

Article

Genesis and Metallogenic Characteristics of the Zhunsujihua Granitic Intrusions in Sonid Left Banner, Inner Mongolia, China

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Abstract: The Zhunsujihua porphyry Mo-Cu deposit is located in the Erenhot–East Ujimqin metallogenic belt in northeastern China. Granodioritic intrusions in the mining area are dominated by granodiorite and granodiorite porphyry, but the Mo mineralization is limited within the granodiorite. Zircon LA-ICP-MS U-Pb dating yields crystallization ages of 301.5 ± 3.0 Ma for granodiorite and 296.0 ± 3.0 Ma for granodiorite porphyry. These ages constrain the magmatic activity at the Zhunsujihua deposit that took place during the subduction of the Paleo-Asian oceanic plate. Whole-rock geochemical data suggest that the granodioritic intrusions belong to calc-alkaline and high-K calc-alkaline series, and are characterized by enrichment in K, Rb, U, Th, and Pb, and depletion in Nb, Ta, Ti, and P. The negative Eu, Ba, and Sr anomalies suggest that they have experienced extensive fractionation of plagioclase. Trace element compositions of zircons from the Zhunsujihua deposit provide constraints on the oxygen fugacity (fO_2) of the magma, which is shown to high values with $\Delta FMQ = +0.5$ to $+5.6$. The wide range of zircon $\varepsilon_{Hf}(t)$ ($+1.3 \sim +9.4$) values, positive whole-rock $\varepsilon_{Nd}(t)$ ($+2.5 \sim +3.9$) values, and relatively low initial $(^{87}Sr/^{86}Sr)_i$ ($0.70367 \sim 0.70561$) ratios indicate that the magmas mainly originated from a juvenile lower crust source derived from depleted mantle, but mixed with pre-existing crustal components. Moreover, the juvenile lower crust represents the main source of Mo for the Zhunsujihua deposit. A high magmatic oxygen fugacity and fractional crystallization played key roles in forming the Zhunsujihua deposit.

Keywords: geochemistry; Inner Mongolia; porphyry Mo-Cu deposit; Sr-Nd-Hf isotopes; Zhunsujihua; zircon U-Pb dating



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1. Introduction

The Xing'an–Mongolia Orogenic Belt (XMOB) is the eastern part of the Central Asian Orogenic Belt (CAOB), which lies between the Siberian and North China Cratons (Figure 1a) and is characterized by widespread arc–basin systems and continental margin accretions [1–3]. In the Paleozoic, the XMOB was dominated by the subduction and termination of the Paleo-Asian oceanic plate with the amalgamation of micro-continent massifs, including Erguna, Xing'an, Songliao, and Liaoyuan blocks (Figure 1b). During the Mesozoic, the XMOB was successively overprinted by the Mongol–Okhotsk tectonic domain in the west and the Circum-Pacific tectonic domain in the east [2,4]. Meanwhile, the region produced numerous magmatic hydrothermal deposits with large reserves of Mo, Cu, Au, Ag, Pb, Sn, and W. It is worth noting that the porphyry deposit represents the most important Mo and Cu deposit, contributing 95% of the Cu and 99% of the Mo reserves [5].

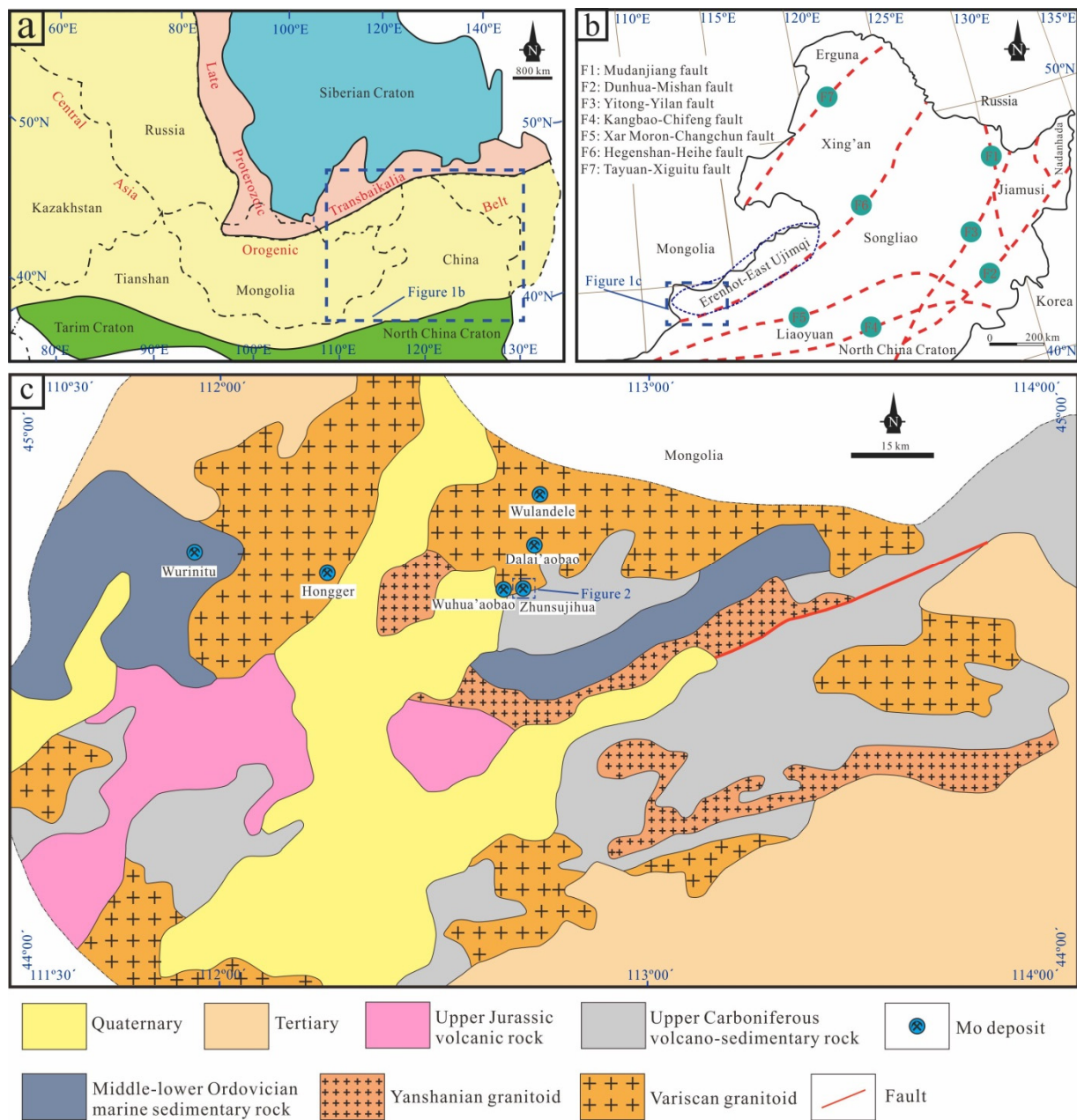


Figure 1. (a) Tectonic frameworks of the CAOB; modified after [6]. (b) Tectonic location map of north-east China; modified after [7]. (c) Geological map of the southwest Erenhot-East Ujimqi district, showing distribution of major Mo-bearing deposits, modified from [8].

The Erenhot–East Ujimqin metallogenic belt in eastern CAOB stretches 184 km from east to west, and 120–160 km from north to south (Figure 1b) [9]. Over the last decade, an increasing number of middle to large-scale Mo deposits have been successively discovered in the belt, such as Wurinitu, Wulandele, Zhunsujihua, and Wuhua’aobao (Figure 1c) [3,10]. In the Paleozoic, the Erenhot–East Ujimqin district was the site of the accretion zone on the southeastern continental margin of the Siberian craton. After the closure of the Paleo-Asian Ocean, this region changed from a compression to an extensional setting, resulting in a series of magmatic activities, accompanied by the mineralization of Mo, Cu, Au, Pb, Zn, and other metals [11]. Most metallic ore deposits in this belt are porphyry-type and hosted in high-K calc-alkaline rocks, and the mineralization mainly occurred in the Yanshanian Period (Jurassic and Cretaceous) (Figure 1c), except for the Zhunsujihua porphyry Mo-Cu deposit, which is a Paleozoic deposit [11]. Therefore, the study of the Zhunsujihua deposit

is of special significance to our understanding of the Late Paleozoic tectonic evolution processes and the associated metallogenesis in the eastern part of CAOB.

Previous studies have revealed that the granitoids in the Zhunsujihua deposit are high-K calc-alkaline series with I-type granite characteristics, and have reported zircon U-Pb dating ages of 299–300 Ma [12], consistent with the molybdenite Re-Os isochron age of 298.1 ± 3.6 Ma [9]. He et al. (2017) [13] investigated the nature and evolution of ore-forming fluids. However, the relationship between magmatic evolution and mineralization has not been well constrained. In this paper, we report zircon U-Pb ages and trace elements of the Zhunsujihua granitoids, along with whole-rock geochemical and Sr-Nd-Hf isotope data, to better constrain the origin and evolution of the intrusions, and their implications for the formation of the deposit.

2. Geological Setting

The Erenhot–East Ujimqin metallogenic belt is located in southwest Xing’an Terrane bounded by the Tayuan–Xiguitu fault in the north, and by the Hegenshan–Heihe fault in the south (Figure 1b) [7]. Several main NE-striking faults developed throughout this region, such as the Chagan Obo–Arongqi fault and Hegenshan–Heihe fault, providing ideal channels for magma intrusion [12]. The secondary faults are mainly NW–NWW trending, and generally filled by later dikes [12].

Outcropping strata in this region include the Ordovician Bayanhushu Formation of marine sedimentary rocks, Carboniferous–Permian Baoligaomiao Formation of volcano-sedimentary rocks, Upper Jurassic volcanic rocks, Tertiary sandstone, and Quaternary sediments (Figure 1c). Phanerozoic granitic intrusions were mainly emplaced during the Variscan and Yanshanian (Figure 1c). The Variscan intrusions are mainly composed of diorite, granodiorite, diabase, diorite porphyry, and granite porphyry; the Yanshanian intrusions are dominated by granite, diorite porphyry, granite porphyry, quartz monzonite porphyry, and aplite.

3. Deposit Geology

The study area is situated in the northwest of Sonid Left Banner, Xilin Gol League, Inner Mongolia Autonomous Region. Its geographic coordinates are from $112^{\circ}41'00''$ E to $112^{\circ}45'00''$ E, and from $44^{\circ}30'00''$ N to $44^{\circ}32'00''$ N, with a mining area of 16.02 km². The total explored resource of the Zhunsujihua deposit is 15.24 Mt Mo and 0.43 Mt Cu with an average grade of 0.127% Mo and 0.793% Cu (reference from the internal data of the Ninth Exploration Institute of Inner Mongolia). The stratigraphic sequences exposed in the Zhunsujihua porphyry Mo–Cu deposit are mainly the Carboniferous–Permian Baoligaomiao Formation of metamorphic siltstone and Ordovician Bayanhushu Formation of metamorphic clastic rock, partially covered by Quaternary sediments (Figure 2) [9]. The strata generally occur in a NE trending monoclinic structure controlled by the regional main fractures; dike rocks and orebodies are mainly controlled by the NW-trending faults (Figure 2) [9]. The Zhunsujihua granite intrusive complex consists of a large body of granodiorite and some granodiorite porphyry dikes and leucogranite dikes, which intruded into the Baoligaomiao Formation strata (Figures 2 and 3) [14]. In addition, a barren Yanshanian granodioritic stock outcrops in the study area (Figure 2).

The granodiorite is medium-grained and equigranular in texture (Figure 4a,d). Plagioclase is the predominant mineral and occupies approximately 40–45% of the rock. Other major minerals include K-feldspar (15–20%), quartz (20–25%), amphibole (5%), and biotite (10%), with accessory minerals of zircon, titanite, apatite, and magnetite (Figure 4d). The granodiorite porphyry has a typical porphyritic structure (Figure 4b,e). The phenocrysts of granodiorite porphyry are plagioclase (~45%), quartz (~50%), and biotite (~5%), while the groundmass comprises quartz, plagioclase, K-feldspar, and biotite (Figure 4e). The granodiorite shows a direct genetic linkage to the Mo mineralization (Figure 4c). In the contact zone between granodiorite and wall rocks, hornification and skarnization are locally developed. No obvious mineralization was observed in the granodiorite porphyry.

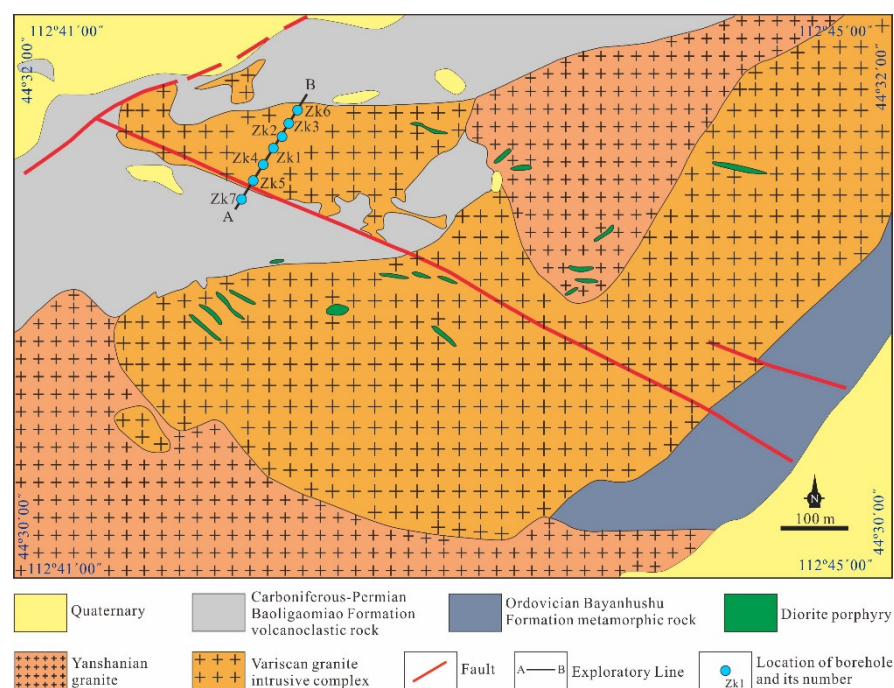


Figure 2. Simplified geological map of intrusions, wall rocks, and structures in the Zhunsujihua porphyry Mo-Cu mining area; modified after [9,13].

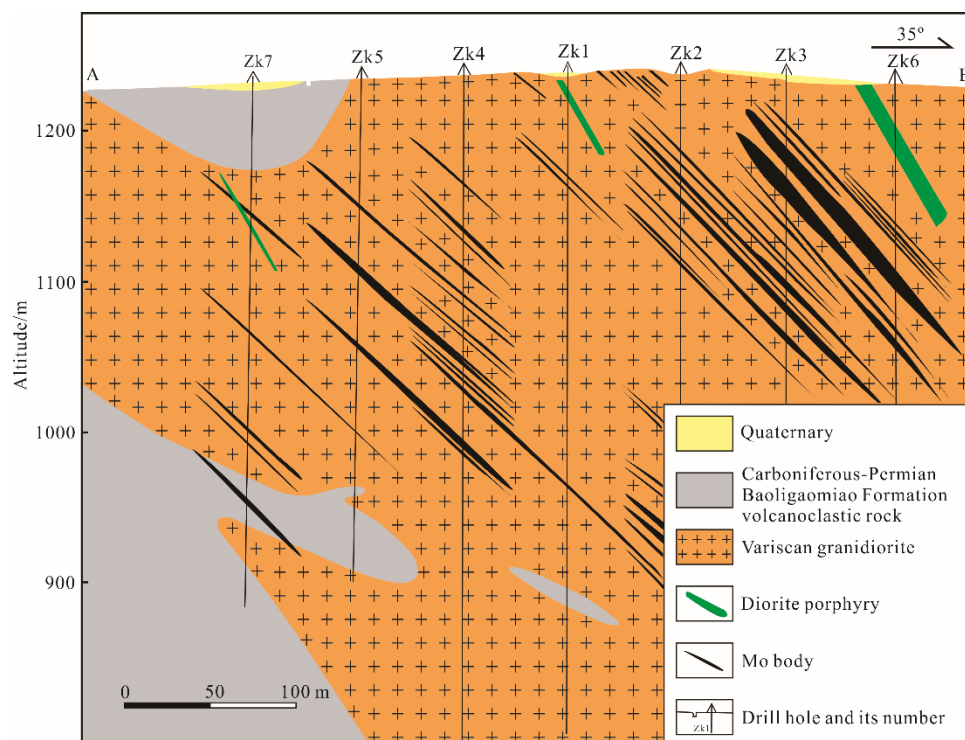


Figure 3. Geological section along No. 8 exploration line of the Zhunsujihua Mo-Cu deposit; modified after [9,13].

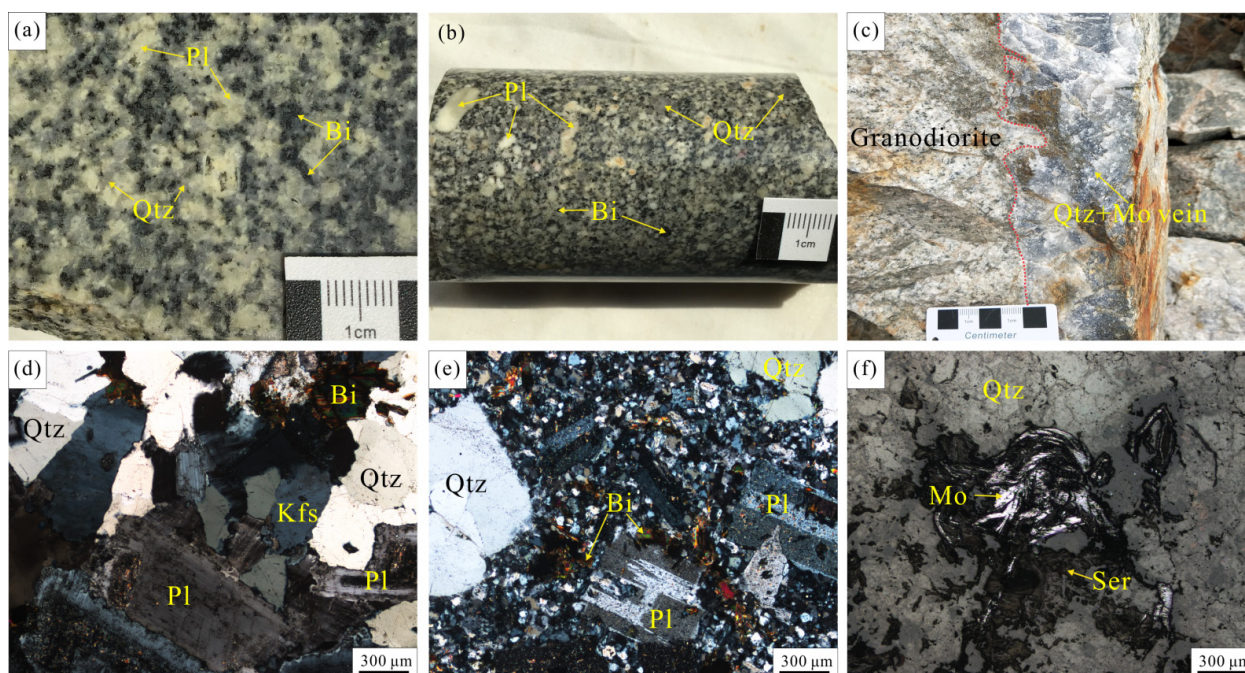


Figure 4. Hand specimens and photomicrographs of rocks from the Zhunsujihua porphyry Mo-Cu deposit and mineralization features. (a) Granodiorite. (b) Granodiorite porphyry. (c) Quartz-molybdenite vein in the granodiorite. (d,e) Granodiorite and granodiorite porphyry under orthogonal polarizing microscope, respectively. (f) Flaky molybdenite in close association with sericite. Abbreviations: Bi = biotite, Kfs = K-feldspar, Mo = molybdenite, Pl = plagioclase, Ser = sericite, Qtz = quartz.

Most of the orebodies of the Zhunsujihua porphyry Mo-Cu deposit occurred in a lenticular shape, with local pinching out in both the strike and dip (Figure 3). The length is generally about 300 m, with a few reaching up to 800 m; the extension depth varies from 10 to 400 m; the thickness of the ore body is generally between 1 and 10 m, with an average of 3 m. Alteration in the mining area shows characteristics typical of those associated with porphyry deposits, including potassic alteration, silicification, sericitization, and carbonation, which are distributed in the interior of the granodiorite body or in the contact zone between granodiorite and country rocks. Weak sericitization and epidotization are observed in the granodiorite porphyry body (Figure 4e). Sericitization and silicification are very closely related to the molybdenum mineralization and are the main precipitation stages of molybdenite (Figure 4f). The ore occurs as dominant sulfide-bearing quartz veins (Figure 4c). Pyrite, molybdenite, and chalcopyrite constitute the main metal minerals. In addition, there are also small amounts of pyrrhotite, azurite, sphalerite, magnetite, etc. Gangue minerals are dominated by quartz and carbonate, with a small amount of sericite, biotite, chlorite, epidote, anhydrite, etc. In the early stage, molybdenite usually occurs as fine scales or stockwork veinlets on the outer edges of quartz veins, and a little occurs inside the veins. In the late stage, molybdenite veins often coexist with chalcopyrite and pyrite veins, which show disseminated or massive occurrences and crosscut the early molybdenite veins [13].

4. Sampling and Analytical Methods

The thirteen least altered samples selected for analyses were all from drilling cores or ore heaps in the Zhunsujihua mining area. Four samples (two of granodiorite and two of granodiorite porphyry) were used for zircon U-Pb dating, in situ Hf isotope, and trace element determination. Whole-rock and trace elements analyses were examined on eight samples (including four granodiorite porphyry and four granodiorite). Three granodiorite porphyry samples and three granodiorite samples were selected for Sr-Nd isotope analyses.

4.1. In Situ Zircon U-Pb and Trace Element Analyses

Cathodoluminescence (CL) images of zircons were taken at the SEM-CL-TIMA Laboratory in Peking University, China. U-Pb isotopes and trace element analyses were conducted simultaneously using LA-ICP-MS at the Key Laboratory of Orogenic Belt and Crustal Evolution, Peking University, China. An Agilent 7500 ce/cs ICP-MS coupled with a 193 nm ArF laser-ablation system (ComPex 102) was used. The analyses were carried out using a 32 μm diameter spot with a flux of 10 J/cm² at rate of 5 Hz. The ablated aerosol was transported into the mass spectrometer by high-purity helium at a rate of 0.65 L/min. The NIST610 and zircon 91,500 were employed as the primary reference materials for instrument optimization and elemental fractionation calibration. The Plešovice zircon was used for data quality control; sixteen zircon spots yielded a Concordia age of 337.6 ± 1.7 Ma (95% confidence, MSWD = 0.18), which agrees well with the recommended value of 337.13 ± 0.37 Ma [15,16]. The data reduction was performed using the Glitter 4.4.2 software and the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ was calculated using the Isoplot/Ex rev. 2.49 Program [17].

4.2. Whole-Rock Geochemistry

Major and trace elements were analyzed at the Analytical Chemistry & Testing Services (ALS) Laboratory, Guangzhou, China. Samples were first cleaned and then crushed in a steel jaw crusher and powered to 200 mesh in an agate mill. The major elements analyses were performed using an X-ray fluorescence spectrometer (XRF) (PANalytical PW2424). Before XRF analysis, the mixtures of 0.4 g of rock powder, 4 g of $\text{Li}_2\text{B}_4\text{O}_7$ (flux), and 4 or 5 drops of NH_4Br (release agent) were fused in a furnace at 1100 °C to form a glass disk. The loss on ignition (LOI) was determined by placing a 1 g sample in a crucible at 980 °C for 20 min before cooling in the desiccator and reweighing. The standards NCSDC73303 and SARM-4 were used to control the analytical precisions. The analytical precisions were generally better than 0.5%. For detailed experimental procedures, refer to [18].

For whole-rock trace elements analyses, 25 mg of crushed sample powder was dissolved in HNO_3 (1.5 mL) and HF (1.5 mL) in a closed Teflon bomb at 150 °C for 24 h. Subsequently, 10 mL of HClO_4 , 1.5 mL of HF, and 1.5 mL of HNO_3 were added to the Teflon bomb and heated in an oven at 150 °C for 10 h to dissolve the sample completely. The cooled solution was placed on a hot plate and evaporated to dryness. After the addition of 1 mL of HNO_3 , the bomb was placed on a hot plate until the sample dissolved. Then, the final solution was fully transferred to a 50 mL colorimetric tube and the volume was metered with 1% HNO_3 . The final solution was subsequently analyzed by ICP-MS (Agilent 7900, USA). The procedures are described in detail by [19]. The MRGeo08 and OREAS-100a standards were employed to monitor the analytical accuracy. The precisions of the ICP-MS analyses were generally better than 5%.

4.3. Whole-Rock Sr-Nd Isotope Analyses

The separation and purification of Rb, Sr, and light rare earth elements (LREEs) were performed in the ultraclean room of the Laboratory of Orogenic Belt and Crust Evolution, Peking University, China. The whole-rock powder samples were dissolved using acids ($\text{HClO}_4 + \text{HNO}_3 + \text{HF}$) in Teflon capsules, and separated by the conventional cation-exchange technique. Isotopic ratios were measured in Shangpu Analysis Technology Co., Ltd. (Wuhan, China) by thermal ionization mass spectrometry (TIMS) using a Triton

instrument (ThermoFisher, Waltham, MA, USA), operating in the positive ionization mode with a 10 kV acceleration voltage and 1011 Ω for the Faraday cups. Rb, Sr, Sm, and Nd concentrations were measured by the isotopic dilution method. All water used in the experiments was purified by a high-purity water machine (Millipore Element, Millipore Corporation, Burlington, MA, USA) to a resistivity of 18.2 $M\Omega \cdot cm^{-1}$. Procedural blanks were 200 pg for Rb and Sr, and 50 pg for Sm and Nd. The mass fractionation correction for $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios was normalized against $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$, respectively. $^{87}Sr/^{86}Sr$ ratios were adjusted relative to the NBS-987 Sr standard = 0.710256 ± 0.000016 (2σ ; $n = 5$), and $^{143}Nd/^{144}Nd$ ratios were adjusted to the JNdi-1 Nd standard = 0.512113 ± 0.000012 (2σ ; $n = 5$). The reproducibility of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ from JR-2 and BIR-1 is approximately 0.002–0.003% (2σ). The detailed analytical procedures for Sr and Nd isotopic measurements are outlined in [20,21].

4.4. In Situ Hf Isotope Analyses of Zircon

In situ zircon Lu-Hf isotope analyses were obtained on the same zircon grains that were previously analyzed for U-Pb isotopes, and performed on a Neptune Plus laser-ablation multi-collector inductively coupled plasma mass spectrometer (LA-MC-ICP-MS) equipped with a GeolasPro HD laser ablation system. A spot size of 44 μm , an ablation time of 26 s, a repetition rate of 8 Hz, and a pulse energy of 8 mJ/cm² were used for analyses. The isobaric interference of ^{176}Lu and ^{176}Yb on ^{176}Hf was corrected by values of $^{176}Lu/^{175}Lu$ (0.02669) and $^{176}Yb/^{172}Yb$ (0.5886). The 91,500 zircon was used as the internal standard with recommended $^{176}Hf/^{177}Hf$ ratios (0.282307) [22]. GJ-1 standard was analyzed to monitor the data quality, which yielded weighted mean $^{176}Hf/^{177}Hf$ ratios of 0.282010 ± 0.000024 (2σ , $n = 4$). This value agrees well with the recommended value of 0.282015 ± 0.000019 (2σ) [23]. $\epsilon_{Hf}(t)$ was calculated based on the decay constant of ^{176}Lu of 1.867×10^{-11} a, and the $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios of chondrite of 0.282785 and 0.0336, respectively. One-stage model ages (TDM1) of the Hf isotope were calculated using the current depleted mantle value of $^{176}Hf/^{177}Hf = 0.28325$, and $^{176}Lu/^{177}Hf = 0.0384$ [24]. Two-stage model ages (TDM₂) were calculated using the average crust value of $^{176}Lu/^{177}Hf = 0.015$ [24]. The detailed analytical procedures are described in [22]. All analyses were carried out in Shangpu Analysis Technology Limited Liability Company, Wuhan, China.

5. Results

5.1. Zircon U-Pb Dating and Trace Element Results

Zircon CL images are shown in Figure 5 and the U-Pb dating results are summarized in Table 1. Most zircons have euhedral crystals that exhibit typical magmatic oscillatory zoning without distinctive older cores or younger overgrowths (Figure 5). Their size varies between 40 and 200 μm in length, and these crystals have variable U (162.4–1086.9 ppm) and Th (74.6–591.6 ppm) contents with a Th/U between 0.12 and 1.51. All these features indicate that the zircons are of magmatic origin [25,26]. The data for sixteen measuring points from granodiorite porphyry are closely distributed, constituting a relevant age group, with a calculated $^{206}Pb/^{238}U$ weighted mean age of 296.0 ± 3.0 Ma (95% confidence, MSWD = 3.0) (Figure 6). Sixteen zircon spots analyses from the granodiorite plotted on concordia yield a well-sorted population with a mean $^{206}Pb/^{238}U$ age of 301.5 ± 3.0 Ma (95% confidence, MSWD = 2.7) (Figure 6). Data for the trace elements in zircon are listed in Table 2. The chondrite-normalized REE diagram for zircon shows a strong left-leaning trend, with an obvious positive Ce anomaly and negative Eu anomaly (Figure 7).

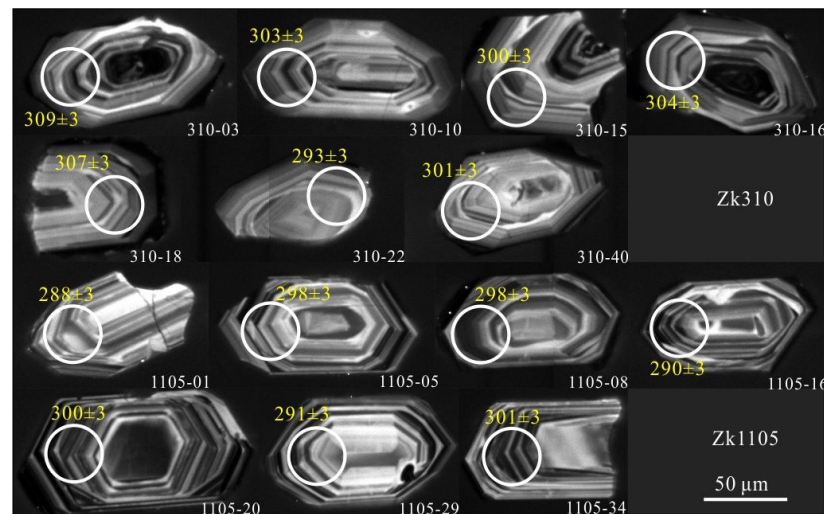


Figure 5. Representative cathodoluminescence (CL) images of dated zircon crystals from granodiorite (Sample ZK310-277) and granodiorite porphyry (Sample ZK1105-135). The yellow numbers represent $^{206}\text{Pb}/^{238}\text{U}$ ages $\pm 1\sigma$ in Ma. LA-ICP-MS pits are marked with circles. The white numbers represent the spot number.

Table 1. Zircon U-Pb LA-ICP-MS analytical results of granodiorite and granodiorite porphyry from Zhunsujihua Mo-Cu deposit.

Spot No.	U	Th	Isotopic Ratios				Dates (Ma)						
	ppm	ppm	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{235}\text{U}$	$\pm 2\sigma$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{235}\text{U}$	$\pm 2\sigma$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm 2\sigma$
Granodiorite													
Z310-03	306.5	461.7	1.51	0.05283	0.002	0.35804	0.02592	0.04915	0.00104	311	10	309	6
Z310-04	543.9	218.6	0.40	0.05265	0.00176	0.34287	0.02184	0.04722	0.00098	299	8	297	6
Z310-10	270.3	114.8	0.42	0.0528	0.00216	0.34988	0.02752	0.04805	0.00104	305	10	303	6
Z310-12	409.3	160.2	0.39	0.05204	0.00184	0.33895	0.02304	0.04723	0.00098	296	8	297	6
Z310-15	185.2	149.7	0.81	0.05189	0.00246	0.34039	0.03116	0.04757	0.00108	297	12	300	6
Z310-16	322.1	161.3	0.50	0.0523	0.00202	0.3486	0.02596	0.04833	0.00104	304	10	304	6
Z310-17	481.0	225.8	0.47	0.05262	0.0018	0.3547	0.02336	0.04888	0.00102	308	8	308	6
Z310-18	231.4	151.5	0.65	0.05234	0.00234	0.35217	0.0304	0.04879	0.00108	306	12	307	6
Z310-21	235.7	145.8	0.62	0.05332	0.00234	0.35136	0.0296	0.04778	0.00106	306	12	301	6
Z310-22	603.3	238.3	0.40	0.05175	0.00172	0.33226	0.0212	0.04656	0.00096	291	8	293	6
Z310-23	630.6	342.4	0.54	0.05123	0.00168	0.34083	0.02148	0.04824	0.001	298	8	304	6
Z310-25	813.3	361.8	0.44	0.05308	0.00166	0.35556	0.02128	0.04858	0.001	309	8	306	6
Z310-26	866.8	350.8	0.40	0.05223	0.00164	0.33666	0.02016	0.04674	0.00096	295	8	294	6
Z310-31	368.3	109.1	0.30	0.0529	0.00204	0.35146	0.02612	0.04818	0.00104	306	10	303	6
Z310-40	865.3	363.6	0.42	0.0529	0.00172	0.34901	0.02172	0.04784	0.001	304	8	301	6
Z310-41	659.6	478.0	0.72	0.05208	0.0018	0.33815	0.02236	0.04709	0.00098	296	8	297	6
Granodiorite porphyry													
Z1105-01	827.1	284.9	0.34	0.05408	0.0016	0.34117	0.00976	0.04577	0.00094	298	8	288	6
Z1105-04	291.9	271.3	0.93	0.05491	0.00242	0.35218	0.01506	0.04652	0.00106	306	12	293	6
Z1105-05	268.8	282.8	1.05	0.05364	0.00216	0.34972	0.01366	0.0473	0.00104	305	10	298	6
Z1105-08	332.2	156.8	0.47	0.05797	0.00218	0.37767	0.01376	0.04726	0.00102	325	10	298	6
Z1105-11	429.4	133.4	0.31	0.06094	0.00264	0.39765	0.0166	0.04733	0.00108	340	12	298	6
Z1105-14	562.1	581.6	1.03	0.05799	0.00186	0.36784	0.01138	0.04601	0.00096	318	8	290	6
Z1105-16	283.5	262.3	0.93	0.05461	0.00216	0.34593	0.0132	0.04595	0.001	302	10	290	6
Z1105-17	202.8	99.8	0.49	0.06361	0.00276	0.42381	0.01764	0.04833	0.00110	329	12	304	6
Z1105-19	329.9	163.6	0.5	0.05687	0.00242	0.38005	0.01396	0.04847	0.00104	327	10	305	6
Z1105-20	252.3	74.6	0.3	0.05284	0.00216	0.34675	0.0137	0.0476	0.00104	302	10	300	6
Z1105-21	634.0	250.4	0.39	0.05599	0.0019	0.36259	0.0118	0.04697	0.00098	314	8	296	6
Z1105-29	461.5	340.8	0.74	0.05477	0.00198	0.34926	0.01212	0.04625	0.00098	304	10	291	6
Z1105-31	166.4	83.6	0.5	0.05226	0.00274	0.3409	0.01726	0.04731	0.00112	298	14	298	6
Z1105-34	1086.9	87.4	0.08	0.05194	0.00154	0.34271	0.0097	0.04786	0.00098	299	8	301	6
Z1105-35	1040.1	122.3	0.12	0.05265	0.00156	0.34381	0.00976	0.04736	0.00096	300	8	298	6
Z1105-37	162.4	130.2	0.8	0.05332	0.00272	0.33992	0.01674	0.04624	0.00108	297	12	291	6

Note: All analyses in the table are used in the mean age calculation.

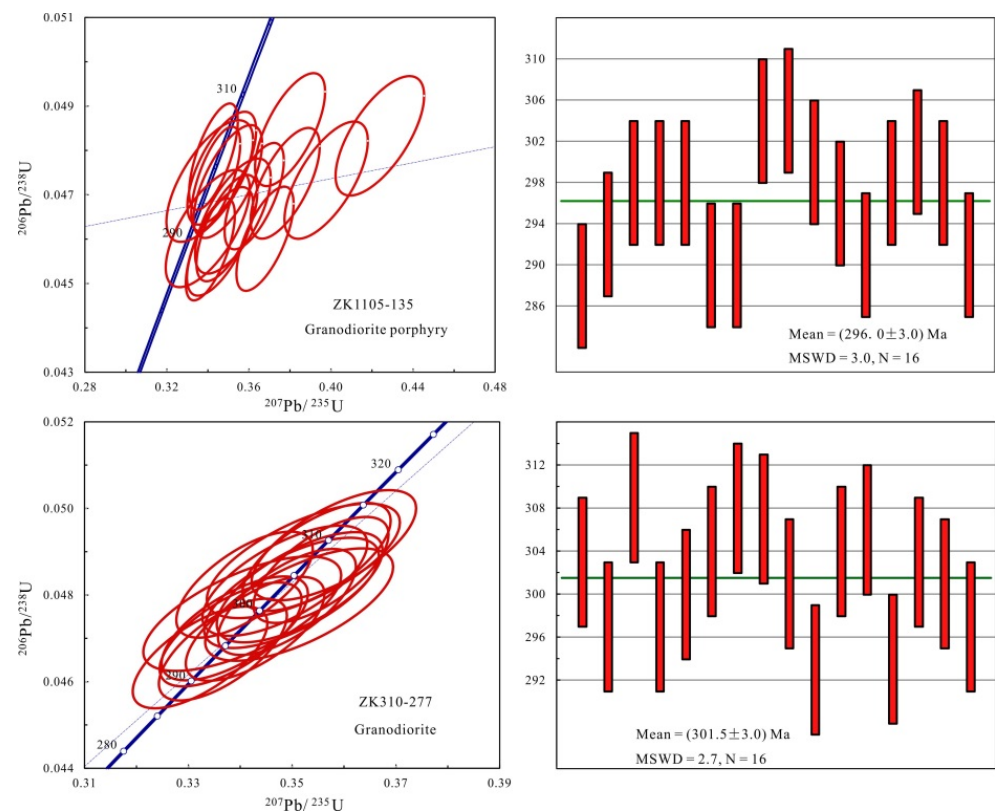


Figure 6. Zircon U-Pb concordia diagrams of the Zhunsujihua granodiorite (Sample ZK310-277) and granodiorite porphyry (Sample ZK1105-135).

Table 2. Trace (ppm) element data, Ce^{4+}/Ce^{3+} values, and $\log f(O_2)$ calculated for zircons from granodiorite, granodiorite porphyry in the Zhunsujihua Mo-Cu deposit.

Spot No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U	Th	Ti	T (°C)	Ce^{4+}/Ce^{3+}	δEu	$\log f(O_2)$	ΔFMQ
ZK1105-01	0.03	5.09	0.07	0.87	2.11	0.62	14.9	6.23	83.9	34.6	163	35.0	345	67.9	230	48	4.18	713	39	0.50	−15.90	+0.5
ZK1105-02	0.03	26.8	0.13	2.18	7.07	3.74	53.2	18.4	211	77.0	331	66.8	623	121	292	271	11.8	813	50	0.88	−10.12	+3.9
ZK1105-03	0.05	26.3	0.45	7.71	16.4	6.78	75.0	23.5	247	86.1	367	73.8	705	139	269	283	8.25	777	11	0.88	−17.27	−2.4
ZK1105-04	0.07	4.87	0.08	0.99	2.28	0.39	16.1	7.24	103	43.8	221	50.4	524	104	562	105	16.3	849	42	0.29	−9.27	+4.0
ZK1105-05	0.07	13.5	0.15	1.76	3.91	1.08	22.4	8.96	112	45.2	209	44.8	441	86.5	332	157	3.46	697	45	0.52	−16.32	+0.5
ZK1105-06	0.05	23.8	0.07	0.89	2.61	0.62	19.5	7.95	103	40.7	188	40.2	387	75.8	657	312	2.34	664	160	0.39	−13.44	+4.2
ZK1105-07	0.09	13.5	0.18	1.76	4.03	0.64	21.3	8.83	112	43.7	206	44.1	437	85.5	429	133	3.33	693	44	0.31	−16.55	+0.3
ZK1105-08	0.07	26.5	0.15	2.54	6.96	2.57	44.6	16.3	189	70.3	299	59.5	553	106	283	262	8.07	774	44	0.66	−12.43	+2.4
ZK1105-09	0.06	12.7	0.12	1.51	3.05	0.37	17.3	7.43	98.2	40.1	191	41.6	408	81.0	203	100	3.58	699	57	0.23	−15.30	+1.4
ZK1105-10	0.08	24.2	0.14	1.67	3.71	1.04	22.7	9.18	118	47.5	220	46.2	451	87.5	330	164	5.29	734	87	0.51	−11.86	+4.0
ZK1105-11	0.07	53.5	0.21	3.21	7.19	2.55	41.0	15.4	187	71.4	319	65.6	626	118	462	341	6.01	746	82	0.67	−11.49	+4.1
ZK1105-12	0.02	4.77	0.12	2.52	5.09	0.63	27.5	9.84	116	42.9	186	37.7	353	67.1	166	84	7.97	773	8	0.24	−18.71	−3.8
ZK1105-13	0.09	8.56	0.11	1.96	3.64	0.22	18.7	6.44	74.0	27.6	122	24.3	233	46.0	156	57	3.17	689	19	0.12	−19.91	−2.9
ZK1105-14	0.02	11.3	0.18	1.07	8.38	2.12	43.9	14.2	147	52.2	221	43.8	416	82.8	162	130	6.15	748	12	0.50	−18.44	−3.0
ZK1105-15	0.09	21.7	0.10	1.47	3.45	0.98	24.5	9.44	120	46.7	216	45.7	448	89.3	484	259	5.29	734	87	0.48	−11.86	+4.0
Average	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	740	52	0.48	−14.59	+1.1
ZK310-01	0.02	39.7	0.07	0.99	2.81	1.09	14.0	4.72	54.3	20.6	96.7	21.6	224	46.1	780	471	2.81	679	190	0.97	−11.93	+5.3
ZK310-02	0.03	20.2	0.04	0.76	2.70	0.67	19.8	8.34	110	45.9	219	47.8	473	94.2	544	219	2.99	684	171	0.51	−12.05	+5.1
ZK310-03	0.03	17.6	0.07	1.38	3.48	1.00	21.3	8.28	104	41.2	188	40.0	390	77.8	336	224	4.77	725	70	0.65	−13.15	+2.9
ZK310-04	0.05	17.6	0.04	0.67	2.22	0.57	16.1	6.59	87.5	35.9	168	36.8	363	72.2	409	160	3.86	706	165	0.53	−10.98	+5.6
ZK310-05	0.06	21.8	0.06	1.09	2.77	0.83	20.3	8.20	106	43.0	202	43.8	431	86.3	481	226	4.20	713	128	0.62	−11.52	+4.8
ZK310-06	0.09	22.2	0.05	0.70	2.72	0.57	18.4	7.75	101	40.9	190	41.1	401	78.6	603	238	3.10	687	182	0.45	−11.63	+5.4
ZK310-07	0.02	5.82	0.11	1.86	5.14	0.71	24.4	7.43	76.0	26.4	110	22.1	210	42.0	368	109	8.70	782	9	0.36	−17.79	−3.1
ZK310-08	0.07	18.1	0.15	2.92	6.76	1.71	36.0	13.4	158	60.8	270	56.1	530	104	388	215	5.59	739	28	0.61	−15.72	+0.0
ZK310-09	0.10	36.2	0.10	1.70	5.27	1.31	32.1	12.4	150	56.9	253	51.8	494	94.4	672	534	7.23	764	99	0.57	−9.94	+5.2
ZK310-10	0.03	27.7	0.08	1.37	3.87	0.67	23.4	9.61	127	51.3	244	54.0	543	110	865	364	2.86	681	127	0.40	−13.35	+3.9
Average	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	716	117	0.57	−12.81	+3.5

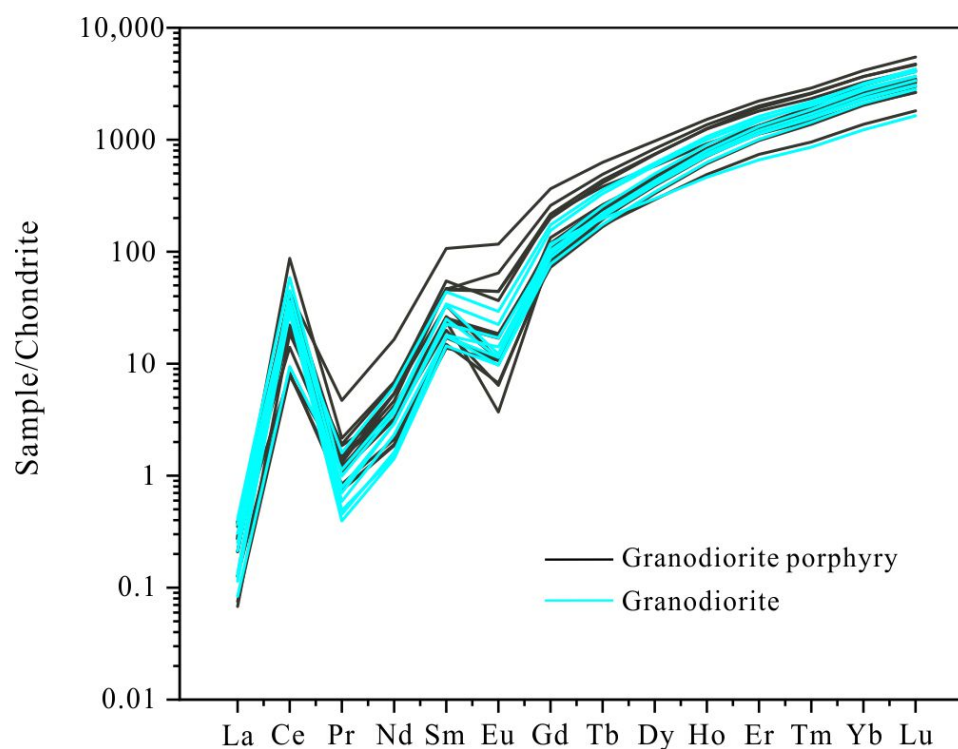


Figure 7. Zircon chondrite-normalized REE distribution patterns of granodiorite porphyry and granodiorite in the Zhunsujhua Mo-Cu deposit (data normalized after [27]).

5.2. Major and Trace Element Compositions

The results of major and trace elements for granodiorite and granodiorite porphyry are summarized in Table 3. The petrographic photos of representative rocks show that the studied samples are virtually unaltered (Figure 4), which is consistent with their low LOI values, ranging from 0.92 to 1.45 wt.% (Table 3) [28]. Granodiorite and granodiorite porphyry have similar geochemical characteristics in terms of both major and trace elements. All the samples are characterized by high silicon contents (SiO_2 : 69–71 wt.%) and are alkali-rich ($\text{K}_2\text{O} + \text{Na}_2\text{O}$: 7.02–7.76 wt.%) with relatively high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios (0.62–0.99), and have low TiO_2 , MgO , and P_2O_5 contents (Table 3). They plot into the granodiorite and granite fields in the SiO_2 vs. ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) diagram (Figure 8), and fall into the calc-alkaline and high K calc-alkaline series in the SiO_2 vs. K_2O diagram (Figure 9). The majority of calculated A/CNK values are over 1.0, with only one exception of 0.99 (Table 3), indicating that these rocks are peraluminous or only slightly metaluminous (Figure 10). In the chondrite-normalized rare earth element (REE) diagram (Figure 11), they are enriched in LREEs at different degrees, relatively depleted in heavy rare earth elements (HREEs), and have a significant fractionation between LREEs and HREEs. The $(\text{La}/\text{Yb})_N$ values of granodiorite and granodiorite porphyry are 10.44–11.93 and 9.37–10.84, respectively. The granodiorite shows an obvious negative Eu anomaly ($\delta\text{Eu} = 0.51\text{--}0.58$), while the granodiorite porphyry shows a weak negative Eu anomaly ($\delta\text{Eu} = 0.65\text{--}0.68$). In the primitive mantle-normalized trace element spider diagram, both granodiorite and granodiorite porphyry show enrichment in certain large-ion lithophile elements (LILEs) (K, Rb, U, Th, Pb), but depletion in Ba and high-field-strength elements (HFSEs) (Nb, Ta, Ti, P) (Figure 11).

Table 3. Major (wt.%) and trace (ppm) elements of granodiorite and granodiorite porphyry from the Zhunsujihua Mo-Cu deposit.

Rocks	Granodiorite					Granodiorite Porphyry		
Samples	ZK310-277	ZK1105-81	ZK1105-206	ZK1105-264	Z1105-155	ZK701-03	ZK310-52	ZK1105-135
SiO ₂	69.43	70.76	69.94	69.72	71.45	71.01	70.51	70.62
TiO ₂	0.34	0.34	0.36	0.35	0.28	0.28	0.28	0.30
Al ₂ O ₃	14.82	14.62	14.83	14.75	15.29	15.06	14.88	15.02
^T Fe ₂ O ₃	3.01	2.86	2.89	2.86	2.31	2.54	2.49	2.80
MnO	0.03	0.05	0.04	0.03	0.04	0.05	0.07	0.05
MgO	0.85	0.82	0.88	0.85	0.75	0.75	0.76	0.84
CaO	2.60	2.61	2.56	2.05	2.19	2.17	2.24	1.90
Na ₂ O	3.85	3.93	3.84	3.90	4.45	4.40	4.37	4.59
K ₂ O	3.41	3.28	3.18	3.86	2.98	2.78	2.70	2.96
P ₂ O ₅	0.11	0.12	0.12	0.12	0.10	0.10	0.10	0.10
LOI	1.41	1.13	1.45	1.39	1.00	0.92	1.09	1.09
Total	98.59	98.87	98.55	98.61	99.00	99.08	98.91	98.91
NK	7.26	7.21	7.02	7.76	7.43	7.18	7.07	7.55
A/CNK	1.00	0.99	1.03	1.03	1.05	1.06	1.05	1.06
A/NK	1.48	1.46	1.52	1.39	1.45	1.47	1.47	1.40
Mg#	36.09	36.44	37.85	37.28	39.37	37.13	37.91	37.50
A.I.	0.68	0.68	0.66	0.72	0.69	0.68	0.68	0.72
Cs	2.93	1.38	1.58	3.44	1.46	1.19	2.03	1.90
Rb	107.5	91.4	97.2	135.0	86.8	78.1	81.6	90.4
Ba	503	510	477	463	397	349	374	400
Sr	309	386	344	372	482	431	445	406
Th	7.51	11.60	7.46	8.18	6.68	7.46	7.24	7.13
U	2.93	2.43	1.15	3.05	2.51	2.39	2.00	2.72
Nb	6.4	6.3	5.9	6.3	5.7	5.3	5.4	5.5
Ta	0.6	0.4	0.5	0.6	0.6	0.5	0.5	0.6
Zr	163	158	160	166	129	143	141	140
Hf	4.2	4.9	4.0	4.2	3.3	3.6	3.5	3.6
La	25.4	27.1	20.9	22.7	21.2	19.8	17.5	20.7
Ce	51.1	58.2	45.1	48.4	41.5	44.6	39.3	45.0
Pr	5.86	6.84	5.32	5.67	4.65	5.19	4.57	5.34
Nd	22.6	25.9	20.5	22.0	17.8	19.2	17.3	20.5
Sm	4.97	5.47	4.38	4.64	3.81	3.99	3.58	4.41
Eu	0.78	0.84	0.76	0.82	0.79	0.83	0.74	0.86
Gd	3.85	4.31	3.58	3.81	3.28	3.31	2.97	3.46
Tb	0.59	0.64	0.54	0.59	0.53	0.48	0.47	0.51
Dy	3.20	3.39	2.90	3.09	2.82	2.77	2.52	2.81
Ho	0.62	0.67	0.56	0.61	0.55	0.53	0.51	0.54
Er	1.69	1.79	1.52	1.68	1.52	1.44	1.42	1.48
Tm	0.26	0.27	0.22	0.25	0.25	0.23	0.22	0.23
Yb	1.53	1.63	1.41	1.56	1.45	1.47	1.34	1.37
Lu	0.26	0.27	0.25	0.26	0.25	0.21	0.23	0.24
Y	18.5	19.6	16.7	18.4	17.0	15.2	15.1	16.1
Ga	20.3	20.4	19.85	19.80	19.35	19.25	19.25	18.75
Tl	0.62	0.43	0.55	0.82	0.52	0.48	0.49	0.59
V	43	39	40	53	33	17	29	31
W	2	2	1	2	1	1	1	2
Sn	1.7	1.7	1.8	1.9	1.5	1.6	1.5	1.9
Mo	2.12	1.98	1.34	1.23	2.29	1.98	2.18	2.56
Bi	0.16	0.25	0.18	0.31	0.45	0.19	0.31	0.08
Cu	29.8	33.9	53.6	80.3	0.9	0.7	0.7	0.7
Pb	9.3	8.5	10.1	8.5	9.5	8.5	8.9	7.6
Zn	24	42	30	25	27	28	43	32
Ag	0.04	0.05	0.08	0.11	<0.01	0.01	<0.01	<0.01
As	3.9	3.7	3.5	4.5	3.3	3.2	4.1	3.0
Be	4.71	4.88	2.82	2.91	3.42	2.86	2.53	2.86
Li	17.3	15.9	16.9	23.9	13.1	14.5	14.9	17.9
ΣREE	122.71	137.32	107.94	116.08	100.40	104.05	92.67	107.45
(La/Yb) _N	11.91	11.93	10.63	10.44	10.49	9.66	9.37	10.84
Sr/Y	16.70	19.69	20.60	20.22	28.35	28.36	29.47	25.22
δEu	0.53	0.51	0.57	0.58	0.67	0.68	0.67	0.65
Ce/Pb	5.49	6.85	4.47	5.69	4.37	5.25	4.42	5.92
Nb/Ta	10.67	15.75	11.80	10.50	9.50	10.60	10.80	9.17

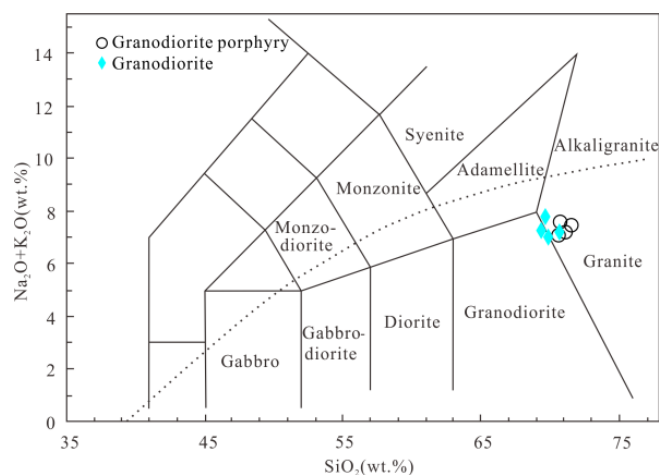


Figure 8. Classification of the Zhunsujihua granite samples on SiO_2 vs. $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ diagram, modified from [29].

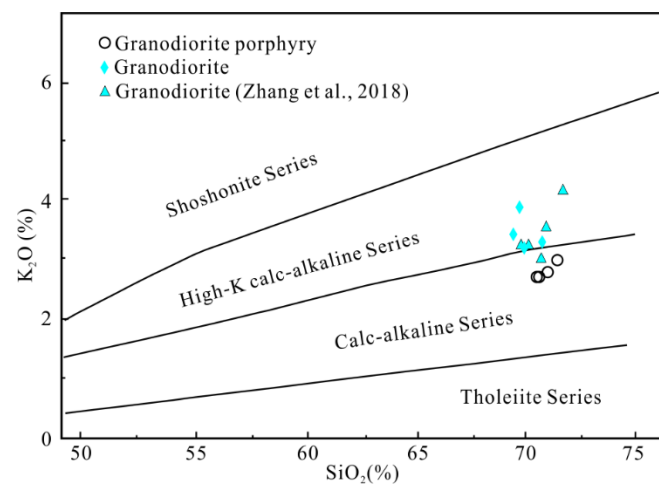


Figure 9. SiO_2 - K_2O diagram for granodiorite porphyry and granodiorite in the Zhunsujihua porphyry Mo-Cu deposit.

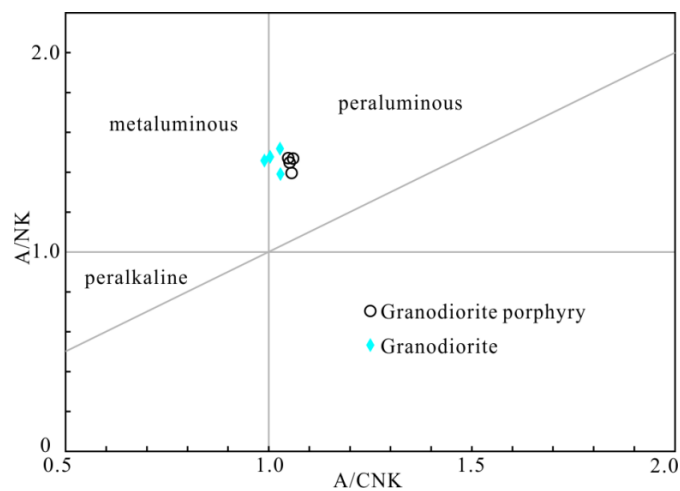


Figure 10. A/NK - A/CNK diagram for granodiorite porphyry and granodiorite in Zhunsujihua porphyry Mo-Cu deposit.

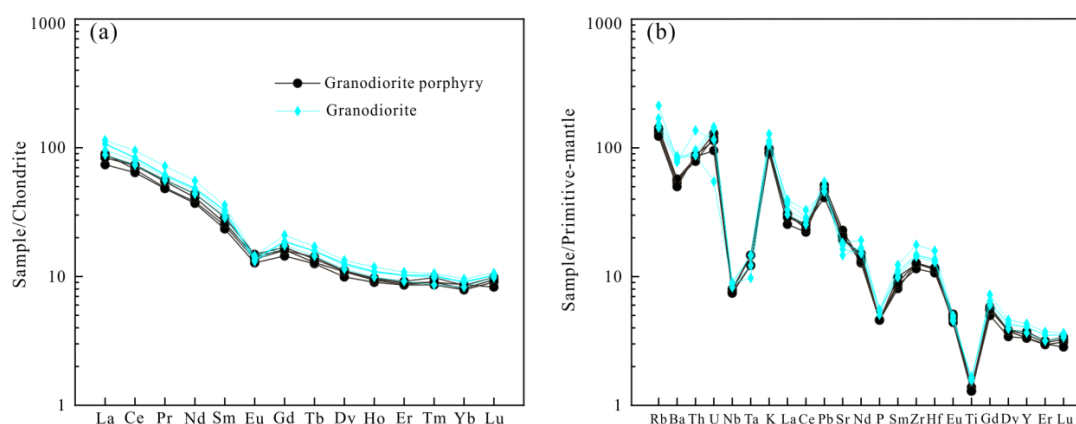


Figure 11. (a) Whole-rock chondrite-normalized REE diagram and (b) whole-rock primitive mantle-normalized trace element spider diagram for the Zhunsujihua granodiorite porphyry and granodiorite. Chondrite and primitive mantle data are both from [27].

5.3. Whole-Rock Sr-Nd Isotopic Compositions and Zircon Hf Isotopes

The results of the whole-rock Sr-Nd isotopic compositions and in situ zircon Lu-Hf isotopic analyses are presented in Tables 4 and 5, respectively. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\epsilon_{\text{Nd}}(t)$ values are calculated at 302 Ma for granodiorite and at 296 Ma for granodiorite porphyry. The granodiorite has $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.70412\text{--}0.70561$, and $\epsilon_{\text{Nd}}(t) = +2.55$ to $+3.39$, yielding two-stage depleted mantle Nd model ages ($T_{\text{DM}2}$) of 787 to 807 Ma. The granodiorite porphyry has $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.70367\text{--}0.70378$, and $\epsilon_{\text{Nd}}(t) = +3.08$ to $+3.86$, yielding $T_{\text{DM}2}$ of 754 to 787 Ma. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of granodiorite are slightly higher than those of granodiorite porphyry, but the $\epsilon_{\text{Nd}}(t)$ values are slightly lower.

Table 4. Sr-Nd isotopic data of the Zhunsujihua granitic intrusions.

Rock		Rb	Sr					Sm	Nd					t	T _{DM2}
Type	Sample	ppm	ppm	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	2 σ	I_{Sr}	ppm	ppm	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2 σ	Ma	$\epsilon_{\text{Nd}}(t)$	Ma
GD	ZS-013	168.5	291	1.67	0.712790	9	0.70561	4.96	24.6	0.1220	0.512646	4	302	+3.04	807
	PG-01	100.0	340	0.85	0.708267	9	0.70462	3.79	15.2	0.1509	0.512678	5	302	+2.55	785
	ZK310-01	151.5	287	1.52	0.710666	9	0.70412	3.55	18.2	0.1180	0.512656	5	302	+3.39	787
GP	ZK701-03	79.4	457	0.50	0.705796	11	0.70368	4.24	20.0	0.1283	0.512663	5	296	+3.08	787
	ZK1105-165	83.8	456	0.53	0.706012	8	0.70378	3.79	18.3	0.1253	0.512664	4	296	+3.21	782
	ZK707-02	74.8	449.3	0.48	0.705695	10	0.70367	2.54	18.9	0.1132	0.512674	9	296	+3.86	754

Note: ^{87}Rb decay $\lambda = 1.42 \times 10^{-11} \text{ year}^{-1}$; ^{147}Sm decay $k = 6.54 \times 10^{-12} \text{ year}^{-1}$; $\epsilon_{\text{Nd}}(t)$ were calculated with modern $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$ and $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$, and T_{DM} were calculated using present-day $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}} = 0.2137$ and $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}} = 0.51315$ [30]. GD = granodiorite; DP = granodiorite porphyry; $I_{\text{Sr}} = (^{87}\text{Sr}/^{86}\text{Sr})_i$.

The $^{176}\text{Yb}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios for zircons from granodiorite are relatively low, ranging from 0.045504 to 0.075724 and from 0.001378 to 0.002395, respectively. The calculated $\epsilon_{\text{Hf}}(t)$ values vary from $+1.3$ to $+8.9$ and the obtained two-stage depleted mantle Hf model ages ($T_{\text{DM}2}$) are 693–1118 Ma. The $^{176}\text{Yb}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios for zircons from granodiorite porphyry are relatively high, varying in a large range of 0.049679–0.137264 and 0.001301–0.004089, respectively. The calculated $\epsilon_{\text{Hf}}(t)$ values vary from $+1.9$ to $+9.4$ and the obtained $T_{\text{DM}2}$ are 666–1151 Ma (Table 5). Both two-stage model ages obtained from Hf isotopes are in good agreement with those obtained from Nd isotopes. The range of $\epsilon_{\text{Hf}}(t)$ variation is significantly larger than the error caused by the analytical error. Therefore, zircons from the Zhunsujihua granitic intrusions have heterogeneous Hf isotopic compositions.

Table 5. Hf isotope data of zircons from granodiorite, granodiorite porphyry of the Zhunsujihua Mo-Cu deposit.

								t				T _{DM1}	T _{DM2}
Spots	¹⁷⁶ Hf/ ¹⁷⁷ Hf	1σ	¹⁷⁶ Yb/ ¹⁷⁷ Hf	1σ	¹⁷⁶ Lu/ ¹⁷⁷ Hf	1σ	(¹⁷⁶ Hf/ ¹⁷⁷ Hf) _i	Ma	ε _{Hf} (t)	2σ	Ma	Ma	
Granodiorite													
ZS-013-01	0.282771	0.000009	0.056992	0.000517	0.001524	0.000007	0.282762	302	6.3	1.2	691	837	
ZS-013-02	0.282693	0.000013	0.071257	0.000242	0.002327	0.000009	0.28268	302	3.4	1.4	820	999	
ZS-013-03	0.282819	0.000011	0.051256	0.000925	0.001717	0.000015	0.28281	302	8.0	1.3	625	744	
ZS-013-04	0.282844	0.00001	0.051047	0.000116	0.001427	0.000006	0.282836	302	8.9	1.3	585	693	
ZS-013-05	0.282808	0.000013	0.062293	0.000436	0.00201	0.000015	0.282797	302	7.5	1.4	647	770	
ZS-013-06	0.282809	0.000011	0.045504	0.000489	0.001567	0.000022	0.2828	302	7.6	1.3	638	763	
ZS-013-07	0.28284	0.000009	0.07263	0.000342	0.002059	0.000018	0.282828	302	8.6	1.2	601	708	
ZS-013-08	0.282644	0.000012	0.075724	0.000799	0.002395	0.000021	0.282631	302	1.6	1.4	894	1097	
ZS-013-09	0.282832	0.00001	0.064437	0.000454	0.001762	0.000013	0.282822	302	8.4	1.3	608	721	
ZS-013-10	0.282631	0.000014	0.054415	0.000639	0.001886	0.000028	0.28262	302	1.3	1.5	901	1118	
ZS-013-11	0.282826	0.000012	0.054308	0.000551	0.001545	0.000016	0.282817	302	8.2	1.4	613	730	
ZS-013-12	0.282842	0.000011	0.050172	0.001044	0.001378	0.000027	0.282835	302	8.9	1.3	586	695	
Granodiorite porphyry													
ZK-701-01	0.282848	0.000009	0.075913	0.001062	0.002044	0.000041	0.282836	296	8.8	1.3	590	694	
ZK-701-02	0.28285	0.000009	0.077624	0.000657	0.002182	0.000013	0.282838	296	8.8	1.2	588	691	
ZK-701-03	0.282832	0.000012	0.057793	0.000922	0.001811	0.000046	0.282821	296	8.3	1.4	609	723	
ZK-701-04	0.282733	0.000016	0.077075	0.001179	0.002575	0.000048	0.282719	296	4.6	1.6	767	925	
ZK-701-05	0.282664	0.000014	0.137264	0.00137	0.004089	0.000056	0.282641	296	1.9	1.5	907	1151	
ZK-701-06	0.28276	0.000012	0.127753	0.003459	0.003783	0.000141	0.282739	296	5.3	1.4	753	941	
ZK-701-07	0.282865	0.000009	0.060611	0.000576	0.001777	0.00003	0.282855	296	9.4	1.3	561	666	
ZK-701-08	0.28284	0.00001	0.054538	0.001071	0.001425	0.000021	0.282832	296	8.6	1.3	590	712	
ZK-701-09	0.282846	0.000011	0.070834	0.001359	0.001946	0.000044	0.282835	296	8.8	1.3	590	713	
ZK-701-10	0.282819	0.000013	0.096886	0.001103	0.002623	0.000049	0.282804	296	7.7	1.4	641	785	
ZK-701-11	0.282857	0.00001	0.049679	0.000655	0.001301	0.00001	0.28285	296	9.3	1.3	564	670	
ZK-701-12	0.282848	0.000011	0.07464	0.000461	0.001968	0.00002	0.282837	296	8.8	1.3	588	708	

6. Discussion

6.1. Timing of Magmatism and Mineralization

The zircon U-Pb ages of the granodiorite and granodiorite porphyry in the Zhunsujihua deposit are 301.5 ± 3.0 Ma and 296.0 ± 3.0 Ma, respectively. These age data are similar to the previously reported U-Pb age of granodiorite (300 ± 2 Ma) and granodiorite porphyry (299.0 ± 2.6 Ma) [12], and are consistent with the reported molybdenite Re-Os isochron age of 297.2 ± 4.3 Ma [31], suggesting that the Zhunsujihua granodioritic intrusions and mineralization are related to Late Carboniferous–Early Permian magmatic–hydrothermal events [31]. Given that the granodiorite is the major host to the orebodies, and no mineralization and alteration were observed in the granodiorite porphyry, it is reasonable to propose that granodiorite was the causative intrusion.

6.2. Petrogenesis of the Magmatic Rocks

All of the granodiorite and granodiorite porphyry samples contain magmatic biotite and hornblende, suggesting that they have a typical I-type affinity [32]. This is further supported by the Sr isotope data ($I_{\text{Sr}} = 0.70367\text{--}0.70561$) and the geochemical features of the granodioritic intrusions, which are metaluminous, high-K calc-alkaline, with $A/\text{CNK} < 1.1$.

Similar Nd and Hf isotope compositions of granodiorite and granodiorite porphyry, together with the same zircon U-Pb ages, indicate that they have a unified magma source region [33]. The positive whole-rock $\epsilon_{\text{Nd}}(t)$ values ($+2.55\text{--}+3.86$) and relatively low $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values ($0.70367\text{--}0.70561$) suggest that the source region might be from the simple juvenile lower crust derived from the depleted mantle and mixed with pre-existing crustal materials. According to the mixing calculations using different end-members, which are shown in the $\epsilon_{\text{Nd}}(t)\text{--}({}^{87}\text{Sr}/^{86}\text{Sr})_i$ diagram (Figure 12a) [34], the source of Zhunsujihua intrusions contains 80–90% juvenile basalt components, with 10–20% ancient crustal materials. The average Ce/Pb and Nb/Ta ratios of granodiorite and granodiorite porphyry are 5.3 and 11.1, respectively, which are close to those of the crust ($\text{Ce}/\text{Pb} = 3.9$ [35]; $\text{Nb}/\text{Ta} = 12\text{--}13$ [36]), but quite different from those of the mantle-derived magma

(Ce/Pb = 27 [37]; Nb/Ta = 17.5 ± 2.0 [38]). Therefore, the magma source region should be dominated by the juvenile lower crustal materials.

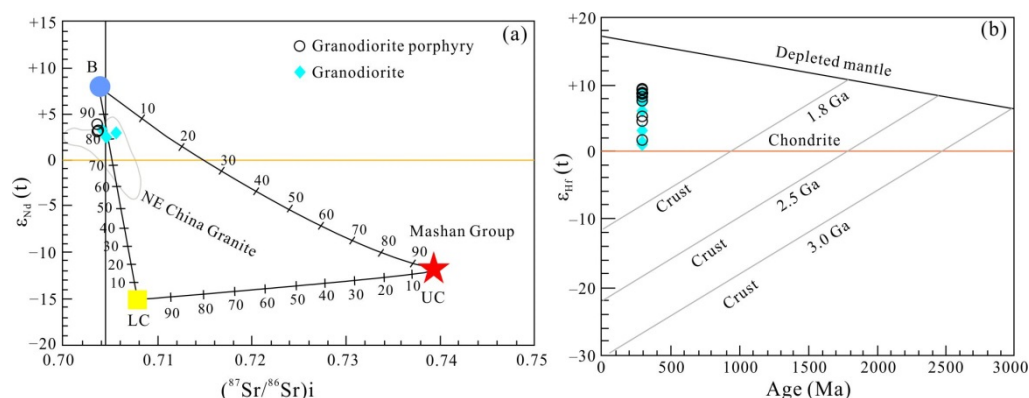


Figure 12. $\epsilon_{\text{Nd}}(t)$ – $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $\epsilon_{\text{Hf}}(t)$ –Age diagrams. (a) The field for NE China Granite is from [34]. Isotope modeling for a simple mixing in the source region of Zhunsujihua granitoid plutons is also shown (only the samples with $(^{87}\text{Rb}/^{86}\text{Sr})_i \leq 10$ are plotted in this diagram). The mantle-derived component is represented by basaltic rock (B) with the following calculated parameters: $\epsilon_{\text{Nd}}(t) = +8$, Nd = 15 ppm, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.704$, Sr = 200 ppm. The upper continental crust (UC) component (the red star) is represented by Proterozoic Mashan Complex metamorphic rocks with $\epsilon_{\text{Nd}}(t) = -12$, Nd = +30 ppm, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.740$, Sr = 250 ppm; for lower continental crust (LC) (the yellow square): $\epsilon_{\text{Nd}}(t) = -15$, Nd = 20 ppm, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.708$, Sr = 20 ppm. All end-number data are derived from [34]. (b) Plot of $\epsilon_{\text{Nd}}(t)$ vs. crystallization ages of zircons for the Zhunsujihua granitic intrusions. The Hf isotopic evolution line of the Archean average crust with $f_{\text{Lu}/\text{Hf}} = 0.015$ is after [39].

The zircon Lu–Hf isotopic system has a higher closure temperature compared with the whole-rock Rb–Sr or Sm–Nd isotopic system [40], so it can be applied to track the source region and identify the magma mingling process more effectively [41]. In the $\epsilon_{\text{Hf}}(t)$ –Age diagram (Figure 12b), all samples plot into the field between the chondrite uniform reservoir reference line and depleted mantle evolution line. The two-stage Hf model ages from 564 to 1150 Ma suggest that the crust–mantle differentiation could be dated back to the Mesoproterozoic. The $\epsilon_{\text{Hf}}(t)$ values of zircons from the Zhunsujihua granodiorite and granodiorite porphyry vary widely (+1.3~+9.4) (Table 5) and even show negative values [12], indicating that the source magma was mainly derived from the juvenile crust, but incorporated ancient crustal components [42]. Mao et al. (1999) [43] concluded that the rhenium contents in molybdenite decrease when going from a mantle source ($\approx 10^{-4}$), to mixtures between mantle and crust ($\approx 10^{-5}$), and then to crust ($\approx 10^{-6}$). The rhenium content of molybdenite in the Zhunsujihua deposit ranges from 9×10^{-6} to 2.8×10^{-5} [31], which also indicates that the ore materials originated from a mixed source between the crust and mantle. Finally, we can conclude that the Zhunsujihua granitic intrusions most likely originated from partial melting of the juvenile lower crust derived from the depleted mantle, but mixed with pre-existing crustal components.

6.3. Tectonic Implications

Both granodiorite and granodiorite porphyry are characterized by enrichments in LILEs and LREEs, and a relative depletion in HFSEs, similar to those of arc volcanic rocks [44]. In the Sr/Y vs. Y and Rb vs. (Y + Nb) diagrams, all rock samples fall into the island arc or the continental margin arc field (Figure 13) [45,46]. It seems that Zhunsujihua granodioritic intrusions were formed in the arc tectonic setting. This is supported by other evidence. From the late Carboniferous to the early Permian, there was a successive volcanic–sedimentary sequence in the region, i.e., the Baoligaomiao Formation [47]. The volcanic rocks of the Baoligaomiao Formation are primarily rhyolite, dacite, and andesite [48], which

show analogous geochemical characteristics to the Zhunsujihua granitic intrusions and igneous rocks in an active continental margin setting [6,47,49]. Furthermore, Chai et al. (2018) [50] reported an arc-like adakitic granodiorite in the Baiyinwula, which yielded a zircon U-Pb age of 318 ± 1.8 Ma; Chen et al. (2000) [51] proposed that Baolidao rocks in Sonidzuoqi was emplaced at ca. 310 Ma under the subduction setting.

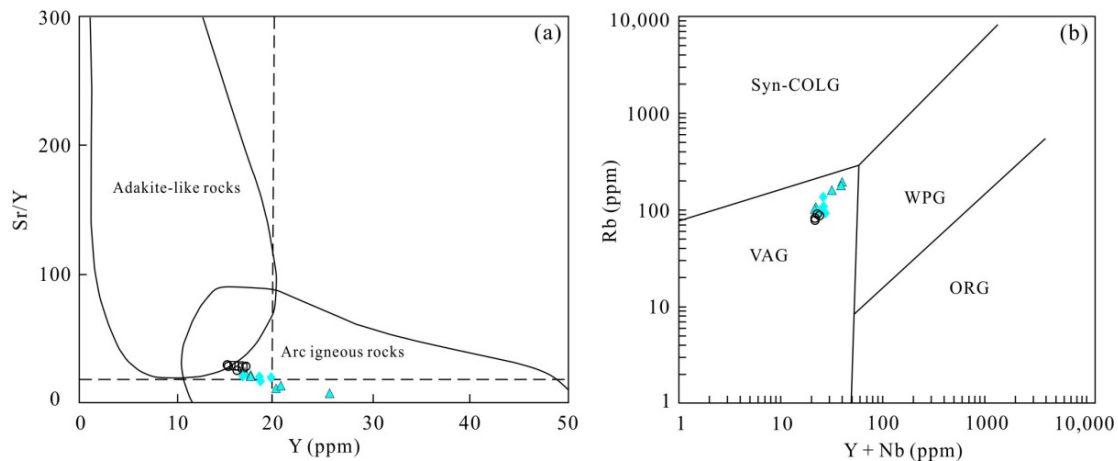


Figure 13. Non-active element diagram of granite tectonic environment discrimination. (a) Sr/Y vs. Y diagram, according to [45]. (b) Rb vs. (Y + Nb) diagram, according to [46]. VAG = volcanic arc granite, WPG = within plate granite, Syn-COLG = syn-collision granite, ORG = ocean ridge granite. Legends are the same as in Figure 9.

6.4. Oxygen Fugacity of Magmas

The oxygen fugacity of the magma is an important parameter of the redox state during fractional crystallization, which affects the mineralization of many metals, especially chalcophile and siderophile elements, such as Cu and Au [52]. Under relatively low oxygen fugacity conditions, the sulfur in magma mainly exists in the form of S^{2-} . The sulphophile elements such as Cu preferentially combine with S^{2-} to form sulfide and remain in the magma chamber. Under high-oxygen fugacity conditions, S^{2-} is easily oxidized to SO_4^{2-} or SO_2 and dissolved in the silicate melt. A higher concentration of Cu and other sulphophile elements can be further transported into magmatic hydrothermal fluids and enriched for mineralization. In this study, we calculated the Ce^{4+}/Ce^{3+} ratio of zircons to represent the relative oxygen fugility of the magma during fractional crystallization based on the following formula [53]:

$$\left[Ce^{4+}/Ce^{3+} \right]_{zircon} = (Ce_{melt} - Ce_{zircon} / D_{Ce^{3+}}^{zircon/melt}) / (Ce_{zircon} / D_{Ce^{4+}}^{zircon/melt} - Ce_{melt}) \quad (1)$$

where $D_{Ce^{3+}}^{zircon/melt}$ and $D_{Ce^{4+}}^{zircon/melt}$ are calculated from the linear fit of trivalent cations (REE^{3+}) and tetravalent cations, including U^{4+} , Th^{4+} , and Hf^{4+} , respectively, and Ce_{zircon} and Ce_{melt} are the Ce contents in zircon and whole rock, respectively. The detailed calculation process is described in [53]. Trail et al. (2012) [54] converted the relative oxygen fugacity to the absolute oxygen fugacity ($\log(f(O_2))$) by calibrating the Ce anomaly of zircon as a function of temperature and oxygen fugacity:

$$\ln(\delta Ce)_D = (0.1156 \pm 0.0050) \times \ln(f(O_2)) + (13860 \pm 708)/T(K) - 6.125 \pm 0.484 \quad (2)$$

where the values of $(\delta Ce)_D$ can be replaced by $[Ce^{4+}/Ce^{3+}]_{zircon}$, and T is the zircon crystallization temperature in K, which can be obtained using the Ti thermometer of zircon [55]:

$$T(K) = (5080 \pm 30) / [(6.01 \pm 0.03) - \lg(Ti)] \quad (3)$$

The oxygen fugacity data of granodiorite and granodiorite porphyry calculated with the above empirical formula are listed in Table 2 and plotted in the $\log f(\text{O}_2)$ - $1000/T$ diagram. As shown in Figure 14, most of the oxygen fugacity ($\log f(\text{O}_2)$) data for granodiorite porphyry and granodiorite are above the FMQ buffer line, with an average value of $\Delta\text{FMQ} + 1.1$ and $\Delta\text{FMQ} + 3.5$, respectively (Table 2). It is notable that the clean zircon is generally considered as a La, Pr-free mineral with La, Pr ≤ 0.1 ppm [56]. Those zircons with La or Pr > 0.1 ppm may contain undetected inclusions, which would result in unreliable oxygen fugacity calculations based on the REE composition of zircons [57]. In other words, the oxygen fugacity values ($\Delta\text{FMQ} = +0.5$ to $+5.6$; Table 2) calculated using REE contents of clean zircons are robust (Figure 14), and it can be concluded that both granodioritic intrusions had a high oxygen fugacity, which was favorable for the migration of ore-forming elements.

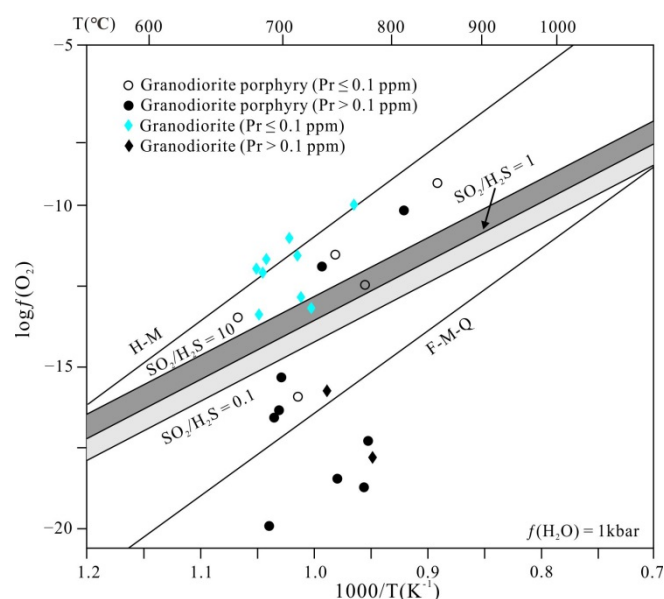


Figure 14. The oxygen fugacity $\log f(\text{O}_2)$ - $1000/T$ diagram of granodiorite porphyry and granodiorite. Abbreviations: F-M-Q = fayalite-magnetite-quartz buffer line, H-M = hematite-magnetite buffer line. SO_2 - H_2S buffer lines are also shown in the diagram.

6.5. Controls on the Formation of the Zhushujihua Mo-Cu Deposit

A previous study has revealed that source regions [58], the magmatic process (e.g., fractionation) [59], and high-oxygen fugacities [60] were all critical for the formation of porphyry Mo deposits. Although many scholars have agreed that the Mo is mainly derived from the ancient lower crust [61,62], our study suggests that partial melting of the juvenile lower crust played an important role in the genesis of granodioritic magma related to the Mo mineralization in the Zhushujihua deposit, which is similar to other porphyry deposits in the XMOB [63] (e.g., the Daheishan Mo deposit [64]; the Badaguan Cu-Mo deposit [65], the Luming Mo deposit [66]). In addition, our data indicate a high oxygen fugacity for the granodioritic magma in Zhushujihua. Such oxidized magmas are common in subduction zones [67]. A high magmatic oxygen fugacity can enable Mo to migrate in the form of Mo^{6+} in the residual melt until fluid exsolution, rather than in the form of Mo^{4+} partitioning into Ti-bearing magmatic minerals or magmatic sulfides [68]. Furthermore, the negative Eu, Ba, and Sr anomalies indicate that the parental magma that formed granodiorite and granodiorite porphyry experienced extensive fractionation of plagioclase or K-feldspar. The differentiation index (DI) of magma was used to quantify the degree of fractional crystallization. The results show that both the granodiorite and granodiorite porphyry have high DI values of 92.3–93.9 and 92.7–94.3, respectively. These values are similar to those (93–97) of the Chalukou porphyry Mo deposit [69]. Li et al. (2014) [69] argued that

the felsic magma with high DI values could maintain long-term fractional crystallization and ultimately contribute to Mo enrichment in the residual magma.

In summary, the Mo (probably also Cu) of the Zhunsujihua deposit was mainly sourced from the juvenile lower crust. A high magmatic oxygen fugacity and fractional crystallization played key roles in forming the Zhunsujihua deposit.

7. Conclusions

The granodioritic intrusions exposed in the Zhunsujihua porphyry Mo-Cu deposit mainly consisted of granodiorite and granodiorite porphyry, and both were emplaced at ca. 296.0–301.5 Ma in a continental margin arc setting.

Granodiorite and granodiorite porphyry have a unified magma source region, both of which were derived from partial melting of the juvenile lower crust, but mixed with ancient crustal components.

The Mo in the Zhunsujihua deposit was mainly sourced from the juvenile lower crust. A high magmatic oxygen fugacity and preliminary enrichment of Mo through fractional crystallization were critically important in the formation of the Zhunsujihua deposit.

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