Research Article

Fluid Evolution of Fuzishan Skarn Cu-Mo Deposit from the Edong District in the Middle-Lower Yangtze River Metallogenic Belt of China: Evidence from Petrography, Mineral Assemblages, and Fluid Inclusions

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The Fuzishan Cu-Mo deposit is located in the Edong district of the Middle-Lower Yangtze River Metallogenic Belt, China. The orebodies mainly occurred as lenticular and bedded shapes in the skarn zone between the Lower Permian Qixia Formation carbonate rocks and the quartz diorite. Four paragenetic stages have been recognized based on petrographic observations: (1) prograde skarn stage, (2) retrograde skarn stage, (3) quartz-sulfide stage, and (4) carbonate stage. Six fluid inclusion types were recognized: $S_1$ (vapor + liquid + halite + other daughter minerals), $S_2$ (vapor + liquid + daughter minerals except halite), $L_V$ (rich liquid + vapor), $V_L$ (rich vapor + liquid), $V$ (vapor), and $L$ (liquid) types. Fluid inclusion studies show distinct variations in composition, final homogenization temperature, and salinity in four stages. Daughter minerals of the primary fluid inclusions include chalcopyrite, molybdenite, hematite, anhydrite, calcite, and halite in the prograde skarn stage and hematite, calcite, and sulfide (?) in the retrograde skarn stage. No daughter minerals occurred in the quartz-sulfide and carbonate stages. Final homogenization temperatures recorded in these stages are from 405 to $>$550°C, from 212 to 498°C, from 150 to 485°C, and from 89 to 223°C, respectively, while salinities are from 3.7 to 42.5, from 2.6 to 18.5, from 2.2 to 17.9, and from 0.2 to 11.5 wt.% NaCl equivalent, respectively. The coexisting $V_L$ and $S_1$ type fluid inclusions show similar homogenization temperature of 550 to about 650°C in the prograde skarn stage, indicating that immiscibility occurred at lithostatic pressure of 700 bars to perhaps 1000 bars, corresponding to a depth of 2.6 km to about 3.7 km. The coeval $V_L$ and $L_V$ types fluid inclusions with homogenization temperature of 350 to 400°C in the late retrograde skarn and quartz-sulfide stages suggest that boiling occurred under hydrostatic pressure of 150 to 280 bars, equivalent to a depth of 1.5 to 2.8 km. Mo mineralization in the retrograde stage predated Cu mineralization which mainly occurred in the quartz-sulfide and carbonate stages. Fluid compositions indicate that ore-forming fluid has high $f_{O_2}$ and rich Cu and Mo concentration in the early stage, while relatively lower $f_{O_2}$ and poor Cu and Mo concentration in the middle to late stages. Microthermometric data show a decreasing trend in temperature and salinity in the fluid evolution process. Decreasing temperature and boiling event may be the main factors that control the ore precipitation.

1. Introduction

Skarn deposits are one of the most important deposit types that form in a wide range of temporal, spatial, and tectonic settings [1–8]. Skarns can provide economically significant resources of Cu, Fe, Au, Zn, W, Mo, and Sn and some rare earth elements (REE) in the world [4, 9]. Among them, skarn (porphyry) Cu-Mo deposits are considered to associate with I-type granites [3, 5].

The Middle-Lower Yangtze River Metallogenic Belt (MLYRMB) is one of the most important metallogenic belts in China, occupying an area of about 30,000 km², which is famous for economic values of Cu-Fe-Au-W-Mo mineralization in the east part of China (Figures 1(a) and 1(b)) [10–15].
Seven ore districts distribute among the MLYRMB, including Edong, Jiurui, Anqing, Luzong, Tongling, Ningwu, and Ningzhen from the west to the east, respectively. The Edong district is in the westernmost part of the MLYRMB. It contains more than 50 porphyry-skarn and skarn deposits and over 800 km$^2$ of igneous rocks [16]. The main types of ore deposits are porphyry-skarn Cu-Mo, skarn Cu-Fe, skarn Fe-Cu, skarn Au-Cu, skarn W-Cu, skarn Fe, and skarn Cu deposits (Figure 2) [17, 18]. Numerous geochronologic data suggest that all these deposits in the Edong district are associated with the Late Mesozoic granitoids [19–23]. Figure 2 shows that the Fe skarn deposits primarily distribute along the southern margin of the Echeng and Jinshangdian batholiths and the southwestern edge of the Lingxiang batholith (e.g., Chengchao, Jinshandian, and Lingxiang Fe deposits). The Fe-Cu skarn deposits mainly occur around the Tieshan batholith (e.g., Tieshan Fe-Cu deposit). However, all the Cu-Mo deposits discovered in this district are associated with porphyry-skarn system, spatially relevant to granodiorite and granite porphyry stocks (e.g., Tongshankou and Fengshandong Cu-Mo deposit) [22, 24]. Besides, the Cu, Cu-Fe, W-Cu, and Au-Cu skarn mineralizations seem more likely to have an intimate relationship with the Yangxin batholith (e.g., Jiguanzui Au-Cu and Tonglvshan Cu-Fe (Au) deposit) [16, 17]. Almost all the skarn Cu, Au-Cu, and Fe-Cu deposits distribute in the northwest part of the Yangxin batholith, which have been the subject of various geochronological, geochemical, and geofluid studies [16, 25–28]. In the southeast part of the Yangxin batholith, almost no economic skarn Cu, Fe-Cu, Au-Cu, and Cu-Mo deposits were discovered except for a few skarn W-Cu deposits (e.g., Ruanjiawan W-Cu deposit) [29]. Recently, the newly discovered Fuzishan skarn Cu-Mo deposit filled the gap in the southeastern margin of the Yangxin batholith (Figure 2). Until now, there has

![Figure 2](https://example.com/figure2.png)
been no research carried out in the Fuzishan skarn Cu-Mo deposit. Previous studies on fluid inclusion characteristics of skarn Fe-Cu-Mo deposits in the Edong district mainly focused on temperature-salinity-pressure evolution of the ore-forming fluids [27, 30–32]. However, they rarely reflect a compositional change during the fluid evolution process and did not provide detailed fluid evolution model as well as detailed transportation and precipitation mechanism for ore metals.

In this study, we carried out a detailed investigation on deposit geology, alterations, and mineral petrography and fluid inclusion study in the Fuzishan Cu-Mo deposit. It is worth mentioning that the Fuzishan deposit is particularly suitable for fluid inclusion study, as it contains complete skarn mineralization stages and various types of skarn minerals and some unfamiliar minerals (e.g., anhydrite) as well as abundant fluid inclusion types in distinct stages. Our aims are (1) to obtain compositional variations of ore-forming fluid between different mineralization stages and temperature-salinity-pressure evolution of ore-forming fluid, (2) to model a detailed fluid evolution process and give a better insight to understand ore metal transportation and precipitation mechanism of the Fuzishan skarn Cu-Mo deposit, and (3) to compare the Fuzishan skarn Cu-Mo deposit with other skarn- (porphyry) Fe-Cu-Mo deposits in the Edong district as well as Cu-Mo deposits around the world.

2. Geological Setting

The MLYRMB is tectonically situated in the northern margin of the Yangtze Craton and along the southeastern
edge of North China Craton and Dabieshan orogenic belt (Figure 1(b)). To the northwest, the MLYRMB is bounded by the Xiangfan-Guangji fault (YCF), and to the northeast by the Tancheng-Lujiang regional strike-slip fault (TLF), and by the Yangxin-Changzhou fault (YCF) to the south. Previous geophysical data revealed the existence of the concealed Yangtze River fault zone in the MLYRMB, which might have formed in Neoproterozoic and reactivated during Triassic and Jurassic-Cretaceous [10, 22, 33]. Its reactivation generated a well-developed network of faults and S-type folds [16, 18]. The formation of Late Mesozoic faults and folds has been considered to be the result of subduction of the Pacific plate [10, 11, 34].

As the westernmost ore district in the MLYRMB, the Edong district is confined in a subtriangular tectonic framework by three main faults: the Ma-Tuan, the Xiangfan-Guangji, and the Tan-Lu faults (Figure 2). The regional stratigraphy was completely exposed from the Cambrian to Quaternary, merely missing the Middle-Lower Devonian and Upper Jurassic strata [17, 26, 27, 29]. Cambrian to Middle Triassic strata comprise more than 6000 m thick shallow-marine carbonates, clastic rocks, shale, and sandstone sequences and are widespread in the middle and south parts of the Edong district (occupying a proportion of almost 50% of the area). The subsequent collision between the Yangtze Craton and the North China Craton made the Paleozoic strata intensely folded during the Late Triassic [28, 35]. Late Triassic to Middle Jurassic strata include mainly continental clastic rocks and coal-bearing shales [16, 22], locally distributing in the west part of the ore district. In the Early Cretaceous, extensive volcanism took place that produced greater than 2000 m thick lavas and volcaniclastics in the Jingniu basin (Figure 2). These volcanic strata can be divided into the Majiashan, Lingxiang, and Dasi formations from bottom to top, with compositions of (trachy-) basalt, (trachy-) andesite, (trachy-) dacite, and rhyolite [22, 26, 36]. SHRIMP zircon U-Pb dating suggests an age of 130 to 124 Ma for the volcanism [36].

The Edong district has undergone extensive plutonic magmatism in Yanshannian, generating six major batholiths, namely, Echeng batholith (100 km²), Tieshan batholith (140 km²), Jinshandian batholith (190 km²), Lingxiang batholith (54 km²), Yinzu batholith (90 km²), and Yangxin batholith (215 km²) (Figure 2). The lithology diﬀers between the batholiths. The Echeng batholith comprises granite and minor quartz diorite, the latter having minor granite porphyry [16, 17]. In addition, more than 30 small granitic to dioritic stocks and dikes surrounded or intruded the major batholiths. All the intrusions cover more than 17% of the area in the Edong district [19], and most of them have intruded into the Devonian to Lower Triassic sedimentary rocks [26]. Besides, a large number of SHRIMP and LA-ICP-MS zircon U-Pb dating data suggest that the intrusive rocks were emplaced between 152 and 132 Ma [22, 26, 28].

The Edong district contains abundant mineral resources, including predominant Fe-Cu-Au-W skarn deposits as well as minor porphyry-skarn Cu-Mo deposits. These skarn deposits are dominantly hosted within the contact zone between Carboniferous, Permian, to Triassic carbonate, clastic rocks, and late Mesozoic intrusions.

3. Geology of the Fuzishan Deposit

The Fuzishan deposit (115°08′00″ to 115°09′06″ E, 29°19′08″ to 29°20′06″ N) is located in southeastern margin of the Yangxin batholith, east portion of the Edong district (Figure 2). The mining area is about 16 km away from the Yangxin County, covering 0.3 km². In the Fuzishan deposit, the outcropped strata include Paleozoic, Mesozoic, to Cenozoic (Figure 3), wherein the Paleozoic strata consist of Middle Silurian quartz sandstone and argillaceous siltstone of Fentou Formation. The Mesozoic strata appear to be dominant, occupying approximately 60% of the total mining area, and are characterized by a set of marine carbonate rocks. They can be chronologically divided into limestone of Middle Carboniferous Huanglong Formation, bioclastic limestone and chert-bearing limestone of Lower Permian Qixia and Maokou Formations, argillaceous limestone and dolomitic limestone of Lower Triassic Daye Formation, and Lower-Middle Triassic Jialingjiang Formation dolomite. The Cenozoic strata are only composed of Quaternary sediments of clay and rock fragments. The carbonate rocks of Silurian to Permian, to a certain extent, are marble in the contact zone due to thermal metamorphism by magmatism. Besides, they also become the significant skarn-forming strata, in which orebodies are hosted. The Lower Permian Maokou Formation is the primary ore-forming strata owing to its widespread skarn zones. Both the Lower-Middle Triassic Jialingjiang Formation and the Lower Permian Maokou Formation show a distinct fault contact relationship (Figure 3).

The intrusive rocks in the Fuzishan deposit are mainly quartz diorite and minor granodiorite porphyry (Figure 3). The quartz diorite shows a close spatial relationship with the orebody and is considered to be related with the Fuzishan porphyry. The quartz diorite presents a middle-granular texture and massive structure and compositionally contains plagioclase (58–68%) and K-feldspar (10–25%), with lesser amounts of amphibole (4–15%) and quartz (2–12%). Zircon and titanite are the main accessory minerals. LA-ICP-MS zircon U-Pb dating yields an age of 138.4 ± 1.7 Ma (our unpublished data), which is similar to the age of Yangxin batholith that previously dated.

In the Fuzishan deposit, a typical fold includes Fuzishan syncline, which is distributed in the northeastern part of the mining area (Figure 3). It is east-west-striking with a core comprised by the jianglingjiang Formation and north and south limbs hosting Daye and Maokou formations, respectively [37]. However, faults are well-developed compared to the folds, which can be divided into three groups, nearly east-west-
striking, northeast-striking, and northwest-striking (Figure 3). The nearly east-west-striking faults have the largest scale, including F1 and F2 faults. F1 is in the contact boundary between the Lower Permian Maokou Formation and the Lower-Middle Triassic Jialingjiang Formation, and it belongs to a thrust fault, which is 73° to 80° south-dipping, extending about 1320 m. Almost all the skarn zone and orebodies occur in parallel with the F1 fault. According to drilling logging, both the quartz diorite and carbonate rocks of Lower Permian Maokou Formation recut the F1 fault below the surface [37]. Therefore, the F1 fault is thought to be the most favorable ore-controlling structure acting as a conduit in transporting hydrothermal fluid and provides sites for ore deposition. Another east-west-striking, south-dipping F2 fault is about at least 300 m in distance from the No. II orebody. The northeast-striking F3 fault has a strike-slip character, whereas the northwest-striking F4 fault is a normal fault. Both F3 and F4 faults are in small-scale located east of the mining area. There is no direct evidence suggesting that F2, F3, and F4 faults control mineralization.

Nine orebodies have been explored in the Fuzishan deposit containing a reserve of 17,374 t Cu and 33 t Mo, with average grades of 0.86% and 0.042%, respectively [37]. Except for the major No. I and No. II orebodies (Figure 3), there also occur seven small orebodies [37]. Most of the orebodies are hosted in the skarn of the contact zone between the quartz diorite and the carbonate rocks of the Lower Permian Maokou Formation (Figure 3) and show lenticular or bedded shapes (Figure 4). The No. I orebody is situated west of the mining area, which extends NW with length of 150 m and
width of 2–20 m and dips to the north at an angle of more than 60° along a distance of 230 m. This orebody occurs at an altitude of +120 m to −110 m and simply comprises copper ores, with an average Cu grade of 0.88%. The No. II orebody occurs in the east part of the mining area. It is 485.5 m in length along the east-west trend, 2.9 m in width, with a dip up to 40° to the north, extending 592.5 m. Besides, the No. II orebody occurs in an altitude ranging from +115 m to −530 m and consists of copper and molybdenum ores with average Cu and Mo grades of 1.78% and 0.063%, respectively.

In the Fuzishan Cu-Mo deposit, the metallic minerals include pyrite, chalcopyrite, bornite, chalcocite, molybdenite, sphalerite, magnetite, and hematite. The ore structures include disseminated (Figures 5(a) and 5(b)), massive (Figure 5(c)), stockwork (Figure 5(d)), veinlet (Figure 5(e)), and speckled (Figure 5(f)). Typical ore textures are euhedral to subhedral granular (Figures 6(a)), metasomatic relic (Figures 6(b)), and solid-solution textures (Figures 6(c) and 6(d)). In the Fuzishan deposit, the Cu mineralization is more widespread than the Mo mineralization, and the Cu-bearing sulfide-disseminated ores are the most pervasive ore type. The majority of disseminated, massive, and stockwork ores are hosted in the skarn zones, either occurring as interstitial fillings or crosscutting along the fractures of skarn minerals and oxides (Figures 5(a)–5(d), 6(b), and 6(e)–6(g)). However, lesser amount of ores tends to fill the fissures and cavities of marble as lumps or veinlets (Figures 5(e) and 6(c)). The Mo-bearing sulfides are only observed in the area associated with chloritization and kaolinization (Figure 5(f)). The Fuzishan deposit also contains different kinds of gange minerals, which are dominated by skarn minerals such as garnet, diopside, actinolite, and epidote (Figures 5(g) and 5(h)), and with relatively less amounts of quartz, calcite, anhydrite, K-feldspar, chlorite, and kaolinite (Figures 5(i)–5(l)).

Hydrothermal alteration related to Cu-Mo mineralization in the Fuzishan deposit comprises skarnification, potassic feldspathization, silicification, chloritization, kaolinization, and carbonization. As mentioned previously, the most extensive skarnification seems to be spatially intimated with Cu orebodies (Figures 5(a) and 5(d)), whereas the Mo mineralization is associated with chloritization (Figure 5(f)). The silicification mainly occurs as quartz + sulfide veins or aggregates (Figures 5(j), 6(a), 6(g), and 6(h)). Both chloritization and kaolinization are only observed in a local area in the Fuzishan deposit, formed by replacing K-feldspar (Figure 5(f)). The carbonization is composed of calcite and minor dolomite. Calcite occurs as aggregates within ores or as late veins crosscutting previously formed minerals (Figures 5(c) and 5(l)).

In terms of field evidences, petrographic observations, mineralogical assemblages, replacement, and crosscutting relationships, four main hydrothermal stages were determined in the Fuzishan deposit, namely, the prograde skarn stage (1), retrograde skarn stage (2), quartz-sulfide stage (3), and carbonate stage (4). Figure 7 illustrates distinct mineral associations in different hydrothermal stages.

The prograde skarn stage is the earliest stage in the hydrothermal evolution history, which is characterized by the formation of anhydrous silicate minerals such as garnet and diopside (Figure 5(g)). Garnet varies from light yellow to reddish brown in colour, and coarse-grained anhedral to euhedral in crystal morphology. The anhedral garnets are optically uniform from the core to the rim, while the euhedral garnets generally contain a light yellow and crackle-rich core, with a brown zoned rim (Figure 6(i)). The anisotropy is possibly explained by variations in the composition of hydrothermal fluid and environment where garnet grows from the core to the rim [26, 38]. Diopside with a dark green colour occurs as fine- to medium-grained, euhedral cubic to anhedral crystals and is more pervasive than garnet in the prograde skarn (Figures 6(e), 6(j), and 6(k)). Particularly, the early anhydrite (Adr I) occurs in this stage and with a lesser amount in diopside skarn. Anhydrite is not pervasively reported in other skarn deposits, and it occurs in the form of thin sheet in white colour coexisting with bornite and chalcopyrite in diopside skarn (Figures 5(a) and 6(e)).

The retrograde skarn stage postdates the prograde stage and is typically accompanied by hydrous mineral assemblages and formation of oxides, as well as minor amount of sulfides. Hydrous minerals include epidote, actinolite, and chlorite. Nevertheless, the epidote is relatively more extensive. Epidote displays bright green colour in hand specimens (Figure 5(h)) and has coarse- to medium-grained, subhedral to anhedral crystals under the microscope (Figures 6(k) and 6(l)). Actinolite is weakly developed, which can only be observed in some thin sections under the microscope. It typically occurs as dark green acicular aggregates in transmitted plane-polarized light, accompanied by epidote, and crosscut by subsequent late anhydrite vein (Adr II) (Figure 6(j)). Collectively, epidote and actinolite generally replaced the prograde skarn minerals to different degrees (Figures 6(j) and 6(l)). Like many other skarn systems, large amount of oxides deposited in this stage, including magnetite and hematite, which occur as euhedral to subhedral, acicular aggregates. They are commonly replaced by the large-scale sulfides (Figures 6(f) and 6(g)). Besides, molybdenite associated with chlorite was also deposited in this stage (Figure 5(f)).

The quartz-sulfide stage is the main stage for the precipitation of extensive Cu-bearing sulfides. Sulfides comprise pyrite, chalcopyrite, bornite, chalcocite, and sphalerite. As mentioned before, these ores occur in different kinds of structures and textures, replacing skarn minerals and oxides, or filling the fractures of skarn and marble. In addition, some transparent minerals also exist in this stage, including quartz, calcite, and late anhydrite (Adr II). Quartz mainly occurs as cryptocrystalline- to fine-grained veins coexisting with sulfides (Figures 5(j), 6(a), 6(d), 6(g), and 6(h)). However, calcite is in light yellow colour and mostly has euhedral granular morphology occurring together with bornite (Figure 5(c)). Specifically, the late anhydrite differs from the early anhydrite, as the latter is characterized by light purple colour, veined to thin-bedded occurrence crosscutting diopside skarn (Figure 5(k)), filling the interstices of diopside crystals together with bornite and chalcocite (Figure 6(e)).

The carbonate stage is the last stage of the hydrothermal activity. Minerals of this stage are represented by calcite,
Figure 5: Photographs of hand specimens showing the mineral assemblages, structures, and different kinds of alterations of the Fuzishan Cu-Mo deposit. (a) Interstitial bornite, chalcocite, and late anhydrite in diopside skarn. (b) Disseminated chalcopyrite overprinting magnetite. (c) Massive bornite ores together with coexisting calcite replacing previously formed garnet, diopside, and epidote. (d) Stockwork bornite and chalcocite ores in diopside skarn. (e) Chalcopyrite and pyrite occurring as small lumps or veinlets in marble. (f) Chloritization and kaolinization together with speckled molybdenum mineralization superimposed on ambiguous potassic feldspathization. (g) Prograde skarn stage containing minerals of garnet and diopside. (h) Retrograde skarn stage epidote replacing prograde skarn garnet. (i) Quartz diorite with potassic feldspathization and minor diopside-bearing skarnization. (j) Silicification comprising light grey quartz and coexisting disseminated pyrite. (k) Late anhydrite displaying as light purple, transparent vein crosscutting diopside skarn. (l) Carbonate stage calcite veins cutting hematite and magnetite. Py: pyrite; Cpy: chalcopyrite; Bn: bornite; Cct: chalcocite; Mol: molybdenite; Mt: magnetite; Hem: hematite; Grt: garnet; Di: diopside; Ep: epidote; Kfs: k-feldspar; Adr I: early anhydrite; Adr II: late anhydrite; Chl: chlorite; Kln: kaolinite; Cal: calcite.
Figure 6: Photomicrographs of representative samples under transmitted plane polarized light (e, i–l) and reflected plane polarized light (a–d, f–h) illustrating mineral assemblages, textures of ores, and alterations in the Fuzishan Cu-Mo deposit. (a) Euhedral pyrite and anhedral chalcopyrite that replace along the margin of pyrite in cryptocrystalline to fine-grained quartz vein. (b) Rosy bornite occurring as relics replaced by grey-white chalcocite in diopside skarn. (c) Chalcopyrite decomposed along the margin or within bornite as irregular bands in marble. (d) Chalcopyrite decomposed in the form of emulsion texture in sphalerite in quartz vein. (e) Bornite, chalcocite, and coexisting late anhydrite in the interstitial space of diopside skarn. (f) Chalcopyrite together with quartz replacing magnetite. (g) Bornite + quartz veinlet crosscutting hematite. (h) Plate-like molybdenite superimposed by subsequent chalcopyrite and bornite in quartz vein. (i) Cracked euhedral garnet replaced by quartz-sulfide stage calcite. (j) Actinolite and epidote replacing diopside, eventually crosscut by the late anhydrite of the quartz-sulfide stage. (k) The cubic diopside in the prograde skarn stage replaced by epidote of the retrograde skarn stage. (l) Garnet nearly replaced by epidote and retaining euhedral crystal morphology.

Py: pyrite; Cpy: chalcopyrite; Bn: bornite; Cct: chalcocite; Mol: molybdenite; Sph: sphalerite; Mt: magnetite; Hem: hematite; Grt: garnet; Di: diopside; Ep: epidote; Kfs: k-feldspar; Adr I: early anhydrite; Adr II: late anhydrite; Cal: calcite.
minor dolomite, and quartz. Calcite occurs as extensive veinlets that crosscut skarn and oxides (Figure 5(l)).

### 4. Analytical Methods

A large number of samples in the Fuzishan Cu-Mo deposit were collected from drill cores and underground tunnels at depths of −260 m, −320 m, and −420 m, respectively. These samples are further used to identify the mineralogical and geochemical studies, from which forty-two doubly polished thin sections (about 200 μm thick) were made for fluid inclusion studies. Fluid inclusions (FIs) of different minerals of the four hydrothermal stages were used for petrographic and laser Raman spectroscopic analyses and microthermometric measurements.

Fluid inclusion petrographic studies were carried out by using the Nikon Eclipse LV100 POL microscope in the National Demonstration Center for Experimental Mineral Exploration Education, China University of Geosciences (Wuhan). Microthermometric measurements were conducted with a Linkam THMS600 heating-freezing stage (from −196 to 550 °C), which is linked with a Leica DM2700 P microscope at China University of Geosciences (Wuhan). Calibration for this heating-freezing stage uses the synthetic FIs supplied by Fluid Inc., USA, with standard values of −56.6 °C, 0.0 °C, and 374.1 °C for ice melting temperature, critical temperature, and CO₂ melting temperature, respectively. The heating/freezing rate is commonly controlled at 0.2–5.0 °C/min but is reduced to <0.2 °C/min near the phase transformation. The uncertainty for the measurements is ±0.5 °C, ±0.2 °C, and ±2.0 °C for the run in the range of −120 °C to −70 °C, −70 °C to 100 °C, and 100 to 600 °C, respectively. Ice melting temperatures were obtained at a heating rate of less than 0.1 °C/min and homogenization temperatures at a rate of ≤1 °C/min.

In order to get the exact microthermometric data for each hydrothermal stage, the primary fluid inclusion assemblages (FIAs) were studied. The primary FIs are formed as isolated, in groups, or sometimes along crystal growth zones [39, 40], and FIAs represent the contemporaneous entrapment in a hydrothermal stage [41, 42]. Secondary FIs occurring in microfractures and transgranular trails are not measured in this study. Three parameters of phase transformation are the final ice melting temperature (Tm), the halite dissolution temperature (Td), and the final homogenization temperature (Th). We use the empirical equations of Hall et al. [43] to calculate salinity for halite-free inclusions and of Sterner et al. [44] for halite-bearing inclusions. Densities are estimated according to the empirical equations of Liu and Duan [45] for halite-free inclusions and of Liu [46] for halite-bearing inclusions.

Laser Raman spectroscopic analyses were conducted at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan), by using a Renishaw RM1000 Raman microscope. The laser source was a 514 nm Ar⁺ ion laser with the excitation source.
operating at 20 mW. Spectrograph aperture was defined as 50 μm. The exposure time was 20–40 s and ranged from 50 to 3500 cm⁻¹.

5. Results

5.1. Petrography and Classification of Fluid Inclusions. On the basis of phase compositions at room temperature and behaviors during the freezing and heating processes, six types of FIs were identified, namely, S₁, S₂, L₀, V_L, L, and V types. Features of each type are described below.

The S₁-type FIs comprise three phases of liquid, vapor, and daughter mineral at room temperature, which are characterized by halite daughter mineral and commonly are rich in liquid phase, with a vapor bubble occupying 15 to 45 vol% at room temperature. The daughter mineral phase of the S₁-type inclusions always contains multiple minerals besides halite, including opaque daughter minerals of chalcopyrite, molybdenite, and hematite, transparent daughter minerals of calcite and anhydrite (Figures 8(a)–8(d)). However, this observation of abundant daughter minerals of FIs in the prograde skarn stage was rarely documented in other skarn or porphyry Cu-Mo deposits, such as only halite + opaque daughter minerals which occur in the porphyry Cu-Mo deposit at Butte [47] and halite + sylvinite + opaque Fe-bearing daughter minerals in the Hongniu-Hongshan skarn Cu deposit [48]. Most S₁-type inclusions range from 4 to 45 μm in size, although irregular (Figures 8(a) and 8(c)) and minor negative crystal shapes dominated (Figures 8(b) and 8(d)). All the S₁-type inclusions show a homogenization nature that halite dissolves before the vapor disappearance. And they were only recognized in garnet and diopside of the prograde skarn stage.

S₂-type FIs contain three phases of liquid, vapor, and daughter mineral same as the S₁ type. However, it typically involves daughter minerals except halite, such as calcite and hematite and sulfide (Figures 8(e)–8(g)). They vary from 4 to 25 μm in size and 10 to 40% vapor bubbles in volumetrical proportion. The shapes of S₂-type inclusions are mostly irregular, with small quantity of elongate and rhombic shapes (Figures 8(f) and 8(g)), and they tend to homogenize into liquid phase. This type of inclusions occurs in both prograde and retrograde skarn stages.

L₀-type FIs comprise two phases of liquid plus vapor at room temperature. They have vapor bubbles of 10 to 40 vol% and size of 2 to 25 μm. This type of inclusions show shapes ranging from rounded, irregular, and elliptical shapes (Figures 8(h)–8(k)). L₀-type inclusions are the most pervasive among all inclusion types, extensively distributed in all stages. Vapor bubbles conformably homogenized into the liquid phase during the heating process.

V_L-type FIs contain two phases of liquid plus dominant vapor phase at room temperature, with vapor bubbles occupying 70 to 90 vol%. They vary from 4 to 20 μm in size and have irregular, elongate, and elliptical shapes. The V_L type commonly coexists with S₁, L₀, and V types within FIs in the prograde, late retrograde skarn, and early quartz-sulfide stage minerals (Figures 8(a), 8(d), and 8(h)). This type of inclusion tends to be homogenized into the vapor phase during the heating process.

The L- and V-type inclusions are recognized only in a small amount and comprise one phase at room temperature. They range from 4 to 20 μm in size and show irregular, rounded, and elongate shapes. Similar to the V_L type, the L- and V-type inclusions occur mostly within FIs in the prograde, late retrograde skarn, and early quartz-sulfide stage minerals (Figures 8(a), 8(e), 8(h), and 8(i)).

5.2. Laser Raman Spectroscopy. Laser Raman spectroscopic analyses reflect the variations of fluid inclusion compositions of different minerals during different hydrothermal stages. The detailed compositions are summarized in Table 1 based on petrographic observations and Laser Raman spectroscopic and microthermometric techniques. Representative Raman spectra are shown in Figure 9.

In the prograde skarn stage, several daughter minerals are identified in S₁-type inclusions. The typical S₁-type inclusion in garnet contains multiple opaque and transparent daughter minerals including red-coloured hematite, cubic-shaped anhydrite, calcite, and chalcopyrite (Figures 9(a)–9(c)); besides, halite was observed as well by its cubic shape and nature of dissolution during the heating process. However, only water was determined in the vapor phase (Figure 9(e)). The S₁-type inclusion in diopside also contains molybdenite, chalcopyrite, and halite (Figures 9(f) and 9(g)).

In the retrograde skarn stage, the daughter mineral phases of fluid inclusions are not so abundant in contrast to the prograde skarn stage. The S₁-type inclusions in epidote comprise calcite (Figure 9(h)) and hematite. The vapor and liquid phases are dominated by water.

In the quartz-sulfide and carbonate stages, fluid inclusions contain no daughter minerals, and only water was identified in vapor and liquid phases.

5.3. Microthermometry. A total of 406 primary FIs from different minerals in different mineralization stages were measured during this study. They included S₁ (56), S₂ (46), L₀ (282), and V_L (22) types. The V_L-type data are relatively less than the other types, as this type of inclusion has an unclear phase boundary, and thus phase transformation is hard to observe during cooling and heating processes. All the data are summarized in Table 2 and shown in Figure 10.

5.3.1. Prograde Skarn Stage. Primary FIs in garnet, diopside, and early anhydrite were selected for microthermometric measurements. S₁-type inclusions are the most abundant, almost occupying up to 60% of all FIs. Quantities of other FIs decreased in the order of V_L, L₀, and S₂ types. Different types of inclusions mainly occurred in cluster, although a small part of S₁-type inclusions distributed in isolation (Figure 8(c)). It was obvious to find that V_L and V types coexist with S₁-type inclusions within any FIs of any mineral in this stage (Figures 8(a) and 8(d)).

Fifty-six S₁-type inclusions were measured, which show halite dissolution temperatures ranging from 127 to 351°C, corresponding to salinities of 28.8 to 42.5 wt.% NaCl equivalent (average = 37.4 wt.% NaCl equivalent). The final
Figure 8: Photomicrographs of representative fluid inclusions in the Fuzishan Cu-Mo deposit. (a) A fluid inclusion assemblage including $S_1$, $S_2$, $L_V$, $V_L$, and V-type inclusions in garnet of the prograde skarn stage. (b) A typical $S_1$-type inclusion containing multiple daughter minerals in garnet of the prograde skarn stage. (c) $S_1$-type inclusion in diopside of the prograde skarn stage. (d) Coexisting $S_1$- and $V_L$-type inclusions in the cubic diopside of the prograde skarn stage. (e) A fluid inclusion assemblage comprising $S_2$, $L_V$, V-type inclusions in epidote of the retrograde skarn stage. (f) A typical $S_2$-type inclusion in epidote of the retrograde skarn stage. (g) $S_2$-type inclusion in epidote of the retrograde skarn stage containing dark opaque daughter mineral, possibly being sulfide. (h) Coexistence of $L_V$, L-, V-, and $V_L$-type inclusions in quartz of the quartz-sulfide stage. (i) Coexisting $L_V$- and V-type inclusions in calcite of the quartz-sulfide stage. (j) $V_L$ and secondary fluid inclusions of the late anhydrite of the quartz-sulfide stage. (k) $L_V$-type inclusions in calcite of the carbonate stage. Cpy: chalcopyrite; Mol: molybdenite; Hem: hematite; Cal: calcite; Adr: anhydrite; H: halite.
homogenization temperatures yield an interval of 422 to >550°C, with a peak value over 550°C (Figures 10(a) and 10(b)), most of which could not be determined due to the high homogenization temperatures greater than the measurement range of the freezing-heating stage in our lab. However, these high-temperature fluid inclusions have very small vapor bubbles with no more than a 5% volume ratio at around 550°C. Other daughter minerals (opaque and transparent minerals except halite) did not dissolve even at final homogenization temperature. The densities vary from 0.82 to 0.99 g/cm³, with an average value of 0.89 g/cm³.

Twenty-four S²-type inclusions were measured. Ice-melting temperatures are −20.8 to −16.4°C, equivalent to salinities between 19.8 and 22.9 wt.% NaCl equivalent, with an average of 21.3 wt.% NaCl equivalent. They showed final homogenization temperatures of 483 to >550°C, with a peak value over 550°C. The S²-type inclusions also contain little vapor bubbles with no more than a 5% volume ratio at around 550°C. The daughter minerals also did not dissolve when reaching the final homogenization temperature. The densities vary from 0.52 to 0.62 g/cm³, with an average value of 0.58 g/cm³.

Thirteen Lᵥ-type inclusions were determined, which show ice-melting temperatures of −19.7 to −13.5°C, corresponding to salinities of 17.3 to 22.1 wt.% NaCl equivalent, with an average of 19.2 wt.% NaCl equivalent. Final homogenization temperatures range from 431 to >550°C, having a peak value over 550°C. Vapor bubbles become very little at about 550°C during the heating process, which are the same as the S₁ and S₂ inclusions. The densities vary from 0.47 to 0.70 g/cm³, with an average value of 0.58 g/cm³. The data of Lᵥ-type coincide well with S₂-type inclusions.

Sixteen Vᵥ-type inclusions measured exhibited ice-melting temperatures of −9.2 to −2.2°C, equivalent to salinities between 3.7 to 13.5 wt.% NaCl equivalent, with an average of 7.2 wt.% NaCl equivalent. Final homogenization temperatures show a range of 405 to >550°C, with a peak value greater than 550°C. Vapor bubbles occupy more than 95% in volume ratio, and the phase boundary is hard to be observed at around 550°C. The densities vary from 0.15 to 0.50 g/cm³ and have an average of 0.27 g/cm³.

5.3.2. Retrograde Skarn Stage. Epidote was the only mineral selected for microthermometric measurements in the retrograde skarn stage. Large amount of FIAs in epidote showed that Lᵥ-type inclusions were extensive, although S₂, Vᵥ, and Vₕ types are relatively less. The Vᵥ- and Vₕ-type FIAs were accompanied by Lᵥ and S₂ types within some FIAs (Figure 8(e)). No S₁-type inclusions were observed in this stage.

Twenty-two S₂-type inclusions were measured, which display ice-melting temperatures of −14.8 to −7.1°C, corresponding to salinities of 10.6 to 18.5 wt.% NaCl equivalent, with an average of 14.3 wt.% NaCl equivalent. Final homogenization temperatures vary from 240 to 471°C, having average of 379°C (Figures 10(c) and 10(d)). The daughter minerals did not dissolve even at final homogenization temperature. The densities range from 0.58 to 0.89 g/cm³ and have an average of 0.73 g/cm³.

Sixty-two Lᵥ-type inclusions were determined, yielding ice-melting temperatures of −17.6 to −5.2°C, equivalent to salinities of 8.1 to 20.7 wt.% NaCl equivalent, with an average of 15.5 wt.% NaCl equivalent. Final homogenization temperatures are between 212 and 498°C, with an average of 350°C. The densities have a range of 0.60 to 0.97 g/cm³, with an average of 0.78 g/cm³.

Two Vᵥ-type inclusion data were obtained. Ice-melting temperatures range from −3.3 to −1.5°C, corresponding to salinities of 2.6 to 5.4 wt.% NaCl equivalent, respectively. The densities range from 0.57 to 0.63 g/cm³.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Host mineral</th>
<th>Determined phase</th>
<th>Component</th>
<th>Characteristic peak (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prograde skarn</td>
<td>Garnet</td>
<td>Daughter mineral</td>
<td>Chalcopyrite</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hematite</td>
<td>1319</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vapor</td>
<td>H₂O</td>
<td>3440</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Halite</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Diopside</td>
<td>Daughter mineral</td>
<td>Chalcopyrite</td>
<td>286</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Molybdenite</td>
<td>408</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hematite</td>
<td>1321</td>
</tr>
<tr>
<td>Retrograde skarn</td>
<td>Epidote</td>
<td>Daughter mineral</td>
<td>Calcite</td>
<td>1085</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sulfide?</td>
<td>—</td>
</tr>
<tr>
<td>Quartz-sulfide</td>
<td>Quartz</td>
<td>Liquid</td>
<td>H₂O</td>
<td>3444</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Calcite</td>
<td>Liquid</td>
<td>H₂O</td>
<td>3450</td>
</tr>
</tbody>
</table>
5.3.3. Quartz-Sulfide Stage. Primary FIAs in quartz, calcite and late anhydrite associated with Cu mineralization were selected for microthermometric measurements. The V or VL types tend to coexist with LV type in some FIAs (Figures 8(h) and 8(i)), while most of FIAs almost contain single LV-type inclusions. Some secondary FIIs occur along transgranular trails (Figure 8(j)). No daughter minerals were observed in fluid inclusions in this stage.

One hundred ninety-four LV-type inclusions were measured, yielding ice-melting temperatures of $-14.1$ to $-1.3\,^\circ C$.

**Figure 9:** Representative Raman spectra of fluid inclusions in the Fuzishan Cu-Mo deposit. (a) Hematite spectra of daughter mineral phase in fluid inclusion of prograde skarn stage garnet. (b) Both anhydrite and calcite spectra of daughter mineral phase in fluid inclusion of prograde skarn stage garnet. (c) Chalcopyrite spectra of daughter mineral phase in fluid inclusion of prograde skarn stage garnet. (d) H$_2$O spectra of vapor phase in fluid inclusion of prograde skarn stage garnet. (e) Molybdenite spectra of daughter mineral phase in fluid inclusion of prograde skarn stage diopside. (g) Chalcopyrite spectra of daughter mineral phase in fluid inclusion of cubic diopside in prograde skarn stage early anhydrite. (h) Calcite spectra of daughter mineral phase in fluid inclusion of retrograde skarn stage epidote. Cpy: chalcopyrite, Mol: molybdenite, Hem: hematite; Cal: calcite; Adr: anhydrite; H: halite; Grt: garnet; Di: diopside; Ep: epidote.
Table 2: Summary of microthermometric data of fluid inclusions from different host minerals and stages in the Fuzishan Cu-Mo deposit.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Host mineral</th>
<th>FI type</th>
<th>Number of Fls studied</th>
<th>Ice-melting temperature Tm (°C) Range</th>
<th>Halite dissolution temperature Td (°C) Range</th>
<th>Final homogenization temperature Th (°C) Mean</th>
<th>Salinity (wt.% NaCl equivalent) Range</th>
<th>Density (g/cm³) Mean Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prograde skarn</td>
<td>Garnet</td>
<td>$S_1$</td>
<td>23</td>
<td>-20.8 to -17.5</td>
<td>127–340</td>
<td>422 to &gt;550</td>
<td>28.8–41.5</td>
<td>36.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_2$</td>
<td>16</td>
<td>-19.7 to -14.0</td>
<td></td>
<td>483 to &gt;550</td>
<td>20.6–22.9</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$L_V$</td>
<td>8</td>
<td>-9.6 to -5.2</td>
<td></td>
<td>431 to &gt;550</td>
<td>17.8–22.1</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_L$</td>
<td>11</td>
<td>180–351</td>
<td></td>
<td>405 to &gt;550</td>
<td>8.1–13.5</td>
<td>10.1</td>
</tr>
<tr>
<td>Diopside</td>
<td>$S_1$</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td>485 to &gt;550</td>
<td>30.9–42.5</td>
<td>38.3</td>
</tr>
<tr>
<td></td>
<td>$S_2$</td>
<td>8</td>
<td></td>
<td>-17.9 to -16.4</td>
<td></td>
<td>488 to &gt;550</td>
<td>19.8–20.1</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>$L_V$</td>
<td>5</td>
<td></td>
<td>-3.5 to -2.2</td>
<td></td>
<td>&gt;550</td>
<td>17.3–18.2</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>$V_L$</td>
<td>5</td>
<td></td>
<td>-3.5 to -2.2</td>
<td></td>
<td>430 to &gt;550</td>
<td>3.7–5.7</td>
<td>5.0</td>
</tr>
<tr>
<td>Retrograde skarn</td>
<td>Epidote</td>
<td>$L_V$</td>
<td>62</td>
<td>-14.8 to -7.1</td>
<td></td>
<td>240 to 471</td>
<td>10.6–18.5</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_L$</td>
<td>2</td>
<td>-17.6 to -5.2</td>
<td></td>
<td>212 to 498</td>
<td>8.1–20.7</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-3.3 and -1.5</td>
<td></td>
<td>350 to 401</td>
<td>2.6–5.4</td>
<td>4</td>
</tr>
<tr>
<td>Quartz-sulfide</td>
<td>Quartz</td>
<td>$L_V$</td>
<td>48</td>
<td>-12.4 to -3.7</td>
<td></td>
<td>192 to 367</td>
<td>6.0–16.3</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_L$</td>
<td>4</td>
<td>-4.4 to -1.7</td>
<td></td>
<td>363 to 485</td>
<td>2.9–7.0</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Calcite</td>
<td>$L_V$</td>
<td>78</td>
<td>-14.1 to -3.5</td>
<td></td>
<td>157 to 382</td>
<td>5.7–17.9</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>Late anhydrite</td>
<td>$L_V$</td>
<td>68</td>
<td>-10.5 to -1.3</td>
<td></td>
<td>150 to 458</td>
<td>2.2–14.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Calcite</td>
<td>$L_V$</td>
<td>9</td>
<td>-2.9 to -1.4</td>
<td></td>
<td>125 to 204</td>
<td>2.4–4.8</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>$L_V$</td>
<td>4</td>
<td>-7.9 to -0.1</td>
<td></td>
<td>89 to 223</td>
<td>0.2–11.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Figure 10: Continued.
equivalent to salinities of 2.2 to 17.9 wt.% NaCl equivalent, with an average of 10.6 wt.% NaCl equivalent. Final homogenization temperatures show a range from 150 to 458 °C, with an average of 273 °C (Figures 10(e) and 10(f)). The densities are between 0.40 and 1.00 g/cm³ and have an average of 0.85 g/cm³.

Only four V L-type fluid inclusions in quartz were determined, as the unclear phase boundary (vapor bubble occupying over 90% of bulk volume) and small size (less than 4 μm) in calcite and late anhydrite. Obtained data show that ice-melting temperatures are from −4.4 to −1.7 °C, corresponding to salinities of 2.9 to 7.0 wt.% NaCl equivalent, with an average of 4.3 wt.% NaCl equivalent. Final homogenization temperatures vary from 363 to 485 °C and have an average of 395 °C. The densities are between 0.41 and 0.62 g/cm³, with an average of 0.56 g/cm³.

5.3.4. Carbonate Stage. Fluid inclusions in late calcite and quartz were quite small and rare. In this stage, L V- and L-type inclusions were observed, from which L V types were mainly isolated in occurrence.

Thirteen L V-type inclusions were measured, obtaining ice-melting temperatures of −7.9 to −0.1°C, which equal to salinities of 0.2 to 11.5 wt.% NaCl equivalent, with an average of 4.0 wt.% NaCl equivalent. Final homogenization temperatures are from 89 to 223°C and have an average value of 156°C (Figures 10(g) and 10(h)). The densities range from 0.89 to 0.98 g/cm³, with an average value of 0.94 g/cm³.

6. Discussion

6.1. Pressure Estimation and Evolution of Ore-Forming Fluids. There are distinct variations in fluid compositions, temperatures, salinities, and pressures during the ore-forming fluid evolution in the Fuzishan Cu-Mo deposit. All microthermometric data are plotted in Figure 11 and are discussed according to the different stages below.

6.1.1. Prograde Skarn Stage (Stage 1). Petrographic characteristics and laser Raman spectroscopy for fluid inclusions in this stage suggest that fluids compositionally contain large amount of ore-forming elements Cu and Mo, as chalcopyrite and molybdenite were identified in the daughter mineral phase of S₁-type inclusions. Moreover, some other daughter minerals, such as hematite and anhydrite, can be indicative of high oxygen fugacity (high fO₂), and SO₄²⁻ is the dominant sulfur-bearing species in the early stage of magmatic-hydrothermal fluids.

Microthermometric data display that final homogenization temperatures of all types of inclusions are quite high, with a peak value of over 550°C. Salinities span a wide range from 3.7 to 13.5 wt.% NaCl equivalent (average of 7.2 wt.% NaCl equivalent) for V L type and 28.8 to 42.5 (average of 37.4 wt.% NaCl equivalent) for S₁-type fluid inclusions. Coexistence of halite-bearing inclusions (S₁ type) and vapor-rich inclusions (V₁, V types) is observed within several FIAs in this stage. Few S₁-type inclusions finally homogenized into the liquid phase by vapor disappearance at around 550°C and average salinity of 37.0 wt.% NaCl equivalent; meanwhile, coexisting V₁-type inclusions with salinity of 5 wt.% NaCl equivalent homogenized to vapor at similar temperatures (Figure 11). We thus reasonably infer that first boiling occurred in the prograde skarn stage, although vast amount of data of S₁- and V L-type inclusions fall in final homogenization temperatures greater than 550°C. We infer that these fluid inclusions very likely homogenize within the 100°C temperature range (homogenization temperature may reach up to 650°C), as they have very small vapor bubbles with no more than 5% in volume ratio for S₁, S₂, and L V inclusions and greater than 95% for V L inclusions at
around 550°C in the same FIA. Thus, we here approximately take 650°C as the upper limit of the final homogenization temperature in this stage, which facilitates later discussion on pressure estimation. Immiscibility between high-salinity brine and low-density vapor has been documented in many skarn and porphyry deposits [3, 4, 48–53]. It is proposed that these fluids are generated via fast decompression and slow cooling of the initial supercritical fluid with intermediate salinities (6 to 8 wt.% NaCl equivalent) exsolved from the magma chamber [54–59]. Therefore, we consider that the same mechanism is also applicable to the Fuzishan Cu-Mo deposit. The initial supercritical fluid unmixing results in the phase separation at about 37.0 wt.% NaCl equivalent high-salinity brine (S1 type) and around 5.0 wt.% NaCl equivalent vapor-rich fluid (V2 type) as well as less than 1.0 wt.% NaCl equivalent vapor (V1 type) at 550°C (Figures 12 and 13).

Trapping pressure can be estimated only if exact trapping temperature is known, or fluid inclusions are trapped during immiscibility and/or boiling conditions [60–62]. Thus, there is no need to correct pressure when selecting the boiling FIA in the prograde skarn stage. All the estimations are made assuming a NaCl-H2O system, as no other soluble salt-bearing daughter minerals (KCl, MgCl2, etc.), except for halite, were observed within any type of fluid inclusions. Hence, other salts are minor in content and negligible. Using the formula provided by Driesner and Heinrich [63], the trapping pressure in this stage was estimated to range from 700 to 1000 bars (green ellipse in Figure 12 and light blue ellipse in Figure 13), corresponding to a lithostatic depth of 2.6 to 3.7 km. There are some data below 550°C yielding the pressures that are lower than 700 bars; this is probably because these inclusions are not in boiling FIA. Consequently, the obtained pressures only represent the minimal trapping pressures.

Hence, other salts are minor in content and negligible. Using the formula provided by Driesner and Heinrich [63], the trapping pressure in this stage was estimated to range from 700 to 1000 bars (green ellipse in Figure 12 and light blue ellipse in Figure 13), corresponding to a lithostatic depth of 2.6 to 3.7 km. There are some data below 550°C yielding the pressures that are lower than 700 bars; this is probably because these inclusions are not in boiling FIA. Consequently, the obtained pressures only represent the minimal trapping pressures.

6.1.2. Retrograde Skarn Stage (Stage 2). Petrographic and laser Raman spectroscopic studies reveal that there are still some S1-type inclusions in this stage, which comprise daughter minerals of hematite, calcite, and sulfide (?). In small part of inclusions, although L1-type inclusions dominate in quantity. In this case, fo2 decreases relative to the prograde skarn stage, which is in accordance with the existence of large amount of oxides (magnetite and hematite) deposited in the retrograde skarn stage. Microthermometric data show that epidote formed in a wide temperature range from 212...
to 498°C, wherein most of the data are between 350 and 450°C and with partially overlapping temperature range of the quartz-sulfide stage (200 to 350°C) (Figure 10(c)). This also suggests that part of sulfides beside molybdenite precipitated in this stage. Salinities are mainly between 8 and 20 wt.% NaCl equivalent, lower than the high-salinity prograde skarn stage. Besides, in both retrograde skarn and quartz-sulfide stages, second boiling did occur due to the coexistence of low-salinity vapor (V type), vapor-rich (V_L type), and moderate-salinity fluid inclusion (L_V type) at temperatures of 350 to 400°C by homogenization into vapor and liquid phases for V_L- and L_V-type inclusions, respectively (Figures 8(e) and 8(h) and purple ellipse in Figure 12 and dark green ellipse in Figure 13). Thus, the trapping pressures for the second boiling event are estimated to range from 150 to 280 bars, equivalent to 1.5 to 2.8 km under hydrostatic conditions. Other inclusions that have final homogenization temperatures greater than 400°C or lower than 350°C in this stage cannot be directly estimated, as they are not trapped in boiling FIAs, generating minimal trapping pressures of 280 to 580 bars or below 150 bars (Figure 12).

6.1.3. Quartz-Sulfide Stage (Stage 3). No sulfide- and oxide-bearing daughter minerals were observed in FIIs, which indicates that sulfides and oxides have already deposited at this stage. Unlike some other skarn systems, no reductive gases, such as CH4, were recognized in the vapor phase. This difference probably suggests a relatively oxidizing environment in or after sulfide deposition.

Final homogenization temperatures and salinities continually decline, having moderate salinities mostly from 4 to 16 wt.% NaCl equivalent and below 400°C in homogenization temperatures. As mentioned above, V-, V_L-, and L_V-type inclusions were simultaneously observed within FIAs of quartz, calcite, and late anhydrite in this stage. A “typical” boiling FIA usually contains high-salinity S_1-type inclusions and low-salinity V_L- or V-type inclusions in many skarn and porphyry deposits [3, 48]. However, in the Fuzishan deposit, there is no S_1-type inclusion found in boiling FIAs of the quartz-sulfide stage, similar to that documented by Shu et al. [62]. Trapping pressures for the quartz-sulfide stage are 150 to 280 bars, corresponding to 1.5 to 2.8 km under hydrostatic conditions when calculated by using boiling FIAs. However, several FIAs simply comprise L_V-type inclusions, yielding a homogenization temperature range of 200 to 350°C for quartz-sulfide stage; thus, their minimal trapping pressures are below 150 bars (Figures 10 and 12).

6.1.4. Carbonate Stage (Stage 4). The last stage is characterized by low-temperature and low-salinity fluid and L_V- and
L-type inclusions in late calcite and quartz. The L_v-type inclusions have homogenization temperatures <250°C and salinities <12 wt.% NaCl equivalent. The minimal trapping pressures for this stage are <100 bars (Figure 12).

In summary, there is a distinct decreasing trend of temperature, salinity, and pressure from early to late stages. If the fluid evolution model of most skarn systems is extended from the porphyry Cu deposit as suggested by Meinert et al. [3], the ore-forming fluid in the Fuzishan Cu-Mo deposit can be illustrated into the following two evolutionary processes (Figure 14). First, when the quartz diorite intruded to shallow depth (about 4 to 5 km in lithostatic condition), the magma had a high temperature (>400°C and up to 700–800°C) and the wall rocks behaved in a ductile nature [64]. Thus, the magmatic system can be regarded as a closed system. A moderate supercritical fluid with salinity of 6 to 8 wt.% NaCl equivalent may be exsolved along with magma saturation during cooling and crystallization. This kind of fluid gathered on top of the magma chamber, ascending to a shallower depth (around 2.6 to 3.7 km) concurrent with intrusions. In this case, continuous exsolved fluid can maintain relatively high temperature and with only minor conductive cooling [57]. Rapid decompressive and nearly homothermal conditions make this supercritical fluid interse its solvus. Thus, immiscibility can occur, yielding a 40 wt.% NaCl equivalent hypersaline fluid and a 5 wt.% NaCl equivalent low-salinity fluid (the blue path in Figure 14). Many prograde skarn minerals form in this hypersaline liquid [3]. Second, when the underlying magma evolves to the final stage, it approaches stagnant crystallization and fast cooling due to lack of concurrent intrusions [57]. The subsequently exsolved fluid will not intersect the solvus as the more gentle path (green path in Figure 14). The temperature declining to about 400°C is considered to be the transition temperature from lithostatic to hydrostatic conditions because of change from ductile to brittle behavior [62, 64, 65]. Consequently, the fluid pressure drops quickly, intersecting its solvus and generating coexisting V, V_1, and L_v-type inclusions in boiling condition in late retrograde skarn and early quartz-sulfide stages. This may account for precipitation of Cu-bearing sulfides (chalcopyrite, bornite, chalcocite, etc.). Such a model is established on the basis of the sole magmatic origin for the formation of prograde skarn, retrograde skarn, and hydrothermal ore precipitation [3, 8, 66]. However, we cannot exclude the contributions of external fluids at present, such as admixture of meteoric and formation waters, which have already been evidenced in some other skarn deposits by some geochemical and isotopic data [1, 67–70].

6.2. Mechanism for Metal Transportation and Precipitation. Transportation of metals in hydrothermal fluid has been thought to be in the form of metal complexes. However, there are still some controversies regarding the type of ligands (e.g., Cl, F, and S) combined with metals (e.g., Cu, Mo) and metal partitioning habit between liquid and vapor [71]. Previous studies experimentally demonstrated that Cu is partitioned strongly into a high-salinity, Cl-rich brine relative to low-salinity vapor in the NaCl-KCl-CuCl-H2O fluid system [72–74] and Mo may share the same behavior [75]. These results provide strong support for the leading role of Cl-rich brine in the evolution of porphyry (skarn) Cu-Mo deposits [71]. Recent analyses of individual vapor and brine fluid inclusions from natural boiling assemblages by using proton-induced X-ray-emission (PIXE) and laser ablation inductively coupled mass spectrometry (LA-ICP-MS) techniques suggest that Cu is preferentially partitioned into low-salinity vapor relative to coexisting brine, yielding a partition coefficient $D_{Cu}^{cl}$ of 1 to 10 [76–78], and similar results were also obtained for Mo [79]. It is suggested that sulfur is the main ligand due to its high concentration in the vapor phase (e.g., H2S, SO2) and strong fractionation for Cu into vapor rather than coexisting brine [77, 80, 81]. A significant amount of Cu or Au, which is transported by such vapor plumes condensing to an aqueous liquid during ascension, may be responsible for some shallow-depth epithermal Cu (Au) deposits in the porphyry environment [82, 83]. However, in the Fuzishan skarn deposit with relatively moderate depth, we suggest that the Cl-rich brine phase is the major carrier for Cu and Mo, as evidenced by pervasive chalcopyrite, molybdenite, and halite daughter minerals in S_1-type inclusions of the prograde skarn stage.

The mechanism for ore precipitation depends on some physicochemical parameters, which include salinity (chloride concentration), redox state (fO2), pH, temperature, and pressure [84–88]. Liu and McPhail [89] pointed out that increasing pressure and pH or decreasing temperature and fO2 as well as chloride concentration could lower the solubility of copper. There are some small variations between Cu and Mo in solubility, because molybdenum tends to saturate in more oxidizing (high fO2), low-acidity (more neutral pH), and lower-temperature conditions compared to chalcopyrite [75, 90–93]. Besides, immiscibility and/or boiling are also suitable mechanisms for ore deposition, as they sharply change physicochemical parameters in hydrothermal fluid. A number of studies indicated that phase separation could cause a decrease in temperature and pressure and increase pH by removing acidic volatiles (CO2, H2S, and SO2) in an ore-forming fluid, consequently resulting in ore precipitation due to instability of metal complexes [94–98].

Combining the finding mentioned above, we can qualitatively interpret that Cu and Mo did not precipitate in the prograde skarn stage of the Fuzishan deposit because of their high solubility in high temperature (>550°C), although immiscibility did occur, similar to that described by Peng et al. [48]. Petrographic studies indicate that molybdenum mineralization was earlier than copper mineralization in temporal sequence, probably due to that molybdenite was saturated prior to chalcopyrite at higher temperatures in the retrograde skarn stage, while chalcopyrite subsequently reached saturation in the quartz-sulfide stage. Microthermometric data show that Cu-bearing sulfides deposited at a temperature below 400°C, consistent with either calculated or measured temperature values at which fluid reached copper saturation [89, 99–101]. It seems that 400°C is an important cutoff point controlling Cu-bearing sulfide precipitation. As discussed above, 400°C is also a transition
from lithostatic to hydrostatic pressure at which the hydrothermal system became open and boiling event occurred. Suitable temperature and boiling may play a very important role in precipitation of Cu-bearing sulfides. Moreover, petrographic observations show existence of late anhydrite in the quartz-sulfide stage (Figure 6(j)). It is unlikely to see anhydrite deposit at a relatively low temperature (below 400°C) due to its high solubility with decreasing temperature [102, 103], unless it is gypsum or anhydrite from external sources. In the Fuzishan deposit, Triassic to Permian carbonate wall rocks contain significant amount of gypsum-bearing layers that may be responsible for the anhydrite saturation at lower temperatures. Alternatively, cooler meteoric water leaching a certain amount of marine sulfates might have circulated into the magmatic hydrothermal system as a result of an open system. The mixing of these two distinct fluids could not only decrease the temperature and chloride concentration but also increase $f_{O_2}$ due to addition of relatively oxidizing and cold meteoric water that carries part of $SO_4^{2-}$ gases (CH$_4$, H$_2$S, etc.) in the vapor phase and no hematite.

Raman spectrometric analyses which indicated no reductive reaction occurred. Suitable temperature and boiling may play a very important role in the hydrothermal system became open and boiling event when the Fuzishan deposit, Triassic to Permian carbonate wall rocks contain significant amount of gypsum-bearing layers that may be responsible for the anhydrite saturation at lower temperatures. Alternatively, cooler meteoric water leaching a certain amount of marine sulfates might have circulated into the magmatic hydrothermal system as a result of an open system. The mixing of these two distinct fluids could not only decrease the temperature and chloride concentration but also increase $f_{O_2}$ due to addition of relatively oxidizing and cold meteoric water that carries part of $SO_4^{2-}$ gases (CH$_4$, H$_2$S, etc.) in the vapor phase and no hematite. In the Fuzishan deposit, Triassic to Permian carbonate wall rocks contain significant amount of gypsum-bearing layers that may be responsible for the anhydrite saturation at lower temperatures. Alternatively, cooler meteoric water leaching a certain amount of marine sulfates might have circulated into the magmatic hydrothermal system as a result of an open system. The mixing of these two distinct fluids could not only decrease the temperature and chloride concentration but also increase $f_{O_2}$ due to addition of relatively oxidizing and cold meteoric water that carries part of $SO_4^{2-}$ gases (CH$_4$, H$_2$S, etc.) in the vapor phase and no hematite.

Sulphur isotope data for these deposits support that skarn Fe mineralization is related to assimilation of Triassic carbonate wall rocks that contain gypsum-bearing layers at the magmatic stage. The same process may also be applicable in the Fuzishan deposit as widespread Permian to Triassic strata exposed in the mining area. In addition, fluid inclusion petrography and laser Raman spectrometry show the presence of abundant daughter minerals (chalcopyrite, molybdenite, hematite, halite, calcite, and anhydrite) in S$_1$-type FIs of the prograde skarn stage and the ore-forming fluid has no CO$_2$ content in the Fuzishan deposit. In contrast, the ore-forming fluid contains CO$_2$ and simple daughter mineral (halite) in Tongshanporphyry-skarn Cu-Mo and comprises daughter minerals such as halite, sylvite, and opaque minerals as well as no CO$_2$ in the Tonglvshan skarn Cu-Fe deposit [30, 107]. Microthermometry conformationally suggests that ore-forming fluid of all the skarn Fe-Cu-Mo deposits undergo an evolution process from high temperature, high salinity, and high pressure in early stage to low temperature, low salinity, and low pressure in late stage. The mechanism for ore precipitation in the Tongshanporphyry-skarn Cu-Mo is mainly temperature decline and fluid mixture with meteoric water [31, 32], and fluid boiling is considered to be the main reason for ore deposition in the Tonglvshan skarn Cu-Fe deposit [107]. However, in the Fuzishan deposit, temperature decline and fluid boiling primarily control the ore precipitation.

6.4. Comparison with Other Cu-Mo Deposits Worldwide. Skarn- (porphyry) Cu-Mo deposits widely formed in oceanic and continental subduction settings and are associated with oxidized I-type granites [3–5]. In the Fuzishan deposit, the early ore-forming fluid is of high $f_{O_2}$ nature and $SO_4^{2-}$ is the dominant sulfur-bearing species in the prograde skarn stage, which is consistent with other giant porphyry and skarn Cu deposit systems worldwide, at which ore-forming fluid is genetically related to oxidized magma [108–112]. In addition, CO$_2$-bearing FIs and different S-type FIs that are homogenized by halite dissolving after vapor disappearance are generally reported in some skarn Cu and porphyry Cu-Mo deposits [47, 52], whereas the Fuzishan deposit does not have this type of FIs, and the fluid inclusion is characterized by occurrence of multiple daughter minerals. Our fluid inclusion studies evidenced that boiling occurred in the prograde skarn stage and quartz-sulfide stage, respectively, which is similar to a fluid evolution model with two-stage fluid phase separation documented in some skarn Cu-Au, Pb-Zn, and Cu deposits [3, 48, 62]. However, in some porphyry Cu-Mo deposits, only one-stage fluid phase is observed [47].

7. Conclusions

On the basis of geology, mineralogy, and fluid inclusion studies in the Fuzishan Cu-Mo deposit, the following conclusions can be drawn:

(1) The Fuzishan deposit is a typical skarn Cu-Mo deposit located in the southeastern margin of Yangxin batholith in the Edong district of the MLYRMB. The paragenetic sequences for ore and gangue minerals can be divided into four stages: prograde skarn stage (1), retrograde skarn stage (2), quartz-sulfide stage (3), and carbonate stage (4). The ore minerals contain molybdenite, chalcopyrite, bornite, and chalcocite, while gangue minerals mainly comprise garnet, diopside, anhydrite, epidote, quartz, and calcite.

(2) Initial fluid in the prograde skarn stage is characterized by high oxygen fugacity, high concentration of Cu and Mo, high temperature, and high salinity.
However, temperature, salinity, and concentration of Cu and Mo in the quartz-sulfide stage generally decrease. This indicates that ore metals have deposited by the variations of physiochemical conditions.

(3) Pressure for first boiling in the prograde skarn stage is about 700 to 1000 bars, corresponding to lithostatic depths of 2.6 to 3.7 km, while in the quartz-sulfide stage, second boiling yields a trapping pressure of 150 to 280 bars, equivalent to hydrostatic depths of 1.5 to 2.8 km.

(4) Ore-forming elements (Cu and Mo) are mainly transported as metal complexes with Cl ligand. Declining temperature and boiling event in the quartz-sulfide stage are the major factors causing the ore precipitation.

Data Availability
The data used to support the findings of this study are included within the article.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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