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Geochemistry, Detrital Zircon U-Pb Geochronology, and Lu-Hf Isotopes of the Metasedimentary Rocks (Xinghongpu Formation, Late Devonian) in the Central South Qinling Orogenic Belt: Implications for Provenance and Tectonics

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Abstract: The Xinghongpu Formation is very important for understanding the Devonian tectonic evolution of the South Qinling orogenic belt. Geochemical, detrital zircon U-Pb-Hf isotopic studies were carried out on the Late Devonian metasedimentary rocks of the Xinghongpu Formation to constrain the depositional age, the provenance, and the tectonic setting. The detrital zircon U-Pb dating results revealed that the depositional age of the Xinghongpu Formation of the Late Devonian was not earlier than 363.2 Ma. The whole-rock geochemistry suggested that (1) this suite of metasedimentary rocks was mainly derived from quartzose sediments of mature continental provenance, with a small contribution from mafic and intermediate igneous provenance, and (2) the metasedimentary sandstone of the Xinghongpu Formation from the Late Devonian was deposited in an active continental margin to continental arc setting. The detailed detrital zircon U-Pb dating showed that the age spectra of detrital zircon could be divided into four groups: (1) 416–480 Ma, accounting for about 23%; (2) 740–850 Ma, accounting for about 19%; (3) 889–1017 Ma, accounting for about 19%; and (4) 1072–1146 Ma, accounting for about 12%. It also contained a group of Early Proterozoic zircons. The age and Hf isotope of the detrital zircons suggested that the clastic sediment deposited in the Xinghongpu Formation mainly came from the South Qinling Orogenic Belt and the North Qinling Orogenic Belt. The detrital zircon Lu-Hf isotopes indicated that most zircons were the products of the ancient crustal remelting, and the mantle-derived magmatic sources contributed to the provenance. The Xinghongpu Fm. formed in an oceanic basin in a continental margin environment with arc systems.

Keywords: detrital zircon; U-Pb dating and Lu-Hf isotope; late Devonian; South Qinling orogenic belt

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1. Introduction

The Qinling orogenic belt (QOB) in central China is a very important part of the Central Orogenic Belt [1,2]. It is between the North China Craton (NCC) in the north and the South China Craton (SCC) in the south. The west of the QOB is connected with the Qilian-Kunlun-Algin orogenic belt and the Pamir Plateau, and the southwest is adjacent to the Songpan-Ganzi fold belt. The east of the QOB is connected with the Tongbai-Hong'an-Dabie-Sulu orogenic belt [3–5]. The QOB has been divided into several parts [1]: the southern margin of the NCC (S-NCC), the North Qinling belt (NQB), and the South Qinling belt (SQB). These three terranes are separated from each other by the Shangdan Suture

Zone (SSZ) in the north and the Mianlue Suture Zone (MSZ) in the south [1,6]. Like the other major collisional orogenic belts in the world, the QOB was also constructed through prolonged processes of arc–arc, arc–continent, and continent–continent collisional events [7–9]. Its main collisional tectonic period was from the late Archaean to the Middle Triassic. The QOB experienced a long and complex collisional process from the rifting system to a plate collisional system, varying from extensional to subducting and then to a collisional environment [10–12]. The tectonic evolution was recorded and can be reflected by the sedimentary layers in the QOB, which was divided into five main parts from the old to the present: (1) the basement rock, which is Archean–Paleoproterozoic metamorphic rocks; (2) Neoproterozoic metasedimentary rocks and igneous rocks; (3) Mesoproterozoic–Paleozoic ophiolitic suites; (4) Paleozoic metasedimentary rocks, migmatites, and HP-UHP metamorphic rocks; and (5) Paleozoic–Mesozoic granitoid plutons [1,6,13]. To constrain the tectonic evolution of the QOB more clearly, a large amount of research has been carried out on the geochemical and geochronological features of the different layers in the QOB. Dong et al. [13] studied the Kuanping ophiolite, which represents a Mesoproterozoic ocean, which helps ensure the time of the amalgamation of the north Qinling Terrain to the North China Craton. The geochemical and geochronological study on the adakitic rocks and the complex in the NQB reflect the subduction of the Qinling oceans and the tectonic setting [14–16]. Furthermore, the pre- and post-collisional processes were also uncovered by the geochemical and geochronological study on granite in the QOB [17,18].

In addition, in recent years, the detrital zircon U-Pb dating and Hf isotope were widely applied in the analysis of tectonic evolution and provenance in basin and orogeny research [19–23]. In addition, some research was carried out with the help of detrital zircon dating in the QOB. Yang et al. [24] analyzed the provenance of the Jiyuan basin with detrital zircon U-Pb data and established the unroofing pattern of the QOB. Zhang et al. [25] investigated the Late Paleozoic and Early Mesozoic tectonic and paleogeographic evolution of central China through the study of the detrital zircon from the western QOB. The tectonic evolution and sedimentary provenance of the basin in the NQB, such as the Liuyehe basin and Lingguanmiao basin, were analyzed with the detrital zircon dating result of metamorphic sedimentary rocks, showing the slab–arc–basin system in the NQB from the Late Paleozoic to the Early Mesozoic [26,27] and the new intracontinental orogeny after the Indosinian orogeny [28]. In addition, the whole-rock geochemistry of metasedimentary rocks was used to study the sedimentary provenance in the QOB [29]. Dai et al. [30] studied the geochemical characteristics of meta-mud-siltstones from the Danfeng ophiolite mélange and found they were formed during the Ordovician to the Silurian, and the sedimentary set should be in a fore-arc basin of the active continental margin. When compared with the NQB, the geological story of the SQB has not been fully uncovered. Especially in our study area, Fengxian town, most of the detrital zircon studies of sedimentary rocks are focused on the Early to Middle Devonian [31–34], while there are fewer reports about the layers of the Late Devonian. This study focused on the Late Devonian Xinghongpu Formation (Fm.) in the Fengxian area, using whole-rock geochemistry, detrital zircon U-Pb dating, and Lu-Hf isotopes to uncover the sedimentary provenance and tectonic setting for the metasedimentary rocks from the Xinghongpu Fm. It was a supplementary study to the research on the sedimentary provenance and tectonic evolution of the SOB.

2. Geological Setting

The SQB has experienced a complex tectonic evolution. From the end of the Neoproterozoic to the beginning of the early Paleozoic, the ancient Qinling Ocean opened and gradually created an intensive extensional environment. This extensional environment lasted until the Middle Ordovician and then transferred to the convergence stage with the Yangtze plate subducting to the North China Craton. Thus, the SQB became the passive continental margin of the Yangtze plate [10]. At the same time, the northern margin of the Yangtze plate entered into a new extensive environment in the early Devonian. During

this process, the Mianlue Ocean formed [11,23], which caused the separation of the passive continental margin of the SQB from the Yangtze plate [3]. During the same period, a rifting zone developed along Minxian-Lixian-Fengzheng-Shanyang, forming a series of marine basins such as Zhengxun, Zhashan, Bansha, Fengtai, Xicheng, and Limin [35]. The Fengxian area is located in the central SQB (Figure 1). The exposed layers in the Fengxian are mainly Devonian, including the Middle Devonian Dafenggou Fm., the Middle–Late Devonian Gudaoling Fm., and the Late Devonian Xinghongpu Fm. and Jiuliping Fm. [36]. The Gudaoling Fm. and the Xinghongpu Fm. have promising potential for the exploration of lead-zinc and gold deposits. In addition, the Cretaceous Donghe group is also widely spread in the study area, which is the deposits of the Mesozoic rift basin [37,38].

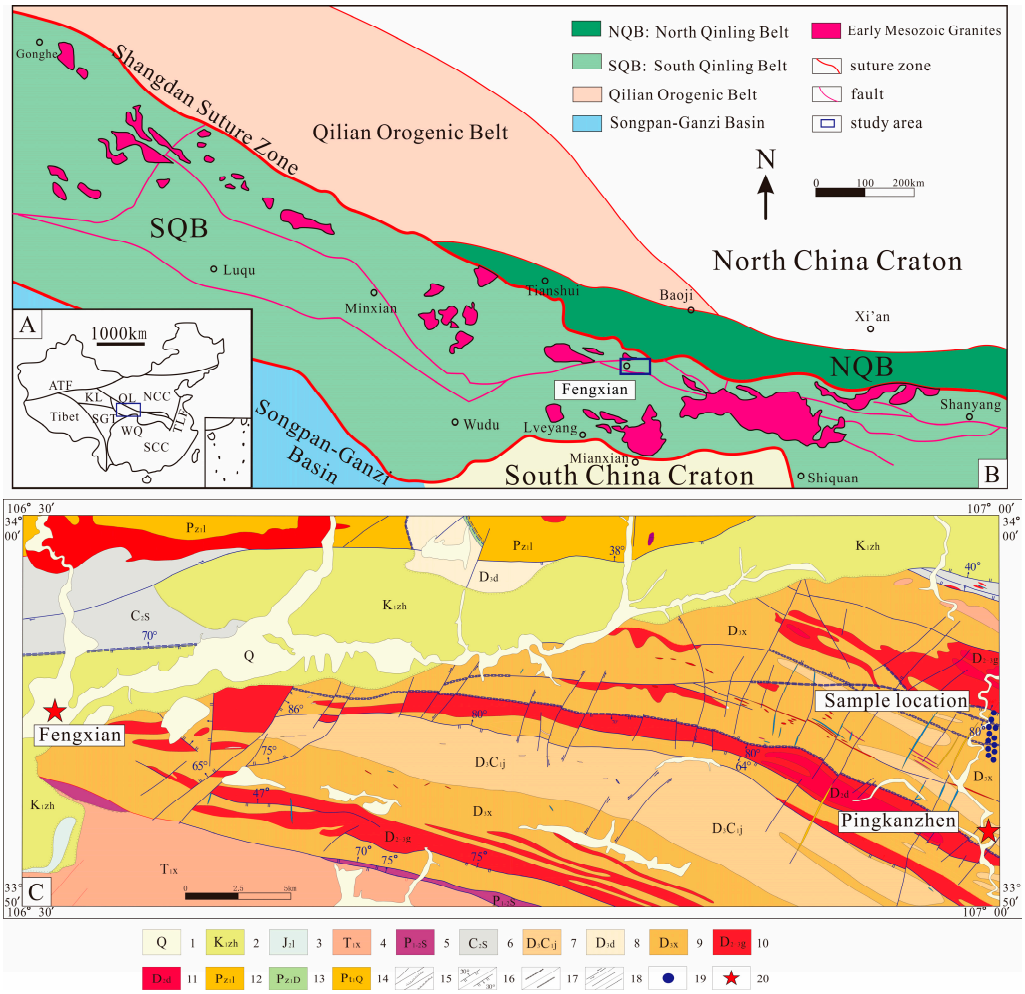


Figure 1. Geological maps of the study area (modified from [36]). (**A**) Geotectonic sketch map of China. (**B**) Tectonic framework map of the Qinglin Orogenic Belt. (**C**) Geological map of the Fengxian district showing sampling location. Legend: 1—Quaternary; 2—the Lower Cretaceous Zhoujiawan Fm.; 3—the Middle Jurassic Longjiawan Fm.; 4—the Lower Triassic Xipo Fm.; 5—the Lower–Middle Permian Shuixiakou Fm.; 6—the Upper Carboniferous Sixiakou Fm.; 7—the Upper Devonian Jiuliping Fm.; 8—the Upper Devonian Dacaotan Fm.; 9—the Upper Devonian Xinghongpu Fm.; 10—the Middle–Upper Devonian Gudaoling Fm.; 11—the Middle Devonian Dafenggou Fm.; 12—the Lower Paleozoic Luohanzi Fm.; 13—the Lower Paleozoic Danfeng Group; 14—the Lower Proterozoic Qinling Group; 15—geological boundary; 16—small fault; 17—brittle-ductile shear zone; 18—regional fault; 19—sampling location; 20—town.

The Xinghongpu Fm. is characterized by a huge suite of muddy sediments, which can be divided into three parts from the bottom to the top [35]. Part 1 generally consists of

slightly metamorphic clastic rocks intercalated with carbonate rocks. This part changed upward with less calcium and more siliceous clastic. Part 2 mainly consists of muddy components, with light green silty metasedimentary rock at the bottom. Calcium deposits appeared as interlayers, such as silty limestone, in the middle and upper parts of this part. The content of calcium in part 2 is higher than in part 1. Part 3 shows a similar lithological variation to part 2. The lower part of part 3 is fine clastic rocks and mudstone without any calcium deposits, while the calcium deposits developed as interlayers in the middle part of part 3. The upper part of part 3 is characterized by thin muddy carbonate rock. The overlying layer of part 3 from the Xinghongpu Fm. belongs to the Jiuliping Fm., which spans the Late Devonian and the Early Carboniferous. It is marked with many more carbonate deposits than what was developed in the Xinghongpu Fm. The metamorphic degree of the sedimentary rocks from the Jiuliping Fm. is also higher than the one developed in the Xinghongpu Fm. Thus, the sedimentary rocks from the Xinghongpu Fm. are more suitable to understand the sedimentary provenance and tectonic setting of the QOB in the Late Devonian. In this study, we picked 12 samples of slightly metamorphic siltstone of the Xinghongpu Fm. along the profile that is 50 km east of Fengxian County and 5 km north of Pingkan Town (Figure 1C). The metamorphic sandstone is yellow or green as a weathered color in the field (Figure 2A) and demonstrates a microscopically blastopsammitic texture (Figure 2B).

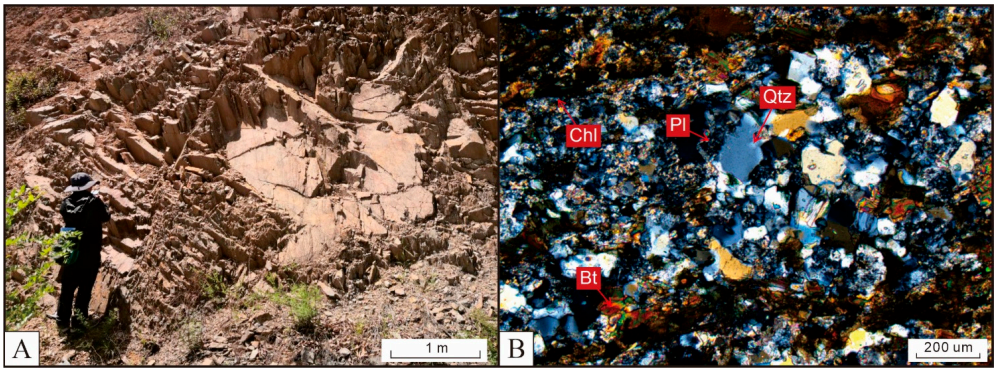


Figure 2. Field photo (**A**) and photomicrographs (**B**) of metamorphic siltstone from the Xinghongpu Fm. Qtz—quartz; Pl—plagioclase; Bt—biotite; Chl—chlorite.

3. Methods

3.1. Whole-Rock Elemental Geochemistry

The chemical analyses were conducted at the geochemistry lab of Geomillion Mineral Testing Technology Co., Ltd., Xi'an, China. Before the experiment, fresh rock pieces without cracks were crushed to a 200 mesh size. The major oxides were analyzed by X-ray fluorescence spectrometry (XRF; equipment model is Axios) with the relative standard derivation (2RSD) of major oxides less than 5%. The procedure for the major element analyses was described by Kimura [39]. The trace elements were analyzed by ICP-MS (equipment model was ICAP Qc), and the detailed procedures for the trace element analysis were described by Liang et al. [40]. The relative standard deviations (RSDs) of trace elements were within 5%.

3.2. LA-ICP-MS Zircon U-Pb Dating

The U-Pb dating and trace element analyses of zircon were conducted synchronously by LA-ICP-MS at the geochemistry lab of Geomillion Mineral Testing Technology Co., Ltd. The laser sampling was performed using a New wave NWR213. An Agilent 7500ce ICP-MS instrument was used to acquire ion signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T connector before entering the ICP. Each analysis incorporated a background acquisition of approximately 10 s (gas blank) followed by 40 s data acquisition from the sample. The

Agilent Chemstation was utilized for the acquisition of each analysis. Off-line selection and integration of background and analyte signals, time drift correction, and quantitative calibration for trace element analyses and U-Pb dating were performed by Glitter 4.4. Zircon 91,500 was used as an external standard for U-Pb dating. Time-dependent drifts of U-Th-Pb isotopic ratios were corrected using linear interpolation (with time). The preferred U-Th-Pb isotopic ratios used for 91,500 were from Wiedenbeck et al. [41]. The uncertainty of the preferred values for the external standard 91,500 was propagated to the ultimate results of the samples. Concordia diagrams were created and weighted mean calculations were performed using Isoplot/Ex_ver3 [42]. The trace element compositions of zircons were calibrated against reference materials (NIST610) combined with Si as an internal standardization. The preferred values of the element concentrations for the NIST reference glasses were from the GeoReM database, http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp (accessed on 25 May 2023). In addition, the age concordance of the zircons was not less than 80%, while the lower ones were eliminated. The zircon U-Pb dating method was described in detail by Duan [43].

3.3. Zircon In Situ Lu-Hf Isotope

The in situ zircon Hf isotope analyses were performed using a New Wave UP213 laser ablation microprobe coupled to a Neptune MC–ICP–MS at the geochemistry lab of Geomillion Mineral Testing Technology Co., Ltd. Meng et al. [44] described the method of testing in situ Lu-Hf isotopes in detail. A stationary spot with a beam diameter of 40 or 55 um was used. Helium was used as a carrier gas and was combined with argon in a mixing chamber before being introduced to the ICP–MS plasma. The values of $^{176}Lu/^{175}Lu = 0.02658$ and $^{176}Yb/^{173}Yb = 0.796218$ were used to correct for the ^{176}Lu and ^{176}Yb isobaric interferences, respectively [45]. The zircon GJ1 was used as the reference standard, yielding a weighted mean $^{176}Hf/^{177}Hf$ value of 0.282008 ± 27 (2σ). All Hf isotope data were reported with an error of 2σ of the mean, and values of ε_{Hf} were calculated using a ^{176}Lu decay constant of 1.865×10^{-11} yr^{-1} [46]. The depleted mantle model ages (TDMs) were calculated based on the measured $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ values concerning the depleted mantle with present-day $^{176}Hf/^{177}Hf = 0.28325$ and $^{176}Lu/^{177}Hf = 0.0384$ [47]. The average continent crustal (TC DM) model ages were calculated for the magma source using the zircon's initial $^{176}Hf/^{177}Hf$ value, assuming a mean crustal value of 0.015 [48].

4. Results

The major element, trace element, and rare earth element contents of 12 samples analyzed in this study are listed in Supplementary Table S2. The zircon U-Pb dating and Lu-Hf isotopic results of the sample PM02-2 are presented in Supplementary Table S1.

4.1. Major Elements

The element composition of the metasedimentary rocks was dominated by SiO_2 (48.7~69.4 wt.%, average 61.1 wt.%), Al_2O_3 (7.55~18.1 wt.%, average 14.2 wt.%), and CaO (1.48~14.9 wt.%, average 5.85 wt.%). In addition, these rocks also contained relative low concentrations of Fe_2O_3 (3.05~7.37 wt.%, average 6.00 wt.%), K_2O (0.54~4.28 wt.%, average 2.56 wt.%), MgO (1.51~5.93 wt.%, average 3.31 wt.%), and Na_2O (0.85~4.46 wt.%, average 1.99 wt.%). The contents of other major elements (MnO, P_2O_5, and TiO_2) were all lower than 1 wt.%. The average contents of SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, P_2O_5, and MnO of our samples were close to PAAS, while the content of CaO was much higher than the one in PASS (Figure 3). The contents of MgO and Na_2O were a bit higher than the ones in PASS.

There was a negative correlation between the contents of SiO_2 and Al_2O_3 and between the contents of Al_2O_3 and CaO (Figure 4). No obvious correlation could be observed between the contents of Al_2O_3 and P_2O_5. However, the samples showed a positive correlation between the contents of Al_2O_3 and TiO_2, between the contents of Al_2O_3 and TFe_2O_3, and between the contents of Al_2O_3 and K_2O. The rocks were compositionally variable, but most

samples shared similar geochemical characteristics (Figure 5), as shown by their respective $lg(SiO_2/Al_2O_3)$ (0.52~0.94) and $lg(TFe_2O_3/K_2O)$ (0.17~1.07) values. Most samples fell within the shale and wacke fields on Herron's sedimentary rock classification diagram [49] (Figure 5), while three samples fell in the Fe-Shale, Fe-sand, and Lith-arenite fields.

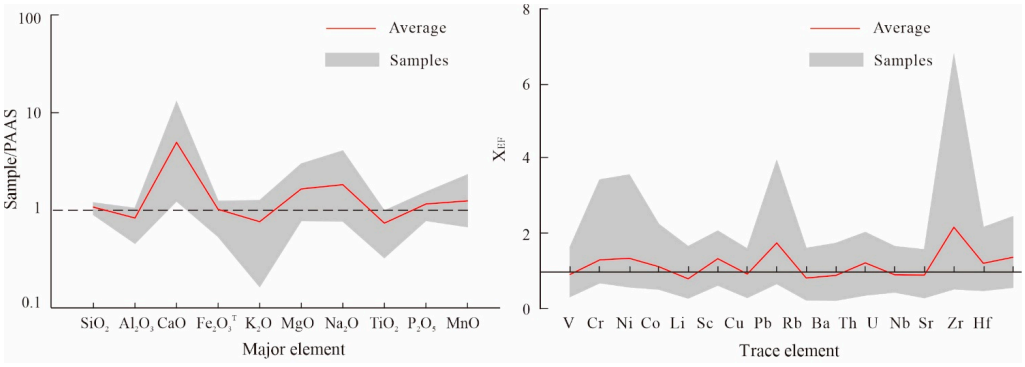


Figure 3. Major elements normalized by PAAS and XEF of trace elements of metasediment rocks from the Xinghongpu Fm.

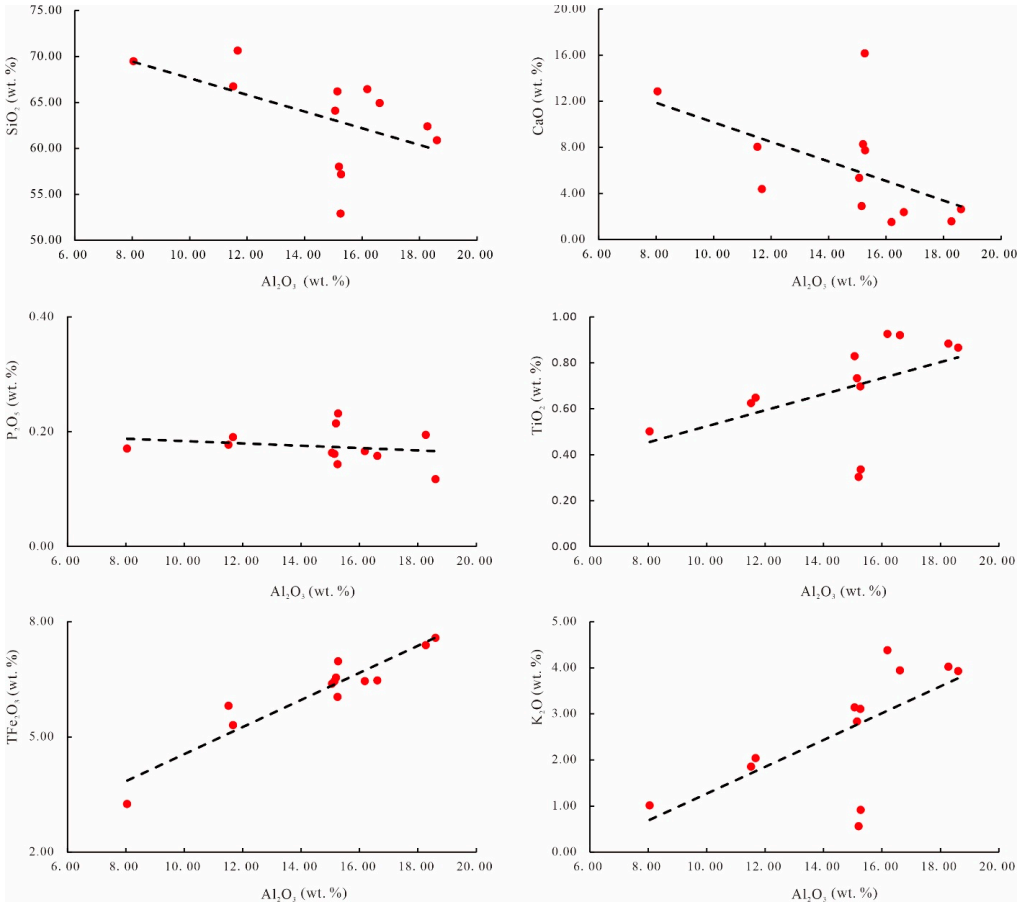


Figure 4. The Harker diagrams of major elements of metasedimentary rocks from the Xinghongpu Fm.

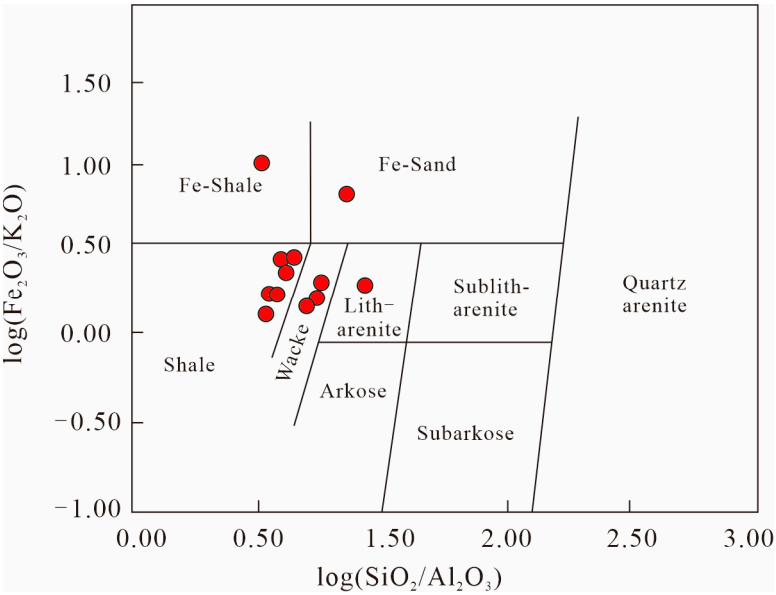


Figure 5. Log(Fe_2O_3/K_2O) vs. log(SiO_2/Al_2O_3) diagram (modified after [49]) for metasedimentary rocks from the Xinghongpu Fm.

4.2. Trace and Rare Earth Elements

Element enrichment factors were used to see the enrichment or depletion of an element by comparing it with a selected standard value. In this study, the trace elemental compositions of the samples were compared with the composition of PAAS [50] through Al-normalization to identify significant deviations [51]. Element enrichment factors of X (X_{EF}) were calculated by $X_{EF} = (X/Al)_{Sample}/(X/Al)_{PAAS}$. $X_{EF} > 1$ represents that element X was relatively enriched in the sample compared with X in PAAS, while $X_{EF} < 1$ represents the situation of depletion [51]. The X_{EF} values of Cr, Co, Ni, Sc, Pb, Th, Sr, Zr, and Hf were larger than 1, showing these trace elements were more enriched in the samples than in PAAS, while the X_{EF} values of Li and Rb were much lower than 1, indicating these elements were depleted. As to the elements V, Cu, Ba, U, and Nb, the X_{EF} values were close to 1, indicating that they behaved similarly to PAAS. The total ∑REE content of the Xinghongpu Fm. metasedimentary rocks varied from 106 ppm to 204 ppm. Moreover, the samples were enriched in LREE (96.1~182 ppm) relative to HREE (10.1~22.0 ppm) and showed prominent negative Eu anomalies (δEu = 0.58~0.89), and the ratio of $(La/Yb)_N$ was 7.89~11.8 (Supplementary Table S2).

4.3. Detrital Zircon U-Pb Dating

The analytical data are presented in Supplementary Table S1. Eighty zircons of the sample PM01 were selected for U-Pb analysis, and 75 spots produced good results. The zircons could be easily divided into two groups based on their CL image (Figure 6). Most zircons contained oscillatory growth zoning and yielded relatively high Th/U values (0.20~2.45), indicating a magmatic origin [44,52,53]. They are typically subhedral to euhedral, subrounded to subangular, and 35~100 μm in size. Two of these zircons were internally homogeneous with low Th/U values (less than 0.1) and were rounded and allotriomorphic in shape, suggesting a metamorphic origin [54–56]. The youngest zircon yielded an age of 363.2 ± 3.2 Ma with a magmatic zircon Th/U ratio (0.84), and the oldest zircon yielded an age of 2502 ± 13 Ma (Figure 7A). The main age peaks of these zircons were at about 440 Ma, 826 Ma, 970 Ma, and 1100 Ma (Figure 7B). They also contained a lot of old zircons, whose ages ranged from 1200 to 2500 Ma.

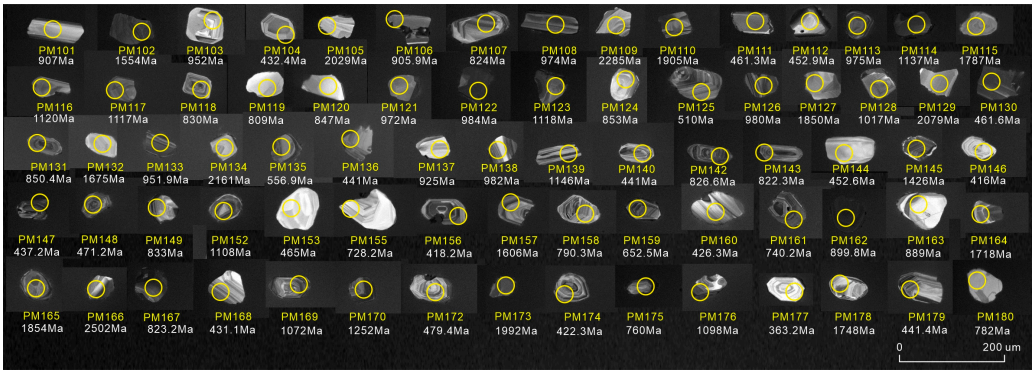


Figure 6. CL image of zircons of PM01 from the Xinghongpu Fm. The CL images of zircons 141, 150, 151, and 171 are not presented because their age concordance was lower than 80%, and zircon 154 was eliminated for its bad result during the test.

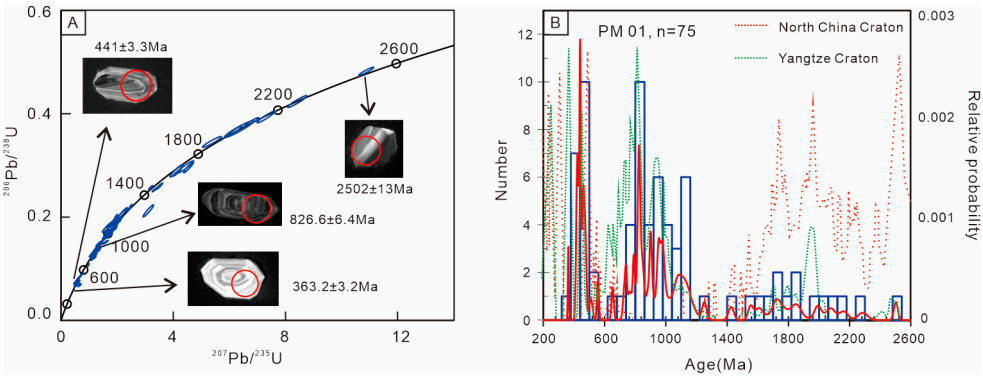


Figure 7. Zircon U-Pb concordia diagram (**A**) and frequency histograms (**B**) of PM01 from the Xinghongpu Fm. The probability densities of the Yangtze craton and the North China craton are from [34].

4.4. Zircon Lu-Hf Isotope

Zircon in situ Lu-Hf isotopic compositions of the dated 75 grains were also measured (Supplementary Table S1). The values of $^{176}Hf/^{177}Hf$ of these analytical spots ranged from 0.281234 to 0.283003, and the values of $^{176}Lu/^{177}Hf$ of these analytical spots ranged from 9.5×10^{-5} to 6.858×10^{-3}. The corresponding values of $\varepsilon_{Hf}(t)$ had a wide range interval from −22.58 to +16.26, with most grains (>70%) giving negative $\varepsilon_{Hf}(t)$. The $\varepsilon_{Hf}(t)$ value showed different characteristics in different age ranges. The number of zircons with positive $\varepsilon_{Hf}(t)$ values nearly equaled the ones with negative $\varepsilon_{Hf}(t)$ values when their ages were older than 1000 Ma, while the zircons with negative $\varepsilon_{Hf}(t)$ values dominated when their ages were younger than 1000 Ma. The model ages (T_{DM2}) were from 401 to 3141 Ma. Almost all the zircons demonstrated that their model ages (T_{DM2}) were larger than their $^{206}Pb/^{238}U$ or $^{207}Pb/^{206}Pb$ ages, while one zircon with 461 Ma as its $^{206}Pb/^{238}U$ age showed the opposite.

5. Discussion

5.1. Depositional Age of the Xinghongpu Fm

Detrital zircon's age was usually used to ensure the earliest depositional age of the layers because the deposition could not happen before the formation of the zircon, which came from its provenance. As shown above, the youngest age found when dating the zircon analyzed in this study was 363.2 ± 3.2 Ma (Figure 7A), indicating that the depositional age of the Xinghongpu Group should be younger than 363.2 Ma. In addition, the biological assemblage of the Xinghongpu Formation was classified into the Ancyrodella rotundiloba alata assemblage zone, which belonged to the Late Devonian.

Combined with the regional geological setting, this implied that the Xinghongpu group should belong to the latest Devonian.

5.2. Provenance

5.2.1. Evidence from Whole-Rock Geochemistry

The sedimentary geochemistry of rocks, detrital zircon geochronology, and zircon Lu-Hf isotope are useful tools widely used to distinguish the provenance of sediments.

Roser and Korsch [57] defined two functions (F1 and F2) to help distinguish the sediments from different provenances, including P1 (primarily mafic and lesser intermediate igneous provenance), P2 (primarily intermediate igneous provenance), P3 (felsic igneous provenance), and P4 (quartzose sediments of mature continental provenance):

$$F1 = -1.773 \times TiO_2 + 0.607 \times Al_2O_3 + 0.76 \times TFe_2O_3 - 1.5 \times MgO + 0.616 \times CaO + 0.509 \times Na_2O - 1.224 \times K_2O - 9.09,$$

$$F2 = 0.445 \times TiO_2 + 0.07 \times Al_2O_3 - 0.25 \times TFe_2O_3 - 1.142 \times MgO + 0.438 \times CaO + 1.475 \times Na_2O + 1.426 \times K_2O - 6.861.$$

Most of our samples fell into the P4 zone, while two fell into the P1 zone, and the others fell into the P2 zone (Figure 8). It suggests that quartzose sediments of mature continental provenance were the main provenance of the Xinghongpu Fm., and the mafic and intermediate igneous provenance also contributed to the Xinghongpu Fm. Floyd and Leveridge [58] proposed the Hf vs. La/Th diagram to distinguish the sedimentary source. Our sample fell into the field of acidic arc source with a mixed felsic and basic source and some ancient crustal material (Figure 9). In the Th/Sc-Zr/Sc diagram (Figure 10), two of our samples show different chemical compositions from the other samples. These two samples should be closely related to a mafic to intermediate igneous source marked by high Fe content (Figures 8 and 9) and very close to the andesite (Figure 10). In addition, the other samples did not show any compositional variation, suggesting they may not have originated from igneous provenance (Figure 10). It suggests they should be controlled by the mature continental source whose main compositional mineral was dominated by quartz and feldspar.

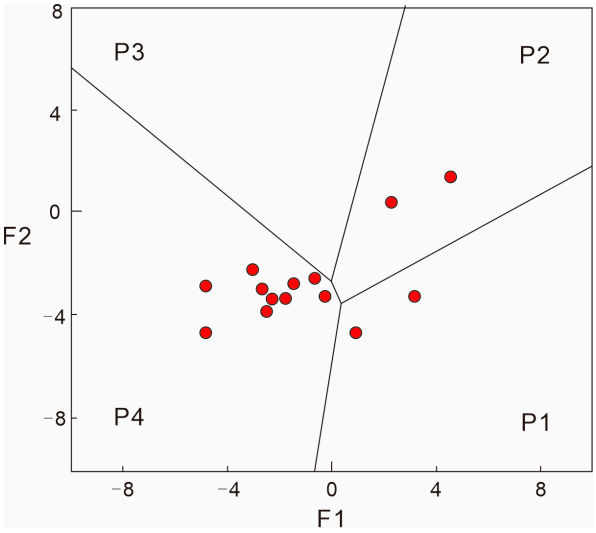


Figure 8. F1-F2 function diagram to distinguish provenance [57]. P1, primarily mafic and lesser intermediate igneous provenance; P2, primarily intermediate igneous provenance; P3, felsic igneous provenance; and P4, quartzose sediments of mature continental provenance.

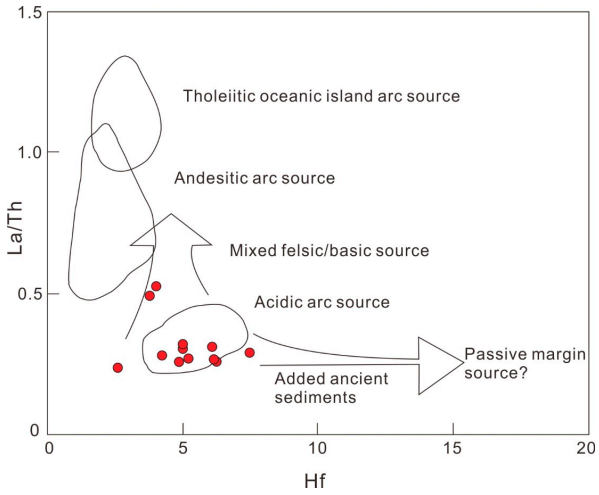


Figure 9. Sedimentary source (Hf vs. La/Th; modified after [58]).

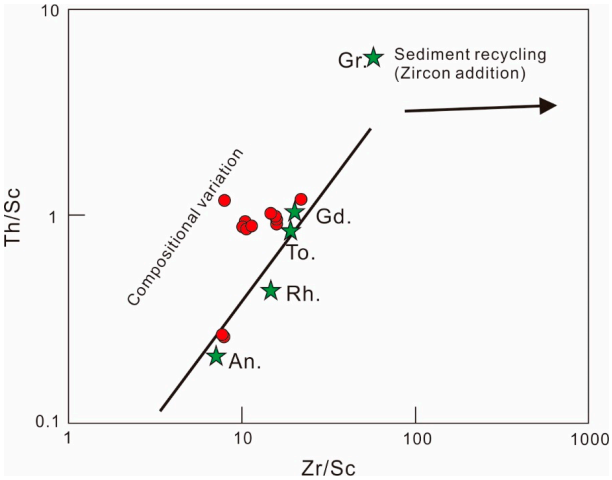


Figure 10. Th/Sc–Zr/Sc diagram after [59]. The data for tonalite (To), granodiorite (Gd), granite (Gr), and rhyolite and andesite are from [60].

5.2.2. Evidence from Detrital Zircon U-Pb Age and Hf Isotope

Combining the U-Pb age with the in situ Hf isotope of the detrital zircons could help constrain the provenance in complex situations. Seventy-five spots of detrital zircons were analyzed for their U-Pb age and the corresponding Lu-Hf isotopes. The age of the zircons ranged widely from 363.2 Ma to 2502 Ma, suggesting a complicated provenance that contained old crust material. Only two zircons from our sample were aged with a Devonian age (363.2 Ma and 416 Ma). Their $\varepsilon_{Hf}(t)$ values were −10.83 and 0.14, respectively. The lack of zircons aged from 364 Ma to 415 Ma indicated that the paleoenvironment of the study area in Devonian was a sag or a basin that could accept the deposits from ancient sources and lacked volcanic activity. It was consistent with understanding the stratigraphy and sedimentology of the Xinghongpu Fm. The zircon frequency histogram of our sample behaved similarly to the zircon frequency histogram of the Yangtze Craton with age peaks of 440 Ma, 826 Ma, 970 Ma, and 1100 Ma, lacking in the zircon frequency histogram of the North China Craton (Figure 7B). However, the Neoproterozoic detrital zircons (~0.8 Ga) from the Yangtze Craton were marked by positive $\varepsilon_{Hf}(t)$ values [25]. However, the $\varepsilon_{Hf}(t)$ values of the zircons (~0.8 Ga) in our sample varied from −17.8 to 6.61 (only three of 17 showed positive values). It indicated that there were at least two sources that contributed to the provenance, suggesting a complex provenance of the Xinghongpu Fm.

The Silurian zircons of our sample were aged from 437.2 Ma to 418.2 Ma, with negative $\varepsilon Hf(t)$ values (−9.9~−0.39). These were consistent with the zircons of granites and gneiss in

the NQB [15,61], suggesting that the NQB should be a provenance zone of the Xinghongpu Fm. This also indicated that the igneous source provided a large amount of material as the clastics for the Xinghongpu Fm. The age of our Ordovician zircons varied from 479.4 Ma to 441 Ma. Most of them showed negative $\varepsilon_{Hf}(t)$ values (−16.75~−0.44), while the zircons aged 461.3 ~ 465 Ma showed positive $\varepsilon_{Hf}(t)$ values (2.21~16.26). The positive group was consistent with the zircons of the amphibolite in the SQB (Shi et al., 2013), while the negative one should come from the gneiss in the NQB. Only one zircon was aged with a Cambrian age of 510 Ma, showing a positive $\varepsilon_{Hf}(t)$ value (9.37). The Neoproterozoic zircons of our sample were aged from 984 Ma to 556.9 Ma, with varying $\varepsilon_{Hf}(t)$ values from −22.58 to 8.98. The latest Neoproterozoic zircons marked by positive $\varepsilon_{Hf}(t)$ values should come from the granitoid in the SQB [62], while the zircons with the age of ~820 Ma and positive $\varepsilon_{Hf}(t)$ value were very consistent with the zircons from dioritic intrusion and migmatite in Yangtze Craton [20]. The other Neoproterozoic zircons of our sample were almost marked by negative $\varepsilon_{Hf}(t)$ value, which was common in the SQB and the NQB. Most of the early Mesoproterozoic zircons (seven of 10) were marked with negative $\varepsilon_{Hf}(t)$ values (−6.42~−1.25), while the other three zircons were marked with positive $\varepsilon_{Hf}(t)$ values. It was consistent with the quartz schist in the NQB [15,63]. In addition, the middle–late Mesoproterozoic zircons of our samples were all marked with positive $\varepsilon_{Hf}(t)$ values, which was similar to the zircons of gneiss in the NQB as well [15]. The Paleoproterozoic zircons were also mostly marked by negative $\varepsilon_{Hf}(t)$ values, while the zircons (aged 1675 Ma, 1606 Ma, and 2161 Ma) were marked by positive $\varepsilon_{Hf}(t)$ values. There was only one zircon with a Neoarchean age, showing a positive $\varepsilon_{Hf}(t)$ value. These Hf isotopic characteristics of zircon are similar to the ones from the NQB [15,63].

Above all, the potential provenance of the Xinghongpu Fm. was from multiple sources, including the SQB, NQB, and Yangtze Craton. However, because the Mianlue Ocean between the SQB and Yangtze Craton opened in the Early Devonian and existed until the Middle–Late Triassic [11,23,25], it would hinder the transport of detrital material from the Yangtze Craton to the SQB in the Late Devonian. The zircons showing similar geochemical features to the Yangtze Craton were all older than 800 Ma. In that period, the SQB was an extensional oceanic zone near the Yangtze Craton and accepted the clastics from Yangtze Craton as depositions. This is why some old zircons of our sample geochemically behaved similarly to the ones in the Yangtze Craton. Thus, the provenance of the Xinghongpu Fm. was mainly the SQB and the NQB.

5.3. Crustal Evolution and Tectonics

The age and Hf isotope of detrital zircons could help understand regional tectonic evolution [23,25,64] and assess plate tectonic reconstructions [22,65] for their wide age range, which was hardly recorded by the whole rock.

5.3.1. Crustal Evolution

The age and the Hf isotopic features of zircons (Figure 11) could provide interpretations on the regional crustal evolution. The main age groups of the detrital zircons of our sample were divided into the four groups below.

Group 1 included the zircons aged from 416–480 Ma, with $\varepsilon_{Hf}(t)$ = −16.8~3.19 and T_{DM2} = 1237~2479 Ma, except for one zircon aged 461.6 Ma with $\varepsilon_{Hf}(t)$ = 16.26 and T_{DM1} = 417 Ma and, in addition, another zircon aged 510 Ma with $\varepsilon_{Hf}(t)$ = 9.37 and T_{DM1} = 750 Ma. These suggested that most of the zircons came from remelting of the ancient crust while there was a depleted-mantle-derived magmatic intrusion or volcanic deposits developing during the Ordovician and Silurian in the study area, representing the early Paleozoic crustal growth event.

Group 2 included the zircons aged from 740–1017 Ma, with $\varepsilon_{Hf}(t)$ = −22.6~8.98 and T_{DM2} = 1626~3078 Ma, except the zircons aged 823.2 Ma, 824 Ma, 982 Ma, and 1017 Ma, with positive $\varepsilon_{Hf}(t)$ values (6.53, 6.61, 8.98, and 6.5), indicating crustal growth events at ~823 Ma in the middle Neoproterozoic and at ~1000 Ma in the transitory stage from the

Mesoproterozoic to the Neoproterozoic. In addition, the other zircons were characterized by negative $\varepsilon_{Hf}(t)$ values, representing the remelting and recycling of the ancient crust.

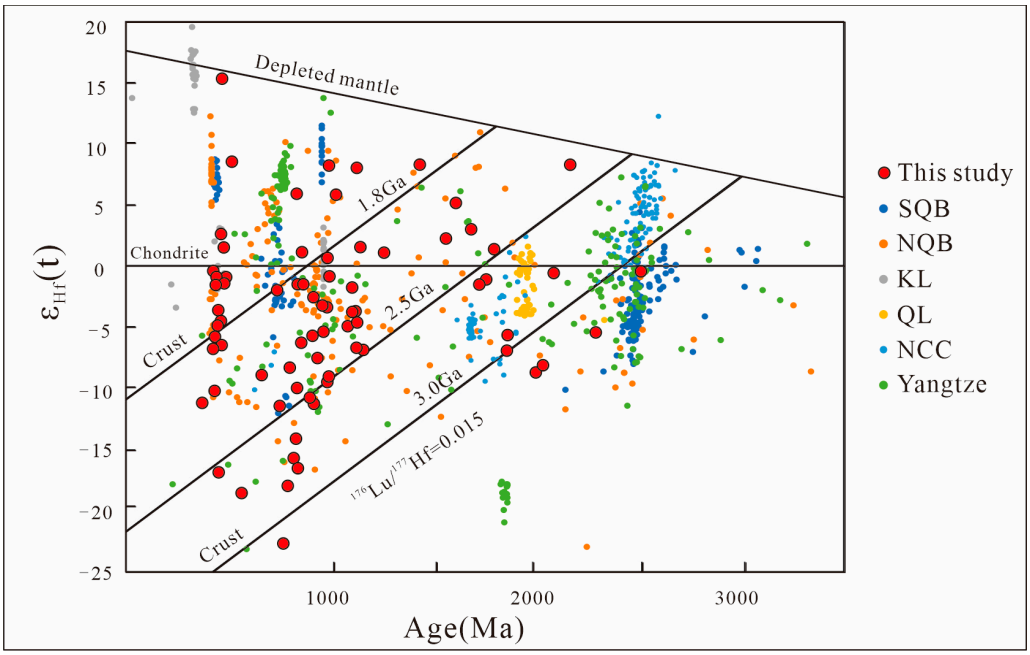


Figure 11. Age (Ma) vs. εHf(t) diagram of PM01 from the Xinghongpu Fm. Data sources: the SQB data were from [15,62,66], the NQB data were from [15,61,63], Kunlun from [67,68], the Qilian data were from [69], the North China Craton (NCC) data were from [70,71], and the Yangtze Craton (Yangtze) data were from [20,72–75].

Group 3 included the zircons aged from 1072–1787 Ma. This group of zircons could be divided into two subgroups according to the ages and different $\varepsilon_{Hf}(t)$ values: subgroup 1 (1072~1146 Ma), with $\varepsilon_{Hf}(t) = -6.42 \sim -1.25$ and T_{DM2} = 1999~2361 Ma, except for two zircons aged 1120 Ma and 1137 Ma with $\varepsilon_{Hf}(t)$ = 2.14~8.81 and T_{DM1} = 1287 Ma and 1562 Ma, and subgroup 2 (1252~1675 Ma), with positive $\varepsilon_{Hf}(t) = -6.42 \sim -1.25$ and T_{DM1} = 1549~1969 Ma. These indicated crustal growth events from the end of the Paleoproterozoic to the early Mesoproterozoic, while in the late Mesoproterozoic, crustal remelting took place and became dominant.

Group 4 included the zircons aged from 1718–2502 Ma, except for one zircon (age 2161 Ma), with a strong positive $\varepsilon_{Hf}(t)$ value (9.02) and T_{DM1} = 2174 Ma. The other zircons had negative or slightly positive $\varepsilon_{Hf}(t)$ values (−8.28~2) and T_{DM2} = 2680–3141 Ma. These suggested that crustal remelting was the main form of crustal evolution in this period.

Above all, the remelting of old crust occurred almost all the time, and the Paleozoic and Neoproterozoic were the main crustal growth periods.

5.3.2. Tectonic Implication

(1) Tectonic implication from detrital zircon

Besides the crustal evolution reflected by the geochemical features of the detrital zircons, the message of tectonic events could also be read out and interpreted. The age of the zircons with strongly positive $\varepsilon_{Hf}(t)$ values was concentrated in 461~465 Ma, ~823 Ma, 982~1017 Ma, and 1426~1606 Ma. It indicated that in these periods, the zircons should be derived from a depleted mantle by magmatism very close to the extensional tectonic environment, while the age of the zircons with strongly negative $\varepsilon_{Hf}(t)$ values was concentrated in ~441 Ma, ~557 Ma, 760~782 Ma, and ~830 Ma. This group of zircons represented the melting of the ancient crust and its recycling, which may have happened in a collisional tectonic setting. Combined with the geological and historical story, the zircons aged 1426~1606 Ma with positive $\varepsilon_{Hf}(t)$ values should be close to the breakup of

the Columbia supercontinent at ~1400 Ma. The Neoproterozoic zircons with strongly positive $\varepsilon_{Hf}(t)$ values should be close to the oceanic subduction during the formation of the Rodinia supercontinent at ~0.9~1.0 Ga, while the zircons with strongly negative $\varepsilon_{Hf}(t)$ values were almost marked by very old T_{DM2} (>2.5 Ga), suggesting they may have been derived from the crust during the formation of the Kenorland supercontinent.

(2) Tectonic setting in the Late Devonian

It has been shown that the chemical compositions of the sediments can be related to plate tectonic processes, making geochemistry a powerful tool for recognizing ancient tectonic settings [50,76–78]. The value of K_2O/Na_2O of sedimentary rock behaves differently from its SiO_2 content in different tectonic settings. Roser and Korsch [57] used K_2O/Na_2O-SiO_2 diagrams to distinguish the sedimentary rocks' tectonic settings successfully: active continental margin, passive continental margin, and island arc. The result shows that our samples are plotted in the fields of the active continental margin and island arc (Figure 12). Large ionic lithophile elements such as Th, Co, Zr, La, and Sc were also successfully used to distinguish the sedimentary rocks' tectonic environment. In the triangle series of diagrams proposed by Bahatia and Crook in 1986 [79], most of our samples are plotted in the continental arc (Figure 12) and active continental margin fields. There are also two samples plotted in the oceanic island arc field. It suggests that in the Late Devonian, the layers of the Xinghongpu Fm. were deposited in an active continental margin setting with arc systems. However, there was rare volcanism during the Devonian in the study area. The latest volcanic deposition occurred in the Late Silurian. Combined with the distributional characteristics of the zircon ages, the sedimentary rock in the Xinghongpu Fm. should contain a lot of re-depositional igneous clastic from Silurian.

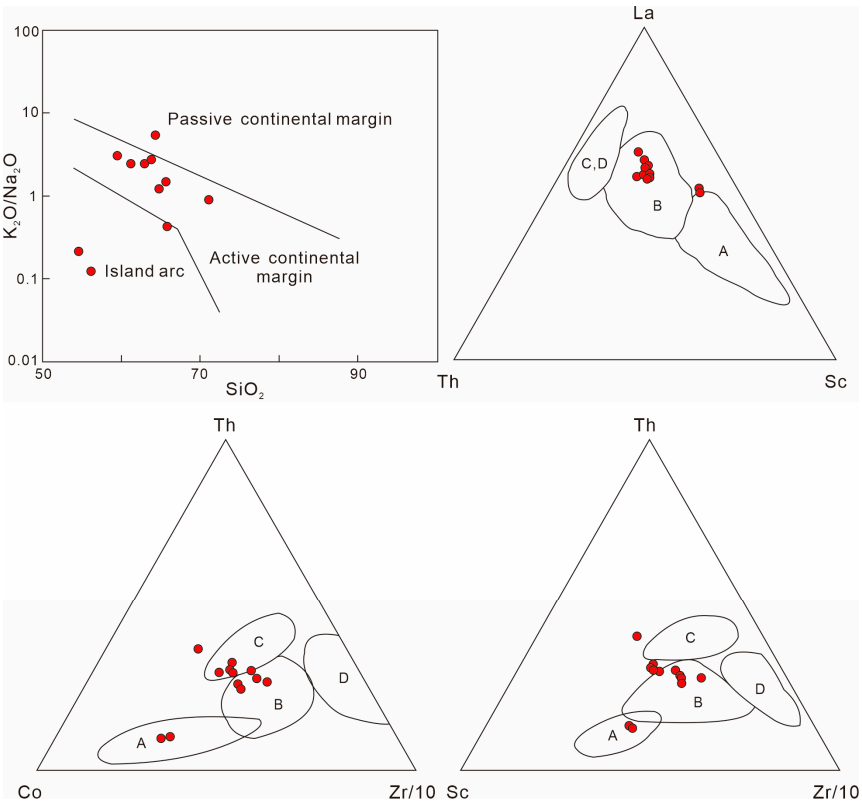


Figure 12. Tectonic discrimination diagrams for the Paleoproterozoic metasedimentary rocks (after Roser and Korsch, 1988 [57]; Bhatia and Crook, 1986 [79]). Abbreviations for tectonic settings: A, oceanic island arc; B, continental arc; C, active continental margin; D, passive continental margin.

6. Conclusions

The Xinghongpu Fm. was not deposited earlier than 363.2 Ma, which constrains its depositional age to the Late Devonian. The provenance of the Xinghongpu Fm. was mainly

from quartzose sediments of mature continental provenance, while mafic and intermediate igneous provenances also contributed a bit. Ancient crusts from the NQB and the SQB were the main sources for the provenance of the metasedimentary layers in the Xinghongpu Fm. The tectonic setting of the Fengxian area in the central SQB is an oceanic basin in an active continental margin environment with arc systems in the Late Devonian. The regional crustal evolution was related to the breakup and formation of supercontinents such as Columbia and Rodinia. The age peak (700~950 Ma) of zircon showed a co-relationship with the formation (1.0~0.9 Ga) and breakup (750~720 Ma) of supercontinent Rodinia, showing recycling continental material marked with negative $\varepsilon_{Hf}(t)$ and the juvenile crust represented by the ones with the positive $\varepsilon_{Hf}(t)$. The zircons aged 2.1~1.7 Ga were all with negative $\varepsilon_{Hf}(t)$ values and may represent the formation of the supercontinent Columbia.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/min13060768/s1: Table S1: Result of zircon U-Pb dating and Hf isotope; Table S2: Result of element geochemistry of samples.

Author Contributions: Conceptualization, Z.Z. and T.Z.; methodology, D.L.; software, T.Z. and H.W.; validation, Z.Z. and B.D.; formal analysis, D.Z.; investigation, Z.Z., B.D. and Y.Z.; resources, Z.Z.; data curation, B.D., C.Z. and Z.L.; writing—original draft preparation, Z.Z.; writing—review and editing, T.Z. and Y.S.; visualization, Z.Z., N.C. and X.Z.; supervision, Z.Z. and T.Z.; project administration, Z.Z., N.C. and X.Z.; funding acquisition, Z.Z. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in supplementary material, which can be downloaded at: www.mdpi.com/xxx/s1.

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