



# Discovery of Yaozhuang Stock and Deep Ore Prospecting Implication for the Western Mangling Orefield in North Qinling Terrane, Central China

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In the western Mangling orefield, the molybdenum (Mo) polymetallic deposits are closely related to the ore-bearing porphyry stocks (individual outcrop size: <1 km<sup>2</sup>). In this study, we have discovered several granitic stocks at Yaozhuang. Systematic petrologic, zircon U-Pb-Hf isotope and whole-rock geochemical studies show that both the granitic stocks of porphyritic granite (157 ± 2 Ma) and the intruding monzogranite dike (153 ± 1 Ma) were emplaced in the Late Jurassic. These granitic stocks are characterized by high SiO<sub>2</sub> (66.83–75.63 wt%), high K<sub>2</sub>O (4.15–5.05 wt%), high Al<sub>2</sub>O<sub>3</sub> (12.90–16.93 wt%), and low MgO (0.06–0.73 wt%) and are metaluminous to weakly peraluminous, being highly fractionated I-A-type transition granites. The content of the total rare Earth element ( $\Sigma$ REE) of the porphyritic granite (139.6–161.7 ppm) is lower than that of the monzogranite (151.4–253.6 ppm). The porphyritic granite has weakly negative Eu anomalies (Eu/Eu\* = 0.77–0.93), whereas the monzogranite has weakly positive Eu anomalies (Eu/Eu\* = 0.97–1.21) and are more enriched in light rare Earth elements. Both of them are enriched in large ion lithophile elements (LILEs, e.g., K, Rb, and Ba) but depleted in high-field-strength elements (HFSEs, e.g., Nb, Ta, Ti, Zr, and Hf). The zircon  $\epsilon_{\text{Hf}}(t)$  values of all the samples range from -16.1 to -6.9, and the two-stage model ages ( $t_{\text{DM2}}$ ) are 1.78–2.16 Ga. The magma may have originated from partial melting of the lower crust (more than 40 km in depth) caused by mantle-derived magma underwelling. The plutons and stocks were emplaced into the intersection of the early EW-trending faults and the late (Yanshanian) NE-trending faults. The fertile magma with high water content (H<sub>2</sub>O > 4%) and high oxygen fugacity (Delta FMQ > 1.5) indicates that the Yaozhuang area has significant potential for porphyry Mo polymetallic ore discovery.

**Keywords:** Yaozhuang granitic stocks, zircon U-Pb age, late Jurassic granite, western Mangling orefield, North Qinling terrane

**Abbreviations:** A, A-type granite; FG, differentiated granite; I, S, and M, undifferentiated I, S, and M-type granite; OGT, undifferentiated I, S, and M-type granite.

## INTRODUCTION

The Qinling orogen is well-known for its multistage magmatism and orogeny (Mattauer et al., 1985; Kröner et al., 1998; Meng and Zhang, 1999; Liu et al., 2016). The magmatism occurred in four major stages: Neoproterozoic, Paleozoic, Early Mesozoic, and Late Mesozoic (Ratschbacher et al., 2003; Wang et al., 2012; Wang et al., 2015b). Previous works have studied the rock assemblage, magma source, and spatiotemporal evolution of intermediate-felsic plutons in the region and described the multistage orogeny in detail (Zhang et al., 1995; Dong et al., 2012; 2016; Wang et al., 2017; Li N. et al., 2018; Bao et al., 2019).

The western Mangling orefield is one of the deep prospecting hotspots in North Qinling terrane in recent years, and the orefield is also an important component of the Qinling Mo polymetallic ore belt (Fan and Xie, 1999; Mao et al., 2011; Yang et al., 2017). The known deposits in the area include Taoguanping, Xigou, Nantai, Mahe Mo deposits, etc. The Late Jurassic–Early Cretaceous Mangling pluton and the western porphyries are developed in the orefield, and the latter is closely related to the local Mo polymetallic mineralization (Mao et al., 2008, 2010; Zeng et al., 2012; Zhai and Santosh, 2013). In recent years, many workers have studied the age, magma evolution, petrogenesis, and mineralization of the Mangling pluton and Nantai, Taoguanping, and Xigou granitic stocks on the western side of the orefield (Ke et al., 2012a, 2012b; Qin et al., 2012; Yang et al., 2014; Hu et al., 2017), whereas granitic stock in the Yaozhuang area was rarely studied. The 1:50,000 gravity survey in Mangling revealed an oval low Bouguer gravity anomaly at Yaozhuang, and the presence of concealed porphyry bodies was speculated at depth (Yang et al., 2020). In the southwest of the study area, the borehole (Northwest Nonferrous Geological Research Institute Co., Ltd.) drilled porphyry at 380–1,400 m, accompanied by NW-extending Mo polymetallic ore (Yang et al., 2019). In the process of field geological survey, Yaozhuang stock and some monzogranite dikes were found near the gravity anomaly. Therefore, we analyzed the zircon U-Pb geochronology, Lu-Hf isotopes, and whole-rock geochemistry of the Yaozhuang stocks and discussed their petrogenesis and prospecting implications for the western Mangling orefield. This work provides new data for studying the late Mesozoic tectonic–magmatic evolution of the North Qinling terrane.

## GEOLOGICAL SETTING

The study area (Yaozhuang, Luonan County) in North Qinling is located in the early Neoproterozoic Kuaping Rift, a narrow EW-trending structure extending along the Luonan–Luanchuan and Qiaorui–Waxuezi deep-seated faults (Zhang S. H. et al., 2019). Among them, there are a large number of NE-trending Yanshanian faults. The intersection of these faults often controls the development of various magmatic deposits (Diwu et al., 2010). Exposed stratigraphy comprises predominantly the Middle–Upper Proterozoic Kuaping Group ( $Pt_{2-3}k$ ), consisting of metamorphosed mafic volcanic rocks, clastic rocks, and

carbonate rocks. The Kuaping Group can be divided into the Guangdongping ( $Pt_{2-3}gd$ ), Sichakou ( $Pt_{2-3}sc$ ), and Xiewan ( $Pt_{2-3}x$ ) formations from bottom to top (Li C. D. et al., 2018). The crystalline basement comprises the Qinling Group amphibolite-facies metamorphic rocks, with local granulite- or eclogite-facies rocks (Liu B. X. et al., 2013; Diwu et al., 2014; Zhang et al., 2015). There are a series of Yanshanian (Jurassic–Cretaceous) granitic stocks in the area. The Mangling pluton is a large EW-trending intrusive complex, containing diorite, biotite monzogranite, and moyite. On the western side of the Mangling pluton, shallow granitic stocks (e.g., Taoguanping, Xigou, Nantai, and Panhe) are present with lithology mainly of porphyritic granite, monzogranite, alaskite, and granodiorite (Figure 1).

The Yaozhuang granitic stocks intruded the Sichakou Formation biotite-quartz schist and the Guangdongping Formation plagioclase-amphibole schist. The individual stock has an exposed area of  $<1\text{ km}^2$  and extends NW or NE (Figure 2A). These stocks comprise mainly porphyritic granite and intruding monzogranite dikes (Figure 2B).

## SAMPLES AND ANALYTICAL METHODS

### Sample Descriptions

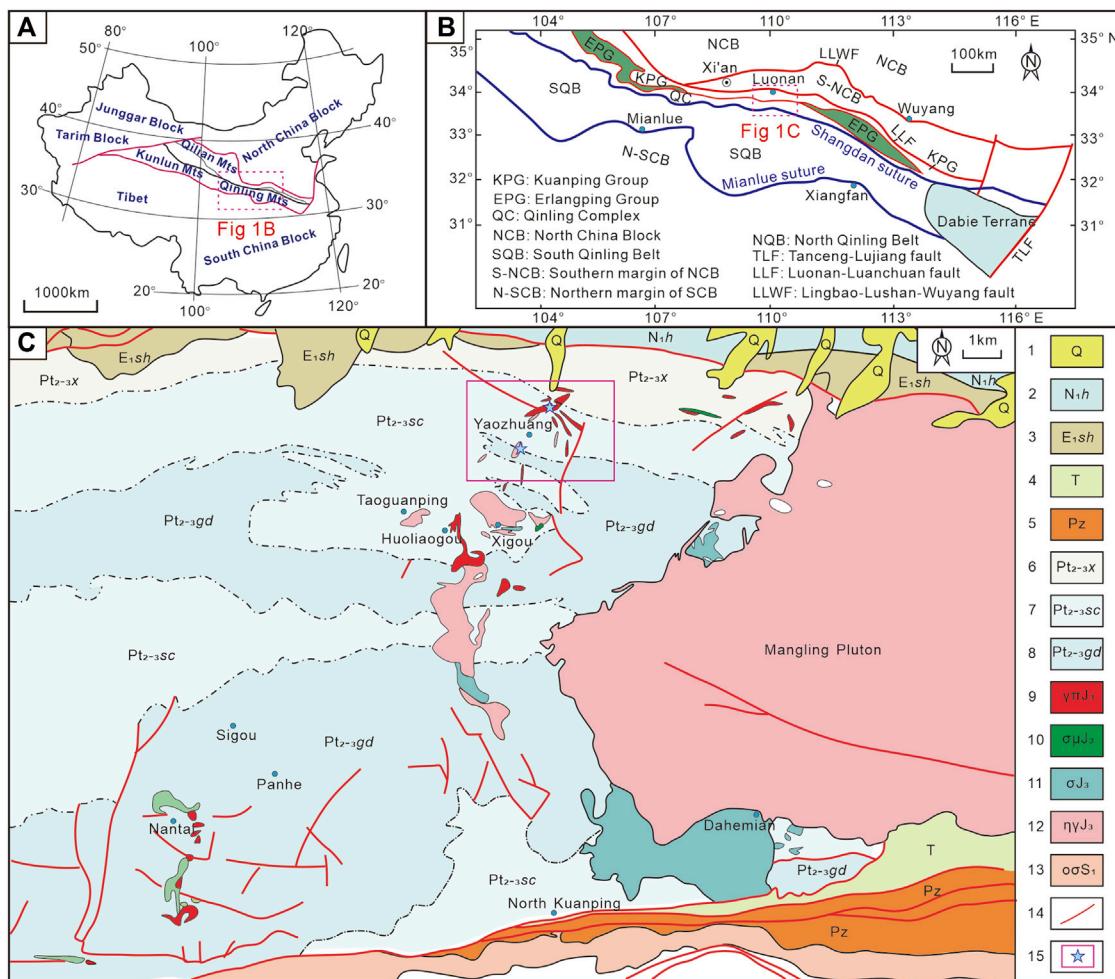
Ten samples (five porphyritic granite and five monzogranite) in this study were collected from Yaozhuang village, Luonan County. The sampling positions are shown in Figure 1.

The porphyritic granite is light gray and massive and composed of phenocrysts (15 vol%) and groundmass (85 vol %). The phenocrysts comprise mainly plagioclase, K-feldspar, and quartz. Plagioclase (size: 1–3 mm) is euhedral–subhedral and polysynthetic twinned. K-feldspar (size: 0.5–4 mm) includes mainly microcline and is euhedral–subhedral and slightly kaolinite altered on the surface. The grain margins are locally rimmed by fine secondary quartz. Quartz (size: 0.8–2 mm) is euhedral granular and colorless. The microcrystalline groundmass is composed mainly of plagioclase, microcline, quartz, and minor biotite. Accessory minerals include apatite and zircon (Figure 2C).

The monzogranite is massive; the ores show hypidiomorphic granular texture and contain K-feldspar (35–40 vol%), plagioclase (30–35 vol%), quartz (20–25 vol%), and minor biotite (<5 vol%). K-feldspar (size: 0.5–2 mm) is euhedral–subhedral, dominated by perthite with minor microcline, and weakly kaolinite altered. Plagioclase grains (size: 0.5–3 mm) are subhedral and partially sericite and K-feldspar altered. Quartz (size: 0.7–3 mm) is anhedral granular with wavy extinction. Biotite (size: 0.4–2 mm) is flaky and chloritized locally (Figure 2D).

### Zircon U-Pb-Hf Isotope Analysis

Zircon grains from one porphyritic granite and one monzogranite sample were separated with conventional heavy liquid and magnetic separation techniques. LA-ICP-MS zircon U-Pb dating was completed at the State Key Laboratory of Continental Dynamics, Northwestern University. The laser ablation system used was a GeoLas 200M from MicroLas



**FIGURE 1 |** Regional geological map of the western Mangling orefield [(A) revised after Ke et al., 2012a; (B) after Dong et al., 2011b].

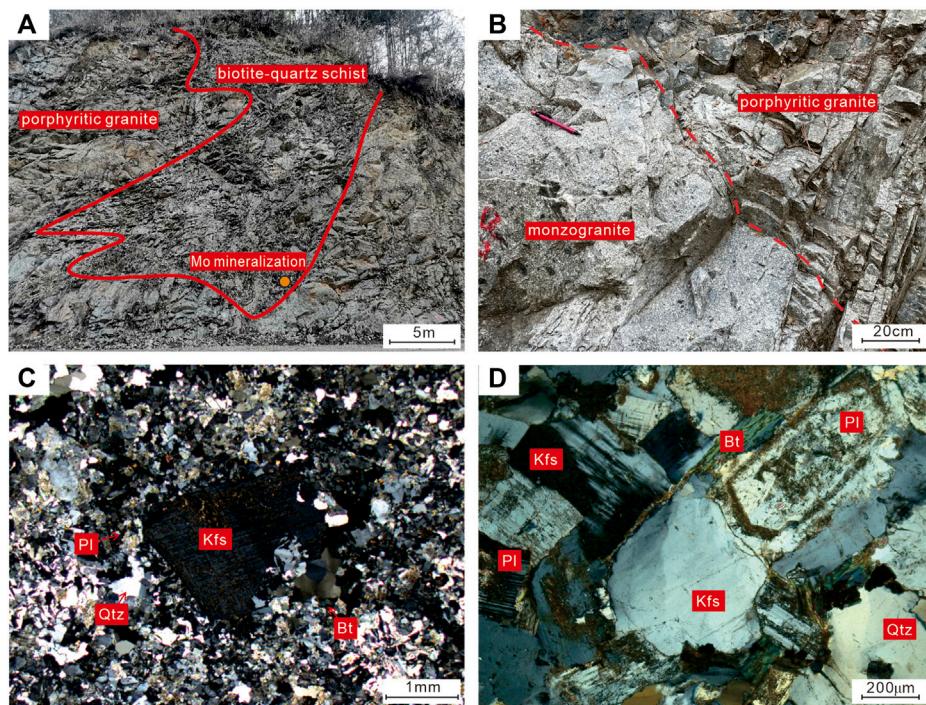
(Germany) with a 30  $\mu\text{m}$  spot size, 10 Hz repetition rate, and 32–36 MJ energy. Ion signal intensities were acquired with a quadrupole Elan 6100 DRC (ICP-MS). The instrument configuration and analytical procedures were as described by Yuan et al. (2003). Zircon GEMOC GJ-1 was used as the external standard to correct elemental fractionation and monitor instrument quality. The zircon U, Th, and Pb contents were calculated by the NIST SRM 610 glass standard (Liu et al., 2010). The method of Andersen (2002) was adopted for common Pb correction, the Glitter program (version 4.0) was used for data processing, and the Isoplot program (version 3.75) was used to calculate the U-Pb age and construct the concordia plot.

The zircon Hf isotope analysis was performed at the Laboratory of Langfang Institute of Regional Geological Survey (China), and the analysis was performed on the U-Pb dating spots. The instrument adopted the GeoLas 200M equipped with a 193 nm ArF excimer system and the Neptune plus multi-receiver plasma mass spectrometry (LA-MC-ICP-MS). The diameter of the laser ablation spot beam is 50  $\mu\text{m}$ , and the denudation depth is

20–40  $\mu\text{m}$ . Helium was used as the carrier gas and mixed with the argon makeup gas. The standard zircon 91500 was used as the external standard to monitor the analytical accuracy. Detailed instrumental conditions and analysis procedures were as described by Yuan et al. (2008).  $^{176}\text{Lu}/^{175}\text{Lu} = 0.02655$  and  $^{176}\text{Yb}/^{172}\text{Yb} = 0.5887$  were used for interference correction (Wu et al., 2007a).

## Whole-Rock Geochemical Analysis

Whole-rock geochemical compositions were determined at the laboratory of the #203 Institute of Nuclear Industry Geology (Xi'an, China). Major element compositions were measured with an Axios X-ray fluorescence (XRF) spectrometer (Panaco, the Netherlands). The analysis error was less than 5%. After correcting the loss on ignition (LOI), the major element oxide contents were back-calculated to 100%. Meanwhile, the standard curve was established with the GeokitPro program (Lu, 2004). The trace elements and rare Earth elements (REEs) were analyzed by the XSERIES II ICP-MS manufactured by Thermo Fisher (United States) with a precision better than 5%.



**FIGURE 2 |** Photos and microstructures of Yaozhuang stock. **(A)** Porphyritic granite intruded into biotite quartz schist; **(B)** monzogranite vein intruded into porphyritic granite; **(C)** porphyritic granite (orthogonal polarization); **(D)** monzogranite (orthogonal polarization); Kfs—K-feldspar, Pl—plagioclase, Qtz—quartz, Bt—biotite;  $\gamma\text{J}_3$ —Late Jurassic porphyritic granite;  $\eta\text{J}_3$ —Late Jurassic monzogranite; Pt<sub>2-3</sub>sc—Middle-Upper Proterozoic Sichakou rock formation.

## ANALYSIS RESULTS

### Zircon U-Pb age

The zircon grains from both samples have lengths of 70–210  $\mu\text{m}$  with aspect ratios of 3:1–3:1 and are mostly transparent and euhedral elongated prismatic. CL images show clear oscillatory zoning (Figure 3A), with clear core–mantle–rim structures. The zircons have Th/U = 0.27–2.8, typical of magmatic zircons (Belousova et al., 2002; Wu and Zheng, 2004).

A total of 25 zircons were analyzed for porphyritic granite sample no. D92-1, among which 21 are concordant (>90%) and 17 spots fall on the concordia, yielding a weighted-mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $157 \pm 2$  Ma (MSWD = 0.15) (Figure 3B). A total of 25 zircons were analyzed for monzogranite sample no. D13-8, with 23 spots being concordant and 21 spots falling on the concordia, yielding a weighted-mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $153 \pm 1$  Ma (MSWD = 0.10) (Figure 3C). Two inherited zircons were identified, with the age of  $847 \pm 7$  Ma. Monzogranite is slightly younger than porphyritic granite (4 Ma), consistent with the field observation that the monzogranite dike intruded the porphyritic granite (Table 1).

### Zircon Hf Isotope Compositions

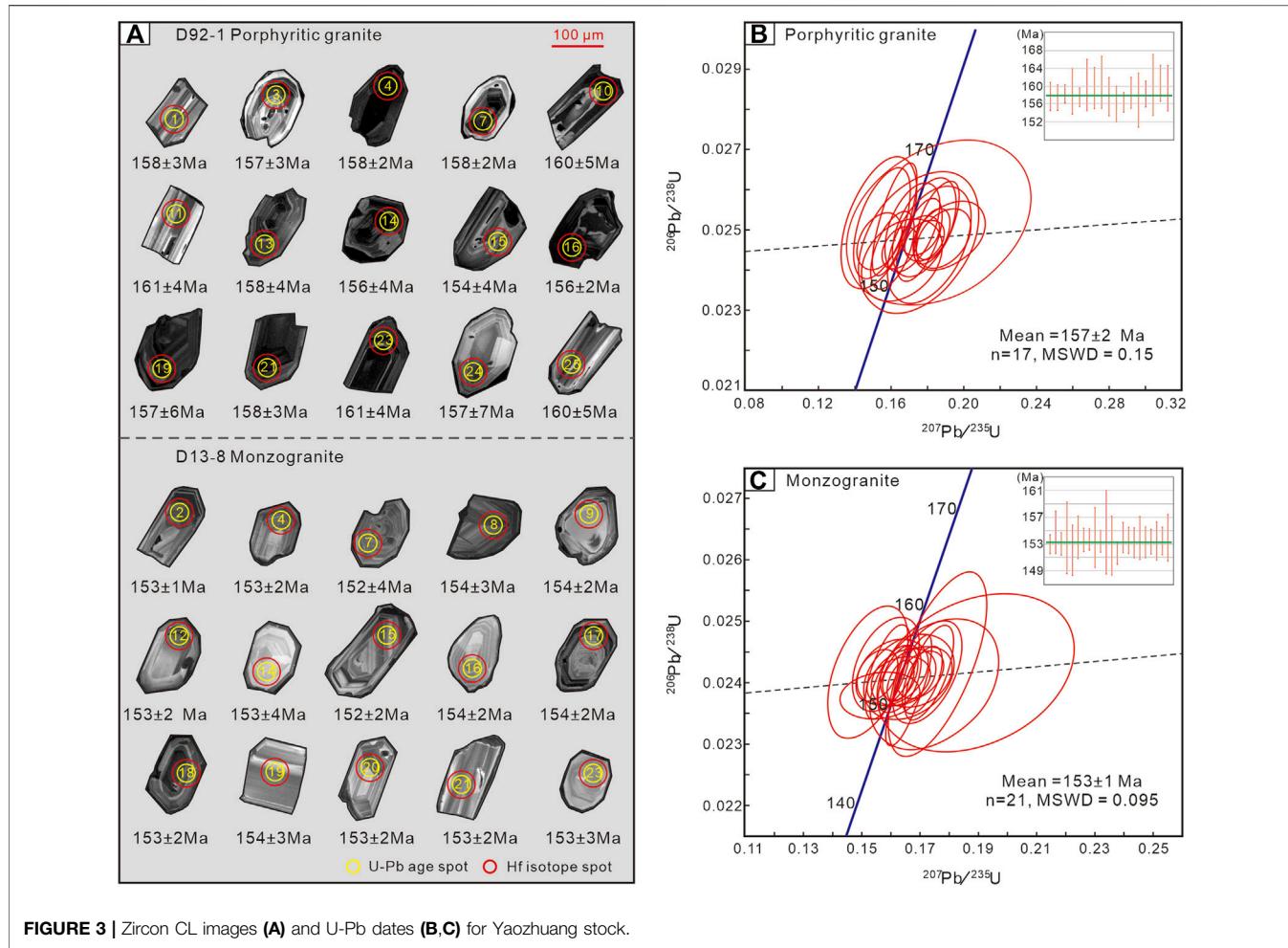
For our two samples, their  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios are <0.002, indicating negligible radiogenic Hf accumulation after the zircon crystallization, and the sample  $^{176}\text{Hf}/^{177}\text{Hf}$  approximates that of the entire system (Vervoort et al.,

1996; Wu et al., 2007a). The samples have  $f_{\text{Lu/Hf}}$  values of −0.97 to −0.94 (avg. −0.95), and  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282301\text{--}0.282485$  (avg. 0.282367; porphyritic granite) and  $0.282225\text{--}0.282372$  (avg. 0.282317; monzogranite). The samples have  $\epsilon_{\text{Hf}}(t)$  values of −13.4 to −6.9 (porphyritic granite) and −16.1 to −11.0 (monzogranite) and two-stage Hf-isotope model ages ( $t_{\text{DM2}}$ ) (representing the age of source material extraction from the depleted mantle) of 1.64–2.05 Ga (porphyritic granite) and 1.89–2.21 Ga (monzogranite) (Table 2).

### Whole-Rock Geochemistry

The major element oxide compositions of the porphyritic granite and monzogranite are similar, with  $\text{SiO}_2 = 66.83\text{--}75.63$  wt%, total alkali ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) = 8.09–10.41 wt%, and  $\text{Al}_2\text{O}_3 = 12.90\text{--}16.93$  wt%. The contents of  $\text{MgO}$  (0.06–0.73 wt%),  $\text{TiFe}_2\text{O}_3$  (0.99–2.23 wt%), and  $\text{CaO}$  (0.46–1.99 wt%) are generally low. The samples are high-K calc-alkaline (Figure 4A) and metaluminous to weakly peraluminous ( $\text{A/CNK} = 0.92\text{--}1.09$ ) (Table 3; Figure 4B).

The monzogranite has a higher total REE ( $\Sigma\text{REE} = 151.4\text{--}253.6$  ppm) than that of porphyritic granite ( $\Sigma\text{REE} = 139.6\text{--}161.7$  ppm). Both rock types have right-inclining chondrite-normalized REE patterns (Figure 5A), with LREE/HREE = 14.4–25.7 and  $(\text{La/Yb})_N = 16.7\text{--}36.4$ . However, the porphyritic granite has weakly negative Eu anomalies ( $\text{Eu/Eu}^* = 0.77\text{--}0.93$ ), whereas the monzogranite has weakly positive Eu



**FIGURE 3 |** Zircon CL images (**A**) and U-Pb dates (**B,C**) for Yaozhuang stock.

anomalies ( $\text{Eu/Eu}^* = 0.97\text{--}1.21$ ). In the primitive mantle-normalized spidergram (Figure 5B), both rock types are enriched in LILEs (e.g., Rb, K, and Ba) but depleted in HFSEs (e.g., Nb, Ta, Ti, Zr, and Hf) (Table 3).

## DISCUSSION

### Time of the Granitic Stock Emplacement

Late Mesozoic (158–112 Ma) magmatism was extensive in the North Qinling terrane (Wang et al., 2011; Liu R. et al., 2013; Lei et al., 2018; Zhang Y. S. et al., 2019; Wang et al., 2020), as represented by the Muhuguan, Mangling, and Laojunshan plutons and the nearby porphyry stocks. Recent geochronological studies had constrained the magmatic peak to be 158–144 Ma (Table 4), which was closely related to the regional Mo polymetallic mineralization (160–150 Ma). Mao et al., 2013, 2017). As shown in Table 4, the age of Mangling pluton seems to be slightly later than the stocks in the west, which may be related to the active emplacement controlled by the intersection of faults, or because the late magma in Mangling pluton may not be emplaced to the

surface. In this study, the newly obtained zircon U–Pb ages for porphyritic granite ( $157 \pm 2$  Ma) and monzogranite ( $153 \pm 1$  Ma) fall within the regional magmatic peak. Combined with the available age data and features of granitic rock distribution, it constrains the magmatism of the western Mangling orefield to about 15 My.

### Petrogenesis

The Yaozhuang granitic stocks are dominantly high-K calc-alkaline and metaluminous–weakly peraluminous (0.74–1.09). The samples do not contain Al-rich minerals (e.g., garnet and corundum) that are common in S-type granites but contain sphene and apatite that are common in I-type granites. The aluminum content index ( $A/\text{CNK} < 1.1$ ) indicates that they are I-type granites (Wu et al., 2007b). Combined with the data of other stocks near the study area, the Zr-10000Ga/Al diagram shows the sample plot in the I-A-type transition area (Figure 6A). The 160–140 Ma period is considered to be the peak period of the transformation mechanism from the paleo-Asia and Tethys tectonic domain to paleo-Pacific tectonic domain (Ding et al., 2011; Dong et al., 2018), accompanied by local crustal compression thickening and later extension. The I-A-type

**TABLE 1 | LA-ICP-MS zircon U-Pb ages of Yaozhuang stock.**

No.	Corrected isotope ratio								Apparent age (Ma)						
	Th	U	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	10	$^{207}\text{Pb}/^{235}\text{U}$	13	$^{206}\text{Pb}/^{238}\text{U}$	13	$^{207}\text{Pb}/^{206}\text{Pb}$	10	$^{207}\text{Pb}/^{235}\text{U}$	13	$^{206}\text{Pb}/^{238}\text{U}$	13
D92-1 porphyritic granite															
1	536	743	0.72	0.0554	0.0029	0.1883	0.0102	0.0248	0.0005	428	115	175	9	158	3
2	512	435	1.18	0.0502	0.0032	0.1605	0.0106	0.0231	0.0004	211	145	151	9	147	2
3	2,608	1,495	1.74	0.0449	0.0022	0.1532	0.008	0.0247	0.0005			145	7	157	3
4	1,380	1,566	0.88	0.0514	0.002	0.176	0.0068	0.0249	0.0003	257	87	165	6	158	2
5	667	796	0.84	0.0494	0.0022	0.1944	0.0091	0.0287	0.0008	165	138	180	8	182	5
6	185	162	1.15	0.0686	0.007	0.2313	0.0232	0.0249	0.0008	887	212	211	19	159	5
7	1,712	1,236	1.38	0.0524	0.0023	0.1784	0.007	0.0247	0.0003	306	94	167	6	158	2
8	429	605	0.71	0.0705	0.002	1.5251	0.0433	0.1567	0.0018	943	64	941	17	939	10
9	653	601	1.09	0.0456	0.0027	0.1549	0.0103	0.0252	0.0009			146	9	160	6
10	1,228	957	1.28	0.0495	0.0024	0.1714	0.01	0.0251	0.0007	172	113	161	9	160	5
11	1,334	1,234	1.08	0.048	0.0021	0.1621	0.0081	0.0253	0.0009	98	100	153	7	161	4
12	970	928	1.04	0.0506	0.0044	0.1861	0.0336	0.0252	0.0014	233	202	173	29	160	5
13	619	1,437	0.43	0.0515	0.0021	0.1757	0.0081	0.0247	0.0007	261	94	164	7	158	4
14	2,747	1,338	2.05	0.0483	0.0024	0.1609	0.0076	0.0245	0.0006	122	111	151	7	156	4
15	477	417	1.14	0.0506	0.0044	0.1661	0.0146	0.0243	0.0007	233	202	156	13	154	4
16	2,396	1,673	1.43	0.0487	0.0019	0.1646	0.0063	0.0246	0.0003	200	91	155	6	156	2
17	264	673	0.39	0.1088	0.0024	4.4053	0.116	0.2936	0.0049	1780	41	1,713	22	1,659	24
18	526	371	1.42	0.0561	0.0037	0.1923	0.013	0.0249	0.0006	457	146	179	11	159	3
19	269	985	0.27	0.053	0.0035	0.1811	0.0152	0.0246	0.001	328	150	169	13	157	6
20	986	554	1.78	0.079	0.0091	0.2865	0.0486	0.0247	0.001	1,172	231	256	38	157	6
21	2,876	2,218	1.3	0.0533	0.002	0.1821	0.0067	0.0248	0.0005	339	83	170	6	158	3
22	606	406	1.49	0.0465	0.0046	0.1532	0.0136	0.0252	0.0011	33	222	145	12	160	7
23	2,131	1,907	1.12	0.0535	0.0022	0.1855	0.008	0.0252	0.0006	350	93	173	7	161	4
24	434	285	1.52	0.0496	0.004	0.1753	0.0218	0.0247	0.0012	176	191	164	19	157	7
25	498	457	1.09	0.053	0.0035	0.1784	0.0116	0.0251	0.0008	332	150	167	10	160	5
D13-8 monzogranite															
1	251	422	0.59	0.0701	0.0015	1.43	0.0326	0.1476	0.0016	931	43	902	14	888	9
2	4,102	1,464	2.8	0.0492	0.001	0.1632	0.0031	0.024	0.0002	167	42	153	3	153	1
3	438	960	0.46	0.0491	0.0027	0.1583	0.0076	0.0243	0.0005	154	130	149	7	155	3
4	587	509	1.15	0.0492	0.0022	0.1628	0.0071	0.024	0.0003	167	101	153	6	153	2
5	127	409	0.31	0.0663	0.0013	1.2166	0.0212	0.1331	0.001	817	39	808	10	805	6
6	139	174	0.8	0.0563	0.0052	0.1891	0.0223	0.0242	0.0008	465	202	176	19	154	5
7	398	932	0.43	0.0505	0.0014	0.1662	0.0052	0.0239	0.0006	220	56	156	5	152	4
8	906	507	1.79	0.048	0.0018	0.159	0.0051	0.0242	0.0005	98	87	150	5	154	3
9	773	952	0.81	0.0467	0.0015	0.1551	0.0047	0.0241	0.0003	35	87	146	4	154	2
10	292	869	0.34	0.0513	0.0017	0.1703	0.0052	0.0241	0.0003	254	76	160	4	154	2
11	384	261	1.47	0.0457	0.0026	0.1521	0.0091	0.0242	0.0007			144	8	154	4
12	1,518	1,013	1.5	0.0493	0.0014	0.1635	0.0045	0.0241	0.0003	167	69	154	4	153	2
13	337	1,144	0.3	0.0518	0.0013	0.176	0.0111	0.0243	0.001	280	62	165	10	155	6
14	64	98	0.66	0.0539	0.0049	0.175	0.0146	0.024	0.0007	365	210	164	13	153	4
15	403	319	1.26	0.048	0.0031	0.1561	0.0091	0.0238	0.0003	102	154	147	8	152	2
16	463	394	1.17	0.048	0.0022	0.1605	0.0081	0.0242	0.0004	98	113	151	7	154	2
17	679	1,658	0.41	0.049	0.0012	0.1626	0.0037	0.0241	0.0003	146	56	153	3	154	2
18	2,023	1,840	1.1	0.0516	0.0013	0.1707	0.0045	0.024	0.0004	265	59	160	4	153	2
19	1,617	728	2.22	0.0522	0.0018	0.1731	0.0056	0.0242	0.0005	295	80	162	5	154	3
20	2,631	1,500	1.75	0.0491	0.0012	0.1628	0.0046	0.0241	0.0004	150	55	153	4	153	2
21	1,120	768	1.46	0.05	0.0017	0.1662	0.006	0.0241	0.0003	195	106	156	5	153	2
22	145	534	0.27	0.1625	0.0025	3.9755	0.2317	0.1765	0.0094	2,483	26	1,629	47	1,048	52
23	197	173	1.14	0.05	0.0031	0.1662	0.0104	0.0241	0.0005	195	151	156	9	153	3
24	451	452	1	0.051	0.0023	0.1692	0.0079	0.0241	0.0003	239	106	159	7	153	2
25	1,261	754	1.67	0.052	0.0025	0.1724	0.0079	0.0242	0.0006	287	111	161	7	154	3

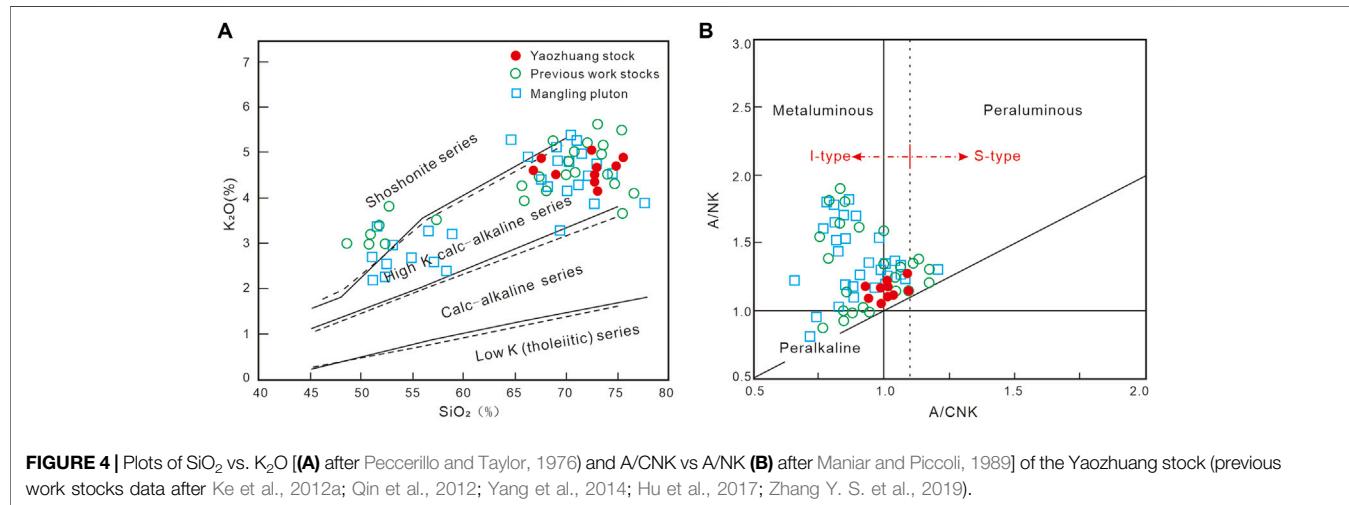
transition granites are just the products of this period. The  $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{CaO}$  vs.  $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$  diagram shows the features of high-fractionation granites (**Figure 6B**). The occurrence of high-fractionation granites is mainly related to high-temperature magma and rich volatiles, while fractionated crystallization often occurs in emplacement along with extensional structures

(Wu et al., 2017). Interestingly, highly fractionated crystallization is of great significance for the enrichment of rare metal minerals (Xu et al., 2021).

Zircon U-Pb age and Hf isotopes can effectively constrain the magma source and crustal evolution (Kinny and Roland, 2003; Xu et al., 2004; Kemp et al., 2007). The similar REEs and trace

**TABLE 2** | Zircon Lu-Hf isotope results in Yaozhuang stock.

No.	Age (Ma)	$^{176}\text{Hf}/^{177}\text{Hf}$	$2\sigma$	$^{176}\text{Yb}/^{177}\text{Hf}$	$2\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$2\sigma$	$I_{\text{Hf}}$	$\epsilon_{\text{Hf}}$	$T_{\text{DM}} (\text{Ma})$	$T_{\text{DM2}} (\text{Ma})$	$f_{\text{Lu/Hf}}$
D92-1 porphyritic granite												
D92-1-01	158	0.282341	0.00002	0.08896	0.00078	0.00202	0.00002	0.282335	-12	1,321	1,956	-0.94
D92-1-03	157	0.282363	0.00002	0.07857	0.001	0.00187	0.00002	0.282358	-11.2	1,285	1,907	-0.94
D92-1-06	159	0.282485	0.00003	0.08048	0.00197	0.00196	0.00005	0.282479	-6.9	1,112	1,637	-0.94
D92-1-07	158	0.28238	0.00003	0.06288	0.00131	0.00161	0.00002	0.282375	-10.6	1,252	1,868	-0.95
D92-1-13	158	0.282367	0.00002	0.0683	0.00016	0.00172	0	0.282362	-11	1,274	1,898	-0.95
D92-1-14	158	0.282374	0.00002	0.07421	0.00322	0.00168	0.00007	0.282369	-10.8	1,263	1,882	-0.95
D92-1-18	158	0.282413	0.00002	0.08681	0.00013	0.00198	0	0.282407	-9.4	1,217	1,798	-0.94
D92-1-19	157	0.282303	0.00002	0.05378	0.00017	0.00137	0	0.282299	-13.3	1,352	2,036	-0.96
D92-1-21	157	0.282301	0.00002	0.08457	0.00119	0.00182	0.00003	0.282295	-13.4	1,373	2,045	-0.95
D92-1-24	160	0.282345	0.00003	0.08197	0.00257	0.00193	0.00006	0.282339	-11.8	1,313	1,946	-0.94
D13-8 monzogranite												
D13-8-04	153	0.282291	0.00003	0.06485	0.00114	0.00179	0.00002	0.282286	-13.8	1,385	2,068	-0.95
D13-8-07	152	0.282346	0.00002	0.07015	0.00035	0.0018	0.00001	0.282341	-11.9	1,307	1,948	-0.95
D13-8-08	154	0.282372	0.00003	0.06953	0.00451	0.00172	0.00011	0.282367	-11	1,267	1,889	-0.95
D13-8-09	154	0.28231	0.00003	0.06009	0.00194	0.00166	0.00005	0.282306	-13.1	1,353	2,024	-0.95
D13-8-10	154	0.282225	0.00002	0.04428	0.00037	0.00107	0.00001	0.282222	-16.1	1,451	2,209	-0.97
D13-8-12	154	0.282361	0.00003	0.07157	0.00016	0.00186	0.00001	0.282356	-11.3	1,288	1,914	-0.94
D13-8-13	155	0.282288	0.00002	0.06579	0.00059	0.00186	0.00001	0.282282	-13.9	1,392	2,075	-0.94
D13-8-14	153	0.282359	0.00003	0.04588	0.00011	0.00116	0	0.282355	-11.4	1,267	1,915	-0.97
D13-8-16	154	0.282312	0.00002	0.09271	0.00052	0.00199	0.00002	0.282306	-13.1	1,362	2,022	-0.94
D13-8-17	154	0.282301	0.00002	0.06552	0.00022	0.00182	0.00001	0.282296	-13.5	1,372	2,046	-0.95
D13-8-23	153	0.282346	0.00002	0.09296	0.00103	0.0019	0.00003	0.28234	-11.9	1,311	1,948	-0.94
D13-8-24	153	0.282297	0.00002	0.08451	0.00034	0.00187	0.00001	0.282291	-13.7	1,380	2,056	-0.94

**FIGURE 4** | Plots of  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$  [(A) after Peccerillo and Taylor, 1976] and  $\text{A/CNK}$  vs  $\text{A/NK}$  [(B) after Maniar and Piccoli, 1989] of the Yaozhuang stock (previous work stocks data after Ke et al., 2012a; Qin et al., 2012; Yang et al., 2014; Hu et al., 2017; Zhang Y. S. et al., 2019).

element patterns (**Figure 5**) and zircon  $\epsilon_{\text{Hf}}(t)$  values of the porphyritic granite and monzogranite suggest a common magma source. The  $\epsilon_{\text{Hf}}(t)$  values of crystalline zircons range from -16.1 to -6.9, and the sample points are located near the evolution line of the lower crust (**Figures 7A,B**). The  $\epsilon_{\text{Hf}}(t)$  and La-La/Sm diagrams (**Figure 8A**) show the source mainly originates from partial melting of the lower crust. Moreover, Ke et al. (2012b) found that the Xigou stock at the western Mangling pluton had low  $\epsilon_{\text{Hf}}(t)$  values (-8.9 to -0.8), which implied that some mantle-derived components may be mixed into the lower crustal melt. A small number of mafic dikes [e.g., lamprophyre dikes of Muhuguan ( $152 \pm 1$  Ma) and gabbro

dikes of Mokou ( $145 \pm 2$  Ma,  $132 \pm 3$  Ma)] also indicates the addition of mantle-derived components (Liu et al., 2013; Liang et al., 2020). The  $\text{Mg}^{\#}$  [atomic Mg/(Mg + Fe)  $\times 100$ ] values of lower crustal melts are usually below 40, and thus,  $\text{Mg}^{\#} > 40$  often indicates mantle material involvement (Wilson, 1989; Kelemen, 1995; Smithies and Champion, 2000). The  $\text{Mg}^{\#}$  values of our samples (33–77, avg. 61) suggest mantle input in the magma source region.

The fractional crystallization of garnet leads to a significant increase in the ratios of  $(\text{La/Yb})_{\text{N}}$  and  $(\text{Dy/Yb})_{\text{N}}$  (Blundy and Wood, 1994; He et al., 2011). The separation crystallization of garnet (or as a residual phase in the source

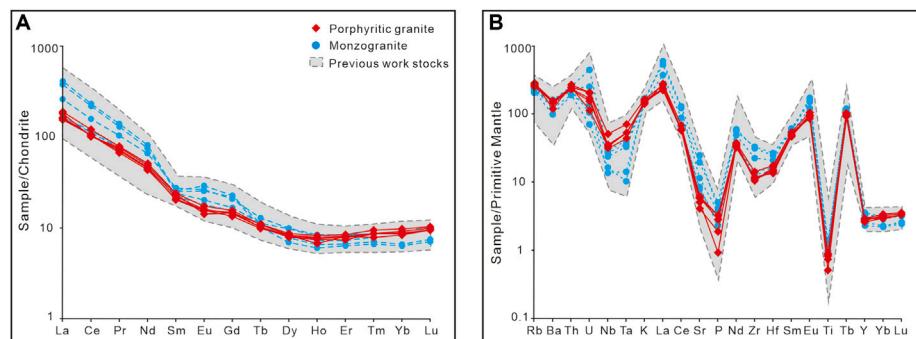
**TABLE 3** | The major elements (wt%) and trace elements (ppm) of Yaozhuang stock.

Sample	D91-1	D91-2	D92-1	D92-2	D92-3	D13-2	D13-3	D13-5	D13-7	D13-8
Lithology	Porphyritic granite					Monzogranite				
SiO <sub>2</sub>	75.63	74.96	72.91	72.89	73.14	67.63	66.83	72.52	73.02	69.03
Al <sub>2</sub> O <sub>3</sub>	12.90	13.19	13.65	13.64	14.10	16.61	16.93	14.02	13.38	15.19
TFe <sub>2</sub> O <sub>3</sub>	0.99	1.22	1.61	1.56	1.50	2.03	2.23	1.60	1.84	2.22
MgO	0.06	0.23	0.73	0.52	0.37	0.46	0.59	0.50	0.42	0.73
CaO	0.49	0.63	1.15	1.11	1.09	0.46	1.66	0.60	1.14	1.99
Na <sub>2</sub> O	4.17	4.11	4.11	4.21	3.94	5.53	5.33	4.26	4.34	4.80
K <sub>2</sub> O	4.89	4.71	4.52	4.35	4.15	4.88	4.61	5.05	4.66	4.52
P <sub>2</sub> O <sub>5</sub>	0.04	0.02	0.06	0.07	0.07	0.08	0.09	0.06	0.05	0.11
MnO	0.04	0.07	0.08	0.09	0.08	0.05	0.09	0.06	0.04	0.09
TiO <sub>2</sub>	0.11	0.16	0.19	0.19	0.18	0.29	0.27	0.21	0.20	0.30
LOI	0.42	0.59	0.68	1.08	1.03	1.58	1.09	1.14	0.87	0.79
Total	99.74	99.89	99.69	99.71	99.65	99.60	99.72	100.02	99.96	99.77
Mg#	33	59	77	68	57	74	69	74	62	68
A/CNK	0.99	1.01	0.99	1.00	1.09	1.09	1.01	1.03	0.94	0.92
La	42.62	38.27	36.49	37.81	44.24	58.25	46.70	39.11	40.43	60.66
Ce	61.37	63.82	63.40	63.37	72.68	131.91	140.52	71.78	67.33	95.32
Pr	7.18	6.90	6.35	6.57	7.41	12.30	13.20	7.33	7.22	9.78
Nd	22.60	21.41	20.27	21.13	23.42	34.97	37.74	23.62	22.90	30.71
Sm	3.59	3.10	3.19	3.34	3.61	3.77	3.85	3.61	3.38	4.13
Eu	0.82	0.89	0.90	0.92	1.00	1.46	1.68	1.17	1.04	1.51
Gd	2.99	3.04	2.77	2.93	3.19	4.48	4.65	3.43	3.16	4.27
Tb	0.41	0.38	0.37	0.38	0.40	0.38	0.41	0.42	0.40	0.48
Dy	2.20	2.11	2.04	2.00	2.10	1.76	1.97	2.49	2.13	2.46
Ho	0.46	0.38	0.43	0.42	0.44	0.34	0.37	0.47	0.41	0.46
Er	1.39	1.33	1.28	1.22	1.33	1.05	1.10	1.37	1.20	1.38
Tm	0.24	0.20	0.22	0.22	0.22	0.17	0.18	0.22	0.20	0.22
Yb	1.65	1.44	1.57	1.45	1.49	1.08	1.12	1.48	1.42	1.55
Lu	0.26	0.24	0.25	0.24	0.24	0.18	0.19	0.24	0.24	0.26
Y	13.11	13.24	12.28	11.70	13.22	10.39	11.78	15.33	13.89	15.90
Rb	177.3	159.7	175.6	168.4	163.5	156.0	138.2	157.2	131.9	144.2
Ba	815.5	1,007.4	1,043.0	984.5	1,054.0	835.4	682.8	940.4	1,120.0	948.5
Th	22.44	19.77	20.61	19.43	20.46	16.02	16.21	19.58	21.23	20.04
U	4.25	3.48	4.21	3.18	2.33	1.47	2.74	2.19	9.46	5.27
Nb	35.45	21.73	24.29	23.06	23.01	11.58	9.67	18.81	20.56	16.71
Ta	2.86	1.75	2.12	2.14	2.14	0.41	0.58	1.48	1.64	1.34
Sr	85.7	106.4	124.7	120.9	128.2	238.0	518.6	166.3	179.3	409.7
Hf	5.05	4.14	4.35	4.62	5.26	8.01	7.50	4.52	4.94	6.43
Zr	113.7	129.4	121.7	121.9	156.2	364.2	351.8	144.3	159.5	250.6
Ga	16.57	17.63	16.71	16.78	17.84	19.80	21.48	18.12	18.07	19.49
Sc	3.81	3.63	4.31	4.24	4.40	3.88	3.73	3.82	3.94	4.65
Cr	13.67	11.02	9.29	9.45	12.50	17.03	19.89	14.75	19.21	16.48
Co	1.04	1.20	1.76	1.61	2.34	3.19	3.19	2.26	2.27	3.81
Ni	3.53	3.08	4.50	4.86	5.35	7.35	8.40	6.46	6.74	6.93
ΣREE	147.8	143.5	139.6	142.0	161.7	252.2	253.6	156.7	151.4	213.2
LREE/HREE	14.39	14.74	14.63	15.03	16.19	25.70	24.40	14.49	15.53	18.24
(La/Yb) <sub>N</sub>	18.52	19.08	16.68	18.70	21.28	36.42	28.14	18.95	20.41	28.09
Eu/Eu*	0.77	0.89	0.93	0.90	0.90	1.09	1.21	1.02	0.97	1.10

area) and the inconspicuous Eu anomaly are usually interpreted as deeper crustal melting (Rudnick and Gao, 2003; Zhang et al., 2018). Yaozhuang stock shows positive correlation on (La/Yb)<sub>N</sub> and (Dy/Yb)<sub>N</sub> (**Figure 8B**). When the depth of the magma source area is >40 km and the pressure is >1.0–1.2 GPa, garnet will exist as the residual face in the magma source area (Rapp et al., 1999). Therefore, it is speculated that Yaozhuang granitic magma comes from the deep source region >40 km.

## Tectonic Implications

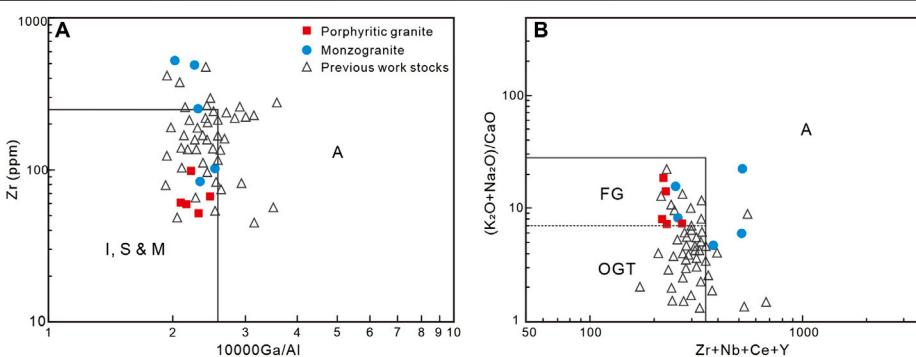
The magmatism in the North Qinling terrane is still debated. Some workers suggested that magmatism occurred after the collision of the North China Plate and the Yangtze Plate (Zhu et al., 2009, 2010; Dong et al., 2013), while others inferred that it was caused by the far-field tectonic transition effect of the Paleo-Pacific subduction beneath the Eurasia plate (Wang et al., 2015; Gao and Zhao., 2017; Yang et al., 2021). The Qinling orogen may have undergone continent-continent



**FIGURE 5 |** Chondrite-normalized REE patterns (**A**) and primitive mantle-normalized spidergram (**B**) of Yaozhuang stock (normalized values after Sun and McDonough, 1989; previous work stocks data after Ke et al., 2012a; Qin et al., 2012; Yang et al., 2014; Hu et al., 2017; Zhang Y. S. et al., 2019).

**TABLE 4 |** Age statistics of granitic batholith and stocks in the North Qinling.

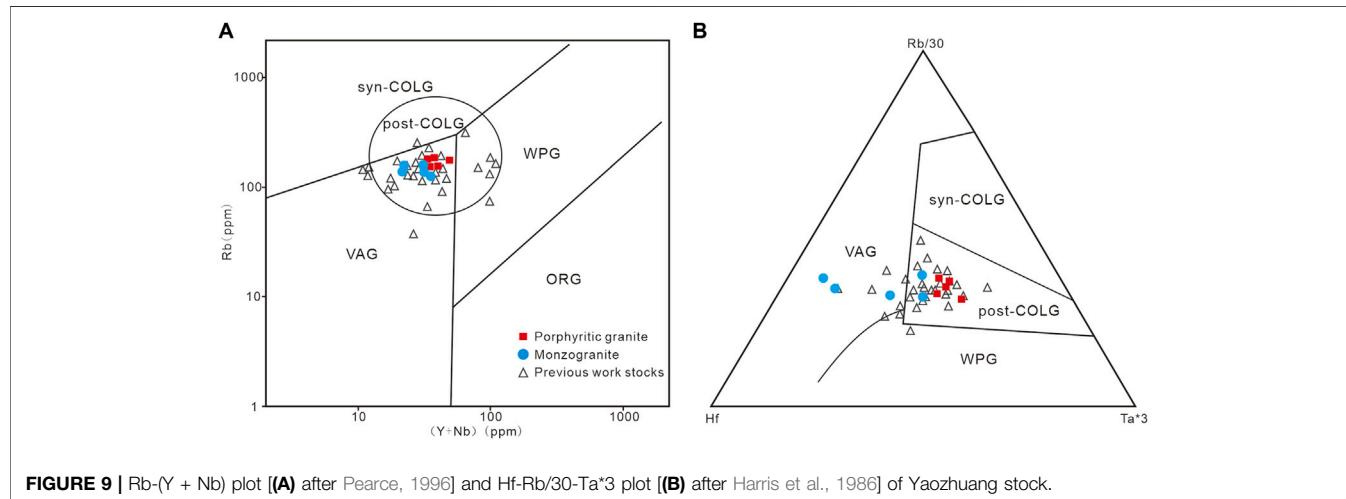
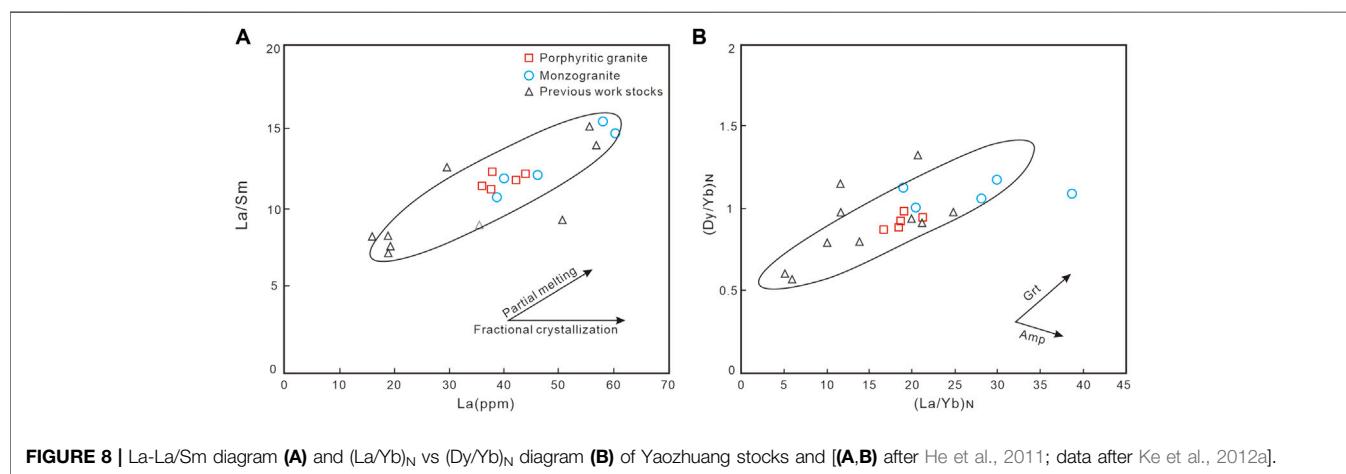
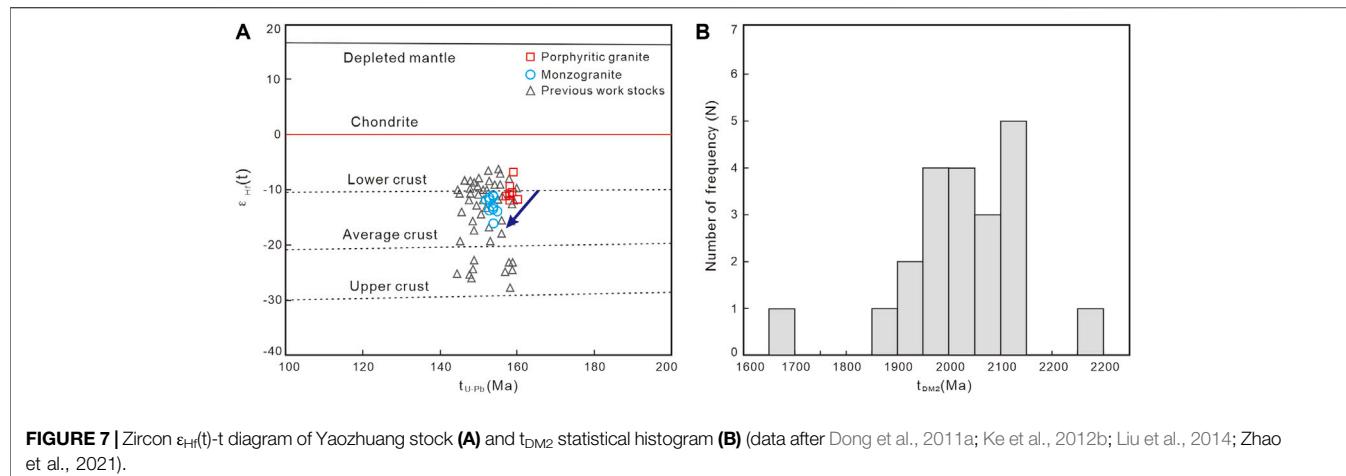
Type	Research object	Chronological method	Age (Ma)	Data sources
Stocks	Taoguanping monzogranite	LA-ICP-MS Zircon U-Pb	157±1	Ke et al. (2012)
	Xigou monzogranite	LA-ICP-MS Zircon U-Pb	153±1	Ke et al. (2012)
	Nantai granite porphyry	LA-ICP-MS Zircon U-Pb	151±1	Ke et al. (2014)
	Muhuguan lamprophyre dike	LA-ICP-MS Zircon U-Pb	152±1	Liu R. et al. (2013)
	Mokou lamprophyre dike	LA-ICP-MS Zircon U-Pb	147±3	Liang et al. (2020)
	Yaozhuang porphyroid granite	LA-ICP-MS Zircon U-Pb	157±2	This study
	Yaozhuang monzogranite	LA-ICP-MS Zircon U-Pb	153±1	This study
Plutons	Mangling biotite diorite	LA-ICP-MS Zircon U-Pb	157±1	Yang et al. (2014)
	Mangling porphyroid biotite monzogranite	LA-ICP-MS Zircon U-Pb	148±1	Yang et al. (2014)
	Mangling medium-grained monzogranite	LA-ICP-MS Zircon U-Pb	144±1	Yang et al. (2014)
	Mangling K-feldspar granite	LA-ICP-MS Zircon U-Pb	124±2	Qin et al. (2012)
	Muhuguan monzogranite	LA-ICP-MS Zircon U-Pb	145±3	Zhang Y. S. et al. (2019)
	Muhuguan dark enclaves (MMEs)	LA-ICP-MS Zircon U-Pb	152±1	Liu R. et al. (2013)
	Laojunshan biotite monzogranite	SHRIMP Zircon U-Pb	111±1	Meng et al. (2012)



**FIGURE 6 |** Zr-10000Ga/Al diagram [(**A**) after Joseph et al., 1987] and (K<sub>2</sub>O + Na<sub>2</sub>O)/CaO-Zr + Nb + Ce + Y diagram [**B**] after Joseph et al., 1987; previous work stocks data after Ke et al., 2012a; Qin et al., 2012; Yang et al., 2014; Hu et al., 2017; Zhang Y. S. et al., 2019].

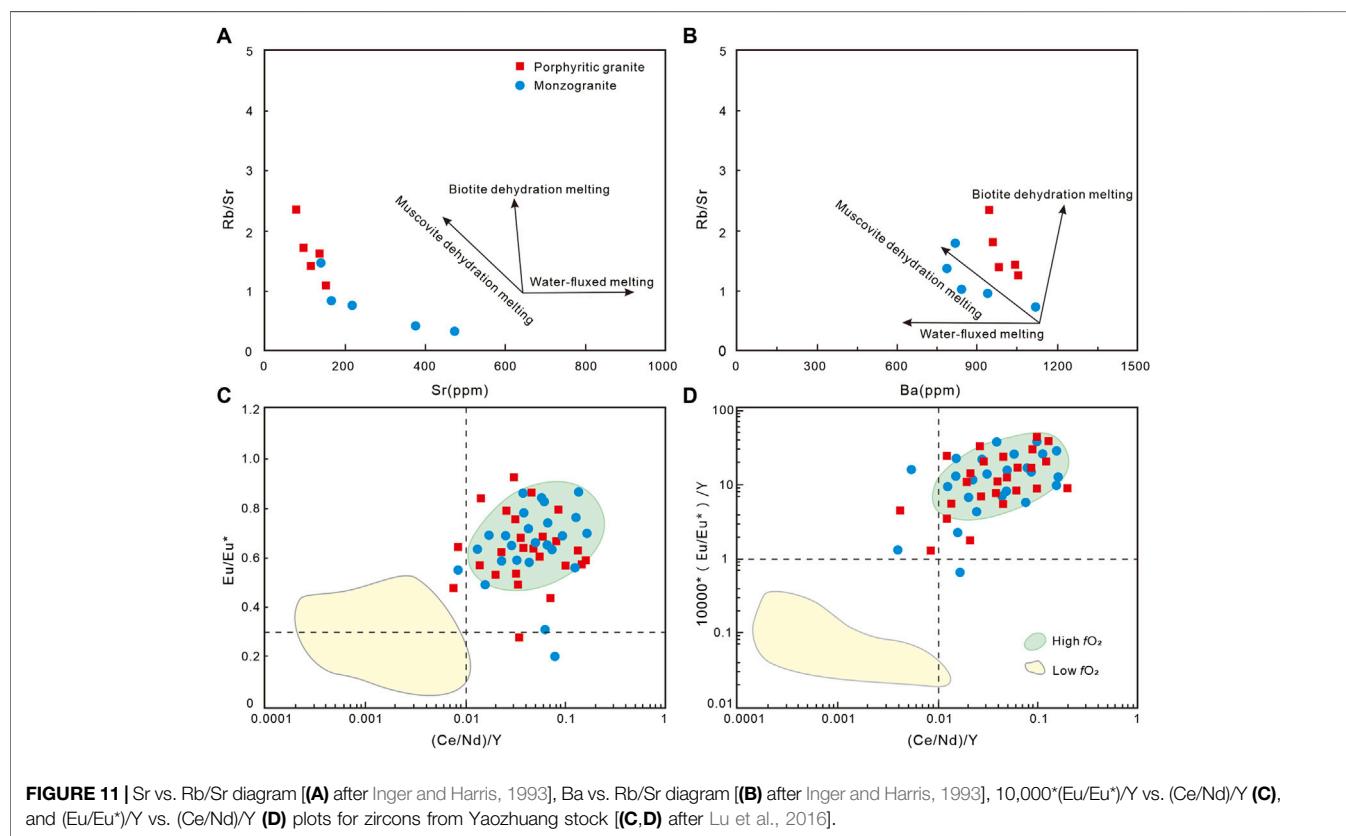
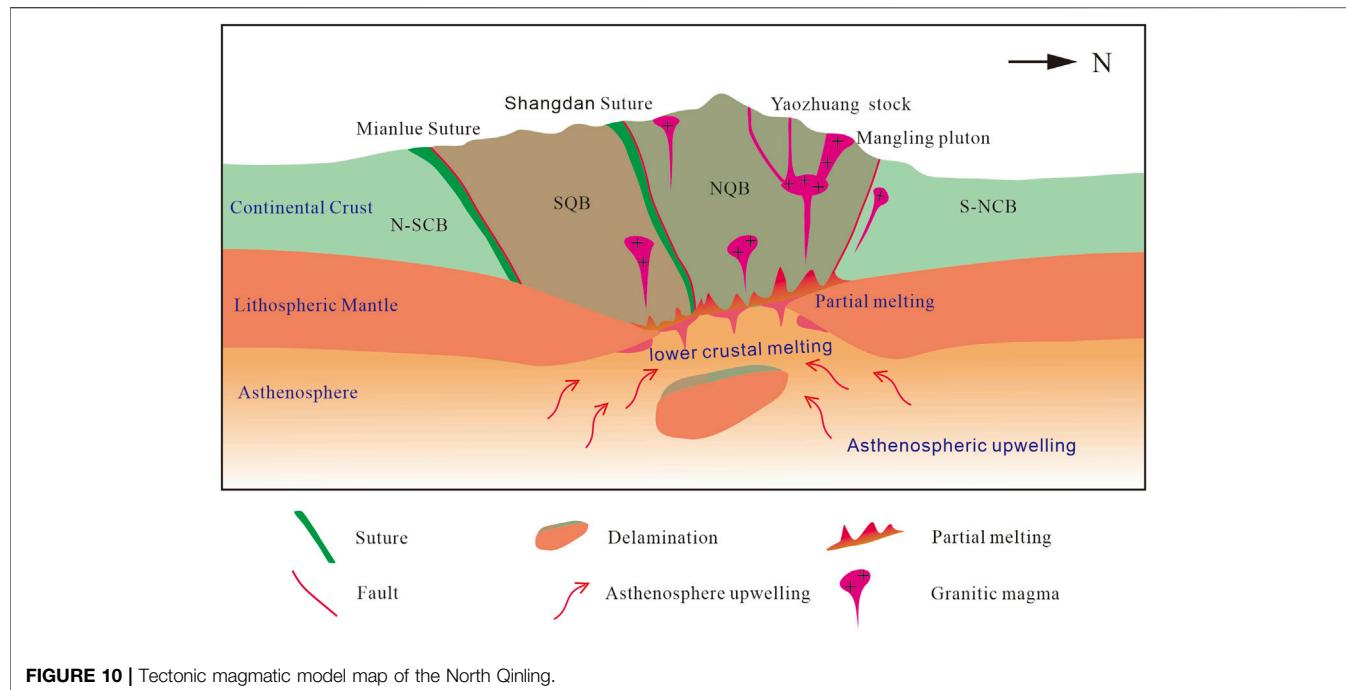
collision in the Middle-Late Triassic (242–221 Ma), followed by an intraplate orogenic stage (Bao et al., 2015; Li et al., 2015; Chen et al., 2019). In the Late Triassic (220–195 Ma), it was the late syncollision or post-collision tectonic environment. Some alkaline syenites, rapakivi granites, and I-type granites are developed in the region (Dong et al., 2011a; 2011b; Ding

et al., 2011; Wang et al., 2013), followed by tectonic quiescence in the early Middle Jurassic (195–160 Ma) (Li N. et al., 2018). In the Late Jurassic (160–140 Ma), there are some bimodal magmatism, mafic microgranular enclaves, and lamprophyre dikes in the Qinling orogeny (Wang et al., 2008; Liang et al., 2020), implying that



Lithospheric extension may have occurred (Liu et al., 2013). Both the Rb vs. ( $\text{Y} + \text{Nb}$ ) and Hf-Rb/30-Ta\*3 diagrams also revealed post-collisional magmatism (Figures 9A,B).

Geophysical data show that there was a WNW-directed uplift in the southern margin of the North China Craton (Xu et al., 2004, 2009; Zhou 2006), which is consistent



with the large Qinling Mo ore belt, regional deep faults and widespread pluton emplacement in the Late Mesozoic. All indicate that the mantle upwelling may

occur in the North Qinling terrane. Underplating melting has provided the heat and material for the coeval magmatism.

Some workers suggested a flat-slab subduction model that the Paleo-Pacific subduction could extend up to 1,300 km inland and cause large-scale magmatism in the Late Mesozoic (Li and Li., 2007; Gao and Zhao., 2017). Zhou (2006) argues that the gravity gradient and lithosphere thickness of the Qinling orogen decreases from south to north, but the gravity gradient and lithospheric thickness in eastern China decrease from west to east and cross with the Qinling orogenic belt. If affected by the Paleo-Pacific subduction, the variation of gravity gradient and lithospheric thickness should be consistent in the NE direction, and a large number of NE-trending magmatism should be found. However, the late Mesozoic magmatism in the Qinling area is nearly E–W in direction. We suggest that the Paleo-Pacific subduction has a limited impact on North Qinling, but a significant impact on the decratonization in North China. The study area is about 1,700 km far away from the Paleo-Pacific subduction zone and should have a negligible impact on the subduction. Therefore, regional tectonics may have been controlled mainly by the collision orogeny. We propose that in the North Qinling terrane, the asthenospheric materials may have upwelled and heated the lithospheric mantle to form mantle-derived magma. Subsequently, the magma underplating may have triggered partial melting of the lower crust, and the resultant magma may have then evolved and fractionated. Finally, the highly fractionated granitic magmas may have intruded into the intersection of the older EW-trending faults and the younger NE-trending faults (Figure 10).

## Implications for Mo Polymetallic Ore Prospecting

The formation of porphyry Mo deposits is controlled by many factors, including the content of water and sulfur in magmatic-hydrothermal solution, oxygen fugacity of magma (Burnham and Berry, 2012), and the migration of metal elements (Sillitoe, 2010; Richards et al., 2012; Park et al., 2021). Porphyry metallogenic magmas not only in subduction settings but also in collision settings have significant water-rich (>4.0%) (Wang et al., 2014a) and high-oxygen fugacity (Delta FMQ > 1.5) (Richards, 2011; Wang et al., 2014b). Previous studies have found that the separation and crystallization of amphibole from the magmatic system require a high water content (4%) (Naney, 1983; Davidson et al., 2007; Ridolfi et al., 2010), but the high water content will inhibit the separation and crystallization of plagioclase (Wang et al., 2021), so that the rare Earth element distribution model of water-rich magma does not show Eu anomaly. The Eu of the studied stock shows no or weakly negative anomalies ( $\text{Eu/Eu}^* = 0.77\text{--}1.21$ , avg. 0.98). Moreover, some contemporaneous diorite rocks are found near the study area, containing a large number of amphibole cumulates (Liu et al., 2014; Yang et al., 2014). These characteristics suggest that the original magma has high water content ( $\text{H}_2\text{O} > 4\%$ ).

Inger and Harris (1993) found that the dehydration and melting of muscovite would lead to the increase of the Rb/Sr ratio and the decrease of Sr and Ba contents in the melt; the trend diagram of dehydration melting and water-fluxed melting was divided (Sylvester,

1998; Meng et al., 2021). From Figures 11A,B, it is seen that the Yaozhuang stock shows a good trend of Muscovite dehydration melting; the fluid formed by dehydration melting of water-bearing minerals in the crust leads to further melting of the rock (Weinberg and Hasalová, 2015). Generally, the melt formed by dehydration melting has a higher K/Na ratio, and water-fluxed melting is just the opposite (Douce and McCarthy, 1998). The K/Na ratios of Yaozhuang stock also (0.86–1.19, avg. 1.05) support the above conclusions.

Interestingly, the water of post-collision ore-forming magma may come from additional water supplementation (Wang et al., 2018). One theory is that the water-rich mantle-derived ultra-potassium magma is mixed with the lower crustal magma to provide water (Yang et al., 2015), and the other explains that the subduction of continental crust dehydration releases free fluids into the magma to increase the water content of the magma (Zheng, 2009.; Zheng, 2019).

Researchers previously proposed that  $10,000^{*}(\text{Eu/Eu}^*)/\text{Y}$  and  $\text{Eu/Eu}^*$  ratios are positively correlated with Ce/Nd ratios, which can well indicate the oxygen fugacity of wet fertile magmatic-hydrothermal solution. The best fertility indicators are zircon  $\text{Eu/Eu}^* > 0.3$ ,  $10,000^{*}(\text{Eu/Eu}^*)/\text{Y} > 1$  ratios, and  $(\text{Ce}/\text{Nd})/\text{Y} > 0.01$  (Lu et al., 2016; Zheng et al., 2021). The above zircon trace element ratios of the Yaozhuang stock plot in the high-oxygen fugacity fertile magma region (Figures 11C,D). In addition, the zircon Delta FMQ values of porphyritic granite (avg. +2.7, the calculation method is derived from Li et al., 2019) and monzogranite (avg. +3.9) in this study are higher than the basic conditions of porphyry mineralization (Delta FMQ > 1.5).

Porphyry-type mineralization is commonly associated with porphyry stocks, where large amounts of ore-forming fluids and materials were focused into the intrusion apex to form disseminated or vein-type ores (Hedenquist and Lowenstern, 1994; Heinrich, 2005; Blundy et al., 2015). Field geological surveys show that the mineralization and alterations are generally developed, such as Mo mineralization and silicic, pyrite, and sericite alterations. The molybdenite filled the wall rock fractures (Figure 2A), which indicates that the Yaozhuang area has the potential to prospect porphyry Mo deposits.

## CONCLUSION

- (1) The newly discovered porphyritic granite and monzogranite in the Yaozhuang area are zircon U-Pb dated to be  $157 \pm 2$  and  $153 \pm 1$  Ma, coeval with the magmatic peak of the region.
- (2) The high-K calc-alkaline Yaozhuang I-type granites are metaluminous-weakly peraluminous, with zircon  $\varepsilon_{\text{Hf}}(t)$  values of  $-16.1$  to  $-6.9$  and  $t_{\text{DM2}}$  ages of  $1.78\text{--}2.16$  Ga. The granites may have formed from partial melting of the lower crust mixed with some mantle components.
- (3) The Yaozhuang granitic stocks were likely formed by the lower crustal delamination in North Qinling. The asthenospheric upwelling may have heated the lithospheric mantle to form mantle-derived magma, which then caused the lower crustal melting and magma mixing. These magmas were finally emplaced into the fault intersections at Yaozhuang.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

PF: conceived the research, investigated the literature, and wrote the manuscript. AX, BZ, and XC: provided research funds, supervision, and revision. WY, JS, HZ, and LW: participated in data analysis and academic support. All authors contributed to the article and approved the submitted version.

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