Characteristics and evolution of ore-forming fluids in the Diyanqinamu Mo deposit, Inner Mongolia: Evidence from LA-ICP-MS analysis of individual fluid inclusion

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Abstract. The Diyanqinamu Mo deposit in Dong Ujimqin Banner of Inner Mongolia is a large deposit. In this study, hydrothermal activity is divided into five stages: quartz - potassium feldspar - fluorite, quartz - muscovite, epidote - magnetite, chlorite - carbonate – pyritization, and argillization. The results show that early exsolved fluid has the characteristic of high temperature (up to 470°C), high oxygen fugacity, and Fe- and sulfide-rich in daughter minerals. LA-ICP-MS analysis of individual fluid inclusion exhibit early fluid is rich in W, Mo, Pb, Zn, Fe, Mn, As, Ag, Sn, and rare earth elements of La, Ce. The ore-forming fluids are NaCl-H2O system and contain gases CO2 and a small amount of H2 and N2. In general, the ore-forming fluids evolved from high temperature (340 °C - 470°C) with high salinity (up to 63.9 wt%NaCl equiv) to low temperature (189 °C - 202°C) with low salinity (as low as 0.18 wt% NaCl equiv). The ore-bearing fluid comes from the exsolution of the volatile-rich magma, and hydrothermal fluid boiling result from the drop of the pressure may have led to Mo precipitation. Based on the alteration, mineralization, and fluid characteristics, the Diyanqinamu Mo deposit is a porphyry deposit related to magmatic activity in Yanshanian.

1. Introduction

The Diyanqinamu deposit is a large Mo deposit discovered in the eastern part of Xingmeng Orogenic belt in recent years. It is also a largesized porphyry Mo deposit found in the Dong Ujimqin Banner at present. The First Geological Exploration Institute of China Metallurgical Geology Bureau submitted an exploration report in 2012, detected resource of 77.8 Mt of molybdenum (average grade 0.097%), 2.32 Mt of lead (average grade 2.61), 2.69 Mt of zinc (with an average grade of 3.04%) and 94.48 tons of silver (average grade of 106.7×10-6) (First Geological Exploration Institute of China Metallurgical Geology Bureau, 2012). Previous studies mainly focused on geochemistry and chronology of intrusive rocks in the Diyanqinamu molybdenum deposit (Leng et al., 2015; Wang, 2015), but there is no comprehensive study on ore-forming fluid.

Based on detailed field observation and petrographic studies, we summarize that quartz K-feldspar geode, the petrological structure of unidirectional solidification texture (UST) of fluorite veins and quartz veins develop in the fine-grained syenite in borehole, recording the transformation process of magmatic to fluid, which is beneficial to study the process of exsolve fluids from magmatic and the feature of the exsolved fluids. LA-ICP-MS analyses of individual fluid inclusions can accurately...
analyze elements in the fluid inclusion and is essential in studying elemental paragenesis mechanisms. In this paper, we apply LA-ICP-MS to precisely analyze the element compositions of early exsolved fluids in Diyanqinamu Mo deposit. Furthermore, combining with petrography, microthermometry, and SEM, to discuss characteristics of porphyry molybdenum ore-forming fluid and their constraints for the mineralization, and further understanding the relationship between early exsolved fluid and mineralization of porphyry Mo deposit.

2. Ore Deposit Geology
The exposed strata in the Diyanqinamu area are Middle-Ordovician, Upper Jurassic, and Quaternary Holocene (First Geological Exploration Institute of China Metallurgical Geology Bureau, 2012). The principal structures in the Diyanqinamu area include fold and fault. The most notable fold is the NW trending anticline, which superimposed on the early near EW trending fold structure. The faults are principally NE and NW trending. Disseminated and stockwork Mo mineralization are developed in altered intrusive rocks or strongly silicified rocks. Jurassic volcanic rocks and pyroclastic rocks are common, whereas the intrusive rocks have not developed in the mining area, and only dikes can be found in a few borehole cores. The intrusive rocks contain granite porphyry, quartz monzonite porphyry, fine-grained syenite, and basic rocks. Due to the intense alteration, dark minerals in the basic rocks have been altered into pyrite and rutile. It is inferred from the alteration products that the primary dark minerals should be mainly biotite, whose composition is similar to lamprophyre. Fluorite and quartz veinlet occur in the fine-grained syenite show UST.

According to the relationship of the field vein cutting, mineral assemblages, and the mineralization and alteration in the Diyanqinamu Mo deposit, the ore-forming process can be divided into five stages and summarized follows.

I: Quartz-potassium feldspar-fluorite stage: the main mineral assemblages include quartz, fluorite, potassium feldspar, molybdenite, zinnwaldite, etc.

II: Quartz-muscovite stage: the main mineral assemblages include quartz, muscovite, pyrite, rutile, fluorite, a small amount of chalcopyrite, molybdenite, etc.

III: Epidote-magnetite stage: the main mineral assemblages include epidote, magnetite, hematite, quartz, calcite, actinolite, chlorite, etc.

IV: Chlorite-carbonate-pyrite stage: the main mineral composition includes chlorite, calcite, quartz, hematite, pyrite, sphalerite, chalcopyrite, etc.

V: Argillation stage: mainly characterized by clayization of feldspar, and the primary mineral is clay minerals (such as illite, etc.), pyrite, galena, sphalerite, etc.

Fig. 1. Field occurrences of the Diyanqinamu Mo deposit. (a) quartz-potassium feldspar - molybdenite veins occurred in the margin of fine-grained syenite; (b) the quartz-pyrite veins in the altered fine-grained syenite are cut by calcite - chlorite - epidote veins, and the latter are cut by calcite - hematite veins; (c) multiphase quartz veins occurred in altered granite porphyry. FGS- fine-grained syenite; GP- granite porphyry; Q-quartz; Kfs- potassium feldspar; Mo- molybdenite; Py- pyrite; Ep- epidote; Chl- chlorite; Hem- hematite.
3. Analytical results

In this study, petrography, microthermometry, LAM, SEM/EDS for daughter minerals, and LA-ICP-MS analysis are carried out to reveal the fluid evolution of the Diyanqinamu deposit.

3.1. Fluid inclusions petrography

The coexist of melt and fluid inclusions in early UST quartz is evidence of melt-flow conversion. Three types of fluid inclusions were recognized according to their phase components at room temperature and phase transitions during microthermometric analysis (Roedder, 1984): the type I daughter-minerals-bearing fluid inclusions (ADV type), the type II aqueous fluid inclusions (AV type), and the type III pure gas fluid inclusions (V type).

ADV type is found in stage I and contain vapour bubble, liquid phase, and one solid daughter mineral at room temperature. They are elliptical or rounded and generally 5-30 μm in diameter. The solid daughter minerals are halite, transparent non-saline minerals, and opaque sub-minerals. A few acicular crystals, possibly Fe-chloride, were also found, and SEM/EDS was used to analyze these inclusions later. ADV type inclusions occur randomly or coexist with AV type.

V type mainly occurs in quartz phenocryst and molybdenite-fluorite veins. They are rounded or negative crystal with the size of 5-12 μm.

AV type contains H₂O vapour and H₂O liquid, occurring in every stage. According to the vapour phase proportion, they can be classified into vapour–rich aqueous (AV₁ type) and liquid-rich aqueous (AV₂ type). AV₁ type is usually rounded, negative crystal, and irregular in shape, with the size of 6-25 μm, and high vapour phase proportions (>40%). They commonly develop in quartz phenocrysts, UST quartz, molybdenite-quartz veins, and molybdenite-fluorite veins. AV₂ type is characterized by lower vapour phase proportions (5%-30%) and rounded, elliptical, strip, and negative crystal, with 6-25 μm in diameter.

The inclusion assemblages in different ore-forming stages have various characteristics. Stage I and II are mainly ADV and AV types, usually characterized by continuous vapour phase proportions and suggest boiling fluids feature. And ADV type in stage II is much less than stage I. In stage III, the inclusions are mainly AV₂ types, with a small amount of AV₁. There are only AV₂ type inclusions in stage IV.

3.2. Fluid inclusions microthermometry

ADV type inclusions have high homogenization temperature and salinity. They mainly homogenize into the liquid phase with daughter minerals disappear, suggesting these inclusions are trapped from supersaturated solution; Very few inclusions homogenize along with the daughter minerals and bubbles disappear at almost the same temperature, suggesting that these inclusions are trapped during fluid boiling. The ADV type inclusions Vapour-liquid phase homogenized to liquid phase at 267-457℃, and daughter crystals usually dissolved upon heating at temperature of 340 to 470℃, and corresponding salinity ranges from 41.49 to 69.63 wt% NaCl equiv.

AV₁ type inclusions homogenized at 260-432℃, with ice-melting temperatures of -15.2 to -0.2℃ and salinities of 0.35-18.72 wt% NaCl equiv.

AV₂ type inclusions homogenized to liquid phase at 189-400℃, with ice-melting temperatures of -5.5 to -0.4℃ and salinities of 0.71-8.55 wt%NaCl equiv.

The homogenization temperature and salinity of ADV type inclusions in stage I range from 340 to 470℃ and 41.49 to 69.63 wt%NaCl equiv, respectively, while that of AV type inclusions range from 260 to 432℃ and 0.35 to 7.86 wt%NaCl equiv, respectively. The homogenization temperature and salinity of AV type inclusions in stage II mainly range from 249 to 320℃ and 0.71 to 2.24 wt%NaCl equiv, respectively. The homogenization temperature and salinity of the AV₂ type inclusions in the late stage range from 189 to 202℃ and 0.18 to 0.53 wt%NaCl equiv, respectively. In general, the mineralization temperature and salinity show a decreasing trend from the early to the late mineralization stage.
3.3. Composition of the fluid inclusions

3.3.1. LAM analyses
The gas and liquid phase components of the fluid inclusions are mainly H2O, while the gas phase components contain a small amount of CO2, N2, CH4, H2S, etc.

3.3.2. SEM/EDS analyses for daughter minerals in fluid inclusion
According to SEM/EDS analyses, daughter minerals in ADV type inclusions of early-stage are mainly NaCl and KCl, and contain a small amount of Fe and Mn compounds.

3.3.3. LA-ICP-MS individual fluid inclusion analyses
We just obtained few valid data for ADV type inclusions in UST quartz due to the small size of fluid inclusions. The element components of these inclusions contain Na, K, Cl, and W, Mo, Fe, Mn, Pb, Zn, As, Cu, Sb, Ag, Ba, Sn, and other ore-forming elements, as well as a small amount of La, Ce and other rare earth elements.

4. Discussion

4.1. Fluid exsolution
Fluorite and quartz veinlets occur in the fine-grained syenite behaviours as UST in the Diyanqinamun Mo deposit are evidence of fluid exsolution from magma, suggesting that the fine-grained syenite magma rich in volatile, and exsolved fluid is the initial ore-forming fluid. Quartz phenocrysts of granite porphyry and quartz monzonitic porphyry develop in quantity melt and melt-fluid inclusions imply magma rich in water. Based on microphysiography, microthermometry, and SEM/EDS analysis of fluid inclusions, characteristics of early exsolved fluid is high temperature, high salinity, CO2-bearing NaCl-H2O system, and the daughter minerals usually are halite, sylvite, iron and manganese chloride. LA-ICP-MS analysis of single fluid inclusions in UST quartz indicate that the ore-forming fluid contains mainly Na, K, Cl, and W, Mo, Pb, Zn, Fe, Mn, As, Cu, Sb, Ag, W, Ba, Sn, and other ore-forming elements, as well as a small amount of La, Ce and other rare earth elements, which are consistent with the known minerals in the mine area. Meanwhile, the rare earth elements in the fluid are also accordant with the bastnaesite, xenotime, and monazite found in the mine area, which further confirms the relationship between fluid and mineralization.

Compared with the classic porphyry Cu deposit, the ore-forming temperature of porphyry Mo deposit is usually less than 500°C. For example, the temperature of the fluid in the early mineralization stage of the Luming and Jiguanshan porphyry Mo deposit are 410-475°C and 320-480°C, respectively (Sun et al., 2015; Chen et al., 2010), and no more than 478°C in Huojihe and Daheishan Mo deposit (Zhang et al., 2015; Shen et al., 2015). Previous studies showed that porphyry W (Mo) deposits in the Xingmeng Orogenic belt all developed a large amount of fluorite, indicating that early ore-forming porphyry is characterized by F-rich, which can reduce the solid-liquid temperature of the magma. Thus the temperature of the fluid exsolution from magma is relatively low, consistent with the microthermometry results of the inclusions in the early UST quartz veins.

4.2. Fluid evolution and mineral precipitation
The early stage is rich in fluid inclusions with high salinity, which coexist with gas-rich fluid inclusions with low salinity, showing the characteristics of boiling inclusion assemblages. As the decrease of temperature and pressure, especially sudden pressure dropping, cause fluid exsolution. The exsolved fluid in the early stage is characterized by high salinity, CO2-bearing, and rich in ore-forming metal element. During fluid boiling, ore-forming metal elements such as Mo, Pb, Zn tend to concentrate in high salinity liquid phase and migrate by chlorine complex.

The fluid inclusions in UST quartz veins of the Diyanqinamu Mo deposit are mainly ADV type, and the homogenization temperature is high (up to 470°C). For stage II, ADV type inclusions are reduced, while AV type inclusions are increased, and ore-forming temperature is slightly lower. For
stage IV, which occur Pb and Zn multi-metal, the homogenization temperature and salinity reduced further. The results of the H-O isotope analysis suggest that the ore-forming fluids are dominated by magmatic water in the early stage, while in the later stage are mainly mixing magmatic water and atmospheric water (Wang, 2015). The H-O isotope analysis results of quartz in the first three stages indicate that the ore-forming fluids are mainly magmatic-hydrothermal fluids in the early stage, with more meteoric water mixing in the late stage (Wang, 2015).

The high temperature and salinity fluids exsolution in the early stage have a remarkable ability to carry metal elements, and contribute to mineralization as Mo, Pb, Zn migrate by chlorine complex in the fluid, and this is also confirmed by SEM/EDS and LA-ICP-MS analysis. The ore-forming fluid of porphyry Mo deposit generally belongs to the NaCl-H2O±CO2 system, containing a small amount of KCl, SO2, H2S, CH4 (Heinrich, 2005). The ore-forming fluids in the Diyanqinamu deposit consistent with this feature. Fluid boiling is a significant mineral precipitation mechanism that can destabilize the ore metal complex and promote Mo ore precipitation (Qu et al., 2021).

5. Conclusions
(1) The Diyanqinamu Mo deposit is a porphyry deposit related to Yanshanian intrusive rocks, and alteration mainly contains K-feldsparthization, silicification, and propylitization, etc.
(2) The results of fluid inclusions research indicate that initial exsolved fluid was characterized by high temperature and high salinity, and carrying amount of Mo, W, Pb, Zn, Cu, Sn, As, Ag and rare earth elements such as La, Ce.
(3) The temperature and salinity gradually decreased from the early to the late mineralization stage. The fluid boiling and temperature drop led to the precipitation of molybdenite.

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