

Article

Geochemical Study of Cretaceous Magmatic Rocks and Related Ores of the Hucunnan Cu–Mo Deposit: Implications for Petrogenesis and Poly-Metal Mineralization in the Tongling Ore-Cluster Region

Ke Shi ^{1,2,3}, Xiaoyong Yang ^{1,*}, Jianguo Du ^{2,3}, Jingya Cao ¹ , Qiu Wan ^{2,3} and Yang Cai ^{2,3}

- ¹ CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Hefei 230026, China; shike890815@163.com (K.S.); jingyacao@126.com (J.C.)
- ² Geological Survey of Anhui Province, Hefei 230001, China; ahdujianguo@126.com (J.D.); att3955@163.com (Q.W.); youngtsai@outlook.com (Y.C.)
- ³ The Coverage Area Deep Resource Exploration Engineering Technology, Innovation Center of Ministry of Natural Resources, Hefei 230001, China
- * Correspondence: xyyang@ustc.edu.cn; Tel.: +86-0551-6465-2201

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Abstract: The Hucunnan porphyry- and skarn-type Cu–Mo deposit is located in the south of the central Shizishan ore field of the Tongling ore-cluster region. The intrusive Hucunnan granodiorite, outcropping in this deposit, has adakitic geochemical features, and its magma is proposed to have originated from partial melting of the oceanic crust mixed with mantle-derived materials. The porphyry-type orebody is hosted in the granodiorite, whereas the skarn-type orebody occurs in the contact zones of intrusions and country rocks. The $\delta^{34}\text{S}$ values of pyrite from the skarn orebodies ranged from +3.9 to +4.7‰ (avg. +4.3‰, $n = 6$), while those of the porphyry orebodies ranged from +5.1 to +6.2‰ (avg. +5.6‰, $n = 4$). $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the pyrites from the skarn orebodies were 38.04–38.45 (avg. 38.26), 15.55–15.66 (avg. 15.59), and 18.16–18.54 (avg. 18.44), respectively ($n = 6$). The pyrites in the porphyry orebodies had $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 38.24–38.36, 15.51–15.662, and 18.10–18.41, respectively (avg. 38.32, 15.58, 18.22; $n = 4$), respectively. The metallogenetic model ages from Re–Os isotopic dating were 138.7 ± 1.9 and 140.0 ± 2.8 Ma, respectively. Geochemical data indicate that the ore-forming fluids in the skarn stage are characterized by high temperature, low acidity, and high oxygen fugacity, and the ore-forming materials were mainly from magma and partly from stratum, proving that the skarn orebody has more stratum materials than the porphyry orebody.

Keywords: EMPA; S–Pb isotopes; Re–Os isotopic dating; metallogenetic model; Hucunnan Cu–Mo deposit; Tongling ore-cluster region

1. Introduction

Porphyry and skarn deposits are widely distributed in the world and represent the most important source of Cu, W, Fe, Mo, Pb–Zn, etc. Various petrogenetic and metallogenetic models that involved porphyry and skarn deposits have been proposed over the past few decades [1–7]. Porphyry-skarn metallogenesis is a dynamic process, and the development of deposits depends on parameters such as the host rock types, geochemistry of the causative intrusions, and local tectonic history. These deposits can form in either convergent arc systems (island arcs or continental arcs) or collisional settings and they are closely related to intermediate to acidic intrusions [8,9]. With the development of adakite

rocks, some scholars believe that the high oxygen fugacity of adakite magma is closely related to porphyry copper deposits [10].

The Middle-Lower Yangtze River Belt (MLYRB) is a well-known metallogenic belt in eastern China that contains more than 200 polymetallic Cu–Fe–Au–Mo deposits. It hosts seven large-scale ore-cluster regions from northeast to southwest: Ningzhen (Cu, Fe, Pb, Zn), Ningwu (Fe), Tongling (Cu, Au, Pb, Zn), Luzong (Fe, Cu), Anqing–Guichi (Cu, Fe), Jiurui (Cu, Au), and E’dong (Fe, Cu) [11–18]. Among them, the Tongling ore-cluster region has high economic value with a high degree of geological exploration and intense studies ([19–29]; Figure 1a), and it is the birthplace of the theory of “stratabound skarn deposit” [11]. Skarn ore deposits are one of the most important ore types in the Tongling ore-cluster region, and the geochronological, geochemical, and fluid evolution features of this type have been reported in numerous studies [30–32]. However, in recent years, porphyry ore bodies were found in the depth, and there have been relatively few studies on the mineralization of porphyry-skarn type deposits in this area [33–35].

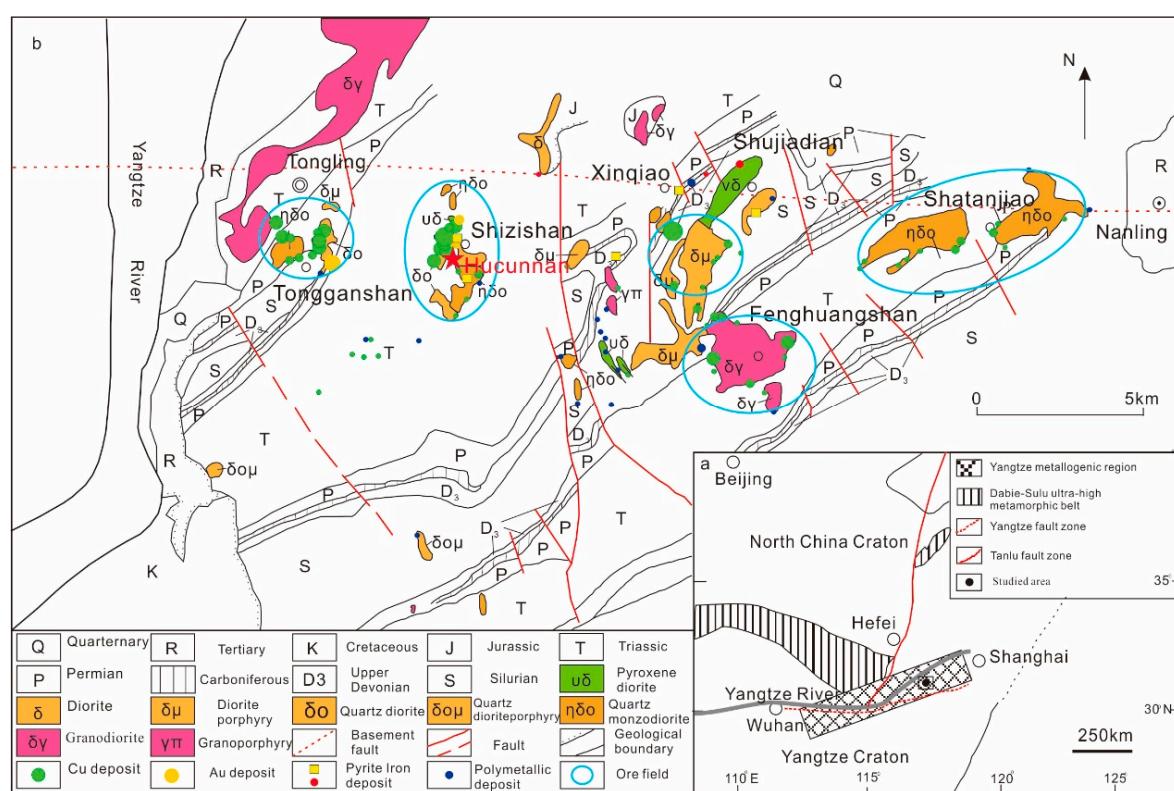


Figure 1. Geological sketch maps of (a) Lower Yangtze River Metallogenic Belt and (b) Tongling ore cluster, East China [26].

As typical porphyry-skarn Cu–Mo polymetallic deposits, the Hucunanan deposit in the Tongling ore-cluster region provides a good example for revealing the magmatic evolution and enrichment and migration of metallogenic materials during the skarn formation process. Previous studies held that the ages of quartz diorites and granodiorite of Hucunanan deposit are 125 Ma and 137.5 Ma, respectively [36]. The H–O isotopic signatures and the study of fluid inclusions show that the ore-forming fluids were dominated by magmatic water in the early stages, and gradually mixed with circulating meteoric water in the late stages [37]. However, there is still a lack of research on the magmatic evolution and source of ore-forming materials.

This study systematically investigated the age, physical conditions (temperature, pressure, and oxygen fugacity), source of mineralization, and petrogenesis of the intrusive rocks in the Hucunanan deposit. Here, the geochemical characteristics of intrusive rock were summarized and the evolution and

source of magma were discussed. We also discussed the S–Pb isotopic compositions of metallic sulfides and the elemental compositions of pyrite and garnet. They can be used to trace the evolution of the environment and the source of ore-forming materials, and play important roles in judging the physical and chemical conditions of ore-forming hydrothermal solution and determining the genetic types of ore deposits [38–41]. The new data provide evidence related to the evolutionary history of ore-forming hydrothermal system, all of which are necessary for understanding the ore-forming process.

2. Geological Setting

The Tongling ore-cluster region is along the lower Yangtze depression in the northern Yangtze block and belongs to the secondary uplift depression, which is also known as the Tongling uplift [11]. Apart from the absence of Lower and Middle Devonian strata, the main stratigraphic system of this region is from Silurian to Triassic (Figure 1b) [42]. The Cu–Au orebodies are mainly located in neritic-facies and littoral-facies carbonate sequences, e.g., the Carboniferous Huanglong and Chuanshan Formations and the Lower Permian Nanlinghu Formation. There are more than 70 magmatic plutons in the Tongling ore-cluster region. They are distributed from east to west for nearly 25 km in the Tongling-Daijiahui magmatic belt (Figure 1b). These magmatic rocks are divided into four rock assemblages [43,44]: (1) Pyroxene diorite–pyroxene monzodiorite combination, (2) quartz diorite–quartz monzodiorite combination, (3) granodiorite combination, and (4) K-feldspar granite. The ages of granodiorites are concentrated in the range of 144–137 Ma, whereas pyroxene diorite–pyroxene monzodiorite and quartz diorite–quartz monzodiorite range from 143–137 Ma and 140–136 Ma, respectively [19]. The quartz monzodiorite and granodiorite are closely related to copper mineralization, and belong to high potassium calc-alkaline and olivine anorthite [25]. There are three groups of faults in the basement of the Tongling ore-cluster region with trending directions of EW, SN, and N-NE. In addition, there are three groups of shallow fault systems, i.e., NE, NS, and NW. These structures controlled the distribution of rocks and deposits in this area.

There are more than 200 ore deposits in the Tongling ore-cluster region, which are divided into five ore fields: Tongguanshan (Cu, Au, Fe), Shizishan (Cu, Au, S, Pb, Zn), Xinqiao–Shujiaidan (Cu, S, Au), Fenghuangshan (Cu, Au, Fe), and Shatanjiao (Pb, Zn, Au, Cu) (Figure 1b) [11]. The metallogenic age gradually changes from east to west, the metallogenic age difference of the adjacent ore fields is about 2 Ma, and the metallogenic ages of the whole ore-cluster region are between 141 and 137 Ma [19]. According to different mineralization, the deposits in the area can be divided into porphyry, sedimentation-hydrothermal superposition reworked type, skarn, hydrothermal, and weathering types (Table 1).

Table 1. Classification of metal ore deposits in the Tongling ore-cluster region.

Type	Subgenera	Mineralization	Example Deposits
Skarn	Contact metasomatism type	Cu, Cu–Fe, Au–Cu, Cu–Mo, Mo	Fenghuashan, Yaoyuan, Bishan
	Stratified skarn type	Cu–S, Cu, S–Cu–Au, Au–As–S	Dongguashan, Xinqiao, Tongshan, Tianmashan
	Ore magma type	Cu–Au, Cu–Fe	Dongshizishan
Hydrothermal		Pb, Zn–Au–Cu, Au–Cu, Pb, Zn	Yaojiali, Baimangshan, Caoshan, Cishan
Porphyry		Cu, Cu–Au, Cu–Mo	Shujiadia, deep of Donggushan, Hucunnan
Sedimentation-hydrothermal superposition reworked type		S–Au, S–Fe, Fe	Simenkou
Gossan		Au–Fe	Ji Guan Shan
Laterite		Au	Long Tan Xiao

3. Geology of Deposit

The Hucunnan Cu–Mo deposit, a medium-sized porphyry- and skarn-type deposit, is located in the south of Shizishan orefield in the Tongling ore-cluster region (Figure 1b). The exposed surface strata, exposed in the mining area, are mainly Middle Triassic Dongmaanshan Formation (T_2d) limestone and dolomite (Figure 2a), and the deep part is Early Triassic (T_1) and Permian (P) sedimentary rocks.

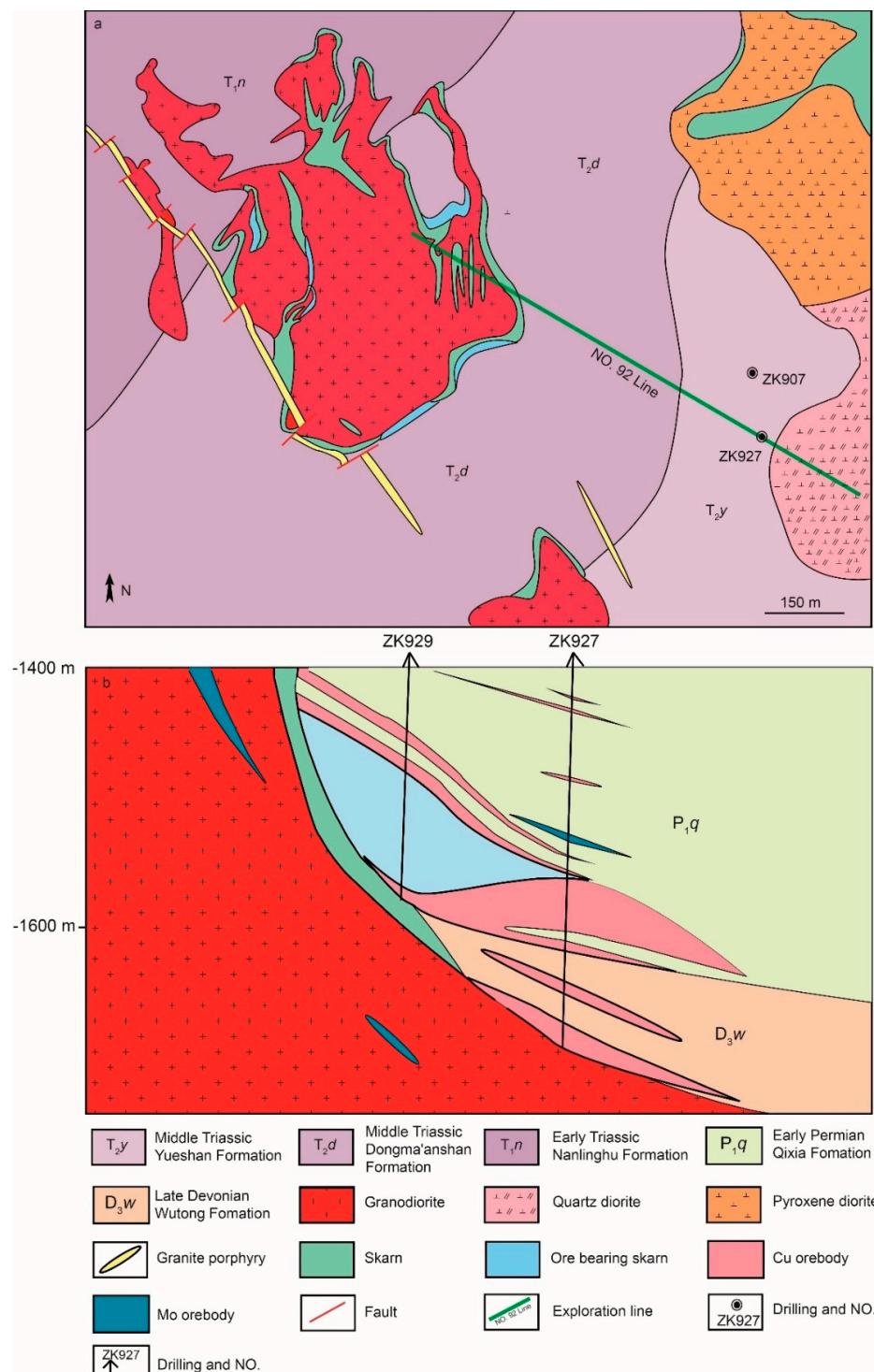


Figure 2. (a) Modified geological sketch map of Hucunnan area; (b) drilling geological profile of Hucunnan Cu–Mo deposit [45].

The fold structures in the mining area are Qingshanjiao anticline and Zhucun syncline. The main faults can be classified into three groups, i.e., SN, NW–W, and N–NE directions, which are important rock- and ore-controlling structures in this area.

The most important intrusive rock of this deposit is Hucun pluton, which is composed of granodiorite (Figure 3a). The granodiorite is light gray and the major minerals are quartz (25%), plagioclase (45%), K-feldspar (20%), amphibole (6%), and biotite (4%) (Figure 3b,c).

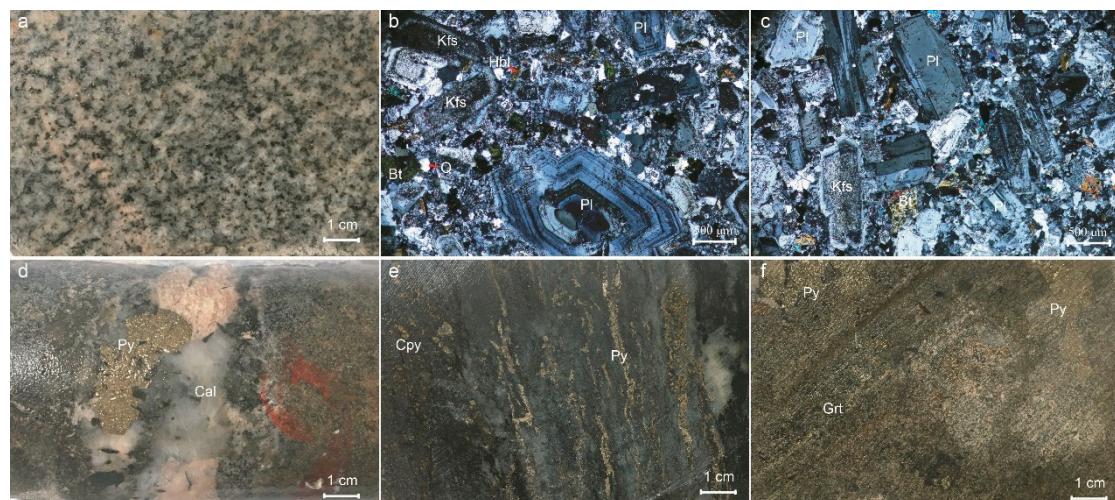


Figure 3. Hand specimens and photomicrographs of rock and mineralogy in the Hucunnan Cu–Mo deposit. (a) Granodiorite hand specimen; (b,c) granodiorite photomicrograph; (d) granular pyrite; (e) vein pyrite; (f) pyrite in skarn. Py, pyrite; Cpy, chalcopyrite; Kfs, K-feldspar; Bt, biotite; Q, quartz; Pl, plagioclase; Hbl, hornblende; Grt, garnet; Cal, calcite.

There are two types of orebodies in the Hucunnan deposit, i.e., skarn and porphyry type. The porphyry-type orebody is located in the granodiorite, and the skarn-type orebody is located in the contacts of intrusions and country rocks (Qixia and Gufeng Formation) (Figure 2b). The Cu mineralization is dominant in the adjacent contact zones of the southwest and northeast sides of the intrusion. Generally, the orebodies strike $N\ 30^\circ$ and dip 10° – 25° to the southeast. The Cu orebody is 6.30–19.40-m thick, with an average grade of 0.54–0.69%. Mo mineralization is dominant in the interior of the NE-trending intrusion. The maximum thickness of Mo orebody is 116.71 m, with an average grade of 0.069–0.107%.

Metal minerals are mainly chalcopyrite, pyrite, and molybdenite, followed by magnetite, sphalerite, and galena. Gangue minerals are mainly quartz, garnet, pyroxene, calcite, plagioclase, and potassium feldspar, followed by biotite, sericite, epidote, and chlorite. The ore structure is diverse, including automorphic–semi-automorphic, heteromorphic, metasomatic, and solid solution separation structures. The structures are mainly disseminated, veined, and reticulated (Figure 3d–f).

Field evidence, petrographic observations, and cross-cutting and replacement relationships indicate that hydrothermal activity occurred in four stages during the formation of the Hucunnan deposit: (1) Skarn stage, (2) oxide stage, (3) quartz–sulfide stage, and (4) quartz–carbonate stage (Table 2).

Table 2. Minerals generated sequence table of the Hucunnan Cu–Mo deposit.

Mineral	Skarn Stage	Oxide Stage	Quartz-sulfide Stage	Quartz-carbonate Stage
Garnet				
Diopside				
Quartz				
Magnetite				
Epidote				
Chlorite				
Pyrite				
Molybdenite				
Chalcopyrite				
Sphalerite				
Kaolinite				
Anhydrite				
Calcite				

4. Samples and Analysis

4.1. Sample Collection

All samples were collected from drills (Nos. ZK907 and ZK927) in the Hucunnan Cu–Mo deposits from −1400 m to −1600 m.

The five samples of granodiorite were from No. ZK927. The rocks were relatively fresh, gray-white, with idiomorphic–semi-idiomorphic granular and block structure. In this work, whole-rock major and trace elements were tested, and the rock-forming minerals (biotite) were analyzed by electron probe micro-analysis (EPMA, JEOL, Beijing, China).

Skarn of different depths and two metallogenic types of pyrite-bearing samples were selected to grind probe plates. Seventeen garnets of skarn, ten pyrites of skarn type (Pysk 1–10; Figure 4a–c), and seven pyrites of porphyry type (PyGD 1–7; Figure 4d–f) were selected for EPMA. Ten samples were selected for S–Pb isotope analysis. Six samples were skarn type (TW 01–06; Figure 4a) and the others were porphyry type (TW 07–10; Figure 4d).

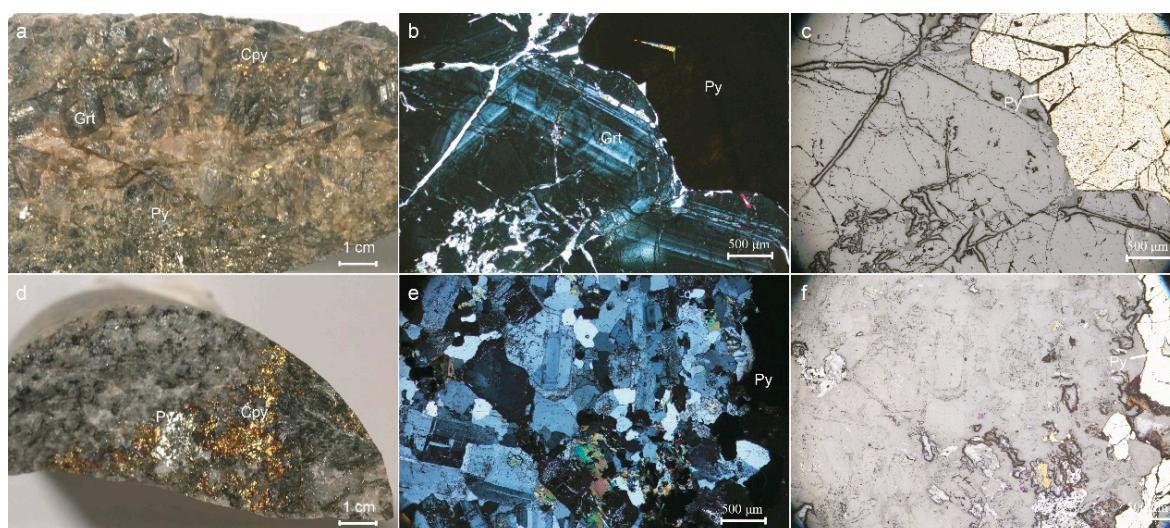


Figure 4. Hand specimens and photomicrographs of samples in the Hucunnan Cu–Mo deposit. (a) Hand specimen of pyrite in skarn; (b) crossed polars photomicrograph of skarn type; (c) reflected light photomicrograph of skarn type; (d) hand specimen of pyrite in porphyry; (e) crossed polars photomicrograph of porphyry type; (f) reflected light photomicrograph of porphyry type. Grt, garnet; Cpy, chalcopyrite; Py, pyrite.

The garnets were usually reddish brown, with mainly rhombic dodecahedron or tetragonal trihedron self-shaped/semi-self-shaped granular structures. The particle size was generally 3–6 mm, with a small part reaching more than 1 cm, and the band structure was obvious. The pyrites were usually bright yellow, automorphic/semi-automorphic, disseminated, and reticulated.

4.2. Analysis

4.2.1. Whole-Rock Major and Trace Elements

Whole-rock major and trace elements of fresh samples were analyzed by ALS Minerals–ALS Chemex (Guangzhou, China).

Major elements were determined by ME-XRF26 spectrometry. A prepared sample was fused with lithium metaborate–lithium tetraborate flux, which also included an oxidizing agent (lithium nitrate), and then poured into a platinum mold. The resultant glass disk was analyzed by X-ray fluorescence (XRF) spectrometry. The XRF analysis was determined in conjunction with a loss-on-ignition at 1000 °C. The resulting data from both determinations were combined to produce a total.

Trace elements and rare earth elements (REE) were determined by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). First, we prepared two pulp subsamples. One subsample was digested with perchloric, nitric, and hydrofluoric acids. The residue was leached with diluted hydrochloric acid and diluted to volume. The solution was then analyzed by ICP-MS for ultra-trace-level elements. The same digestion solution was also analyzed by ICP-AES for trace-level elements. Results were corrected for spectral interelement interference. The other subsample was added to lithium metaborate/lithium tetraborate flux, mixed well, and fused in a furnace at 1025 °C. The resulting melt was then cooled and dissolved in an acid mixture containing nitric, hydrochloric, and hydrofluoric acids. This solution was then analyzed by ICP-MS. According to the actual situation of the sample and the digestion effect, the comprehensive value was the final test result.

4.2.2. EPMA

The element composition of pyrite was determined using a JEOL JXA-8230M electron microprobe at the School of Resources and Environmental Engineering, Hefei University of Technology, Hefei, China. The analytical conditions were as follows: Accelerating voltage of 15 kV, probe current of 20 nA, and peak diameter of 5 μm .

4.2.3. Sulfur Isotope

The S isotope was tested at the Chinese Academy of Geological Sciences, Beijing, China. Samples contained no more than 100 μg of sulfur and three to five times the amount of V_2O_5 , wrapped in 9-mm \times 5-mm tin cups. They were automatically sampled in the combustion reactor with an oxygen supply and sufficient combustion under 1020 °C. All gas was combusted under helium load flow into and through the WO_3 filler and redox reaction of Cu wire tube, and all gas was oxidized adequately. At the same time, a small amount of SO_3 was generated through the reduction of SO_2 by the Cu wire. Gas was separated from SO_2 and other impure gases by a column (PN 260 070 80 Sulphur Separation Column for IRMS/HT) and then tested by mass spectrometry. Three international standard substances, IAEA-SO-5, IAEA-SO-6, and NBS 127, were used. The accuracy of standard sample analysis was better than 0.2‰.

4.2.4. Pb Isotope

The Pb isotope was tested at the Chinese Academy of Geological Sciences, Beijing, China. For determination of Pb isotope composition, all the methods were static. $^{202}\text{Hg}^+$ was measured to monitor the interference of $^{204}\text{Hg}^+$ to $^{204}\text{Pb}^+$ in argon. $^{205}\text{Tl}^+$ and $^{203}\text{Tl}^+$ were measured to use $^{203}\text{Tl}/^{205}\text{Tl}$ as an external standard calibration instrument for mass fractionation effect. Before testing

the samples, the parameters of Neptune Plus were optimized using NIST 981 200 $\mu\text{g/L}$ standard solution, including plasma parameters (rectangular tube position and carrier gas velocity) and ion lens parameters, in order to achieve maximum sensitivity. The sample after chemical separation underwent mass spectrometry with 2% HNO_3 solution, and the signal intensity of $^{208}\text{Pb}^+$ was about 8 V (the concentration of Pb in solution was about 200 $\mu\text{g/L}$). The sample was injected by free atomizer. The lead isotope ratio was normalized by $^{203}\text{Tl}/^{205}\text{Tl} = 0.418922$.

4.2.5. Re–Os Isotope

The Re–Os isotope analysis of molybdenite was completed at the Chinese Academy of Geological Sciences, Beijing, China. The isotope dilution Carius tube reverse water sample technique was used to seal and melt the sample for 24 h at 220 °C [46], direct distillation was used to separate and enrich Os [47], acetone extraction was used to separate and purify Re [48], and four-stage rod mass spectrometry (thermoelectric company x-series) was used to determine isotope ratios.

5. Results

5.1. Whole-Rock Geochemistry

The major and trace element results are listed in Supplementary Materials Table S1 and plotted in Figures 4 and 5, respectively.

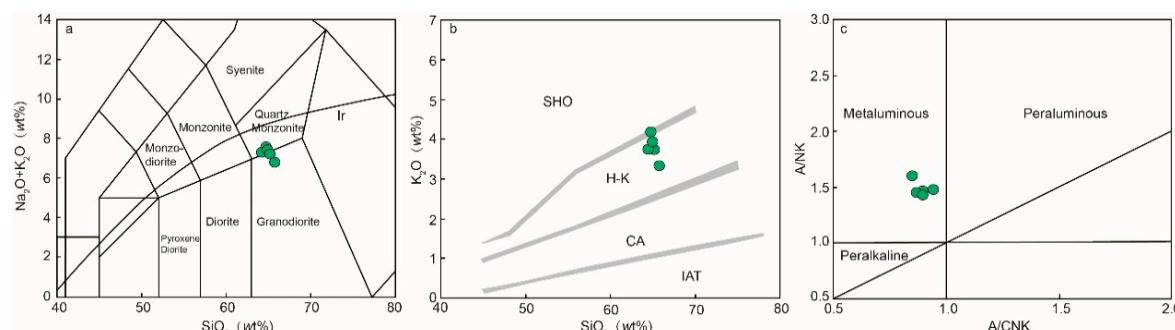


Figure 5. Classification diagrams of lithochemical compositions of Hucunnan granodiorites: (a) Total alkali vs. silica (TAS) [49]; (b) K_2O - SiO_2 [50]; (c) A/NK vs. A/CNK [51]. Ir—The Irvine dividing line, the top is alkaline, and the bottom is sub-alkaline; SHO—Potassium basalt series; H-K—High potassium calcium basic series; CA—Calc-alkaline series; IAT—Low potassium series.

The Hucunnan samples (SiO_2 , 64.49–65.77 wt.%) are granodiorites, based on geochemistry (Figure 5a). The total alkali contents ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) mainly ranged from 6.77 wt.% to 7.47 wt.%, of which K_2O contents ranged from 3.34 wt.% to 4.17 wt.% and Al_2O_3 contents from 14.45 wt.% to 15.50 wt.%. They are mostly plotted in the field of high-K calc-alkaline series on the SiO_2 versus K_2O diagram (Figure 5b). The alkali-aluminum ratios $\text{A}/\text{NK} = \text{Al}_2\text{O}_3/(\text{K}_2\text{O} + \text{Na}_2\text{O})$ ranged from 1.43 to 1.59, and aluminum supersaturations $\text{A}/\text{CNK} = \text{Al}_2\text{O}_3/(\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O})$ ranged from 0.85 to 0.95, indicating that they are metaluminous (Figure 5c).

The primitive mantle-normalized trace element distribution patterns (Figure 6a) show that large ion lithophile elements (LILEs) Rb (121.5–159.5 ppm), Ba (858–1010 ppm), Sr (657–727 ppm), and Th (8.68–10.05) were enriched, and there was a deficit of high-field strong elements (HFSEs) Nb (12.0–12.8 ppm), Y (14.5–16.4 ppm), and Yb (1.36–1.69 ppm). REE was 131.66–157.48 ppm, light rare earth elements (LREE)/HREE were between 11.93–12.99, and the chondrite-normalized REE pattern was right-inclined (Figure 6b). $(\text{La}/\text{Yb})_n$ was 16.14–19.57, indicating a high degree of fractional distillation of HREE and LREE in this intrusion.

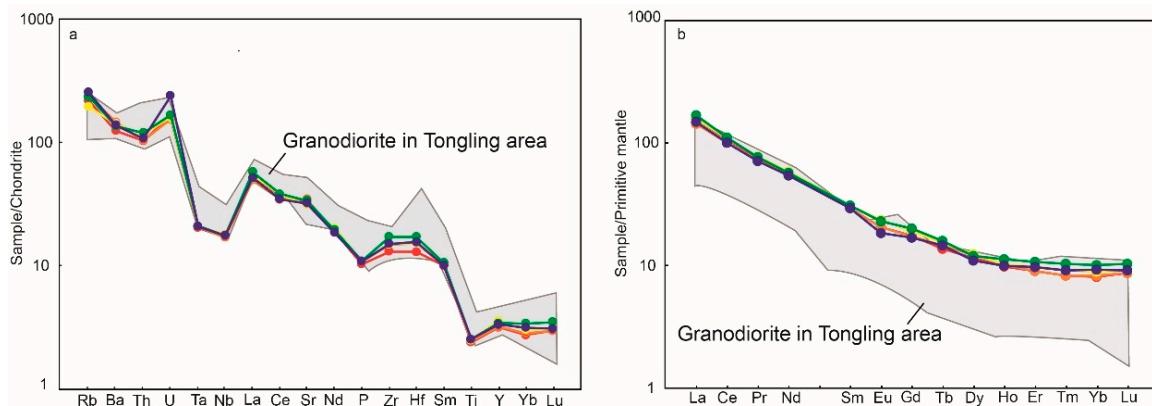


Figure 6. (a) Primitive mantle-normalized trace element variation; (b) chondrite-normalized rare earth element pattern. Data are taken from [52].

5.2. Mineral Geochemistry

5.2.1. Biotite Composition

The EPMA result of the biotite is listed in Supplementary Materials Table S2.

Biotites of the Hucunnan granodiorite belong to magnesia biotite series (Figure 7). SiO₂ content ranged from 36.95 wt.% to 39.85 wt.%, FeO from 13.71 wt.% to 16.88 wt.%, MgO from 13.22 wt.% to 15.87 wt.%, and Al₂O₃ from 12.20 wt.% to 13.79 wt.%.

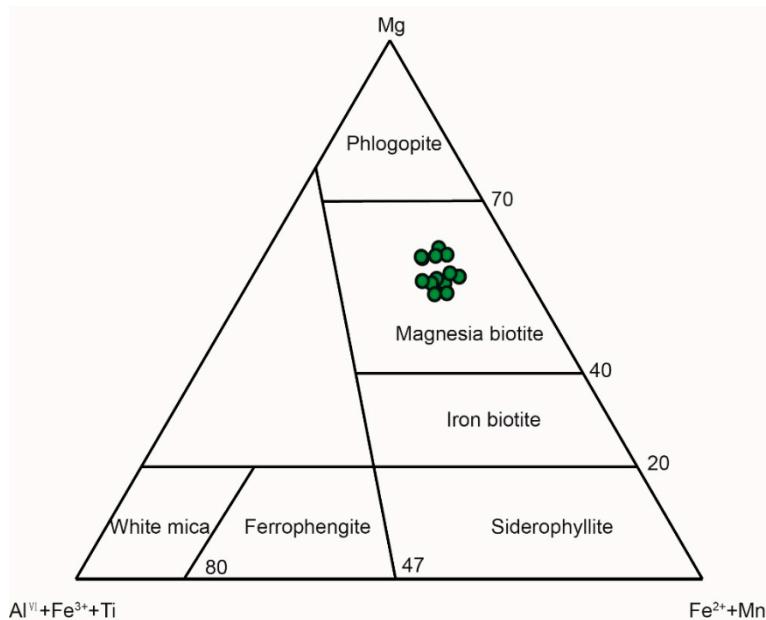


Figure 7. Biotite classification map [53].

5.2.2. Garnet Composition

The EPMA results of the garnet are listed in Supplementary Materials Table S3.

The individual garnets had high SiO₂ and CaO contents: SiO₂ contents were 32.45–36.38 wt.% (avg. 35.26 wt.%, $n = 17$) and CaO contents were 29.45–33.58 wt.% (avg. 32.61 wt.%, $n = 17$). FeO contents were 17.23–27.42 wt.% (avg. 24.91 wt.%, $n = 17$). Al₂O₃ contents were 0.07–7.20 wt.% (avg. 24.91 wt.%, $n = 17$). The contents of TiO₂, Cr₂O₃, MnO, and MgO were relatively low, i.e., 0.00–0.14 wt.% (avg. 0.04 wt.%, $n = 17$), 0.00–0.24 wt.% (avg. 0.03 wt.%, $n = 17$), 0.18–0.83 wt.% (avg. 0.34 wt.%, $n = 17$), and 0.00–0.33 wt.% (avg. 0.08 wt.%, $n = 17$), respectively.

5.2.3. Pyrite Composition

A total of 17 EPMA spot analyses were completed on pyrite, 10 on PysK and 7 on PyGD from the Hucunnan deposit. The EPMA results of the pyrite are listed in Supplementary Table S4.

Fe contents were 45.95–47.95 wt.% (avg. 47.06 wt.%, $n = 10$) in PysK samples and 46.72–47.76 wt.% (avg. 47.73 wt.%, $n = 7$) in PyGD samples. S contents were 50.76–53.85 wt.% (avg. 52.11 wt.%, $n = 10$) in PysK samples and 51.63–54.31 wt.% (avg. 52.78 wt.%, $n = 7$) in PyGD samples. Cu contents were 0.002–0.061 wt.% (avg. 0.034 wt.%, $n = 10$) in PysK samples and 0.011–0.041 wt.% (avg. 0.026 wt.%, $n = 3$) in PyGD samples.

5.3. Isotope Geochemistry

5.3.1. S Isotope

The S isotope composition of different orebody types is shown in Supplementary Materials Table S5. Our results show that the $\delta^{34}\text{S}$ values of pyrite from the skarn orebodies ranged from +3.9‰ to +4.7‰ (avg. +4.3‰, $n = 6$), while those of the porphyry orebodies ranged from +5.1‰ to +6.2‰ (avg. +5.6‰, $n = 4$).

The S isotope composition of the different orebody types at Hucunnan differed slightly, but the two generally had little change and were close, which indicates that different types of orebodies may have the same S source but were slightly different in the evolution process.

5.3.2. Pb Isotope

The Pb isotope composition of different types of orebodies is shown in Supplementary Table S6. The pyrite in the skarn orebodies had $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 38.04–38.45, 15.55–15.66, and 18.16–18.54 (avg. 38.26, 15.59, 18.44; $n = 6$), respectively. The pyrite in the porphyry orebodies had $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 38.24–38.36, 15.51–15.662, and 18.10–18.41 (avg. 38.32, 15.58, 18.22; $n = 4$), respectively.

The Pb isotope composition of the Hucunnan deposit was similar to that of the feldspar of granitoids in the Tongling ore cluster ($^{208}\text{Pb}/^{204}\text{Pb} = 38.090\text{--}38.460$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.470\text{--}15.600$, $^{206}\text{Pb}/^{204}\text{Pb} = 17.940\text{--}18.420$) (Tang et al., 1998, [42]), which indicates that the Hucunnan deposit and the intermediate-felsic intrusions in Tongling may have shared a similar Pb source.

5.3.3. Re–Os Isotope Dating

The results of Re–Os isotope are listed in Supplementary Materials Table S7. The content of ^{187}Re was 8686.80 and 17863.42, and ^{187}Os was 20.28 and 41.33. Both of them changed greatly. The metallogenetic ages of Hucunnan Cu–Mo deposit are 138.70 ± 1.87 and 140.03 ± 2.8 Ma, from Late Jurassic to Early Cretaceous.

6. Discussion

6.1. Petrogenesis of the Hucunnan Granodiorite

The granodiorite of the Hucunnan Cu–Mo deposit is consistent with the magmatic rock related to copper ore in the Shizishan ore field, both of which belong to the high-K calcium alkaline series.

The chemical compositions of biotite can also reflect oxidation conditions during magma crystallization. The concentrations of Fe^{3+} , Fe^{2+} , and Mg^{2+} in biotite, which is paragenetic with K-feldspar and magnetite, can be used to calculate magmatic oxygen fugacity [54–58]. From the $\text{Fe}^{3+}\text{--}\text{Fe}^{2+}\text{--}\text{Mg}$ diagram of biotite in the intrusion (Figure 8a), it can be seen that the sample points of biotites fall between the two buffer lines of $\text{Ni}\text{--}\text{NiO}$ and $\text{Fe}_2\text{O}_3\text{--}\text{Fe}_3\text{O}_4$, indicating that biotite was crystallized under the condition of high oxygen fugacity [57]. The contents of MgO and FeO in biotite can determine the source of magmatic material. In the $\text{MgO}\text{--}\text{FeO}/(\text{FeO} + \text{MgO})$ diagram for biotites

(Figure 8b), data are mainly plotted in the crust–mantle mixed-source area, indicating that Hucunnan granodiorite has the characteristics of crust–mantle mixed source.

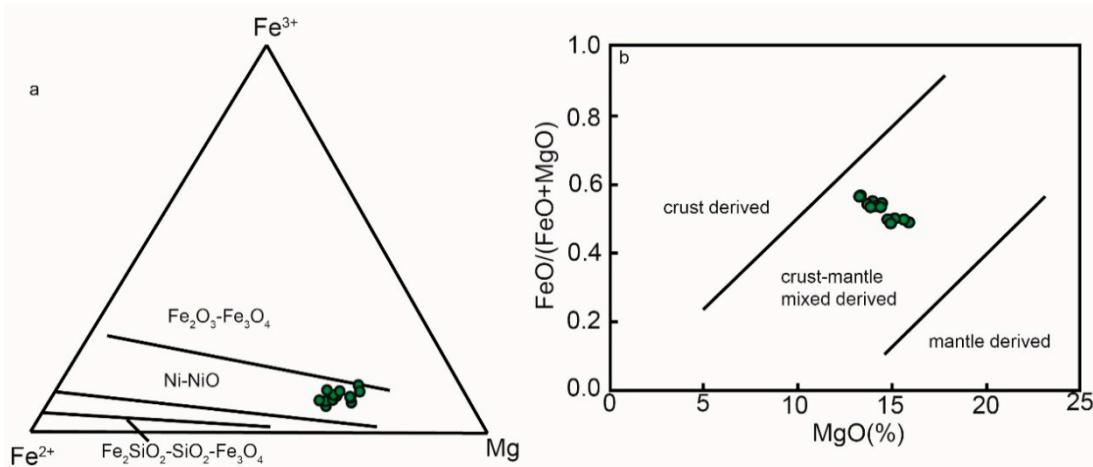


Figure 8. (a) $\text{Fe}^{3+}\text{-Fe}^{2+}\text{-Mg}$ [58], and (b) $\text{FeO}/(\text{FeO} + \text{MgO})$ vs. MgO for biotites from Hucunnan granodiorite [59].

The Hucunnan granodiorite was enriched in K, Al, and Na; enriched in large ion lithophile and light rare earth elements; depleted in high-field-strength elements Nb, Ta, and Ti; and obviously enriched in Sr and Ba, but Rb was low. The Rb/Y - Nb/Y diagram (Figure 9a) shows that the distribution of Hucunnan granodiorite was basically along the line of the evolution of crustal contamination or subduction zones. These characteristics reflect that the original magma came from the lithospheric mantle, and the lithospheric mantle source area may have been caused by plate subduction and may also reflect crust mixing during the magma rising process.

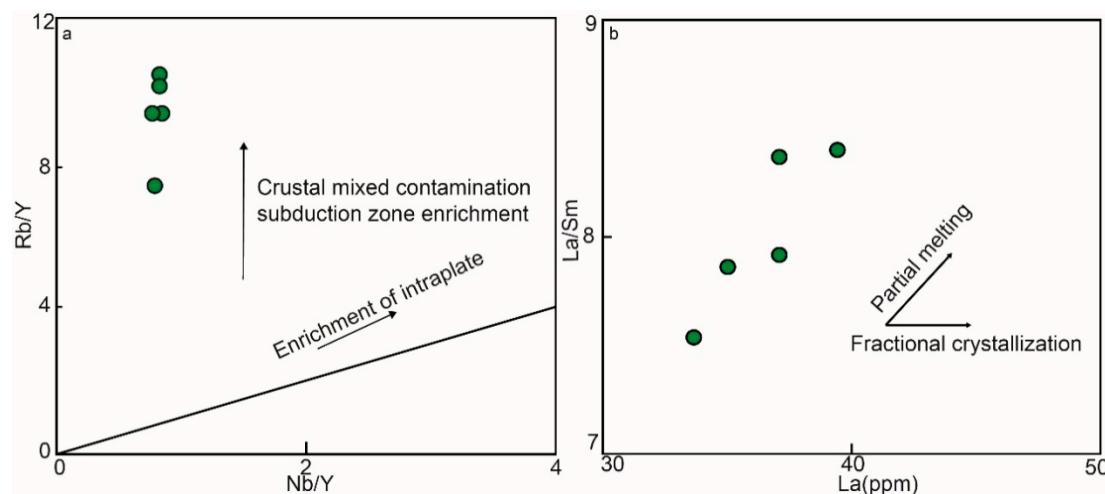


Figure 9. (a) Rb/Y - Nb/Y and (b) La/Sm - La for Hucunnan granodiorite.

In the La/Sm - La diagram (Figure 9b), the La/Sm ratio and La content of the sample show an obvious linear increasing trend on the partial melting evolution line, indicating that partial melting occurred in the process of magma evolution. In the Harker diagram (Figure 10), Al_2O_3 , CaO , P_2O_5 , TiO_2 , and MgO decreased with the increase of SiO_2 , indicating that with the evolution of magma, hornblende, pyroxene, sphene, biotite, and other minerals in the magma gradually underwent precipitation crystallization separation, and crystallization differentiation occurred during the evolution of magma. However, Na_2O , did not change with SiO_2 .

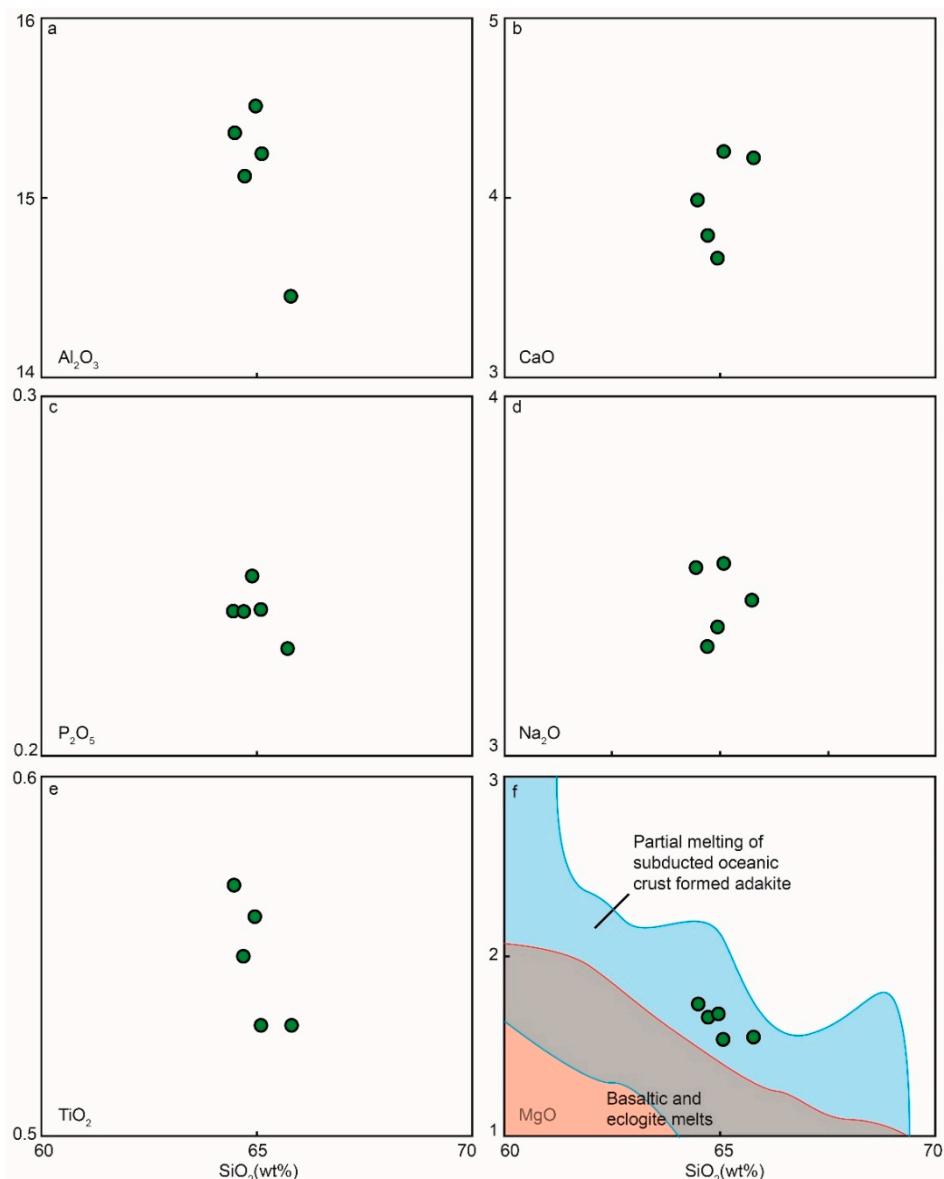


Figure 10. Harker diagram of SiO₂ versus other major elements of Hucunnan granodiorite: (a) SiO₂ vs. Al₂O₃, (b) SiO₂ vs. CaO, (c) SiO₂ vs. P₂O₅T, (d) SiO₂ vs. Na₂O, (e) SiO₂ vs. TiO₂, (f) SiO₂ vs. Mg.

MgO and SiO₂ of granodiorite in the area were negatively correlated, reflecting the typical characteristics of subducted oceanic crust melting adakite (Figure 10f) [60]. In the Sr/Y-Y diagram (Figure 11a), all samples show a negative correlation trend and fall within the area of adakite with an affinity of melting of oceanic subduction, which is obviously different from that of melting of thickened lower continental crust (Figure 11b).

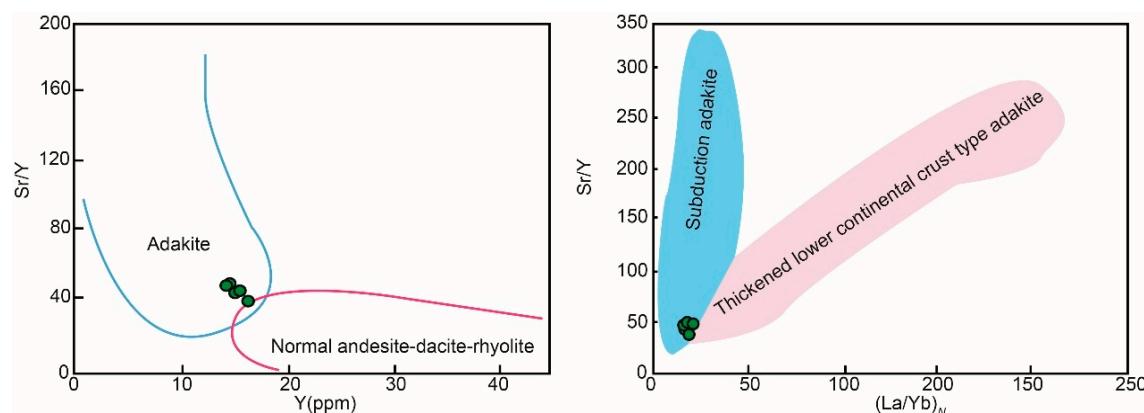


Figure 11. (a) Sr/Y – Y and (b) Sr/Y – $(\text{La}/\text{Yb})_N$ for Hucunnan granodiorite [61].

To sum up, we believe that the Hucunnan granodiorite is adakite that originated from the partial melting of oceanic crust, mixed with mantle-derived materials. After melting, the magma underwent crystallization differentiation of hornblende, pyroxene, sphene, biotite, and other minerals, and the crystallization environment had high oxygen fugacity.

6.2. Evolutionary Characteristics of Garnet

Garnet is the main skarn mineral in the Hucunnan deposit. In this study, the main elements of garnet at different locations were measured by electron probe. According to the distance from intrusion, the elements from far to near were zk927-b24, zk907-b59, and zk927-b26, respectively.

As one of the common minerals in skarn-type polymetallic deposits, garnet can be used to indicate the diagenetic and metallogenic process of skarn and serve as a direct indicator of mineralized species and genera [62,63]. In the Hucunnan Cu–Mo deposit, the end-member compositions were andradite ($\text{And} = 61.91\text{--}97.88\%$), grossularite ($\text{Gro} = 1.19\text{--}34.16\%$), spessartite ($\text{Spe} = 0.43\text{--}2.11\%$), pyrope ($\text{Pyr} = 0.00\text{--}1.53\%$), and almandine ($\text{Alm} = 0.00\text{--}1.74\%$), which belong to the series of andradite and agrossularite solid solutions. The molecular contents of the andradite are similar to the end components of garnet in skarn-type Cu–Mo deposits in the world (Figure 12a).

As skarn gradually moves away from the contact zone and the influence of alteration, its mineral composition also shows a certain change trend. The contents of andradite and grossularite in the Hucunnan deposit were linearly correlated (Figure 12b), and the composition of garnet gradually changed from andradite to grossularite with the direction close to the intrusion. This indicates that the metasomatism of fluid may have decreased gradually with the change of spatial position. There was a negative correlation between FeO and Al_2O_3 (Figure 12c), and a slight positive correlation between SiO_2 and CaO (Figure 12d). With the increase of Fe content, Al content in garnet decreases obviously, which reflects the variation characteristics of composition in the $\text{Ca}\text{--}\text{Fe}\text{--}\text{Ca}\text{--}\text{Al}$ garnet solid–melt system and was formed under nonequilibrium condition [64].

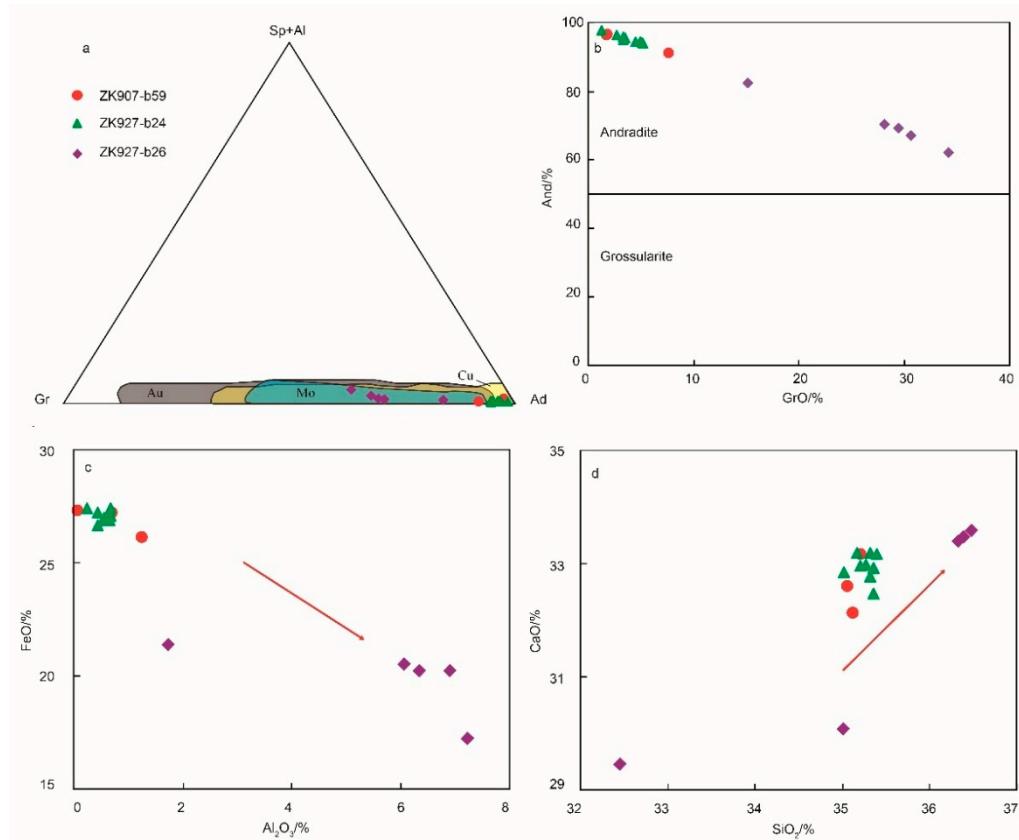


Figure 12. (a) Classification of garnets [65], (b) And–GrO of garnets, (c) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ of garnets, and (d) $\text{CaO}-\text{SiO}_2$ of garnets from Hucunnan Cu–Mo deposit. And, andradite; Gr, grossularite; Sp, spessartite; Al, almandine.

Skarn mineral composition is closely related to intrusive rock composition, surrounding rock composition, depth, oxygen fugacity, temperature, pressure, etc. [66]. Based on comprehensive research on the main mineral composition and symbiotic combination of skarn in skarn deposits, the changes in physical and chemical conditions in the process of diagenesis and mineralization of the deposit can be revealed. Changes in the mineral compositions of garnet have important indicative significance for the formation environment of skarn [63]. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of garnet mineral in the Hucunnan deposit were 0.00–0.04, indicating that it was formed in an oxidized environment. The end members of the minerals are composed of $\text{Gro}_{1.19-34.16}\text{And}_{61.91-97.88}\text{Spe} + \text{Pyr} + \text{Alm}_{0.62-3.85}$, which is dominated by andradite, indicating that it was formed under more oxidized conditions [67]. Previous experiments on the physical and chemical conditions for the formation of andradite showed that its main formation temperature was 450–600 °C, and it was in an oxidation-weak alkaline environment with pH 4.0–11.0 [68], indicating that the ore-forming fluids in the skarn stage of the Hucunnan deposit can be characterized by high temperature, low acidity, and high oxygen fugacity.

6.3. Mineralization and Material Source

The metallogenetic model ages of the Hucunnan Cu–Mo deposit are 138.70 ± 1.87 Ma and 140.03 ± 2.8 Ma, which are consistent with the main metallogenetic ages of the Tongling ore-cluster region [19]. The diagenetic age of Hucunnan granodiorite measured by predecessors is 137.5 ± 1.2 Ma [36], indicating that the age of diagenesis and mineralization is basically the same. Therefore, the formation of the Hucunnan Cu–Mo deposit may be closely related to the Hucunnan granodiorite.

Variations of Fe and S contents (Figure 13a) are predominantly related to trace metal substitution in pyrite [69]. The well-defined negative correlation between Cu and Fe in the Hucunnan deposit (Figure 13b) indicates Cu^{2+} substitution for Fe^{2+} in pyrite [70]. Previous studies suggested that Cu can

be structurally bound in pyrite, reaching weight percent levels [70,71], and can also be concentrated in pyrite due to micro- or nanoparticle inclusions of chalcopyrite [72]. We propose that the negative correlation of Cu and Fe is due to Cu^{2+} solid solution in pyrite because of the low Cu contents in the studied pyrite samples and pyrite coexisting with chalcopyrite. The elemental compositions of pyrite in skarn type and porphyry type have similar evolutionary trends, indicating that they may have had the same source of ore-forming materials.

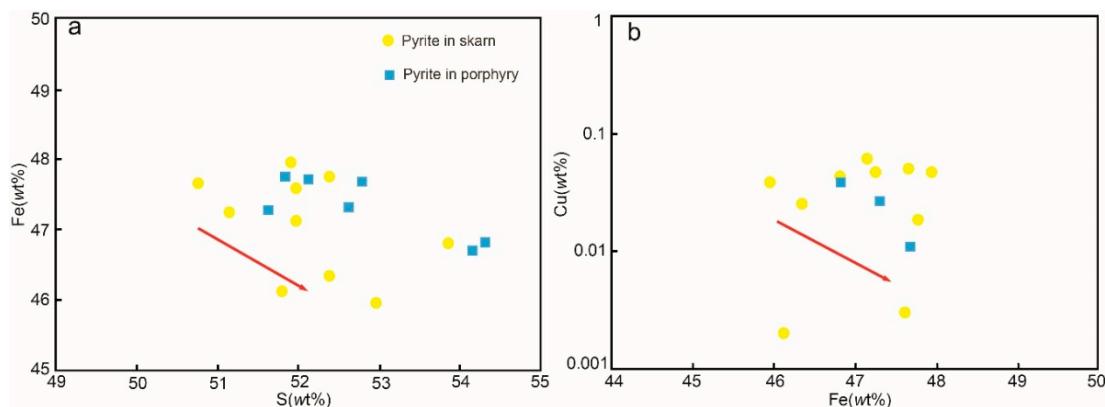


Figure 13. (a) Fe–S and (b) Cu–Fe of pyrites from the Hucunnan Cu–Mo deposit.

The sulfur isotopic composition of metal sulfide is widely used to trace the source of sulfur in ore deposits. $\delta^{34}\text{S}$ will vary greatly from one source to another. From mantle sulfur, $\delta^{34}\text{S}$ will be $0 \pm 3\text{\textperthousand}$, from sea sulfur, it will be $+20\text{\textperthousand}$, and from sedimentary sulfur, it will be negative [73].

The S isotopes show that the $\delta^{34}\text{S}$ values of sulfide were generally less than $10\text{\textperthousand}$ in the Tongling ore-cluster region, mainly concentrated in the 2\textperthousand – 8\textperthousand range, while the carboniferous strata of pyrite in the $\delta^{34}\text{S}$ values were $0.6\text{\textperthousand}$ – $29.5\text{\textperthousand}$ [74,75]. The $\delta^{34}\text{S}$ values of the Hucunnan deposit were consistent with other deposits in the area, indicating that most of the sulfur in this deposit did not originate from the strata (Figure 14), but from magma of acidic intrusive rocks in the area. Meanwhile, the $\delta^{34}\text{S}$ value of skarn ore was lower than that of porphyry ore, indicating that the ore-forming hydrothermal underwent further evolution during the intrusion process and more stratigraphic materials were involved in the skarn mineralization stage.

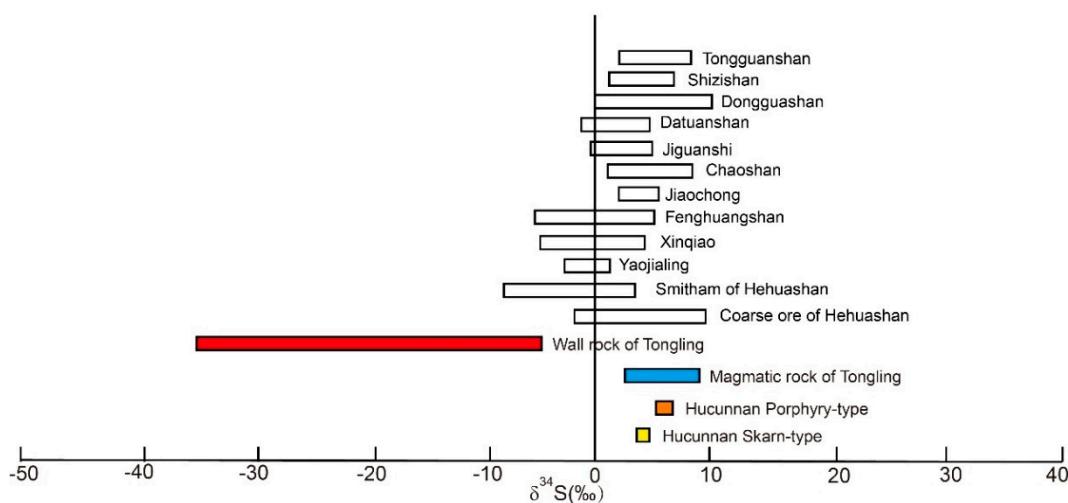


Figure 14. Distribution of sulfur isotope (data after [76–92]).

By projecting the isotopic composition of lead in various types of ore onto the diagram of $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ (Figure 15a), it can be seen that the projection

points of the isotopic composition of lead in two types of ore are relatively concentrated, suggesting that they may have had the same origin or evolutionary process [93]. The Pb isotope is located between the upper crust and the mantle. It is inferred that Pb in the Hucunnan deposit is mainly mantle-derived, which may be contaminated by crustal material (Figure 15b).

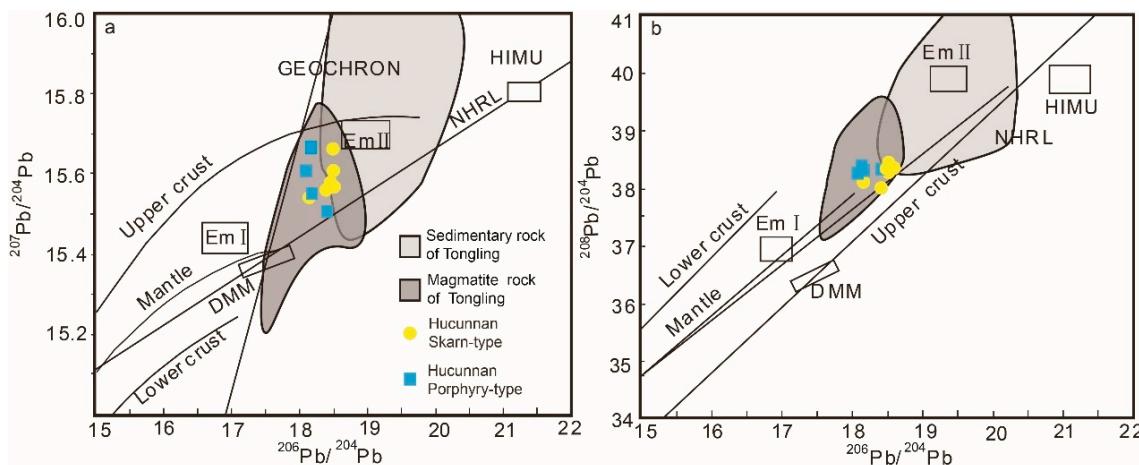


Figure 15. Pb isotope of the Tongling ore-cluster region [28]: (a) $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$; (b) $^{208}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$. DMM, depleted mantle component; EM I and II, enriched mantle components [94]; Geochron, zero isochron line; NHRL, northern hemisphere reference line [95]. Lines of mantle, lower crust, and upper crust of China are after [96].

The $^{206}\text{Pb}/^{204}\text{Pb}$ values of ore lead in the Hucunnan deposit were 18.10–18.54, with an average value of 18.35, which is comparable to the $^{206}\text{Pb}/^{204}\text{Pb}$ value of rock lead in the Yanshan period (18.30) and the value of post-magmatic hydrothermal deposits in the Middle and Lower Yangtze River [97,98], showing that the ore-forming materials were originated from magma. In the diagram of Pb isotope of ore, the ore sample point of Hucunnan deposit also mainly falls in the magmatic area, and a small amount of skarn ore falls in the boundary area between sedimentary and magmatic rock, which shows that ore-forming materials have the characteristics of magma source, and some stratigraphic materials were added in the skarn stage.

In conclusion, we believe that the formation of the Hucunnan Cu–Mo deposit was closely related to the intrusion of granodiorite. The ore-forming materials were mainly from magma and partly from strata. The skarn orebody has more stratigraphic materials than the porphyry orebody.

6.4. Metallogenic Geological Background

According to previous studies, during the Late Jurassic period (165 ± 5 Ma to 145 Ma), the ancient Pacific plate began to subduct, resulting in the eastern part of China being extruded and uplifted as a whole to form a plateau, suffering from erosion and missing the deposition of the Late Jurassic, and the lithosphere rapidly thickened [99,100]. A fluid or melt formed by the dehydration of the oceanic crust produced metasomatism of the mantle wedge to a low degree of partial melting of the mantle wedge or mixing with mantle magma to form alkaline basaltic magma. Then, it entered the post-collisional orogenic stress transition period (145–130 Ma). The tectonic stress transitioned from compression to tension. The alkaline basaltic magma from the enriched mantle bottom invaded the lower crust, which not only caused the crust to thicken, but also caused partial melting of the crust to form a deep magma chamber, with a part of the deep magma acidic like adakite. The adakite magma mixed with the lower crust source magma, evolved, and transgressed upward, forming intrusive rocks, mainly composed of intermediate acid in the Tongling area. Later, it entered the extensional period (130–80 Ma), during which the lithosphere was desecrated and thinned, the asthenosphere underwent upwelling, and large-scale volcanic eruption occurred in the region [27]. In the tectonic discrimination

diagrams (Figure 16), the data of Hucunnan granodiorite are mostly plotted in the field of volcanic arc granite (VAG). Combined with its diagenetic age, it would have been against the dynamic background of the transformation from compression to tension.

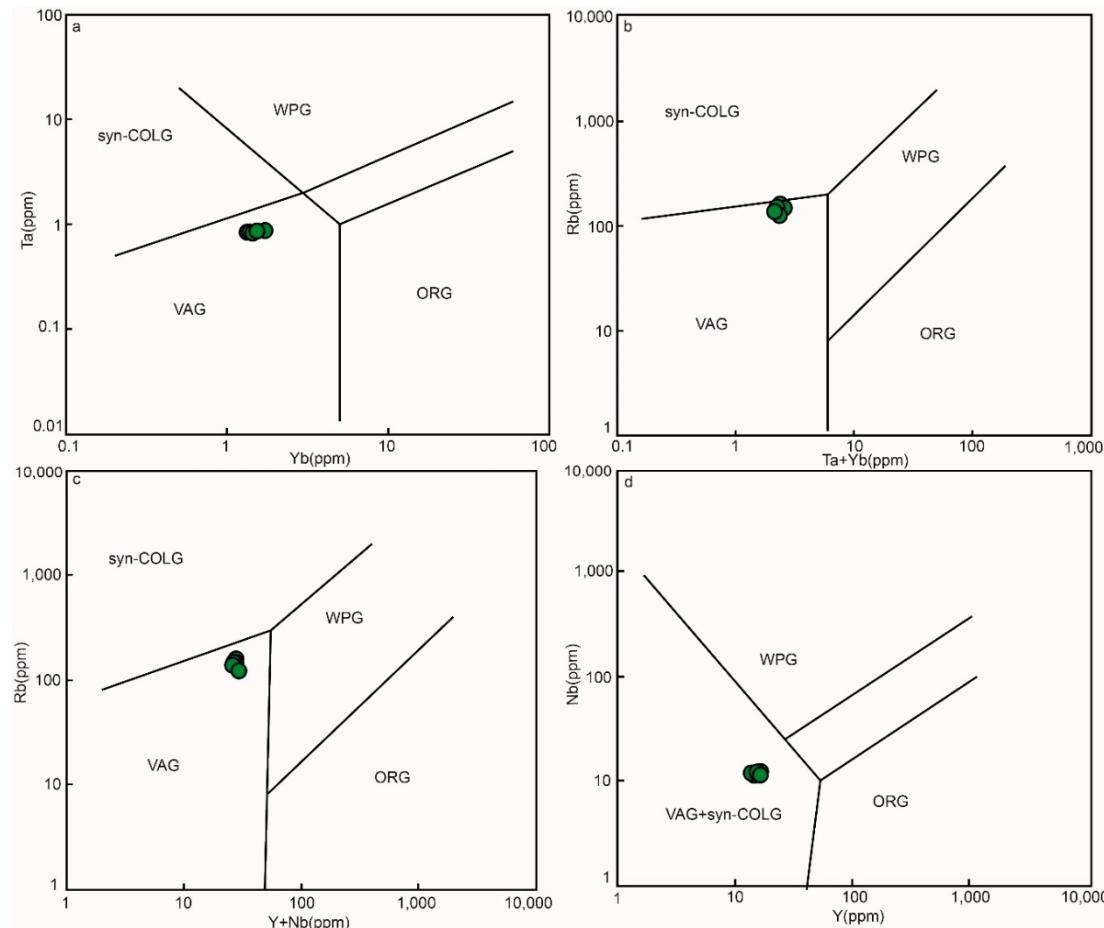


Figure 16. Tectonic discrimination of Hucunnan granodiorite: (a) Ta vs. Yb, (b) Rb vs. (Yb + Ta), (c) Nb vs. Y, and (d) Rb vs. (Y + Nb); after [101]. VAG, volcanic arc granite; ORG, oceanic ridge granite; Syn-COLG, syn-collision granite; WPG, intra-plate granite.

6.5. Metallogenesis Model

According to previous studies, the diagenetic ages of granodiorite in the Tongling ore cluster are mainly from 147–137 Ma, and the metallogenetic ages are mainly from 141–137 Ma [19]. The diagenetic age of Hucunnan granodiorite is 137.5 ± 1.2 Ma [36], and the ages of the metallogenetic model are 138.70 ± 1.87 Ma and 140.03 ± 2.8 Ma, which are consistent with the overall diagenetic and metallogenetic age of the region, indicating that magmatism and mineralization are inseparable. Research on the major elements of biotite and garnet showed that the ore-forming environment of the Hucunnan Cu–Mo deposit was characterized by high oxygen fugacity. This is consistent with the view that large-scale Cu–Mo polymetallic mineralization is closely related to high oxygen fugacity magmas [102–109]. Previous studies on the ore-forming fluid of the deposit showed that the time changes of redox conditions, acid balance, and temperature in the ore-forming fluid led to the temporal separation of copper and molybdenum in Hucunnan skarn deposit [37]. Research on the major elements and S–Pb isotopes of pyrite showed that the ore-forming materials of skarn and porphyry orebody in this deposit have similar sources. They are mainly from magma and are mixed with some stratigraphic materials. Compared with porphyry orebody, skarn orebody has more stratigraphic materials. Combined with

the geochemical characteristics of the rocks, the compositional patterns are summarized as follows (Figure 17).

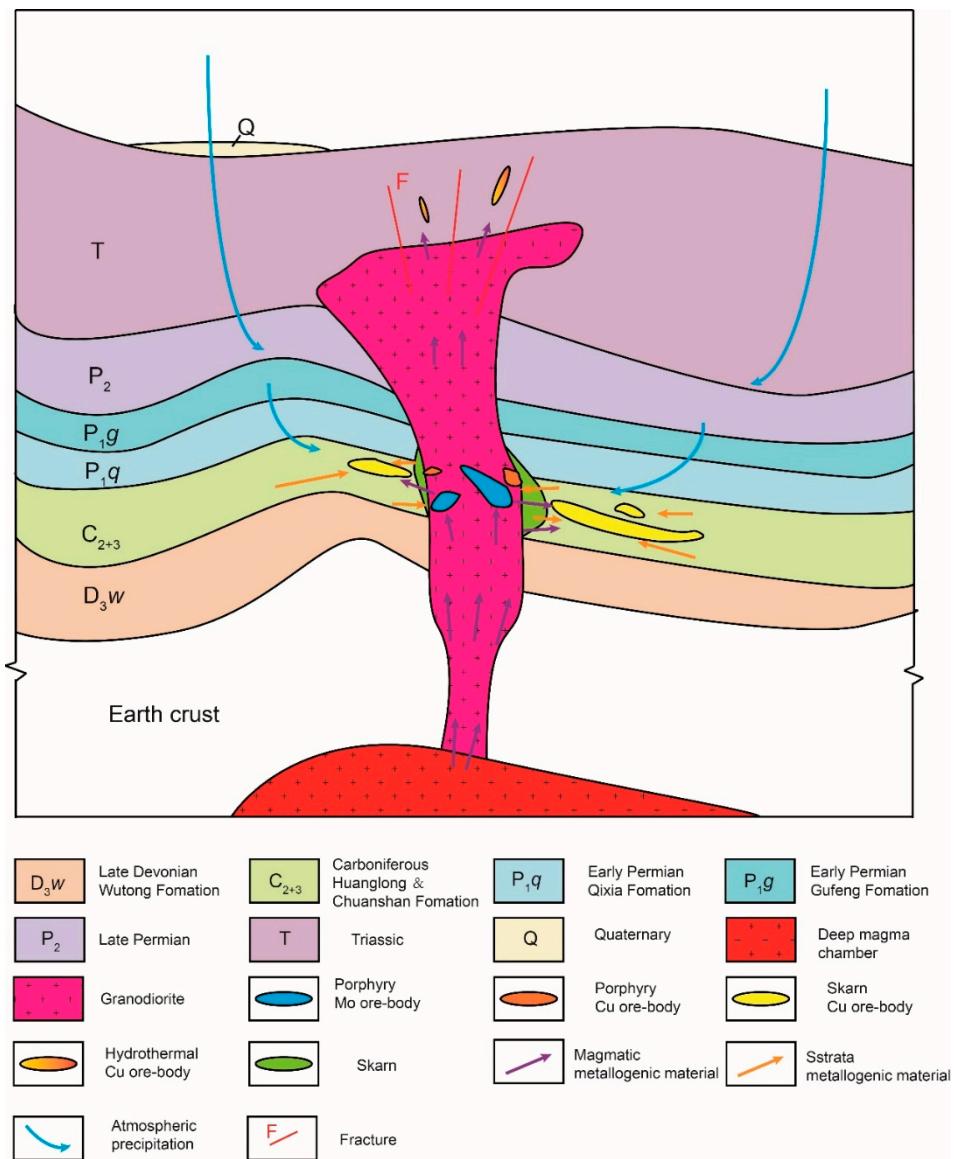


Figure 17. Metallogenetic model map of the Hucunnan Cu–Mo deposit.

During 145–135 Ma, the regional tectonic stress field changed to a stress relaxation stage of transition from compression to tension. Before that, the collision and welding of the North China plate and Yangtze plate from north to south and the subsequent subduction northwest to the ancient Pacific plate resulted in lithospheric thickening and melting due to decompression. A fluid or melt formed by the dehydration of the oceanic crust made metasomatism of the mantle wedge to a low degree of partial melting of the mantle wedge or mixed with mantle magma to form alkaline basaltic magma, and the underplating of the lower crust rock formed adakitic magma. The two kinds of magma show mixed coalescence, evolution, and random rise and emplacement along the east–west deep fault. During the upwelling process, crystallization of apatite, sphene, amphibole, pyroxene, and plagioclase and assimilation and contamination of crustal materials took place, forming the Hucunnan granodiorite. Magmatism in the area not only brought ore-forming materials, but also provided a lot of heat energy for groundwater circulation. The ore-forming hydrothermal fluid rose to the shallow intrusion, forming lenticular orebodies and vein and veinlet disseminated ore in the intrusive body

and its silicate surrounding rock, developing slightly zonal K-silicified hydrothermal alteration and forming porphyry deposits. Skarnization formed in the contact zone between the rock body and carbonate formation, with strong contact thermal metamorphism. Under the influence of thermal activity and volatilization, the ore-forming materials in the strata were activated and migrated into the ore-forming hydrothermal solution, and were enriched in favorable spaces, such as interlayer fissures and fold ends, to form skarn orebodies, usually occurring along the strata. In addition, a small amount of ore-forming hydrothermal fluids continued to intrude along the fractures, forming a small-scale hydrothermal orebody near the surface, which is the end metallogenic effect of the metallogenic system.

7. Conclusions

- (1) The geochemical affinity of this granodiorite related to Cu–Mo mineralization is adakite, the metallogenic model ages of the Hucunnan Cu–Mo deposit are 138.70 ± 1.87 Ma and 140.03 ± 2.8 Ma, and the ages of diagenesis and mineralization are basically the same. Magma originated in the mantle and subducted oceanic crust and mixed with some crustal material. It formed under the dynamic background of a transformation from compression to extension.
- (2) The chemical compositions of biotites show that the magma formed in a high oxygen fugacity environment, and garnets show that the ore-forming fluids in the skarn stage are characterized by high temperature, low acidity, and high oxygen fugacity.
- (3) The formation of the Hucunnan Cu–Mo deposit was closely related to the intrusion of granodiorite. The ore-forming materials were mainly originated from magma and partly from strata. The skarn orebody has more stratigraphic materials than the porphyry orebody. The porphyry/skarn metallogenic system was formed under the joint action of stratum structure magmatic rocks.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/2/107/s1>, Table S1: Major (wt.%) and trace element (ppm) results of Hucunnan granodiorites; Table S2: Chemical compositions of biotites in the Hucunnan deposit; Table S3: Chemical composition of garnets in the Hucunnan deposit; Table S4: Chemical composition of pyrites in the Hucunnan deposit; Table S5: S isotopes of ores in the Hucunnan deposit; Table S6: Pb isotopes of ores in the Hucunnan deposit; Table S7: Re–Os isotopes of molybdenites in the Hucunnan deposit.

Author Contributions: K.S. wrote the paper; X.Y., J.D., and J.C. designed the experiments; Q.W. and Y.C. took part in the field investigation. All authors have read and agreed to the published version of the manuscript.

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