The Magmatic-Hydrothermal Ore-Forming Processes of the Tonggou Cu-Zn Deposit, NW China: Constraints from Magnetite Chemistry and Fluid Inclusions

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Abstract: The Tonggou deposit is a porphyry Cu and vein-type Cu-Zn mineralization system located in the Bogda Orogenic Belt, north of Eastern Tianshan. Systematic fluid inclusion analyses were performed on granular quartz from the magnetite–quartz stage and pyrite–chalcopyrite–quartz stage from the porphyry Cu mineralization. During the early stage of porphyry Cu mineralization, the ore-forming fluids were at high temperatures (450–501 °C) and high salinity (51.2–55.2 wt.% NaCl equiv.) H2O-NaCl hydrothermal fluids with fluid boiling. These fluids evolved to high temperature (412–450 °C) and intermediate to low salinity (8.3–14.2 wt.% NaCl equiv.) H2O-NaCl hydrothermal fluids during the pyrite–chalcopyrite–quartz stage. In addition, magnetite from the Tonggou deposit was studied as a marker for the ore-forming process evolution of porphyry and vein-type mineralization. Sampled magnetite can be divided into MagI (allotriomorphic magnetite from altered granodiorite), MagII (magnetite from altered granodiorite found in veinlets or as granular aggregates), MagIII (from the magnetite–quartz stage of porphyry mineralization), and MagIV (from the polymetallic sulfide–epidote–quartz stage of vein-type mineralization). Magnetite LA-ICP-MS data indicate a hydrothermal origin. The contents of Ti, Si, Al, and Ta are controlled by temperature, and these elements gradually decrease from MagI to MagIV. Moreover, fO2 has considerable influence on the substitution of Sn, V, and Mn in magnetite, and the contents of these elements generally decrease from MagI to MagIV—increasing only in MagIV. Indeed, high fO2 in the polymetallic sulfide–epidote–quartz stage (MagIV) of vein-type mineralization is shown by the presence of a replacement texture in ilmenite grains within hydrothermal magnetite. On the other hand, magnetite samples from the Tonggou deposit have relatively low Ti + V contents compared to other porphyry Cu deposits—plotting in the skarn field of the (Ti + V) vs. Sn diagram—and shows negative correlations in the (Ti + V) vs. Sn diagram. These data indicate that the porphyry Cu mineralization at Tonggou formed at relatively lower fO2 conditions than the Tonggou vein-type mineralization and other typical porphyry Cu deposits. Finally, porphyry and vein-type mineralization at Tonggou are both sourced from the porphyry system, as a result of ore-forming fluid transfer to a different location.

Keywords: magnetite; trace element composition; fluid inclusion; Tonggou deposit; Eastern Tianshan

1. Introduction

Magnetite is a common mineral in intermediate to acidic rocks and metallic deposits, which is stable at a wide range of temperatures [1–4]. Indeed, magnetite may display different chemical compositions depending on its formation temperature, mineralization style, and genetic processes involved in its formation. For instance, magnetite crystallized from silicate and sulfide melts at high temperatures is expected to be enriched in Ti, Si, Al, Ba, Ta, Sc, and Y [3]. Thus, due to its wide temperature stability across different ore-forming
processes, magnetite trace element analysis by LA-ICP-MS has increasingly been used to discuss the ore-forming conditions of different deposits [1,4–6].

Based on elemental concentrations and ratios in magnetite, several studies have established geochemical discrimination diagrams for various types of deposits [4,7,8]. On the other hand, some research efforts have been devoted to distinguishing magnetite from igneous, hydrothermal, and sedimentary origins on the basis of elemental variations [1,9,10]. Therefore, some studies have focused on the trace-element geochemistry of magnetite to fingerprint the evolution of the ore-forming hydrothermal fluids and reconstruct the mineralization processes [1,2,11]. However, compositional variations in magnetite from porphyry Cu systems dependent on mineralization style (e.g., porphyry and vein types) are still poorly understood, as are their specific implications for ore-forming conditions and ore-forming fluid evolution. In addition, the study of fluid inclusions is a primary method for getting the information about the ore-forming fluids (e.g., temperatures, salinities, and pressures), which is the key to revealing the ore genesis and ore-forming progress of the hydrothermal deposits [12].

The Tonggou Cu-Zn deposit is located in the Eastern Tianshan section of the Central Asian Orogenic Belt (CAOB)—one of the world’s largest Phanerozoic subduction-accretionary orogens (Figure 1a) [13–15]. This area hosts a number of porphyry Cu deposits, for instance, Tuwu-Yandong, Fuxing, and Sanchakou, located in the Jueluotage Belt [16–18]. Tonggou porphyry Cu and vein-type Cu-Zn mineralization both formed in Late Carboniferous (302–303 Ma; [19,20]), which provide an ideal target to study the chemical variations among different types and generations of magnetite.

This paper presents new magnetite compositional data, acquired using LA-ICP-MS, coupled with a petrographic investigation—i.e., detailed classification and texture analysis from different mineralization stages of the Tonggou deposit. We provide new insight into ore-forming conditions as well as genetic relationships between different mineralization types in porphyry Cu systems. In addition, we acquired fluid inclusion data from porphyry mineralization to constrain the evolution of the ore-forming fluids. The present study could potentially be applied to other similar vein mineralization in porphyry Cu systems.
2. Regional Geological Setting

2.1. Regional Geology

The Eastern Tianshan area is located in the southern part of the CAOB, bordered by the Junggar Block to the north and the Precambrian Tarim Block to the south (Figure 1b). Eastern Tianshan can be divided from north to south into the Bogda-Harlik Orogenic Belt, the Jueluotage Belt, the Central Tianshan massif, and the Beishan terrane [21]. This area witnessed the evolution and closure of the Paleo-Asian Ocean [22–24], and the formation of a number of economic Au, Fe, porphyry Cu-Mo, magmatic Cu-Ni, and VMS Cu-polymetallic deposits [25–28]. Porphyry Cu-Mo mineralization in Eastern Tianshan is mainly distributed along the Jueluotage Belt, while the Tonggou porphyry deposit is located in the Bogda Orogenic Belt, with coexisting vein mineralization.

The Bogda Orogenic Belt, situated north of Eastern Tianshan, consists of Devonian, Carboniferous, Permian, and Jurassic strata [29]. The Devonian strata mainly consist of marine and terrigenous sediments, tuffaceous sandstone, and volcanic rocks. The Carboniferous strata show fault contacts with the Devonian rocks and are divided into the Lower Carboniferous Qijiaojing Formation and the Upper Carboniferous Liushugou and Qijiagou Formations, respectively. The Lower Carboniferous Formation mainly consists of
marine volcanic ignimbrites, tuffaceous sandstone, and bimodal volcanic lavas, while the Upper Carboniferous Formation is dominated by marine (pillow) basaltic lava and felsic ignimbrites, with minor sandstone and siltstone. The Lower and Upper Carboniferous Formations are separated by regional faults. The Permian strata unconformably overlie the Carboniferous rocks and are mainly composed of terrestrial conglomerate, sandstone, and siliceous mudstone, intercalated with bimodal volcanic lavas. In the southeastern region of the study area, Jurassic clastic sediments unconformably overlie the Permian strata [19,29].

Meanwhile, Late Carboniferous to Early Permian intermediate-to-felsic intrusions occur sporadically in the Bogda Orogenic Belt [30–33]. These intermediate-to-felsic intrusions are associated with a series of Cu polymetallic vein deposits [19], such as the Tonggou, Weicaogou, and Miao’ergou deposits (Figure 1c). In addition, porphyry Cu mineralization has been discovered at the top of the Tonggou granodiorite. Moreover, Re-Os and U-Pb isotopic ages indicate that both porphyry and vein Cu polymetallic mineralization at Tonggou formed in the Late Carboniferous (303 Ma, [19,20]).

2.2. Deposit Geology

The Tonggou deposit is located in the western part of the Bogda Orogenic Belt. The exposed strata mainly correspond to the Late Carboniferous Qijiaojing Formation—consisting of argillite, siltstone, and fine sandstone.

Porphyry Cu mineralization occurs at the top (or contact zone) of the Tonggou granodiorite (Figure 2a). The strata in Tonggou porphyry mineralization belong to the First Segment of Devonian Qijiaojing Formation and consist of metamorphic fine sandstone and siltstone. Metallic minerals are mainly hematite, magnetite, pyrite, and chalcopyrite (Figure 3a–g), with lesser amounts of galena. Porphyry Cu mineralization mainly occurs as disseminated, veinlet, and stockwork veins, accompanied by potassic and propylitic alteration. Widespread gangue minerals contain abundant K-feldspar, chlorite, epidote, quartz, calcite, and lesser anhydrite. Magnetite is widely present in the porphyry Cu mineralization and is partially replaced by hematite (Figures 3e and 4). Based on mineral assemblages and crosscutting relationships, hydrothermal mineralization at Tonggou can be classified into two stages: the magnetite–quartz stage (stage I) and the pyrite–chalcopyrite–quartz stage (stage II).

Vein-type Cu-Zn mineralization occurs 1.5 km south of the porphyry Cu mineralization and is mainly hosted by Late Carboniferous Qijiaojing Formation argillite, siltstone, and fine sandstone. The 36 economic ore bodies discovered are mainly distributed in the E-W trend faults, which are widely developed and act as the ore-controlling structures in the Tonggou deposit. For vein-type Cu-Zn mineralization, the shapes and sizes of the ore bodies are controlled by faults, mainly occur as disseminated, veinlet disseminated, lenticular, and vein-shaped [19]. Metallic minerals are mainly magnetite, pyrite, chalcopyrite, and sphalerite, with lesser amounts of hematite, ilmenite, galena, and bornite (Figures 3h,i and 4). Gangue minerals, including quartz, calcite, chlorite, and epidote, occur widely in the Tonggou deposit and are similar to the propylitic alteration of porphyry mineralization [34]. The hydrothermal mineralization at Tonggou can be divided into three stages: the pyrite–quartz stage (stage 1), the polymetallic sulfide–epidote–quartz stage (stage 2), and the pyrite–calcite stage (stage 3).
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Figure 3. Representative photographs and photomicrographs of magnetite samples at the Tonggou porphyry and vein mineralization. (a) A MagI sample from altered granodiorite; (b) reflected-light photomicrograph of MagI; (c) A MagII sample accompanied with pyrite from altered granodiorite; (d) reflected-light photomicrograph of veinlet-disseminated MagII; (e) reflected-light photomicrograph of euhedral MagII; (f) A MagIII sample from magnetite–quartz stage; (g) reflected-light photomicrograph of MagIII; (h) the specimen of MagIV representing polymetallic sulfide–epidote–quartz stage; (i) reflected-light photomicrograph of MagIV. Ccp—chalcopyrite; Hem—hematite; Mag—magnetite; Py—pyrite; Qz—quartz.
**3. Samples and Analytical Methods**

3.1. Sample Preparation

Quartz samples were selected for fluid inclusion analyses, specifically granular quartz from magnetite–quartz stage (stage I) and stage-II pyrite–chalcopyrite–quartz veins (Figure 5a–c). In addition, representative samples were collected from the altered granodiorite and wall rocks of the different mineralization stages. Magnetite samples include two from granodiorite (Mag$_I$ and Mag$_{II}$), one from stage-I porphyry Cu mineralization (Mag$_{III}$), and another from stage 2 of vein-type Cu-Zn mineralization (Mag$_{IV}$). Mag$_I$ from altered granodiorite is allotriomorphic and occurs as isolated or granular aggregates (Figure 3a,b). Mag$_{II}$ from altered granodiorite is subidiomorphic and occurs as veinlet or granular aggregates accompanied by pyrite (Figure 3c–e). Mag$_{III}$ from stage I is allotriomorphic and occurs alongside quartz (Figure 3f,g). Mag$_{IV}$ (stage 2) is allotriomorphic and is partially replaced by chalcopyrite (Figure 3h,i). In addition, some Mag$_{IV}$ samples exhibit ilmenite replacement, which indicates that magnetite from stage 2 formed at high oxygen fugacity conditions.

3.2. Analytical Methods

Fluid inclusion petrography and microthermometric analyses were performed at the Xinjiang Key Laboratory for Geodynamic Processes and Metallogenic Prognosis of the Central Asian Orogenic Belt, Xinjiang University, China. Microthermometric measurements were performed using a Linkam THMS-600 heating-freezing stage mounted on a Carl Zeiss AxioLab microscope with 10× and 50× ultra-long working distance objectives. The heating–freezing rate was generally from 0.2 to 5 °C/min but was reduced to less than 0.2 °C/min near phase transformations. Uncertainties of freezing and heating measurements were ±0.1 °C from −120 to 31 °C, ±1 °C from 31 to 300 °C, and ±2 °C above 300 °C. Homogenization temperature data for fluid inclusions were calculated using the software MacFlinCor [35].
Figure 5. Specimen photographs and photomicrographs of FIAs in quartz from the porphyry Cu mineralization of Tonggou deposit. (a) Granular quartz sample from magnetite–quartz stage; (b) granular quartz vein; (c) chalcopyrite–quartz vein; (d) granular quartz sample from magnetite–quartz stage show growth bands; (e) Boiling FIA (S- and V-type FIs) in the core of sample TGP6-1; (f) L-type FIA and V-type FIA in the core of sample TGP6-1; (g) L-type FIA and V-type FIA in the transition of sample; (h) L-type FIA and V-type FIA in the rim of sample TGP6-1; (i, j, k) L-type FIA and V-type FIA in sample BY-7; L (liquid phase), V (vapor phase), S (daughter mineral).

Energy dispersive spectrometer (EDS) and back-scattered electron (BSE) analyses were performed on magnetite in the Beijing Kerongen Science and Technology Ltd., Beijing, China, prior to LA-ICP-MS analysis. EDS analyses were carried out to obtain Fe, O, Al, Mg, Si, and Ti concentrations, while BSE images were obtained for inclusion identification in magnetite (Figure 6).
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Figure 6. (a) BSE image of Mag I from sample FG-1; (b) BSE image of Mag II from sample BY-9; (c) BSE image of Mag III from sample BY-1; (d) BSE image of Mag IV from sample TG-002; (e) replacement texture of Mag IV in reflected-light photomicrograph from sample TG-002; (f) replacement texture of Mag IV in BSE image from sample TG-002; (g) EDS analysis on ilmenite; (h) EDS analysis on magnetite; (i) EDS analysis on chalcopyrite.

Trace element analyses of magnetite were performed with LA-ICP-MS at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Detailed operating conditions for the laser ablation system, the ICP-MS instrument, and data reduction are as described by Zong et al. [36]. Laser sampling was performed using a GeolasPro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7900 ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP-MS. A “wire” signal smoothing device is included in this laser ablation system [37]. Laser spot size and frequency were set to 44 μm and 5 Hz, respectively. Trace element compositions of magnetite were calibrated against various reference materials (BHVO-2G, BCR-2G, and BIR-1G) without using an internal standard [38]. Each analysis incorporated a background acquisition of approximately 20–30 s followed by 50 s of data acquisition from the sample. The Excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction, and quantitative calibration for trace element analysis [38].

4. Results

4.1. Petrography of Fluid Inclusions

The standard for distinguishing different generations of FIs within hydrothermal quartz was proposed by Goldstein and Reynolds [39]. FIs along growth bands are considered as separate FIA. Primary FIs occur as isolated inclusions or random groups, while pseudosecondary inclusions are found in infilled internal cracks. Based on fluid inclusion
petrography, three types of fluid inclusions were identified in our samples according to their phase compositions at room temperature (25 °C) and the phase transitions observed during heating and cooling. The three types of inclusions include liquid-rich aqueous inclusions (L), vapor-rich aqueous inclusions (V), and NaCl daughter mineral-bearing three-phase inclusions (S) (Figure 5d–k).

L-type FIs generally consist of a liquid phase and a minor vapor phase at room temperature, with 10 to 30 vol.% of vapor bubble (Figure 5f–k). With maximum dimensions of 20 µm, these FIs occur randomly in quartz and are present in granular quartz and stage 2 of porphyry Cu mineralization. VL-type FIs consist of a liquid with a vapor bubble—which accounts for 60–90% of the FI volume (Figure 5f–h,j,k). This type of FI is typically elliptical and 10–15 µm in size. These FIs were trapped in granular quartz and stage 2 mineralization and occurred randomly in quartz. S-type FIs are comprised of halite, liquid phase, and vapor bubble that account for 15–20% of the total volume at room temperature and are generally less than 15 µm in diameter (Figure 5e). This type of FI is only present in the core of granular quartz and is accompanied by minor V-type FIs.

4.2. Fluid Inclusion Microthermometry

In total, 19 FIAs and 131 FIs were chosen for microthermometric analysis. Detailed data are listed in Table 1. The homogenization temperature vs. salinity diagram of the different FIAs is presented in Figure 7.

Figure 7. Homogenization temperature vs. salinity in the NaCl-H₂O system for FIAs from porphyry Cu mineralization in the Tonggou deposit. Isobars were calculated using the equations of Driesner and Heinrich [40].
Table 1. Microthermometric data from FIA in quartz from porphyry Cu mineralization of the Tonggou deposit.

| Sample       | Host Mineral                      | FIA  | FI Type | Number | Gas–Liquid Ratio (%) | Tm (Ice) (°C) | Tm (NaCl) (°C) | Salinity (wt% NaCl Equiv.) | Th (°C) | Note |
|--------------|-----------------------------------|------|---------|--------|-----------------------|---------------|---------------|---------------------------|---------|------|
| TGP6-1       | Quartz from granular quartz       | FIA-1| V       | 3      | 80                    | From −7.9 to −7.0 | 458–465       | 10.5–11.6 (avg.11.1)       | 480–492 | core |
|              |                                   |      | S       | 2      | 20                    |               |               |                           | 495–501 |      |
|              |                                   |      | V       | 4      | 70                    | From −7.1 to −6.6 |               |                           | 9.9–10.6 |      |
|              |                                   |      | V       | 3      | 70                    | From −6.3 to −5.6 |               |                           | 8.7–9.6  | transition |
|              |                                   |      | L       | 6      | 15                    | From −13.1 to −9.8 |               |                           | 13.8–17.1 | rim |
|              |                                   |      | V       | 2      | 90                    | From −5.5 to −5.1 |               |                           | 8.0–8.5  |      |
|              |                                   |      | L       | 8      | 25                    | From −10.2 to −8.7 |               |                           | 12.5–14.2 |      |
|              |                                   |      | L       | 5      | 30                    | From −10.1 to −8.2 |               |                           | 12.0–14.1 |      |
|              |                                   |      | L       | 6      | 20                    | From −10.6 to −9.3 |               |                           | 13.2–14.6 |      |
|              |                                   |      | L       | 7      | 15                    | From −10.9 to −10.1 |               |                           | 14.1–14.9 |      |
| TGP5-1       | Quartz from granular quartz vein  | FIA-8| S       | 3      | 20                    |               | 439–445       | 51.2–52.7               | 489–496 | core |
|              |                                   |      | V       | 3      | 80                    | From −6.9 to −6.3 |               | 9.6–10.4               | 458–470 |      |
|              |                                   |      | L       | 7      | 20                    | From −13.5 to −11.8 |               | 15.8–17.5             | 446–469 |      |
|              |                                   |      | V       | 2      | 70                    | From −6.7 to −6.2 |               | 9.5–10.1             | 432–446 |      |
|              |                                   |      | L       | 6      | 15                    | From −12.6 to −11.9 |               | 15.9–16.6             | 416–433 | transition |
|              |                                   |      | L       | 7      | 20                    | From −11.2 to −10.5 |               | 14.5–15.2             | 386–412 | rim |
|              |                                   |      | L       | 5      | 30                    | From −10.1 to −9.3 |               | 13.2–14.3             | 371–395 |      |
| BY-7         | Quartz from pyrite–chalcopyrite–quartz vein | FIA-13| L       | 6      | 10                    | From −9.2 to −8.5 |               | 12.3–13.1             | 412–430 |      |
|              |                                   |      | L       | 6      | 20                    | From −9.5 to −8.8 |               | 12.7–13.4             | 421–432 |      |
|              |                                   |      | V       | 3      | 80                    | From −5.7 to −5.3 |               | 8.3–8.8               | 441–449 |      |
|              |                                   |      | L       | 8      | 30                    | From −10.3 to −9.5 |               | 13.4–14.2             | 435–443 |      |
| BY-7         | Quartz from pyrite–chalcopyrite–quartz vein | FIA-16| V       | 2      | 60                    | From −5.9 to −5.6 |               | 8.7–9.1               | 445–450 |      |
| BY-8         | Quartz from pyrite–chalcopyrite–quartz vein | FIA-17| V       | 3      | 80                    | From −6.2 to −5.8 |               | 8.9–9.5               | 436–441 |      |
|              |                                   |      | L       | 6      | 20                    | From −9.9 to −9.2 |               | 13.1–13.9             | 430–441 |      |
|              |                                   |      | L       | 7      | 15                    | From −9.6 to −8.9 |               | 12.8–13.6             | 425–439 |      |
|              |                                   |      | L       | 6      | 10                    | From −9.1 to −8.4 |               | 12.2–13.0             | 415–428 |      |
Granular quartz from porphyry mineralization displays a clearly zonal structure. Grain cores contain abundant L-, V-, and S-type FIs. Final ice-melting temperatures of L-type FIs range from $-13.5 \, ^\circ C$ to $-9.8 \, ^\circ C$, corresponding to salinities of 13.8–17.5 wt.% NaCl equiv. Total homogenization of L-type FIs to the liquid phase occurred at temperatures of 446–471 $^\circ C$. Final ice-melting temperatures of V-type FIs range from $-7.9$ to $-6.3 \, ^\circ C$, corresponding to salinities of 9.6–11.6 wt.% NaCl equiv. Total homogenization of V-type FIs to the vapor phase occurred at temperatures of 458–492 $^\circ C$. For S-type FIs, the following homogenization mechanism was observed: halite crystals dissolved first, and the disappearance of the vapor phase occurred later. S-type FIs finally homogenized to a single liquid phase at temperatures of 489–501 $^\circ C$. Halite crystals within S-type FIs dissolved at temperatures of 439–465 $^\circ C$, corresponding to salinities of 51.2–55.2 wt.% NaCl equiv.

The granular quartz transition area contains abundant L- and V-type FIs. L-type FIs all homogenize to the liquid phase at temperatures of 416–433 $^\circ C$. Final ice-melting temperatures of L-type FIs range from $-12.6 \, ^\circ C$ to $-9.1 \, ^\circ C$, corresponding to salinities of 13.0–16.6 wt.% NaCl equiv. Final ice-melting temperatures of V-type FIs range from $-6.7$ to $-5.6 \, ^\circ C$, corresponding to salinities of 8.7–10.1 wt.% NaCl equiv. Total homogenization of V-type FIs to the vapor phase occurred at temperatures of 420–446 $^\circ C$.

Granular quartz rims also contain abundant L- and V-type FIs. Final ice-melting temperatures of L-type FIs range from $-8.2 \, ^\circ C$ to $-11.2 \, ^\circ C$. Their salinities are estimated to range between 12.0 and 15.2 wt.% NaCl equiv., and these FIs homogenized to a liquid phase at temperatures ranging from 365 $^\circ C$ to 412 $^\circ C$. On the other hand, V-type FIs all homogenized to the liquid phase at temperatures of 391–403 $^\circ C$. Final ice-melting temperatures of L-type FIs range from $-5.5 \, ^\circ C$ to $-5.1 \, ^\circ C$, corresponding to salinities of 8.0–8.5 wt.% NaCl equiv.

Abundant L- and V-type FIs occur in quartz from stage 2. Final ice-melting temperatures of L-type FIs range from $-10.3 \, ^\circ C$ to $-8.4 \, ^\circ C$, and their salinities are estimated between 12.2 and 14.2 wt.% NaCl equiv. L-type FIs are homogenized to a liquid phase at temperatures of 412 $^\circ C$ to 443 $^\circ C$. V-type FIs all homogenize to the liquid phase at temperatures of 436–450 $^\circ C$. Final ice-melting temperatures of L-type FIs range from $-6.2 \, ^\circ C$ to $-5.3 \, ^\circ C$, corresponding to salinities of 8.3–9.5 wt.% NaCl equiv.

4.3. Magnetite Chemistry

LA-ICP-MS spot analyses were conducted on four magnetite samples, with two, eight, seven, and eight spots on Mag$_I$, Mag$_{II}$, Mag$_{III}$, and Mag$_IV$, respectively. Representative bulk trace-element compositions (Si, Al, Ti, Mn, Ca, P, Mg, V, Cr, Co, Ni, Cu, Zn, Ga, Zr, Ba, As, Ge, Sn, Sc, Sr, Y, Nb, Mo, W, Hf, Ta, and Bi) are summarized in Table 2. In addition, EDS analyses were conducted to acquire elemental concentrations of ilmenite crystals in magnetite, which show a phenomenon of alteration of the ilmenite (Figure 6e–i).
| Sample          | Generation | Mg   | Al  | Si   | Ca   | Sc  | Ti  | V   | Cr  | Mn  | Co  | Ni  | Cu  | Zn  | Ga  | Ge  | Sn  | W   | Pb  | Bi  |
|-----------------|------------|------|-----|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| FG1-01          | 1          | 1007 | 10 | 806 | 28,084 | 5225 | 23.4 | 723 | 234 | 34  | 471 | 401.5 | 470.6 | 7 | 590 | 12.3 | 6.7 | 0.9 | 0.6 | 8.7 | 35.7 |
| FG1-02          | 1          | 915  | 8736 | 18,636 | 5153 | 45.3 | 872 | 310 | 136 | 429 | 232.4 | 633.2 | 6 | 655 | 26.2 | 6.4 | 0.9 | 0.9 | 4.9 | 3.4 |
| BY-9(1)-01      | 2          | 1956 | 20,850 | 33,635 | 4226 | 37.6 | 222 | 356 | 879 | 294 | 7.6 | 491.1 | 86 | 3908 | 19.1 | 5.7 | 0.4 | 3.4 | 42.6 | 4.7 |
| BY-9(1)-02      | 2          | 2151 | 3452 | 17,063 | 1316 | 3.6 | 19  | 240 | 138 | 534 | 95.1 | 732.4 | 17 | 1229 | 2.62 | 4.9 | 0.0 | 0.8 | 11.9 | 0.7 |
| BY-9(1)-03      | 2          | 1404 | 20,099 | 33,527 | 4561 | 31.7 | 319 | 383 | 1215 | 545 | 7.1 | 466.8 | 80 | 3841 | 18.9 | 4.7 | 1.1 | 2.8 | 45.1 | 2.5 |
| BY-9(1)-04      | 2          | 1531 | 20,763 | 32,390 | 4406 | 34.2 | 516 | 342 | 862 | 620 | 7.4 | 497.8 | 82 | 3740 | 18.2 | 3.8 | 0.0 | 3.0 | 33.9 | 2.1 |
| BY-9-01         | 2          | 1685 | 19,564 | 32,353 | 4604 | 34.1 | 352 | 347 | 1008 | 581 | 14.9 | 516.3 | 75 | 3232 | 17.0 | 5.4 | 0.6 | 2.3 | 28.9 | 1.9 |
| BY-9-02         | 2          | 1817 | 10,291 | 26,291 | 287 | 17.5 | 287 | 305 | 785 | 945 | 62.1 | 688.5 | 47 | 1909 | 9.34 | 5.2 | 0.0 | 1.7 | 23.9 | 0.7 |
| BY-9-03         | 2          | 1864 | 15,439 | 31,205 | 3675 | 29.9 | 655 | 359 | 884 | 158 | 15.8 | 457.4 | 59 | 2629 | 14.5 | 6.3 | 0.2 | 1.8 | 38.3 | 2.9 |
| BY-9-04         | 2          | 2002 | 22,472 | 40,869 | 4933 | 29.8 | 247 | 412 | 1844 | 617 | 16.4 | 606.1 | 108 | 3795 | 27.0 | 3.6 | 0.5 | 3.3 | 32.0 | 2.2 |
| BY-1-02         | 3          | 623  | 6285 | 29,965 | 777 | 0.5 | 294 | 2  | 17 | 518 | 463.3 | 761.1 | 2 | 261 | 0.0 | 2.0 | 0.5 | 0.0 | 2.3 | 6.4 |
| BY-1-03         | 3          | 954  | 3605 | 21,831 | 444 | 0.6 | 626 | 3 | 13 | 497 | 426.6 | 706.5 | 2 | 251 | 0.2 | 3.6 | 1.5 | 0.1 | 2.2 | 4.2 |
| BY-1-04         | 3          | 437  | 1559 | 21,602 | 357 | 0.1 | 69 | 1 | 12 | 451 | 552.6 | 1199.7 | 5 | 240 | 0.0 | 2.5 | 0.4 | 0.0 | 0.9 | 1.2 |
| BY-1-05         | 3          | 585  | 5391 | 30,415 | 668 | 0.4 | 280 | 2 | 15 | 367 | 525.3 | 885.7 | 3 | 206 | 0.4 | 3.7 | 0.4 | 0.0 | 1.5 | 1.4 |
| BY-1-06         | 3          | 611  | 3775 | 23,137 | 386 | 0.6 | 354 | 2 | 11 | 448 | 451.7 | 757.2 | 2 | 260 | 0.4 | 2.6 | 0.0 | 0.0 | 1.6 | 3.1 |
| BY-1-07         | 3          | 909  | 6470 | 32,784 | 672 | 1.0 | 421 | 5 | 19 | 521 | 360.1 | 599.1 | 1 | 251 | 1.0 | 2.6 | 0.6 | 0.1 | 3.2 | 7.6 |
| BY-1-08         | 3          | 618  | 3371 | 22,733 | 548 | 0.6 | 380 | 2 | 13 | 371 | 497.4 | 826.2 | 3 | 254 | 0.4 | 5.2 | 0.2 | 0.0 | 1.7 | 4.2 |
| TG002-2-01      | 4          | 2642 | 5245 | 15,177 | 362 | 4.5 | 59 | 30 | 11 | 612 | 2.3 | 3.9 | 22,282 | 481 | 4.6 | 41.0 | 6.2 | 3023.3 | 2.1 | 13.4 |
| TG002-2-02      | 4          | 980  | 2928 | 9821 | 249 | 2.9 | 18 | 14 | 2 | 498 | 0.5 | 0.6 | 2010 | 163 | 2.2 | 39.0 | 5.4 | 3414.5 | 1.3 | 4.7 |
| TG002-2-03      | 4          | 560  | 2514 | 9170 | 430 | 2.7 | 18 | 24 | 2 | 606 | 4.4 | 0.3 | 16,829 | 217 | 0.9 | 32.9 | 9.4 | 4653.6 | 2.6 | 28.3 |
| TG002-2-04      | 4          | 907  | 1512 | 15,492 | 1270 | 2.5 | 25 | 18 | 8 | 447 | 1.9 | 7.9 | 10,069 | 182 | 1.1 | 61.8 | 9.1 | 5735.6 | 1.8 | 15.0 |
| TG002-01        | 4          | 400  | 2351 | 14,150 | 561 | 2.6 | 41 | 28 | 15 | 487 | 0.3 | 0.5 | 517 | 151 | 1.7 | 76.5 | 16.2 | 4616.2 | 1.7 | 3.7 |
| TG002-02        | 4          | 520  | 2756 | 9581 | 188 | 3.3 | 44 | 24 | 1 | 583 | 1.1 | 2.9 | 111 | 55 | 1.7 | 44.7 | 14.9 | 4204.6 | 0.5 | 10.4 |
| TG002-03        | 4          | 482  | 2332 | 9911 | 413 | 2.6 | 12 | 15 | 27 | 447 | 0.4 | 0.0 | 58,878 | 208 | 1.6 | 45.3 | 6.1 | 3376.0 | 2.1 | 14.5 |
5. Discussion

5.1. Controlling Factors on Magnetite Compositions

Trace elements in magnetite always depend on the formation temperatures of the rock or ore, as well as oxygen fugacity ($f_{O2}$), fluid/melt composition, host rock composition, and coexisting minerals during mineral deposit formation [2,4,41]. Titanium is favored in high-temperature ulvospinel–magnetite solid solutions and is incorporated into magnetite by coupling substitution with Fe$^{2+}$ for Fe$^{3+}$ [3,42]). Ti concentrations gradually drop from MagI to MagIV, which is consistent with a higher formation temperature for MagIII (~500 °C, as described in Section 4.2.) than for MagIV (~400 °C; [19]). These results are coherent with the affinity of magnetite for Ti at higher temperatures. Furthermore, Si, Al, and Ta in magnetite are found to decrease gradually from MagI to MagIV, which implies a positive correlation of these elements with Ti (Figure 8).

![Figure 8](image_url) Comparative box plot of SiO$_2$, Al$_2$O$_3$, Ti, Ba, Sc, Y, Ta, V, Co, Ni, Sn, and Mn concentrations of the different magnetite generations.

On the other hand, some trace element concentrations (e.g., Sn, V, Mn) are controlled by oxygen fugacity since these elements have several valence states. For instance, in magnetite, Fe$^{3+}$ is substituted by Sn$^{4+}$ more readily than Sn$^{2+}$ [41]. This is consistent with the fact that MagIV contains higher ratios of Sn than MagIII (Figure 8). In addition, V and Mn generally decrease from MagI to MagIII, following the same trend as Ti. However, V and Mn do not decrease with Ti in MagIV (Figure 8). This can be explained by the appearance of ilmenite replacing MagIV (Figure 3i), which indicates that high f$_{O2}$ is characteristic of stage 2 (polymetallic sulfide–epidote–quartz stage). Thus, Ti in magnetite can be considered a temperature indicator, while Sn, V, and Mn are dependent on both temperature and f$_{O2}$ [3,10].

In addition, considering the different partition coefficients of trace elements between magnetite and coexisting minerals, the compositions of certain trace elements in magnetite may also be affected by the co-precipitation of other minerals [1]. For instance, chalcophile...
elements (Co, Ni, Cu, Zn, and Bi) partition more readily into sulfides than magnetite [2]. Indeed, there is a decreasing trend in Co, Ni, and Zn contents from MagIII to MagIV (Figure 8). However, Cu and Bi are not depleted in MagIV as expected (Figure 8), despite the coexistence of sulfides with MagIV. It may be a reasonable explanation that MagIV precipitated earlier than the sulfides, which is supported by the occurrence of secondary chalcopyrite replacing magnetite (Figure 6e). Similar cases have been described in the Yuleken porphyry Cu deposit in East Junggar [4].

5.2. Evolution of Ore-Forming Fluids

FIs identified in the cores of granular quartz grains are LV-, VL-, and S-type FIs with high temperatures (450–501 °C) and high salinity (51.2–55.2 wt.% NaCl equiv.). In addition, fluid boiling occurred in the core of granular quartz, as demonstrated by coexisting vapor-rich (VL-type) and high-salinity (S-type) FIs, which homogenized at similar temperatures, suggesting they were trapped during phase separation [43]. In view of the fact that the homogenization temperature and salinity of boiling FIsAs are extremely high (~500 °C), they most likely originated from phase separation of magmatic water due to decompression. In addition, homogenization temperature and salinity decrease gradually from core to rim in granular quartz, which indicates an increasing contribution of meteoric water in ore-forming fluids during the later stage.

On the other hand, FIs from porphyry Cu mineralization (stage 2) have similar homogenization temperatures and salinities to vein-type Cu mineralization in the Tonggou deposit (this study and [19]). In addition, they both formed in Late Carboniferous Porphyry Cu Systems (303 Ma; [19,20]) and occur in adjacent geographical locations. Thus, we consider that the porphyry and vein-type Cu mineralization belong to the same porphyry Cu system.

5.3. Metallogenetic Processes

Based on magnetite chemistry, some researchers have proposed discrimination diagrams for distinguishing magnetite of different origins or from various deposit types [1,3,4,7,44]. Tonggou magnetite of different origins was mostly plotted within the magmatic range in the Ni/Cr vs. Ti diagram (Figure 9a). Due to the higher solubility of Ni in hydrothermal fluids with respect to Cr, hydrothermal magnetite has relatively low Ni/Cr ratios [1].

In the (Ti + V) vs. (Ca + Al + Mn) diagram proposed by Dupuis and Beaudoin [7], magnetite from Tonggou plots close to the skarn field (Figure 9b), indicating relatively low Ti + V contents compared to other porphyry Cu deposits. As discussed above, the temperature is a controlling factor for trace element incorporation and correlates positively with Ti, with the early stage of porphyry Cu mineralization showing the highest formation temperatures (~500 °C) and Ti contents of the Tonggou deposit. By observing our data plotted in the (Ti + V) vs. (Ca + Al + Mn) diagram (Figure 9c) by Nadoll et al. [2], it is evident that magnetite from Tonggou is high-temperature magnetite (generally >300 °C). However, V concentrations in Tonggou magnetite are influenced by both temperature and fO2 and are lower than in other porphyry Cu deposits (e.g., Yuleken Cu deposit; [4]). In addition, zircons from Tonggou granodiorite have high Ce/CeN* values (227–234) and Ce4+/Ce3+ ratios (159–286; [20]). Furthermore, Sn is characterized by negative correlations with Ti + V, as seen in the (Ti + V) vs. Sn diagram (Figure 9d). It is worth noting that porphyry Cu mineralization at Tonggou likely formed at relatively high fO2 conditions, though lower than other porphyry Cu deposits (e.g., Yuleken) and Tonggou vein-type mineralization.
Thus, although both porphyry and vein-type mineralization are sourced from the Tonggou porphyry system, the vein-type mineralization may have formed at a higher $f\text{O}_2$ than the porphyry mineralization. Generally, large and intermediate porphyry Cu deposits are associated with intrusive rocks derived from oxidized magmas [45]. This is consistent with the fact that the vein Cu-Zn mineralization at the Tonggou deposit is economically significant, while the porphyry Cu mineralization is less economically relevant.

6. Conclusions

Magnetite in the Tonggou deposit can be divided into allotriomorphic Mag$_I$ from altered granodiorite, subidiomorphic Mag$_{II}$ from altered granodiorite, allotriomorphic Mag$_{III}$ from the magnetite–quartz stage of porphyry mineralization, and allotriomorphic Mag$_{IV}$ from the polymetallic sulfide–epidote–quartz stage of vein-type mineralization.

LA-ICP-MS analyses reveal that trace elements in magnetite of the Tonggou deposit vary systematically from porphyry to vein-type mineralization. In addition, the content of Ti, Si, Al, and Ta in magnetite is positively correlated with high temperatures, while $f\text{O}_2$ has a considerable influence on Sn, V, and Mn.

Ore-forming fluids of the Tonggou porphyry mineralization were high temperature and high-salinity H$_2$O-NaCl hydrothermal fluids in the early stage, which derived from a magmatic fluid.

The occurrence of ilmenite replacing Mag$_{IV}$ in the polymetallic sulfide–epidote–quartz stage is characterized by high $f\text{O}_2$ and intermediate to high temperatures. Porphyry and

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Figure 9. (a) Ti vs. Ni/Cr ratio in magnetite, where the boundary is defined by Dare et al. [1]. (b) (Ca + Al + Mn) vs. (Ti + V) discrimination diagram for magnetite from the Tonggou deposit, where the fields for Kiruna, IOCG, PCD, skarn, Fe-Ti-V, and BIF deposits were defined by Dupuis and Beaudoin [7]. (c) (Al + Mn) vs. (Ti + V) diagram for magnetite (modified after [1]) from the Tonggou deposit. (d) Sn vs. (Ti + V) diagram for magnetite from the Tonggou deposit.
vein-type mineralization are sourced from the Tonggou porphyry system and are the result of the transfer of ore-forming fluids to a different location.

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References

1. Dare, S.A.S.; Barnes, S.J.; Beaudoin, G.; Méric, J.; Boutroy, E.; Potvin-Doucet, C. Trace elements in magnetite as petrogenetic indicators. Mineral. Deposita 2014, 49, 785–796. [CrossRef]
2. Nadoll, P.; Angerer, T.; Mauk, J.L.; French, D.; Walshe, J. The chemistry of hydrothermal magnetite: A review. Ore Geol. Rev. 2014, 61, 1–32. [CrossRef]
3. Canil, D.; Grondahl, C.; Lacourse, T.; Pisiak, L.K. Trace elements in magnetite from porphyry Cu-Mo-Au deposits in British Columbia, Canada. Ore Geol. Rev. 2016, 72, 1116–1128. [CrossRef]
4. Wu, C.; Chen, H.-Y.; Hong, W.; Li, D.-F.; Liang, P.; Fang, J.; Zhang, L.-J.; Lai, C. Magnetite chemistry and implications for the magmatic-hydrothermal oreforming process: An example from the Devonian Yuleken porphyry Cu system, NW China. Chem. Geol. 2019, 522, 1–15. [CrossRef]
5. Huang, X.-W.; Zhou, M.-F.; Qiu, Y.-Z.; Qi, L. In-situ LA-ICP-MS trace elemental analyses of magnetite: The Bayan Obo Fe-REE-Nb deposit, North China. Ore Geol. Rev. 2015, 65, 884–899. [CrossRef]
6. Li, D.-F.; Chen, H.-Y.; Hollings, P.; Zhang, L.; Sun, X.-M.; Zheng, Y.; Xia, X.-P.; Xiao, B.; Wang, C.-M.; Fang, J. Trace element geochemistry of magnetite: Implications for ore genesis of the Talate skarn Pb-Zn (-Fe) deposit, Altay, NW China. Ore Geol. Rev. 2018, 100, 471–482. [CrossRef]
7. Dupuis, C.; Beaudoin, G. Discriminant diagrams for iron oxide trace element fingerprinting of mineral deposit types. Mineral. Deposita 2011, 46, 319–335. [CrossRef]
8. Pisiak, L.K.; Canil, D.; Lacourse, T.; Plouffe, A.; Ferbey, T. Magnetite as an indicator mineral in the exploration of porphyry deposits: A case study in till near the Mount Polley Cu-Au deposit, British Columbia, Canada. Econ. Geol. 2017, 112, 919–940. [CrossRef]
9. Chen, W.-T.; Zhou, M.-F.; Gao, J.-F.; Hu, R.-Z. Geochemistry of magnetite from Proterozoic Fe-Cu deposits in the Kangdian metamorphic province, SW China. Mineral. Deposita 2015, 50, 795–809. [CrossRef]
10. Chen, W.-T.; Zhou, M.-F.; Li, X.-C.; Gao, J.-F.; Hou, K.-J. In-situ LA-ICP-MS trace elemental analyses of magnetite: Cu-(Au, Fe) deposits in the Khetri copper belt in Rajasthan Province, NW India. Ore Geol. Rev. 2015, 65, 929–939. [CrossRef]
11. Liu, Y.; Fan, Y.; Zhou, T.; Xiao, X.; White, N.-C.; Thompson, J.; Hong, H.; Zhang, L. Geochemical characteristics of magnetite in Longqiao skarn iron deposit in the Middle-Lower Yangtze Metallogenic Belt, Eastern China. Mineral. Deposita 2019, 54, 1229–1242. [CrossRef]
12. Ni, P.; Chi, Z.; Pan, J.-Y.; Wang, G.-G.; Chen, H.; Ding, J.-Y. The Characteristics of Ore-Forming Fluids and Mineralization Mechanism in Hydrothermal Deposits: A Case Study of Some Typical Deposits in China. Bull. Mineral. Petrol. Geochem. 2018, 37, 369–395.
13. Sengör, A.M.C.; Natal'In, B.A.; Burtman, V.S. Evolution of the Altaiad tectonic collage and Palaeozoic crustal growth in Eurasia. Nature 1993, 364, 299–307. [CrossRef]
14. Jahn, B.M.; Wu, F.; Chen, B. Granitoids of the Central Asian Orogenic Belt and continental growth in the Phanerozoic. Earth Env. Sci. Trans. R. Soc. 2000, 350, 181–193.
15. Wang, J.-B.; Wang, Y.-W.; He, Z.-J. Ore deposits as a guide to the tectonic evolution in the East Tianshan Mountains, NW China. Geol. China 2006, 33, 461–469.
41. Carew, M.J. Controls on Cu-Au Mineralization and Fe Oxide Metasomatism in the Eastern Fold Belt, N.W. Ph.D. Thesis, James Cook University, Douglas, QLD, Australia, 2004.

42. Buddington, A.F.; Lindsley, D.H. Iron-titanium oxide minerals and synthetic equivalents. *J. Petrol.* **1964**, *5*, 310–357. [CrossRef]

43. Ramboz, C.; Pichavant, M.; Weisbrod, A. Fluid immiscibility in natural processes: Use and misuse of fluid inclusion data: II. Interpretation of fluid inclusion data in terms of immiscibility. *Chem. Geol.* **1982**, *37*, 29–48. [CrossRef]

44. Zhang, Y.; Hollings, P.; Shao, Y.-J.; Li, D.-F.; Chen, H.-Y.; Li, H.-B. Magnetite texture and trace-element geochemistry fingerprint of pulsed mineralization in the Xinqiao Cu-Fe-Au deposit, Eastern China. *Am. Mineral.* **2020**, *105*, 1715–1723. [CrossRef]

45. Shen, P.; Hattori, K.; Pan, H.-D.; Jackson, S.; Seitmuratova, E. Oxidation condition and metal fertility of granitic magmas: Zircon trace-element data from porphyry Cu deposits in the Central Asian orogenic belt. *Econ. Geol.* **2015**, *110*, 1861–1878. [CrossRef]