Fluid inclusion and H–O isotope evidence for immiscibility during mineralization of the Yinan Au–Cu–Fe deposit, Shandong, China

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Abstract

The fluid inclusion and H–O isotope studies have provided the evidences for the source of ore-forming fluids, and helped to recognize two types of immiscibility and their relationships with mineralization. Hydrogen and oxygen isotopic geochemistry shows that the earlier ore-forming fluids during the anhydrous skarn stage (I) and the hydrous skarn-magnetite stage (II) were mainly derived from magmatic water, while the later fluids during the quartz-sulfide stage (III) and the carbonate stage (IV) were mainly from magmatic water mixed with small amounts of meteoric water. Various types of fluid inclusions, including abundant vapor- or liquid-rich two-phase aqueous inclusions, daughter minerals-bearing multiphase inclusions, CO2–H2O inclusions, and less abundant liquid inclusions, vapor inclusions and melt inclusions, are present in hydrothermal minerals of different stages. The liquid–vapor fluid inclusions are mainly composed of H2O, with significant amounts of CO2 and a small amount of CH4. In the opaque-bearing fluid inclusions, the hematite and fahlore (tetrodahedrite) were identified. The homogenization temperature of the aqueous fluid inclusions decreases from Stage I (520–410 °C), through Stage II (430–340 °C) and III (250–190 °C), to Stage IV (190–130 °C). The coexistence of melt inclusions with simultaneously trapped vapor- or liquid-rich two-phase aqueous inclusions and daughter minerals-bearing multiphase inclusions in garnet, diopside and epidote of Stages I and II suggests an immiscibility between silicate melt and hydrothermal fluid. It is an effective mechanism on scavenging and transporting ore-forming components from magmas. The aqueous fluid inclusions with various vapor/liquid ratios (from <10% to >65%) commonly coexist with simultaneously trapped liquid inclusions, vapor inclusions, daughter minerals-bearing multiphase inclusions and CO2–H2O inclusions in the quartz of Stage III, and the different kinds of the fluid inclusions have similar homogenization temperatures. This indicates that the boiling – another kind of immiscibility, widely took place during Stage III. It resulted in the precipitation and enrichment of gold, copper and iron.

Keywords: Immiscibility; Boiling; Fluid inclusion; H–O isotopes; Yinan Au–Cu–Fe deposit; Shandong

1. Introduction

There are three types of mineralization associated with immiscibility in nature: (1) The separation of immiscible magmatic melt leads to the formation of metallic and silicate melt. For instance, the immiscibility of copper–nickel sulfide melt and silicate melt can form the copper–nickel sulfide deposits (Naldrett, 1989); (2) during the late stage of magmatic crystallization, the silicate melt immiscibly separates from the H2O–CO2–H2S bearing volatiles, leading to the formation of ore-bearing gas–water hydrothermal fluids. These fluids can form deposit by means of replacement and filling (Jin et al., 1999; Fulignati et al., 2001; Campos et al., 2002; Reyf, 2004; Cesare et al., 2007); and (3) boiling and phase separation occur in various ore-bearing gas–water hydrothermal fluids along with decompression, resulting in the precipitation and concentration of ore-forming minerals (Reed and Spycher, 1985; Zhu, 1999; Graupner et al., 2001; Gu et al., 2003; Calagari, 2004; Coulibaly et al., 2008). Therefore, immiscibility between hydrous silicate melt and hydrous saline melt (and aqueous solutions) is responsible for many ore deposits in particular (Roedder, 1992). The fluid inclusions and H–O isotopes are microscopic records of the sources and evolution of ore-forming fluids, as well as the immiscibility process during mineralization.

As a typical Au–Cu–Fe polymetallic skarn deposit, the Yinan deposit has become a serious crisis mine after more than 50 years of exploitation. From 1957, when it was discovered, to 2006, it was mined constantly and has produced 6000,000 t of ore which yielded 20,000 t of copper, 1050,000 t of iron, 300,000 oz of gold, and 3,800,000 oz of silver. The serious shortage of reserves turns...
successful resource exploration into a top priority. Although the most recent exploration in 2007–2009 (new discovered resource of 19,000 t of copper, 6000,000 of iron and 4,80,000 oz of gold) indicated a significant progress on ore prospecting in the deep and peripheral mining area (Gu et al., 2008a), the scientific research of this deposit is still limited. Therefore, the in-depth understanding of the mineralization laws and ore-controlling factors has been constrained. The samples of different stages in the Yinan deposit provide a wealth of material for the study of fluid inclusions and H–O isotopes. From this, we seek to identify the source of ore-forming fluids, recognize the types of immiscibility, and discuss the relationships between immiscibility and mineralization.

2. Regional geological setting

The Yinan Au–Cu–Fe deposit is located in the western Shandong Province (Luxi area) on the west side of Tanlu fault zone, on the southeast margin of the North China plate. It is composed of the Tongjing and Jinchang Mines which are about 6 km away from each other (Fig. 1). The basement formed in the Luxi area after experiencing a series of geological processes such as sedimentation, metamorphism, magmatism, magmatic activities, cymatogeny and craton consolidation from Archean to Paleoproterozoic. Then the rocks were uplifted and experienced denudation. As a result, the Late Paleoproterozoic to Mesoproterozoic sediments were removed from the geologic record resulting in unconformity surface. During the Neoproterozoic, the Taishan continental craton cracked longitudinally, forming the Yishu rift. The Neoproterozoic to Paleozoic strata deposited on the rift basin and formed the cap rock above the unconformity surface (Cao, 1995; Song and Li, 2001; Hou et al., 2004).

During the Yanshanian, the Tanlu fault system had experienced sinistral strike-slip movement, and this tension action induced the invasion and emplacement of intermediate-acidic magmas along the composite positions of NE trending faults (branch faults of the Tanlu fault zone) and the NW faults in cap rock. Consequently, extensive tectonic magmatic activities occurred in the Luxi area (Zou and Shen, 2001; Zhu et al., 2002; Shen et al., 2003; Wu et al., 2007). Various types of polymetallic deposits (hydrothermal metasomatic and breccia type) are related to intermediate-acidic magmatic activities of the Yanshan period in this area (Xu et al., 1999, 2002; Liu et al., 2002).

3. Geology of the Yinan deposit

The deposit is produced in the contact zones between the Tongjing and the Jinchang intermediate-acidic complexes of Yanshanian and the strata from Neo-Archean to Cambrian (Fig. 2). It is
controlled by magmatic rocks, strata lithology and structures, showing typical characteristics of skarn deposits (Gu et al., 2008b).

The Tongjing complex (in the Tongjing mining area) outcrops as stocks, and on its edges there is sill intruded into the wallrock, showing irregular shape on the surface area with approximately 4.4 km². There is mainly quartz diorite in the western part and quartz diorite porphyrite in the eastern part of this complex (Fig. 2A), and the respective K–Ar ages of the whole-rock are 125.5 Ma and 117.5 Ma (Zheng and Luo, 1996). The quartz diorite is intruded by quartz diorite porphyrite or forms xenoliths, indicat-
ing that the emplacement of quartz diorite may be earlier than quartz diorite porphyrite. Most recent LA–ICP–MS dating of zircon from quartz diorite yields a mean age of 135.8 ± 2.7 Ma (Li, 2009).

The Jinchang complex (in the Jinchang mining area) is composed of intrusion and dykes: the Jinchang intrusion is located in its western part and the Yeguanmu dyke is situated at its eastern part.

The ring-like and radial dykes are distributed around the complex (Fig. 2B). The Jinchang intrusion shows round-shaped at the surface, with an area of about 0.2 km². There is porphyritic medium- and fine-grain monzonitic granite in its center, surrounded with granite porphyry, and gradually transiting to veins and dykes towards the outside. The Yeguanmu dyke shows dumbbell shape in the surface of the NE-direction extension with an area of about 0.1 km². It is mainly composed of granite porphyry, and the K–Ar age of the whole-rock is 121 Ma. The geochemical studies indicate that (Gu et al., 2008b), the calc-alkaline ore-forming complex plutons are relatively silicic, alkalic, and magnetite-bearing with high coefficient of oxidation (Fe₂O₃/(Fe₂O₃ + FeO) > 0.5), and they are broadly similar to the oxidized, Au skarn-related plutons defined by Meinert (1989, 1998, 2000).

In the mining area, the stratigraphic sequences include Neoarchean Taishan Group (A₊₉), Neoproterozoic Tumen Group (Z₉), Lower Cambrian Chuangqiang Group (ε₉) and Middle-Upper Cambrian Jiulong Group (θ₉) (Fig. 3A). The Archean Taishan Group is the crystalline basement, and is angular unconformably overlain by the cover composed of the Proterozoic and Cambrian strata. The Archean basement is mainly composed of granitic gneiss, plagioclase amphibolite and hornblende granulite. The Neoproterozoic Tumen Group is a set of shallow marine sedimentary facies. Gray–white medium- and fine-grain sandstone and pebbly sandstone are at the bottom, and the gray-yellow and gray–purple shale intercalated with lamella marl are at its middle and upper parts. The Cambrian Changqiang Group is mainly a set of fine clastic rocks, calcareous mudstone and shale interbedded with lamella marl, oolitic limestone, calcarenite and dolomitic limestone. The Cambrian Jiulong Group is mainly composed of thin-bedded limestone, wormkalk, oolitic limestone, bioclastic limestone and argillaceous dolomite, intercalated with shale in some region. The strata above the unconformity plane are gently inclined to the surrounding center on the Yanshanian intermediate-acidic complexes (dip angle <15°). Far from the intrusion, the attitude of stratum tends to horizontal, showing the characteristics of a dome structure (Gu et al., 2008a).

There are a total of 14 layers of ores in this deposit. All of them are produced in the contact zones of Yanshanian intermediate-acidic complexes and Neoproterozoic–Cambrian wallrock, in which two layers of ores are produced on the unconformity surface of Archean basement and in the Neoproterozoic strata, and 12 layers of ores occur in the Cambrian strata (Fig. 3A; Gu et al., 2008a). The outputs of ore-bodies are controlled by the contact zone between intrusion and wall rock and the tectonic weak zone in the Neoproterozoic–Cambrian wall rock (unconformity surface, interlayer fractured zone, and decollement zone). The shapes of ore-bodies are variable, including bedded-, lenticular- or irregular-shapes (Fig. 3B and C). Generally, the ore-bodies are 140–200 m long on the direction of strike, and are 100–150 m on the direction of dip; their thicknesses range from 0.5 to 11.6 m. The average grade of ore body: Au 1–5 g/t, Cu 0.5–0.8%, TFe 27–33% (Gu et al., 2008a).

The ores are mainly with massive, disseminated, vein-stockwork shaped, banded and brecciated textures (Fig. 4). The meta-somatic relic, poikilitic, skeletal and pseudomorph textures are less common. Magnetite is abundant and it occurs as massive bodies or vein-stockworks cementing fragments of anhedral to subhedral garnet and diopside. Chalcopyrite occurs as disseminations or as veinlets accompanying with quartz. Banded ore with alternating bands composed of anhedral to subhedral garnet and epidote (Fig. 4A). The brecciated ores are pervasively developed, that is, later quartz and sulfide veinlets often cut early skarn minerals and magnetite, indicating that the Cu mineralization occurred later than the deposition of the skarn and magnetite (Fig. 4B–E). The latter assemblage (quartz + sulfide) is then broken and cemented by later quartz and calcite (Fig. 4C–E). The native Au is mostly associated with quartz and sulfide (Fig. 4F). According to the mineral paragenesis and interspersed relationship between veins, the mineralization process can be divided into four stages: the anhydrous skarn stage (I, garnet + diopside), the hydrous skarn-magnetite stage (II, epidote + magnetite + specularite ± tremolite ± actinolite ± quartz), the quartz-sulfide stage (III, quartz + chalcopyrite + pyrite + native gold ± chlorite), and the carbonate stage (IV, calcite ± quartz).

Wall-rock alteration are widely distributed in the contact zones between complexes and wall rocks, in the areas nearby the interlayer fractures, and under or above the unconformity surfaces, with the range of alteration up to 200–300 m or even more. Endoskarn and relative altered ores occur within intrusions associated with K-feldspar alteration, and consist of garnet, pyroxene and minor vesuvianite. Exoskarn typically occurs in an external zone associated with marbles or hornfels, and consists of garnet and diopside. Retrograde alteration is widely distributed in the fractured zone; it consists of quartz, calcite, chlorite and sericite, accompanied by sulfide minerals such as chalcopyrite, pyrite, bornite, and minor amounts of pyrrhotite, galena and sphalerite.

4. Characteristics of fluid Inclusions and H–O isotopes

4.1. Methods of investigation

Hydrothermal minerals of different stages from drill holes and tunnels were selected for thermometric analysis. The microthermometric studies were carried out in the fluid inclusion laboratory at Chengdu University of Technology. The phase transitions of the fluid inclusions were observed at temperatures from −196 °C to 600 °C using a Linkham THMSG-600 heating/freezing stage. Temperature measurement is accurate to ±0.1 °C at −22 °C and the error increases gradually to ±2 °C at 400 °C relative to standard material. Temperatures were controlled at 20 °C/min during heating or freezing process, and less than 4 °C/min near the phase transition point.

Certain inclusion constituents were determined using a Renishaw Invia Reflex-type confocal Laser Raman microspectrometry (LRM) in the fluid inclusion laboratory at China University of Geosciences (Beijing). The test conditions: 514.5 nm light of an argon–ion laser, 20 mW laser power, 7 mW laser power at sample surface, 1800 grooves/mm grating, spectral resolution of 2 cm⁻¹, spatial resolution of 1 μm (×100 lens), 60 s scan time, scan range of 0–4000 cm⁻¹. The wavenumber accuracy was ±1 cm⁻¹.

The H–O isotopes were analyzed in the stable isotope laboratory of Mineral Resources Institute, Chinese Academy of Geological Sciences, using the methods of (Clayton and Mayeda, 1963) in a Finnigan MAT253-type mass spectrometer. Oxygen gas was produced by quantitatively reacting the samples with BrF₅ in externally heated nickel reaction vessels. Hydrogen was determined by quantitatively reacting the H₂O with zinc at temperature of 550 °C. The results adopted the SMOW as their standards, with a precision of ±2‰ for δD and ±0.2‰ for δ¹⁸O.

4.2. Characteristics of primary fluid inclusion

Representative host minerals including garnet (Stage I), diopside (Stage I), epidote (Stage II), quartz (Stage III) and calcite (Stage
IV) of four stages were selected for analysis. These host minerals contain both primary and secondary fluid inclusions. The fluid inclusions are usually small in diameter, generally ranging from 5 to 10 μm, with a minimum size of <1 μm and maximum size of 25–30 μm. Various shapes of inclusions include negative crystal shaped, spheroidal, ellipsoidal, elongate, square, rectangular and

![Sketch geological map showing the relationship between strata and ore bodies in the Yinan Au–Cu–Fe ore deposit.](image)
irregular. Only primary inclusions are chosen to analyze and discuss in the following text.

Based on the components and phase transitions characteristic of inclusions at room temperature (25°C), several types of fluid inclusions have been identified, including abundant vapor- or liquid-rich two-phase aqueous inclusions (V + L), daughter mineral-bearing multiphase inclusions (S + V + L), CO2–H2O inclusions (CO2 + V + L), and less abundant liquid inclusions (L), vapor inclusions (V), possibly melt inclusions (M) (Figs. 5 and 6). The combinations of inclusions are different in various hydrothermal minerals. The inclusions in garnet (Stage I) are mainly V + L type inclusions, and occasionally S + V + L, M and L type inclusions. The inclusions in diopside (Stage I) are mainly V + L and S + V + L type inclusions (opales, halite and sylvite), and occasionally M and L type inclusions. The inclusions in epidote (Stage II) are mainly V + L and opaque-bearing S + V + L type inclusions, followed by transparent minerals-bearing (halite) S + V + L type inclusions, and occasionally V and M type inclusions. Some M type inclusions also occasionally occur in the coexisting quartz (Stage II). The inclusions in Stage III quartz are various, including V + L, S + V + L, CO2 + V + L, L and V type inclusions. The inclusions in calcite (Stage IV) are mainly V + L type inclusions, and the next are L type inclusions. Inclusions in Stages II and IV quartz veinlets are too small to be chosen for micro-thermometric analysis.

It is clear from the inclusion analysis that vapor–liquid two-phase aqueous inclusions are the most widely distributed. Their vapor–liquid ratios (vapor filling degrees) vary from 1% to 75% and usually are in the range of 5–35%. Their main components are composed of H2O, with significant amounts of CO2 and a small amount of CH4 (Fig. 6A, B and D). CO2–H2O inclusions are composed of vapor CO2, liquid CO2 and H2O. The CO2 (mainly vapor CO2) phase accounts for 10–90% of the total volume of inclusions.

Fig. 4. Typical ores and mineral association in the Yinan Au–Cu–Fe deposit. (A) Banded garnet–epidote–magnetite ore, underground exposure; (B) Au-bearing magnetite–chalcopyrite ore; (C) fractured garnet–magnetite ore cemented by chalcopyrite and crosscut by later calcite veins; (D) magnetite fractured and cemented by quartz and calcite, which both crosscut by later calcite veinlets; (E) fragments of chalcopyrite with scattered garnet and magnetite ore is cemented by quartz; (F) Anhedral native gold at the margin of pyrite or between pyrite and quartz, reflected light, single nicol. Gr-garnet, Ep-epidote, Mt-magnetite, Cpy-chalcopyrite, Py-pyrite, Au-native gold, Qz-quartz, Cal-calcite.
Fig. 5. Typical fluid inclusions in the Yinan Au–Cu–Fe deposit. (A) Melt inclusions in garnet; (B) multiphase inclusions with different daughter minerals in diopside (Di); (C) vapor–liquid two-phase inclusions in epidote; (D) vapor-rich inclusions in quartz; (E) liquid-rich inclusions in calcite; (F) coexistence of vapor-, liquid-rich two-phase inclusions with opaque-bearing three-phase inclusions in diopside; (G) multiphase inclusions with two bubbles and different daughter minerals in diopside; (H) multiphase inclusions with different daughter minerals in diopside; (I) CO₂–H₂O inclusions, vapor–liquid two-phase inclusions and liquid inclusions in quartz; (J) coexistence of two-phase inclusions of various vapor/liquid ratios with halite-bearing three-phase inclusions in quartz; (K) multiphase inclusions with different daughter minerals in quartz; (L) coexistence of melt inclusions with halite-, sylvite-, opaque- or rod crystal-bearing multiphase inclusions and vapor–liquid two-phase inclusions; (M) coexistence of melt inclusions with halite-bearing multiphase inclusions in quartz, two-phase inclusions with various vapor/liquid ratios, and vapor inclusions. M-melt, V-vapor, L-liquid H₂O, VCO₂-vapor CO₂, LCO₂-liquid CO₂, H-halite crystal, Ht-hematite crystal, O-opaque crystal, Sy-sylvite crystal, R-rod crystal.
Daughter mineral-bearing multiphase inclusions contain liquid, vapor and solid phases, of which the vapor bubble occupies 5–10% of the cavity volume and solid minerals account for 3–20% of the inclusion volume. Their liquid and vapor phase are mainly H2O identified by laser Raman. There are two types of daughter minerals: transparent and opaque. The cubic halite is by far the most common solid phase, accompanied by minor equant to anhedral sylvite (Fig. 5). The opaque are difficult to analyze by laser Raman, only the hematite and fahlore (tetrahedrite) (Fa) were identified (Fig. 6E and F). Hematite (Ht) was readily recognized by their red color, and its Raman spectra is consistent with the hematite Raman shift near two A1g modes (225 and 498 cm−1) and five Eg modes (247, 293, 299, 412 and 613 cm−1) (de Faria et al., 1997). The micro-Raman spectra of fahlore occurs between 200 and 400 cm−1. Fitting of the spectrum occurs near 325 and 352 cm−1, and the appearance of the spectra change (near 382 cm−1) may be related to the Sb/(Sb + As) (Mernagh and Trudu, 1993; Kharbish et al., 2007). The host mineral of fahlore is diopside (Di) (stage I) whose Raman shift is near 667 and 1012 cm−1 (Xu et al., 1996) (Fig. 6). It cannot exclude the possibility that there exist other opaque like chalcopyrite and magnetite according to the petrographic observation. Melt inclusions occasionally occur in the garnet, diopside, epidote and quartz, being composed of several silicate daughter minerals and bubbles. The silicate daughter minerals have different interference colors from the ones of host minerals under the orthogonal polarizing microscope, and there was no phase change when they underwent heating up to 600 °C.

It is worth noticing that there are different types of inclusions that appear to be coeval in the same domain of the diopside (Stage I), epidote (Stage II) and quartz (Stage III) under the microscope. In the quartz, the vapor–liquid two-phase aqueous inclusions with various vapor/liquid ratios (from <10% to >65%) commonly coexist with simultaneously trapped other types of inclusions, showing the characteristics of boiling (immiscibility).

4.3. Homogenization temperature and salinity

Micro-thermometric analysis was performed principally on primary fluid inclusions in the hydrothermal minerals representing different mineralization stages. Two common thermometric procedures, freezing and heating, were employed to determine the homogenization temperatures (th), melting temperatures of CO2 clathrate (tmcl) and approximate salinities (NaCl eq) in wt.% respectively. Last ice melting temperatures (tice), daughter homogenization temperatures (tm) or melting temperatures of CO2 clathrate (tmcl) were measured to calculate salinities according to the formula proposed by Potter et al. (1978), Collins (1979), Hall et al. (1988) and Bodnar (1993). A summary of data is presented in Table 1 and Fig. 7.

The homogenization temperatures of inclusions in garnet (Stage I) vary from 427 to 549 °C, with an average of 487 °C. The ones in diopside (Stage I) vary between 369–484 °C, with an average of 433 °C. The eΘw of fluid inclusions in Stage I minerals were not listed owing to the possibility of large error. The salinity of one halite-
bearing inclusion is 56.7% NaCl eq in the garnet. While the salinity of nine halite-bearing inclusions is 49.6–70.2% NaCl eq in the diopside (average 56.3% NaCl eq). Sometimes sudden movements of bubbles were occasionally observed between 18 and 30 °C in the diopside and could indicate small quantities of CO2 according to Hedenquist and Henley (1985).

The ones in epidote (Stage II) vary between 290 °C and 438 °C, with an average of 368 °C. The $t_{\text{ice}}$ of the vapor–liquid two-phase fluid inclusions change in the range of −21.1 °C to −6.4 °C, and the calculated salinity data are 9.7–21.3% NaCl eq (average 18.1% NaCl eq). The salinity of two halite-bearing inclusions is 52.0–53.5% NaCl eq (average 52.9% NaCl eq).

The ones in quartz (Stage III) range between 130 °C and 335 °C, with most of 150–300 °C and an average of 226 °C. The $t_{\text{ice}}$ of V + L fluid inclusions change in the range of −13.5 °C to −4.0 °C and the calculated salinity data are 6.5–17.3% NaCl eq (average 11.7% NaCl eq). The salinity of 23 S + V + L inclusions is 41.5–57.1% NaCl eq (average 47.8% NaCl eq). The $t_{\text{incl}}$ of CO2 + V + L inclusions are within the range 4.7–6.9 °C, and the calculated salinity is approximately 5.9–9.4% NaCl eq (average 8.1% NaCl eq). It is equal to the estimated salinity using $t_{\text{ice}}$ of vapor–liquid aqueous inclusions (Table 1).

During the freezing–heating process, a small amount of incipient melting of the liquid–vapor two-phase fluid inclusions in quartz can be observed. The first (eutectic) melting temperatures are in the range of −31.2 °C to −27.5 °C, which are lower than the standard eutectic point (−26.8 °C) in the pure H2O–NaCl system. Low eutectic temperatures suggest that the hydrothermal fluids are polysaline and multi-cation (K+, Ca2+, Mg2+) in addition to the Na+ (Ruano et al., 2002; Lu et al., 2004). The first eutectic melting temperature of CO2 clathrate melting.

Table 1
Microthermometric and salinity data of fluid inclusions from the Yinian Au–Cu–Fe deposit.

<table>
<thead>
<tr>
<th>Host mineral/mineralization stage</th>
<th>Inclusion types</th>
<th>Homogenization temperature ($t_{\text{hom}}$/°C)</th>
<th>Last ice melting temperatures ($t_{\text{fcl}}$/°C)</th>
<th>Melting temperature of halite ($t_{\text{tmcl}}$/°C)</th>
<th>Salinity w (NaCl eq)%</th>
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</thead>
<tbody>
<tr>
<td>Garnet/I</td>
<td>V-L</td>
<td>427–549 (32)</td>
<td>487</td>
<td>477</td>
<td>56.7 (1)</td>
</tr>
<tr>
<td>Diopside/I</td>
<td>S-V-L</td>
<td>421 (1)</td>
<td>421</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epidote/II</td>
<td>V-L</td>
<td>369–484 (23)</td>
<td>433</td>
<td>419–574 (9)</td>
<td>49.6–70.2 (9)</td>
</tr>
<tr>
<td>Quartz/III</td>
<td>S-V-L</td>
<td>190–515 (9)</td>
<td>442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite/IV</td>
<td>V-L</td>
<td>290–438 (30)</td>
<td>368</td>
<td>440–452 (2)</td>
<td>52.0–53.5 (2)</td>
</tr>
</tbody>
</table>

Note: V-L refers to the vapor–liquid two-phase brine inclusions. S-V-L means the halite-bearing multiphase inclusions; f: the anhydrous skarn stage, II: the hydrous skarn-magnetite stage; III: the quartz-sulfide stage, IV: the carbonate stage. $t_{\text{fcl}}$: Temperature of CO2 homogenization; $t_{\text{fmcl}}$: temperature of CO2 clathrate melting.

example with 11.6‰ value. The oxygen isotopes still have the characteristics of magmatic fluid generally. The δD_{H2O} values are low and within the range of −112‰ to −82‰. The wide range may record the degassing of parent magma chamber, as this isotopic fractionation results in lighter δD values of magmatic water (Suzuki and Epstein, 1976). The data are also similar to the H–O isotopic compositions (δD −110‰ to −65‰, δ^{18}O 6.0–9.0‰) of initial mixing magmatic water in the granite of Au–Cu and Fe–Co series defined by Zhang (1985), indicating the ore-forming fluids at this stage are still dominated by the magmatic water, but the possibility of mixing with a minor amount of meteoric water cannot be ruled out. According to Zhang (1985), the initial mixing magmatic water refers to the magmatic water exsolved out by the initial magma which is formed by the anataxis of crust affected by the
interaction with surface water (atmospheric water, sea water). It leaches/exchanges the (sub-) solidified rocks and forms ore-bearing rebalanced-mixing magmatic hydrothermal fluids (Zhang, 1985). The rebalanced mixing magmatic water is usually rich in D compared with the initial mixing magmatic water. Therefore, there is a relatively large variation on the δD/H2O values of magnetite and specularite precipitated from the initial- and rebalanced-mixing magmatic hydrothermal fluids. Until the quartz-sulfide stage (III) and the carbonate stage (IV), the δD/H2O values (−87‰ to −67‰) of ore-forming fluids still remain the characteristics of magmatic water. However, the δ18O/H2O values (−2.9‰ to −0.4‰) are significantly low, showing the hydrothermal characteristics of meteoric water with the δ18O drift. All the above-mentioned features indicate the ore-forming fluids in this stage were from magmatic water mixed with meteoric water.

The hydrogen and oxygen isotopic compositions of the hydrothermal minerals from the Yinan deposit reflect the complexity of the ore-forming process about the skarn deposits to a certain extent. However, the above characteristics are consistent with the general laws of typical skarn-type Cu–Au deposits whose ore-forming fluids are dominated by magmatic water at the early stage and mixed with the meteoric water during the late stage (Table 2, Fig. 7). For example, the δ18O/H2O values of ore-forming fluids range between 7.6‰ and 12.9‰, and the δD/H2O values range between −63‰ and −54‰ in the US Elkhorn skarn-type gold deposit during the early skarn stages (Bowman et al., 1985). In the Mashan Au–S deposit in Tongling, Anhui Province, the δ18O/H2O values are 6.9–10.7‰, and the δD/H2O values are −69‰ to −62‰ in quartz (Stage II) of the skarn stage in the Yinan Au–Cu–Fe deposit, after Qiu et al. (1996). In the Mashan Au–S deposit in Tongling, Anhui Province, the δ18O/H2O values are 6.9–10.7‰, and the δD/H2O values are −69‰ to −62‰ in the quartz-sulfide stage (Tian et al., 2005), indicating that the hydrothermal fluids of these two above-mentioned deposits are dominated in magmatic water without or with very small amount of meteoric water during the forming process of skarn and ore bodies. In the Xiaotongguanshan Cu–Au deposit, Tongling, from 5.1‰ to 10.7‰ at the early skarn stage, the δ18O/H2O values of ore-forming fluids are downgraded as 0.8–5.1‰ at the late quartz-sulfide and carbonate stages, showing that the ore-forming fluids are dominated by magmatic water at an early stage, whereas meteoric water entered the mineralizing system at a late stage (Tian et al., 2005). The hydrogen and oxygen isotopic compositions (δ18O 2.7–9.2‰, δD −102‰ to −76‰) of fluid inclusion water in quartz from the Copper Canyon Cu–Au deposits, United States, suggest that the ore-bearing fluids are most likely composed of magmatic water that had mixed with some meteoric water during mineralization (Batchelder, 1977).

### Table 2

<table>
<thead>
<tr>
<th>Sample no./deposit</th>
<th>Mineral/mineralization stage</th>
<th>δ18O (%)</th>
<th>δD/H2O (%)</th>
<th>δ18O/H2O (%)</th>
<th>T (°C)</th>
<th>Data source</th>
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<td>KG16-9</td>
<td>Garnet/I</td>
<td>5.4</td>
<td>−73</td>
<td>6.8</td>
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<td>KS10-12</td>
<td>Magnetite/II</td>
<td>4.6</td>
<td>−107</td>
<td>8.3</td>
<td>340</td>
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<td>MW280-B1</td>
<td>Magnetite/II</td>
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<td>−112</td>
<td>8</td>
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<tr>
<td>KG16-9</td>
<td>Specularite/II</td>
<td>2.2</td>
<td>−82</td>
<td>7.9</td>
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<tr>
<td>KS10-2</td>
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<td>6</td>
<td>−84</td>
<td>11.6</td>
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</tr>
<tr>
<td>5</td>
<td>Quartz/III</td>
<td>8.1</td>
<td>−87</td>
<td>−0.4</td>
<td>260</td>
<td>Tian et al. (1996)</td>
</tr>
<tr>
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<td>10.55</td>
<td>−72</td>
<td>−2.9</td>
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<tr>
<td>S10-8</td>
<td>Calcite/IV</td>
<td>12.7</td>
<td>−67</td>
<td>−2.4</td>
<td>120</td>
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</tr>
<tr>
<td>Xiaotongguanshan Cu–Au deposits in Tongling</td>
<td>Garnet etc./I</td>
<td>7.0–15.4</td>
<td>−50 to −108</td>
<td>5.1–10.7</td>
<td>260–720</td>
<td>Tian et al. (2005)</td>
</tr>
<tr>
<td></td>
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<td>13.5–15.9</td>
<td>350–400</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Quartz, Calcite/III</td>
<td>14.6–17.4</td>
<td>−54 to −63</td>
<td>2.0–5.1</td>
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<td></td>
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<td></td>
<td>Calcite/IV</td>
<td>13.4–13.5</td>
<td>−77</td>
<td>0.8–0.9</td>
<td>150</td>
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</tr>
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<td>Elkhorn gold deposit in America</td>
<td>Skarn/II, II</td>
<td>−63 to −54</td>
<td>7.6–12.9</td>
<td>525</td>
<td>Bowman et al. (1985)</td>
<td></td>
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<tr>
<td>Copper Canyon Cu–Au deposits in America</td>
<td>Quartz/III</td>
<td>11.3–15.1</td>
<td>−102 to −76</td>
<td>2.7–9.2</td>
<td>280–395</td>
<td>Batchelder (1977)</td>
</tr>
</tbody>
</table>

**Note:** The calcite samples are tested by Analysis and Testing Center of Beijing Institute of Geology Research, Nuclear Industry, and the other sample analysis is carried out by Mineral Resources Institute of Chinese Academy of Geological Sciences; the ′ t′ refers to the average homogenization temperatures of fluid inclusions.

*a* Refers to stable isotope data of other skarns for comparison.

![Fig. 8. Plot of δD vs δ18O for the ore-forming fluids in the Yinan Au–Cu–Fe deposit.](image)

5.2. Immiscibility and mineralization

Melt inclusions are the magmatic droplets (silicate melts) captured by various types of igneous minerals during their forming process. As the host minerals cool, they quenched and condensed into glass, or further crystallized to an assemblage of silicate daughter minerals and fluid phases (liquid- and vapor-phases). Within garnet, diopside and epidote, occasionally in paragenetic quartz (Stage II) of the skarn stage in the Yinan Au–Cu–Fe deposit, the melt inclusions composed of felsic solids and vapors had no phase changes when being heated to 600 °C, indicating that they were captured in the high-temperature magmatic melts. Interestingly, these melt inclusions often coexisted with the vapor- or liquid-rich two-phase aqueous inclusions of various vapor–liquid ratios and daughter minerals-bearing multiphase inclusions, even coexisting within the same tiny view (Fig. 5L and M). Meanwhile, there is no petrographic evidence to demonstrate that they were captured in the different stages. Thus, the above-mentioned phe-
nomenon implies an immiscible state coexisting of melt and fluid (Roedder and Combs, 1967). The calculated salinities of the coexisting hypersaline inclusions in diopside are up to 70.2 wt.% NaCl_eq, implying a magmatic origin (Harris et al., 2003). There are no melt inclusions in the post-skarn stages (the quartz-sulfide stage and the carbonate stage). The above facts further emphasize the genetic relationship between mineralization and magmatism. That is, the ore-forming fluids came from gas–water hydrothermal fluids exsolved by the magmas; the diagenesis and the mineralization experienced the evolution of melt ➔ melt + fluid ➔ fluid. It is usually considered that, with the crystallization of silicate minerals and a progressive decrease of temperature and pressure during the magma evolution, the volatile/silicate melt ratio gradually increases. When the volatiles reach the supersaturation, immiscibility occurs, forming the volatile-rich, high-salinity hydrothermal fluids and the residual silicate melts. At this point, the melt and fluid were trapped by crystallizing minerals simultaneously. Previous literatures have also shown that, silicate melts and multiphase salt-rich inclusions are interpreted as having originally formed as immiscible phases at magmatic temperatures during the magmatic–hydrothermal transition stage (Kamenetsky et al., 1999).

There into, volatile-rich highly saline hydrothermal fluids represented by the salt-rich inclusions are effective in scavenging ore-forming components from magmas (Candela, 1989), and have the potential to transport metals (Davidson and Kamenetsky, 2001). They are often the main contributors of hydrothermal fluids and metals in the ensuing skarn- and/or porphyry-mineralization systems (Eastoe, 1978; Candela, 1989; Bodnar, 1995; Meinert et al., 1997, 2003; Hedenquist et al., 1998; Kamenetsky et al., 1999; Harris et al., 2003). The wide occurrence of salts-rich, opaque-bearing (magnetite, chalcopyrite) multiphase fluid inclusions in diopside implies that the fluids are exsolved from the magma at elevated temperature during the early skarn stage (Campos et al., 2002), confirming the important role of the magmatic hydrothermal fluids mentioned above.

There is another kind of immiscibility widely spread in the Yinan Au–Fe–Cu deposit. As already noted, the boiling inclusions are developed in the diopside (Stage I), epidote (Stage II) and quartz (Stage III), particularly prevalent in quartz. In the same zone of one mineral, the aqueous fluid inclusions with various vapor/liquid ratios (from <10% to >65%) commonly coexist with liquid inclusions, vapor inclusions, daughter minerals-bearing multiphase inclusions and CO2–H2O inclusions trapped simultaneously. Petrographic observations show that they are primary inclusions and have similar homogenization temperatures. However, the salinity of vapor–liquid two-phase aqueous fluid inclusions is very different from the one of the paragenetic daughter minerals-bearing multiphase inclusions (varies in the range of 9.7–23.1% NaCl_eq and 52.0–53.5% NaCl_eq in epidote, 6.5–17.3% NaCl_eq and 41.5–57.1% NaCl_eq in quartz, respectively), indicating that they were captured in different fluids with dissimilar nature, namely, one is the low-salinity and low-density fluid, while the other is high-salinity and high-density fluid. This is interpreted as evidence for boiling (immiscibility) (Lu et al., 2004). Sometimes, in some vapor–liquid two-phase inclusions with medium vapor/liquid ratios (40–60%), there was no obvious change of the bubbles being heated above 400°C, indicating that they were captured in the heterogeneous fluid phase (liquid-phase + vapor-phase) at the boiling state. Petrographic observation and micro-thermometric analysis reveal that, the boiling occurred in a wide range of temperatures from 130°C to 430°C, and most of the temperatures were concentrated in the range of 190–280°C at the quartz-sulfide stage.

Serving as one of the main ways of natural fluid immiscibility, boiling of ore-forming fluids is considered as an important mechanism in the metal precipitation and enrichment in many hydrothermal deposits (Roedder, 1984; Reed and Spycher, 1985; Logan, 2000; Shen et al., 2000, 2001; Yao et al., 2001; Ruano et al., 2002; Gu et al., 2003; Calagari, 2004; Zhou et al., 2007). Speciation and reaction progress calculations confirm that boiling would be a more efficient depositional mechanism than cooling or mixing of the ore fluid with groundwater (Graney et al., 1991). Due to boiling, the vapor-phase H2O, as well as H2S, CO2, HCl and other acidic components is constantly escaping from the original homogeneous fluid phases. The increasing pH values and the decreasing temperatures will promote the instability of metal complexes and lead to the precipitation of metal oxides (magnetite), sulfides (chalcopyrite, pyrite) and native gold (Reed and Spycher, 1985):

\[
\begin{align*}
3\text{Fe}^{2+} + 4\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_4 (magnetite) + 6\text{H}^+ + \text{H}_2 \\
\text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{HS}^- & \rightarrow \text{CuFeS}_2 (chalcopyrite) + 2\text{H}^+ \\
\text{Fe}^{2+} + 2\text{HS}^- & \rightarrow \text{FeS}_2 (pyrite) + 2\text{H}^+ \\
\text{Au(HS)}^2_2 + \text{H}^+ + 0.5\text{H}_2\text{O} & \rightarrow \text{Au} (\text{native gold}) + 2\text{H}_2\text{S}
\end{align*}
\]

The opaque-bearing (magnetite, chalcopyrite) multiphase fluid inclusions abound in epidote and quartz indicating that the boiling was the main mechanism leading to the precipitation of metallic minerals. It is generally accepted that boiling is mainly caused by the sudden pressure decrease (lithostatic pressure converts into hydrostatic pressure). The rapid pressure release is either related to fracturing or resulted from the hydrofracturing occurring when the fluid pressure exceeds the resistance of overlying rocks. Therefore, in addition to the micro-geological evidences (occurrence of plenty of boiling fluid inclusions), lots of brecciated structures often developed in the ore deposit are the macro-geological marks of the boiling fluids. During the hydrous skarn-magnetite stage (II) and the quartz-sulfide stage (III) in the Yinan deposit, early fractured skarn minerals and magnetite are often cemented by later quartz and sulfide, and then the latter are broken and cemented by later quartz, calcite (Fig. 4C–E). Meanwhile, there is also breccia-type ore developed on the edge of the intrusion in somewhere. All these are important characterization of mineralizing fluid boils.

Multiple boiling events are well characterized by the occurrence of multistage brecciated ores and wide range of boiling temperatures (Roedder, 1971; Willian and Nash, 1974; Calagari, 2004). At the beginning of each shattering event, fluid inclusions were trapped with relatively low salinity (unsaturated). As the boiling process continued, the liquid phase became increasingly more saline. Hence, successive generations of halite-bearing inclusions were trapped. Fractures or hydraulic fractures were healed by the precipitation of quartz and sulfides. As a result of choking of the fluid conduits, permeability was reduced and the ascending fluids experienced lithostatic pressure once again. By rising internal pressure of the fluid, another episode of shattering and concomitant release of fluid and boiling took place.

In summary, we believe that there may have been two different kinds of immiscibility during the whole evolution process from the magmatic crystallization differentiation to hydrothermal mineralization in the Yinan Au–Cu–Fe deposit. The early immiscibility of magma melt and the vapor–liquid phase fluids led to the unmixing and separation of ore-bearing water–gas hydrothermal fluids; while the later immiscibility (boiling) of vapor- and liquid-components resulted in the precipitation and enrichment of gold, copper and iron.

6. Conclusion

The Yinan Au–Cu–Fe deposit is a typical skarn deposit produced in the contact zone between the Yanshanian intermediate-acidic intrusive rocks and the Neoproterozoic–Cambrian strata. H–O isotope studies have shown that, the ore-forming fluids of early unhydrothermally altered skarn stage (I) and hydrous skarn-magnetite stage (II) were mainly
derived from magmatic water; while late quartz-sulfide stage (III) and carbonate stage (IV) indicated the fluids were dominantly magmatic origin with a component of meteoric water. The fluid inclusion studies have shown that, the early skarn minerals were formed from an immiscible mixture of silicate melt and vapor–liquid phase fluids. This immiscibility directly led to the ore-bearing gas–water hydrothermal fluids separating out from the magmatic system, laying the material foundation for the later hydrothermal mineralization; at the later hydrothermal stage, the immiscibility (boiling) occurred in ore-forming fluids as an indicator of the vapor and liquid phase separation. Furthermore, the decompression and boiling may occur repeatedly, thus resulting in a large number of precipitations and enrichment of gold, copper and iron.

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