U–Pb Zircon Ages and Geochemistry of the Wuguan Complex and Liuling Group: Implications for the Late Paleozoic Tectonic Evolution of the Qinling Orogenic Belt, Central China

Ming Guan, Jiahao Li *, Guoqing Jia, Shenglian Ren and Chuanzhong Song

School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China
* Correspondence: lijiahao@hfut.edu.cn

Abstract: The tectonic evolution of the Qinling orogen is key to understanding the process of convergence between the North China Block (NCB) and the South China Block (SCB). The Wuguan Complex and Liuling Group, situated along the southern margin of the Shangnan–Danfeng suture zone (SDSZ) between the North Qinling Terrane (NQT) and the South Qinling Terrane (SQT), are important indicators of the late Paleozoic tectonic evolution of the Qinling orogen. In this paper, the detrital zircon U–Pb geochronology and geochemical analysis of the Wuguan Complex and Liuling Group are carried out. Detrital zircons from two metasedimentary rock samples of the Liuling Group yield a major age peak at 460 Ma and two subordinate peaks at 804 Ma and 920 Ma, with a few older grains having formed between 1000–2549 Ma. One metasedimentary rock sample of the Wuguan Complex has a similar age spectrum as that of the Liuling Group, which shows the main age peak at 440 Ma and two subordinate peaks at 786 and 927 Ma, indicating all detrital zircon age results have the same source area. Geochemical analyses suggest that the sedimentary rocks of the Liuling Group and part of the Wuguan Complex were deposited in the tectonic setting of the continental island arc (CIA), while the geochemical characteristics of the other group of sedimentary rocks of the Wuguan Complex indicate the mixing of basic rock sources. The protolith of garnet amphibolite and hornblende schist, which were collected from the Wuguan Complex, were classified as andesite and basalt, with the nature of arc andesite and oceanic island basalt, respectively. In combination with regional data, we suggest that the Liuling Group and the Wuguan Complex were deposited in a fore-arc basin. Additionally, the Wuguan Complex was subsequently incorporated into the tectonic melange by the northward subduction of the Paleo-Qinling Ocean. Zircons from the subduction-related metamorphic igneous rocks in the Wuguan Complex yielded a weighted mean age of 365 ± 19 Ma, indicating that the Paleo-Qinling Ocean between the SQT and NQT was still subducted at the end of Devonian.

Keywords: Qinling orogen; Liuling Group; Wuguan Complex; detrital zircon U–Pb age; fore-arc basin geochemistry

1. Introduction

The Qinling–Tongbai–Dabie–Sulu orogen, a giant orogenic belt that extends more than 1000 km from east to west (Figure 1a), is considered to be the product of the collision of the North China Block (NCB) and South China Block (SCB) [1–3]. As an important part, the Qinling orogen is proven to be a composite orogenic belt with two main suture zones, namely the Shangnan–Danfeng suture zone (SDSZ) and the Mianxian–Lueyang suture zone (MLSZ), and multiple orogenic activities. A long-term oceanic subduction and accretion process occurred before the continental collision [1,2,4–7]. Because of the complex and multi-stage evolution, the timing and details of the collision between the NCB and SCB are disputed [1–4,8].

The two suture zones within the orogenic belt indicate at least two stages of collisional events. A large amount of paleomagnetic data and Triassic high-pressure and
ultra-high-pressure metamorphic rocks in the Tongbai–Hongan–Dabie–Sulu orogenic belt indicate that the final collision between the NCB and the SCB along the MLSZ occurred in the Mesozoic [8–18]. However, the exact time of closure of the Paleo-Qinling Ocean leading to the collision between the North Qinling Terrane (NQT) and South Qinling Terrane (SQT) along the SDSZ is still controversial, with a range of predictions, including Silurian–Devonian [19,20], early Devonian [21] and no earlier than the late Devonian [6,22]. Therefore, it is essential to determine the time of the closure of the Paleo-Qinling Ocean, which can provide constraints on the tectonic evolution of the Qinling orogenic belt during the Paleozoic.

The Wuguan Complex and Liuling Group exhibit a linear arrangement along the southern margin of the SDSZ. The Wuguan Complex is considered to be a tectonic complex consisting of the Neoproterozoic to late Paleozoic sedimentary strata and multi-stage magmatic rock assemblages [6,22–24], and the Liuling Group is regarded as a set of Devonian sedimentary strata [6,19,25]. Previous studies identified the Wuguan Complex to be a mixture of Qinling continental arc and fore-arc sedimentary materials that were deposited in a fore-arc basin [6,22,24]. However, the provenance and depositional setting of the Liuling Group are still hotly debated, and different models have been developed: (1) a passive continental margin basin in the northern margin of the Yangtze Block [26]; (2) a foreland basin after the closure of the Paleo-Qinling Ocean [3,27,28]; (3) an active continental margin or fore-arc basin [29,30]; and (4) a post-orogen-related extensional basin [21,31].

In this paper, we present our petrographic, geochemical, systematic zircon U–Pb isotopic data of metamorphosed sedimentary and igneous rocks from the Wuguan Complex and Liuling Group and provide constraints on the provenance and depositional setting of the Wuguan Complex and Liuling Group. This study can provide data support for the constraint of the Paleozoic tectonic evolution of the Qinling orogen.

2. Geological Setting

The Qinling orogenic belt is a composite orogenic belt between NCB and SCB [4]. It is bounded by the Luonan–Luanchuan Fault (LLF) in the north and the Mianlue–Bashan–Xiangguang Fault (MBXF) in the south. It can be divided into NQT and SQT by the SDSZ (Figure 1b).

Figure 1. (a) The main tectonic divisions in the Chinese mainland, showing the location of the study area (after [32]). (b) Simplified geologic map of the eastern Qinling orogen (after [19]) and locations of
the studied samples for zircon U–Pb dating. (c,d) The structural profiles across the Liuling Group and the Wuguan Complex. The Shangnan–Danfeng suture zone (SDSZ) dips to the north with different angles in different sections. The Maanquao-Mianyuzui suture zone (MMSZ) dips to the south with a steep angle.

2.1. North Qinling Terrane

From north to south, the Kuanping Group, Erlangping Group, Qinling Group, and Danfeng Group are outcrops within NQT (Figure 1b). The Kuanping Group, located in the northernmost part of the NQT, is composed of mafic volcanic rocks that formed ~943 Ma [33] and terrigenous clastic rocks [34]. The detrital zircon age of metasedimentary rocks shows peaks at ~2500 Ma, ~1750 Ma, ~1000–900 Ma and 650 Ma [34], respectively. The Erlangping Group comprises ophiolite units, clastic rocks and carbonate rocks that formed in the early Paleozoic back-arc basin [31,35–39]. As an old basement in the NQT, the Qinling Group comprises orthogneisses, paragneisses, marble and lenticular or lamellar amphibolites. The deposition age of the protolith of paragneisses is 960–850 Ma, with the main age population of detrital zircons of 1800–1300 Ma [23,34,40]. Previous studies have shown that the northern Qinling Group experiences high-pressure (HP) to ultra-high-pressure (UHP) metamorphism at ca. 500 Ma [41–45]. Neoproterozoic and Paleozoic magmatism are well-developed in the NQT, which mainly occurred at 979–815 Ma and 507–399 Ma [42], respectively. Along the SDSZ, the Danfeng Group is mainly composed of a set of ophiolite remnants of the oceanic crust of the Paleo-Qinling Ocean. The rock assemblage includes serpentinite, mafic volcanic/intrusive rocks and radiolarian siliceous rocks [46]. Previous geochronological studies have indicated that it formed between 530 and 400 Ma [38,46,47].

2.2. South Qinling Terrane

The South Qinling Terrane is mainly composed of a Precambrian basement, sedimentary cover and intrusive rocks. The Precambrian basement includes a crystalline basement that underwent high-grade metamorphism and a transitional basement that underwent low-grade metamorphism [31]. The crystalline basement includes the Yuzidong Group [48], Douling Group [49] and Foping Group [50]. The Yuzidong Group is considered an Archean crystalline basement [48]. The Douling Group comprises a ~3.0 Ga basement, 746–730 Ma gneiss and sedimentary rocks older than 443 Ma [51]. The transitional basement mainly consists of Precambrian volcano-sedimentary sequences, including the Wudang and Yaolinghe groups, with a wide distribution range. The Wudang Group is about 810–720 Ma in age [52], while the volcanic rocks in the Yaolinghe Group are mainly divided into three phases: ~850 Ma, 760–730 Ma and 680–650 Ma [53].

The Sinian to Ordovician sedimentary cover of the SQT is mainly carbonate, shale and sandstone, which is consistent with the deposits in the northern margin of the Yangtze Block. The Silurian sedimentary rocks are mainly distributed in the southern part of the SQT, and their lithology is deep-water siliceous clastic rock and turbidite. The Devonian sedimentary rocks are mainly distributed in the northern part of the SQT and comprise meta-greywacke, slate, phyllite and carbonate rocks. The Carboniferous to Triassic rocks are less exposed.

The Liuling Group is located in the northern margin of the SQT. It is bounded by Mianyuzui ductile shear zone, is adjacent to the Wuguan Complex in the north and is bounded by the Shanyang–Fengzhen fault to the south [4]. The Liuling Group in the Shangnan area comprises metasandstone, phyllite and schist and has been subject to metamorphism from greenschist facies to green epidote–amphibolite facies [22]. Recent detrital zircon geochronology studies indicate that the sedimentation of the Liuling Group lasted until the middle and late Devonian [26].

The Wuguan Complex is located in the northernmost margin of the SQT, between the SDSZ and the Mianyuzui ductile shear zone. It comprises metamorphosed clastic rocks,
metapelites and minor amphibolite, metaquartzite and marble. Previous geochronology studies in the Wuguan Complex indicate that it is a set of tectonic melange with a variety of geological bodies from the Neoproterozoic to late Paleozoic [6,19,22–24]. The Wuguan Complex has generally experienced intermediate-grade metamorphism and strong ductile deformation, with the peak metamorphic conditions reaching to the high amphibolite facies [54].

3. Samples and Analytical Techniques

3.1. Samples Descriptions

Two metamorphosed clastic samples (GQ20 and TW43) within the Liuling Group, one metamorphosed clastic sample (TW61) and two metamorphosed igneous rock samples (TW55 and TW68) within the Wuguan Complex were collected for petrography and LA–MC–ICP–MS zircon U–Pb dating in this study. In addition, eleven metamorphosed clastic rock samples of the Liuling Group, five metamorphosed clastic rock samples and two metamorphogenic igneous rock samples of the Wuguan Complex were collected for major and trace element analysis. The sample locations are shown in Figure 1, and their location coordinates, mineral assemblages and dating results are shown in Table 1.

Table 1. Sampling localities, mineral assemblages and zircon U–Pb ages of the studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Coordinates</th>
<th>Lithology</th>
<th>Mineral Assemblage</th>
<th>Youngest Detrital Zircon Age or Crystallization Age/Ma</th>
<th>Peak Ages/Ma</th>
</tr>
</thead>
<tbody>
<tr>
<td>GQ20</td>
<td>Liuling Group</td>
<td>33°26′19″ N, 110°47′50″ E</td>
<td>Biotite quartz schist</td>
<td>Qtz (‒40%) + Bt (‒35%) + Ep (‒15%) + Pl (‒10%)</td>
<td>395 ± 10</td>
<td>452, 827, 1072, 1523</td>
</tr>
<tr>
<td>TW43</td>
<td>Liuling Group</td>
<td>33°31′7″ N, 110°38′57″ E</td>
<td>Garnet mica quartz schist</td>
<td>Qtz (‒30%) + Mus (‒35%) + Bt (‒15%) + Grt (‒15%) + Chl (‒3%) + Ap (‒1%) + IIm (‒1%)</td>
<td>360 ± 11</td>
<td>460, 781, 942, 1882, 2502</td>
</tr>
<tr>
<td>TW61</td>
<td>Wuguan Complex</td>
<td>33°34′42″ N, 110°40′33″ E</td>
<td>Garnet staurolite mica schist</td>
<td>Mus (‒30%) + St (‒20%) + Qtz (‒25%) + Grt (‒10%) + Chl (‒13%) + Ap (‒1%) + IIm (‒1%)</td>
<td>409 ± 12</td>
<td>440, 779, 927</td>
</tr>
<tr>
<td>TW55</td>
<td>Wuguan Complex</td>
<td>33°34′37″ N, 110°39′46″ E</td>
<td>Garnet amphibolite</td>
<td>Grt (‒15%) + Hbl (‒20%) + Bt (‒15%) + Pl (‒10%) + Qtz (‒25%) + Ep (‒5%) + Czo (‒3%) + Py (‒3%) + Cal (‒3%) + Rt (‒1%)</td>
<td>365 ± 19</td>
<td></td>
</tr>
<tr>
<td>TW68</td>
<td>Wuguan Complex</td>
<td>33°33′18″ N, 110°44′22″ E</td>
<td>Hornblende schist</td>
<td>Hbl (‒60%) + Qtz (‒30%) + Pl (‒10%)</td>
<td>446 ± 13</td>
<td></td>
</tr>
</tbody>
</table>


Sample GQ20 is a biotite quartz schist with a fine-grained blastic texture from the Liuling Group (Figure 2a). It mainly consists of quartz fragments and elongated biotite laths. Quartz mostly appears in the form of a single crystal with a straight grain boundary. Biotites are lamellar and distribute along the cleavage with preferred orientation (Figure 2b).

Sample TW43 is a garnet mica schist with a lepiod blastic texture (Figure 2c) and mainly contains quartz, muscovite, biotite, garnet and minor apatite. Garnets occur as large porphyroblasts surrounded by muscovite and contain inclusions of quartz, biotite, apatite and chlorite (Figure 2d). Muscovite is present as scaly crystal or a matrix in the sumplets. Biotite is present mainly within the sumplets. Quartz is mostly a polycrystalline aggregate.

Sample TW61 is a garnet–staurolite mica schist with a medium-fine-grained blastic texture (Figure 2e) and mainly contains muscovite, staurolite, garnet and minor apatite and plagioclase (Figure 2e). Muscovite is present as a scaly crystal. Staurolite is euhedral–hypidiomorphic with crossed twinning (Figure 2f). Quartz grains with recrystallized and suture edges are distinctly preferred. Chlorite exhibits tabular aggregate or scattered-needle morphologies. Garnet porphyroblasts are crushed, with nearly perpendicular cracks.
Figure 2. Field photographs and micrographs of studied samples from the Liuling Group and Wuguan Complex. (a) Biotite quartz schist (Sample GQ20) from the Liuling Group. (b) The mineral assemblage of biotite quartz schist (Sample GQ20), with schistosity defined by biotite. (c) Garnet mica quartz schist (Sample TW43) from the Liuling Group. (d) The mineral assemblage of the garnet mica quartz schist (Sample TW43). Late muscovite surrounds the early garnet grains, which contain a large number of inclusions. (e) Garnet staurolite mica schist (Sample TW61) from the Wuguan Complex. (f) The mineral assemblage of garnet staurolite mica schist, with schistosity defined by muscovite. (g) Garnet amphibolite (Sample TW55) from the Wuguan Complex. (h) Porphyroblasts of the garnet and hornblende within the biotite quartz plagioclase symplectites (Sample TW55). (i) Hornblende schist (Sample TW68) from the Wuguan Complex (Sample TW68). (j) Hornblende schist (Sample TW68) is dominated by hornblende with referred orientation.
Sample TW55 was collected from the garnet amphibolite, which occurred as a two-hundred-meter-thick layer in the metasedimentary rocks (Figure 2g). Foliations in the garnet amphibolite often occurred parallel to those in country rocks. It shows a porphyroblastic texture (Figure 2g) and mainly contains garnet, hornblende, quartz, biotite, plagioclase and minor epidote, clinzoisite, ilmenite and calcite (Figure 2h). Plagioclase, hornblende and garnet porphyroblasts can be seen on the outcrop. Microscopic observation shows that they are surrounded by xenomorphic biotite and quartz.

Sample TW68 was collected from the hornblende schist, which occurred as a 200 m thick layer (Figure 2i). Due to the strong ductile deformation, the foliation of hornblende schist is consistent with that of the surrounding rock. It has a fine-grained blastic texture and contains hornblende, quartz and plagioclase. They are strongly oriented and are defined by a clear foliation (Figure 2j).

3.2. Analytical Techniques

Zircons were separated by conventional magnetic and heavy-liquid methods and were subsequently purified by hand-picking under a binocular microscope. About 200 zircon grains were mounted on adhesive tape, enclosed in epoxy resin and polished to approximately half their thickness. The internal structures of the zircons were revealed by cathodoluminescence (CL) imaging. High-resolution U-Th-Pb data of zircons were generated using laser ablation–inductively coupled plasma–mass spectrometer (LA–ICP–MS) at the Geological Laboratory, School of Resource and Environmental Engineering, Hefei University of Technology, P. R. China. The LA–ICP–MS system consists of an Agilent 7500a ICP–MS coupled with a COMPex PRO 102 ArF-Excimer laser source ($\lambda = 193$ nm). The laser energy was 80 mJ, with a repetition rate of 6 Hz, a spot size of 32 µm diameter and 50 s ablation time. The 91500 and Plešovice were used as external calibration standards, and NIST SRM 610 was used to optimize the instrument. Zircon 91500 was analyzed twice for every eight analyses; NIST SRM 610 was analyzed once and Plešovice was analyzed twice for every sixteen analyses. Errors of individual LA–IC–PMS analyses are quoted at the 1σ level. The results were calculated using ICP–MS-Data Cal 10.8 [55] and ISOPLOT 3.23 software [56]. Common Pb was corrected following Andersen (2002) [57]. The U–Pb ages used in this study are $^{207}\text{Pb}/^{206}\text{Pb}$ ages for grains older than 1.0 Ga and $^{206}\text{Pb}/^{238}\text{U}$ ages for younger grains. The analytical data are presented in Table S1.

The whole-rock major and trace element analyses were carried out at Nanjing FocuMS Technology Co., Ltd., Nanjing, China. Major oxides were determined by an Agilent 5110 ICP-OES instrument, and the trace elements were determined by an Agilent7700x ICP-MS instrument, sourced from Agilent Technologies, California, USA. Geochemical reference materials of USGS, basalt (BCR-2, BHVO-2), andesite (AVG-2), rhyolite (RGM-2) and granodiorite (GSP-2), were treated as quality controls. Measured values of these reference materials were compared with the preferred values in the GeoReM database [58]. The deviation was better than 20% for trace elements between 0.5–5 ppm, better than 10% for those between 5–50 ppm and better than 5% for those exceeding 50 ppm. All of the chemical compositions of the samples are shown in Table S2.

4. Results

4.1. U–Pb Ages

Zircons from sample GQ20 were mostly colorless and short columnar, and they ranged in size from 40 to 150 µm. CL imaging revealed that the majority had clear oscillatory zoning (Figure 3a). Of the spot analyses, 66 out of 72 were more than 90% concordant. All spots had a variable U (63.9–2416 ppm) and Th (32.1–1514 ppm) abundance and a Th/U ratio of 0.09–2.25. Except for one zircon whose Th/U ratio was less than 0.1, the remaining zircons had Th/U ratios greater than 0.2, suggesting a magmatic origin. Sixty-six concordant zircon analyses yielded ages ranging from 2549 ± 25 Ma to 395 ± 10 Ma, with the main peak at 452 Ma and subordinate peaks at 827, 1072 Ma, 1523 Ma and 2494 Ma (Figure 4b). Twenty-six spots yielded the youngest weighted mean U–Pb age of 441 ± 9 Ma
Among them, the youngest spot yielded $^{206}\text{Pb}/^{238}\text{U}$ age of 395 ± 10 Ma, with a Th/U ratio of 0.28.

**Figure 3.** Representative cathodoluminescence images of zircons from the Wuguan Complex and Liuling Group. (a) The majority of zircons from sample GQ20 with clear oscillatory zoning; (b) Zircons from sample TW43 with a magmatic, oscillatory zoned core and a thin, brightly luminescent rim; (c) Zircons from sample TW61 with an oscillatory or planar zoned core and a thin, brightly luminescent rim; (d) Zircons from sample TW55 with dark and exhibited oscillatory zoning or straight, banded patterns; (e) Zircons from sample TW68 with cores exhibited oscillatory or planar zoning.
Zircons from sample TW43 were mostly colorless or transparent, with a subangular to subrounded shape and a size range from 40 to 200 µm. CL imaging revealed that most of them have a magmatic, oscillatory zoned core and a thin, brightly luminescent rim (Figure 3b). Of the spot analyses, 73 out of 80 were more than 90% concordant. All spots had a variable abundance of U (27.7–1476 ppm) and Th (17.8–1204 ppm). They had a relatively high Th/U ratio of 0.07–1.89, with most of them greater than 0.1, indicating a magmatic origin. Seventy-three concordant zircon analyses yielded ages ranging from 2511 ± 35 Ma to 360 ± 11 Ma, with the main population at 460 Ma and subordinate populations at 781, 942 Ma, 1882 Ma and 2502 Ma (Figure 4d). The youngest zircon was subrounded with a magmatic, oscillatory zoned core and a thin brightly luminescent rim in the CL image (Figure 3b) and yielded a $^{206}$Pb/$^{238}$U age of 360 ± 11 Ma in the core, with a Th/U ratio of 0.68. Excluding this zircon, the other seventeen youngest zircons yielded a weighted mean U–Pb age of 455 ± 8 Ma (MSWD = 1.5) (Figure 4c).
Zircons from sample TW61 were mostly colorless and transparent, short columnar or subrounded in shape, and their grain sizes ranged from 50 to 150 µm. CL imaging showed that the majority had a magmatic, oscillatory zoned core and a thin, brightly luminescent overgrowth rim (Figure 3c). A total of 80 spot analyses were performed on 80 zircons, of which 70 analyses were more than 90% concordant. They contained a variable abundance of U (23.9–1518 ppm) and Th (7.74–1477 ppm), and the Th/U ratios were 0.09–1.95. Only one spot analyzed gave a low Th/U ratio <0.1, suggesting that most zircons were of magmatic origin. Seventy concordant zircon analyses ranged in age from 2464 ± 43 Ma to 409 ± 12 Ma, with the main population at 440 Ma and subordinate populations at 779 Ma, 927 Ma, 1605 Ma and 2473 Ma (Figure 4f). The youngest group gave a weighted mean U–Pb age of 440 ± 5 Ma (MSWD = 1.2, n = 13) (Figure 4e), among which the youngest grain dated had a 206Pb/238U age of 409 ± 12 Ma (Figure 3c). It was colorless and anhedral, with several angular fragments, with a dark CL image and a Th/U ratio of 1.19.

Zircons from sample TW55 were mostly subangular to subrounded in shape. The CL image showed that the majority have core–rim structures. Zircon cores were dark and exhibited oscillatory zoning or straight, banded patterns, whereas the rims were bright and commonly had planar or fir-tree zoning. Some zircons only exhibited planar or fir-tree zoning (Figure 3d). A total of 40 spot analyses were performed on 40 zircon grains, of which 24 analyses were more than 90% concordant. Sixteen oscillatory or banded zoned cores contained a high abundance of Th (15.2–438 ppm) and U (67.1–623 ppm), and the Th/U ratios were 0.23–1.03, yielding an age distribution of 1949 ± 49 Ma to 365 ± 19 Ma (Figure 4g), of which the youngest grain yielded a 206Pb/238U age of 365 ± 19 Ma with a Th/U ratio of 0.34, indicating the protolith crystallization age. The planar/fir-tree zoned rims and individual grains had relatively low concentrations of Th (0–29.2 ppm) and U (8–2383 ppm), and the Th/U ratios were 0–0.035, suggesting a metamorphic origin. Eight concordant analyses yielded an age distribution from 402 ± 13 Ma to 330 ± 11 Ma, of which the two youngest zircons had a weighted mean U–Pb age of 332 ± 15 Ma (MSWD = 0.102), representing the metamorphic age.

Zircons from sample TW68 were subangular or subrounded in shape, and their grain sizes ranged from 50 to 150 µm. CL images revealed core–rim structures in most grains. Zircon cores exhibited oscillatory zoning, whereas the rims commonly had planar or fir-tree zoning of varying brightness and widths. A few zircons only exhibited planar or fir-tree zoning (Figure 3e). Only 14 of the total 16 spot analyses were more than 90% concordant. The oscillatory zoned cores contained a high abundance of Th (28.6–768 ppm) and U (108–768 ppm), and the Th/U ratios were 0.08–1.62, yielding a concordant age distribution of 3102 ± 43 Ma to 446 ± 13 Ma (Figure 4h). The two youngest zircons yielded a weighted mean U–Pb age of 452 ± 18 Ma (MSWD = 0.36), indicating the protolith crystallization age. The planar/fir-tree zoned rims and individual grains had a low abundance of Th (0.9–16.2 ppm) and U (50.6–477 ppm), and the Th/U ratios were 0.003–0.11, suggesting a metamorphic origin. Four spot analyses yielded a concordant age distribution, from 412 ± 11 Ma to 349 ± 14 Ma. The youngest zircon yielded a 206Pb/238U age of 349 ± 14 Ma, representing the metamorphic age.

4.2. Geochemistry
4.2.1. Metasedimentary Rocks of the Liuling Group

Seven metasedimented elastic rocks from the Liuling Group contained 54.85–74.21 wt.% SiO2, 9.85–20.28 wt.% Al2O3, 0.33–10.42 wt.% CaO, 0.53–0.89 wt.% TiO2, 2.68–4.95 wt.% MgO, 1.76–7.67 wt.% K2O, 0.24–3.69 wt.% Na2O and 3.91–8.34 wt.% Fe2O3.T. In the Fe2O3.F + MgO-Na2O-K2O diagram (Figure 5a), most of the samples are plotted near the boundary between lithic sandstone and arkose fields, indicating that the protolith of the metasedimented elastic rocks is less mature, which is consistent with the abundance of plagioclase in the samples.
Figure 5. (a) Chemical classification diagram for discriminating siliciclastic sediments using (Fe$_2$O$_3$T + MgO)-Na$_2$O-K$_2$O (after [59]). (b) Total alkali–SiO$_2$ (TAS) diagram for the classification of meta-igneous rocks from the Wuguan Complex (after [60]).

In comparison with the average upper continental crust (UCC), the metasedimentary rocks of the Liuling Group show distinct negative Sr, P, Ta and Nb anomalies but a high enrichment of Cs, V, Cr, Ni and Sc (Figure 6a). The chondrite-normalized rare earth element (REE) patterns (Figure 6b) of the samples are characterized by high fractionation between LREE and HREE (La/Yb$_N$ = 7.2–14.9) and have total REE contents of 126–277 ppm, obvious negative Eu anomalies (Eu/Eu* = 0.59–0.70) and no Ce anomalies (Ce/Ce* = 0.87–0.99).

Figure 6. Spider diagrams and REE patterns of metamorphosed clastic and meta-igneous rocks from the Wuguan Complex and Liuling Group. (a, b) Normalized to average upper crustal values (after [61,62]). (c) Chondrite-normalized REE patterns of metamorphosed clastic (after [63]). (d) Primitive mantle-normalized multi-elemental diagrams of amphibolite from the Wuguan Complex (after [64,65]).
4.2.2. Metasedimentary Rocks of the Wuguan Complex

Five metamorphosed clastic rocks from the Wuguan Complex contained 47.09~66.92 wt.% SiO$_2$, 12.67~20.96 wt.% Al$_2$O$_3$, 0.57~9.77 wt.% CaO, 0.75~3.46 wt.% TiO$_2$, 2.72~5.41 wt.% MgO, 0.74~2.67 wt.% K$_2$O, 0.64~3.18 wt.% Na$_2$O and 5.46~15.63 wt.% Fe$_2$O$_3$$^T$. In the Fe$_2$O$_3$$^T$+MgO-Na$_2$O-K$_2$O diagram (Figure 5a) [59], all of the samples are plotted in the greywacke and the lithic sandstone fields, suggesting that the protolith of the metamorphosed clastic rocks is less mature.

According to different REE contents, the five samples of metasedimentary rocks in the Wuguan Complex can be divided into two groups. In comparison with the average upper continental crust, two samples of the first group show significant negative anomalies of Sr, P, Ta and Nb and positive anomalies of Cs, V, Cr and Ni (Figure 6a), whereas the other three samples of the second group are characterized by the extremely high enrichment of V, Ti and Sc and negative anomalies of K, Rb, U, Cs, Ba and Th (Figure 6b). In the chondrite-normalized REE patterns (Figure 6c), all samples were characterized by a high fractionation between LREE and HREE (La/Yb$_N$ = 5.3~14.1). They have total REE contents of 132~284 ppm, with no Ce anomalies (Ce/Ce* = 0.93~0.96). The first group of samples has more significant negative Eu anomalies (Eu/Eu* = 0.64~0.73), which are 0.83~0.99 in the second group.

4.2.3. Meta-Igneous Rocks of the Wuguan Complex

Garnet amphibolite (TW55) contains 61.29 wt.% SiO$_2$, 14.52 wt.% Al$_2$O$_3$, 9.77 wt.% CaO, 0.67 wt.% TiO$_2$, 4.45 wt.% MgO, 2.15 wt.% K$_2$O, 1.90 wt.% Na$_2$O and 6.93 wt.% Fe$_2$O$_3$$^T$. Additionally, hornblende schist (TW68) contains 51.26 wt.% SiO$_2$, 12.46 wt.% Al$_2$O$_3$, 8.87 wt.% CaO, 2.83 wt.% TiO$_2$, 5.30 wt.% MgO, 0.68 wt.% K$_2$O, 2.66 wt.% Na$_2$O and 14.14 wt.% Fe$_2$O$_3$$^T$. In the total alkali versus silica (TAS) classification (Figure 5b), the protoliths of garnet amphibolite and hornblende schist were classified as andesite and basalt, respectively.

Both the garnet amphibolite and hornblende schist exhibited chondrite-normalized REE patterns characterized by an enrichment of light rare earth elements (LREE) (La/Yb$_N$ = 5.3~6.6) (Figure 6c), and there were almost no Ce anomalies (Ce/Ce* = 0.95~0.96). The garnet amphibolite (TW55) had total REE contents of 140 ppm and an obvious Eu anomaly (Eu/Eu* = 0.77). In contrast, the hornblende schist (TW68) had total REE contents of 195 ppm and a weak Eu anomaly (Eu/Eu* = 0.91).

The garnet amphibolite (TW55) falls into the volcanic arc field in the Hf/3-Th-Nb/16 diagram (Figure 7a). Additionally, in the La/Yb-Sc/Ni and La/Yb-Th diagram (Figure 8c, d), it is plotted in the continental margin arc (CIA) field. The depletion of the HFSE, such as Nb, Ta and Ti, indicates its formation was related to subduction (Figure 6d). These geochemical data indicate that the protolith of the garnet amphibolite is continental arc andesite.

![Figure 7. (a) Hf/3-Th-Nb/16 diagram (after [66]). (b) TiO$_2$-K$_2$O-P$_2$O$_5$ diagram (after [67]).](image-url)
The hornblende schist (TW68) plots on the boundary between the enriched mid-ocean-ridge basalt (E-MORB) and ocean island basalt (OIB) in the Hf/3-Th-Nb/16 diagram (Figure 7a). However, its primitive mantle-normalized multi-element pattern is completely different from the MORB and is similar to the OIB (Figure 6d). In the Zr/Y-Zr and Ti/100-Zr-Y*3 diagram (Figure 8a,b), it shows the characteristic of within-plate basalt (WPB). The TiO₂-K₂O-P₂O₅ diagram (Figure 7b) indicates that this formed in an oceanic environment. Therefore, the protolith of the hornblende schist should be the OIB.

5. Discussion
5.1. Provenance of the Sedimentary Rocks of the Liuling Group and Wuguan Complex

The youngest detrital zircon grains from different samples were used to define the maximum depositional ages in this study. Detrital zircons from two metasedimentary rock samples (GQ20 and TW43) of the Liuling Group and one metasedimentary rock sample (TW61) of the Wuguan Complex had similar zircon age spectra and youngest age peaks (Figure 4b,d,f), indicating the same source. The difference in the youngest single detrital zircon grain in three samples (395 ± 10 Ma, 360 ± 11 Ma and 409 ± 12 Ma, respectively) may suggest that they have different depositional ages. A total of 209 zircons were analyzed, and these could be divided into five age groups: 360–540 Ma (n = 89), 719–1000 Ma (n = 69), 1051–1342 Ma (n = 20), 1469–2162 Ma (n = 18) and 2381–2549 Ma (n = 11). The youngest zircon in the samples yielded a ²⁰⁶Pb/²³⁸U age of 360 ± 11 Ma, and the 365 ± 19 Ma meta-igneous interlayer of the Wuguan Complex in this study defined the lower limit of
depositional age. This indicates that the deposition of the Liuling Group and Wuguan Complex might have continued until the late Devonian.

The ages of magmatism in the NQT have been well-documented and summarized [38,42]. The Paleozoic magmatism in the NQT can be divided into three periods: 507–470 Ma, 460–422 Ma and 415–399 Ma [42,71]. Meanwhile, a large number of subduction-related mafic and granitic rocks with ages of 520–420 Ma have been reported in the Danfeng and Erlangping Group [1,37]. Neoproterozoic magmatic activity mainly occurred in 979–815 Ma [42,71]. For eclogites and retrometamorphic eclogites in the Qingling Group, many scholars have obtained the ages of 770–820 Ma on the core of zircons, representing the crystallization ages of the protolith [41–45]. Furthermore, the Qinling Group contains ca. 867–729 Ma amphibolite–facies mafic rocks [43], and the Qinling and Kuanping groups also contain ca. 730–610 Ma mafic–granitic dykes. The paragneiss of the Qinling and Kuanping groups in the NQT has a detrital zircon age population of 600–2980 Ma [19,23,33]. Therefore, the NQT contains all ages of detrital zircons from the metasedimentary rocks of the Liuling Group and the Wuguan Complex, and they have similar age spectrum (Figure 9a,b).

Figure 9. Relative probability diagrams of U–Pb ages for (a) NQT, (b) metasedimentary rocks of the Liuling Group and Wuguan Complex in this study, and (c) SQT. The data for the NQT and SQT are from [23,50,71,72] and [23,50,51,73–75], respectively.
The Phanerozoic magmatism in the SQT was characterized by the occurrence of late Triassic granitoids [37,38,42], minor basalt and a mafic–ultramafic dyke with an age of 433 ± 4 Ma in the southern margin of the SQT [76]. The Neoproterozoic magmatism developed in the SQT and northwestern margin of the Yangtze Block and mainly occurred in the periods 760–710 Ma and 860–705 Ma, respectively. The U–Pb age clusters at ca. 2000 Ma–2500 Ma can also be seen in the age spectrum of the SQT (Figure 9c). By comparison, it is clear that detrital zircons with age populations at 435 Ma and 926 Ma in our samples cannot be derived from the South Qinling or the northwest margin of the Yangtze Block. For the Neoproterozoic and Paleoproterozoic–Archean detrital zircons, the SQT and northwestern margins of the Yangtze Block might be potential sources. In that case, the Liuling Group and Wuguan Complex should deposit in a foreland basin with a dual source. However, the meta-sedimentary rocks from the Liuling Group and Wuguan Complex are dominated by lithic sandstone and arkose with an active continental margin and continental arc source (Figures 6a and 7a). This indicates that they have a proximal source with low maturity of structure and composition. In addition, subduction-related meta-andesite and meta-basalt with OIB affinity were also detected in the Wuguan Complex. These facts imply that the Liuling Group and the Wuguan Complex were deposited in a forearc basin rather than a foreland basin. Therefore, we propose that all of the detrital zircons in the Liuling Group and Wuguan Complex were derived from the NQT rather than the SQT or the NW margin of the Yangtze Block.

5.2. Depositional Setting of the Liuling Group

Most scholars supported the idea that the Wuguan Complex was deposited in a forearc basin [3,6,19,22,24,28]. However, the sedimentary setting of the Liuling Group is still controversial. It was once considered to be deposited in a passive continental margin [28], foreland basin [3,27,28], fore-arc basin [29,30] or a post-orogen-related extensional basin [21,31].

Relatively stable trace elements such as rare earth and large-ion lithophile elements can effectively identify the tectonic setting of sedimentary rocks [77]. The UCC-normalized multi-element patterns of the metasedimentary rocks from the Liuling Group display distinct negative Sr, P, Ta and Nb anomalies and the enrichment of V, Cr, Ni, Sc and Cs, which are similar to the sedimentary rocks in the active continental margin and continental arc setting (Figure 6a). On the Ti/Zr-La/Sr (Figure 10a), Th-Co-Zr/10 (Figure 10b), Th-Sr-Zr/10 (Figure 10c) and La-Th-Sc (Figure 10d) tectonic discrimination diagrams, all metasedimentary rock samples from the Liuling Group fall within the CIA and ACM fields. Furthermore, on the La/Th-Hf diagram of Floyd and Leveridge [59] (Figure 10e), all of the sedimentary rock samples from the Liuling Group and the first group of samples from the Wuguan Complex fell into the field of an acidic arc source, whereas the second group of samples from the Wuguan Complex fell into the field of the mixed felsic and basic source. On the Th/Sc-Zr/Sc diagram (Figure 10f), all of the samples from the Liuling Group and the first group of samples from the Wuguan Complex plot were between the andesite and the felsic volcanic rocks but close to the felsic volcanic rocks, and the other samples plot close to the basalt source. These characteristics imply a mixed source dominated by felsic rocks related to the island arc, with some intermediate and mafic–ultramafic rocks for the sedimentary rocks of the Liuling Group and the Wuguan Complex, supporting the fore-arc depositional setting.
Figure 10. Trace-element tectonic-setting discrimination diagrams for metamorphosed clastic rocks in the Wuguan Complex and Liuling Group. (a) Ti/Zr-La/Sc, (b) Th-Co-Zr/10, (c) Th-Sc-Zr/10 and (d) La-Th-Sc spots (after [77]). (e) La/Th-Hf diagram (after [39]). (f) Th/Sc-Zr/Sc plot (after [78]). Abbreviations: OIA = oceanic island arc; CIA = continental island arc; ACM = active continental margin; PM = passive margin.

5.3. Nature of the Wuguan Complex

The Wuguan Complex is linearly distributed along the SDSZ, with different rock compositions in different areas. Recent studies have recognized the Cambrian–Ordovician MORB or OIB-related basalts, as well as late Ordovician–early Silurian and late Devonian–early Carboniferous arc-related volcanic and sedimentary rocks in the Wuguan Complex [6,22].
Samples of metasedimentary and meta-igneous rocks in the Wuguan Complex were collected in this study. Their tectonic settings are quite different. The depositional age and characteristics of trace elements of the first group are similar to those of the Liuling Group. They show negative anomalies of Sr, P, Ta and Nb and positive anomalies of Cs, V, Cr and Ni, and the UCC-normalized multi-element patterns are similar to the sediments in the active continental margin (ACM) and continental island arc (CIA) setting (Figure 6a).

However, the second group of metasedimentary rocks from the Wuguan Complex shows high content of V, Ti and Sc but low content of K, Sr, U, Cs, Ba and Th, indicating the mixing of basic rock sources (Figure 10e), and the UCC-normalized multi-element patterns are similar to those of sedimentary rocks within the oceanic plate (WOP) setting (Figure 6b).

The protoliths of the meta-igneous rocks are continental island arc andesite and oceanic island basalt, respectively. Therefore, just as the previous researchers suggested, the Wuguan Complex is a set of tectonic melange composed of island arc materials and forearc sediments of different ages, and it is not a continuous lithostratigraphic unit [6,22,24].

5.4. Implications for the Late Paleozoic Tectonic Evolution of the Qinling Orogen

The Qinling orogen has undergone a complex evolutionary history. Previous studies demonstrated that the NQT developed a “trench–basin” system in the early Paleozoic [2,79,80]. The collision between the NQT and the NCB formed the Andean continental margin in the Early Paleozoic [1,5,29,38,71,81]. The final collision between the NCB and SCB occurred in the Mesozoic [2,79,80,82]. Compared with the early Paleozoic arc-continent collision and Mesozoic continent–continent collision, the details of tectonic evolution in late Paleozoic are not clear.

In this study, the geochemical analysis and zircon U–Pb dating of the metasedimentary rocks of the Liuling Group suggest that they were deposited in a fore-arc basin and with detritus only derived from the NQT. Additionally, the Wuguan Complex is a set of tectonic mélangé that contains island arc materials and forearc sediments of different ages. The youngest group of detrital zircons (360 ± 11 Ma) from the Liuling Group and the syn-sedimentary andesite layer (365 ± 19 Ma) in the Wuguan Complex imply that the subduction of the Paleo-Qinling Ocean and the sedimentation of the forearc basin lasted at least until the end of Devonian.

In this study, 332 ± 15 Ma for the metamorphic age of the garnet amphibolite and 349 ± 14 Ma for the metamorphic age of the amphibolite schist in the Wuguan Complex were both obtained in this study, consistent with 320–340 Ma obtained by predecessors [6,22]. These consistent metamorphic ages indicate that there was an early Carboniferous regional metamorphic event. Regionally, the Liuling Group and Wuguan Complex correspond to the Nanwan Group and Guishan Complex in the Tongbai–Hong’an orogen, which is in the east of the Qinling orogen. The Guishan Complex underwent a medium-pressure amphibolite facies metamorphic event in the hanging wall of the subduction zone 310–340 Ma [83]. Correspondingly, as the footwall of the subduction zone, the Xiongdian eclogite belt developed in the south of the Nanwan Group and Guishan Complex in the same period [38]. The Guishan Complex and the Xiongdian eclogite belt were considered paired metamorphic belts that might be indicative of a subduction–accretion process prior to continental collision [83]. This also indicates that the collision of NQT and SQT was not earlier than the early Carboniferous.

6. Conclusions

The Liuling Group formed in a forearc basin, with detritus derived from the NQT.

The Wuguan Complex is a tectonic mélangé composed of island arc materials and forearc sediments of different ages.

The youngest age population of detrital zircons from the Liuling Group and the age of the syn-sedimentary andesite layer in the Wuguan Complex suggest that the subduction of the Paleo-Qinling Ocean and the sedimentation of the forearc basin lasted at least until the end of the Devonian.
The early Carboniferous metamorphism occurred in the Wuguan Complex, which may be related to the collision of the SQT and NQT.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12081026/s1, Table S1: U-Pb data of LA-CP-MS analyses of detrital zircons from metasedimentary and meta-igneous rock samples of the Wuguan Complex and Liuling Group. Table S2: Chemical composition of the metasedimentary and meta-igneous rocks from the Wuguan Complex and Liuling Group.

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