

Article

Geochronology and Geochemistry of the Xianshuihu Formation Volcanic Rocks in the Beishan Orogenic Belt, Northwest China: Implications for the Early–Middle Ordovician Tectonic Setting

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Abstract

The Beishan orogenic belt, in the southern margin of the Central Asian Orogenic Belt (CAOB), records a complex Paleozoic tectonic history, yet the nature and timing of its early magmatism remain debated. This study presents new petrological, geochemical, zircon U–Pb geochronological, and Lu–Hf isotopic data, combined with fossil biostratigraphic constraints, for volcanic rocks of the Xianshuihu Formation to constrain their formation age, petrogenesis, and tectonic setting. LA-ICP-MS zircon U–Pb dating of rhyolitic tuff yields a weighted mean age of 472.6 ± 3.7 Ma, indicating Early to Middle Ordovician volcanism and falling within the range of published ages (490.2 ± 2.9 Ma and 462 ± 3 Ma) for related volcanic units. Zircons from the rhyolitic tuff have $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.283077–0.283371, and positive $\varepsilon_{\text{Hf}}(t)$ values of +19.7 to +28.2, plotting in the depleted mantle field. The volcanic rocks have mostly primitive mantle-like Zr/Hf (33.40–39.13) and Nb/Ta (7.53–18.87), but low Nb/U (3.81–9.29), Ce/Pb (4.03–7.91), and Mg# (52–62). They are enriched in LILEs (e.g., Ba, U, Pb) and LREEs, depleted in HFSEs (Nb, Ta, P, Ti), with limited HREE fractionation. These geochemical fingerprints indicate arc-related magmatism and, when integrated with the deep-marine depositional environment indicated by graded and rhythmic bedding and graptolite fossils, are consistent with a continental arc setting. Our data do not support a direct link between these volcanic rocks and the ophiolite-bearing ocean basins in the Beishan area. Instead, we tentatively interpret them as products of southward subduction of the Zoolen Ocean beneath the Hanshan Block, which induced continental arc magmatism during the Early–Middle Ordovician.

Keywords: Beishan; early–middle ordovician; continental arc; Xianshuihu Formation; geochronology; geochemistry

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1. Introduction

Orogenic belts provide an essential framework for understanding continental accretion and the supercontinental cycle [1,2]. The Central Asian Orogenic Belt (CAOB) is one

of the world's largest accretionary orogenic belts, recording the amalgamation of multiple ocean plates, subduction zones, and convergent accretion related to the Paleo-Asian Ocean [2–5].

The Beishan, situated between the Siberian, Tarim, and Kazakhstan Plates, strikes roughly east–west in the southern part of the CAO. It is thought to record the evolution of the Paleo-Asian Ocean throughout the Paleozoic [6–8] and has become a research hotspot due to its crucial role in understanding the CAO. Previous studies in the Beishan have mainly focused on ophiolites [9–11], granites [12–20], and Carboniferous volcanic rocks, such as those of the Baishan Formation [21–23]. Several tectonic models have been proposed: (1) the Hongshi–Baihe–Pengbo Mountains suture divides the Beishan orogenic belt into the Kazakhstan Plate and the Tarim Plate [24]; (2) using the Luotuo–Hongshi–Heiying Mountains and Liuyuan–Daqi Mountains as boundaries, the Siberian, Kazakhstan, and Tarim Plates are distinguished from north to south [25]; (3) the Kazakhstan Plate is located north of the Hongliuhe–Niujuanzi–Xichangjing ophiolite belt, whereas the Tarim Plate lies to the south [26]. More recently, a fourth model has been proposed based on extensive regional surveys and comparative analyses [27]. In this model, the Beishan area is divided into the CAO and the Tarim Plate along the Hongliuhe–Niujuanzi–Xichangjing suture. The Hongshi–Baihe–Pengbo Mountains suture is interpreted as a supra-subduction zone (SSZ) ophiolite that developed from the Queershan–Yuanbaoshan island arc (QYIA). Furthermore, the QYIA is considered to record the early–mid Paleozoic evolution of the Paleo-Asian Ocean [28,29]. Understanding the formation of the QYIA is therefore crucial for deciphering the early Paleozoic tectonic evolution of the CAO.

The QYIA is mainly composed of volcanic rocks, intrusive rocks, and arc-margin clastic and carbonate rocks. However, few studies have investigated its Ordovician geological setting, and no consensus has been reached. Wang et al. [30] suggested that the Xirehada volcanic rocks formed in an extensional environment during the Ordovician. In contrast, Chen et al. [14] proposed a continental marginal arc setting based on data from the Xianshuihu Formation in Hurengbasike. Thus, the Ordovician tectonic setting of the QYIA remains poorly constrained.

In this study, we present new stratigraphic, petrographic, geochemical, zircon U–Pb geochronological, and Lu–Hf isotopic data, together with fossil and sedimentological constraints, for the Xianshuihu Formation. The results indicate Early–Middle Ordovician volcanism and arc-like geochemical signatures with a juvenile, mantle-derived source. Deep-marine sedimentary records further support an arc-related basin rather than an intracontinental rift. These data collectively suggest a continental marginal arc setting, tentatively related to southward subduction of the Zoolen Ocean beneath the Mingshui–Hanshan Block.

2. Geological Background

The Beishan orogen, a key component of the CAO, is situated between the Siberian Craton to the north and the Tarim Plate to the south (Figure 1a). It is separated from the Tarim Plate by the Hongliuhe–Niujuanzi–Xichangjing suture [27]. This area is characterized by three approximately east–west trending ophiolite belts or regional faults (Figure 1a), which divide the orogen into two tectonic units from north to south: the Queershan–Yuanbaoshan and Mingshui–Hanshan units (Figure 1a). Together, these two units constitute the northern Beishan orogen.

The formation age of the Hongliuhe–Niujuanzi–Xichangjing suture remains debated. Most scholars suggest an Early Paleozoic origin, with proposed ages ranging from the Early Cambrian [31–33] to the Middle Ordovician [34,35] or Early Silurian [36–38]. However, some studies argue for a Late Permian formation [39]. In the Xiaohuang Mountains

area, mafic-ultramafic rocks record hot emplacement along deep-seated faults during the Early Paleozoic [27], consistent with an Early Paleozoic origin for this suture.

The northernmost tectonic belt is the Hongshi–Baihe–Pengbo Mountains ophiolite belt. Regional geological characteristics and isotopic ages indicate that the oceanic basin represented by this tectonic belt opened in the Early Carboniferous [30,40,41] and closed in the Early–Middle Permian [42]. It is interpreted as an SSZ ophiolite that developed on the basis of the QYIA [27].

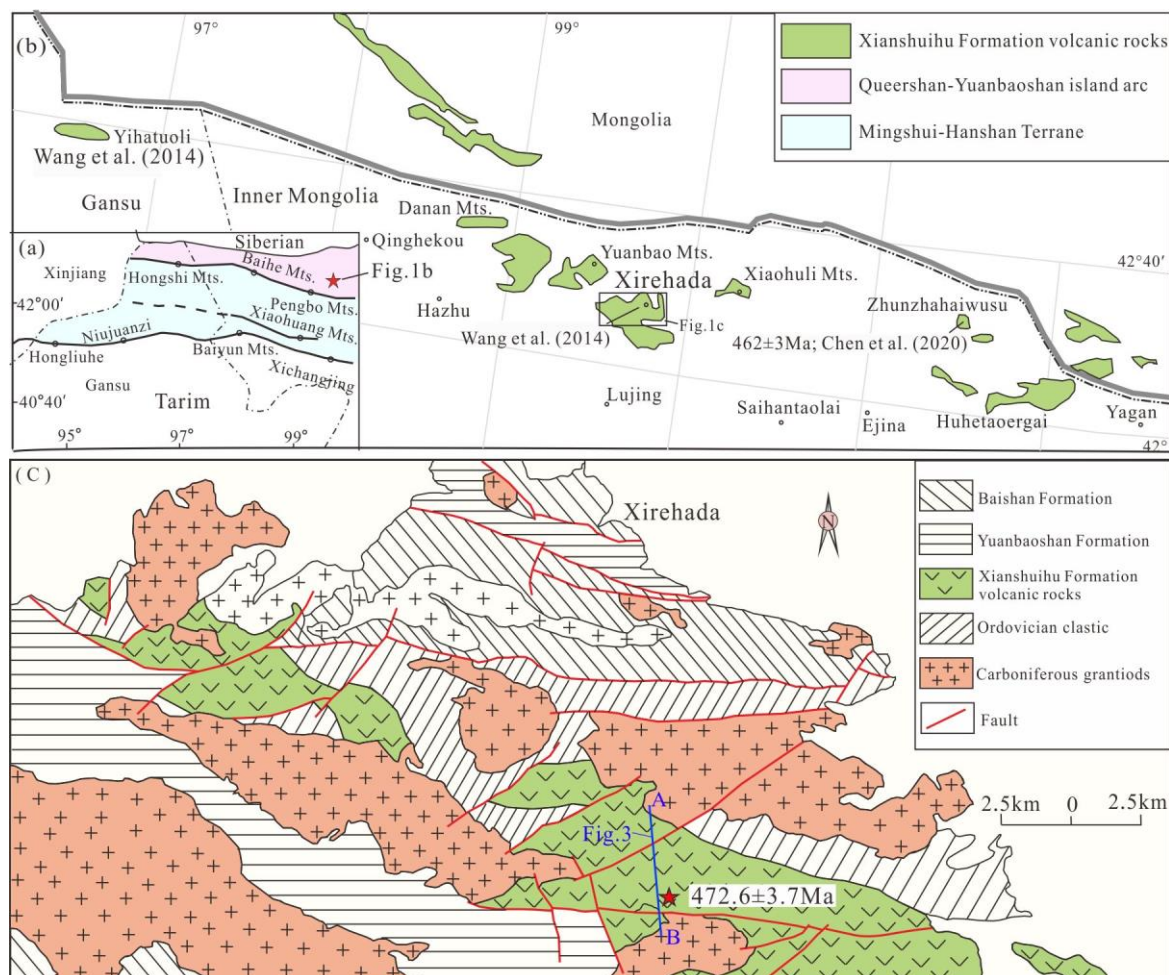


Figure 1. Tectonic sketch map (a), distribution of Ordovician volcanic rocks (b) [14,30], and schematic geologic map with section and sampling location (c) of the Xirehada area. Red stars: isotope sampling points; A and B: start and end points of the profile in Figure 3.

The QYIA is mainly composed of Ordovician–Devonian volcanic rocks, intrusive rocks, and contemporaneous arc-derived clastic and carbonate rocks. The Xianshuihu Formation volcanic rocks, which form part of this arc sequence, are distributed along a north-east-east-trending belt near the China–Mongolia border (Figure 1b). These rocks are mainly exposed in the Yihatuoli, Danan Mountains, Yuanbao Mountains, Xirehada, Xiaohuli Mountains, Zhunzhahaiwusu, and Huhetaoergai areas (Figure 1b). However, the tectonic setting of the QYIA during the Ordovician and thus the geodynamic environment in which the Xianshuihu Formation erupted remains controversial.

3. Field Observations and Sample Description

Detailed field surveys indicate that the Xirehada area in western Inner Mongolia is underlain by Xianshuihu Formation volcanic rocks, Silurian Yuanbaoshan Formation clastic rocks, and Carboniferous Baishan Formation intermediate to acidic volcanic rocks.

In addition, various intrusive rocks, such as gabbro, diorite, quartz diorite, granodiorite, and monzogranite, are also present in the area. These units are partially overlain by Meso-Cenozoic strata (Figure 1c). The Xianshuihu Formation is highly fragmented due to tectonic activity and magmatic intrusion (Figure 1c). Notably, the basal clastic rocks, which are in conformable contact with the Xianshuihu Formation, exhibit graded bedding (Figure 2a) and rhythmic bedding (Figure 2b), and graptolite fossils are present in the gray metasedimentary siltstone (Figure 2c,d).

The Xianshuihu Formation volcanic rocks comprise dark green andesitic basalt, green-black basaltic andesite, gray-green andesite, andesitic breccia tuff, gray dacitic breccia tuff, and rhyolitic tuff (Figure 3).

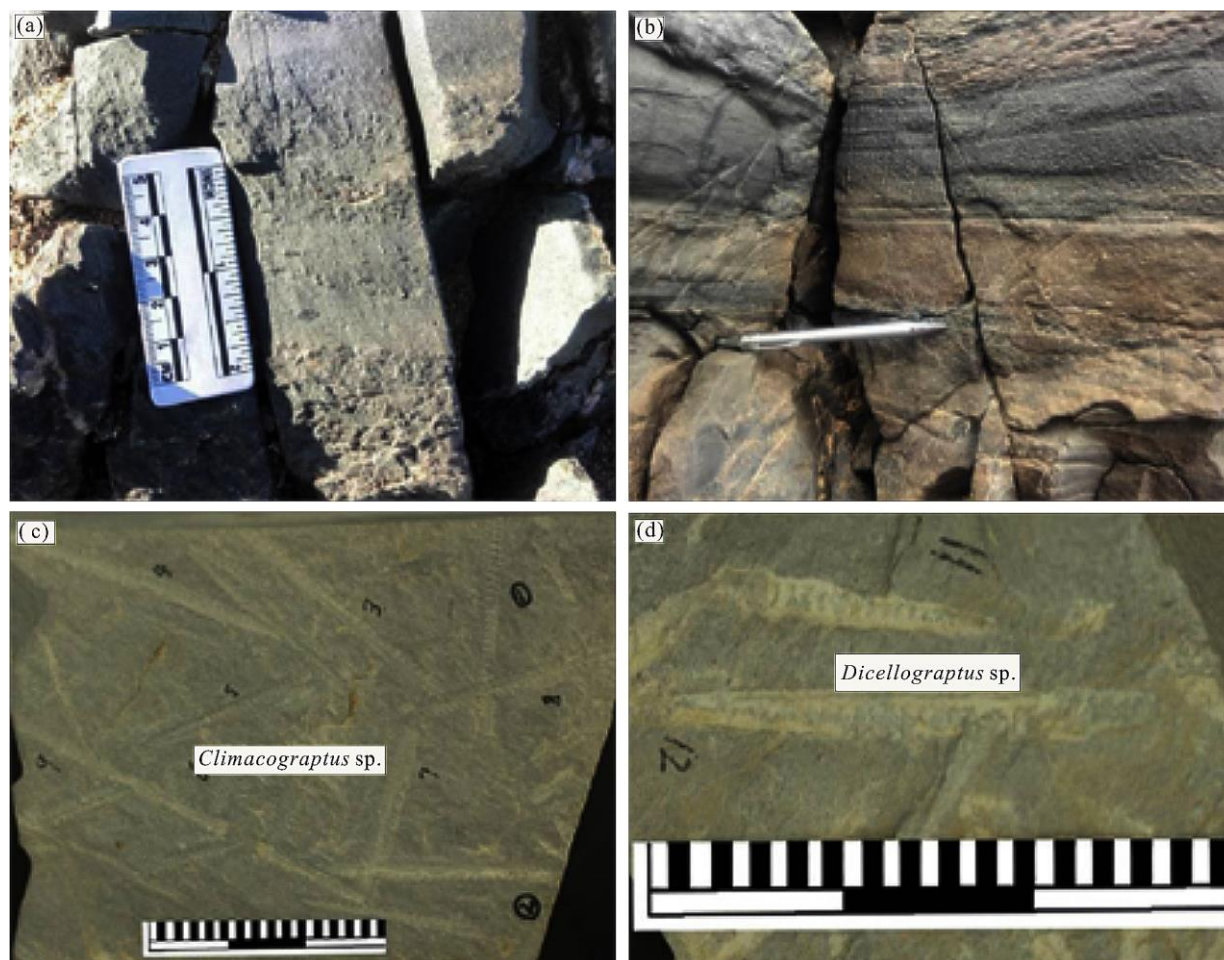


Figure 2. Characteristics of clastic rocks at the base of the Xianshuihu Formation. (a) Graded bedding; (b) rhythmic bedding; (c,d) fossils.

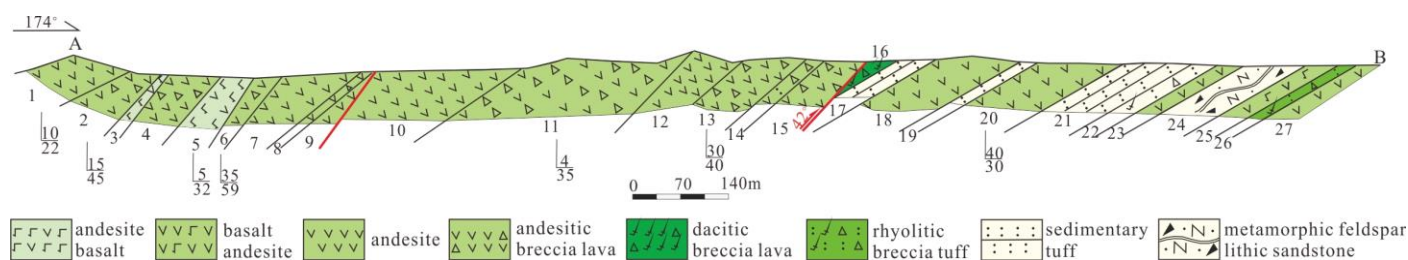


Figure 3. Representative stratigraphic section of the Xianshuihu Formation in the Xirehada area.

The andesite (Figure 4a,b) exhibits a porphyritic texture and a massive structure. The matrix displays an intergranular to intersertal texture. Phenocrysts (8%–10% plagioclase,

5%–10% dark mineral) range from 0.25 to 1.75 mm in size and are randomly distributed, locally exhibiting a glomeroporphyritic texture. Plagioclase phenocrysts are subhedral, plate-shaped, with polysynthetic twinning; some are partially altered to clay, chlorite, and limonite. Dark minerals consist mainly of pyroxene, which occurs as subhedral columnar crystals and is commonly replaced by chlorite, secondary amphibole, and limonite, forming pseudomorphs. The matrix is cryptocrystalline; under the microscope, it consists of grains <0.2 mm with a composition similar to that of the phenocrysts.



Figure 4. Photographs of volcanic rocks from the Xianshuihu Formation. (a,b) andesite, macroscopic and microscopic views, respectively; (c,d) andesitic breccia tuff, macroscopic and microscopic views, respectively; (e,f) rhyolitic tuff, macroscopic and microscopic views, respectively. Cpx: clinopyroxene; P: plagioclase.

Andesitic breccia tuff (Figure 4c,d) exhibits a breccia lava structure and a massive structure. It consists of breccia (~10%), debris (~3%), and lava cement (phenocrysts ~5%, matrix 80%–85%). The volcanic breccias are subrounded to irregular in shape, ranging from 2 to 24 mm in size, and displaying a disorderly distribution, although some long axes are oriented. Their lithology is andesite. The volcanic debris are irregular and scattered, with sizes between 0.4 and 2 mm, and are composed of basalt, andesite and other

rock types. The lava cement consists of phenocrysts and matrix. Phenocrysts are mainly plagioclase, ranging from 0.4 to 1.25 mm in diameter, whereas the matrix, composed of plagioclase and dark minerals, is finer than 0.4 mm.

Andesitic tuff consists of volcanic debris and lava cement, exhibiting a tuff lava texture and a massive structure. The volcanic debris includes volcanic agglomerate (~25%) and breccia (~5%), and is mostly subangular rock debris ranging from 0.3 to 2 mm, with a small amount of volcanic breccia between 2 and 7 mm. The lava cement is predominantly andesitic, composed of plagioclase phenocrysts (~25%) and matrix (~45%).

Rhyolitic tuff (Figure 4e,f) is composed of tuff, minor volcanic breccia, and lava cement, displaying a tuffaceous texture and a massive structure. The tuff is dominated by angular to subangular vitroclastic and crystal fragments, with no evidence of rounding, sorting, or sedimentary reworking. Its characteristics are similar to those of andesitic tuff lava, except that the lava cement is rhyolitic rather than andesitic.

4. Analytical Methods

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

Zircon separations, mounting, and optical (transmitted light and reflected light) and cathodoluminescence (CL) imaging were performed at the Hebei Regional Institute of Geology and Mineral Resources, Langfang, China. Zircon grains were separated using conventional manual panning, heavy liquid, and magnetic separation techniques. Approximately 100 zircon grains with complete crystal shapes and no cracks or inclusions were selected under a binocular microscope. They were then mounted in epoxy resin on a glass plate and polished. The CL images were used to select appropriate locations for U–Pb analysis.

Zircon U–Pb dating was conducted at the Inner Mongolia Institute of Geological Survey, Hohhot, China, using a Geolas HD 193 nm laser ablation system (Coherent GmbH, Göttingen, Germany) coupled with a Neptune Plus ICP-MS (Thermo Fisher, Dreieich, Göttingen, Germany). Helium was used as the carrier gas. The laser beam diameter was 32 μm , with an energy density of 10 J/cm² and a repetition rate of 6 Hz. The 91500 zircon standard was used for external calibration every eight sample analyses. Common lead correction was performed following Andersen [43]. Data reduction was carried out using the ICPMSDataCal program [44], and U–Pb concordia diagrams were constructed using Isoplot 3.0 [45].

4.2. Whole-Rock Major and Trace Elements

Fresh, weakly altered samples were selected and powdered to less than 200 mesh under contamination-free conditions. Whole-rock major and trace element compositions were determined at the Hebei Regional Institute of Geology and Mineral Resources, Langfang, China. Major element oxides were measured by an ICAP6300 X-ray fluorescence (XRF) spectrometer, with analytical precision generally better than 2%–5%. FeO was not obtained by XRF; it was determined separately by wet chemical analysis. H₂O[−] is the weight loss after drying at ~110 °C (hygroscopic moisture), whereas H₂O⁺ (structurally bound water) is determined by ignition at high temperature. Trace elements were analyzed using an X-Series 2 inductively coupled plasma-mass spectrometer (ICP-MS). The relative standard deviation (RSD) is better than 5%.

4.3. In Situ Zircon Lu–Hf Isotopic Analyses

In situ zircon Lu–Hf isotopic analyses were conducted at the Inner Mongolia Institute of Geological Survey, Hohhot, China, using the same Geolas HD 193 nm laser ablation

system and Neptune Plus ICP-MS as described above. To ensure direct comparability between Lu–Hf isotopic data and U–Pb ages, the analyses targeted the same zircon grains that yielded concordant U–Pb ages, with a laser spot size of 44 μm . The ^{176}Yb and ^{176}Lu interferences were corrected by monitoring ^{173}Yb and ^{175}Lu , mass bias was corrected with an exponential law ($^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$), and $^{176}\text{Hf}/^{177}\text{Hf}$ was normalized to 91500. $\varepsilon\text{Hf}(t)$ was calculated using $\lambda = 1.865 \times 10^{-11} \text{ a}^{-1}$, $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$ and $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$. The laboratory provided the analytical results and processing parameters; however, the original reference-material data for this session were not released with the report. Detailed operating conditions and analytical methods followed those described by Hu [46].

5. Results

5.1. Zircon U–Pb Ages

Twenty-five zircon grains from sample TW5213 (location: 42°11'35" N, 99°52'20" E) of the rhyolitic tuff were selected for LA-ICP-MS zircon U–Pb dating analysis. The results are listed in Supplementary Table S1. The zircon grains are generally colorless, transparent, and euhedral to subhedral, ranging from 50 to 110 μm in length, with length-to-width ratios of 1:1 to 2:1. CL images reveal oscillatory zoning (Figure 5), characteristic of magmatic zircon. The zircon grains have Th contents of 53–407 ppm, U contents of 150–816 ppm, and Th/U ratios of 0.33–0.83, all greater than 0.3. Additionally, Th and U show a good correlation (Figure S1). These features are consistent with a magmatic origin [43,47].

Prior to age calculation, analyses were screened using a priori criteria: (i) discordance >20%, calculated as $100 \times [(^{206}\text{Pb}/^{238}\text{U} \text{ age})/(^{207}\text{Pb}/^{235}\text{U} \text{ age})]$; (ii) $^{207}\text{Pb}/^{235}\text{U}$ ages anomalously older or younger than the corresponding $^{206}\text{Pb}/^{238}\text{U}$ age, indicating elevated common Pb or Pb loss; and (iii) CL evidence of inherited cores [48,49]. The three zircon grains (spots 8, 14, and 21) failed these criteria and were excluded. The remaining 22 zircon grains yield a broadly unimodal $^{206}\text{Pb}/^{238}\text{U}$ age cluster ranging from 458 to 490 Ma, with no distinct sub-populations or systematic age–discordance correlation [50]. The MSWD of 2.0 is slightly above 1 but is acceptable for a magmatic zircon population affected by minor common-Pb correction and Pb loss [51]. We therefore interpret the 458–490 Ma range as a single crystallization population, with the minor dispersion attributed to analytical uncertainty, minor Pb loss, and a small antecrystic/inherited component; the weighted mean age is $472.6 \pm 3.7 \text{ Ma}$ (1σ , MSWD = 2.0, $n = 22$) (Figure 5). This age indicates that the rhyolitic tuff was emplaced in the Early to Middle Ordovician.

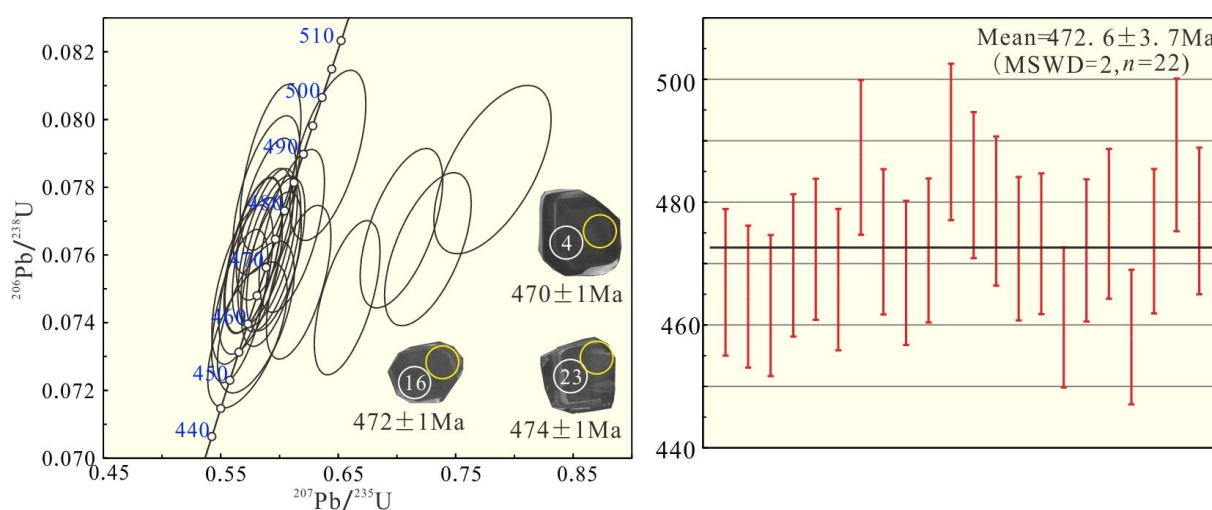


Figure 5. U–Pb concordia diagrams with cathodoluminescence (CL) images of representative zircons analyzed from sample 5213.

5.2. Whole-Rock Geochemistry

The whole-rock major and trace element compositions of the studied samples are presented in Supplementary Table S2. They display relatively high LOI values of 1.7% to 2.58%, suggesting that they may have undergone alteration. This inference is corroborated by petrographic observations: plagioclase phenocrysts are partially altered to clay minerals, chlorite, and limonite, and pyroxene is commonly replaced by chlorite, secondary amphibole, and limonite, forming pseudomorphs. High field-strength elements (e.g., Zr, Ti, Nb, Y, and Ta) are generally immobile during alteration [52,53], whereas most LILEs (such as K, Ba, Rb, and Sr) are easily mobilized [54,55], and should therefore be treated with caution in petrogenetic interpretations. No systematic correlations are observed in the LOI vs. Ba, Rb, Ba/Nb, and Ba/Rb diagrams (Figure S3), suggesting alteration did not exert a first-order control on these elements and ratios. Accordingly, our petrogenetic and tectonic interpretations rely primarily on HFSEs, REEs, and their mutual ratios (e.g., Zr/Hf, Nb/Ta, Th/Yb, La/Yb), which are robust to alteration.

The basaltic–andesitic rocks display SiO₂ contents ranging from 49.34% to 56.25% and TiO₂ from 0.71% to 1.14%. These rocks exhibit high Al₂O₃ concentrations (16.57%–19.10%), moderate MgO (4.81%–6.96%) and FeO (5.35%–6.78%) concentrations, and Fe₂O₃ values ranging from 1.38% to 2.38%. The Mg⁺ [100 × Mg²⁺/(Mg²⁺ + TFe²⁺)] varies from 52 to 62, where TFe²⁺ represents total iron (FeO_{total}) recalculated as Fe²⁺. In contrast, the rhyolitic rocks (Sample 5213) exhibit elevated SiO₂ concentrations together with relatively low Al₂O₃, MgO, FeO, and TiO₂ contents. In the total alkalis vs. silica (TAS) diagram (Figure 6a), Sample 5213 plots in the rhyolite field, whereas the other samples lie within the basalt–basaltic-andesite field. In the Zr/TiO₂–Nb/Y classification diagram (Figure 6b), all samples are projected into the subalkaline series, with Sample 5213 also falling in the rhyolite field, whereas the remaining samples plot in the andesite and basaltic andesite fields.

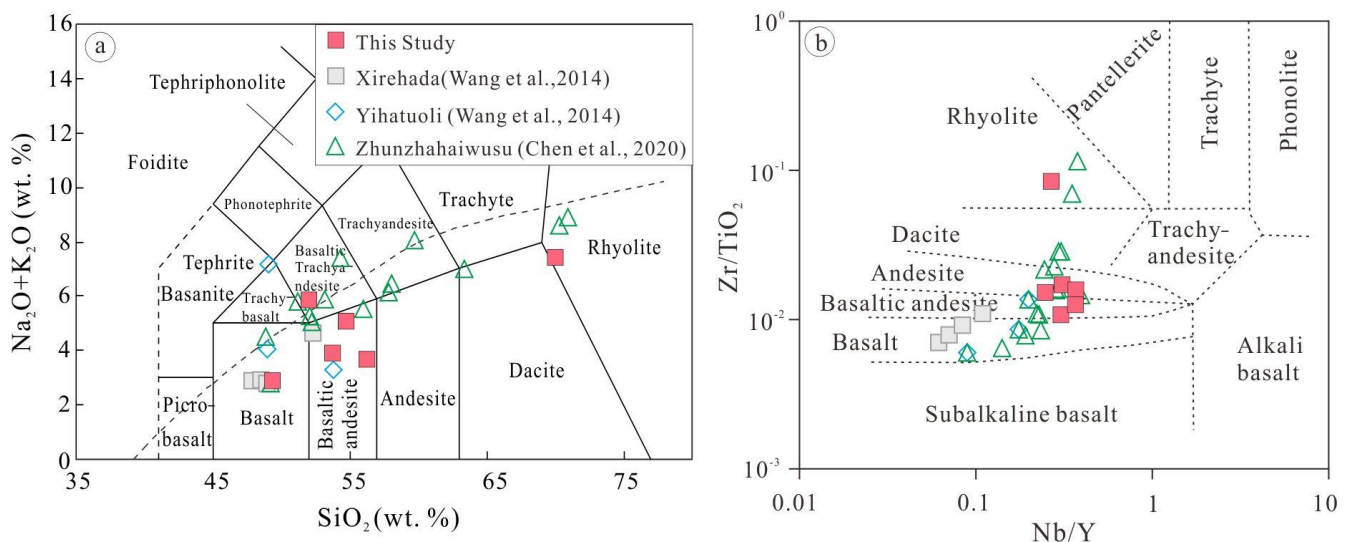


Figure 6. (a) Total alkalis vs. silica (TAS) diagram (after [56,57]) and (b) Zr/TiO₂–Nb/Y (after [58]) diagram for lithological classification of volcanic rocks from the Xianshuihu Formation. The comparative data is from references [14,30].

The chondrite-normalized REE diagram (Figure 7a) shows that the basaltic–andesitic rocks are characterized by slight Eu anomalies ($\delta\text{Eu} = 0.92\text{--}1.07$) and pronounced enrichments in LREEs, with relatively flat HREEs, and $\sum\text{LREE}/\sum\text{HREE}$ ratios ranging from 5.26 to 7.46, and (La/Yb)_N ratios ranging from 4.94 to 8.60. In contrast, the rhyolitic rocks exhibit

similar patterns (Figure 7c) except for intensely negative Eu anomalies (0.74). These characteristics are broadly similar to those of the Xirehada basalts, as well as the Hurengbasike and Yihatuoli volcanic rocks from the Xianshuihu Formation.

In the primitive mantle-normalized multielemental diagrams (Figure 7b,d), these rocks show enrichments in large ion lithophile elements (LILEs), such as U and Th, and depletions in high field strength elements (HFSEs), such as Nb, Ta, and Ti.

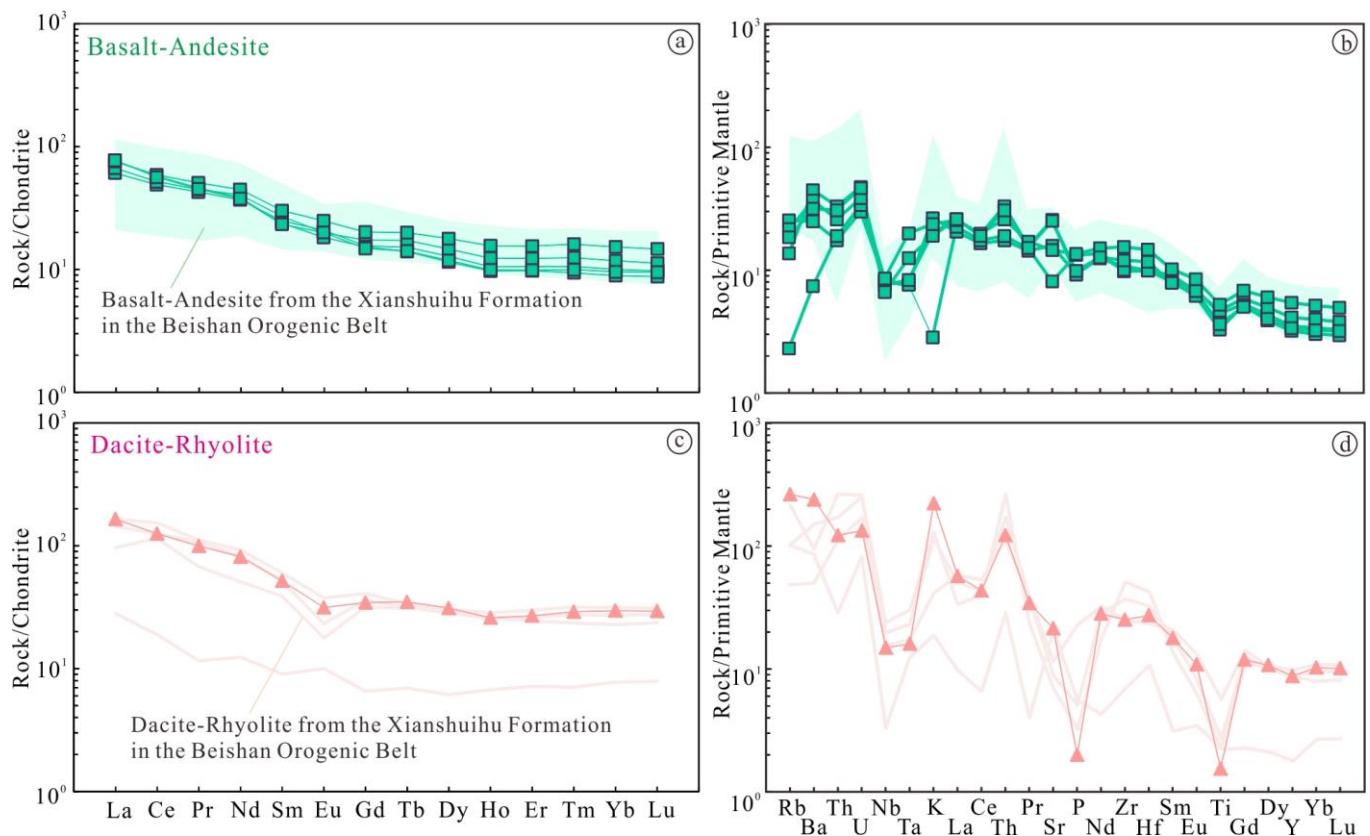


Figure 7. Chondrite-normalized rare earth element (REE) patterns and primitive mantle-normalized multielemental diagrams. (a,b) for the Basalt-Andesite, (c,d) for the Dacite-Rhyolite. Chondrite values and primitive mantle values are from [59].

5.3. In Situ Zircon Hf Isotopes

Ten zircon grains with concordant $^{206}\text{Pb}/^{238}\text{U}$ ages close to the weighted mean age were selected for in situ Hf isotopic analysis. The Hf isotope data are presented in Supplementary Table S3. The analyzed zircons yielded low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranging from 0.002212 to 0.005424, indicating negligible accumulation of radiogenic Hf after their formation. Thus, the measured $^{176}\text{Hf}/^{177}\text{Hf}$ values can reflect the Hf isotopic composition at the time of zircon crystallization [60]. The $^{176}\text{Hf}/^{177}\text{Hf}$ ratios range from 0.283077 to 0.283371, with corresponding $\varepsilon_{\text{Hf}}(t)$ values ranging from +19.7 to +28.2 and $f_{\text{Lu/Hf}}$ values from −0.93 to −0.84. The single-spot 2SE uncertainties on the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are 0.000023–0.000049, corresponding to $\varepsilon_{\text{Hf}}(t)$ uncertainties of approximately ± 0.8 –1.7 units. The depleted-mantle source interpretation is therefore robust with respect to the available uncertainty constraints, although session-specific reference-material data would provide stronger analytical validation. All data plot in the depleted mantle field on the t – $\varepsilon_{\text{Hf}}(t)$ diagram (Figure 8).

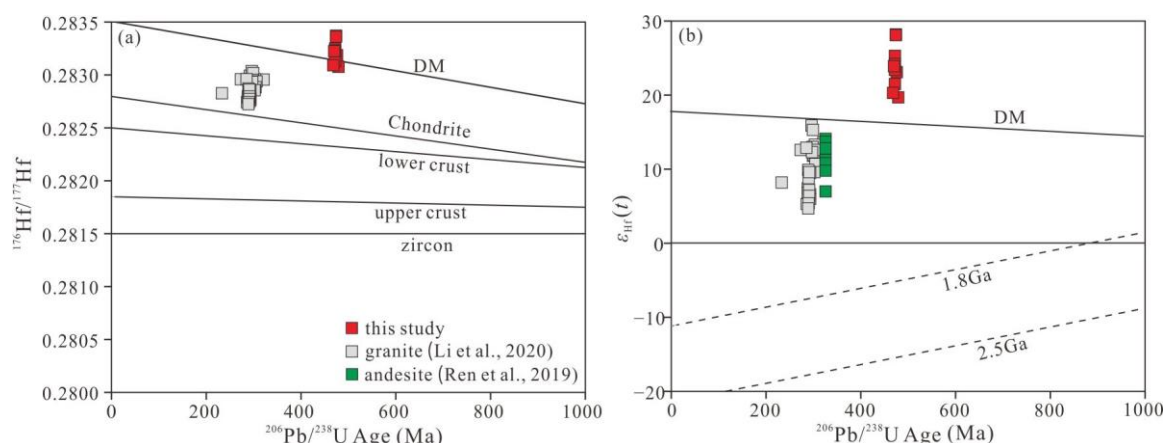


Figure 8. Diagrams of (a) $^{206}\text{Pb}/^{238}\text{U}$ ages vs. $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and (b) $^{206}\text{Pb}/^{238}\text{U}$ ages vs. $\epsilon_{\text{Hf}}(t)$ values. The comparative data is from references [16,23].

6. Discussion

6.1. Stratigraphic Age

The age of the Xianshuihu Formation has long been debated due to the lack of reliable geochronological and paleontological constraints. This study provides new zircon U–Pb ages and fossil evidence that collectively constrain its depositional age. The Early Paleozoic evolution of the Beishan area was closely linked to the closure of the Paleo-Asian Ocean and the development of the southern Central Asian Orogenic Belt [61,62], providing a regional tectonic framework for interpreting the stratigraphic age of the Xianshuihu Formation.

A rhyolitic tuff sample from the upper part of the Xianshuihu Formation yielded a weighted mean LA-ICP-MS zircon U–Pb age of 472.6 ± 3.7 Ma (Middle Ordovician). In addition, fossil specimens of *Climacograptus* sp. and *Dicellograptus* sp. recovered from grayish-green meta-siltstone of the lower part of the Xianshuihu Formation indicate age ranges of the Early Ordovician to Early Silurian (O_1 – S_1) and Middle to Late Ordovician (O_2 – O_3), respectively. These paleontological constraints are consistent with, and further refine, the geochronological results. The presence of deep-marine graptolites and turbidite-like deposits is consistent with an arc-related basin influenced by a magmatic arc barrier, which may have controlled biogeographic provincialism in East Asia during the Paleozoic [63].

Chen et al. [14] reported zircon U–Pb ages of 490.2 ± 2.9 Ma and 462 ± 3 Ma for rhyolitic crystal tuff and rhyolite, respectively, from the Hurengbasike area in northern Baisheshan. Xin et al. [27] obtained a minimum $^{206}\text{Pb}/^{238}\text{U}$ age of 482 Ma from grayish-black fine meta-sandstone in the Xirehada area. Our new weighted mean age of 472.6 ± 3.7 Ma falls within the range defined by these previous studies, but it differs in two important respects. First, we integrate the new U–Pb age with graptolite biostratigraphic constraints (*Climacograptus* sp. and *Dicellograptus* sp.) from the lower part of the formation, which collectively refine the depositional age to the Early–Middle Ordovician (ca. 472–482 Ma). Second, the concordance between the volcanic zircon age (this study and [14]) and the minimum detrital zircon age [27] demonstrates that volcanism and sedimentation were essentially synchronous, a relationship not previously documented for this formation.

Notably, the concordant ages between volcanic rocks and meta-sedimentary rocks indicate that the Xianshuihu Formation represents a volcano-sedimentary sequence formed during a short time interval in the Early to Middle Ordovician, which is typical of active continental margin or island arc settings where volcanism and sedimentation occur synchronously [64].

Collectively, the integrated geochronological and paleontological evidence presented above constrains the depositional age of the Xianshuihu Formation to the Early to Middle Ordovician, consistent with the Early Paleozoic plate tectonic framework of Asia [65].

6.2. Magma Source and Petrogenesis

Although the samples are limited, the stratigraphic section (Figure 3) shows that the Xianshuihu Formation constitutes a coherent volcanic eruption sequence, in which lavas, volcanoclastic rocks, and sedimentary interbeds are vertically superimposed. The analyzed samples were collected from different lithological units of this eruption sequence, and thus represent the overall geochemical character of the sequence. Using these representative samples, we evaluate the petrogenesis of the predominantly calc-alkaline andesites, for which several models have been proposed, including (1) partial melting of lower crust induced by mantle-derived basaltic magmas [66,67]; (2) fractional crystallization of mantle-derived basaltic magmas [68]; (3) crust–mantle magma mixing [69]; and (4) partial melting of mantle wedge metasomatized by subduction-related fluids [70,71].

The studied volcanic rocks exhibit Zr/Hf ratios ranging from 33.40 to 39.13, close to the primitive mantle value (36.7). Their Nb/Ta ratios are mostly 15.79–18.87, also near the primitive mantle value (17.5 ± 2), except for samples 5206 and 5207, which yield lower values of 7.53 and 9.27, respectively. In the Zr vs. Nb diagram (Figure 9), most samples plot within the depleted mantle field. These features argue against a predominant lower crustal partial-melting origin and are broadly consistent with mantle-derived or juvenile crustal sources [72]. Similar juvenile, mantle-derived signatures have been widely documented in Paleozoic granitoids of the northern Beishan orogenic collage [73]. However, the Hf isotopic data were obtained only from zircon grains in rhyolitic sample TW5213. The $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (0.283077–0.283371) and $\varepsilon_{\text{Hf}}(t)$ values (+19.7 to +28.2) are exceptionally high for ca. 470 Ma zircon. We therefore restrict the Hf-based source inference to the rhyolitic unit and consider the depleted-mantle interpretation.

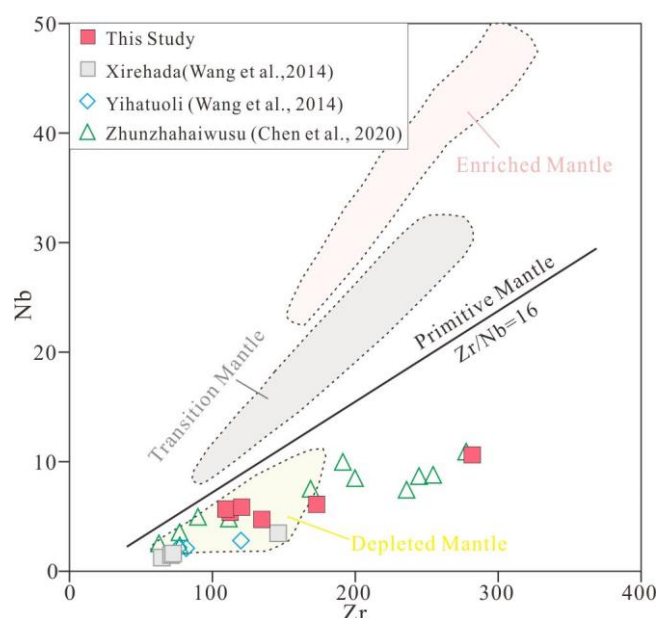


Figure 9. Zr vs. Nb diagram for the volcanic rocks from the Xianshuihu Formation. The comparative data is from references [14,30].

The rock assemblage is dominated by andesites, with limited variations in MgO contents (4.81%–6.96%), $\text{Mg}^\#$ values (52–62), and transition metal concentrations ($\text{Cr} = 66.42 \times 10^{-6}$ – 123.00×10^{-6} , $\text{Ni} = 45.08 \times 10^{-6}$ – 85.24×10^{-6}). Combined with the lack of significant correlation between major oxides and SiO_2 content and the weak Eu anomalies ($\delta\text{Eu} =$

0.92–1.07 in basaltic–andesitic rocks), these features collectively suggest that fractional crystallization of basaltic magmas was not the dominant process, similar to the limited fractional crystallization inferred for other high-Mg arc magmas in the region [74]. The homogeneous Hf isotopic compositions ($\epsilon_{\text{Hf}}(t) = +19.7$ to $+28.2$) from sample TW5213 may also argue against large-scale magma mixing if they represent a single magmatic system [75]. Collectively, these observations are most consistent with the fourth model: partial melting of a mantle wedge metasomatized by slab-derived fluids. This interpretation is further supported by the Th/Yb vs. Ba/La (Figure 10a) and Ba/Nb vs. Nb/La (Figure 10b) diagrams, in which the samples define a trend characteristic of subduction-related fluid metasomatism. We therefore conclude that the Xianshuihu Formation andesites were generated by partial melting of mantle wedge metasomatized by slab-derived fluids.

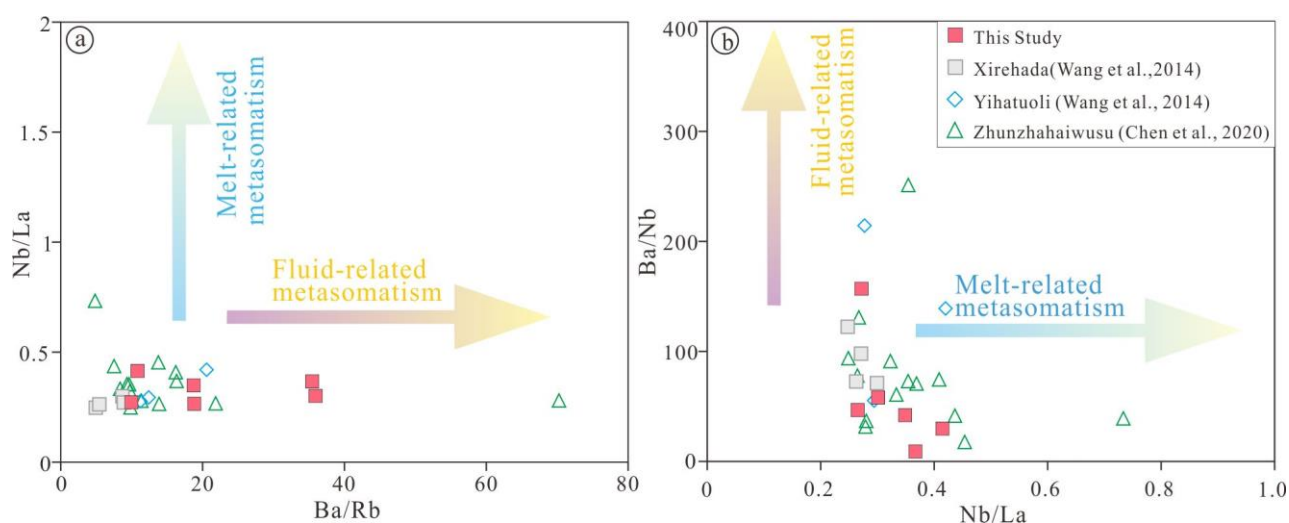


Figure 10. (a) Th/Yb vs. Ba/La and (b) Ba/Nb vs. Nb/La diagrams for the volcanic rocks from the Xianshuihu Formation. The comparative data is from references [14,30].

Nevertheless, several geochemical features indicate that the magma was not a primary mantle melt. The $\text{Mg}^{\#}$ values (52–62), together with the relatively low MgO, Cr, and Ni contents, are lower than those of typical primary mantle melts ($\text{MgO} = 10\text{--}12$ wt.%, $\text{Cr} = 250$ ppm, $\text{Ni} = 90\text{--}670$ ppm) [76]. The Nb and Ta contents range from 4.73 to 10.62 ppm and from 0.31 to 0.81 ppm, respectively, falling between primitive mantle and continental crust values. The Nb/U ratios (3.81–9.29) are significantly lower than the mantle value (47 ± 10) but close to the continental crust value (9–12) [77]. The Ce/Pb ratios (4.03–7.91) are significantly lower than the primitive mantle value (25 ± 5) and fall within the continental crust range (<15) [77]. These low Nb/U and Ce/Pb ratios are consistent with crustal contamination during magma ascent [78–82]. However, they are not diagnostic, because similar ratios can also arise from source characteristics, such as the involvement of subduction-related sediment-derived fluids or melts in the mantle wedge [83]. Moreover, the uniformly positive $\epsilon_{\text{Hf}}(t)$ values ($+19.7$ to $+28.2$) and the absence of inherited zircon or ancient crustal components in zircons from sample TW5213 rule out crustal contamination during magma ascent. Taken together, these observations suggest that source enrichment by subduction-related fluids/melts was likely the dominant process.

In summary, the volcanic rocks of the Xianshuihu Formation were most likely derived from partial melting of mantle wedge metasomatized by subduction-related fluids.

6.3. Tectonic Setting

The tectonic setting of the Xianshuihu Formation volcanic rocks remains debated. Wang et al. [30] proposed a rift setting, whereas other researchers have suggested a continental marginal arc or island arc setting [14,27].

The Xianshuihu Formation is part of the Paleozoic accretionary collage of the Beishan orogen, which lies in the southern CAOB. Regional studies have documented widespread juvenile, mantle-derived magmatism with positive $\varepsilon_{\text{Hf}}(t)$ and $\varepsilon_{\text{Nd}}(t)$ values [29,73]. In the northern Beishan orogenic collage, zircon Hf isotopic mapping of Paleozoic granitoids indicates significant contributions from depleted mantle sources, with limited involvement of ancient continental crust [73]. This is consistent with the positive $\varepsilon_{\text{Hf}}(t)$ values reported here for the rhyolitic sample TW5213, although those data alone cannot be extrapolated to the entire volcanic suite. The absence of a thick, ancient continental basement in the immediate study area argues against a purely intracontinental rift setting. In addition, Early Paleozoic arc-related volcanic rocks, accretionary complexes, and ophiolitic mélanges are widely distributed in the Beishan region, indicating a long-lived subduction–accretion system [31–35]. This regional framework is more consistent with a subduction-related setting than with a rift model.

Our new data provide further constraints on the tectonic setting. First, the volcanic rocks investigated in this study are characterized by enrichments in Ba, U, and Pb, relative depletions in Nb, Ta, P, and Ti, and light rare earth element (LREE) enrichments with limited heavy REE (HREE) fractionation. These geochemical features are typical of subduction-related arc magmatism [84,85] and are inconsistent with a within-plate rift setting. Second, the positive $\varepsilon_{\text{Hf}}(t)$ values of sample TW5213 indicate a juvenile mantle source rather than significant involvement of ancient continental crust, which argues against a rift setting. In addition, on the $\log(\text{Zr})$ vs. $\log(\text{TiO}_2)$ discrimination diagram (Figure 11a), most samples plot within the volcanic arc field, although some samples from the Xirehada, the Hurengbasike, and the Yihatuoli areas of the Xianshuihu Formation fall into the overlapping area between volcanic arc and mid-ocean ridge basalt (MORB) fields. On the $\log(\text{Ta/Yb})$ vs. $\log(\text{Th/Yb})$ diagram (Figure 11b), the Xirehada basalts plot in the oceanic island arc field, whereas the remaining samples predominantly fall within the continental marginal arc field. We therefore consider the rift model less likely and favor a continental marginal arc setting.

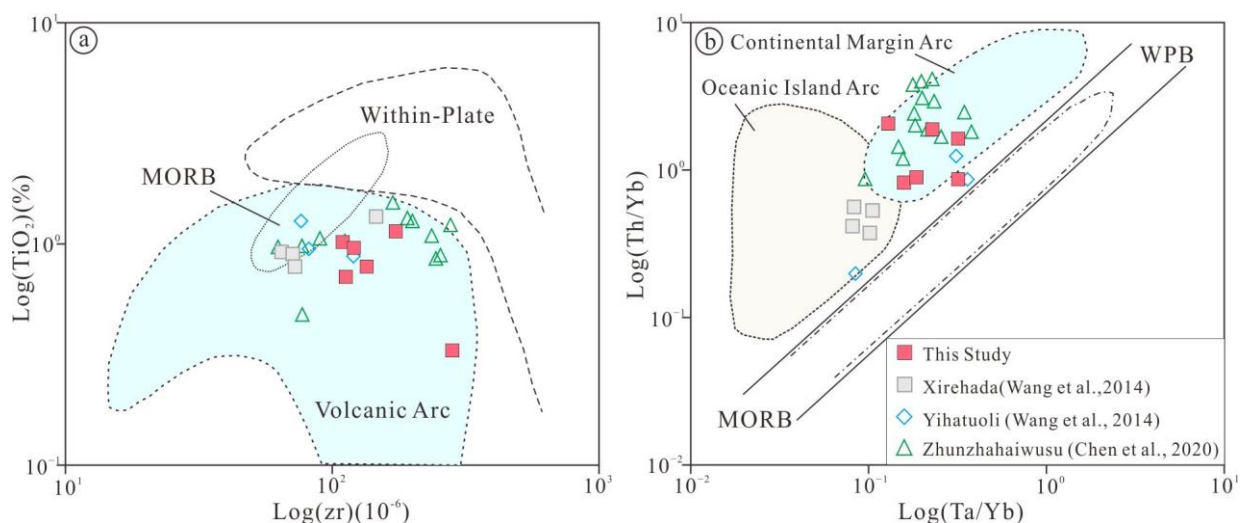


Figure 11. Tectonic discrimination diagrams for the volcanic rocks from the Xianshuihu Formation. (a) $\log(\text{Zr})$ vs. $\log(\text{TiO}_2)$ diagram [86], (b) $\log(\text{Ta/Yb})$ vs. $\log(\text{Th/Yb})$ diagram [87,88]. The comparative data is from references [14,30].

In addition, sedimentary features of the Xianshuihu Formation provide further constraints on its tectonic setting. The basal clastic rocks exhibit graded bedding (Figure 2a) and rhythmic bedding (Figure 2b), which are common in turbidite or submarine fan deposits across diverse deep-marine settings, such as active continental margins or arc-related basins [89,90]. These structures indicate rapid deposition from density currents, a process that is widespread in convergent settings where tectonic instability and high sedimentation rates prevail. Graptolite fossils (*Climacograptus* sp. and *Dicellograptus* sp.) recovered from gray meta-sedimentary siltstone (Figure 2c,d) indicate a deep-marine environment, as graptolites are generally considered to be inhabitants of deep-marine environments, often preserved in fine-grained sediments of continental slopes, deep-sea basins, or arc-related troughs [91–94]. These sedimentological and paleontological features therefore establish a relatively deep subaqueous setting. Integrated with the calc-alkaline andesite–rhyolitic tuff assemblage and the arc-type geochemical signature described above, they are consistent with a continental marginal arc setting in which rapid subsidence, volcanism, and sediment supply co-occur [89].

Collectively, the integrated evidence from regional tectonics, geochemistry, and stratigraphy–sedimentology is most consistent with a continental marginal arc setting for the Xianshuihu Formation during the Early–Middle Ordovician.

6.4. Geological Implications for the Early Paleozoic Evolution

As a key component of the CAOBS, the Beishan orogenic belt was predominantly situated within the Paleo-Asian Ocean tectonic domain during the Paleozoic [95], recording a complex geological evolution of the Paleo-Asian Ocean. The Queershan–Yuanbaoshan Paleozoic island arc belt, located north of the Hongshishan–Baiheshan–Pengboshan ophiolite belt, provides critical constraints on the regional tectonic evolution.

Previous studies have recognized three ophiolite belts in the Beishan area from south to north: (1) the Xichangjing–Niujuanzi–Hongliuhe ophiolite belt; (2) the Mingshui–Shibanjing–Xiaohuangshan ophiolite belt; and (3) the Hongshishan ophiolite belt [87,88]. Among them, the Xichangjing–Niujuanzi–Hongliuhe ophiolite belt formed during the Early Paleozoic [37,38,96,97] and likely represents the Early Paleozoic suture zone in the Beishan area [27]. The Hongshishan ophiolite belt formed during the Late Paleozoic [98], whereas the Shibanjing–Xiaohuangshan ophiolite belt is interpreted as a deep-seated fault formed under an Early Paleozoic extensional tectonic regime, with exposed intermediate–mafic intrusive rocks representing magmatic origin [27].

The Xianshuihu Formation investigated in this study is distributed in a northwest–southeast direction on the northern side of the Hongshishan ophiolite belt. The volcanic rocks are products of Early–Middle Ordovician continental marginal arc magmatism. Considering the distribution of tectonic units in the area [27,99], the tectonic setting in which the Xianshuihu Formation formed does not appear to be directly related to the evolution of the ocean basins represented by the three ophiolite belts mentioned above, and its formation mechanism warrants further consideration.

Several competing models have been proposed for the Early Paleozoic tectonic evolution of the Beishan area:

(1) Hongliuhe–Niujuanzi–Xichangjing suture model. This model interprets the Early Paleozoic evolution of the Beishan area as the result of northward subduction of the Tarim Plate beneath the Kazakhstan Plate, with the Xichangjing–Niujuanzi–Hongliuhe ophiolite belt representing the Early Paleozoic suture zone [27,37,38,96]. It is supported by the presence of Early Paleozoic ophiolites and accretionary complexes along this belt and by regional evidence for northward subduction and arc magmatism farther south [100,101].

However, it predicts arc magmatism at a location farther south than the Xianshuihu Formation, and the Xianshuihu Formation shows no direct petrogenetic link to the ophiolite-bearing ocean basins of this belt [27].

(2) Rift model. Wang et al. [30] interpreted the Xirehada volcanic rocks as having formed in an extensional environment during the Ordovician. This model is supported by the occurrence of extensional structures in some parts of the region and by bimodal-like volcanic rocks in some sections [102]. However, it cannot explain the arc-like trace-element signatures (LILE and LREE enrichment, HFSE depletion, elevated Ta/Yb), or the deep-marine sedimentary record (graded and rhythmic bedding, graptolite fossils), and it does not consider the regional subduction–accretion framework [31–35].

(3) *Zoolen southward-subduction model*. Jian et al. [103] proposed that the Zoolen Ocean, located in southern Mongolia north of the Beishan area, began to subduct southward from the Late Cambrian, producing trench-like TTG-type rocks at 498–461 Ma and an accretionary magmatic arc at 484–469 Ma. This model is supported by: (i) the timing of arc magmatism in this study (472.6 ± 3.7 Ma) overlaps with the 484–469 Ma Zoolen arc; (ii) the southward subduction polarity is consistent with the northward younging of arc magmatism and the distribution of the Xianshuihu Formation along the northern margin of the Mingshui–Hanshan Block; and (iii) the absence of a direct link between the Xianshuihu Formation and the ophiolite-bearing ocean basins within the Beishan area [27] suggests that the arc was not generated by subduction of the Hongliuhe–Niujuanzi–Xichangjing Ocean.

Among these models, the Zoolen model is considered the most probable. We therefore tentatively suggest that the Xianshuihu Formation volcanic rocks were generated by southward subduction of the Zoolen Ocean beneath the Mingshui–Hanshan Block, which is also consistent with the interpretations of Chen et al. [14] and Xin et al. [27]. This continental marginal arc magmatism during the Early–Middle Ordovician not only documents the southward subduction process of the Zoolen Ocean but also provides important evidence for the accretionary history of the southern CAOB. The occurrence of deep-marine sedimentary facies (turbidite-like bedding and graptolite-bearing fine-grained sediments) further supports the existence of an active continental margin setting rather than a passive margin or intracontinental rift. Collectively, the Queershan–Yuanbaoshan island arc belt records a key phase of Early Paleozoic arc magmatism and sedimentation in response to the consumption of the Paleo-Asian Ocean, contributing to the lateral growth of the CAOB.

Based on the integrated evidence presented above, we propose a tectonic model to illustrate the Early–Middle Ordovician evolution of the Beishan orogenic belt (Figure 12).

During the Early–Middle Ordovician (ca. 475 Ma), the Zoolen Ocean to the north of the Beishan area may have begun to subduct southward beneath the Mingshui–Hanshan Block [103]. This southward subduction would have triggered partial melting of the mantle wedge metasomatised by slab-derived fluids, generating the calc-alkaline andesitic magmas of the Xianshuihu Formation. These magmas ascended through the continental crust, and erupted in a continental marginal arc setting. Concurrently, the subduction zone would have created a fore-arc basin on the trenchward side of the arc, where rapid deposition of turbidite-like graded and rhythmic bedding occurred, along with the preservation of deep-marine graptolite fossils. Thus, the Xianshuihu Formation volcanic rocks most likely document an Early–Middle Ordovician continental marginal arc system associated with southward subduction of the Zoolen Ocean, contributing to the accretionary growth of the southern CAOB. This model remains a hypothesis. The subduction polarity of the Zoolen Ocean and its linkage to the Beishan orogenic belt require further study.

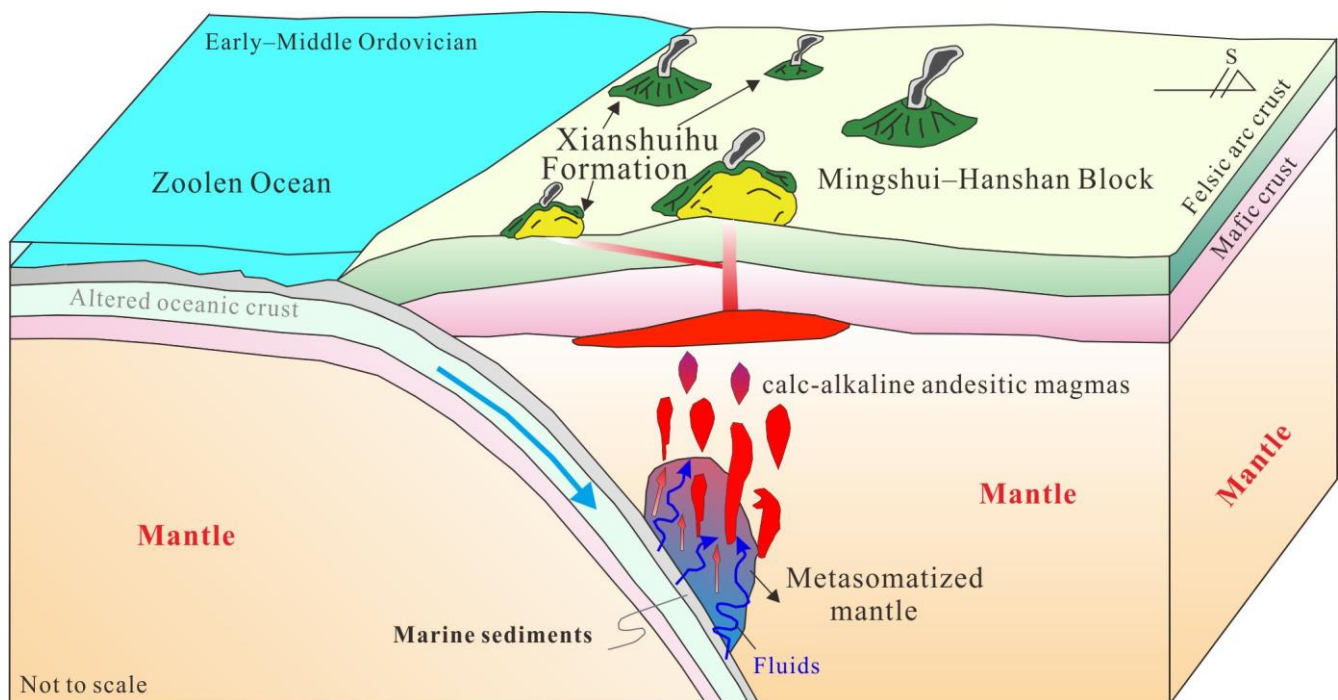


Figure 12. Schematic illustration summarizing an integrated petrogenetic model for the volcanic rocks from the Xianshuihu Formation.

7. Conclusions

Based on the integrated study of petrology, geochronology, geochemistry, and Lu–Hf isotopes of the Xianshuihu Formation volcanic rocks in the Beishan orogenic belt, the following conclusions can be drawn:

(1) Zircon LA-ICP-MS U–Pb dating of rhyolitic tuff from the Xianshuihu Formation yields a weighted mean age of 472.6 ± 3.7 Ma, indicating that the volcanic rocks erupted during the Early to Middle Ordovician. Coexisting graptolite fossils (*Climacograptus* sp. and *Dicellograptus* sp.) provide a broad biostratigraphic constraint consistent with this age.

(2) The rhyolitic sample displays high positive $\varepsilon_{\text{Hf}}(t)$ values (+19.7 to +28.2), together with mostly primitive mantle-like Zr/Hf and Nb/Ta ratios, and low Nb/U, Ce/Pb, and $\text{Mg}^\#$ values. These features indicate that the magma was generated by partial melting of the mantle wedge metasomatised by subduction-related fluids.

(3) The geochemical signatures (enrichment in LILEs and LREEs, depletion in HFSEs, elevated Ta/Yb ratios), together with sedimentary structures (graded and rhythmic bedding) and deep-marine graptolite fossils, are most consistent with a continental marginal arc setting. We tentatively propose that these volcanic rocks were most likely generated by southward subduction of the Zoolen Ocean beneath the Mingshui–Hanshan Block. This model should be regarded as the most probable among the alternatives and contributes to the Early–Middle Ordovician accretionary history of the southern Central Asian Orogenic Belt.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16111103/s1>, Figure S1: Zircon CL images with U–Pb and Lu–Hf analytical spots and corresponding ages; Figure S2: Zircon U–Th concentration correlation diagram; Figure S3: LOI vs. Ba, Rb, Ba/Nb and Ba/Rb diagrams. Table S1: Zircon U–Pb geochronological data for the investigated rhyolitic tuff lava sample (TW5213) from the Xianshuihu Formation in the Beishan Orogenic Belt; Table S2: Bulk-rock compositions of major (wt%) and trace (ppm) elements for the samples from the Xianshuihu Formation in the Beishan Orogenic Belt [14,30];

Table S3: In situ zircon Hf isotopic data for rhyolitic tuff sample (TW5213) from the Xianshuihu Formation in the Beishan Orogenic Belt.

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