Methane-rich fluid evolution of the Baogutu porphyry Cu–Mo–Au deposit, Xinjiang, NW China

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A B S T R A C T

Baogutu is the first porphyry Cu–Mo–Au deposit discovered in Western Junggar, Xinjiang, NW China. The ore-bearing intrusion is a dioritic intrusive complex that includes stage 1 diorites and minor stage 2 diorite porphyries. The stage 1 diorites have produced concentric potassic and propylitic alteration zone and overprinted phyllic alteration and host much of the Cu–Mo–Au mineralization at Baogutu. The Baogutu porphyry Cu–Mo–Au deposit consists of unusually disseminated and minor vein-style mineralization. The fluid evolution occurred in stage 1 diorite from late magmatic stage to hydrothermal stage (stages 1B and 1C) is constructed based on alteration and fluid inclusion analysis by microthermometry, Raman Spectroscopy and Quadrupole Mass Spectrometer.

Five fluid types are distinguished and they are L1 (liquid-rich 2-phase), L2 (liquid-vapor 2-phase), V1 (vapor-rich 2-phase), V2 (mono-phase vapor), and H (multi-phase solid). The dominant inclusions rich in reductive CH4 plus H2O while minor inclusions rich in CH4 and CO2. The inclusions in quartz from the late magmatic stage contain the most brine inclusions and less other inclusions with CH4-rich and H2O-rich compositions. The inclusions in quartz from stage 1B contain all fluid types and have CH4-rich and CH4 + H2O compositions with rare CO2. The inclusions in quartz from stage 1C are characterized by more vapor inclusions without brine inclusions and a clear CO2 concentration in a few assemblages with CH4 + CO2 composition.

Using microthermometry, we estimate fluid trapping conditions at T~400 °C and P = 1500 to 3100 bar in late magmatic stage, T = 200 to 400 °C and P = 50 to 320 bar in disseminated quartz in stage 1B, T = 180 to 400 °C and P = 20 to 260 bar in vein quartz in stage 1B, and T = 170 to 400 °C and P = 20 to 230 bar in stage 1C. Such late magmatic conditions are compatible with the fluid evolution as a result of CH4-rich inclusions derived from mantle magma. Such hydrothermal conditions in stages 1B and 1C with small P-T fluctuations are compatible with the dominant disseminated mineralization at Baogutu that indicates a weak fracturing. The overall fluid path at Baogutu is toward lower pressure and small changed temperature, with composition transit of fluid from a high halite CH4-rich system to low halite CH4 + CO2 system. It may lead to the formation of this Cu–Mo–Au deposit.

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1. Introduction

The Central Asian Orogenic Belt (Altaids or Altaid collage, Xiao et al., 2009) lies between the Siberian and Russian cratons to the north, and Tarim and North China cratons to the south (Fig. 1a). The late Paleozoic tectonics of the Central Asian Orogenic Belt (CAOB) was characterized by continuous accretion along the southern active margin of Siberia and the northern active margin of the North China craton (Fig. 1a, Xiao et al., 2009, 2010). It led to the formation of the giant metal deposits (Fig. 1). The fifteen most important porphyry Cu (Mo–Au) deposits are distributed in the CAOB (Rui et al., 1984; Kudryavtsev, 1996; Rui et al., 2002; Qin et al., 2002; Nie et al., 2004; Cooke et al., 2004, 2005). They are Baogutu (in this study), Tuwu-yandong, Wunuhetushan, and Duobaoshan in China, Erdenet, Tsa-gaan-Suvarga, and Oyu Tolgoi in Mongolia, Boshekol, Samarsk, Kounrad, Aktogai, Borly, Sayak, and Koksai in Kazakhstan, and Kal'makyr in Uzbekistan (Fig. 1a). Most are porphyry Cu–Mo and Cu deposits exception for Oyu Tolgoi, Samarsk, and Kal'makyr which are porphyry Cu–Au deposits (Kudryavtsev, 1996; Zhukov et al., 1997; Heinhorst et al., 2000; Rui et al., 2002; Nie et al., 2004; Sillitoe, 2010).

Baogutu is the first porphyry Cu–Mo–Au deposit discovered in West Junggar, Xinjiang, China (Fig. 1b). Four diamond drill holes totaling 1200 m completed by the Institute of Geology and Geophysics, Chinese Academy of Sciences in 1985–1990, one of them encountered copper mineralization (>0.1% Cu) over a 30 m interval (Shen et al.,
Since 2002, 62 diamond drill holes totaling 34,000 m have been completed by the Institute of Geology, Xinjiang Geoexploration Bureau for Non-ferrous Metals, in Baogutu. Disseminated and vein-style mineralization was discovered at the Baogutu porphyry Cu–Mo–Au deposit (Zhang et al., 2005, 2006b). An evaluation in 2009 showed that Baogutu complex contained metal 6×10⁶ tonnes averaging 0.28% Cu, 1.8×10⁶ tonnes averaging 0.011% Mo, 14 tonnes averaging 0.1 ppm Au, and 390 tonnes averaging 1.8 ppm Ag (Zhang, unpublished data). Based on these data, Baogutu is Xinjiang’s second largest porphyry copper deposit, after Tuwu–Yandong located in Eastern Tianshan, NW China (Fig. 1a). It consists of unusually dominant dissemination (>80%) relative to most porphyry deposits.

Methane rich fluid inclusions have been widely reported in different types of metallic ore deposits and petroleum basins (e.g., Dubessy et al., 2001; Charlou et al., 2002; Hurai et al., 2002). Methane rich fluid inclusions also are reported in some rocks, such as the skarn near the giant REE–Nb–Fe deposit at Bayan Obo, Northern China (Fan et al., 2004) and the mafic–ultramafic intrusion in Cu–Ni sulfides deposit in Eastern Tianshan Mountain, NW China (Liu and Pan, 2006). However, methane rich fluid inclusions are typically not detected in most porphyry Cu deposits (Rusk and Reed, 2002). CO₂ has been identified in inclusions from most porphyry Cu deposits (e.g., Butte: Rusk and Reed, 2002; Bajo de la Alumbrera: Ulrich et al., 2002; Bingham: Redmond et al., 2004; Landtwing et al., 2005; and El Teniente: Klemm et al., 2007; Rusk et al., 2008; Landtwing et al., 2010). By contrast, fluid inclusions in quartz from Baogutu porphyry Cu–Mo–Au deposit trap methane rich fluids based on the analysis results of the Raman Spectroscopy and Quadrupole Mass Spectrometer. The presence of CH₄ in fluids from diorite at Baogutu is an interesting feature. In this paper, we attempt to elucidate the evolutionary history of methane rich fluids that is responsible for alteration and mineralization of the Baogutu porphyry Cu–Mo–Au system associated with intermediate intrusive rocks (e.g., diorite).

2. Regional geology

The Western Junggar terrain is located in the central section of the CAOB (Fig. 1a). It consists mainly of Palaeozoic island arc and back-arc basin rocks (Shen and Jin, 1993; Chen and Jahn, 2004; Xiao et al., 2008; Shen et al., 2009). They were accreted onto the Kazakhstan plate as the Tarim, Kazakhstan and Siberian plates converged (Chen and Jahn, 2004; Chen and Arakawa, 2005; Xiao et al., 2008). This geodynamic process led to the formation of volcanic-hosted and intrusion-related gold deposits (Shen and Jin, 1993; Shen et al., 1996, 2007, 2008) and porphyry copper deposits (Shen and Jin, 1993; Zhang et al., 2006a,b; Wang and Xu, 2006; Shen et al., 2008, 2009). They constitute the Hatu gold and the Baogutu copper belts, respectively. The two metallogenic belts are separated by the Darbut fault (Fig. 1b).

The Western Junggar terrain consists mainly of Lower Carboniferous volcanic rocks which are widespread throughout southeastern Western Junggar, particularly near the Darbut fault (Fig. 1b). Shen and Jin (1993) studied two Early Carboniferous volcanic belts (Anqi and Darbut volcanic belts) in the Western Junggar terrain which are separated by the Anqi fault (Fig. 1b). The volcanic rocks in the Anqi volcanic belt contain tholeiitic rocks which are inferred to reflect the magmatism under conditions of regional extension and back-arc basin (Shen and Jin, 1993). The volcanic rocks in the Darbut volcanic belt consist of tholeiitic and calc-alkaline assemblages, as well as felsic volcaniclastic sequences, indicating a transitional setting from back-arc basin to arc (Shen and Jin, 1993; Shen et al., 2009) or an immature arc setting.

Three Early Carboniferous stratigraphic units in Anqi and Darbut volcanic belts have been identified. From oldest to youngest, these are the Tailegula, Baogutu, and Xibeikulas Group (Shen and Jin, 1993). The Tailegula group consists of basaltic–andesitic flows and pillow lavas and felsic tuff with intercalations of silica rock. Pillow basalt and chert of the Tailegula group in the Anqi volcanic belt yielded Rb–Sr ages of 328 ± 31 Ma (Shen et al., 1993; Li and Chen, 2004) and 323 ± 22 Ma (Li and Chen, 2004), respectively. The felsic tuff of the Tailegula group has a U–Pb zircon LA-ICP-MS age of 357.5 ± 5.4 Ma (Guo et al., 2010). Gold mineralization is stratabound within the Tailegula group and defines the Hatu gold metallogenic belt in the northern part of the Darbut fault (Fig. 1b). The Baogutu group includes volcaniclastic siltstone and sandstone, as well as lithic–vitric felsic tuff with intercalations of pebbly graywacke and the lens of limestone, marl and bioclastic limestone. The felsic tuff of the Baogutu group in the Darbut volcanic belt have a U–Pb zircon SHRIMP age of 328.1 ± 1.8 Ma (Wang and Zhu, 2007) and a U–Pb zircon LA-ICP-MS age of 323.1 ± 3.0 Ma (Guo et al., 2010). The Xibeikulas group consists of graywacke with graded bedding, volcaniclastic siltstone and mudstone with formed bedding.

These Early Carboniferous sequences are intruded by ore-bearing diorite stocks at about ∼325 Ma (Fig. 2; Tang et al., 2009; Shen, unpublished data) and barren granite batholiths at ∼300 Ma (Chen and Jahn, 2004; Wang et al., 2004; Su et al., 2006; Han et al., 2006; Wang and Xu, 2006). The diorite stocks and its adjacent wall rocks are spatially and temporally related to copper mineralization, and define the Baogutu metallogenic belt in the southern part of the Darbut fault (Fig. 1b). Shen et al. (2009) used whole rock geochemical analyses to confirm that the intrusions are diorites and quartz diorites with a transitional character from tholeite to calc-alkaline. Mantle-normalized trace element patterns depict three types including distinctly fractionated REE pattern, enriched LREE and large ion lithophile elements (LILE) pattern, and little enrichment of LREE and LILE pattern. We therefore further suggest that the ore-bearing diorite stocks still formed in a Darbut immature arc or initial arc.

The regional structure is characterized by faults that display dominant northeast trends including the Darbut, Anqi, and Hatu faults, although NS- and WE-trending structures are also present (Fig. 1b). Of these, the Darbut fault is the most important because it was the locus of intense magmatism and associated mineralization. The main structures in the south of the Darbut fault are a series of approximately N-trending faults and folds which are almost orthogonal to those to the north of the Darbut fault (Fig. 1b). The Xibeikulas syncline is dominant structure which is traversed by several major N- and NE-striking faults (Fig. 2). The Xibeikulas syncline consists of Xibeikulas Group in core and Baogutu Group and Tailegula Group in two limbs. The ore-bearing diorite stocks intruded the core and two limbs of the Xibeikulas syncline (Fig. 2).

3. Local geology

3.1. Host wall-rocks

The local geology comprises Early Carboniferous volcaniclastic, sediment, and volcanic rocks belonging to the Baogutu Group and Xibeikulas Group (Fig. 3). The Baogutu group, which is dominant host wall-rocks around the mineralized complex, is composed of volcaniclastic and volcanic rocks. They contain the dominant felsitic lithic–vitrif tuff, silty tuff and volcaniclastic siltstone and minor andesite. The disseminated and vein mineralization occurred mainly in the volcaniclastic siltstone, silty tuff and lithic–vitrific tuff. The barren Xibeikulas group, occurs in the western part of the mineralized complex, consists of greywacke, tuffaceous mudstone and tuffaceous siltstone.

3.2. Intermediate complex

The mineralized complex intruded the eastern limb of the Xibeikulas syncline into the Lower Carboniferous Baogutu and Xibeikulas Groups and occupies localized dilatant sites which provided
by a structural intersection of the N- and ENE-trending faults (Figs. 2 and 3).

The host rocks at Baogutu have been described in different ways by previous workers, mainly as granodiorite and quartz diorite (Shen and Jin, 1993) or granodiorite porphyries (Zhang et al., 2005, 2006b; Cheng and Zhang, 2006; Zhang et al., 2006a; Song et al., 2007) respectively. We have identified the ore-bearing intrusion as a dioritic intrusive complex that includes equigranular diorite, weakly porphyritic diorite, and diorite porphyry, with rare granodiorite (Table 1). Two intrusive phases recognized by us at Baogutu based on the cross-cutting relationships are the main-stage (stage 1) equigranular to weakly porphyritic diorites and minor late-stage (stage 2) diorite porphyries. Moreover, two breccias variants (mineralized hydrothermal breccias and very weak mineralized matrix-rich breccias) have been also identified. Alteration and mineralization were closely related to the main-stage diorites. Spatial relationships between the discrete intrusive phases are shown in Figs. 3 and 4.

3.3. Ore bodies

The orebodies define an area that is 1100 m × 800 m and extend for more than 800 m downwards. They are hosted in the diorite complex and adjacent wall rocks based on the 62 drill holes (Figs. 3 and 4). The orebodies are covered by Quaternary overburden. The 0.2% Cu contour defines a wedge-shaped zone approximately 800 m wide and more than 700 m deep in a cross-sectional view (Fig. 4). Mineralization is more strongly developed in the northern and eastern parts of the complex, and Cu and Mo grades gradually increase with increasing depth. Highest-grade zones (>0.4% Cu or >0.03% Mo) occur at depths of 300–700 m depth below the surface at the northwestern and eastern parts of the complex associated with higher fracture intensities and/or intensively developed hydrothermal breccias (e.g., Fig. 4). The orebody dips northeast at an angle of about 45 to 55° implying that significant tilting may have occurred after ore formation, given that porphyry deposits typically have sub-vertically oriented ore shells (e.g., Hedenquist et al., 1998; Wilson et al., 2003).

The mineralized complex well-develops the disseminated, minor vein-style Cu-Mo-Au mineralization. Cu–Au mineralization is localized in the main parts of the complex and at its contact with the adjacent wall rocks. Au mineralization, which gold grades range from 0.03 to 0.4 g/t Au with average 0.1 g/t, is by-product. Economic Mo mineralization (common >0.01% with minor >0.06%) has been detected at depth in the complex. The Baogutu ore-bearing complex could have the Cu–Mo–Au assemblage.

3.4. Ages of ores and their host porphyries

The ages of the ores and their porphyries at Baogutu are determined. The molybdenite from two veins of the Baogutu complex have been dated by the Re–Os method, yielded age of 310.1±3.6 Ma and 310.4±3.6 Ma (Song et al., 2007). Main-stage quartz diorite in the Baogutu complex yielded Rb–Sr ages of 322±30 Ma (Shen et al., 1993). We obtained a U–Pb zircon SHRIMP age of 325.1±4.2 Ma (Shen, unpublished data). Late-stage diorite porphyry of the Baogutu complex yielded U–Pb zircon LA-ICP-MS age of 309.9±1.9 Ma (Tang et al., 2009). These data indicate that the Baogutu complex range in age from 325 to 309 Ma and the molybdenites ores 310 Ma.
4. Materials and methods

4.1. Sample selection

Selected sample originates from 3 diamond drill holes (Fig. 3) within the hypogene alteration zones (phylllic and potassic) in the stage 1 diorites. Fluid inclusions were studied in quartz crystals from stage 1 diorites and different vein stages, corresponding to the spatial and temporal evolution of the magmatic–hydrothermal system at Baogutu; the evolution was determined from geologic relationships and petrographic investigation of successive quartz generations.

About 100 core samples containing stage 1 diorites and various vein types from various depths were collected for laboratory analyses. Over 70 samples were observed for inclusion type, abundance, spatial distribution, and size. Approximately 30 of these samples were further analyzed by microthermometry. Over 800 inclusions were

<table>
<thead>
<tr>
<th>Intrusion history</th>
<th>Intrusion composition</th>
<th>Location</th>
<th>Texture</th>
<th>Mineralogy assemblage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main stage (stage 1)</td>
<td>Equigranular diorite Weakly porphyritic diorite Hydrothermally-cemented breccias</td>
<td>Center and depth of the complex Expos to the outer of the equigranular diorite Center and bottom of the complex</td>
<td>Equigranular hypidiomorphic, fine- to medium-grained (1–3 mm) Weak porphyritic texture, 20–30% phenocryst (0.5–3 mm), and coarse groundmass (0.05–0.5 mm) 50–60% clasts up to 3–5 cm wide with hydrothermal minerals cement</td>
<td>Plagioclase (30–40%), hornblende (15–20%), biotite (10–15%), pyroxene (&lt;5%), and quartz (&lt;5–10%) Plagioclase (30–40%), hornblende (15–20%), biotite (10–15%), and quartz (5–15%) Contain complex and wall-rock clasts, with hydrothermal minerals cement without matrix; breccias can be well mineralized Plagioclase, hornblende, and biotite phenocrysts in quartz (5–15%) plagioclase, and hornblende groundmass</td>
</tr>
<tr>
<td>Late stage (stage 2)</td>
<td>Diorite porphyry</td>
<td>Distributes around the porphyritic-like diorite</td>
<td>Porphyritic, 10–20% phenocrysts (2–3 mm) and microcrystalline (&lt;0.01 mm) and (0.02–0.05 mm) groundmass</td>
<td>As above hydrothermal breccias, but rich in matrix and lack the hydrothermal minerals cement with weak mineralization</td>
</tr>
<tr>
<td>Matrix-rich breccias</td>
<td>Center and bottom of the complex</td>
<td>Composed of 70–80% clasts and matrix with minor hydrothermal minerals cement</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Summary description of the intrusion sequence and rock types of the Baogutu complex.
analyzed by microthermometry. The inclusions range from less than 3 to ∼8 μm in diameter, with the vast majority of inclusions being less than 6 μm. Most inclusions analyzed by microthermometry were between 4 and 6 μm in diameter. All analysis is carried out at the Institute of Geology and Geophysics, Chinese Academy of Sciences.

4.2. Methods

4.2.1. Microthermometry

The microthermometric study of fluid inclusions was carried out with a Leitz microscope and a Linkam THMS 600 programmable heating-freezing stage (e.g. Shepherd et al., 1985; Lu et al., 2004). The precision of temperature measurements on cooling runs is about ±0.1 °C. On heating runs, the precision is ±2 °C. Ice-melting temperatures were observed at a heating rate of no more than 0.1 °C/s. Homogenization temperatures were observed at a heating rate of 1 °C/s. Homogenization of halite-bearing inclusions was obtained on a heating cycles of about 5 °C.

4.2.2. Raman spectroscopy

In order to confirm the suggested fluid inclusion volatile species, representative samples were analyzed using a Renishaw 1000 Raman microspectrometer according to the method of Burke (2001). With this technique, inclusions are homogenized in a heating stage mounted on a microscope attached to a Renishaw 1000 Raman microprobe. The laser beam with a wavelength of 514.5 nm and a spot size of about 1 μm, was focused on the bubble for each fluid inclusion through a light microscope. The Raman peaks of the CH4 and H2O are 2914–2916 cm⁻¹ and 3500 cm⁻¹, respectively. The Raman peaks of the CO2 are about 1281 and 1386 cm⁻¹ in this study.

4.2.3. Quadrupole mass spectrometer

In order to further determine gaseous composition of fluid inclusions and contents, four samples were analyzed using a Prisma TM QMS200 Quadrupole Mass Spectrometer according to the method of Zhu and Wang (2000). The dried washed sample weighing 50 mg was put in a clean quartz tube, and heated to 100°C. Then, valve was turned on and the gas pipe was vacuumed. When the pressure in the quartz tube was less than 6×10⁻⁶ Pa, the burst stove was heated to 550°C at the speed of 1 °C/3 s. The vacuum valve was turned on for determination of gaseous composition.

5. Alteration and veins

5.1. Alteration zonation and alteration stages

We carried out alteration mapping and document the alteration characteristics of the study Baogutu complex. The intrusive complex
has been subjected to intense hydrothermal alteration, especially within and adjacent to the ore-bearing intrusion (Fig. 5). Based on observations from outcrops (Fig. 3) and 10 drill holes (Fig. 4), detailed examination of alteration overprinting relationships was carried out on 766 polished thin sections using transmitted and reflected light microscopy. Figs. 5 and 6 show the distribution of alteration minerals in detail plan and across an east–west vertical cross section at the Baogutu deposit, respectively. We divided the alteration into two stages and five sub-stages at Baogutu and identified disseminations and/or vein generations within each of the paragenetic stages (Table 2). The alteration and mineralization occurred in the stage 1 diorites are emphasized only here.

Within the stage 1 diorites overprinted by the hydrothermal breccias, Ca–Na silicate alteration assemblage (stage 1A), potassic alteration assemblage (stage 1B) and phyllic alteration assemblage (stage 1C) have been recognized; the Ca–Na silicate alteration zone was not clearly outlined; the potassic zone have been subdivided into the inner potassic subzone in the complex (a range of 1200 m×1400 m) and outer potassic subzone in the wall rocks (100 m to 500 m in width); the phyllic zone (700 to 1000 m in area) overprinted in the potassic zone rather than the concentric ring around the potassic zone as mapped previously (Cheng and Zhang, 2006; Zhang et al., 2006b). Cu and Mo sulfides are associated spatially and temporally with potassic and phyllic assemblages. The distal propylitic and early inner Ca–Na silicate alteration assemblages lack significant sulfides. Within the stage 2 diorite porphyries, pervasive potassic alteration (stage 2A) occurred in the groundmass of porphyries with mineralization. The matrix-rich breccias (stage 2B) have weak alteration in cement with very weak mineralization (Table 2).

5.2. Quartz generations and vein sequences

5.2.1. Quartz in late magmatic stage

Constraints on the spatial and temporal evolution of the magmatic–hydrothermal system at Baogutu were based on the geologic constraints of quartz-bearing samples, both late magmatic and hydrothermal. The earliest fluids in the magmatic–hydrothermal system are preserved in interstitial quartz (I-quartz) hosted in the diorites (Fig. 7a). Most of these quartzes have anhedral forms due to latest growth within the crystallizing magma. Commonly, they show no evidence for recrystallization. Therefore, they are thought to represent the late magmatic stage of the magmatic–hydrothermal system.

5.2.2. Quartz in hydrothermal stage 1B

Hydrothermal processes in the Baogutu were deduced largely from the distribution of the different hydrothermal quartz in diorites and veins. The earliest quartz type, the disseminated quartz (D-quartz), is represented by anhedral granular quartz with variable amounts of biotite, magnetite, chlorite, and rutile (Fig. 7b). As a result of the hydrothermal metasomatism, D-quartzes occur in the potassic diorites and wall-rocks of the Baogutu Group, in close proximity to the intrusive rocks. Petrographically later quartz type, the hydrothermally cemented quartz (H-quartz), is subhedral granular quartz with variable amounts of biotite and magnetite (Fig. 7c). The H-quartz (now matrix) occurs in the mineralized hydrothermal breccias (Fig. 8b) which located in the centre and deepest parts of Baogutu complex (Fig. 4) and is associated with potassic alteration.

The stage 1B corresponds to local quartz veinlets or veins without a distinct alteration halo. The vein type includes the early quartz–chalcopyrite–pyrite–biotite ± pyrrhotite veinlets (B1-veinlets, Fig. 8c),
Table 2
Major characteristics of alteration and veins in the Baogutu complex (in relative age sequence, oldest at top).

<table>
<thead>
<tr>
<th>Stage</th>
<th>Alteration type</th>
<th>Alteration assemblage</th>
<th>Mineralization type</th>
<th>Vein type</th>
<th>Vein distribution</th>
<th>Texture</th>
<th>Vein thickness</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Ca–Na silicate alteration</td>
<td>Act–Qtz–Mt ± Ep</td>
<td>Intense disseminated</td>
<td>D-quartz</td>
<td>Abundant in diorites</td>
<td>Disseminated</td>
<td>Not used</td>
<td></td>
</tr>
<tr>
<td>1B</td>
<td>Potassic alteration</td>
<td>Bio–Qtz–Mt ± Rut ± Chl in diorites; Bio–Qtz–Mt–Ksp–Apa in wall rocks</td>
<td>Moderate breccias overprint with Qtz–Bio–Cp–Py assemblage</td>
<td>B1-veinlets</td>
<td>Moderately abundant in diorites</td>
<td>Veins with irregular parallel walls</td>
<td>5 mm</td>
<td>Used</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bio–Qtz–Mt ± Rut ± Cal</td>
<td>Qtz–Cp–Py veins</td>
<td>B3-veins</td>
<td>Moderately abundant in diorites and wall rocks</td>
<td>Veins with wavy walls</td>
<td>1–2 cm</td>
<td>Used</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bio–Qtz–Mt ± Rut ± Cal</td>
<td>Barren Bio–Qtz veins</td>
<td>B4-veinlets</td>
<td>Common in diorites and wall rocks</td>
<td>Veins with wavy walls</td>
<td>1–2 cm</td>
<td>Used</td>
</tr>
<tr>
<td>1C</td>
<td>Phyllic alteration</td>
<td>Ser–Qtz–Py ± Chl ± Cal</td>
<td>Qtz–Mo–Cp veins with phyllic alteration envelopes</td>
<td>C1-veins</td>
<td>In diorites</td>
<td>Veins with wavy walls</td>
<td>1–2 cm</td>
<td>Used</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ser–Qtz–Py ± Chl ± Cal</td>
<td>Qtz–Cp–Py veins with phyllic alteration envelopes</td>
<td>C2-veins</td>
<td>In diorites</td>
<td>Veins with wavy walls</td>
<td>&lt;1 cm</td>
<td>Used</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ser–Qtz–Py ± Chl ± Cal</td>
<td>Pyr–(Qtz–Cal) veins</td>
<td>C3-veins</td>
<td>In diorites</td>
<td>Veins with wavy walls</td>
<td>&lt;1 cm</td>
<td>Not used</td>
</tr>
<tr>
<td>2A</td>
<td>Potassic alteration</td>
<td>Bio–Qtz–Mt</td>
<td>Gpy–(Qtz–Cal) veins</td>
<td>C4-veinlets</td>
<td>In stage 1 diorites</td>
<td>Veins with regular walls</td>
<td>&lt;1 cm</td>
<td>Not used</td>
</tr>
<tr>
<td>2B</td>
<td>Potassic alteration</td>
<td>Gyp–Qtz–Cal–Bio</td>
<td>Weak breccias overprint with Gyp–Qtz–Cal–Bio–Cp–Py assemblage</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
</tr>
</tbody>
</table>

Mineral abbreviations: act = actinolite, alb = albite, ap = apatite, bio = biotite, bn = bornite, cal = calcite, cc = chalcocite, chl = chlorite, cp = chalcopyrite, ep = epidote, gyp = gypsum, ksp = K-feldspar, mo = molybdenite, mt = magnetite, prl = pyrophyllite, pyrhottite = pyr, py = pyrite, qtz = quartz, rut = rutile, sl = sphalerite, ser = sericite.
quartz–chalcopyrite–pyrite–molybdenite–biotite veinlets (B2-veinlets), and the late quartz–chalcopyrite ± pyrite veins (B3-veins, Fig. 8d). They are similar to A-type veins occurred in porphyry deposits (Sillitoe, 2010). Of these, B1-veinlets are predominant. B1- and B2-veinlets (<1 cm width) are filled with subhedral quartz, anhedral biotite, chalcopyrite, pyrite and pyrrhotite. Subhedral quartz is the predominant gangue mineral and contains abundant fluid inclusions. The internal symmetry or open vugs (Fig. 7d) and the irregular walls suggest that they formed in the brittle rocks. They occur throughout the inner potassic alteration subzone and also extend into the adjacent volcanic–sedimentary wall rocks of the Baogutu Group. B3-veins are planar and continuous veins. The veins are more than 5 cm wide and cut the wall rocks of the Baogutu Group.

5.2.3. Quartz in hydrothermal stage 1C
The late vein type includes C1-veins, C2-, C3- and C4-veinlets. C1-veins have a quartz–molybdenite–chalcopyrite–pyrite assemblage, and are similar to the B-type veins occurred in porphyry deposits (Sillitoe, 2010). C1-veins are typically thick (1–5 cm), molybdenite-rich, and have been observed within diorites (Fig. 8e). Vein walls are parallel and slightly wavy. C2-veinlets have a quartz–chalcopyrite–pyrite–biotite ± pyrrhotite assemblage with obvious phyllic alteration halos (including quartz and sericite) from 1 mm to 2 cm thick and formed within diorites as well as in the adjacent wall rocks (Fig. 8f, g). C2-veins are the same as the D-type veins occurred in porphyry deposits (Sillitoe, 2010). C3-veinlets are characterized by a pyrrhotite–calcite ± quartz assemblage (Fig. 8h) and vary from <3 mm to 1 cm wide and occur only within the strong sericite alteration domains. The latest C4-veinlets have a gypsum–calcite ± quartz assemblage (Fig. 8g) and vary from 1 to 5 mm wide and cut the phyllic zone and related veins. Quartz in stage 1C is mostly granular and oriented perpendicular to the vein walls, suggesting that veins formed in the brittle rocks. Quartz veins in stage 1C cut the potassic zone and related veins which indicate that they generally postdate veins in stage 1B.

6. Fluid inclusion petrography and microthermometry

6.1. Fluid inclusion types
The classification of fluid inclusion types observed in this study is primarily based on phase proportions at room temperature. All descriptions strictly refer to fluid inclusion assemblages (Wilkinson, 2001). Samples examined for fluid inclusion study are representative of the different quartz stages described above and include I-quartz, D-quartz, H-quartz, vein quartz (B1-veinlets, B2-veinlets, B3-veins, C1-veins, C2-veins). Five fluid types are distinguished in this study based on petrographic and microthermometric criteria. They are L1 (liquid-rich 2-phase), L2 (liquid-vapor 2-phase), V1 (vapor-rich 2-phase), V2 (mono-phase vapor), and H (multi-phase solid). The fluid inclusion types distinguished in this study are presented in Table 3 and shown in Fig. 9.

Fig. 7. Photomicrographs showing the features of the different quartzs from Baogutu Cu–Mo–Au deposit. (a) I-quartz (interstitial quartz) hosted in weakly porphyritic biotite diorite in late magmatic stage; (b) D-quartz (disseminated quartz) in biotite diorite in stage 1B; (c) H-quartz (hydrothermally cemented quartz) occurred in matrix of the hydrothermal breccias in stage 1B; (d) B1-veinlets in stage 1B with internal symmetry. All photomicrographs were taken under cross polarized light exception for (b). Abbreviations: Pl: plagioclase; P-Bio: primary biotite; S-Bio: secondary biotite; Mt: magnetite; Ser-: sericite; Q: quartz.

Fig. 8. Photographs of mineralization from Baogutu Cu–Mo–Au deposit. (a) Intensive disseminated ore in stage 1B, medium-grained diorite with disseminated hydrothermal biotite, chalcopyrite and magnetite, note the abundant of chalcopyrite and magnetite; (b) breccia ore in stage 1B; (c) veinlet ore in stage 1B, quartz–chalcopyrite–pyrite veinlets overprinted in the disseminated mineralization in diorite; (d) vein ore in stage 1B, quartz–chalcopyrite–pyrite veins in diorite; (e) vein ore in stage 1C, quartz–molybdenite–chalcopyrite veins with phyllic alteration halos; (f) vein ore in stage 1C, quartz–chalcopyrite–pyrite veinlets with phyllic alteration halos occurred in possitic alteration zone; (g) vein ore in stage 1C, diorite porphyry with abundant quartz–chalcopyrite–pyrite veinlets; (h) vein ore in stage 1C, pyrrhotite–calcite ± quartz veinlets is cut by and gypsum–calcite ± quartz veinlets. Abbreviations: Q: quartz; Cp: chalcopyrite; Py: pyrite; Mo: molybdenite; Pyr: pyrrhotite; Gyp: gypsum.
<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Drill hole no.</th>
<th>No.</th>
<th>Depth (m)</th>
<th>Host quartz (stage)</th>
<th>Alteration zone</th>
<th>Fl type</th>
<th>Th (°C)</th>
<th>Tm (ice) or Ts (halite) (°C)</th>
<th>Salinity (wt.% NaCl equiv)</th>
<th>P (bars)</th>
<th>Basis for P estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZK102-528</td>
<td>ZK102</td>
<td>528</td>
<td>284</td>
<td>I-quartz (late magmatic)</td>
<td>Diorite</td>
<td>H</td>
<td>265-281 (23)</td>
<td>400-530 (13)</td>
<td>47.4-63.9</td>
<td>1542-3128</td>
<td>Halite disappearance</td>
</tr>
<tr>
<td>ZK102-530</td>
<td>ZK102</td>
<td>530</td>
<td>284</td>
<td>I-quartz (late magmatic)</td>
<td>Diorite</td>
<td>H</td>
<td>209-284 (15)</td>
<td>420-482 (15)</td>
<td>47.4-57.1</td>
<td>1565-3103</td>
<td>Halite disappearance</td>
</tr>
<tr>
<td>ZK203-260</td>
<td>ZK203</td>
<td>260</td>
<td>310</td>
<td>D-quartz (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>309-310 (2)</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZK211-783</td>
<td>ZK211</td>
<td>783</td>
<td>310</td>
<td>D-quartz (stage IB)</td>
<td>Potassic</td>
<td>L1</td>
<td>279-282 (9)</td>
<td>345-395 (9)</td>
<td>41.5-46.4</td>
<td>99-1020</td>
<td>Halite disappearance</td>
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<tr>
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<td>330</td>
<td>310</td>
<td>D-quartz (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>271-399 (19)</td>
<td>-2.2---5.4 (8)</td>
<td>3.71-8.41</td>
<td>54-160</td>
<td>LV curve</td>
</tr>
<tr>
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<td>245</td>
<td>310</td>
<td>D-quartz (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>375-358 (2)</td>
<td>-0.9---10.9 (6)</td>
<td>1.57-14.87</td>
<td>63-194</td>
<td>LV curve</td>
</tr>
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<td>ZK211</td>
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<td>310</td>
<td>B1-veinlets (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>201-348 (13)</td>
<td>-2.8---4.0 (3)</td>
<td>4.6-6.45</td>
<td>72-112</td>
<td>LV curve</td>
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<td>Potassic</td>
<td>L1</td>
<td>324-336 (2)</td>
<td>-3.7 (1)</td>
<td>3.06</td>
<td>6.01</td>
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<td>B1-veinlets (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>205-355 (23)</td>
<td>-1.8---11 (11)</td>
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<td>310</td>
<td>B1-veinlets (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>310-300 (10)</td>
<td>-0.8---4.1 (8)</td>
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<td>LV curve</td>
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<td>1</td>
<td>310</td>
<td>B2-veinlets (stage IB)</td>
<td>Potassic</td>
<td>L1</td>
<td>201-269 (3)</td>
<td>-1.2---9.3 (2)</td>
<td>20-13.8</td>
<td>41--129</td>
<td>LV curve</td>
</tr>
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<td>ZK211-373</td>
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<td>373</td>
<td>310</td>
<td>B2-veinlets (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>302-381 (19)</td>
<td>-6.1---13.6 (7)</td>
<td>0.9-14.3</td>
<td>77-127</td>
<td>LV curve</td>
</tr>
<tr>
<td>ZK102-530</td>
<td>ZK102</td>
<td>530</td>
<td>284</td>
<td>B2-veinlets (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>234-261 (3)</td>
<td>344-550 (3)</td>
<td>41.45-66.75</td>
<td>593-612</td>
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<tr>
<td>ZK211-527</td>
<td>ZK211</td>
<td>527</td>
<td>310</td>
<td>B3-veins (stage IB)</td>
<td>Potassic</td>
<td>H</td>
<td>178-194 (13)</td>
<td>-5---9 (9)</td>
<td>7.9-12.8</td>
<td>20-52</td>
<td>LV curve</td>
</tr>
<tr>
<td>ZK211-209</td>
<td>ZK211</td>
<td>209</td>
<td>310</td>
<td>B3-vein (stage IB)</td>
<td>Potassic</td>
<td>L2</td>
<td>221-309 (27)</td>
<td>-5---9 (9)</td>
<td>7.9-12.8</td>
<td>20-52</td>
<td>LV curve</td>
</tr>
<tr>
<td>ZK102-272</td>
<td>ZK102</td>
<td>272</td>
<td>310</td>
<td>C2-veinlet (stage IB+IC)</td>
<td>Phyllic</td>
<td>V1</td>
<td>210-460 (16)</td>
<td>-2.1---21.1 (7)</td>
<td>2.7-23</td>
<td>18-237</td>
<td>LV curve</td>
</tr>
</tbody>
</table>
H inclusion is halite saturated at room temperature, generally has negative crystal shapes, and is typically between 4 and 6 μm in size. It contains liquid plus solid phases plus 10 to 20 vol.% vapor at room temperature (Fig. 9a). In contrast to most porphyry Cu deposits (e.g., Alumbrera, Bingham, Santa Rita, Red Mountain); most H inclusions at Baogutu contain no other daughter minerals in addition to halite, minor H inclusions contain several solid phases (e.g. halite, sylvite, opaque). Halite crystals are larger than the other solids and can be readily distinguished by their cubic shape. Sylvite (when present) is smaller and divided into two groups: L1 and L2. The L1 inclusions have a small vapor bubble of 10 to 20% inclusion volume. The L2 inclusions have a large vapor bubble that occupies about 30% of the inclusion volume. No daughter crystals and CO₂ were observed. They are scattered in individually quartz grains (Fig. 9b–f).

Aqueous inclusions contain liquid and <30–40 vol.% vapor and lacks halite daughter minerals at room temperature (Fig. 9b–f). They occur as negative crystal shape, rounded or irregular shaped inclusions and divided into two groups: L1 and L2. The L1 inclusions have a small vapor bubble of 10 to 20% inclusion volume. The L2 inclusions have a large vapor bubble that occupies about 30–40% of the inclusion volume. No daughter crystals and CO₂ were observed. Aqueous inclusions are generally widespread in veins and range in size from around 3 up to 8 μm. There is a continuous gradient in bubble size between L1 and L2 inclusions; therefore, distinguishing between L1 and L2 inclusions at room temperature is sometimes difficult. They are scattered or occur along secondary or pseudosecondary trails.

### 6.2. Fluid inclusion microthermometry

We observe that most inclusions are randomly scattered and minor are aligned along cross-cutting healed micro-fractures at Baogutu. It differs from the individual quartz crystals and vein sections with continuous growth zonation and no significant crack filling or dissolution discontinuities at the El Teniente porphyry Cu–Mo deposit, Chile (Klemm et al., 2007). It also differs from typical vein reactivation textures documented at Butte, Montana (Rusk and Reed, 2002), Bingham, Utah (Redmond et al., 2004; Landtwing et al., 2005), Copper Canyon, Nevada (Nash, 1976), Bajo de la Alumbrera, and Argentina (Ulrich et al., 2001). Careful attention was required during sampling to distinguish between potassic alteration features and the later alteration overprint and veins occurred in stages 1B and 1C in order to identify the superimposition of some generations of inclusions in samples. Our descriptions of potassic assemblages and related veins rely heavily on petrographic specimens determined to have undergone only limited later alteration. Based on these, some inclusions which are relatively large (>4 μm) and preferably polygonal-shaped scattered in late magmatic–hydrothermal stage at Baogutu are measured in this study (Table 3).

Two common thermometric procedures, freezing and heating, were employed to determine the approximate salinity (wt.% NaCl equivalent) and homogenization temperature (Th), respectively. Freezing was carried out mainly for non-halite-bearing liquid-rich inclusions, and the temperature of the melting point of ice was recorded. The collected data were converted into corresponding salinity values by using diagrams for NaCl-H₂O system (Shepherd et al., 1985). The heating stage was used for all types of inclusion. For non-halite bearing inclusions the homogenization temperature of liquid and vapor (predominant L+V→L and rare L+V→V) was recorded. In the halite-bearing inclusions, two points: (1) Th (temperature of vapor and liquid homogenization) and (2) Ts (NaCl) (the temperature at which halite dissolves) were recorded. The solid phase is predominantly halite, occasionally accompanied by sylvite; therefore, almost all inclusions measured are halite-bearing inclusions and Ts (KCI) (the temperature at which sylvite dissolves) was not recorded. The only Ts (NaCl) values were converted into wt.% NaCl by using phase diagrams of binary system NaCl–H₂O (Shepherd et al., 1985). The unidentified opaque minerals seldom form more than 1% of the volume of an inclusion and therefore, do not significantly affect its homogenization temperature. In the case of V2 inclusions, the final melting temperature of ice was difficult to determine, because of the high vapor/liquid ratios.

#### 6.2.1. L-quartz in late magmatic stage

Fluid inclusions in the interstitial quartz occurred in the diorites contains the predominant halite saturated inclusions and minor vapor inclusions. They are thought to represent the late magmatic stage of the magmatic–hydrothermal system. All hyper-saline fluid inclusions are homogenized by halite dissolution. Final homogenization temperatures by halite dissolution ranged from 401° to 550 °C (Fig. 10a, Table 3). Salinities calculated from these halite dissolution temperatures range between 47 and 65 wt.% NaCl equiv (Fig. 10a).

#### 6.2.2. D-quartz in stage 1B

Fluid inclusions in the disseminated quartz occurred in the potassic zone homogenize mainly between 200° and 400 °C (Fig. 10b, Table 3). The hyper-saline fluid inclusions are homogenized by halite dissolution.
Final homogenization temperatures by halite dissolution ranged from 315° to 440 °C. Salinities calculated from these halite dissolution temperatures range between 39 and 46wt.% NaCl equiv (Fig. 10b). Aqueous inclusions have a salinity mainly range of 3.7 to 9.7wt.% NaCl equiv and homogenize from 200° to 390 °C. Minor vapor inclusions have the high apparent homogenization temperatures (395° to 442 °C) to aqueous inclusions (Table 3).

6.2.3. Vein quartz in stage 1B

Fluid inclusions in quartz occurred in B1-, B2-veinlets and B3-veins have similar characterization (Fig. 10c). They are characterized by dominant L2 inclusions and abundant V1, L1 inclusions. V2 inclusion is rare. L1 inclusion homogenize between 180° and 310 °C, with one discrete population occurring between 200° to 240 °C. L2 inclusions have the high apparent homogenization temperatures (220° to 380 °C). The temperature of homogenization of V1 and V2 fluid inclusions varies from 270° to 390 °C. Salinities of L1 and L2 inclusions range from 1.7 to 23wt.% NaCl equiv (Fig. 10d). Salinities of V1 inclusions vary from 3.7 to 12.08 wt.% NaCl equiv.

In summary, fluid inclusions in vein quartz form stage 1B homogenize between 180 °C and 420 °C, with a bimodal distribution of 180 °C to 260 °C and 260° to 420 °C. It indicates that the ore-forming fluids at Baogutu could have two different sources (magmatic fluid with an influx of a low-salinity fluid of external origin).

6.2.4. Vein quartz in stage 1C

Fluid inclusions in quartz gangue occurred in C1- and C2-veins have similar characterizations. Veins are characterized by L2, V1 and V2 inclusions. L1 inclusion homogenize between 170° and 270 °C (Table 3, Fig. 10d). L2 inclusion homogenize between 170° and 390 °C (Table 3), with 85% of fluid inclusions homogenizing at temperatures 210–330 °C. V1 inclusions have the high apparent homogenization temperatures (180° to 460 °C) and concentrated in between 250° and 390 °C (Fig. 10d; Table 3). The temperature of homogenization of V2 fluid inclusions (>320 °C) overlaps the homogenization temperatures of coexisting V1 fluid inclusions (Table 3). Salinities of the L1 overlap the salinities of coexisting V fluid inclusions and range from 1.3 to 23wt.% NaCl equiv (Fig. 10d).

6.3. Results of Raman spectroscopy

In contrast to most porphyry Cu deposits (Butte, Alumbrera, Bingham, Santa Rita, Red Mountain), at Baogutu, clathrate formation was not observed in any of the inclusions assemblages. Raman spectroscopy is used in this study in order to detected gaseous composition of fluid inclusions. The results of more than 70 individual fluid inclusions from one assemblage (I-quartz) formed in late magmatic stage and three assemblages (D-quartz, B- and C-vein quartzes) formed in hydrothermal stage are plotted in Fig. 11. I-quartz...
fluid inclusions include H₂O-rich (Fig. 11a) and CH₄-rich with micro-
CO₂ (Fig. 11b). So, fluids brought from late magmatic stage by
the quartz in diorite are CH₄–H₂O type. D-quartz fluid inclusions in
stage 1B include H₂O-rich (Fig. 11c), CH₄-rich (Fig. 11d), CH₄ + H₂O
(Fig. 11e), and H₂O + CH₄ (Fig. 11f) with notable absence of CO₂.
Vein-quartz fluid inclusions in stage 1B have similar gaseous com-
position which include CH₄ + H₂O (Fig. 11g) and CH₄-rich (Fig. 11h),
without CO₂. Vein-quartz fluid inclusions in stage 1C are characterized
by CH₄ + H₂O (Fig. 11i) and CH₄ + CO₂ (Fig. 11j). CO₂ with a similar
abundance as CH₄ is detected only in a few analyses.

In summary, fluids carried by these quartzes in late magmatic stage
and hydrothermal stage 1B are rich in reductive gaseous species CH₄
and H₂O, with absence of CO₂; while fluids carried by these quartzes
in hydrothermal stage 1C are rich in CH₄ and H₂O plus minor CO₂.

6.4. Results of quadrupole mass spectrometer

In order to further determine gaseous composition and their
content of fluid inclusions, Quadrupole Mass Spectrometer is used in
this study. The analytical results for four respective samples formed
during from stage 1B to stage 1C are listed in Table 4. This result show
that the fluid inclusions in stage 1B contain H₂O (82.12%), CH₄
(12.89%), CO₂ (3.49%) and minor N₂ (1.14%), C₂H₆ (0.22%), and H₂S
(0.04%), indicating that fluid is rich in CH₄ and H₂O plus minor CO₂.
However, the fluid inclusions in stage 1C contain H₂O (75.73–77.53%)
CH₄ (8.041–11.46%), CO₂ (10.43–11.29%) and minor N₂ (1.89–2.54%)
C₃H₆ (0.21–0.27%), and H₂S (0.006–0.009%) indicating that fluid is
rich in CH₄, H₂O and CO₂. The fluid inclusions (ZK102-272) in stage 1B
overprinted by stage 1C have gaseous composition and content which
vary between stage 1B and stage 1C. Therefore, fluids that are brought by the Baogutu diorite are rich in reductive volatiles CH₄ and H₂O in stage 1B and change gradually from reductive volatiles to oxidative volatiles from stage 1B to stage 1C.

7. Discussion

7.1. Pressure estimation and deep magmatic system

Pressure estimation from fluid inclusions can be obtained by fluid data in the binary system NaCl–H₂O as an approximation (Hedenquist et al., 1998; Driesner and Heinrich, 2002, 2007) and outlined in Table 3. Pressures determined for nonboiling assemblages are derived from the homogenization temperature and represent minimum values (Rusk et al., 2008). Boiling assemblages will give absolute fluid entrapment temperatures (Roedder, 1984), although compositional deviations of the fluids from the binary model system introduce systematic uncertainties. At Baogutu, the lack of the significance boiling assemblages shows that pressures determined only represent the minimum values.

Almost brine inclusions in quartz at Baogutu consistently show homogenization by halite dissolution after bubble disappearance. Such homogenization behavior is relatively common in halite saturated inclusions in magmatic–hydrothermal ore deposits (Ulrich et al., 2001; Bouzari and Clark, 2006). They have been interpreted to indicate entrapment of a halite-saturated hydrothermal brine (Croke and Kesler, 1979; Wilson et al., 1980), homogeneous trapping at high pressures (Bodnar, 1994; Rusk et al., 2008), or post-entrapment H₂O loss or volume shrinkage (Sterner et al., 1988). Halite-homogenizing inclusions at Baogutu do not occur widely on boiling trails, which would be clear evidence for post-entrapment modification. The analyzed fluid inclusion assemblages showed no petrographic evidence of post-entrapment disturbance. Moreover, halite homogenization at temperatures well above homogenization of the bubble in brine inclusions do not yield unreasonably high trapping temperatures, suggesting that significant post-entrapment modification may not occur. We therefore suggest that homogenization by halite dissolution at Baogutu could record the entrapment at high pressures.

The depth of formation of porphyry Cu–Mo deposits is typically difficult to determine and in many deposits it is poorly known (Seedorff et al., 2005). Fluid inclusions may provide estimates of trapping pressure, but the resultant depth estimates are not straightforward because pressures may be either lithostatic or hydrostatic or somewhere in between (Rusk et al., 2008). In some cases depth can be reliably inferred from geologic relationships. At Baogutu, we have indirect geologic estimates of depth. Baogutu complex includes dominant equigranular diorite and weakly porphyritic diorite, indicating crystallization formed in depth. Baogutu complex is emplaced into folded rocks of the Xibeikulasi fold (Fig. 2). The carapace of eogenetic Carboniferous Darbut Volcanics is missing over the Baogutu complex in the Baogutu district (Fig. 3), supporting deep erosion.

Halite saturated inclusions in l-quartz were trapped at temperatures of about 401–550 °C, then pressures of l-quartz formation were calculated from the homogenization temperature of brine inclusions and were in the range of 1500 to 3100 Pa (Table 3). Under lithostatic pressures, where rock density is 3 gm/cm³, l-quartz within Baogutu complex formed at depths of 5 to 10 km. This depth estimate coincides with that for the crystallization of the host Baogutu complex. The Baogutu complex was, however, emplaced prior to porphyry Cu–Mo–Au mineralization at Baogutu, so this estimate yields crystallization depths rather than directly mineralization depths.

D-quartz from stage 1B precipitated from moderate-temperature fluids (200–400 °C), probably during transition from a lithostatic to a hydrostatic regime or a hydrostatic regime. Here, pressures have been calculated from the homogenization temperature of brine inclusions, yielding values of <320 bars. The estimated depth may be <3.2 km. Petrographically later inclusions in stage 1B quartz have similar characteristics as D-quartz but with minor brine inclusions. The uncertainty in the values derived from vapor-rich inclusions is greatest owing to the very poor visibility of the liquid phase. Pressure estimates for V1 inclusions commonly exceed 84 bars, up to 260 bars. Aqueous L1 and L2 Inclusions were trapped at temperatures of about 180–390 °C and have an estimated pressure from 10 to 150 bars. Geologic evidence with tension internal symmetry in quartz veins indicates that fluid pressures of these low-moderate temperature inclusions (180–390 °C) are in hydrostatic conditions during fluid entrapment; hence, a depth of <2.6 km is estimated.

The internal symmetry or open vugs and the irregular walls in stage 1C suggest that they formed in still brittle rocks. Vein quartz in stage 1C, therefore, precipitated from low-moderate temperature fluids (170–400 °C) in a hydrostatic regime. Similarly, estimates for the vapor-rich inclusions (V1 and V2) yield values of <230 bars, whereas minimum pressures for L1 and L2 aqueous liquids range between 10 and 210 bars. The estimated depth may be <2.3 km.

7.2. Unusual methane-rich magmatic–hydrothermal fluid system and its evolution

7.2.1. Unusual methane-rich magmatic–hydrothermal fluid system

Our unpublished data for lead isotope composition of pyrites at Bagutu span a narrow range (206Pb/204Pb=17.86 to 18.50, 207Pb/204Pb=15.44 to 15.60, 208Pb/204Pb=37.49 to 38.28) and plot in the mantle evolution curve. Shen and Jin (1993), Song et al. (2007) and our unpublished data for δ³⁴S from the fluid systems at Bagutu close to zero, indicating that they derived from the mantle source region (Gemmell and Large, 1992). Therefore, fluids at Baogutu are derived from mantle.

In most porphyry Cu–Mo–Au deposit, CO₂ has been identified in inclusions, but other gases such as CH₄, H₂S, and N₂ are typically not detected (Rusk and Reed, 2002). The fluids involved in the late magmatic diorite are predominance of NaCl brines and CH₄. The fluids involved in hydrothermal quartz are CH₄-rich in stage 1B and CH₄ + CO₂ in stage 1C. The fluids at Baogutu belong to a NaCl–H₂O–CH₄–(CO₂) system.

Lithospheric upper mantle is relatively oxidized (Lécuyer and Ricard, 1999; Catling et al., 2001), with volatile components dominated by CO₂ (Lowenstein, 2001). CO₂-rich fluids equilibrate with peridotites on the depths of less than 130 km or up to 200 km in the mantle, respectively, whereas CH₄-rich fluids equilibrate with metal–silicate melts on the depths of greater than 200 km in the much reduced athesospheric mantle (Simakov, 1998). CO₂ fluid instead of

Table 4
Gaseous composition (mol%) of fluid inclusions from quadrupole mass spectrometry.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Veins</th>
<th>Stage</th>
<th>H₂O</th>
<th>N₂</th>
<th>He</th>
<th>Ar⁺</th>
<th>O₂</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZK102-458</td>
<td>B1-veinlet</td>
<td>Stage 1B</td>
<td>82.12</td>
<td>1.142</td>
<td>–</td>
<td>0.135</td>
<td>–</td>
<td>3.493</td>
<td>12.89</td>
<td>0.22</td>
<td>0.041</td>
</tr>
<tr>
<td>ZK102-272</td>
<td>B1-veinlet</td>
<td>Stage 1B+1C</td>
<td>81.84</td>
<td>1.612</td>
<td>–</td>
<td>0.274</td>
<td>–</td>
<td>5.875</td>
<td>9.051</td>
<td>0.439</td>
<td>0.076</td>
</tr>
<tr>
<td>ZK211-509</td>
<td>Cl-vein</td>
<td>Stage 1C</td>
<td>75.73</td>
<td>1.896</td>
<td>–</td>
<td>0.258</td>
<td>–</td>
<td>10.43</td>
<td>11.46</td>
<td>0.215</td>
<td>0.009</td>
</tr>
<tr>
<td>ZK211-526</td>
<td>Cl-vein</td>
<td>Stage 1C</td>
<td>77.53</td>
<td>2.548</td>
<td>–</td>
<td>0.306</td>
<td>–</td>
<td>11.29</td>
<td>8.041</td>
<td>0.278</td>
<td>0.006</td>
</tr>
</tbody>
</table>

– not detected; * values for reference.
CH₄ fluid is abundant in the upper mantle; it is likely that the parent magma and inclusion fluids of the Baogutu diorite derive from the transition zone of the mantle or asthensphere underneath the Paleozoic orogens of the Western Junggar.

7.2.2. Methane-rich magmatic–hydrothermal fluid system evolution

Magmatic volatiles separating from calc-alkaline magmas predominantly consist of water and chloride salts (Heinrich, 2005), and magmatic fluids are therefore commonly discussed with reference to the experimentally well-studied phase relations in the binary system NaCl–H₂O (Hedenquist et al., 1998; Driesner and Heinrich, 2002, 2007), even though quantitative pressure–temperature–composition (P–T–X) relationships are shifted by the common presence of other volatiles (Heinrich, 2005). Our interpretation of the P–T–X fluid evolution is illustrated in Fig. 12 based on the binary system NaCl–H₂O, as described by Heinrich (2005).

The fluid inclusions in I-quartz found in diorite at Baogutu are characterized as CH₄-rich, H₂O-rich and high-saline inclusions and they belong to a NaCl–H₂O–CH₄ system by the results of Raman Spectroscopy (Fig. 11). Almost hyper-saline fluid inclusions homogenize by halite dissolution suggesting a very high salinity in primary fluid and homogeneous trapping at high pressures (Bodnar, 1994; Rusk et al., 2008). The significant post-entrapment modification may not occur at Baogutu. We therefore suggest that the halite-homogenizing inclusion assemblages could record the entrapment of a single-phase brine at pressures well above the liquid-vapor phase boundary (Bodnar, 1994). There is a trend from nonboiling brines with ~60 wt.% NaCl equiv toward lower salinity, essentially following a high-temperature isotherm of the two-phase boundary (Fig. 12).

Significant salinity and density variations of fluids present during potassic alteration with biotite–quartz–magnetite assemblages and probably the initial stages of copper deposition can be explained by a P–T path of general cooling and decompression of one magmatic fluid. In D-quartz occurred in the potassic zone, fluid inclusions contain the dominant aqueous liquids of type L1 and L2 (>60%) and common V1 inclusions (<30%) with minor V2 and H inclusions at Baogutu. The fluid inclusions consist of dominant low-salinity (<23 wt.% NaCl equiv) and minor high-salinity (>38 wt.% NaCl equiv) magmatic fluids. The fluids belong to a NaCl–H₂O–CH₄ system (Fig. 11). The low pressure (up to 320 bar) fluids trapped above 250 °C are interpreted as the earliest inclusion assemblages in hydrothermal stage. Ascent and cooling in the single-phase field would cause this magmatic fluid to first intersect the two-phase surface on the liquid side of the critical curve (Fig. 12) and produces a low density vapor. Therefore, D-quartz contains abundant L2 and V1 inclusions.

In the vein quartz occurred in the stage 1B potassic zone, fluid inclusions have more vapor inclusions and lower salinity and temperature than that in D-quartz. Almost quartz-sulfide veins lack alteration envelopes indicating the chemical equilibrium between fluid and early-formed potassic altered rocks. It also indicates that the compositions of the major vapors or liquids do not vary much during the hydrothermal evolution of the system during stage 1B and the formation of vein quartz during stage 1B did not modify the early-formed fluid chemistry significantly. The homogenization temperature in the vein quartz is near to that in the D-quartz. Estimate pressures show a much wider scatter from 20 to 260 bars which indicates that multiple cycles of sealing of the fracture system caused a repeated increase in pressure, probably due to mineral precipitation. The transition between disseminated and vein mineralization in stage 1B involves essentially isothermal cooling at pressures under the two-phase surface (Fig. 12).

In the vein quartz occurred in the stage 1C phyllic zone, fluid inclusions contains most abundant vapor inclusions without brine inclusions in Baogutu. The fluid inclusions consist of most abundant low-salinity (<23 wt.% NaCl equiv) fluids. Most vapor-rich inclusions results from the renewed hydraulic fracturing (pressure loss) which produced low density vapor. However, the vein quartz in stage 1C and 1B have the similar ranges of the homogenization temperatures (Fig. 10c, d) and relatively clear pressure variations (Fig. 12). It shows

Fig. 12. Phase diagram of the system NaCl–H₂O (Hedenquist et al., 1998; Driesner and Heinrich, 2002, 2007), showing all assemblages and single-phase assemblages. Red and black squares represent stage 1B and stage 1C samples, respectively.
that the change physical process (mainly pressure loss) contribute to the transition from potassic to sericitic alteration.

Quartz-sulfide veins formed in stage 1C cut the potassic zone and have phyllic alteration envelopes. It indicates that there are a chemical disequilibrium between fluid in stage 1C and early-formed potassic altered rocks in stage 1B. The fluid inclusions lack high-salinity magmatic fluids. In addition, the fluid in stage 1C contains CH₄ and H₂O and detected CO₂ which could belong to a NaCl–H₂O–CH₄–CO₂ system. Therefore, the transition between vein mineralization in stages 1B and 1C involves different chemical process and lower pressures at under the two-phase surface. This part of the fluid evolution is associated with feldspar-depressive alteration.

The changes in alteration style from potassic to phyllic can be explained by transfer of CO₂ to the vapor. It is supported by the fact that oxidation of CH₄ to CO₂ and H₂O by chloritization and muscovite of biotite in stage 1C. The early-formed potassic alteration assemblages have been overprinted by a pervasive phyllic alteration (sericite–quartz–pyrite–chlorite–carbonate) assemblage. Where biotite has been sericitized and partly chloritized and plagioclase has been altered to sericite (fine-grained muscovite), calcite, and chlorite. The oxidation of methane into carbon dioxide and water liberates 8 mol of e— per mole of methane. These electrons are captured during iron reduction related to chloritization of biotite (Tarantola et al., 2007, 2009):

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
12\text{Fe}_2\text{O}_3(\text{biotite}) & \rightarrow 8\text{Fe}_3\text{O}_4(\text{chlorite}) + 2\text{O}_2 \\
\text{CH}_4 + 12\text{Fe}_2\text{O}_3(\text{biotite}) & \rightarrow \text{CO}_2 + 8\text{Fe}_3\text{O}_4(\text{chlorite}) + 2\text{H}_2\text{O}
\end{align*}
\]  

(1a) 
(1b) 
(1c)

The hydrothermal evolution at Baogutu is characterized by the chemical reaction of a potassic to a phyllic alteration due to a fluid composition evolution. Pressure variations exceeding the lithostatic to hydrostatic difference are documented in some porphyry-type ore deposits (e.g., Bajo de la Alumbrera: Ulrich et al., 2002; El Teniente: Klemm et al., 2007). In contrast to it, the small pressure fluctuations have been indicated at Baogutu, suggesting that the fracture system caused a change in pressure weakly developed, which can cause the unobvious phase separation or boiling. It coincide with the geological facts that dominant dissemination and minor vein mineralization at Baogutu.

7.3. Evolution model of methane-rich magmatic–hydrothermal system

The conclusions drawn in the following sections are based on a limited fluid inclusion database and could change if more data were collected. A plausible model can be constructed from a consideration of the phase relationships in the H₂O–NaCl system (Fig. 12). The interpretation of fluid evolution in Fig. 13 is only one possible scenario guided by average trapping temperatures and salinities observed in the fluid inclusions as well as the characters of the alteration and mineralization at Baogutu. Temporal evolution of the Baogutu porphyry Cu–Mo–Au deposit is illustrated in Fig. 13.

7.3.1. Baogutu stock emplacement

In the Late Paleozoic, oceanic crust of the Junggar terrain was subducted beneath the Altai orogen and Kazakhstan plate (Chen and Arakawa, 2005; Xiao et al., 2008, 2009). Volatiles, copper and other metals were extracted from the hydrated tholeiitic basalt and pelagic sediments of the subducting oceanic crust. This metal- and volatile-rich melt then ascended into the overlying mantle wedge, inducing partial melting that generated an intermediate magma. The dioritic magma ascended from the mantle wedge and confining pressures decreased rapidly (e.g., Mungall, 2002; Sillitoe, 2010). This allowed volatiles and metals to be released and transported, with minor crustal interaction and assimilation (Shen et al., 2009), to the upper crust. Dioritic magma accumulated in upper crustal magma chambers beneath the site now occupied by the Baogutu intrusive complex. The Baogutu complex (temperatures >400 °C) occupies a structural intersection of N- and ENE-trending faults within the Xibeikulasi synclinorium at depths of 5 to 10 km (Figs. 2 and 13a).

7.3.2. Early K silicate alteration and formation of the dissemination and veins

Porphyry Cu (Mo–Au) deposits form in the upper crust, where fluid overpressures which generated in the cupola of a crystallizing magma hydrofracture the overlying rock (Burnham, 1979), allowing magma and fluids to intrude, forming porphyry dikes surrounded by stockwork fractures (Rusk et al., 2008; Hou and Cook, 2009). Fluids permeate the fractured rock forming veins which led to the dominant vein-style mineralization developed in most porphyry Cu (Mo–Au) deposits. Therefore, sulfides in most porphyry Cu (Mo–Au) deposits occur primarily in veinlets or breccia pipes (e.g. Kay and Mpodozis, 2001; Richards et al., 2001; Richards, 2005; Cooke et al., 2005; Davies et al., 2008). Baogutu differs in that Cu–Fe sulfide mineralization formed mostly as disseminations in the biotite-altered rocks, with lesser amounts in vein stockworks and hydrothermal breccias. It results from the weak tockwork fracturing and hydrothermal brecciation when hydrothermal fluid produced concentric potassic and propylitic alteration zones (Fig. 13b).

At the site of formation of the biotite–magnetite–quartz–sulfides dissemination, hydrothermal fluids had temperatures of <400 °C and pressures of <320 bars, and consisted of hypersaline brine and low-saline fluid. Fluid decompression can account for the presence of brine inclusions that homogenize by halite dissolution in quartz samples from the D-quartz in stage 1B. These D-quartzes did not contain brine inclusions that homogenize by disappearance of the vapor bubble, which account for without phase separation when the rock fractured. Biotite alteration and propylite alteration in stage 1B formed when the magmatic–hydrothermal brines interacted with the diorite and wall rocks of the Baogutu Group, respectively (Fig. 13b).

The highest concentrations of chalcopyrite occur in quartz veins in stage 1B within the Baogutu diorites based on our logging cores. Fluid inclusion microthermometry suggests that chalcopyrite was deposited with the quartz at temperatures between 180° and 420 °C and pressures <260 bars. These fluids were in similar temperatures and slightly lower pressure than those that caused the biotite–magnetite–quartz–sulfides alteration. Thus chalcopyrite-bearing veins most likely formed as the Baogutu diorite cooled and crystallized and denuded (Fig. 13c).

7.3.3. Phyllic alteration and formation of the veins

Intense phyllic alteration overprinted the potassic alteration zone and produced additional Cu–Mo ore at Baogutu. The highest concentrations of molybdenite occur in quartz veins within the Baogutu diorite. Fluid inclusion microthermometry suggests that molybdenite was deposited with the quartz at temperatures between 160° and 400 °C. These fluids have lower pressure (<230 bars) than that the quartz-sulfide veins and alteration (<260 bars) in stage 1B. Thus molybdenite-bearing veins most likely formed as the Baogutu diorite denuded continually (Fig. 13d).

8. Conclusions

Detailed fluid inclusion petrography and microthermometry followed by Raman Spectroscopy analyses and Quadrupole Mass Spectrometer analyses allowed construction of the evolution of the methane-rich magmatic–hydrothermal fluids at Baogutu.

The fluids in late magmatic stage and stage 1B rich in reductive CH₄ plus H₂O, while the fluids in stage 1C rich in reductive CH₄ plus H₂O
and CO₂. Oxidization of the CH₄ to CO₂ characterizes the transition from stage 1B (potassic alteration) to stage 1C (phyllitic alteration).

The Baogutu dioritic magma emplaced at unusually depth (5–10 km) and the estimated magmatic emplacing conditions are at T = 400 °C and P = 1500 to 3100 bar. The dominant disseminated mineralization and minor vein mineralization indicates small temperature and pressure fluctuations from stage 1B to stage 1C. The estimated fluid trapping conditions are at T = 200 to 400 °C and P = 50 to 320 bars in D-quartz in stage 1B, T = 180 to 400 °C and P = 20 to 263 bars in vein quartz in stage 1B, and T = 170 to 400 °C and P = 10 to 230 bars in vein quartz in stage 1C.

The overall fluid path at Baogutu is toward lower pressure and small changed temperature, with some composition transit of fluid from a NaCl–H₂O–CH₄ system to NaCl–H₂O–CH₄–CO₂ system and led to the formation of Cu–Mo–Au from stage 1B to stage 1C.
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References


