Research Article

Fluid Inclusion and Oxygen Isotope Constraints on the Origin and Hydrothermal Evolution of the Haisugou Porphyry Mo Deposit in the Northern Xilamulun District, NE China

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The Haisugou porphyry Mo deposit is located in the northern Xilamulun district, northeastern China. Based on alteration and mineralization styles and crosscutting relationships, the hydrothermal evolution in Haisugou can be divided into three stages: an early potassic alteration stage with no significant metal deposition, a synmineralization sericite-chlorite alteration stage with extensive Mo precipitation, and a postmineralization stage characterized by barren quartz and minor calcite and fluorite. The coexistence of high-salinity brine inclusions with low-salinity inclusions both in potassic alteration stage (~440°C) and locally in the early time of mineralization stage (380–320°C) indicates the occurrence of fluid boiling. The positive correlations between the homogenization temperatures and the salinities of the fluids and the low oxygen isotopic compositions ($\delta^{18}\text{O}_{\text{fluid}} < 3\text{‰}$) of the syn- to postmineralization quartz together suggest the mixing of magmatic fluids with meteoric water, which dominated the whole mineralization process. The early boiling fluids were not responsible for ore precipitation, whereas the mixing with meteoric water, which resulted in temperature decrease and dilution that significantly reduced the metal solubility, should have played the major role in Mo mineralization. Combined fluid inclusion microthermometry and chlorite geothermometer results reveal that ore deposition mainly occurred between 350 and 290°C in Haisugou.

1. Introduction

The global molybdenum resource comes almost completely from porphyry-type deposits. In some of these deposits Mo is recovered as byproduct (i.e., porphyry Cu-Mo ($\pm$ Au) deposits), whereas, in others, the deposits are characterized by high abundances of Mo but virtually no Cu or Au (i.e., purely porphyry Mo deposits) such as the Climax-type deposits along the North American Cordillera [1–3]. China has more than half of the world's molybdenum metal [4], and many of the Mo deposits are similar to the Climax-type Mo deposits where molybdenite is almost the only sulfide [5]. Most of China's Mo deposits are located in the Qinling-Dabie orogenic belt in Central China (>8.5 Mt Mo metal [4, 6, 7])

and the eastern section of the Central Asian orogenic belt in northeastern China (>11 Mt Mo metal [8, 9]). Unlike the Climax-type Mo deposits, which typically develop in back-arc or intracontinental rifts and are associated with alkaline magmas [1], the porphyry Mo deposits in the Chinese Qinling-Dabie orogenic belt are related to high-K calc-alkaline to shoshonitic magmas generated in syn- to postcollisional tectonic settings and therefore have been suggested to belong to a new class of Dabie-type (or collision-type) porphyry Mo deposits [7, 10–12]. However, recently Audétat and Li [13] argued that some of the previously proposed Dabie-type deposits can still be classified as Climax-type. Northeastern China has become the largest Mo ore region in China with the continuous discoveries of many porphyry

Mo deposits in recent years, including the giant Chalukou (2.46 Mt Mo), Caosiyao (1.79 Mt Mo), Daheishan (1.09 Mt Mo), Luming (0.89 Mt Mo), and Diyanqin'amu (0.78 Mt Mo) porphyry Mo deposits [8]. These deposits are mainly Mo-only or Mo-dominant (with minor Cu) deposits, and many of the deposits have Yanshanian (Jurassic to Early Cretaceous) ages and have been suggested to be related to the subduction or subsequent slab rollback of the Paleo-Pacific oceanic plate [8].

The nature and evolution of the fluids associated with porphyry Mo mineralization have been well documented through mineralogical, stable isotopic, melt and fluid inclusion studies [2, 3, 7, 10, 12–14]. It is generally accepted that both the Climax- and the Dabie-type Mo deposits are related to hydrothermal fluids with high contents of F and H₂O but variable CO₂ [7, 13]. Fluid boiling assemblages have been recognized in almost all porphyry Mo deposits [7, 10, 12, 13]. However, it was proposed that boiling is not the major factor controlling Mo precipitation for the Climax-type Mo deposits [13], although it has been suggested to have played a role in ore deposition for the Chinese Dabie-type Mo deposits by some Chinese geologists [7, 10, 12]. Till present the origin and evolution of fluids forming the porphyry Mo deposits in NE China have been rarely investigated [15–17], and the formation conditions and mechanisms remain unclear.

The newly discovered Haisugou porphyry Mo deposit located in the northern Xilamulun district, NE China, is a typical Mo-only deposit where >95% of the sulfides are molybdenite [8, 18, 19]. The quartz veins or breccias with variable alterations prior to, synchronous to, and immediately after molybdenite precipitation are widely distributed within the ore-related granite and thus provide an excellent opportunity to investigate the fluids (as fluid inclusions hosted in quartz) throughout the hydrothermal evolution processes. The present study aims at tracing the genesis and the hydrothermal evolution leading to alteration, metal concentration, and formation of the Haisugou porphyry Mo deposit through detailed study of fluid inclusion microthermometry, oxygen isotope, and chlorite chemistry. In addition, a comparison is also made to reveal the similarities and differences between the Haisugou Mo deposit and other Mo deposits in China and worldwide.

2. Regional Geology

Northeastern China lies in the eastern section of the Central Asian orogenic belt, a major Phanerozoic orogenic belt that separated the Siberia Craton to the north and the Tarim and North China Cratons to the south [20]. In the easternmost part of the Central Asian orogenic belt, the prolonged evolution processes in Paleozoic including subduction, accretion, and final closure of the Paleo-Asian ocean along the Xilamulun-Changchun suture resulted in the amalgamation of several microcontinents and the formation of what is now NE China (Figure 1(a) [21]). The major blocks in NE China include, from north to south, the Erguna, Xing'an, Songliao, and Liaoyuan (also known as the Bainaimiao arc belt [22, 23]) terranes, which are bounded by a series of nearly E- or NE-trending faults including the Tayuan-Xiguitu suture, the Hegenshan-Heihe suture, and the Xilamulun-Changchun

suture (Figure 1(a)). South to the Liaoyuan terrane is the northern margin of the North China Craton, which is separated from the Liaoyuan terrane by the Chifeng-Kaiyuan Fault (Figure 1(a)).

In Paleozoic, due to the southward subduction of the Paleo-Asian oceanic plate beneath the northern margin of the North China Craton, extensive subduction-related intrusions have been recognized in the region, forming a typical Andean-type continental margin [24, 25]. In Triassic, NE China went into a postcollisional intraplate evolution stage, as indicated by the occurrence of many alkaline rocks including ultramafic-syenite complexes, lamprophyres, and A-type granites [24–28]. Since Jurassic, NE China has been reactivated as a result of the westward subduction of the Paleo-Pacific oceanic plate [23, 29]. The majority of the igneous rocks in NE China have Yanshanian ages [23, 29, 30] and have been attributed to the tectonic-thermal events related to the Paleo-Pacific plate subduction or subsequent slab rollback [23, 29]. Coinciding with the Yanshanian magmatism, many hydrothermal ore systems formed in NE China, and many of them are Mo-dominant porphyry deposits [8, 9, 31], with less of skarn or epithermal types [31–34].

The Xilamulun district is named after the Xilamulun-Changchun suture, which divided the district into two parts (Figure 1(b)). The northern part (north of the suture) lies within the Songliao terrane, and the southern part (south of the suture) is part of the Liaoyuan terrane and the northern margin of the North China Craton (Figure 1(b)). There are two NNE-striking faults in this region, the Great Xing'an Range Fault in the west and the Nenjiang Fault in the east (Figure 1(b)), both of which are much younger than the E-trending Xilamulun-Changchun Fault; they were caused by the NW-directed subduction of the Paleo-Pacific plate [37]. The Xilamulun district contains Archean gneiss and Paleozoic schist and marble in the south and Mesozoic sedimentary, intrusive, and volcanic rocks in the north (Figure 1(b)). The Xilamulun district has more than 25 Mo deposits, six of which are of Triassic ages, while the rest are of Late Jurassic to Early Cretaceous ages (Figure 1(b) [8]). The Haisugou deposit is located in the northern Xilamulun district, and the magmatism and Mo mineralization occurred in Early Cretaceous [8, 18].

3. Deposit Geology

3.1. General Characteristics. The Haisugou porphyry Mo deposit is about 50 kilometers to the north-northwest of the Lindong town, Barin Zuoqi in Inner Mongolia. It was discovered in 2010 and exploration is still on-going, and its resources have not been defined. The Haisugou granite is the major host to the orebodies (Figures 1(c) and 2), which outcrops less than 1 km². The granite intrudes into the Lower Permian Qingfengshan Formation limestone and sandstone (Figure 1(c)). At the contact zone between the granite and the limestone, massive skarns have been recognized (Figure 2(d)); stratabound skarn zones also occur in hornfels [8]. However, there is no obvious mineralization on the skarns or within the sedimentary wallrocks. To the west of the mining area, there is a granodiorite stock (Biliutai granodiorite in

FIGURE 1: (a) Tectonic subdivisions of northeastern China and location of the Xilamulun district (from Wu et al. [21]). (b) Geological map of the Xilamulun district and the locations of major Mesozoic Mo deposits (from Shu et al. [8]). (c) Simplified geological map of the Haisugou porphyry Mo deposit (from Shu et al. [18]).

Figure 1(c)). This stock has Triassic ages [41] and has no obvious alteration and mineralization.

The Haisugou granite is porphyritic with fine-grained groundmass (Figures 2(a) and 2(b)). Plagioclase is the major phenocryst, which occupies ~20 vol% of the rock, and it is typically zoned and rimmed by K-feldspar. Other phenocrysts include biotite and amphibole (Figure 3(a)). The groundmass is composed of plagioclase, K-feldspar, quartz, and biotite. Geochemically, the granite contains 68–75 wt% SiO₂,

12.6–15.1 wt% Al₂O₃, 3.1–4.1 wt% Na₂O, and 3.3–4.7 wt% K₂O, belongs to the high-K calc-alkaline series, and is characterized by relatively high LREE, low HREE, depletion of Ti, Ba, and Nb, and a moderate negative Eu anomaly [18]. Dioritic microgranular enclaves are distributed throughout the granite, which are generally several centimeters in diameter, and are rounded, ellipsoidal, or lenticular in shape (Figure 2(c)). Recent geochronological study indicated that the emplacement age of the granite is 137.6 ± 0.9 Ma (zircon

FIGURE 2: Hand-specimen photographs from the Haisugou Mo deposit showing the granite and the alteration and vein types from different hydrothermal stages. (a) Polished granite sample showing the major minerals including plagioclase, quartz, K-feldspar, biotite, and amphibole. (b) Barren quartz-K-feldspar veinlets in granite recording the earliest hydrothermal alteration in Haisugou. (c) Mafic microgranular enclaves in granite. (d) Garnet-pyroxene skarn in limestone in the contact zone between the country rocks and the granite. (e) Slightly mineralized P-stage quartz vein with K-feldspar halos. (f) S-stage quartz-sericite-molybdenite vein. (g) S-stage molybdenite-quartz-calcite-sericite vein. (h) S-stage quartz-molybdenite vein with chlorite and epidote halos. (i) Hydrothermal breccias containing clasts of S-stage molybdenite-quartz-sericite-chlorite aggregates cemented by B-stage barren quartz and fluorite. (j) Hydrothermal breccias containing clasts of S-stage molybdenite-quartz-chlorite aggregates cemented by B-stage barren quartz. The scale bar is 1 cm in each photograph. Cal: calcite; Chl: chlorite; Ep: epidote; Fl: fluorite; Grt: garnet; Kfs: K-feldspar; MME: mafic microgranular enclave; Mol: molybdenite; Pyx: pyroxene; Qtz: quartz; Ser: sericite.

FIGURE 3: Representative photomicrographs from the Haisugou Mo deposit showing the alteration and mineralization in different hydrothermal stages. (a) Photomicrograph of the Haisugou granite showing the major phenocryst minerals. (b) Plagioclase of the granite altered to sericite and calcite. (c) P-stage barren quartz vein surrounded by K-feldspar halos. (d) Hornblende of the granite altered to magnetite and chlorite. (e) S-stage quartz-calcite-molybdenite vein with chlorite halos. (f) S-stage quartz-molybdenite-chlorite-epidote vein with sericite halos. (g) S-stage molybdenite-quartz-sericite vein. (h) Molybdenite flakes in S-stage quartz vein. (i) Molybdenite flakes and chalcopryite in S-stage breccia ores. (a), (b), (f), and (g) were taken under crossed polarized light, (c), (d), and (e) under plane polarized light, and (h) and (i) under reflected light. The scale bar is 0.5 mm in each photomicrograph. Bt: biotite; Cal: calcite; Ccp: chalcopryite; Chl: chlorite; Ep: epidote; Hbl: hornblende; Kfs: K-feldspar; Mag: magnetite; Mol: molybdenite; Pl: plagioclase; Qtz: quartz; Ser: sericite.

U-Pb dating [18]) and the mineralization age is 136.4 ± 0.8 Ma (molybdenite Re-Os dating [8]). The two age datasets are well consistent within error, suggesting that the granite is the synmineralization intrusion.

3.2. Alteration and Mineralization. The Haisugou granite is hydrothermally altered and mineralized. Based on hand lens examination of field samples supplemented by petrographic

observation of thin sections, a series of alteration types with various degrees of mineralization have been recognized (Figures 2 and 3). A simplified paragenetic sequence of the alteration and mineralization at Haisugou is shown in Figure 4.

The earliest alteration minerals are hydrothermal K-feldspar and minor secondary biotite and magnetite. The K-feldspar mainly occurs as halos surrounding barren quartz

	Preminalization P-stage	Synmineralization S-stage	Postmineralization B-stage
K-feldspar	—		
Biotite	—		
Magnetite	—		
Chlorite		—	
Sericite		—	
Epidote		—	
Quartz	—	—	—
Calcite			—
Fluorite			—
Molybdenite	—	—	
Pyrite	—	—	
Chalcopyrite		—	

FIGURE 4: Schematic paragenetic sequence of the Haisugou Mo deposit.

veins (generally <10 mm wide, Figures 2(b) and 3(c)), although some molybdenite-bearing quartz veins (1–5 mm wide) also have K-feldspar halos (Figure 2(e)). These two types of quartz veins with K-feldspar halos are the main potassic alteration assemblages at Haisugou. In addition, hydrothermal K-feldspar veinlets (<5 mm wide, without obvious quartz) are also common in the mineralized granite [8]. Hydrothermal biotites are rare but, when observed, they occur as halos along irregular barren quartz veinlets. Magnetites are also rare and can locally be found in the potassically altered barren quartz veins, or as emplacement of hornblende in the granite (Figure 3(d)).

The early potassic alteration is overprinted by later sericite-chlorite alteration. The general alteration assemblages are molybdenite-rich quartz-sericite $\pm$ chlorite $\pm$ epidote $\pm$ calcite veins (Figures 2(f)–2(h) and 3(d)–3(g)) or quartz-molybdenite-chlorite breccias (Figures 2(i) and 2(j)). The veins are often seen to cut the potassically altered barren quartz veins. It is also common in the granite that plagioclase is altered to sericite $\pm$ calcite (Figure 3(b)) and hornblende is replaced by chlorite (Figure 3(d)). This alteration stage is the main mineralization stage at Haisugou and directly controls bulk Mo mineralization. Sulfide minerals, mostly molybdenite with trace pyrite and chalcopyrite, occur mainly in these quartz veins (Figures 2(f)–2(h), 3(h) and 3(i)) with sericite $\pm$ chlorite $\pm$ calcite halos and to a lesser extent as disseminated grains in the granite. The quartz-sulfide veins are <1 to ~10 cm wide (Figures 2(f)–2(h)). Breccia ores with centimeter-sized, angular-subangular clasts of quartz-molybdenite-chlorite fragments cemented by late barren quartz have also been recognized (Figures 2(i) and 2(j)).

Barren quartz veins are also seen to postdate preexisting potassic and sericite-chlorite alterations (Figures 2(i) and 2(j)). Unlike the barren quartz in the potassic alteration stage, these barren quartz veins are wider (0.2–2 cm) but have no obvious alteration halo. This stage barren quartz also occurs as fillings cementing the above-mentioned hydrothermal breccias (Figure 2(j)). Other minerals including calcite and very rare fluorite are also seen in the barren quartz veins (Figure 2(i)), altogether indicating a relatively later and cooler fluid evolution stage and a postmineralization timing.

Based on the above observation, the alteration and mineralization of the Haisugou porphyry Mo deposit can be generally divided into three stages (Figure 4): an early potassic alteration stage (P-stage), a synmineralization sericite-chlorite alteration stage (S-stage), and a postmineralization barren quartz stage (B-stage). The following text focuses on fluid inclusion and oxygen isotopic studies related to the quartz in these three different stages.

4. Analytical Methods

Altered granite and different quartz veins or breccias samples in Haisugou were collected for observation and analyses. For fluid inclusion study, the quartz samples representing the three hydrothermal evolution stages were selected and are summarized in Table 1. Prior to microthermometric analysis, a qualitative detection of the individual fluid inclusion compositions including vapor phase, liquid phase, and daughter minerals was carried out using a RM-1000 Laser Raman scanning spectrometer at Peking University. An excitation wave length of 514.5 nm was used as the laser source with a power of 22 mW. The scanning range was 200–4000 cm^{-1} . The spectral resolution was $\pm 2 \text{ cm}^{-1}$ with a minimum diameter of the laser beam of 2 μm . Fluid inclusion microthermometric data were measured using an INSTEC HCS622XY programmable heating-cooling stage attached to a Nikon ECLIPSE LV100POL transmitted light microscope at Peking University. Stage calibration was carried out using synthetic fluid inclusions at the triple point of CO_2 (-56.6°C) and the freezing point of pure water (0.0°C). Estimated accuracy is $\pm 0.1^\circ\text{C}$ for measurements of final ice-melting temperatures and within 4°C for halite dissolution and final homogenization temperatures. Heating/cooling rates were commonly restricted to $\sim 10^\circ\text{C}/\text{min}$ and reduced to $< 1^\circ\text{C}/\text{min}$ near phase transformation. The salinity of the halite-bearing fluid inclusions was calculated from halite dissolution temperatures [42], and, for the liquid-vapor inclusions, the salinity was calculated from the final ice-melting temperatures [43]. All the salinity data are reported in weight percent NaCl equivalent (wt% NaCl equiv).

TABLE 1: Descriptions of the samples used for fluid inclusion microthermometry in this study.

Sample number	Sample description	Assemblages for fluid inclusion microanalyses
<i>P-stage</i>		
HSG09-04	Quartz and K-feldspar vein, with minor molybdenite	HSG09-04.1, HSG09-04.2, HSG09-04.3, HSG09-04.4
HSG09-08a	Barren quartz and K-feldspar vein	HSG09-08a.1, HSG09-08a.2
HSG09-15	Quartz-sulfides (molybdenite + chalcopyrite) vein with K-feldspar halo	HSG09-15.1
HSG09-32	Quartz and K-feldspar vein with no obvious sulfide	HSG09-32.1, HSG09-32.2, HSG09-32.3, HSG09-32.4, HSG09-32.5, HSG09-32.6
HSG09-44	Quartz-molybdenite vein with K-feldspar halo	HSG09-44.1, HSG09-44.2, HSG09-44.3, HSG09-44.4, HSG09-44.5
<i>S-stage</i>		
HSG09-09a	Quartz-molybdenite hydrothermal breccias cemented by barren quartz	HSG09-09a.1, HSG09-09a.2, HSG09-09a.3, HSG09-09a.4
HSG09-08b	Quartz-molybdenite vein with sericite halo, cutting early quartz-K-feldspar vein	HSG09-08b.1, HSG09-08b.2, HSG09-08b.3, HSG09-08b.4
HSG09-21	Coarse quartz-molybdenite-sericite vein, with extremely rich molybdenite mineralization	HSG09-21.1, HSG09-21.2
HSG09-25a	Quartz-molybdenite hydrothermal breccias cemented by barren quartz	HSG09-25a.1, HSG09-25a.2, HSG09-25a.3
HSG09-34	Quartz-molybdenite-sericite vein	HSG09-34.1, HSG09-34.2, HSG09-34.3, HSG09-34.4, HSG09-34.5, HSG09-34.6, HSG09-34.7
<i>B-stage</i>		
HSG09-09b	Barren quartz cementing quartz-molybdenite breccias	HSG09-09b.1, HSG09-09b.2
HSG09-25b	Barren quartz cementing quartz-molybdenite breccias	HSG09-25b.1, HSG09-25b.2, HSG09-25b.3
HSG09-49	Barren quartz vein cutting quartz-molybdenite vein	HSG09-49.1, HSG09-49.2, HSG09-49.3, HSG09-49.4

FIGURE 5: Representative photomicrographs of fluid inclusions hosted in quartz of different hydrothermal stages. (a) Primary V-type fluid inclusions in P-stage quartz. (b) Linear distributed pseudosecondary fluid inclusions (along intragrain fractures) and secondary fluid inclusions (cutting through quartz grain boundaries). (c) Pseudosecondary fluid inclusions along intragrain fractures. (d) Secondary trails of fluid inclusions crosscutting quartz boundaries. (e) A P-stage S-type fluid inclusion containing a liquid phase, a vapor phase, a halite, a sylvite, and an opaque mineral. (f) Coexisting S-type, V-type, and L-type inclusions in P-stage quartz, noting opaque minerals are common in all types of inclusions. (g) Coexisting S-type and V-type inclusions in S-stage quartz. (h) Coexisting L-type and V-type inclusions in S-stage quartz. (i) and (j) L-type fluid inclusions in S-stage molybdenite-bearing quartz. (k) A P-stage S-type fluid inclusion containing a liquid phase, a vapor phase, a halite, a hematite, and an opaque mineral. (l) B-stage L-type fluid inclusions. The scale bar is 30 μm in each photomicrograph. P-, S-, and B-stage refer to pre-, syn-, and postmineralization stage, respectively.

For oxygen isotope composition analysis, the quartz separation from the three different paragenetic stages and one magmatic hornblende sample as well as one magmatic quartz sample from the fresh granite were chosen (Table 1). The samples were first carefully selected under a binocular microscope (~1 g for each sample) and crushed into 200 mesh and then reacted with BrF_5 to liberate oxygen from the quartz separates. The resultant oxygen was converted to CO_2 on a platinum-coated carbon rod, the isotopic composition of which was determined using a Finnigan MAT-253 mass spectrometer at the Stable Isotope Laboratory of Mineral Resources Institute, Chinese Academy of Geological Sciences. The isotopic data are reported relative to the Standard Mean Ocean Water (SMOW). The analytic precision is better than 0.2‰. The $\delta^{18}\text{O}$ values of water in equilibrium with the hydrothermal quartz were calculated using the equation of [44] with the estimated average trapping temperatures of fluid inclusions in the same quartz samples. The $\delta^{18}\text{O}$ values of water in equilibrium with the magmatic quartz and hornblende were calculated based on the fractionation factors given by Yong-Fei [45] and Matsuhisa et al. [46], respectively, assuming a magma crystallization temperature of 730°C as calculated using the hornblende geothermometer [47].

Chlorite is common in S-stage, which occurs either in molybdenite-bearing quartz veins (Type I chlorite, Figures 3(e) and 3(f)) or as replacement of hornblende (Type II chlorite, Figure 3(d)). Major elements in individual chlorite grains of both types were determined using a JEOLJXA-8100 electron microprobe housed in Peking University. The beam current is 10 nA and the spot size is 2 μm . For instrument calibration, several synthetic minerals, natural minerals, and relevant standard minerals were used. The estimated precision for each element was better than $\pm 2\%$.

5. Results

5.1. Fluid Inclusion Petrography and Microthermometry. Fluid inclusions analyzed in this study are all hosted in quartz (Figure 5). In order to better understand the fluids exactly representing the three hydrothermal stages, only primary and pseudosecondary inclusions have been focused on according to the criteria given by Goldstein and Reynolds [48]. The primary inclusions were difficult to identify due to the lack of clear quartz growth zonation under transmitted light microscope. Nevertheless, a small number of the inclusions have been believed to be primary as they occur as isolated

FIGURE 6: The Laser Raman spectra of fluid inclusions. The analyzed objects are the daughter mineral in a P-stage S-type inclusion (a), the liquid phase in a P-stage V-type inclusion (b), the vapor phase in a B-stage L-type inclusion (c), the liquid phase in a S-stage L-type inclusion (d), and the daughter mineral in a S-stage L-type inclusion (e). The results show that H₂O is the dominant component of the liquid and vapor phases of all types of fluid inclusions in different stages (a–e), with very small amounts of CH₄ (d). Daughter minerals hematite (a) and chalcopyrite (e) were also identified. P-, S-, and B-stage refer to pre-, syn-, and postmineralization stage, respectively.

individuals with large size in relation to the size of the host quartz crystal (Figure 5(a)) [49]. Most of the fluid inclusions investigated in this study are pseudosecondary, which are linearly distributed along healed intragrain fractures (Figures 5(b) and 5(c)). Secondary fluid inclusions are widespread and often align in trails and go through quartz grain boundaries (Figures 5(b) and 5(d)); they have an unknown origin in relation to the host quartz vein and therefore were avoided in this study. All the fluid inclusions were investigated following the approach of using fluid inclusion assemblages (FIAs, criteria of Goldstein and Reynolds [48]).

Based on the phases observed at room temperature and phase transformation upon heating, three major types of fluid inclusions have been defined in Haisugou. S-type inclusions at least contain a liquid phase, a vapor phase, and a halite (Figures 5(e)–5(g) and 5(k)). Sylvite and anhydrite are also present in some cases. Sylvite was distinguished from halite by its subcubic crystal (Figure 5(e)) whereas anhydrite was identified by its transparent anisotropic prisms. The bubble commonly fills ~10 to 30 vol% of the inclusions (Figures 5(e)–5(g) and 5(k)). During heating, halite in most of these S-type inclusions dissolved before the homogenization of the vapor bubble into the liquid, although a few of them homogenized by final halite dissolution. L-type inclusions are composed of a liquid phase and a vapor phase (Figures 5(f), 5(h)–5(j) and 5(l)) and homogenized to the liquid phase upon heating. The vapor phase occupies < 50 vol% of the L-type inclusions. V-type inclusions are also composed of a liquid phase and a vapor phase (Figures 5(f)–5(h)) but would homogenize to vapor phase. V-type inclusions have a vapor bubble commonly occupying >50 vol% of the total inclusion. Opaque daughter crystals are common in all types of inclusions hosted in P- and S-stage quartz (Figures 5(e)–5(k)) but could not always be identified. Nevertheless, some dark crystals were determined to be chalcopyrite and the red crystals (Figure 5(k)) were hematite based on Laser Raman

spectroscopic analyses (Figure 6). Laser Raman analyses also revealed that the liquid and vapor phases of all types of fluid inclusions in different stages contain dominant H₂O with none to very small amounts of CH₄ but lack CO₂ (Figure 6). The primary and pseudosecondary S-, L-, and V-type inclusions have similar shapes (negative or rounded to sub-rounded) and similar size (typically 5 to 20 μ m) and often coexist in the same FIAs (Figures 5(f)–5(h)). The microthermometric results are presented as averages of assemblages with 1 σ uncertainty and are summarized in Table 2 and plotted in Figure 7.

In five quartz samples from the P-stage veins, 18 FIAs were measured. Most of the FIAs contain all three types of fluid inclusions (Table 2). The homogenization temperatures of the S-type fluid inclusions from 16 FIAs range from 363 to 504°C, whereas the halite dissolution temperatures are between 267 and 382°C, corresponding to salinities between 35.8 and 45.5 wt% NaCl equiv (Figure 7). 10 V-type FIAs have homogenization (to vapor phase) temperatures of 393–469°C; final ice-melting temperatures from –3.1 to –0.5°C correspond to salinities between 0.9 and 5.1 wt% NaCl equiv (Figure 7). L-type inclusions from 17 FIAs have homogenization (to liquid phase) temperatures ranging from 333 to 469°C, final ice-melting temperatures ranging from –7.3 to –2.3°C, and calculated salinities from 3.9 to 10.8 wt% NaCl equiv (Figure 7). In the same FIAs, the coexisting S-, V-, and L-type fluid inclusions commonly yielded similar homogenization temperatures (Table 2 and Figure 7), indicative of fluid boiling in P-stage.

A total of 20 FIAs from S-stage molybdenite-quartz veins or breccias were measured. Most of the FIAs only contain L-type fluid inclusions, although S- and V-type inclusions have also been identified, respectively, in four assemblages (Table 2). L-type inclusions were present in all 20 FIAs and yielded homogenization temperatures of 325–382°C and final ice-melting temperatures of –6.5 to –1.8°C, corresponding

FIGURE 7: Homogenization temperature versus salinity plot of fluid inclusion assemblages (in color). Error bars are at 1σ level. Individual fluid inclusion analyses in each assemblage are also plotted in black and white. P-, S-, and B-stage refer to pre-, syn-, and postmineralization stage, respectively.

FIGURE 8: Homogenization temperature versus calculated oxygen isotopic value plot of magmatic hornblende and quartz, and hydrothermal quartz from three different paragenetic stages in Haisugou. The compositions of primary magmatic water [35] and the Mesozoic meteoric water in the northern Xilamulun district, northeastern China [36], are also shown for comparison. P-, S-, and B-stage refer to pre-, syn-, and postmineralization stage, respectively.

to calculated salinities of 3.0–9.9 wt% NaCl equiv (Figure 7). Four FIAs containing S-type inclusions yielded homogenization temperatures of 355–407°C, halite dissolution temperatures between 230 and 382°C, and calculated salinities of 33.5 to 45.5 wt% NaCl equiv (Figure 7). V-type fluid inclusions in four FIAs homogenized at 240–384°C, with final ice-melting temperatures of -2.0 to -0.6 °C and calculated salinities of 1.1 to 3.4 wt% NaCl equiv (Figure 7). The coexistence of different types of inclusions in some of the FIAs suggests that fluid boiling has occurred locally during Mo participation.

In B-stage, only L-type inclusions were recognized in all nine FIAs from three postmineralization barren quartz samples. They yielded homogenization temperatures between

177 and 244°C, final ice-melting temperatures between -2.9 and -1.3 °C, and calculated salinities between 2.2 and 4.8 wt% NaCl equiv (Figure 7).

5.2. Oxygen Isotope. The magmatic hornblende and quartz samples have measured $\delta^{18}\text{O}$ values of 6.4 and 8.8‰, respectively, and the calculated $\delta^{18}\text{O}$ values of the fluid in equilibrium with them are 8.4 and 7.9‰, respectively (Table 3 and Figure 8). For hydrothermal quartz, five samples from P-stage have measured $\delta^{18}\text{O}$ values between 7.3 and 9.2‰, corresponding to calculated $\delta^{18}\text{O}_{\text{fluid}}$ values between 3.8 and 6.3‰; the measured $\delta^{18}\text{O}$ values of seven samples from S-stage range from 3.7 and 7.4‰, corresponding to calculated

TABLE 2: Microthermometric results for FIAs from different stages.

FIA number <i>P-stage</i>	Boil.	FI type	T_m	SD	N	T_H	SD	N	T_h	SD	N	Salinity	SD	N
HSG09-04.1	Y	S	-5.3	1.6	5	286	6	2	504	13	2	37.1	0.5	2
		L						5	433	90	5	8.3	2.1	5
HSG09-04.2	Y	S	-2.1	0.6	2	293	26	6	456	28	5	37.7	1.9	6
		V	-6.1	1.6	2				428	18	3	3.5	0.9	2
		L							456	6	2	9.2	2.1	2
HSG09-04.3	Y	S	-1.0	0.0	1	278	34	5	375	25	5	36.6	2.4	5
		V	-4.0	0.2	2				348	0	1	1.7	0.0	1
HSG09-04.4		L	-2.3	0.0	1				351	7	2	6.4	0.3	2
		L							333	4	2	3.9	0.0	1
HSG09-08a.1	Y	S	-3.1	0.0	1	328	14	4	486	20	3	40.5	1.2	4
		V	-4.2	1.7	7				469	0	1	5.1	0.0	1
HSG09-08a.2	Y	S	-0.5	0.0	1	317	13	3	465	14	3	39.5	1.1	3
		L	-4.2	0.6	6	344	52	4	467	27	2	6.6	2.4	7
HSG09-15.1	Y	S	-0.5	0.0	1				472	11	4	42.1	4.7	4
		V	-4.2	0.6	6				442	0	1	0.9	0.0	1
		L							458	54	7	6.7	0.8	6
HSG09-32.1	Y	S	-1.1	0.0	1	313	21	6	393	31	5	39.3	1.7	6
		V	-5.2	1.0	6				402	18	2	1.9	0.0	1
HSG09-32.2	Y	S	-4.4	0.3	3	362	27	3	412	50	7	8.2	1.3	6
		L							417	28	3	43.6	2.6	3
HSG09-32.3	Y	S	-0.8	0.0	1	267	0	1	390	25	4	7.1	0.5	3
		V	-4.1	0.5	2				367	0	1	35.8	0.0	1
		L							392	0	1	1.4	0.0	1
HSG09-32.4	Y	S	-0.9	0.0	1	294	20	3	414	27	2	6.5	0.7	2
		V	-4.2	1.7	6				415	6	2	37.8	1.4	3
HSG09-32.5	Y	S	-5.2	0.0	1	292	5	2	445	0	1	1.6	0.0	1
		L							418	16	7	6.6	2.4	6
HSG09-32.6	Y	S	-1.6	0.7	2	353	35	5	409	14	2	37.5	0.4	2
		V	-3.1	0.0	1				337	0	1	8.1	0.0	1
HSG09-44.1	Y	S	-7.3	0.6	4	280	0	1	480	19	4	42.9	3.5	5
		L							433	30	2	2.7	1.2	2
HSG09-44.2	Y	S	-2.2	0.5	2	304	15	4	363	0	1	5.1	0.0	1
		V	-4.9	0.5	2				390	0	1	36.7	0.0	1
HSG09-44.3	Y	S	-3.7	0.9	8	373	31	8	447	20	4	10.8	0.7	4
		L							415	37	4	38.5	1.2	4
		L							348	11	2	3.6	0.8	2
		S							447	10	2	7.7	0.7	2
		L							481	23	8	44.8	3.3	8
		L								22	8	6.0	1.3	8

TABLE 2: Continued.

FIA number	Boil.	Fl type	T_m	SD	N	T_H	SD	N	T_h	SD	N	Salinity	SD	N
HSG09-44.4	Y	V	-1.7	0.8	2			2	423	11	2	2.9	1.4	2
		L	-4.7	0.2	2			2	424	3	2	7.4	0.3	2
HSG09-44.5	Y	S				382	0	1	372	0	1	45.5	0.0	1
		L	-2.8	0.5	3			3	401	9	3	4.7	0.7	3
<i>S-stage</i>														
		S					0	1	325	0	1	33.5	0.0	1
HSG09-09a.1	Y	V	-0.6	0.1	2	230			346	0	2	1.1	0.2	2
		L	-3.8	1.0	7			4	335	11	4	6.1	1.5	7
HSG09-09a.2		V	-1.0	0.0	1			1	240	0	1	1.7	0.0	1
HSG09-09a.3		L	-3.7	1.1	12			13	321	28	13	6.0	1.6	12
HSG09-09a.4		L	-3.1	1.0	9			8	297	24	8	5.1	1.5	9
		L	-3.1	0.6	18			19	293	34	19	5.1	0.8	18
HSG09-08b.1	Y	S				333	46	3	359	46	3	41.1	3.9	3
		L	-4.6	0.5	4			3	384	9	3	7.3	0.8	4
HSG09-08b.2		L	-6.2	0.0	2			2	405	23	2	9.5	0.0	2
		S				313	46	2	350	22	2	39.3	3.7	2
HSG09-08b.3	Y	V	-2.0	0.3	3			3	384	14	3	3.4	0.4	3
		L	-6.4	1.2	3			4	369	38	4	9.7	1.5	3
HSG09-08b.4		S				382	0	1	341	0	1	45.5	0.0	1
		L	-6.5	0.4	3			3	421	12	3	9.9	0.5	3
HSG09-21.1		V	-1.6	0.6	2			2	358	4	2	2.7	0.9	2
HSG09-21.2		L	-5.3	0.9	5			4	385	27	4	8.2	1.1	5
HSG09-25a.1		L	-4.3	0.4	4			5	364	13	5	6.8	0.6	4
HSG09-25a.2		L	-3.2	1.4	11			11	347	37	11	5.1	2.0	11
HSG09-25a.3		L	-2.8	1.4	7			8	342	48	8	4.5	2.1	7
HSG09-34.1		L	-3.3	1.1	4			3	293	93	3	5.3	1.7	4
HSG09-34.2		L	-1.8	1.1	2			2	272	50	2	3.0	1.8	2
HSG09-34.3		L	-3.0	1.6	5			6	297	69	6	4.8	2.4	5
HSG09-34.4		L	-4.3	2.2	8			8	298	73	8	6.7	3.2	8
HSG09-34.5		L	-3.5	0.4	6			6	288	53	6	5.8	0.5	6
HSG09-34.6		L	-2.9	0.6	5			5	281	20	5	4.9	0.9	5
HSG09-34.7		L	-3.2	0.9	3			3	278	33	3	5.2	1.3	3
		L	-4.3	0.9	6			7	290	25	7	6.8	1.3	6
<i>B-stage</i>														
HSG09-09b.1		L	-1.9	1.0	10			11	244	42	11	3.1	1.6	10
HSG09-09b.2		L	-2.2	0.7	8			8	209	60	8	3.7	1.2	8
HSG09-25b.1		L	-1.4	0.8	5			5	177	11	5	2.4	1.3	5
HSG09-25b.2		L	-2.4	1.4	14			16	231	48	16	4.0	2.1	14
HSG09-25b.3		L	-1.3	0.7	3			3	204	29	3	2.2	1.2	3
HSG09-49.1		L	-2.0	0.5	7			8	211	59	8	3.3	0.8	7
HSG09-49.2		L	-2.5	1.5	6			6	227	39	6	4.2	2.2	6
HSG09-49.3		L	-2.9	0.1	2			2	199	35	2	4.8	0.2	2
HSG09-49.4		L	-2.2	0.7	8			9	240	40	9	3.7	1.1	8

Note. Temperature values are reported in degrees Celsius ($^{\circ}\text{C}$), and salinity values in wt% NaCl equiv. N refers to the number of available analyses, SD refers to 1 standard deviation, Boil. refers to boiling assemblage, and Y refers to Yes. T_m = final ice-melting temperature, T_H = halite dissolution temperature, and T_h = homogenization temperature of the H_2O phases.

TABLE 3: Summary of oxygen isotope data of igneous and hydrothermal minerals in Haisugou.

Sample number	Measured mineral	Measured $\delta^{18}\text{O}_{(\text{VSMOW})}$ (‰)	Crystallization temperature (°C)	Calculated $\delta^{18}\text{O}_{\text{fluid}}$ (‰)
<i>Magmatic stage</i>				
HSG43	Hornblende in fresh granite	6.4	730	8.4
HSG03	Magmatic quartz in fresh granite	8.8	730	7.9
<i>P-stage</i>				
HSG09-32	Vein quartz with no obvious sulfide	7.7	415	4.0
HSG09-08a	Barren quartz-K-feldspar vein	9.2	457	6.3
HSG09-04	Barren quartz-K-feldspar vein	7.5	416	3.8
HSG09-15	Weakly mineralized quartz vein with K-feldspar halo	7.9	453	4.9
HSG09-44	Quartz-molybdenite vein with K-feldspar halo	7.3	430	3.9
<i>S-stage</i>				
HSG09-09a	Quartz-molybdenite hydrothermal breccias cemented by barren quartz	6.3	306	-0.4
HSG09-21	Coarse quartz-molybdenite-sericite vein	7.0	370	2.2
HSG09-25a	Quartz-molybdenite hydrothermal breccias cemented by barren quartz	3.7	335	-2.0
HSG09-34	Quartz-molybdenite-sericite vein	6.9	289	-0.4
HSG09-28	Quartz-molybdenite-sericite-chlorite vein	6.6	323	0.5
HSG09-27	Quartz-molybdenite-chalcopyrite vein with sericite halo	6.7	323	0.6
HSG09-08b	Quartz-molybdenite vein with sericite halo, cutting early quartz-K-feldspar vein	7.3	384	2.9
HSG09-40	Coarse quartz-molybdenite-sericite vein	7.5	323	1.4
<i>B-stage</i>				
HSG09-09b	Barren quartz cementing quartz-molybdenite breccias	6.9	229	-3.1
HSG09-49	Barren quartz vein cutting quartz-molybdenite vein	6.0	224	-4.3
HSG09-25b	Barren quartz cementing quartz-molybdenite breccias	7.5	216	-3.2
HSG09-42	Quartz-calcite vein with little pyrite	5.7	223	-4.6
HSG09-50	Barren quartz-calcite vein cutting quartz-molybdenite vein	5.5	223	-4.8

Note. The crystallization temperatures of hydrothermal quartz samples are represented by the average homogenization temperatures of the fluid inclusion assemblages they host.

FIGURE 9: Histogram showing ranges of calculated temperature values of two types of chlorite in Haisugou.

$\delta^{18}\text{O}_{\text{fluid}}$ values between -0.4 and 2.9‰ ; in B-stage, five samples have measured $\delta^{18}\text{O}$ values between 5.5 and 7.5‰ , corresponding to calculated $\delta^{18}\text{O}_{\text{fluid}}$ values ranging from -4.8 to -3.1‰ (Table 3 and Figure 8).

5.3. Chlorite Geothermometry. Chlorites analyzed at Haisugou are from the S-stage quartz-molybdenite veins (Type I chlorite, Figures 3(e) and 3(f)) and from the mineralized granite where chlorite replaces hornblende (Type II chlorite, Figure 3(d)). Chlorite compositions of both types are similar with $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios ranging from 0.49 to 0.55 (Table 4). Chlorite composition variations have been proposed to be closely related to the formation temperatures and thus it has been used as a geothermometer [50–52]. In this study we employed three different empirical equations to calculate the temperatures [38–40]. The results show that all three methods yielded highly consistent results with a standard deviation less than 5% of the average temperature value for each analysis (Table 4). Nine Type I chlorite analyses have average temperature values between 261 and 302°C (average = 281°C , Figure 9), whereas 19 Type II chlorite analyses have average temperatures ranging from 285 to 352°C (average = 317°C , Figure 9).

6. Discussion

The results of this study indicate that the major Mo mineralization in the Haisugou porphyry deposit, NE China, was coeval with sericite-chlorite alteration but postdated earlier potassic alteration and predated the later barren quartz. The available fluid inclusion and oxygen isotopic data from different hydrothermal evolution stages allow us to interpret the fluid origin, the evolution from pre- through syn- to postmineralization fluids, and mechanisms of metal participation.

6.1. Fluid Nature and Sources. The volatile components of the fluids from all stages are mainly H_2O with trace CH_4 in some cases, but without any detectable CO_2 . The major daughter mineral in the S-type fluid inclusions is halite. It is therefore reasonable to come to the conclusion that the fluids

belong to a dominantly $\text{NaCl-H}_2\text{O}$ system. Other identified or inferred daughter crystals in fluid inclusions also include sylvite, anhydrite, hematite, and chalcopyrite (Figures 5 and 6). Taking into consideration the fact that the fluids were related to molybdenite deposition, we can plausibly confirm that the cations in the fluids include but are not limited to Na, K, Ca, Fe, Cu, and Mo, and the anions include Cl and S. Fluorine is also present but is believed to be insignificant, as supported by the occurrence of very limited amounts of fluorite in the B-stage mineral assemblages (Figure 2(i)).

The formation of porphyry-type mineral deposits is typically associated with magmatic fluids, with or without involvement of meteoric water [49, 53, 54]. In Haisugou, fluid boiling in P-stage has been evidenced by the pervasive boiling assemblages where coexisting brines and lower-salinity fluids yielded similar homogenization temperatures (Figure 7 and Table 2). This confirms that the fluids in P-stage are directly a result of phase separation from exsolved magmatic fluid. Oxygen isotopic values of quartz samples from this stage are between 3.8 and 6.3‰ , similar to but slightly lower than typical magmatic fluids (Figure 8) and also slightly lower than the primary magmatic minerals (hornblende and quartz) in Haisugou granite (Figure 8 and Table 3), suggesting that a subordinate contribution of meteoric water in this stage could not be ruled out.

In S-stage, boiling assemblages have also been recognized but only occur in part of the samples, in which S-type high-salinity inclusions are coexisting with low-salinity V-type and/or L-type inclusions, and they have comparable homogenization temperatures (Figure 7 and Table 2). It should be noted that the homogenization temperatures of the boiling assemblages are higher than most of the other assemblages in S-stage (Figure 7 and Table 2). The above observations suggest that fluid boiling has occurred, at least locally, during the early stage of mineralization. In addition, it is also notable that the homogenization temperatures of the four S-type FIAs in S-stage decrease along with the decreasing salinities (Figure 7), suggesting that the high-salinity fluids resulting in earlier fluid boiling should have been mixed with a fluid endmember with lower temperature and lower salinity before entrapment, which could most likely be meteoric water. In fact, most of the FIAs in the S-stage quartz samples only contain L-type

TABLE 4: Representative electron microprobe analyses of chlorite and calculated temperatures.

Sample	Type I chlorite					Type II chlorite				
	H08-2.2	H08-2.3	H08-5.1	H08-5.3	H09-1.2	H09-1.3	H09-2.4	H09-28.6	H09-6.2	H09-6.9
SiO ₂	27.58	28.64	27.12	27.26	27.22	27.70	26.50	25.95	25.57	24.84
Al ₂ O ₃	16.23	16.11	16.92	17.36	16.95	16.83	17.59	17.43	18.06	19.30
TiO ₂	0.10	0.11	0.02	0.05	0.05	0.20	0.06	0.06	0.08	0.11
Cr ₂ O ₃	0.19	0.21	0.08	0.05	0.15	0.06	0.08	0.07	0.07	0.07
FeO	28.32	28.72	29.91	28.29	29.30	28.77	28.31	28.96	28.56	29.21
MnO	0.34	0.33	0.41	0.43	0.32	0.50	0.37	0.37	0.35	0.34
MgO	14.36	14.91	14.41	15.82	14.58	14.89	15.24	14.67	14.51	13.30
CaO	0.15	0.21	0.04	0.04	0.15	0.14	0.07	0.07	0.10	0.13
NiO	0.04	0.02	0.00	0.00	0.01	0.00	0.02	0.01	0.02	0.04
Na ₂ O	0.00	0.00	0.00	0.07	0.02	0.03	0.06	0.07	0.10	0.06
K ₂ O	0.02	0.04	0.03	0.00	0.03	0.05	0.01	0.02	0.02	0.03
Si	2.97	3.02	2.89	2.87	2.90	2.93	2.83	2.81	2.77	2.70
Al ^{IV}	1.03	0.98	1.11	1.13	1.10	1.07	1.17	1.19	1.23	1.30
Al ^{VI}	1.04	1.01	1.02	1.02	1.03	1.03	1.04	1.03	1.07	1.17
Fe	2.55	2.53	2.67	2.49	2.61	2.54	2.53	2.62	2.59	2.65
Mg	2.31	2.34	2.29	2.48	2.32	2.35	2.43	2.37	2.34	2.15
Fe/(Fe + Mg)	0.53	0.52	0.54	0.50	0.53	0.52	0.51	0.53	0.52	0.55
T ₁ (°C)	274	265	292	295	290	284	304	310	318	335
T ₂ (°C)	268	255	294	303	292	283	315	322	335	357
T ₃ (°C)	275	262	301	308	299	289	321	329	341	364
Average	273	261	296	302	294	285	313	320	331	352
SD	4	5	5	6	4	3	8	9	12	15

Note. SD refers to 1 standard deviation. The temperatures were calculated using three different methods: T_1 [38], T_2 [39], and T_3 [40].

inclusions, and all the L-type FIAs display a well positive correlation between homogenization temperatures and salinities (Figure 7), implying that mixing of magmatic and meteoric fluids was common in this stage. Such ingress of meteoric water was also recorded by oxygen isotopic results of the S-stage quartz. In Figure 8 it is clear that all the S-stage quartz samples have oxygen isotopic compositions lower than magmatic fluid but significantly higher than the Mesozoic meteoric water in this region ($\delta^{18}\text{O} = -16\text{‰}$ [36]) and that as temperatures drop from ~ 400 to <300 , the oxygen isotope values decrease from 3.9 to -0.4‰ . All the above facts indicate that the magmatic fluid ($\delta^{18}\text{O} > 5\text{‰}$) was cooled and diluted by the meteoric water ($\delta^{18}\text{O} = -16\text{‰}$) during ore deposition.

The B-stage FIAs only contain L-type inclusions. Fluids in these assemblages have lower homogenization temperatures, lower salinities, and lower $\delta^{18}\text{O}$ values (Figures 7 and 8), indicating that more meteoric water was added to the system, making the fluids much cooler and diluted, and mineralization ceased.

To sum up, the early premineralization (P-stage) fluids are dominantly magmatic and are results of fluid boiling; a small amount of meteoric water has been involved in the system. Boiling of magmatic fluids also occurred locally in the early time of the synmineralization S-stage; the majority of the fluids responsible for mineralization are admixtures of magmatic and meteoric water. The B-stage fluids have more portions of meteoric water, which postdated the major mineralization. Although it is widely accepted, based on stable isotope [14, 50, 51, 53] and fluid inclusion [33, 34, 52, 55] studies, that fluids that are related to porphyry/skarn mineralization have a dominantly magmatic fluid component [34, 53, 56, 57], in the Haisugou porphyry Mo deposit, however, meteoric water has been greatly involved, even since the early potassic alteration stage (P-stage).

6.2. Hydrothermal Evolution and Metal Deposition. The alteration and mineralization of the Haisugou porphyry Mo deposit are associated with at least three episodes of fluid activities. The fluid inclusion and oxygen isotopic data from this study suggest that different processes including fluid boiling and fluid mixing have occurred during the hydrothermal evolution. Fluid boiling occurred in the P-stage and locally the early time of the S-stage (Figure 7). In P-stage, fluid boiled at $\sim 440^\circ\text{C}$, generating high-salinity brines (35.8 and 45.5 wt% NaCl equiv, Table 2) and low-salinity fluids (V- and L-type inclusions) with salinities < 12 wt% NaCl equiv and leading to extensive potassic alteration, with limited molybdenite deposition. In S-stage, boiling also generated fluids with both high and low salinities (Figure 7 and Table 2), and both fluids were cooled and diluted by meteoric water, resulting in sericite and chlorite alteration, as well as extensive Mo participation. Such involvement of meteoric water also dominated the postmineralization B-stage evolution, and barren quartz formed as a consequence.

Several processes have been proposed to be the major factors controlling porphyry (or skarn)-style mineralization including decompression, phase separation (or boiling), cooling, interaction with rocks, and mixing with external waters

[33, 34, 53, 54, 58–64]. In Haisugou both fluid boiling and mixing with external (meteoric) water have occurred as proposed above. Decompression should also have occurred, which could be the direct cause of fluid boiling [64]. In addition, fluid cooling should be always undoubtedly a process throughout the hydrothermal evolution with the crystallization and cooling of the concurrent magmas and the incursion of meteoric water. Interaction with wallrocks could have also occurred, as has been recognized in many porphyry mineralization systems [61, 62], but our study could not confirm if this occurred in Haisugou.

As mentioned above, the P-stage boiling of magmatic fluid resulted in insignificant mineralization, implying that a simple fluid boiling process at $\sim 440^\circ\text{C}$ would not lead to Mo participation. In S-stage, fluid boiling occurred in the earlier time with fluid temperature $>320^\circ\text{C}$, but mixing with meteoric water dominated the whole mineralization process from >400 to $<250^\circ\text{C}$, suggesting that fluid mixing might have played a key role in molybdenite deposition. Fluid mixing not only reduced the fluid temperature (Figure 7) and therefore reduced the metal solubility, but also caused dilution which would change the fluid salinity, acidity, and redox properties, altogether promoting metal deposition [65]. As for fluid boiling, however, it has been recently suggested that it is not a major cause for Mo precipitation in many porphyry Mo deposits [13]. This is because the initial supercritical (single-phase) fluid has a relatively low salinity (e.g., ~ 7 wt% NaCl equiv [2, 56, 59]), and the two-phase field is intersected on the vapor limb once boiling occurs; that is, brine will condense out of a vapor-like bulk fluid, rather than the other way around. In this case the condensation of small amounts of brine out of a vapor-like bulk fluid should not significantly influence the properties of the bulk system, and therefore fluid boiling in the porphyry Mo system is unlikely associated with metal precipitation [13]. In summary, metal deposition in Haisugou was mainly caused by mixing with meteoric water and related cooling, whereas boiling (and perhaps related decompression) seems less important to Mo mineralization.

Fluid mixing and mineralization were closely associated with sericite and chlorite alteration in Haisugou (Figures 2 and 3), which is consistent with previous understanding that meteoric water is necessary to produce sericite alteration [35, 66]. Microthermometry of FIAs indicates that mineralization took place at ~ 420 to $\sim 240^\circ\text{C}$, peak at 350 – 290°C (Figure 7). These data are also well consistent with the results from chlorite geothermometer, which gives a temperature range of 352 – 285°C for the chlorite from the S-stage molybdenite-bearing veins (Type I chlorite, Figure 9). However, it should be noted that the chlorite replacing hornblende in the Haisugou granite (Type II chlorite) has lower temperatures (302 – 261°C , Figure 9), probably implying that such two types of chlorite were not formed at the same time and that the replacement of hornblende by chlorite took place slightly later than the formation of the quartz-chlorite-sericite-molybdenite veins. The similarity between the fluid inclusion homogenization temperatures and the calculated Type I chlorite temperatures suggests that Mo mineralization and related chlorite alteration in Haisugou mainly occurred

at 350–290°C. Since the MoS₂ solubility below 400°C is extremely low, most porphyry Mo deposits are believed to mineralize at ~400°C [64], significantly higher than the inferred mineralization temperatures in Haisugou. This probably can be attributed to the existence of other Mo complexes in the hydrothermal fluids in Haisugou that were capable of transporting Mo at relatively lower temperatures [64].

6.3. Comparison with Other Porphyry Mo Systems. One of the major differences in the Haisugou Mo deposit in NE China compared to the Chinese Dabie-type Mo deposits [7, 10, 12] is the absence of CO₂ in the ore-forming fluids. In fact, in many investigated porphyry Mo deposits in NE China, CO₂ has been reported to be either absent or very minor in amount [15–17]. This could probably be explained by the differences in ore-forming depths because in a deeper level the elevated pressure favors higher CO₂ solubility in NaCl-H₂O fluids [67, 68]. If this is true, then most of the NE China Mo deposits should have formed in shallower levels than the Mo deposits in the Chinese Dabie Belt, which is not reliable. An alternative explanation is that the magmatic-hydrothermal systems related to the NE China Mo deposits were originated from the subduction of the oceanic slabs, which must be infiltrated by seawater and definitely have lower CO₂/H₂O ratios compared to the intracontinental magmatic-hydrothermal systems with higher ratios of CO₂/H₂O that formed the Dabie-type Mo deposits [7, 10, 12].

Another dramatic difference is the lack of fluorine-rich minerals (e.g., fluorite) in Haisugou and many other Mo deposits in NE China [15, 17], which are, however, widespread in Dabie-type and Climax-type Mo deposits [3, 7, 13]. Although fluorite has been recognized in the B-stage veins (Figure 2(i)), it is very rarely present indicating F in the fluids is very low compared with the Dabie-type and Climax-type Mo deposits, in which fluorite is one of the common alteration minerals [3, 7, 13]. The low-F contents in porphyry Mo systems have been attributed to a flat slab subduction setting, in which the major F-bearing mineral, phengite, would remain stable because it can be stable at depths of 70–300 km depending on the geotherm [69].

The Haisugou porphyry Mo deposit in NE China seems different from both the Dabie-type and the Climax-type Mo deposits in terms of the CO₂ and F contents in the magmatic-hydrothermal systems. However, such low CO₂ and F contents in NE China Mo deposits (including Haisugou) are very similar to the low-F type (also referred to as Endako-type, arc-related type, or subduction-type) porphyry Mo deposits along the west coast of the American continents [70, 71]. Moreover, the Haisugou deposit, as well as many other Mo deposits in NE China [16–19], is associated with calc-alkaline magmas, which is also consistent well with the low-F type porphyry Mo deposits. We therefore believe that many of the NE China Mo deposits can be classified to the low-F type. In addition, the low-F type porphyry Mo deposits commonly developed in active continental-margins [71, 72], which is also consistent with our recent understanding to many of the Yanshanian Mo deposits in NE China that have been proposed to be related to the Paleo-Pacific plate subduction or subsequent slab rollback [8].

7. Conclusion

(1) The hydrothermal evolution of the Haisugou porphyry Mo deposit in NE China can be divided into three stages: a premineralization P-stage characterized by potassic alteration with no significant metal deposition, a synmineralization S-stage characterized by extensive Mo precipitation with sericite and chlorite alteration, and a postmineralization B-stage characterized by barren quartz and minor calcite and fluorite.

(2) The fluids associated with the mineralization in Haisugou are dominantly of a NaCl-H₂O system with no detectable CO₂. Fluid boiling occurred in P-stage (at ~440°C) and locally in the early time of the S-stage (380–320°C), resulting in the coexistence of high-salinity brines with low-salinity fluids. Mixing with meteoric water dominated the whole mineralization process from >400 to <250°C and continued to postmineralization B-stage, as indicated by the positive correlations between the homogenization temperatures and the fluid salinities and between the homogenization temperatures and oxygen isotopic compositions of the hydrothermal quartz.

(3) Mixing and related fluid cooling could be the most likely controlling factors for Mo mineralization in Haisugou, whereas fluid boiling seemed less important. The Mo deposition took place at ~420 to ~240°C and mainly between 350 and 290°C based on fluid inclusion microthermometry and chlorite geothermometer.

(4) The Haisugou deposit, as well as many other Mo deposits in NE China, is different from the Dabie-type or Climax-type porphyry Mo deposits in terms of the low CO₂ and F contents. It is similar to the low-F type Mo deposits that developed in arc settings, which also confirms the previous understanding that the formation of many of the Yanshanian Mo deposits in NE China, including Haisugou, is related to the Paleo-Pacific plate subduction or subsequent slab rollback.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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