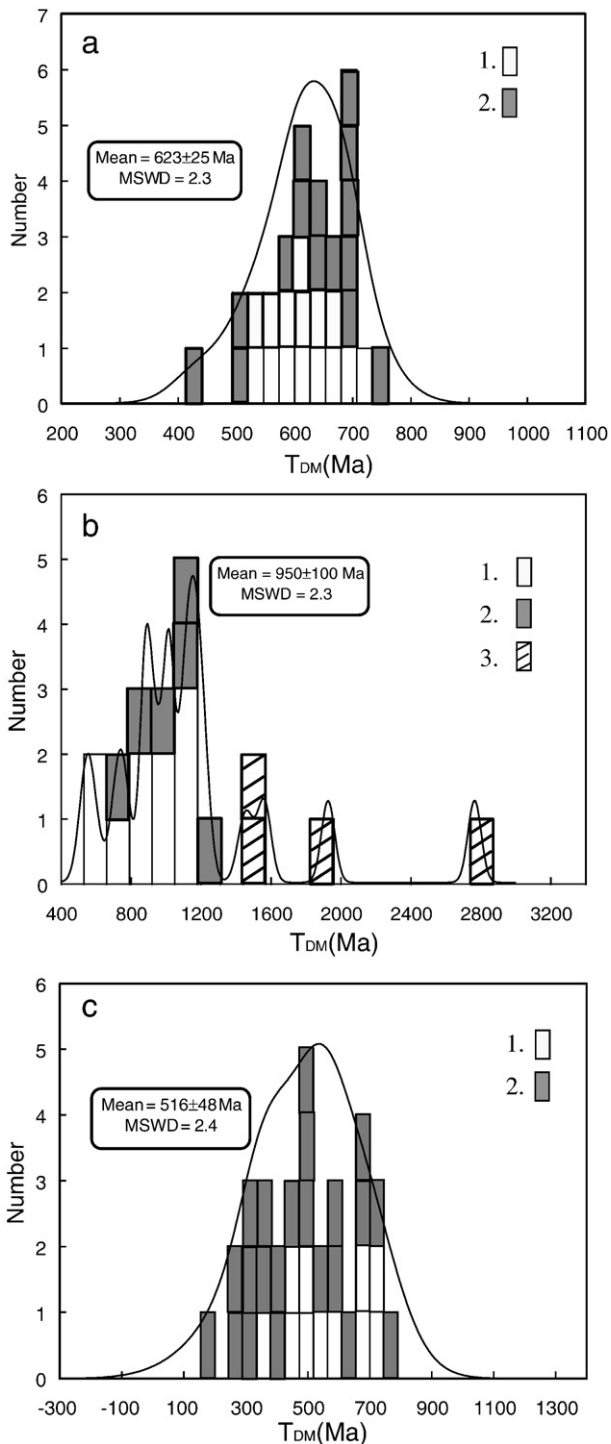


Fig. 5. Histograms of zircon Hf model ages (T_{DM}) for samples 07XD06 (a), 07XX07 (b), and 07XX08 (c). 1, magmatic domain; 2, metamorphic domain; 3, inherited domain.

Twenty-two trace element analyses were done on 18 zircon grains in sample 07XX07 (Table S3 and Fig. 4b). Ten analyses on magmatic cores have relatively high Th, U, and Y contents (45.4–437, 83.3–1937 and 209–773 ppm, respectively), and Th/U ratios of 0.16–0.97. The chondrite normalized REE patterns are enriched in HREE ($Lu_N/Sm_N=55–239$ and $Lu_N=530–2020$), and have large negative Eu anomalies ($Eu/Eu^*=0.04–0.67$) (Fig. 4b). Except for analysis #4 which has an abnormally high Ti content of 103 ppm, the other 9 analyses have Ti contents of 2.46–9.63 ppm, corresponding to formation temperatures of 631–738 °C (Watson and Harrison, 2005). Whereas eight analyses on the metamorphic zircon grains have low

Th (1.27–4.50 ppm) and moderate U (85.4–189.3 ppm) contents, and very low Th/U ratios of 0.01–0.03. The middle REE (MREE) and HREE patterns are nearly flat ($Lu_N/Sm_N=5–16$ and $Lu_N=7–27$) with a relatively small negative Eu anomalies ($Eu/Eu^*=0.33–0.70$); the light REE (LREE) contents are generally below detection limits (Fig. 4b). Their Ti contents vary from 2.00 to 4.03 ppm, yielding formation temperatures of 617–667 °C the activity of $TiO_2=1$ (Watson and Harrison, 2005). Four inherited zircon grains have similar REE patterns as those of the magmatic zircons.

Fourteen trace element analyses were done on 12 zircon grains from sample 07XX08 (Table S3 and Fig. 4c). The magmatic cores have similar chondrite-normalized REE patterns with HREE enrichments ($Lu_N/Sm_N=136–320$ and Lu_N up to 1000). All show large negative Eu anomalies ($Eu/Eu^* < 0.5$) and significant positive Ce anomalies. They have Ti contents of 4.62–9.17 ppm, yielding crystallizing temperatures of 677–733 °C the activity of $TiO_2=1$ (Watson and Harrison, 2005). In contrast, the metamorphic zircon crystals show relatively flat HREE patterns ($Lu_N/Sm_N=2–15$ and $Lu_N=11–84$), and small negative Eu anomalies ($Eu/Eu^*=0.67–0.74$). Their Ti contents vary from 2.75–5.92 ppm, corresponding to formation temperatures of 639–697 °C the activity of $TiO_2=1$ (Watson and Harrison, 2005).

4.3. Zircon Lu-Hf isotopes

Thirty Lu-Hf isotope analyses were done on 28 zircon grains from sample 07XD06 (Hujiawan, Table S4), including sixteen analyses performed in previously dated zircon domains (Fig. 2). Fifteen analyses on magmatic cores show $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ ratios of 0.001021–0.003195 and 0.282724–0.282888, respectively. Whereas the other fifteen analyses on metamorphic zircons have similar $^{176}Hf/^{177}Hf$ ratios of 0.282741–0.282942, but relatively low $^{176}Lu/^{177}Hf$ ratios of 0.000149–0.000684. All the zircon crystals yield $\epsilon_{Hf}(t)$ ($t=400$ Ma) values ranging from 6.8 to 14.8 with a weighted mean of 10.6 ± 0.6 (MSWD=9.2) (Fig. S2a), corresponding to depleted mantle Hf model ages (T_{DM}) of 431 ± 42 to 752 ± 51 Ma with a weighted mean of 623 ± 25 Ma (MSWD=2.3) (Fig. 5a).

Twenty Lu-Hf isotope analyses were done on 18 previously dated zircon grains from sample 07XX07 (Suijiahe, Table S4). Ten analyses on magmatic zircon crystals have very large variation of $^{176}Hf/^{177}Hf$ ratios of 0.282442–0.282865 and relatively high $^{176}Lu/^{177}Hf$ ratios of 0.000101–0.000907. While six analyses on metamorphic zircon crystals exhibit similar variation of $^{176}Hf/^{177}Hf$ ratios of 0.282373–0.282735, but substantially lower $^{176}Lu/^{177}Hf$ ratios of 0.000003–0.000060. Using a protolith age of 420 Ma, the calculated $\epsilon_{Hf}(t)$ values of all these zircon grains range from –4.9 to 12.4 with a weighted mean of 2.2 ± 2.7 (MSWD=98). The large MSWD value precludes any geologic meaning of the average value (Fig. S2b). Their Hf model ages are also quite variable (543 ± 42 to 1211 ± 41 Ma with a weighted mean of 950 ± 100 Ma) (Fig. 5b). The other four analyses on xenocrystic cores have high $^{176}Lu/^{177}Hf$ ratios of 0.000476–0.001280, with relatively low $^{176}Hf/^{177}Hf$ ratios of 0.281268–0.282224.

Thirty-three Lu-Hf isotopic analyses were done on 30 zircon grains of sample 07XX08 (Suijiahe, Table S4). The magmatic zircon grains show high $^{176}Hf/^{177}Hf$ ratios of 0.282730–0.282989 and $^{176}Lu/^{177}Hf$ ratios of 0.000152–0.000372. Whereas the metamorphic zircon grains have similar high $^{176}Hf/^{177}Hf$ ratios of 0.282713–0.283112, with quite lower $^{176}Lu/^{177}Hf$ ratios of 0.000004–0.000075. All of these zircon crystals yield $\epsilon_{Hf}(t)$ values of 7.1–21.3 with a weighted average of 13.0 ± 1.2 (MSWD=9.4) at $t=410$ Ma (Fig. S2c). Their Hf model ages vary from 193 ± 164 to 747 ± 102 Ma with a weighted mean of 516 ± 48 Ma (MSWD=2.4) (Fig. 5c).

5. Discussion

5.1. Hf composition of metamorphic zircon

In the three samples, the metamorphic zircon domains show the similar range of $^{176}Hf/^{177}Hf$ ratios and $\epsilon_{Hf}(t)$ values to those of the

magmatic cores, although their $^{176}\text{Lu}/^{177}\text{Hf}$ ratios are lower (Table S4). This suggests that the metamorphic zircon crystals may have formed by dissolution-precipitation of pre-existing magmatic zircon in a closed system (Zheng et al., 2005, 2006). This is further confirmed by comparing core and rim analyses for four zircon grains in samples 07XD06 and 07XX08 (#2, #3, #8, and #9 in sample 07XD06, and #5, #6, #20, and #21 in sample 07XX08) (Table S4). These data are consistent not only with the experimental studies on cation diffusion rates for Hf which is characterized by very low diffusion rates in zircon (Cherniak and Watson, 2003), but also with the geochemical investigations that HP-UHP metamorphic fluid is internally buffered with respect to the host rocks in the Dabie-Sulu orogenic belt (Fu et al., 2002; Zheng et al., 2003 and references therein). Similar situations have also been documented by Schmidberger et al. (2005) and Zheng et al. (2006). Therefore, the Lu-Hf isotopic compositions of both the metamorphic and magmatic zircons may be used to decipher the nature of the protolith of the three samples.

5.2. Ages and origin of the protoliths

In all three eclogite samples most zircon crystals show core-rim structures. The cores are characterized by igneous growth zoning, or no zoning, a stronger CL intensity, relatively high Th/U ratios and high trace element concentrations, a clear negative Eu anomaly and a positive Ce anomaly, as well as HREE enriched patterns. These data suggest that the cores are magmatic zircon crystals inherited from the protoliths (Hoskin and Black, 2000; Corfu et al., 2003). As discussed previously, their age is best estimated by the oldest cluster of concordant analyses for each sample. The intrusion age of the protolith of the three samples is thus estimated at 406 ± 5 , 420 ± 7 and 411 ± 11 Ma (Fig. 3a,b,c). These ages remarkably similar, and straddle the Silurian-Devonian boundary. These indicate that the protoliths of these eclogites all intruded close to the Silurian-Devonian boundary.

In situ zircon Hf isotope analysis may be used to further constrain the nature of the protoliths (Schmidberger et al., 2005; Zheng et al., 2005, 2006; Wu et al., 2007, 2008). The zircon crystals in sample 07XX08 (Sujiahe) have very high positive $\varepsilon_{\text{Hf}}(t)$ value of 13.0 ± 1.2 (Fig. S2a) and young T_{DM} age of 516 ± 48 Ma (Fig. 5c). These data suggest that the protolith was derived from a depleted mantle with isotopic composition close to the Depleted Mantle reference curve. Previous Nd-O-H isotope and trace element studies for eclogites in the Huwan shear zone suggested that the protoliths of some eclogites in this zone were oceanic crust (Li et al., 2001; Fu et al., 2002; Gao et al., 2002). All these results, therefore, argue for the presence of the late Silurian Paleotethyan oceanic crust.

In contrast, the zircon crystals in sample 07XX07, from the same locality, exhibit a large range in $\varepsilon_{\text{Hf}}(t)$ values from -4.9 to 12.4 , and T_{DM} ages of 543 ± 42 to 1211 ± 41 Ma (Table S4 and Fig. 5b and S2b). The negative $\varepsilon_{\text{Hf}}(t)$ values imply the incorporation of a small quantity of older crustal materials during the protolith formation. The occurrence of xenocrystic zircon grains with very old U-Pb ages (Table S1 and S2) also argues for the involvement of old crustal material during its protolith intrusion. Nevertheless, most of the zircon grains have positive $\varepsilon_{\text{Hf}}(t)$ values some of which are as high as 12.4 . The lowest T_{DM} age is just slightly little older than the protolith age. These suggest that juvenile material was involved in its protolith formation. Accordingly, it is reasonable to infer that the protolith of sample 07XX07 should also be oceanic crust that incorporated more evolved crustal component(s).

The zircon grains in sample 07XD06 at Hujiawan have $\varepsilon_{\text{Hf}}(t)$ values of 6.8 – 14.8 and T_{DM} ages of 623 ± 25 Ma (Table S4 and Fig. 5a and S2a). The youngest T_{DM} ages are very close to the time of the protolith formation, also suggesting that the protolith was derived from the depleted mantle; whereas the oldest T_{DM} ages may demonstrate the incorporation of older material during the protolith formation. Fu

et al. (2002) reported that an eclogite from Hujiawan had a high $\varepsilon_{\text{Nd}}(t)$ value of 4.9 and $\delta^{18}\text{O}$ values of 8.8% , and MORB-like trace element patterns, and thus its protolith presumably was derived from oceanic crust. In contrast, Li et al. (2001) suggested that the protoliths of eclogites at Hujiawan were island arc basalts on the basis of their enrichment in LIL elements and depletion in HFS elements, and relatively low $\varepsilon_{\text{Nd}}(t)$ values. This geochemical evidence, however, may also be ascribed to depleted oceanic crust that incorporated different proportions of crustal materials during its intrusion (Li et al., 1997). The same protolith formation age as the eclogite at Sujiahe and the relatively large variation of $\varepsilon_{\text{Hf}}(t)$ values suggest that the protoliths of the eclogites at Hujiawan were also depleted oceanic crust that had experienced different degrees of crustal contamination.

As discussed above, the protoliths of the three eclogites were oceanic crust that experienced different degrees of crustal contamination (Li et al., 2001; Fu et al., 2002). These eclogites that occurred as layers or lenses in sediments indicate that they may represent tectonic fragments of an ophiolite complex. We propose that the protoliths of these eclogites be formed in a continental marginal environment, and be variably contaminated by more evolved continental material. The same situation has also been proposed for Neoproterozoic ophiolites in the Anhui Province, southeast China (Li et al., 1997). Some eclogites in the Huwan shear zone have protolith ages of 716 ± 28 – 766 ± 14 Ma (2σ) (Hacker et al., 2000; Liu et al., 2004b), which preserve a distinctive signature of continental crust from the Yangtze Craton (Hacker et al., 1998, 2000). The coexistence of Paleozoic oceanic crust and Neoproterozoic continental crust with similar metamorphic ages in the Huwan shear zone can be explained by Neoproterozoic continental crust split from the northern part of the Yangtze Craton and Paleozoic oceanic crust produced within an oceanic marginal basin of the Yangtze Craton. The close spatial and temporal associations between HP oceanic and continental crust in the Huwan shear zone implies that the HP continental rocks may have played a key role in exhumation and preservation of the oceanic rocks through buoyancy-driven uplift because of their low densities. Similar processes have been documented in the Alpine Orogeny (Bousquet et al., 2002; Lapen et al., 2007).

5.3. Carboniferous eclogite-facies metamorphism

The metamorphic zircon rims in samples 07XX07 and 07XX08 have relatively low Th/U ratios and low trace element contents (Table S3). All of the metamorphic zircons are characterized by relatively flat REE patterns, low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, and slight negative Eu anomalies (Table S3 and Fig. 4a,b). This suggests that they be formed in the presence of garnet and absence of feldspar, and thus under eclogite-facies conditions (Schaltegger et al., 1999; Hermann et al., 2001; Rubatto, 2002; Rubatto and Hermann, 2003; Whitehouse and Platt, 2003; Bingen et al., 2004; Zheng et al., 2005; Wu et al., 2006b, 2008). Their formation temperatures were calculated at 655 and 638 °C, which are comparable to the peak metamorphic temperatures of eclogites in the Huwan shear zone (Fu et al., 2002; Liu et al., 2004b; Ratschbacher et al., 2006). The metamorphic zircon crystals in the two samples yield identical ages of 309 ± 2 , 306 ± 7 and 308 ± 6 Ma (Fig. 3b,c, S1a), with a weighted mean of 309 ± 4 Ma (2σ , MSWD=0.092). Therefore, 309 ± 4 Ma is taken as the best estimate for the timing of eclogite-facies metamorphism.

The metamorphic zircon grains in sample 07XD06 show similar geochemical features as the metamorphic zircon in samples 07XX07 and 07XX08, except for enrichment in HREEs and relatively high $^{176}\text{Lu}/^{177}\text{Hf}$ ratios. Their HREE contents (Fig. 4a) and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios (Table S4), however, are still lower than those of the corresponding magmatic zircon crystals. These imply that the metamorphic zircon might have formed during the prograde stage of metamorphism (Wu et al., 2006b), or the metamorphic zircons did not equilibrate with garnet in this sample. This is consistent with their

somewhat older age of 312 ± 11 Ma (2σ , MSWD=0.33), compared to those of the metamorphic zircon crystals in samples 07XX07 and 07XX08.

Sun et al. (2002) obtained zircon U–Pb ages of 307 ± 4 , 311 ± 17 , and 312 ± 5 Ma (2σ) for three eclogites from Xiongdi and Hujiawan, which are identical, within error, to our results. In contrast, Liu et al. (2004a) reported SHRIMP zircon U–Pb dating results of two eclogite samples from Qianjinhepeng and Huwan in the eastern part of Huwan shear zone. The metamorphic rims on zircon from one sample (QJH01) gave a range of $^{206}\text{Pb}/^{238}\text{U}$ ages from 315 ± 17 to 229 ± 12 Ma, with the youngest age interpreted as the maximum age of the eclogite-facies metamorphism. Combined with the regional geological structural pattern that the architecture of the western Dabie orogen is a huge antiform (Hacker et al., 1998, 2000; Zhong et al., 1999), the Huwan shear zone was inferred to be an integral part of the entire Triassic Dabie-Sulu HP/UHP terrane (Hacker et al., 2000; Liu et al., 2004a,b; Jahn et al., 2005). Because there is a NW–SE fault separating eclogites at Xiongdi and Hujiawan from the main part of the Huwan shear zone (Fig. 1), using the metamorphic ages of eclogites at Xiongdi and Hujiawan to constrain the metamorphic history of the whole Huwan shear zone should be viewed with caution (Liu et al., 2004; Jahn et al., 2005). Our two eclogite samples 07XX07 and 07XX08 were collected from Sujiahe, which is clearly in the main segment of the Huwan shear zone (Fig. 1). Their metamorphic age of 309 ± 4 Ma (2σ), therefore, provides strong evidence for Carboniferous eclogite-facies metamorphism of the Huwan shear zone. The discordant metamorphic age of 229 ± 12 Ma (1σ) of QJH01 was obtained by Liu et al. (2004a) from a zircon with porous structure and a very high U content of 3132 ppm (Liu et al., 2004a). This type of zircon, however, may be isotopically reset at low temperatures of ca. 120–200 °C (Geisler et al., 2003) and is likely to have experienced significant radiation damage due to its high initial uranium content. The age of 229 ± 12 Ma is thus regarded as partially reset. In contrast and in view of the new results, the more concordant maximum age of 315 ± 17 Ma is probably a more realistic estimate of the eclogite-facies metamorphism in the same sample (Liu et al., 2004a).

The dominant deformation fabric in the Huwan shear zone clearly post-dates the eclogite-facies metamorphism (Ratschbacher et al., 2006). This deformation is recorded by several zircon ages ranging from ca. 210–280 Ma (Gao et al., 2002; Sun et al., 2002; Liu et al., 2004a,b), $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite ages of ca. 210–270 Ma (Webb et al., 1999; Xu et al., 2000; Ratschbacher et al., 2006), as well as Rb–Sr mineral isochron ages of 210–225 Ma (Jahn et al., 2005). Available data converge towards a more consistent geochronology of the Huwan shear zone, with Carboniferous eclogite-facies metamorphism along the entire length of the shear zone, followed by Permo-Triassic post-eclogite-facies metamorphism and deformation.

The Carboniferous, 309 ± 4 Ma (2σ , MSWD=0.092), age for eclogite-facies metamorphism in the Huwan shear zone contrasts with the Triassic age estimates for the HP to UHP events recorded in the southern part of the Qinling orogen and the Hong'an Block (Zhai et al., 1998; Sun et al., 2002; Liu et al., 2004a; Jahn et al., 2005; Wu et al., 2008). Such a large 100 Ma interval is too long for a single subduction cycle. These metamorphic ages, therefore, argue for two separate subduction–exhumation events in the western Dabie orogen, one in the Carboniferous and the other in the Triassic.

5.4. Tectonic implications

According to the results in this study and previous studies, a more detailed model for the collision processes between the southern North China and the northern Yangtze cratons now can be proposed. The collision of the North China Craton and the Qinling terrain occurred in the middle Paleozoic (ca. 450–500 Ma) along the Shangdan suture zone (Fig. 6a) (Kröner et al., 1993; Gao et al., 1995; Zhang et al., 1997; Zhai et al., 1998; Meng and Zhang, 1999). The ages of Paleotethyan

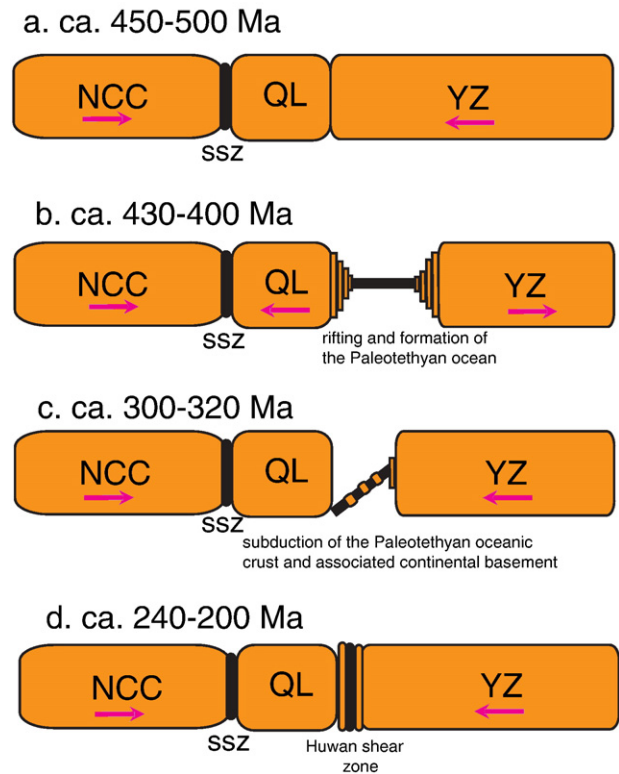


Fig. 6. Schematized model showing the amalgamation processes of the Yangtze and North China cratons along the Qinling-Dabie-Sulu orogen. NCC=the North China Craton; QL=the Qinling terrain; YZ=The Yangtze Craton; SSZ=the Shangdan suture zone. Detailed explanations are given in the text.

ocean formation range from ca. 406 to 430 Ma, which are a slightly younger than the collision of the North China Craton and the Qinling terrain. This strongly supports the hypothesis that rifting occurred at the northern part of the Yangtze Craton, synchronous with the middle Paleozoic collision, and was followed by the opening of the Paleotethyan ocean during the Late Paleozoic. This resulted in the splitting of the South Qinling (Meng and Zhang, 1999, 2000) and the continental basement of Huwan from the Yangtze Craton (Fig. 6b). Subduction of the Paleotethyan oceanic crust and associated continental basement represent a separate tectonic event, resulting in the 309 ± 2 Ma (2σ) eclogite-facies metamorphism in the Huwan shear zone (Fig. 6c). Extensive Triassic isotopic ages of HP–UHP metamorphic rocks in the south Qinling and Dabie-Sulu belt record the Triassic continent–continent collision (Fig. 6d); a separate tectonic event that led to the final coalescence of the Yangtze and North China cratons. The amalgamation of the Yangtze and North China cratons was, therefore, a multistage process spanning at least 200 Ma.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.10.031.

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