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Zircon U-Pb, Molybdenite Re-Os and Quartz Vein Rb-Sr Geochronology of the Luobuzhen Au-Ag and Hongshan Cu Deposits, Tibet, China: Implications for the Oligocene-Miocene Porphyry–Epithermal Metallogenic System



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Abstract: The Gangdese metallogenic belt in Tibet is an important copper and iron polymetallic, metallogenic belt in western China. The Luobuzhen epithermal Au-Ag and Hongshan porphyry Cu deposits, as two new discovery deposits in the last few years, are located in the western Gangdese metallogenic belt. In this paper, we present quartz vein Rb-Sr isochron, zircon U-Pb and molybdenite Re-Os ages for a better understanding of the minerallogenetic epoch of the deposits. Geochronological data show that the Rb-Sr isochron age of a quartz vein in a Luobuzhen Au-Ag deposit is 21.1 ± 1.8 Ma (MSWD (mean standard weighted deviation) = 0.19), zircon U-Pb ages from diorite and granodiorite porphyry in Hongshan Cu deposit are 50.0 ± 0.4 Ma (MSWD = 0.94) and 23.7 ± 0.1 Ma (MSWD = 0.73), respectively, and a Re-Os isochron age of molybdenite in Hongshan Cu deposit is 23.0 ± 2.0 Ma (MSWD = 0.014). These data suggest that the Luobuzhen epithermal Au-Ag and Hongshan porphyry Cu deposits formed at ca. 23–21 Ma, which were controlled by the same magmatic hydrothermal events. Formation of both the Luobuzhen and Hongshan deposits were obviously earlier than the Miocene porphyry metallogenetic events in the Gangdese porphyry copper belt.

Keywords: isotopic geochronology; epithermal deposit; porphyry deposit; metallogenic system; gangdese metallogenic belt; Tibet

1. Metallogenic Geological Background

Porphyry deposits and epithermal deposits often appear together in space and time, forming a complete set of the porphyry-epithermal metallogenic system, e.g., the Zijinshan Cu-Au deposit in Fujian, China, or Lepanto-Far Southeast Cu-Au deposit in the Philippines, etc. [1–7]. Establishing the temporal relationship between the porphyry deposit and the epithermal deposit is a necessary condition to determine the porphyry-epithermal metallogenic system. The Gangdese metallogenic belt, located in the southern Tibet, is characterized by a great number of porphyry and skarn deposits [8–12]. Porphyry deposits always occur together with the skarn deposits, and form a porphyry-skarn metallogenic system, e.g., the Zhibula and Langmujiaguo skarn copper deposits developed around the Qulong porphyry Cu-Mo deposit [10,12,13]. However, the porphyry-epithermal metallogenic system has not been reported so far. In recent years, the Luobuzhen epithermal Au-Ag and Hongshan porphyry Cu deposits were discovered in the western Gangdese metallogenic belt, they are adjacent to each other in space, and which likely form a new porphyry-epithermal metallogenic system.

However, it is not clear whether or not the formation of these two deposits was associated with the same magmatic hydrothermal event. To determine the temporal relationship between these two deposits, we have performed field surveys and detailed geochronological studies. New geochronological data show that the metallogenic time of the Luobuzhen epithermal Au-Ag deposit is basically the same as that of the Hongshan porphyry Cu deposit, which both belong to the same magmatic hydrothermal mineralization event in the late Oligocene to the early Miocenee.

The Gangdese metallogenic belt is located in the south of Lhasa terrane (Figure 1a) which originated from the Australian plate [14], and is a part of a typical continental orogenic porphyry metallogenic belt [9,15,16]. In the Early Cretaceous Epoch, the northern margin of the Lhasa block collided with the Qiangtang block, and in the Paleocene, the Himalayan orogenic belt formed, and this resulted in the formation of the shortened and thickened continental crust [11,14,17–19]. The Precambrian crystalline basement in the middle of the Lhasa block underwent multiple metamorphism, and was covered by a large number of Carboniferous-Permian metasedimentary rocks and Cretaceous volcanic sedimentary strata. The nascent crust on the north and south sides were mainly composed of Mesozoic and Cenozoic marine, alternating marine and continental strata, and volcanic sedimentary strata [14,20]. Since the Paleozoic, the Lhasa block had undergone the polycyclic tectonic-magmatic evolution. Magmatism in the Lhasa block was mainly activated in the Cretaceous, Eocene and Miocene Periods, and they are younger from north to south [19]. Magmatic activities in the Early Cretaceous were related to the southward subduction of the Bangong-Nujiang Tethyan Ocean [14,21] or the northward subduction of the Neo-Tethys Ocean [14,22]. Late Cretaceous-Eocene magmatic rocks were formed during the collision of the Indian and Asian continents [19,23,24]. Miocene magmatic rocks were formed during the post-collision extension of the Indian and Asian continents [11,25].

The Gangdese porphyry copper belt, located in south-central Tibet, is nearly long 600 km from Gongbujiangda County in the east to Angren County in the west (Figure 1a) [26,27]. The porphyry deposits are spatially controlled by the east-west thrust faults that run parallel to the main collisional orogenic belt, and also by the normal fault system across the Lhasa block, where these deposits exhibit typical distribution characteristics with east-west trending zonation and north-south trending stringing [26,28]. Mineralization ages from porphyry exhibit multiple stages and are mainly produced in three periods, including 177–169 Ma in Xiongcun porphyry Cu-Au deposit, 54–45 Ma in Jiru and 18-12 Ma in Qulong, Tinggong and Zhunuo (Figure 1a) [15,29-31]. The metallogenic quartz diorite porphyry in 177-169 Ma originated from a partial melting of the Mantle, which was related to the northward subduction of the Neo-Tethys Ocean [15,29]. The metallogenic porphyry in 54–45 Ma was formed from a partial melting of the metasomatic mantle, which was related to the collision of the Indian and Asian continents [11,32]; The super-large porphyry copper deposits in Qulong, Tinggong, Zhunuo, etc., were formed in 18–12 Ma. Metallogenic porphyry had the characteristics of adakitic magma, and resulted from the partial melting of lower crustal materials, an injection of enriched mantle or the hybridization of upper crustal materials, and was the product of crustal extension after the collision and uplift of the Indian and Asian continents [16,30,33].

Luobuzhen Au-Ag and Hongshan Cu deposits are located in the northern margin of the western volcanic-magmatic arc of the Gangdese continental margin (Figure 1b). The main exposed strata in this region is the Eocene Linzizong Group, which is a set of intermediate-acid volcaniclastic rocks, and can be divided into the Dianzhong Formation, Nianbo Formation and Pana Formation from bottom to top. The volcanic rocks in the Dianzhong Formation belong to the calc-alkaline–high-K calc-alkaline series, and have the characteristics of island arc volcanic rocks, and were produced in the late subduction period of the Neo-Tethys Ocean lithosphere to the initial collision stage of the Indian and Asian continents. The volcanic rocks in the Nianbo Formation are of the calc-alkaline series, and were produced in the collision stage of the Indian and Asian continents. The volcanic rocks in the Nianbo Formation are of flat, 35]. The fault system in the region was the Eocene low-angle thrust fault in the NWW direction, the Miocene extensional structure in the NWW direction, and a normal fault in the NS direction. The intermediate-acid intrusive

rocks intruded into the volcanic rock stratum of the Linzizong group in the form of batholith, strain or dike, forming a complex volcanic-magmatic system. The intrusive rocks can be divided into Eocene and Miocene magmatic activities.

Eocene intermediate-acid rocks have the characteristics of island arc granite; the geochemical characteristics of Miocene intermediate-acid rocks show the affinity of adakite magma [12,30].



Figure 1. Map showing (**a**) the simplified geology of the Lhasa terrane, and the distribution of major porphyry and Au Epithermal, deposits in the Gangdese belt, (**b**) Geological map of the Luobuzhen-Hongshan area.

2. Geological Characteristics of Deposit

2.1. Luobuzhen Epithermal Au-Ag Deposit

The strata exposed in the Luobuzhen Au-Ag deposit district is the Pana Formation, which generally inclines northeastward with the dip angle of 73–81°, and mainly consists of dacite and rhyolite. Diorites are distributed in the south of the deposit district and outcrop in the form of batholith, and the zircon U-Pb age is about 50 Ma [12]. Granite porphyries are controlled by east-west faults, and intrude into diorites and the Pana Formation in the form of dikes of different sizes, and its zircon U-Pb age is 17 Ma (Figure 2a) [12]. Granite porphyry is grey-white, and is of massive structure and porphyritic texture, and the matrix is of a cryptocrystalline texture. Phenocrysts in granodiorite are

plagioclase, quartz and biotite. Main components in the matrix are micro quartz and feldspar, and accessory minerals are mainly apatite, magnetite and zircon. A series of thrust faults in the NWW direction occurs at the deposit district, and this group of faults is 600–3000 m long and 40–80 m wide and trend towards the south, while their dip angle is 40–82°.



Figure 2. Geological map of the Luobuzhen Au-Ag polymetallic deposit and Sample photos. (a) geological sketch map of Luobuzhen Au-Ag polymetallic deposit, (b) symbiosis of gold and galena, (c) pyrite is metasomatized by galena and chalcopyrite, (d) Au-Ag orebody in fractured zones, (e) altered rock type of gold ore, (f) sulfide and quartz in Au-Ag ore. Qz: quartz, Ser: sericite, Py: pyrite, Cpy: chalcopyrite, Gn: galena, Sp: sphalerite, Gl: native gold, Sul: metal sulfide.

Au-Ag orebodies are controlled by faults in the NWW direction and are hosted in the volcanic rocks of the Pana Formation or the contact part between the volcanic rocks of Pana Formation and Eocene diorite (Figure 2a). The orebodies are mainly composed of quartz veins, altered rocks and breccia, with a length of 80–1000 m, a thickness of 0.8–14.6 m, a depth of over 600 m, a gold grade of 1.2–4.3 g/t, and a symbiotic (associated) silver grade of 9.1–177.5 g/t. The ore is characterized by the disseminated structure and mesh-vein structure and secondly of the brecciated structure which is represented by early magmatic breccia cemented by quartz and carbonate minerals. Metal minerals in the ore are mainly natural gold, dyscrasite, galena, sphalerite, arsenopyrite and pyrite.

Gangue minerals are quartz, chalcedony, sericite, calcite and chlorite. Natural gold occurs in the cracks of pyrite in a xenomorphic granular manner and coexists with galena, sphalerite and chalcopyrite (Figure 2b–f). The dyscrasite is metasomatized in galena as xenomorphic granular or irregular aggregates. The arsenopyrite is mostly distributed in a scattered and disseminated manner in medium-fine grained idiomorphic-hypidiomorphic crystals. The alteration types of the surrounding rock mainly include sericitization, silicification, chloritization, carbonation, etc. Among them, the beresitization is closely related to the gold mineralization. Three-dimensional zoning is obvious during the alteration of surrounding rock, and the veins and surrounding rocks show a horizontal zoning from sericitolitization, carbonatation to propylitization, and there are zoning characteristics from deep chlorite, sericite, fine-grained quartz veins to shallow illite, geyserite and chalcedony layers vertically. According to the paragenesis of minerals and transection relationship of vein bodies in the field and microscope, three metallogenic stages in the Luobuzhen Au-Ag deposit have been recognized. In the first stage, the paragenetic minerals include quartz and pyrite, the quartz is metasomatic in surrounding rocks on both sides, and coexists with a certain amount of pyrite. In the second stage, the paragenetic minerals include quartz, chalcedony, gold and sulfides, while the quartz and microcrystalline chalcedony veins are formed, and arsenopyrite, sphalerite and other sulfides are contained. In the third stage, the paragenetic minerals include quartz and carbonate vein, and in addition the quartz-calcite veins are formed, which cut through the early vein bodies.

2.2. Hongshan Porphyry Cu Deposit

The Hongshan porphyry Cu deposit is about 2 km away from this Luobuzhen Au-Ag polymetallic deposit. The strata exposed in the deposit district is mainly the Pana Formation of the Linzizong Group (Figure 3) which consists of grey white dacitic tuff, andesite, andesic tuff, etc. Diorite (Figure 4a,b) outcrops in the form of batholith, and is the most important granite in the deposit district, and later granodiorite porphyry intrudes into the diorite in the form of strain or dike. Granodiorite porphyry is grey-white and with porphyritic-like texture and massive structure. The phenocryst is mainly composed of potassium feldspar and quartz, and the potassium feldspar is of an idiomorphic platy structure, and the cleavage plane is wide and smooth, and the content is about 10%; the matrix is mainly composed of feldspar, quartz and biotite, in which the feldspar is of platy or granular structure, and the content is about 65%; the quartz is colorless, transparent and granular, and the content is about 20%; the content of biotite is about 5%(Figure 4c,d).



Figure 3. Geological map of the Hongshan Porphyry Copper Deposit.

Copper orebodies mainly host in the granodiorite porphyry bodies, diorites in its external contact zone and volcanic rocks of Pana Formation, and occur as the irregular ellipsoidal structure, and are distributed in NE-SW direction, and the mineralized area is about 0.6 km². It is controlled by a reticular fissure system, and the mineralization forms are mainly disseminated and reticulated. Ore minerals mainly include pyrite, chalcopyrite and molybdenite, with minor bornite. Gangue minerals mainly

include quartz, sericite and chlorite. The ore is characterized by a veinlet-disseminated structure, and an earthy, honeycomb, massive, colloidal and scattered structure. Hydrothermal alteration includes silicification, sericitization, cyanolitization and carbonation. Hydrothermal alteration in the contact zone between granodiorite porphyry and diorite is beresitization, while it is propylitization in volcanic rocks of the Pana Formation.



Figure 4. Field and Microscopic Photographs of Samples from Hongshan Porphyry Copper Deposit. (a) photograph of diorite specimen, (b) microscopic photo of diorite, (c) photograph of granodiorite specimen, (d) microscopic photograph of granodiorite, (e) quartz sulfide veins in copper ore, (f) microscopic characteristics of Sulfide. Qz: quartz, Ser: sericite, Pl: plagioclase,Hbl: amphibole, Bit: biotite, Py: pyrite, Cpy: chalcopyrite, Mol: molybdenite, Hem: hematite, Mag: magnetite, Sul: metal sulfide.

3. Sampling and Analytical Methods

Seven gold ore samples are collected from Luobuzhen Au-Ag polymetallic deposit for Rb-Sr isotopic analysis. Gold ore with 2.16–4.3 g/t Au has been altered. The sulfide-quartz vein in the altered host rock is the product of the main metallogenic stage, and the quartz in the vein body is smoky gray and of poor idiomorphism (Figure 3e,f). One granodiorite and granite porphyry samples are collected from Hongshan porphyry Cu deposit respectively for zircon U-Pb dating. Sulfide-quartz veins are developed in the granodiorite and granite porphyry and undergo different degrees of alteration, including sericitization and silicification. Five molybdenite samples used for Re-Os isotope testing are selected from sulfide-quartz veins in Hongshan porphyry Cu deposit (Figure 4e,f).

Rb-Sr isotope analysis was carried out at the Isotope Lab of Beijing Institute of Geology of China National Nuclear Corporation, China. Quartz vein samples were selected and cleaned in the ultrasonic cleaning machine with ultra-pure water. Samples were dissolved and decomposed by hydrofluoric and perchloric acid with ⁸⁵Rb + ⁸⁴Sr mixture diluent. Rubidium and strontium are separated and purified with the ion exchange method. The strontium isotope was analyzed by a single rhenium filament. Quartz samples were dissolved with a drop of high-purity water and were placed at the rhenium ribbon, and then were dried under 1 Ampere. A drop of propellant was added into all samples, and then these samples were made to dry. The electric current for heating slowly increased at 2 A, and kept for about 2–3 s, and then dropped to 0 A in turn. The rubidium isotope was measured by using three ribbons. The sample was also dissolved with a drop of high-purity water and was placed at the outer tantalum ribbon. The electric current for heating slowly increased at 1.5–1.7 A and kept for about 3–5 s, and then dropped to 0 A in turn. The isotope ratios were obtained by a

high-precision solid-state thermal ionization mass spectrometer, IsoProbe-T. The analytical instrument is equipped with 9 Faraday cups and 4 ion count detectors. Sr and Rb isotopes were analyzed by a static multi-receiving way. The sample-diluent mixture is measured by a mass spectrometry, and the strontium isotope ratios were given after a mass fractionation correction and diluent subtraction. During the calibration of the strontium isotope diluent, the mathematical iteration is done by changing the fractionation correction factor of the diluent so that the ratio of strontium isotope in the sample is approximate to the standard value, thus achieving the purpose of correcting the mass fractionation effect of the diluent isotope ratio. The mass fractionation was corrected with the ⁸⁶Sr/⁸⁸Sr value of 0.1194, and an NBS987 value of 0.710250 \pm 0.00007 Rb and Sr background values are 2 \times 10⁻¹⁰g and 2 \times 10⁻¹⁰g, respectively. The age data were processed by the Isoplot/Ex Version 3.23 program [36].

Zircon LA-ICP-MS U-Pb isotopic analysis was completed in Wuhan SampleSolution Analytical Technology Co., Ltd., China. The GeolasPro laser ablation system is composed of a COMPexPro 102 ArF (Coherent, Silicon Valley, CA, USA) 193 nm excimer laser and MicroLas optical system, and the ICP-MS model is Agilent 7700e. Helium gas is used as the carrier gas for ablation, and the diameter of the laser beam spot is $32 \,\mu$ m, and the international standard zircon 91500 and glass standard material NIST610 are internal standards. The 206 Pb/ 238 U age precision of zircon single point analysis is better than 3%. Data processing and concordia plot drawing are finished by ICPMSDataCal and Isoplot/Ex Version 3.23 program [36].

Molybdenite Re-Os isotope analysis was performed using an inductively coupled plasma mass spectrometer (ICPMS) at the Re-Os Isotope Chronology Laboratory of National Research Center for Geoanalysis. The selected molybdenite samples were crushed in an agate mortar, and then molybdenite for Re-Os dating was handpicked under a binocular microscope to remove the impurities. The molybdenite samples were accurately weighed and placed at the bottom of the Carius tube using a long slim-necked funnel. The liquid nitrogen was slowly added into an insulation cup with a half level of ethanol, and then it was made to mix. The Carius tube was placed into the flask under the freezing conditions at the bottom of the Carius tube. ¹⁸⁵Re and ¹⁹⁰Os mixture diluent, 2 mL of 10 mol/L HCl, and 6 mL of 16 mol/L HNO₃ were placed at the bottom of the Carius tube using a long slim-necked funnel. After being frozen at the bottom of the tube, the slim neck of the Carius tube was sealed with a propane oxygen flame. When its temperature was reduced to 25 °C, it was placed into a stainless steel sleeve, and in turn it was placed into an air-blast oven, and then gradually heated up to 230 °C, and kept warm for 10 h. When samples became cooled, they were taken out. Before samples were directly used for the measurement of ICP-MS, Os is purified by distillation. The residual liquid was used to separate Re from it. Put 10 mL 5 mol/L NaOH into the residual liquid and transfer it into an alkaline medium. The supernatant was put into a 120 ml Teflon separatory funnel, and 10 mL acetone was added, and this further extracted the Re 2 mL 5 mol/L NaOH solution was added into the separatory funnel and shaken for 2 min in order to wash off the impurities in the acetone phase. When the water phase was removed, and the acetone was discharged into a 100 mL glass beaker with 2 mL water. The sample solution was heated up 50 °C until it was dry, then there were added a few drops of concentrated HNO_3 until it evaporated, and we lastly removed the residual Os. The residue was dissolved with several milliliters of 2% diluted HNO₃. The Re isotope ratio was determined using ICP-MS. If the amount of salt in the Re solution was over 1 mg/mL, Na must be removed using the cation exchange column. The Re-Os isotope analysis process was finished by an inductively coupled plasma source mass spectrometer TJA X-series ICP-MS manufactured by America TJA. The blank Re, Os and ¹⁸⁷Os values were $0.0024 \pm 0.0003 \,\mu g/g$, $0.00036 \pm 0.00005 \,\mu g/g$, and $0.00002 \pm 0.00002 \,\mu g/g$, respectively, which are far less than the Re and Os contents in samples and standard samples. Common Os is calculated by measuring the ¹⁹²Os/¹⁹⁰Os ratio according to the atomic chart and isotope abundance chart. National standard sample HLP is used to monitor the chemical process and to analyze the data reliability. The average Re-Os age for HLP is 220.8 ± 2.4 Ma, which is consistent with the standard value of 221.4 ± 5.6 Ma within the error range, so the measured molybdenite data is accurate and reliable. The detailed process of analysis was described in some listed references [37].

4. Results

4.1. Quartz Vein Rb-Sr Isotopic Age

Rb-Sr content and isotopic data from seven quartz samples in the Luobuzhen Au-Ag deposit are shown in Table 1. Rb content in quartz veins range from 2.05 μ g/g to 2406 μ g/g, Sr content ranges from 1.28 μ g/g to 657 μ g/g, ⁸⁷Rb/⁸⁶Sr ratios range from 4.616 to 145.102, and ⁸⁷Sr/⁸⁶Sr ratios range from 0.70803 ± 0. 000017 to 0.74960 ± 0. 000022. The Rb-Sr isochron age of quartz veins calculated by the ISOPLOT program is 21.1 ± 1.8 Ma, and the initial ratio of ⁸⁷Rb/⁸⁶Sr is 0.7065 ± 0.0015 (MSWD = 0.19) (Figure 5a).

| Sample Number | Name of the Sample | Rb(µg/g) Sr(µg/g) | | ⁸⁷ Rb/ ⁸⁶ Sr | ⁸⁷ Sr / ⁸⁶ Sr | ±1σ | |
|------------------|-----------------------|-------------------|------|------------------------------------|-------------------------------------|----------|--|
| LBZ01 | quartz | 2.05 | 1.28 | 4.616 | 0.70803 | 0.000017 | |
| LBZ02 | quartz | 2406 | 657 | 10.606 | 0.70907 | 0.000019 | |
| LBZ03 | quartz | 12.1 | 2.72 | 12.911 | 0.71057 | 0.000014 | |
| LBZ04 | quartz | 101 | 10.7 | 27.244 | 0.71398 | 0.000012 | |
| LBZ05 | quartz | 55.6 | 3.81 | 42.254 | 0.71958 | 0.000017 | |
| LBZ06 | quartz | 35.8 | 2.52 | 52.176 | 0.72310 | 0.000011 | |
| LBZ07 | quartz | 309 | 5.51 | 145.102 | 0.74960 | 0.000022 | |

Table 1. Rb-Sr isotope analysis of quartz in the Luobuzhen Au-Ag deposit.



Figure 5. Diagrams of Rb-Sr isochron (**a**), 1/Sr versus ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ (**b**) and 1/Rb versus ${}^{87}\text{Rb}/{}^{86}\text{Sr}$ (**c**) of quartz from the Luobuzhen deposit (modified after [38]).

4.2. Zircon U-Pb Ages

Zircon U-Pb isotopic data in diorite and granodiorite porphyry samples from the Hongshan porphyry copper deposit are shown in Table 2. Most zircons are short-acicular, yellow to colorless, transparent crystals. The CL images show oscillatory zoning and indicate the magmatic growth. The Th content of zircon in the diorite sample varies from 166 ppm to 710 ppm, the U content varies from 168 ppm to 712 ppm, and the Th/U ratios vary from 0.25 to 1.72. The zircon grains have yielded concordant 206 Pb/ 238 U ages of 48.9 to 51.5 Ma with a weighted mean 206 Pb/ 238 U age of 50.0 ± 0.4 Ma (MSWD = 0.94) (Figure 6a). The Th content of zircon in the granodiorite porphyry zircons varies from 16 ppm to 203 ppm, the U content varies from 36 ppm to 188 ppm, and the Th/U ratios vary from 0.69 to 1.33. The zircon grains have yielded concordant 206 Pb/ 238 U age of 23.7 ± 0.1 Ma (MSWD = 0.73) (Figure 6b).

| Lithology | Spote | Th U | | Th/II | Ratio | | | | | | | Age (Ma) | | | Concordance | | |
|--------------|---------|------|-----|-------|--------------------------------------|---------|-------------------------------------|---------|-------------------------------------|---------|--------------------------------------|----------|-------------------------------------|-----|-------------------------------------|-----|----|
| Littiology | 59013 - | ppm | ppm | 11yU | ²⁰⁷ Pb/ ²⁰⁶ Pb | 1σ | ²⁰⁷ Pb/ ²³⁵ U | 1σ | ²⁰⁶ Pb/ ²³⁸ U | 1σ | ²⁰⁸ Pb/ ²³² Th | 1σ | ²⁰⁷ Pb/ ²³⁵ U | 1σ | ²⁰⁶ Pb/ ²³⁸ U | 1σ | % |
| Granodiorite | HS-1.1 | 94 | 65 | 1.44 | 0.0447 | 0.01623 | 0.0223 | 0.00807 | 0.00362 | 0.0001 | 0.00103 | 0.00007 | 22 | 8 | 23.3 | 0.6 | 94 |
| | HS-1.2 | 24 | 79 | 0.30 | 0.04927 | 0.01092 | 0.02451 | 0.00539 | 0.00361 | 0.00009 | 0.00088 | 0.00018 | 25 | 5 | 23.2 | 0.6 | 93 |
| | HS-1.3 | 44 | 116 | 0.38 | 0.04849 | 0.01244 | 0.02443 | 0.00624 | 0.00366 | 0.00009 | 0.00154 | 0.00014 | 25 | 6 | 23.6 | 0.6 | 95 |
| | HS-1.4 | 36 | 72 | 0.50 | 0.04793 | 0.01582 | 0.02398 | 0.00788 | 0.00363 | 0.00011 | 0.00158 | 0.00015 | 24 | 8 | 23.4 | 0.7 | 98 |
| | HS-1.5 | 16 | 50 | 0.31 | 0.04732 | 0.01544 | 0.02389 | 0.00774 | 0.00366 | 0.00014 | 0.00174 | 0.00028 | 24 | 8 | 23.6 | 0.9 | 99 |
| | HS-1.6 | 51 | 65 | 0.78 | 0.04452 | 0.01167 | 0.02244 | 0.00585 | 0.00366 | 0.0001 | 0.00118 | 0.00009 | 23 | 6 | 23.6 | 0.6 | 97 |
| | HS-1.7 | 31 | 73 | 0.43 | 0.04669 | 0.01281 | 0.02377 | 0.00648 | 0.00369 | 0.00011 | 0.0013 | 0.00018 | 24 | 6 | 23.7 | 0.7 | 99 |
| porphyry | HS-1.8 | 203 | 118 | 1.72 | 0.04379 | 0.01546 | 0.02242 | 0.00788 | 0.00371 | 0.00012 | 0.00162 | 0.00006 | 23 | 8 | 23.9 | 0.8 | 96 |
| | HS-1.9 | 31 | 125 | 0.25 | 0.04557 | 0.00867 | 0.02279 | 0.00428 | 0.00363 | 0.00011 | 0.00113 | 0.00017 | 23 | 4 | 23.4 | 0.7 | 98 |
| | HS-1.10 | 51 | 188 | 0.27 | 0.04811 | 0.0031 | 0.02446 | 0.00153 | 0.00369 | 0.00005 | 0.00149 | 0.00006 | 25 | 2 | 23.7 | 0.3 | 95 |
| | HS-1.11 | 52 | 145 | 0.36 | 0.04377 | 0.00338 | 0.02224 | 0.00169 | 0.00369 | 0.00004 | 0.00121 | 0.00006 | 22 | 2 | 23.7 | 0.3 | 92 |
| | HS-1.12 | 60 | 143 | 0.42 | 0.04566 | 0.00291 | 0.02343 | 0.00146 | 0.00372 | 0.00005 | 0.00135 | 0.00004 | 24 | 1 | 23.9 | 0.3 | 99 |
| | HS-1.13 | 20 | 36 | 0.55 | 0.04628 | 0.00841 | 0.02314 | 0.00416 | 0.00363 | 0.00009 | 0.00138 | 0.0001 | 23 | 4 | 23.4 | 0.6 | 98 |
| | HS3-1 | 612 | 680 | 0.90 | 0.0493 | 0.0051 | 0.0514 | 0.0044 | 0.0078 | 0.0002 | 0.0026 | 0.0001 | 50.9 | 4.2 | 49.8 | 1.2 | 97 |
| | HS3-2 | 518 | 585 | 0.88 | 0.0513 | 0.0057 | 0.0529 | 0.0051 | 0.0078 | 0.0002 | 0.0025 | 0.0001 | 52.3 | 4.9 | 49.9 | 1.4 | 95 |
| | HS3-3 | 483 | 531 | 0.91 | 0.0531 | 0.0065 | 0.0525 | 0.0059 | 0.0077 | 0.0002 | 0.0026 | 0.0001 | 51.9 | 5.7 | 49.3 | 1.3 | 94 |
| | HS3-4 | 557 | 647 | 0.86 | 0.0517 | 0.0051 | 0.0552 | 0.0046 | 0.0079 | 0.0002 | 0.0029 | 0.0001 | 54.5 | 4.5 | 50.4 | 1.4 | 92 |
| | HS3-5 | 466 | 518 | 0.90 | 0.0529 | 0.0057 | 0.0547 | 0.0054 | 0.0080 | 0.0005 | 0.0026 | 0.0002 | 54.1 | 5.2 | 51.2 | 2.9 | 94 |
| | HS3-6 | 166 | 168 | 0.99 | 0.0582 | 0.0086 | 0.0560 | 0.0057 | 0.0080 | 0.0004 | 0.0025 | 0.0002 | 55.3 | 5.5 | 51.5 | 2.4 | 92 |
| | HS3-7 | 439 | 459 | 0.96 | 0.0513 | 0.0065 | 0.0505 | 0.0056 | 0.0077 | 0.0002 | 0.0026 | 0.0001 | 50.0 | 5.4 | 49.8 | 1.3 | 99 |
| Diorite | HS3-8 | 425 | 482 | 0.88 | 0.0462 | 0.0069 | 0.0457 | 0.0060 | 0.0076 | 0.0002 | 0.0023 | 0.0001 | 45.3 | 5.8 | 48.9 | 1.4 | 92 |
| | HS3-9 | 660 | 675 | 0.98 | 0.0535 | 0.0046 | 0.0549 | 0.0040 | 0.0077 | 0.0002 | 0.0026 | 0.0001 | 54.3 | 3.8 | 49.6 | 1.0 | 90 |
| | HS3-10 | 391 | 454 | 0.86 | 0.0538 | 0.0075 | 0.0531 | 0.0054 | 0.0077 | 0.0003 | 0.0026 | 0.0002 | 52.6 | 5.2 | 49.3 | 1.7 | 93 |
| | HS3-11 | 571 | 653 | 0.87 | 0.0523 | 0.0057 | 0.0527 | 0.0058 | 0.0076 | 0.0002 | 0.0026 | 0.0001 | 52.2 | 5.6 | 48.9 | 1.2 | 93 |
| | HS3-12 | 171 | 249 | 0.69 | 0.0554 | 0.0180 | 0.0455 | 0.0093 | 0.0076 | 0.0005 | 0.0026 | 0.0004 | 45.1 | 9.0 | 49.1 | 3.0 | 91 |
| | HS3-13 | 306 | 355 | 0.86 | 0.0539 | 0.0089 | 0.0552 | 0.0079 | 0.0078 | 0.0003 | 0.0025 | 0.0002 | 54.6 | 7.6 | 50.1 | 1.9 | 91 |
| | HS3-14 | 341 | 437 | 0.78 | 0.0523 | 0.0056 | 0.0530 | 0.0049 | 0.0078 | 0.0002 | 0.0025 | 0.0001 | 52.4 | 4.8 | 49.8 | 1.3 | 94 |
| | HS3-15 | 389 | 453 | 0.86 | 0.0533 | 0.0061 | 0.0554 | 0.0061 | 0.0079 | 0.0002 | 0.0026 | 0.0001 | 54.8 | 5.9 | 50.4 | 1.3 | 91 |
| | HS3-16 | 439 | 536 | 0.82 | 0.0490 | 0.0069 | 0.0520 | 0.0060 | 0.0080 | 0.0003 | 0.0026 | 0.0002 | 51.4 | 5.8 | 51.1 | 1.6 | 99 |
| | HS3-17 | 416 | 413 | 1.01 | 0.0551 | 0.0071 | 0.0514 | 0.0042 | 0.0076 | 0.0002 | 0.0028 | 0.0001 | 50.9 | 4.1 | 49.0 | 1.4 | 96 |
| | HS3-18 | 348 | 430 | 0.81 | 0.0546 | 0.0076 | 0.0533 | 0.0064 | 0.0077 | 0.0002 | 0.0022 | 0.0001 | 52.7 | 6.2 | 49.7 | 1.3 | 94 |
| | HS3-19 | 451 | 500 | 0.90 | 0.0481 | 0.0054 | 0.0493 | 0.0046 | 0.0079 | 0.0002 | 0.0025 | 0.0001 | 48.8 | 4.4 | 51.0 | 1.2 | 95 |
| | HS3-20 | 608 | 712 | 0.85 | 0.0540 | 0.0049 | 0.0571 | 0.0044 | 0.0080 | 0.0002 | 0.0024 | 0.0001 | 56.4 | 4.2 | 51.1 | 1.1 | 90 |
| | HS3-21 | 710 | 533 | 1.33 | 0.0464 | 0.0052 | 0.0477 | 0.0050 | 0.0080 | 0.0002 | 0.0025 | 0.0001 | 47.3 | 4.8 | 51.4 | 1.3 | 91 |

Table 2. LA-ICP-MS Zircon U-Pb Ages of the granites in Hongshan.





Figure 6. Zircon Cathodoluminescence Photographs and U-Pb Age Maps of Diorite (**a**) and Granodiorite Porphyry (**b**) from the Hongshan deposit.

4.3. Molybdenite Re-Os Age

Re-Os analysis data in five molybdenite samples from the Hongshan porphyry Cu deposit are listed in Table 3. The content of common Os in molybdenite is less than ng/g, and all ¹⁸⁷Os come from β decay of ¹⁸⁷Re. The model ages of molybdenite calculated as per the contents of ¹⁸⁷Re and ¹⁸⁷Os range from 23.08 ± 0.45 Ma to 23.20 ± 0.33 Ma, and yield an isochron age of 23.0 ± 2.0Ma (Figure 7).

| SampleID | w(Re)/(| (ng/g) | w (Normal Os)/(ng/g) | | w(¹⁸⁷ Re) | /(ng/g) | w(¹⁸⁷ Os) | /(ng/g) | Model Age/ma | | |
|----------|-----------------|--------|-------------------------|--------|-----------------------|---------|-----------------------|---------|-----------------|------|--|
| | Tested Value | σ | Tested Value | σ | Tested Value | σ | Tested Value | σ | Tested Value | σ | |
| VZK2-20 | 677,887 | 19,144 | 0.3056 | 0.0126 | 426,065 | 12033 | 164.6 | 1.0 | 23.19 | 0.71 | |
| VZK1-1 | 449,238 | 3888 | 2.475 | 1.542 | 282,355 | 2444 | 109.2 | 0.7 | 23.20 | 0.33 | |
| VZK1-19 | 628,637 | 9604 | 0.6023 | 0.0754 | 395,111 | 6037 | 152.5 | 1.1 | 23.16 | 0.45 | |
| VZK3-4 | 641,181 | 9906 | 0.2209 | 0.1192 | 402,995 | 6226 | 155.0 | 1.0 | 23.08 | 0.45 | |

Table 3. Molybdenite Re-Os isotopic data of Hongshan deposit.



Figure 7. Re-Os isochron ages of molybdenite from the Hongshan porphyry copper deposit.

5. Discussion

Quartz-sulfide veins in breccia-type ores from the Luobuzhen Au-Ag deposit cut across in dacite and diorite breccia, indicating that the Au-Ag mineralization is younger than formation time of dacite and diorite which have been reported as 50.1 Ma and 48 Ma, respectively [12]. The research suggests that the metallogenic temperature in the epithermal Au-Ag deposit is lower, and the Rb-Sr isotope system of hydrothermal minerals (i.e. quartz) can keep closed during the mineralization process, and can be used to directly determine the mineralization age [39,40]. The ore-forming fluid of the Luobuzhen Au-Ag deposit is characterized in a medium-low temperature, a low salinity and a medium-low density, and it contains a small amount of CO₂, N₂, CH₄ and other gases [12]. The primary inclusions in the main stages of the metallogenesis mainly include rich-liquid 2-phase inclusions, pure-liquid inclusions and 3-phase inclusions with the calcite seed crystals [12]. These types of inclusions have coexisting characteristics. The measured values of Rb and Sr are significantly different in the samples, probably due to the uneven distribution of inclusions in the quartz. As mentioned earlier, the formation of gold-bearing quartz veins in the Luobuzhen gold-silver deposit has undergone three stages of

fluid mineralization.

When quartz-gold-sulfide hydrothermal fluid fills along the fissures, the quartz-pyrite veins formed in the early stage recrystallize to a certain extent, while the hydrothermal activity in the quartz-carbonate vein stage is very weak, and the influence on the early gold-bearing quartz veins can be neglected. The metallogenic stages of the three fluids belong to the same hydrothermal alteration metallogenic stage. The metallogenic fluids are of the same origin and form almost simultaneously, so they have the same initial strontium. Each analytical point has different Rb/Sr values, and could produce a good age result. There is no linear relationship between 1/Sr and $\frac{87}{\text{Sr}}$ / $\frac{86}{5}$ Sr(Figure 5c), which are relatively stable, indicating that the $\frac{87}{\text{Sr}}$ / $\frac{86}{5}$ Sr initial value remains basically unchanged during the growth of the quartz, and the test data are reasonable. All analysis points are plotted in the isochron line, and suggest that the Sr isotope of quartz is uniform and well-sealed. Rb-Sr isochron age in quartz veins is 21.1 ± 1.8 Ma, which indicates that these quartz veins formed in the Miocene. Based on the paragenesis among quartz, natural gold and galena, a Rb-Sr isochron age can represent the metallogenic age of the deposit. 17 Ma in granite porphyry [12] is obviously later than Robzhen metallogenic time and is interpreted as a post-metallogenic magmatic event.

Both zircon U-Pb and molybdenite Re-Os systems have high closure temperature and are not easily affected by the late diagenetic, hydrothermal, metamorphic and tectonic events, which can be used to accurately indicate the diagenetic and metallogenic ages [41,42]. A weighted average age of zircon U-Pb from diorite and granodiorite porphyry in the Hongshan porphyry Cu-Mo deposit is 50.0 ± 0.4 Ma and 23.7 ± 0.1 Ma, which indicates that the granodiorite and granite porphyry was formed in the Eocene and Oligocene, respectively. Weighted average age of molybdenite Re-Os in sulfide-quartz vein/stringer is 23.0 ± 2.0 Ma, which indicates that the deposit was formed in the Miocene. The Re-Os age of molybdenite is quite different from that of the diorite, but it is consistent with that of granodiorite porphyry within the error range, which indicates that Hongshan Cu deposit was the product of magmatic hydrothermal activities after the emplacement of Oligocene granodiorite porphyry. The diagenetic ages of granites in Youqiumi and Dongshibu areas around Hongshan deposit are 15.2 Ma and 17 Ma, respectively [12,43], which are obviously later than the metallogenic epoch of the Lobuzhen epithermal gold-silver deposit and the Hongshan porphyry copper deposit, and belong to post-metallogenic magmatic events.

Sr isotope composition of hydrothermal minerals in the metallogenic period and Re content in molybdenite are often used to trace the source of metallogenic materials [44–46]. The surrounding rocks around the Luobuzhen Au-Ag deposit include Pana volcanic rocks, Eocene diorite, Oligocene granodiorite porphyry and Miocene granite porphyry. The average ⁸⁷Sr/⁸⁶Sr initial values of the Pana volcanic rocks is 0.70543 [34]. The Eocene diorite yielded ⁸⁷Sr/⁸⁶Sr initial values of 0.7046–0.7063 [12]. The ⁸⁷Sr/⁸⁶Sr initial value of Oligocene granodiorite porphyry is 0.70649 (Unpublished data).

The Miocene granitoid plutons yielded ⁸⁷Sr/⁸⁶Sr initial values of 0.7071–0.7078 [31]. The initial ⁸⁷Sr/⁸⁶Sr values of Miocene granite and Oligocene granodiorite porphyry are similar, which may be that they were formed in similar magmatic source areas [44–46]. ⁸⁷Sr/⁸⁶Sr initial value of the quartz in the Luobuzhen Au deposit is 0.70803–0.72310 with an average of 0.71405, and is consistent with the ⁸⁷Sr/⁸⁶Sr initial value of the Oligocene granodiorite porphyry and Miocene granite. Considering the metallogenic age of the Luobuzhen deposit, there is a genetic relationship between Au mineralization and Oligocene granodiorite porphyry. The ⁸⁷Sr/⁸⁶Sr initial value of the most quartz in Luobuzhen Au-Ag deposit falls between continental crust and basalt source area [47], which indicates that the metallogenic material was originated from crust-mantle mixed source. Re is mainly enriched in the mantle, which makes it valuable to infer its material source from Re content [45,46]. Re content in molybdenite is 100–1000 μ g/g, which indicates that the metallogenic material comes from the mantle. When it is 10–100 μ g/g, the metallogenic material comes from crust-mantle mixture. When it is 1–n μ g/g or lower, the metallogenic material comes from the crust [45,46]. Re content in Re-Os isotopes of the molybdenite in the Hongshan porphyry Cu-Mo deposit is 449–678 μ g/g with an average of 599 μ g/g, which indicates that the metallogenic material of the deposit comes from the mantle. The research results of fluid inclusions and H, O, S and Pb isotopes also support the above conclusions [12,48].

There are the same metallogenic materials and a small age gap of ca. 2 Ma in the formation time between the Luobuzhen epithermal Au-Ag deposit and Hongshan porphyry Cu deposit, which suggests that two deposits were formed during the same magmatic hydrothermal mineralization event. Both the Luobuzhen epithermal Au-Ag deposit and the Hongshan porphyry copper deposit are centered on ca. 23.7 Ma Oligocene granodiorite porphyry intrusions, which form a porphyry-epithermal metallogenic system (Figure 8). Of course, this conclusion needs to be supported by more studies on the mineralization process. The mostly diagenetic ages of the Miocene metallogenic rock bodies in the Gangdese porphyry copper belt are 17. 8–14.8 Ma [27,31,33,49]. Take the Zhunuo Cu deposit for example, zircon SHRIMP U-Pb age of ore-bearing granite porphyry is 15.6 Ma [27]. Though both the Hongshan Cu deposit and Zhunuo Cu deposit are located at the same tectonic location, about 20 km between two deposits, the age gap of ore-bearing rock bodies in these two deposits is about 8 Ma. In addition, there are ca. 22 Ma inherited zircons in the Zhunuo granite porphyry [27], which indicates that these two deposits are not contemporaneous with metallogenic magmatic activities. 24 Ma magmatic events also can be found in Chongjiang and Nuri [27,50–52]. These metallogenic granite porphyries are characterized by high Sr, low Y, and without Eu anomaly. Their Rb-Sr, Sm-Nd and Pb isotopic values are similar to that of the Miocene Gangdese metallogenic porphyry. These results suggest that they were derived from the mantle-derived source region, and formed in the thickened lower crust [51,53].

Generally, collision between the Indian and Asian continents began at 65–55 Ma and ended the collision at 40–45 Ma, in which about 50 Ma magmatic activities are related to the underplating of mantle-derived magma induced by slab break-off of the Neo-Tethys Ocean [11,35,54]. At 25 Ma, tectonic setting in the Gangdese orogenic belt has changed from convergent to extensional strike-slip [55,56]. The underplating of asthenosphere mantle-derived magma resulted in formation of the thickened nascent lower crust, and the felsic magma produced by partial melting of the lower crust is mixed with mantle-derived magma in a finite manner, and a metallogenic system associated with the porphyry bodies formed in crustal extension environment. Zircon U-Pb age of the granodiorite in the Hongshan Cu deposit is 50.0 ± 0.4 Ma, which is consistent with the underplating time of mantle-derived magma during the continental collision.

The diagenetic age of granite porphyry is 23.7 ± 0.1 Ma, which is obviously older than that of the Miocene metallogenic porphyry in the Gangdese porphyry Cu deposit. Although they are different from Miocene metallogenic magmatic activities in the Zhunuo and Qulong deposits, they are still consistent with the crust-mantle interaction time in the extensional strike-slip process of the Gangdese orogenic belt.

Some scholars believe that both the Xiongcun porphyry Cu-Au deposit and peripheral volcanic structure controlled the Dongga and Donggapu epithermal Au deposits, and formed a Middle Jurassic porphyry-epithermal metallogenic system [57]. However, the metallogenic ages of the Dongga and Donggapu Au deposits are still blank, so it is problematic that they are the products of the same magmatic-hydrothermal activities. The model of the Luobuzhen-Hongshan epithermal-porphyry metallogenic system indicates that it is possible to find the epithermal Au deposit in the overlying magmatic rocks of the Oligocene-Miocene porphyry Cu-Mo deposit, which has great implications for exploration for the epithermal and porphyry deposits in the Gangdese metallogenic belt.



Figure 8. System of the Hongshan-Luobuzhen area.

6. Conclusions

The metallogenesis consists of the Luobuzhen epithermal hydrothermal Au-Ag deposit and the Hongshan porphyry copper deposit represent a consistent spatial-temporal evolution, and showing that the two deposits were controlled by the same tectonic-magmatic metallogenic system. This metallogenic system is centered around the Miocene granitic porphyry and gradually becomes a porphyry copper deposit from the center to the outside. This model resembles the classical porphyry-epithermal hydrothermal metallogenic system.

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