

Article

Geochronology, Petrogenesis, and Metallogenic Implications of Quartz Monzonite Porphyry in the Shanlixu Copper–Gold Deposit in the Lujiang–Chuzhou Area, Middle–Lower Yangtze River Valley Metallogenic Belt, China

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Abstract: The Lujiang–Chuzhou Metallogenic Area is an important component of the Middle–Lower Yangtze River Valley Metallogenic Belt. Despite being an important copper–gold deposit in this area, the Shanlixu skarn Cu–Au deposit has not yet been systematically studied. According to LA–ICP–MS zircon U–Pb dating, the quartz monzonite porphyry from the Shanlixu deposit is aged 137.5 ± 1.7 Ma; while it differs from the timing of the magmatism and related mineralization in the Lujiang–Chuzhou Area, it is consistent with magmatic activity elsewhere in the Middle–Lower Yangtze River Valley Metallogenic Belt. The Ce^{4+}/Ce^{3+} values of zircon in the quartz monzonite porphyry vary from 204.5 to 886.5, indicating that the intrusion might have formed in an environment with high oxygen fugacity. Additionally, the quartz monzonite porphyry exhibits high contents of Al_2O_3 , Sr, Ba, and $Mg^\#$ ($Mg^\# = Mg^{2+}/(Mg^{2+} + Fe^{2+})$) and low ratios of Y, Nb, Ta, and K_2O/Na_2O , showing geochemical characteristics similar to those of adakitic rocks. Based on these characteristics, it is suggested that the intrusion might have been derived from the partial melting of subducted oceanic crust under a continental arc margin setting. Furthermore, it is strongly indicated that the quartz monzonite porphyry from the Shanlixu deposit, in the Lujiang–Chuzhou Area, is closely related to Cu–Au mineralization, as suggested by the age of the intrusion, which is approximately 137 Ma. These findings provide a new direction for research and exploration in this region.

Keywords: zircon U–Pb dating; geochemistry; Lujiang–Chuzhou Area; Middle–Lower Yangtze River Valley Metallogenic Belt



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1. Introduction

The Middle–Lower Yangtze River Valley Metallogenic Belt (MLYB), characterized by numerous large porphyry, skarn, and hydrothermal iron, copper, and gold polymetallic deposits, is the main polymetallic metallogenic belt in China and the world. It has become one of the most recent “hotspots” of ore deposit geology [1–14]. The Lujiang–Chuzhou Metallogenic Area (LCMA), located in the middle part of the MLYB and adjacent to the Qingling–Dabie Metallogenic Belt in the northwest (Figure 1), is mainly composed of porphyry and skarn copper and gold polymetallic deposits, including the Shaxi Cu–Au deposit [15], the Langyashan Cu deposit [16], and the Shanlixu Cu–Au deposit, which is a typical skarn deposit in the area closely related to Shanlixu quartz monzonite porphyry.

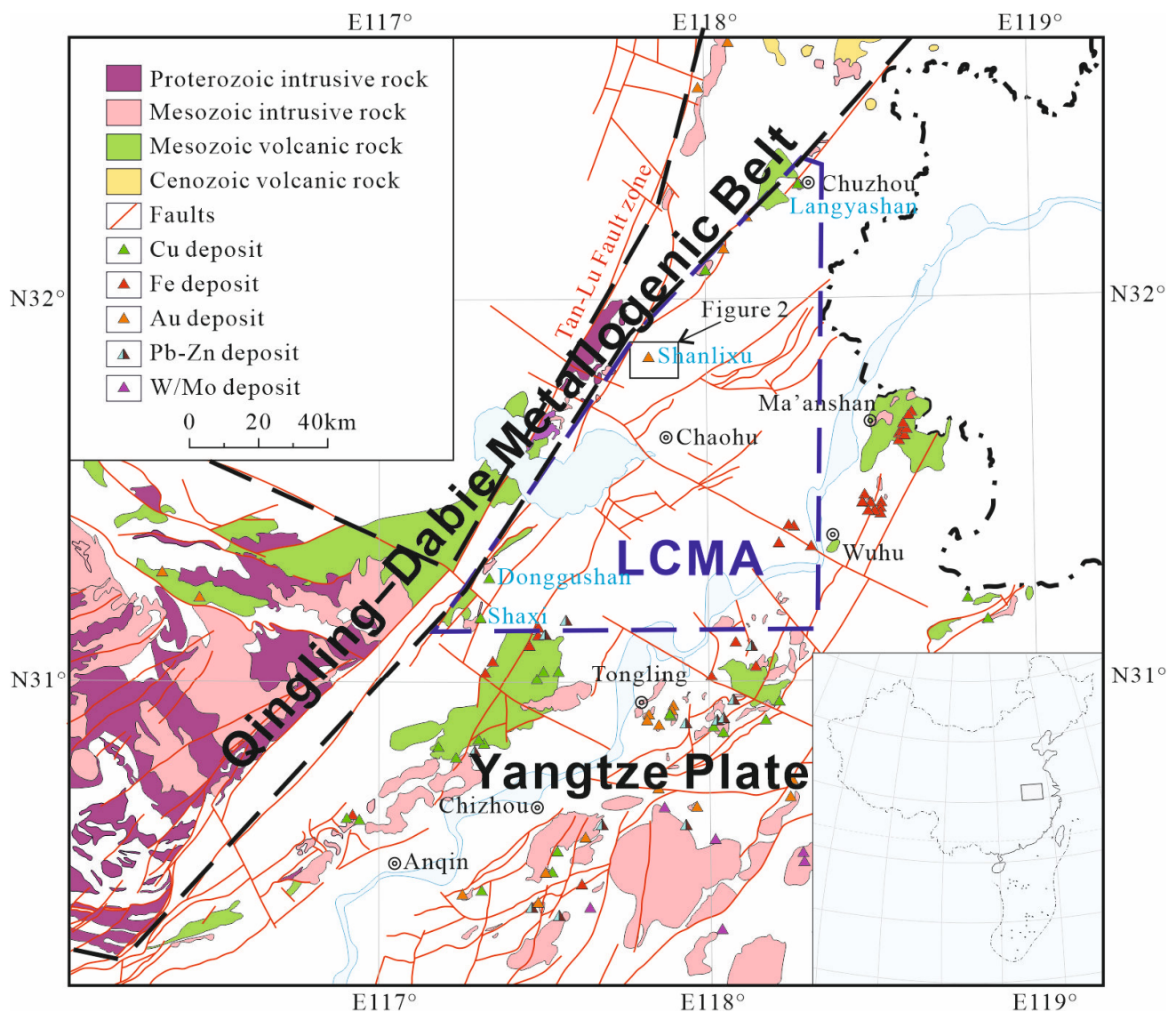


Figure 1. Geological maps of igneous rock and deposits in the MLYB, the inset refers to Figure 2.

Previous research mainly focused on the Shaxi Cu-Au deposit and the Langyashan Cu deposit, including their geological features [16–18], metallogenic intrusion characteristics [19–23], geofluids [24], and metallogenic chronology [25,26]. However, little research on the Shanlixu Cu-Au deposit has been carried out so far [27], similarly to comprehensive diagenesis and metallogenesis studies in this region.

In this study, in situ zircon trace elements and Hf composition, zircon U-Pb dating, and whole-rock geochemistry data are presented to determine the timing, magma source, and petrogenesis of Shanlixu quartz monzonite porphyry. Moreover, we discuss the restriction of igneous rock formation conditions, the tectonic setting, and its significance for mineralization according to this new dataset.

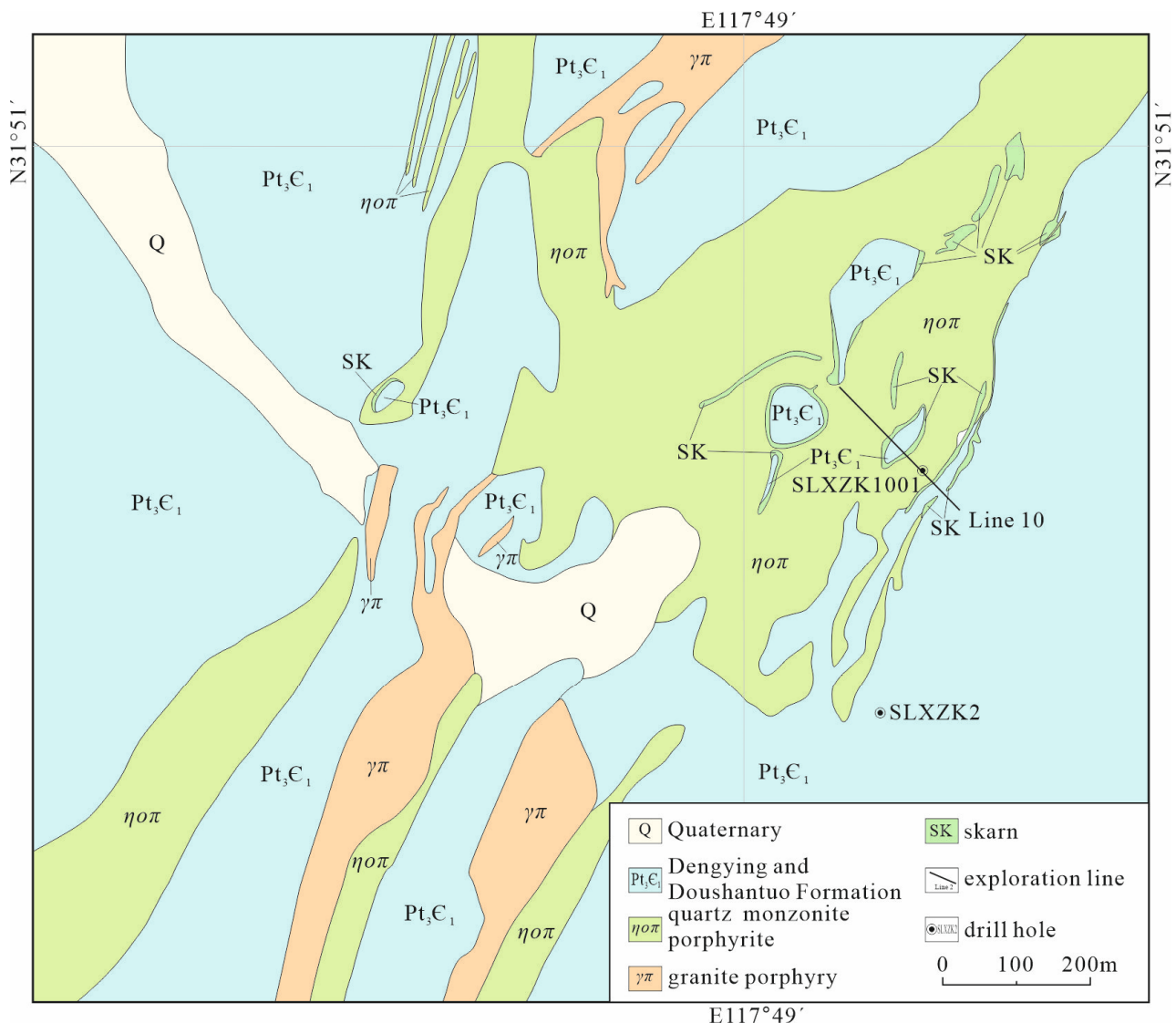


Figure 2. Geological maps of the Shanlixu Cu-Au deposit.

2. Regional and Deposit Geology

The LCMA, in the transition zone between the Dabie orogenic belt and the MLYB, is located close to the southeast of the Tan–Lu fault zone (Figure 1) and characterized by intense deformation. The strata are dominated by marine clastic and carbonate rocks, including Neoproterozoic Sinian, Early Paleozoic Cambrian–Silurian, Late Paleozoic Devonian–Permian, and Mesozoic Triassic. Additionally, Early Cretaceous andesite–trachyandesite–pyroclastic and intermediate-basic and -acid intrusive rocks are mainly magmatic rocks that can be found in the LCMA. The main types of intrusive rocks are gabbro diorite, diorite porphyry, quartz diorite, monzonite quartz, and monzonite porphyry, mostly dated 130 Ma [28–32]. These intrusive rocks are closely associated with porphyry and skarn-type Cu-Au mineralization.

The Shanlixu Cu-Au deposit is situated in the south central part of the LCMA, which is the transitional zone between the Yangtze Plate and the Qinling–Dabie orogenic belt. The exposed strata mainly consist of Neoproterozoic Suwan (phyllite and quartz sandstone), Doushantuo (slate, siltstone, marble, and micrite), and Dengying (dolomite, micrite, limestone, quartz sandstone, and siltstone) formations, and the Shanlixu deposit includes quartz monzonite porphyry and granite porphyry (Figure 2).

The Shanlixu Cu-Au deposit represents a typical skarn-type deposit in the LCMA, where ore bodies are primarily distributed in the contact zone between quartz monzonite porphyry and carbonate rocks, under quartz monzonite porphyry control (Figure 3). The major metallic minerals include pyrite, chalcopyrite, magnetite, chalcocite, and bornite, while gangue minerals comprise diopside, garnet, and calcite, followed by quartz, epidote, and chlorite. Alterations in the Shanlixu Cu-Au deposit encompass carbonatization, sericitization, chloritization, and silicification.

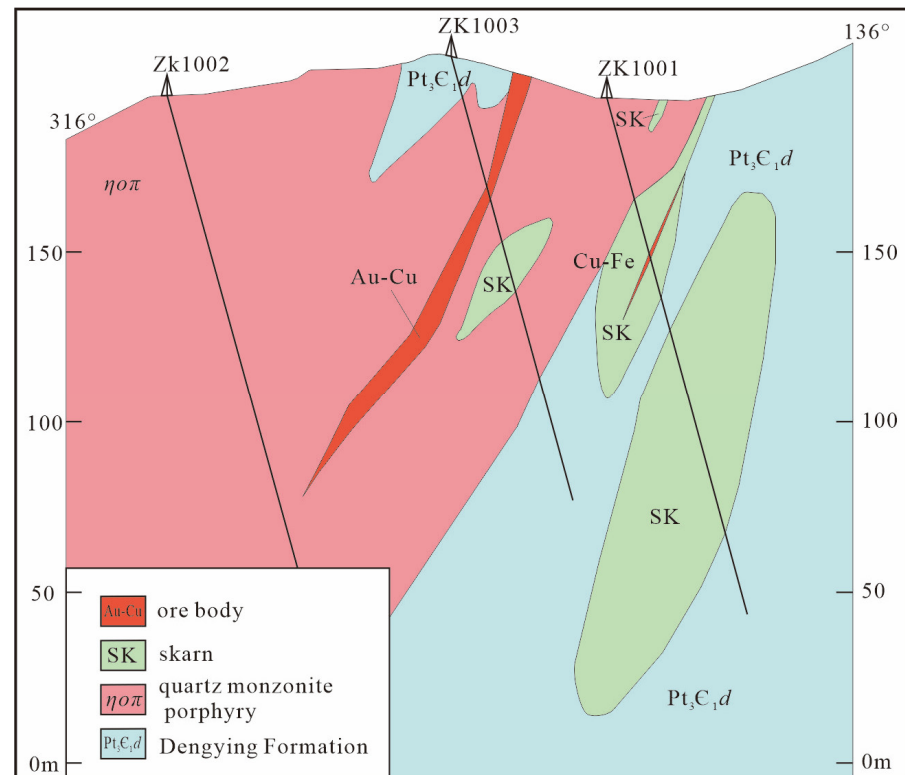


Figure 3. Geological cross-section of the Shanlixu Cu-Au deposit's No. 10 exploration line.

3. Samples and Analytical Methods

3.1. Sample Characterization

Six quartz monzonite porphyry samples were collected from drill holes SLXZK 2 (ZK 2) and SLXZK 1001 (ZK 1001) for whole-rock and zircon analyses in the Shanlixu Cu-Au deposit. Quartz monzonite porphyry is light gray, with a porphyritic texture and a massive structure (Figure 4). The phenocryst contains plagioclase (~4%–15%), quartz (~4%–6%), and biotite (~4%–5%). The phanerocrystalline porphyry groundmass is dominated by plagioclase (~30%–55%), quartz (~5%–10%), and alkali feldspar (~20%). Magnetite, apatite, and zircon are the main accessory minerals.

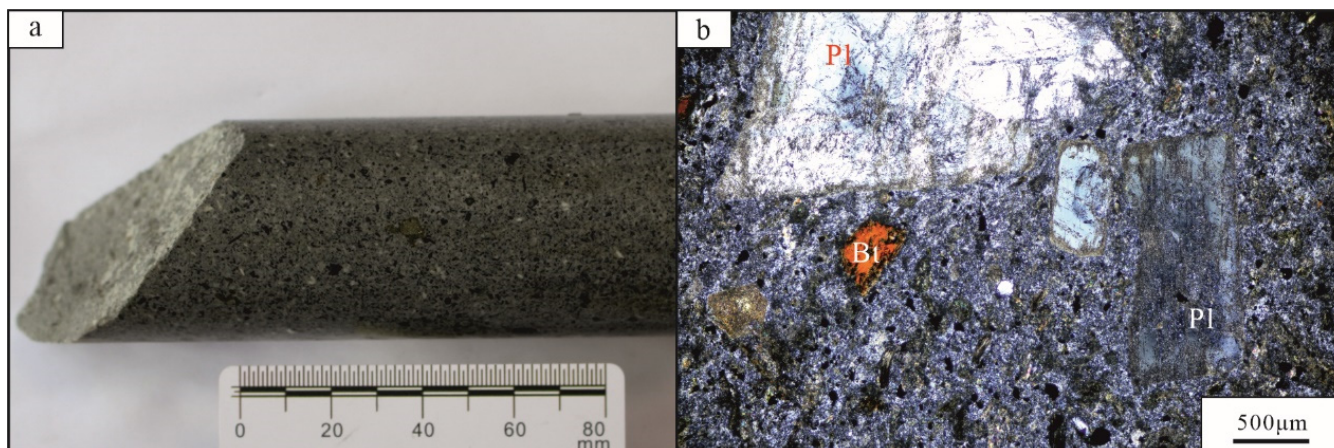


Figure 4. Hand specimen (a) and microphotographs (b) of Shanlixu quartz monzonite porphyry. Bt = biotite; Pl = plagioclase.

3.2. Analytical Methods

Zircon U-Pb dating, in situ Hf isotopic, and trace element analyses were carried out at the Key Laboratory for the Study of Focused Magmatism and Giant Ore Deposit, MNR, Xi'an Center of China Geological Survey. The U-Pb dating and trace element analyses were synchronously conducted using the GeoLas Pro laser ablation system coupled with an Agilent 7700x ICP-MS. Zircon 91500 and NIST610 were used as external standards to correct for isotopic fractionation and trace element calculations, respectively. Data processing was performed via Glitter 4.4 [33], and the age calculations and concordia diagrams were completed with Isoplot/Ex ver 3 [34]. In situ Hf isotopic analyses were conducted with the GeoLas Pro laser ablation system coupled with a Finnigan Neptune MC-ICP-MS. All analytical spot locations were the same or close to the U-Pb dating. The detailed analytical technique was based on Meng et al.'s method (2014) [35].

Whole-rock major and trace element compositions were determined at ALS Chemex (Guangzhou) Co., LTD (Guangzhou, China). The major element composition analyses were carried out using a PANalytical PW2424 X-ray fluorescence spectrometer (XRF), and the trace element content were determined using Agilent 7900 ICP-MS.

4. Results

4.1. Zircon U-Pb Dating

The zircons from Shanlixu quartz monzonite porphyry are mostly euhedral, transparent, short, and prismatic, with lengths of 50–300 μm and length-to-width ratios between 1:1 and 3:1. The cathodoluminescence (CL) image below reveals that most crystals have euhedral, concentric zoning (Figure 5a). The Th/U ratio of the zircon grains is 0.01–0.19, consistent with a typical magmatic origin [36,37]. Twenty spots were analyzed; the analytical data and spot locations are presented in Table 1 and Figure 5a, respectively. The $^{206}\text{Pb}/^{238}\text{U}$ ages of 19 plots fall within the range of 131 to 145 Ma, with a weighted average age of 137.5 ± 1.7 Ma and an MSWD of 1.6 (Figure 5b,c). This age is interpreted as the crystallization age of Shanlixu quartz monzonite porphyry, indicating that the intrusion was established in the Early Cretaceous.

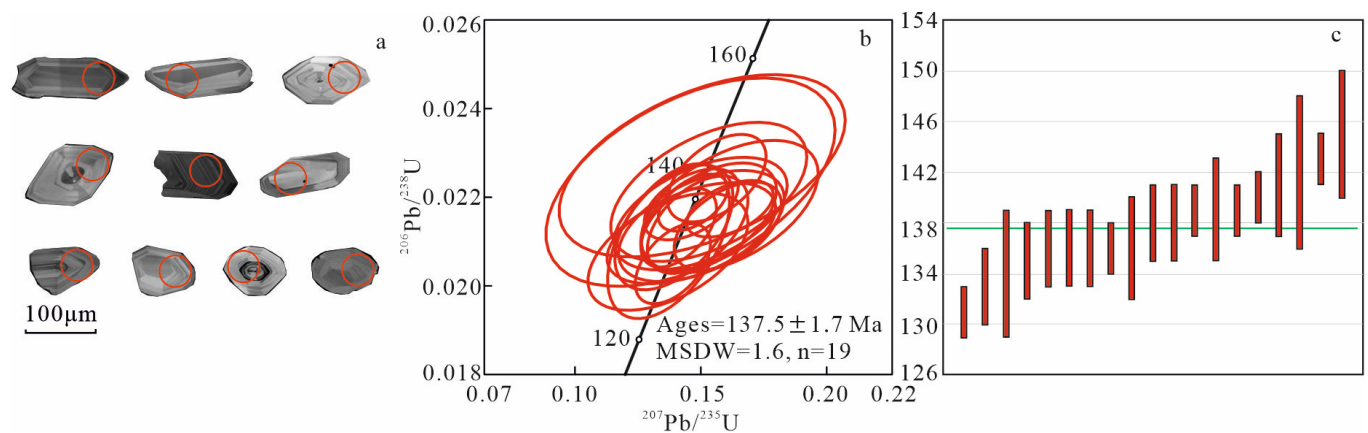


Figure 5. Zircon CL images (a), U-Pb concordia (b) and weighted mean ages (c) of quartz monzonite porphyry in the Shanlixu Cu-Au deposit.

Table 1. Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) zircon U-Pb data for sample ZK2-16 from Shanlixu quartz monzonite porphyry.

Plot	Th	U	Th/U	U-Pb Isotope Ratios						Ages (Ma)			
	ppm	ppm		$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ
1	32.46	423.27	0.08	0.05484	0.002	0.16155	0.00702	0.02174	0.00027	152	6	139	2
2	6.33	507.13	0.01	0.04935	0.002	0.14122	0.00613	0.02131	0.00036	134	5	136	2
3	47.4	729.43	0.06	0.04985	0.002	0.1469	0.00562	0.02188	0.00027	139	5	140	2
4	22.25	480.74	0.05	0.05079	0.008	0.15053	0.02323	0.02271	0.00085	142	21	145	5
5	277.67	1495.27	0.19	0.04934	0.004	0.159	0.0132	0.02421	0.00065	150	12	154	4
6	28.03	404.84	0.07	0.04942	0.002	0.14618	0.00763	0.02184	0.00033	139	7	139	2
7	35.57	444.71	0.08	0.05196	0.003	0.15633	0.00801	0.02243	0.0004	147	7	143	2
8	13.43	1017.68	0.01	0.05103	0.005	0.14993	0.01405	0.02163	0.00052	142	12	138	3
9	24.12	514.04	0.05	0.05475	0.003	0.16071	0.00871	0.02135	0.00041	151	8	136	3
10	11.17	240.95	0.05	0.0481	0.004	0.13694	0.01299	0.02077	0.00054	130	12	133	3
11	27.92	298.68	0.09	0.0489	0.002	0.1389	0.0061	0.0205	0.00036	132	5	131	2
12	27.04	271.93	0.10	0.05033	0.004	0.15022	0.01346	0.02135	0.00051	142	12	136	3
13	21.98	330.58	0.07	0.04758	0.003	0.1372	0.00989	0.02101	0.00071	131	9	134	5
14	21.95	300.89	0.07	0.04693	0.007	0.14589	0.02347	0.02234	0.00096	138	21	142	6
15	22.7	325.59	0.07	0.04971	0.005	0.14623	0.01369	0.02119	0.00047	139	12	135	3
16	24.4	269.05	0.09	0.05092	0.003	0.14874	0.00816	0.02138	0.00045	141	7	136	3
17	103.05	901.35	0.11	0.04653	0.003	0.1393	0.00958	0.02132	0.00058	132	9	136	4
18	13.95	290.53	0.05	0.05114	0.003	0.15308	0.011	0.02156	0.0005	145	10	138	3
19	26.15	887.54	0.03	0.05544	0.005	0.16145	0.01437	0.02179	0.00061	152	13	139	4
20	32.7	312.97	0.10	0.05051	0.005	0.15315	0.01591	0.02212	0.00064	145	14	141	4

4.2. Whole-Rock Major and Trace Elements

The major and trace element data for Shanlixu quartz monzonite porphyry are listed in Table 2. The SiO_2 and total alkalis ($\text{TA} = \text{K}_2\text{O} + \text{Na}_2\text{O}$) contents of the Shanlixu quartz monzonite porphyry range from 57.64 wt.% to 63.62 wt.% and from 7.47 wt.% to 9.43 wt.%, respectively. In the Q-A-P and TAS diagram, most samples fall into the quartz monzonite and monzonite field (Figure 6a,b). The K_2O content of the samples ranges from 2.52 wt.% to 3.82 wt.%, falling in the high-potassium calc-alkaline series field (Figure 6c). Six samples are metaluminous, with ACNK values from 0.74 to 0.92 (Figure 6d).

Table 2. Major and trace element analyses of Shanlixu quartz monzonite porphyry.

Sample No.	ZK2-18-1	ZK2-18-2	ZK2-19	ZK1001-7	ZK1001-8	ZK2-16
Major oxides (wt.%)						
SiO ₂	63.25	63.62	63.45	58.52	61.34	57.64
TiO ₂	0.41	0.40	0.41	0.51	0.55	0.71
Al ₂ O ₃	15.45	15.44	15.41	15.70	15.44	14.19
Fe ₂ O ₃	3.34	3.46	3.32	3.84	4.78	5.05
MnO	0.03	0.03	0.03	0.05	0.07	0.05
MgO	2.46	2.50	3.00	4.03	3.84	4.59
CaO	2.92	2.64	2.47	4.27	4.06	4.29
Na ₂ O	5.71	5.65	5.74	5.82	4.81	3.65
K ₂ O	2.92	2.89	2.52	3.61	2.86	3.82
P ₂ O ₅	0.19	0.19	0.19	0.29	0.24	0.39
LOL	2.85	2.23	2.68	2.91	1.19	4.14
Total	99.84	99.36	99.50	99.89	99.55	98.88
A/CNK	0.86	0.90	0.92	0.74	0.84	0.79
A/NK	1.23	1.24	1.27	1.16	1.40	1.40
Trace elements (ppm)						
Ga	20.7	21.2	21.1	20.8	21.9	19.70
Rb	41.2	42.0	35.5	52.4	47.7	64.5
Sr	981	1015	883	1090	1465	901
Y	6.9	6.8	6.9	10.2	9.8	11.7
Zr	110	131	111	160	168	242
Nb	5.2	5.0	5.0	6.2	6.6	7.8
Ta	0.27	0.26	0.27	0.34	0.36	0.44
Cs	0.84	0.81	0.68	0.55	1.58	0.90
Ba	1685	1760	1570	1920	1870	2170
La	19.8	21.0	19.5	39.7	30.8	44.4
Ce	38.7	41.2	38.7	79.7	59.8	87.0
Pr	4.61	4.92	4.71	9.52	7.08	10.25
Nd	18.2	18.8	17.9	36.8	27.1	38.9
Sm	3.11	3.17	3.01	6.10	4.44	6.27
Eu	0.93	0.91	1.01	1.48	1.23	1.84
Gd	1.97	2.05	2.10	3.48	2.83	3.91
Tb	0.27	0.26	0.26	0.41	0.38	0.52
Dy	1.40	1.35	1.44	2.06	1.94	2.35
Ho	0.24	0.25	0.25	0.36	0.36	0.46
Er	0.65	0.61	0.62	0.95	1.02	1.14
Tm	0.09	0.09	0.10	0.12	0.13	0.15
Yb	0.57	0.54	0.58	0.82	0.83	0.95
Lu	0.08	0.09	0.09	0.12	0.12	0.15
Hf	2.9	3.5	2.9	4.1	4.0	5.4
Th	2.78	2.84	2.80	6.40	4.20	6.55
U	1.28	1.34	1.46	1.76	1.24	1.60
Pb	13.6	13.3	8.2	8.2	13.4	14.4
Eu/Eu*	1.07	1.02	1.17	0.90	0.99	1.06

The chondrite-normalized REE patterns exhibit an enrichment of light rare-earth elements compared to heavy rare-earth elements, with a (La/Yb)_N ratio of 24.1–33.5 (Figure 7a). No significant Eu anomaly is observed, and the δEu values ($\delta\text{Eu} = w(\text{Eu})/w(\text{Eu}^*) = 2 \times w(\text{Eu})_{\text{N}}/[w(\text{Sm})_{\text{N}} + w(\text{Gd})_{\text{N}}]$) range from 0.90 to 1.17. The samples are rich in Sr and depleted in Y, with high Sr/Y ratios (Sr/Y = 77.0–149). In the spider diagram, all the samples show positive Ba, La, Sr, and Pb and negative Nb, Ta, and Ti anomalies (Figure 7b).

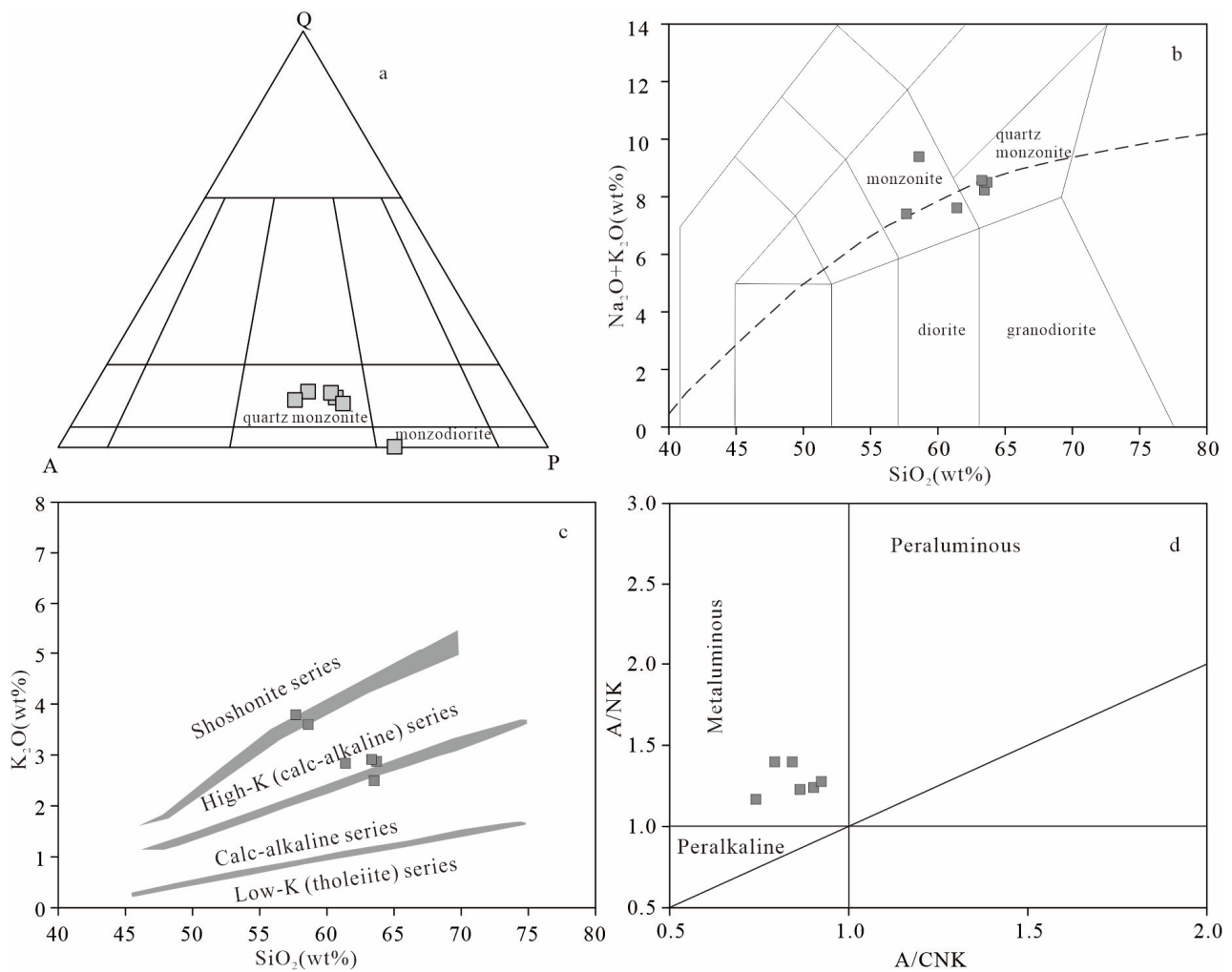


Figure 6. Q-A-P diagram (a), TAS diagram (b), K_2O versus SiO_2 diagram (c), and ACNK versus ANK diagram (d) of quartz monzonite porphyry in the Shanlixu Cu-Au deposit (after Middlemost, 1994 [38]; Peccerillo and Taylor, 1976 [39]; and Maniar and Piccoli, 1989 [40]).

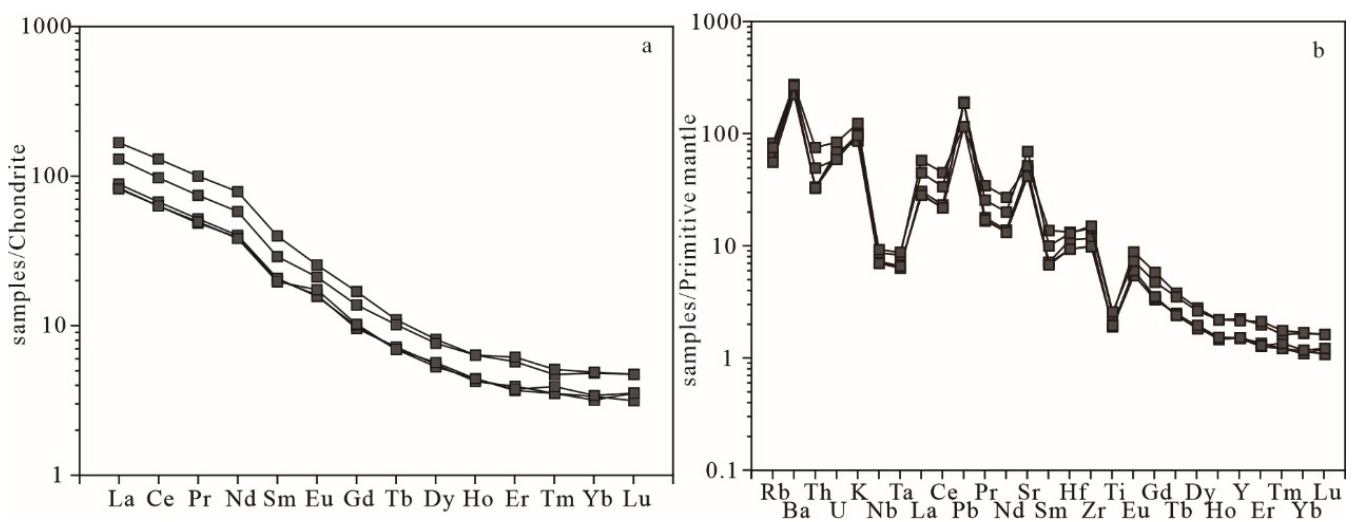


Figure 7. Chondrite-normalized REE (a) and primitive mantle-normalized trace element (b) patterns for quartz monzonite porphyry in the Shanlixu Cu-Au deposit (the normalized values for chondrite and the primitive mantle are from Sun and McDonough, 1989 [41]).

4.3. Zircon Hf Isotopes

Twenty spots from sample SLXZK2-16 were analyzed for their Lu-Hf isotopic composition, using the same locations as the zircon U-Pb analyses. The results are presented in Table 3, with the following ranges: $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of zircon, from 0.282487 to 0.282675; calculated initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, from 0.282486 to 0.282672; $\epsilon_{\text{Hf}}(t)$ values, from -0.40 to -7.19 , with an average of -3.97 ; and calculated two-stage model ages (T_{DM}^{C}) from 1.22 to 1.64 Ga, with an average age of 1.44 Ga.

Table 3. Lu-Hf isotope composition of zircon for sample SLXZK2-16 from Shanlixu quartz monzonite porphyry.

Plot	$^{176}\text{Yb}/^{177}\text{Hf}$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	2σ	$(^{176}\text{Hf}/^{177}\text{Hf})_i$	$\epsilon_{\text{Hf}}(t)$	$T_{\text{DM}}^{\text{C}}(\text{Ga})$
1	0.033177	0.000735	0.282617	0.000056	0.282615	-2.50	1.35
2	0.027947	0.000669	0.282550	0.000037	0.282548	-4.94	1.50
3	0.087252	0.001908	0.282591	0.000050	0.282586	-3.50	1.41
4	0.055179	0.001556	0.282544	0.000054	0.282540	-5.03	1.51
5	0.067574	0.001548	0.282611	0.000087	0.282607	-2.47	1.36
6	0.060019	0.001466	0.282604	0.000059	0.282601	-3.02	1.38
7	0.051788	0.001291	0.282675	0.000066	0.282672	-0.40	1.22
8	0.034262	0.000833	0.282566	0.000094	0.282564	-4.34	1.46
9	0.038824	0.000923	0.282558	0.000055	0.282555	-4.68	1.48
10	0.088521	0.002019	0.282572	0.000064	0.282567	-4.33	1.46
11	0.084104	0.001905	0.282601	0.000050	0.282596	-3.36	1.40
12	0.033035	0.000780	0.282548	0.000038	0.282546	-5.02	1.51
13	0.024184	0.000643	0.282487	0.000038	0.282486	-7.19	1.64
14	0.040120	0.000972	0.282547	0.000036	0.282545	-4.93	1.50
15	0.035760	0.000852	0.282546	0.000039	0.282544	-5.10	1.51
16	0.070178	0.001635	0.282550	0.000036	0.282546	-5.02	1.50
17	0.043288	0.001069	0.282542	0.000042	0.282540	-5.24	1.52
18	0.042199	0.001021	0.282615	0.000034	0.282612	-2.62	1.36
19	0.086998	0.002026	0.282612	0.000033	0.282606	-2.81	1.37
20	0.040587	0.001137	0.282603	0.000021	0.282600	-2.98	1.38

4.4. Zircon Trace Elements

The zircon trace element compositions are presented in Table 4. The zircon grains show various concentrations of Th (6.33–278 ppm) and U (241–1495 ppm), and the Th/U ratios range from 0.01 to 0.19. Zircons have Ti concentrations ranging from 2.27 to 7.90 ppm, Y from 64 to 1328 ppm, Lu from 52.6 to 100 ppm, and Hf from 8545 to 11,747 ppm, while the total REE compositions range from 515 to 1031 ppm. The chondrite-normalized REE patterns of the zircon grains are homogeneous, characterized by HREE enrichment relative to the LREE (Figure 8), with positive Ce ($\text{Ce}/\text{Ce}^* = 12\text{--}384$, $\text{Ce}/\text{Ce}^* = 2 \times w(\text{Ce})_{\text{N}}/[w(\text{La})_{\text{N}} + w(\text{Pr})_{\text{N}}]$) and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.58\text{--}0.92$). It has the typical characteristics of magmatic zircon [42,43].

Table 4. LA-ICPMS results of zircon trace element composition for sample ZK2-16 from Shanlixu diorite porphyrite. “bdl” = below the detection limit.

Spot No.	Ti	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Th	U	Th/U	ΣREE	Eu/Eu*	Ce/Ce*
1	4.14	737	0.01	5.51	0.01	0.41	1.60	1.32	12.1	4.65	58.1	24.2	118	27.1	294	62.1	9716	0.36	32.5	423	0.08	609	0.65	101.91
2	3.04	1263	0.01	1.72	0.01	0.21	1.04	1.08	11.8	5.98	92.6	42.1	213	48.5	513	100	11,747	0.67	6.33	507	0.01	1031	0.58	46.82
3	4.63	793	bdl	5.04	0.01	0.17	1.50	1.69	12.0	4.78	63.2	26.3	125	28.3	299	60.3	10,092	0.51	47.4	729	0.06	628	0.86	
4	3.81	722	bdl	3.52	0.01	0.23	1.80	1.21	10.5	3.74	53.5	22.7	116	26.8	289	65.1	10,212	0.31	22.3	481	0.05	594	0.66	
5	7.90	1328	0.03	21.8	0.06	1.62	5.89	4.27	32.9	11.7	132	46.6	200	41.8	396	76.7	10,292	1.05	278	1495	0.19	972	0.74	101.33
6	3.73	752	0.00	4.80	0.01	0.28	1.39	1.39	11.5	4.29	54.7	23.5	118	28.2	304	66.1	9707	0.46	28.0	405	0.07	618	0.74	107.04
7	5.10	984	bdl	7.98	0.01	0.61	1.95	2.03	15.3	5.98	76.3	31.6	156	35.2	382	77.7	9724	0.41	35.6	445	0.08	793	0.80	
8	3.20	919	0.00	1.34	0.00	0.06	0.97	1.25	11.4	5.13	72.0	30.7	148	32.5	318	62.6	11,043	0.66	13.4	1018	0.01	684	0.70	90.87
9	4.07	680	0.00	3.35	0.01	0.18	1.20	1.12	8.50	3.61	49.2	21.1	106	24.8	263	56.0	8954	0.23	24.1	514	0.05	537	0.78	85.38
10	3.57	689	0.00	3.86	0.01	0.22	0.68	1.07	8.35	3.13	49.6	21.5	112	26.2	298	65.7	8636	0.30	11.2	241	0.05	590	0.82	166.81
11	3.48	646	bdl	7.24	0.02	0.38	1.75	1.14	11.5	3.97	47.4	20.0	97.1	22.2	248	54.5	9796	0.25	27.9	299	0.09	515	0.58	
12	2.27	649	0.00	5.73	0.01	0.35	1.63	1.23	11.1	4.42	51.8	20.6	103	23.7	260	52.6	9091	0.26	27.0	272	0.10	536	0.65	115.80
13	6.01	934	0.00	6.52	0.02	0.43	1.74	1.58	14.0	5.51	71.1	30.4	148	33.6	357	76.1	8921	0.31	22.0	331	0.07	747	0.68	93.96
14	5.90	852	0.01	6.47	0.00	0.36	2.72	1.84	11.5	5.09	66.3	27.4	130	29.5	329	68.6	9262	0.28	22.0	301	0.07	679	0.86	384.44
15	4.38	698	bdl	5.05	0.01	0.53	1.50	1.38	10.3	4.29	52.1	22.3	109	25.9	283	61.9	9417	0.41	22.7	326	0.07	577	0.80	
16	6.35	802	0.17	5.24	0.07	0.50	1.29	1.10	10.6	4.23	58.1	25.5	123	29.4	318	68.6	8577	0.32	24.4	269	0.09	646	0.63	12.10
17	5.03	1132	0.02	12.0	0.04	0.83	2.94	3.53	23.3	8.49	103	38.0	172	36.1	372	71.0	10,946	0.73	103	901	0.11	843	0.92	81.91
18	5.58	910	0.02	4.30	0.01	0.39	1.40	1.53	10.9	4.77	66.0	28.4	141	33.6	355	78.1	9376	0.40	14.0	291	0.05	725	0.85	73.51
19	4.98	996	0.02	2.59	0.01	0.15	1.42	1.85	12.9	5.82	76.0	32.7	154	34.7	358	72.7	10,983	0.47	26.2	888	0.03	753	0.89	60.75
20	7.67	861	0.01	7.66	0.02	0.55	2.29	1.92	15.1	5.46	71.5	28.5	128	29.3	310	61.3	8545	0.33	32.7	313	0.10	662	0.75	102.21

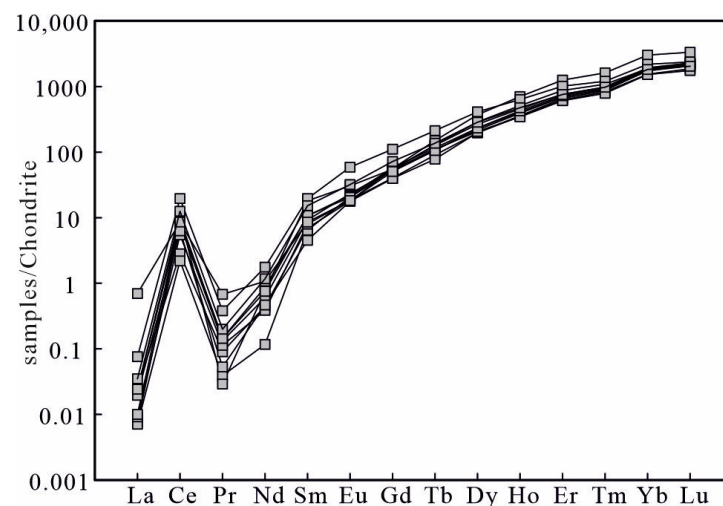


Figure 8. Chondrite-normalized REE patterns of zircon for sample ZK2-16 from Shanlixu quartz monzonite porphyry.

5. Discussion

5.1. Timing of Magmatism and Related Mineralization

As an important metallogenic belt in Eastern China, the MLYB features numerous porphyry, skarn, and hydrothermal Fe-Cu-Au polymetallic deposits associated with Mesozoic magmatic activity. Previous studies have shown that Mesozoic magmatism and mineralization were divided into three stages, respectively, 145–135 Ma, 135–125 Ma, and about 100 Ma [9,44–46]. According to this, skarn Cu-Au mineralization ages mainly fall between 145 and 135 Ma [9,44,47,48].

As an important component of the MLYB, Mesozoic magmatism and mineralization in the LCMA mainly occurred around 130 Ma (Table 5), when a series of porphyry and skarn Cu-Au deposits were formed, such as the Langyashan Cu deposit [25], the Shaxi Cu-Au deposit [49], and the Machang Au deposit [50]. Although Donggushan biotite granite (99 Ma) and Yefushan quartz syenite (140.2 Ma) had different zircon U-Pb ages, related other igneous formations [51,52], other U-Pb ages besides 130 Ma were rare in the LCMA.

Table 5. The ages of major plutons in the LCMA.

Pluton	Lithology	Ages (Ma)	Analytical Method	Reference
Chuzhou	quartz monzonite porphyry	127.17 ± 0.40	biotite ^{40}Ar - ^{39}Ar	[29]
Chuzhou	granodiorite	125 ± 1	zircon U-Pb	[32]
Chuzhou	quartz monzonite	127 ± 1	zircon U-Pb	[32]
Chuxian	quartz monzonite	121.8 ± 1.9	zircon U-Pb	[31]
Chuxian	quartz monzonite	124.0 ± 1.4	zircon U-Pb	[31]
Shangyaopu	quartz monzonite porphyry	129.90 ± 0.23	biotite ^{40}Ar - ^{39}Ar	[29]
Shangyaopu	quartz monzonite	126.6 ± 1.8	zircon U-Pb	[31]
Shangyaopu	quartz monzonite	123.4 ± 1.9	zircon U-Pb	[31]
Yeshan	quartz diorite porphyry	131.22 ± 0.77	^{40}Ar - ^{39}Ar	[28]
Shanlichen	quartz diorite porphyry	130.07 ± 0.48	^{40}Ar - ^{39}Ar	[28]
Outang	quartz monzonite	124.6 ± 2.9	zircon U-Pb	[30]
Outang	quartz monzonite	129.2 ± 4.1	zircon U-Pb	[30]
Machang	quartz monzonite	123.1 ± 2.0	zircon U-Pb	[31]
Machang	quartz monzonite	129.3 ± 1.6	zircon U-Pb	[50]
Huangdaoshan	quartz monzonite porphyry	129 ± 1.7	zircon U-Pb	[50]
Tuncang	quartz monzonite	130.8 ± 1.9	zircon U-Pb	[50]
Huangdaoshan	quartz monzonite porphyry	130 ± 1	zircon U-Pb	[53]
Shaxi	diorite porphyry	128.3 ± 1.5	zircon U-Pb	[20]
Shaxi	quartz diorite porphyry	129.4 ± 1.4	zircon U-Pb	[54]
Shaxi	quartz diorite porphyry	127.1–129.3	zircon U-Pb	[49]
Yefushan	quartz syenite	140.2 ± 1.8	-	[52]
Donggushan	granite	96.7 ± 1.3 Ma	zircon U-Pb	[51]

The zircon U-Pb age obtained from Shanlixu quartz monzonite porphyry was 137.5 ± 1.7 Ma in this study. This intrusion was the product of magmatic activity dated 145–135 Ma, with the related skarn Cu-Au mineralization also occurring in 145–135 Ma. This was considerably different from the time of magmatism and the related mineralization (about 130 Ma) in the LCMA [52], but it was consistent with the time of magmatic activity in the MLYB, i.e., 145–135 Ma [9,47,48,55,56]. Although diagenesis and metallogenesis dated 145–135 Ma was infrequent in the LCMA, 145–135 Ma was an important metallogenic period in Tongling, Anqing, Jiurui, and many other metallogenic areas in this region, during which a series of large and medium Cu-Au deposits were formed, such as the Dongguashan Cu deposit [57,58], the Sujadian Cu deposit [59], and the Anqin Cu deposit [60], among others. The results of this study show that 145–135 Ma is also an important metallogenic period in the LCMA.

5.2. Petrogenesis and Magmatic Source

5.2.1. Temperature and Oxygen Fugacity

Temperature and oxygen fugacity during igneous formation have important implications for petrogenesis and metallogenesis [61–64]. According to the zircon Ti geothermometer based on Waston (2006) [65], the crystallization temperature of Shanlixu quartz monzonite porphyry ranges from 668.6 to 744.9 °C, with an average of 703.9 °C, while its zircon saturation temperature is 712.6–760.8 °C. This is consistent with the zircon crystallization temperature, indicating that the formation of quartz monzonite porphyry occurs in a relatively high-temperature environment.

The $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratios of zircon can effectively indicate the oxygen fugacity of magma during the rock-forming process [64]. Based on Ballard et al.'s method (2002) [64], the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratios of zircon from Shanlixu quartz monzonite porphyry ranged from 204.5 to 886.5, with an average of 478.2. In the $\text{Ce}^{4+}/\text{Ce}^{3+}$ vs. Eu/Eu^* diagram, the sample plots from the quartz monzonite porphyry fall into the area with high oxygen fugacity (Figure 9a). Considering the significant Ce positive and weak Eu negative anomalies, this indicates that the quartz monzonite porphyry in this deposit may have formed in an environment with high oxygen fugacity. The $\log f\text{O}_2$ value, obtained following Trail et al. (2012) [66], was -19.19 – -5.68 . The samples were mostly plotted between the MH and FMQ buffers in the $\log f\text{O}_2$ -T diagram (Figure 9b) and between the MH and NNO buffers in the $\text{Ce}^{4+}/\text{Ce}^{3+}$ - $10^4/T$ diagram (Figure 9c).

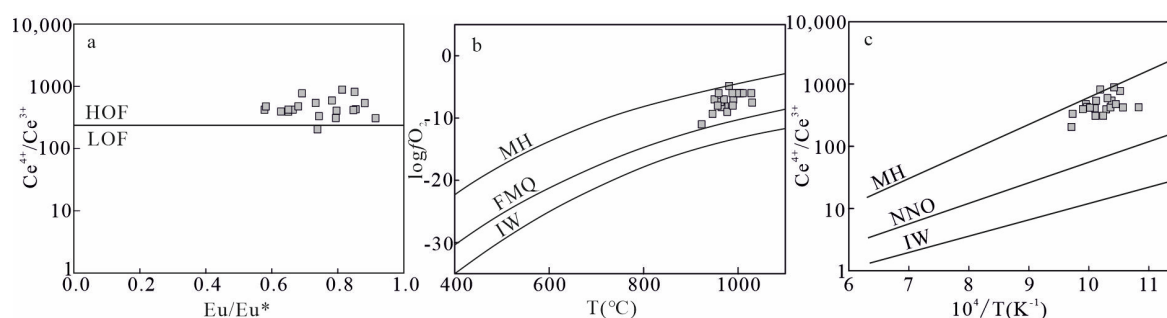


Figure 9. The $\text{Ce}^{4+}/\text{Ce}^{3+}$ versus Eu/Eu^* (a), $\log f\text{O}_2$ versus T (b), and $\text{Ce}^{4+}/\text{Ce}^{3+}$ versus $10^4/T$ (c) diagrams of Shanlixu quartz monzonite porphyry. HOF = high oxygen fugacity; LOF = low oxygen fugacity; MH = magnetite–hematite buffer; FMQ = fayalite–magnetite–quartz buffer; IW = iron–wüstite buffer; and NNO = nickel–nickel oxide buffer.

5.2.2. Magmatic Source

Shanlixu quartz monzonite porphyry is characterized by high concentrations of Rb and Sr and low concentrations of Y, Nb, and Ta. It exhibits light REE (LREE) enrichment, relative to heavy REE (HREE), and shares a similar geochemical composition to mantle-derived or crust–mantle composite granite [67]. This suggests that Shanlixu quartz monzonite

porphyry has features aligned with a mantle-derived or crust–mantle mixture source [67,68], and with high Sr/Y ratios ($\text{Sr}/\text{Y} = 77.0\text{--}149$), it displays similar geochemical characteristics to adakitic rocks.

There are various views on the genesis of adakitic rocks: (1) the partial melting of basaltic oceanic slab in the subduction zone [69,70]; (2) the partial melting of thickened or delaminated lower crust [71–74]; (3) and the assimilation and fractional crystallization of ultra-potassic magma [75,76]. Shanlixu quartz monzonite porphyry contains relatively high MgO content (2.46–4.59 wt.%) and $\text{Mg}^\#$ values (58.9–67.6). In the $\text{Mg}^\#$ - SiO_2 (Figure 10a) and MgO - SiO_2 diagrams (Figure 10b), most samples fell into the areas of subducted oceanic crust-derived adakites and delaminated lower crust-derived adakitic rocks, reflecting typical characteristics of subducted oceanic crust-derived adakites. Apart from one sample which may have been affected by potassic alteration, the Shanlixu quartz monzonite porphyry samples had high Al_2O_3 contents (15.41–15.70 wt.%) and low $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios (0.44–0.62), notably different from thickened, continental lower crust-type adakites [77,78]. In the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ - Al_2O_3 diagram, the samples fell into the area of adakites derived from oceanic slab melting (Figure 10c), meaning that, with Sr/Y and $(\text{La}/\text{Yb})_N$ ratios ranging from 77.0 to 149 and from 24.1 to 34.7, respectively, Shanlixu quartz monzonite porphyry corresponds to adakites derived from the partial melting of subducted oceanic crust (Figure 10d). Furthermore, Shanlixu quartz monzonite porphyry is consistent with other adakites in the MLYB with lower Th/La ratios (0.14–0.16) and K_2O contents (2.52–3.61 wt.%), and it is noticeably different from adakites derived from the partial melting of continental crust [77,79].

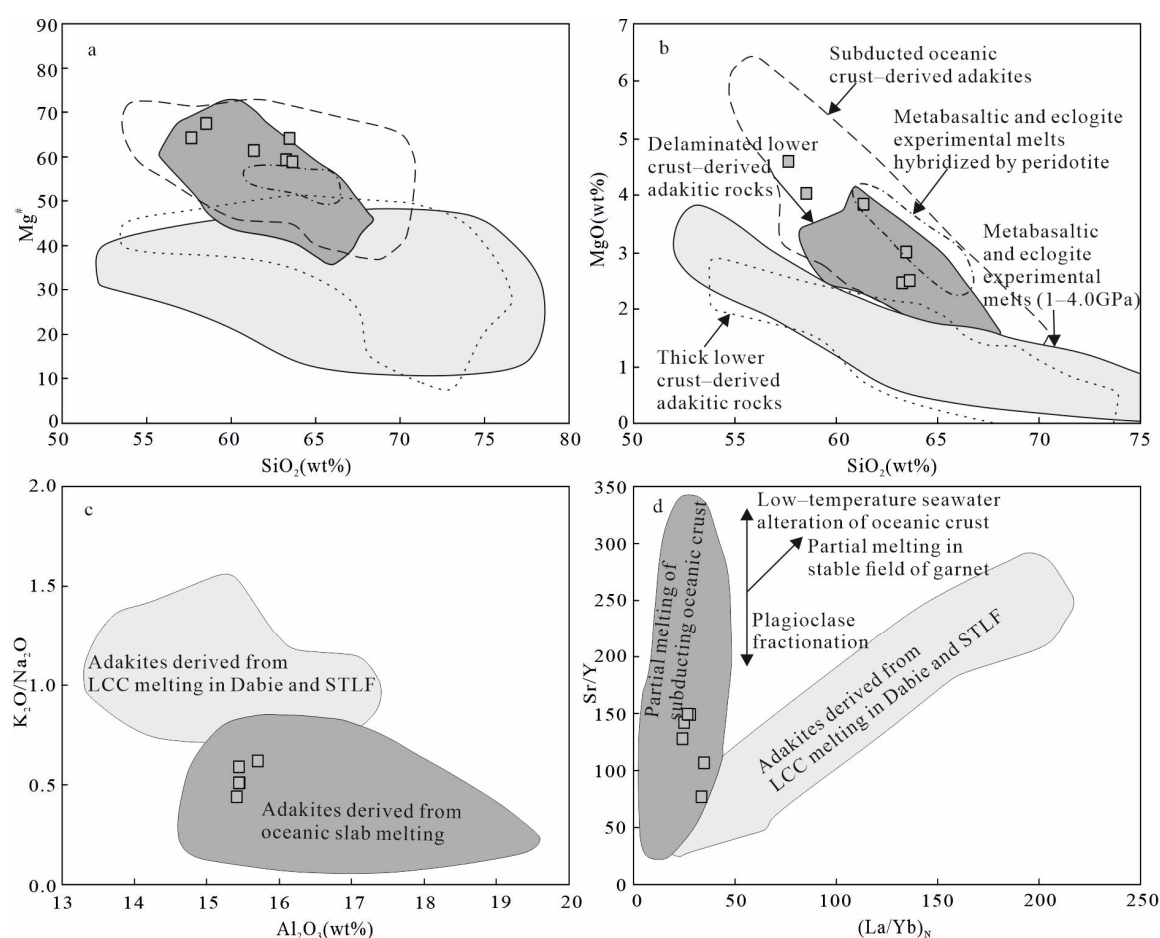


Figure 10. Geochemical discrimination diagrams for Shanlixu quartz monzonite porphyry. $\text{Mg}^\#$ versus SiO_2 (a) and MgO versus SiO_2 (b) diagrams for adakite discrimination. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ versus

Al_2O_3 (c) and Sr/Y versus $(\text{La}/\text{Yb})_N$ (d) diagrams to distinguish lower crust-derived adakitic rocks from slab-derived adakites (after Stern and Kilian, 1996 [80]; data for LCC melting in Dabie and STLf are from Wang et al., 2007 [79], Huang et al., 2008 [77], and Perford and Atherton, 1996 [74]; data for oceanic slab melting are from Kamei et al., 2009 [81]; data for subducting oceanic crust are from Defant and Drummond, 1990 [70], Stern and Kilian, 1996 [80], and Aguilon-Robles et al., 2001 [82]).

The Sr/La and Th/U ratios are utilized to distinguish adakites derived from subducted oceanic crust or continental lower crust [67,83]. Shanlixu quartz monzonite porphyry exhibits relatively high Sr/La ratios (20.29–49.55) and low Th/U ratios (1.92–4.09), suggesting that it is derived from the partial melting of subducted oceanic crust. The initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of zircon from Shanlixu quartz monzonite porphyry range from 0.282486 to 0.282672, with $\epsilon_{\text{Hf}}(t)$ values ranging between -7.17 and -0.40 and two-stage model ages of zircons falling within the range of 1.21–1.64 Ga, respectively. The zircon Hf isotopic composition of Shanlixu quartz monzonite porphyry is notably higher than that of continental lower crust rocks at 2.55 Ga and the continental lower crust in the MLYB (<-60) [84], but similar to Early Cretaceous volcanic rocks derived from the enriched lithospheric mantle in the Ningwu Area (Figure 11a). In the $\epsilon_{\text{Hf}}(t)$ versus age diagram, the samples fall between 1.5 Ga and 1.8 Ga in terms of the average crustal evolution path (Figure 11b), indicating that Shanlixu quartz monzonite porphyry may be mantle-derived.

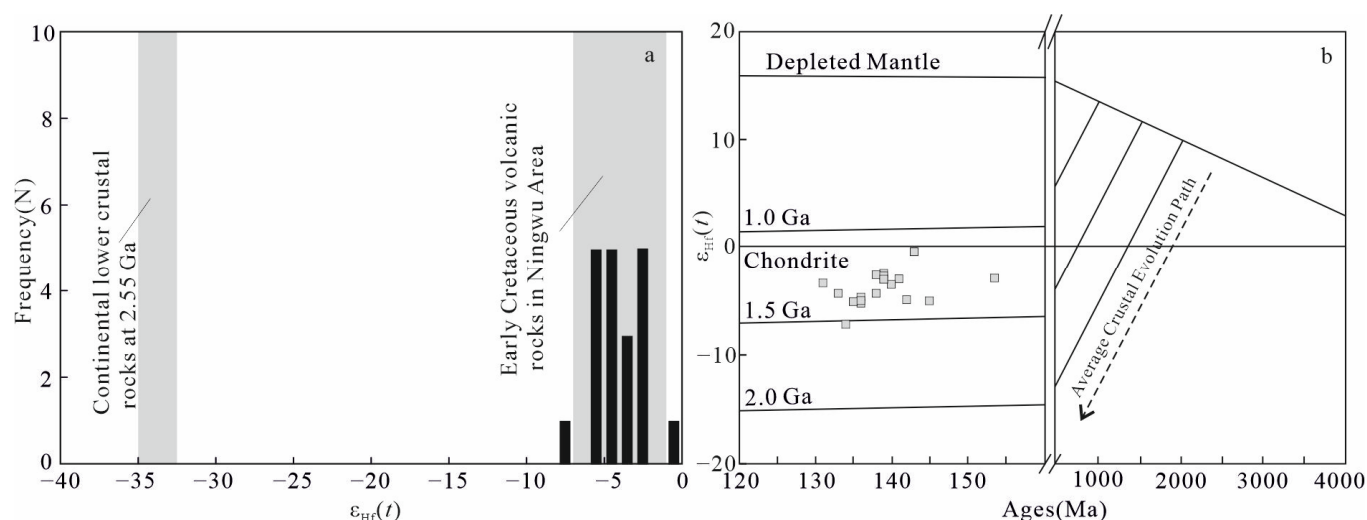


Figure 11. Histogram of zircon $\epsilon_{\text{Hf}}(t)$ values (a) and $\epsilon_{\text{Hf}}(t)$ versus age (b) diagram of Shanlixu quartz monzonite porphyry. (Data of continental lower crustal rocks at 2.55 Ga are from Vervoort and Patchett, 1996 [85], while data of Early Cretaceous volcanic rocks in the Ningwu Area are from Hou and Yuan, 2010 [86]).

5.3. Tectonic Implications

The Mesozoic intrusions associated with Cu-Au mineralization in the MLYB are linked to subduction [87–92]. The characteristics of adakitic rocks present in Shanlixu quartz monzonite porphyry suggest its derivation from the partial melting of a subducted oceanic slab. The quartz monzonite porphyry shows LILE and LREE enrichment and Ti, P, and Nb depletion, similar to magmatic arc granites [93]. In the $(\text{Yb} + \text{Ta})\text{-Rb}$ and $(\text{Y} + \text{Nb})\text{-Rb}$ diagrams, the samples fall into the volcanic arc granite field (Figure 12a,b). Furthermore, as Th/Ta ratios are reliable for distinguishing between different tectonic settings [94], Shanlixu quartz monzonite porphyry's Th/Ta ratios between 10.3 and 18.8 are consistent with an active continental margin setting (Figure 12c). The La/Yb and Th/Yb ratios are 33.6–48.4 and 4.8–7.8, respectively. In the Th/Yb-La/Yb diagram, the samples fall into the field of continental arc margin settings (Figure 12d). In addition, the high Ba/Zr (9.0–15.3)

and Ba/Nb (278–352) ratios of quartz monzonite porphyry are also compatible with arc magmatism [95–97].

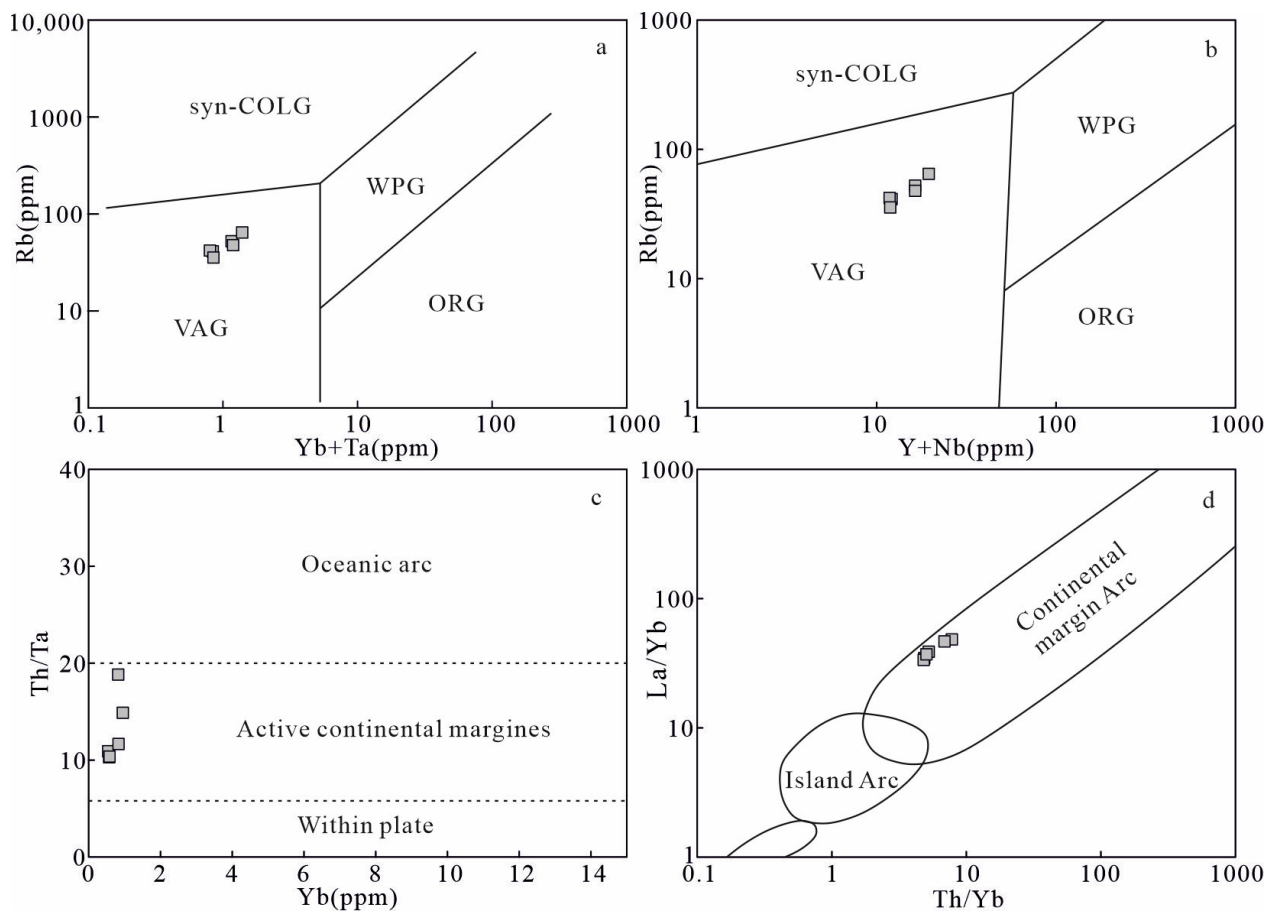


Figure 12. Geotectonic trace element discrimination diagrams for Shanlixu quartz monzonite porphyry. Ta versus Y (a), Rb–Yb + Nb (b), Th/Ta versus Yb (c), and La/Yb versus Th/Yb diagrams (d) (after Pearce et al., 1984 [93]; Gorton and Schandl, 2000 [94]; and Condie, 1989 [98]).

In summary, the geochemical data and intrusion diagrams support the notion that the Shanlixu deposit formed under a continental arc margin setting.

5.4. Implications for Cu–Au Mineralization

Cu–Au mineralization is strongly associated with Mesozoic adakites in the MLYB [99–101]. Numerous studies have demonstrated that an environment with high oxygen fugacity in a plate-convergent margin is more favorable for the formation of Cu–Au deposits [62,102–107]. Specifically, magma formed by the partial melting of oceanic crust usually contains a high Cu composition, conducive to Cu mineralization [108]. Shanlixu quartz monzonite porphyry is genetically related to the partial melting of subducted oceanic crust and contains a significant amount of mantle-derived materials. With a high Ce positive anomaly of zircon, Shanlixu quartz monzonite porphyry is considered to have high oxygen fugacity, indicating that it may be the ore-forming rock in this deposit, and is associated with skarn Cu–Au deposits.

Zircon U–Pb dating shows that Shanlixu quartz monzonite porphyry formed around 137 Ma. It is noticeably different from the major ore-forming ages in the CLMA (~130 Ma) but consistent with those in the MLYB. Based on the above study, it is suggested that, except for 130 Ma Cu–Au mineralization, an earlier Cu–Au mineralization of around 137 Ma may exist in the CLMA. This is similar to other metallogenic areas in the MLYB, such as Tonling, Chizhou, Anqing, and Jiurui, among others. This provides new insights for the exploration of Cu–Au deposit in the CLMA.

6. Conclusions

The zircon U-Pb data of Shanlixu quartz monzonite porphyry indicate that the intrusion dates back to 137.5 ± 1.7 Ma, suggesting that it occurred during the early stage of the Early Cretaceous. Based on the petro-geochemical analysis and high Ce^{4+}/Ce^{3+} values of zircon, it can be inferred that Shanlixu quartz monzonite porphyry formed in an environment with high oxygen fugacity through the partial melting of subducted oceanic crust under a continental arc margin setting. The characteristics of adakitic rocks further support this notion. Additionally, Shanlixu quartz monzonite porphyry is strongly related to skarn Cu-Au mineralization. Considering the intrusion age of the quartz monzonite porphyry, a 137 Ma Cu-Au mineralization may be a new important metallogenic period, providing a new direction for research and exploration in the LCMA.

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