



Geological and Fluid Inclusion Constraints on Gold Deposition Processes of the Dayingezhuang Gold Deposit, Jiaodong Peninsula, China

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Abstract: The Dayingezhuang gold deposit, hosted mainly by Late Jurassic granitoids on Jiaodong Peninsula in eastern China, contains an estimated 170 t of gold and is one of the largest deposits within the Zhaoping fracture zone. The orebodies consist of auriferous altered pyrite–sericite–quartz granites that show Jiaojia-type (i.e., disseminated and veinlet) mineralization. Mineralization and alteration are structurally controlled by the NE- to NNE-striking Linglong detachment fault. The mineralization can be divided into four stages: (K-feldspar)–pyrite–sericite–quartz, quartz–gold–pyrite, quartz–gold–polymetallic sulfide, and quartz–carbonate, with the majority of the gold being produced in the second and third stages. Based on a combination of petrography, microthermometry, and laser Raman spectroscopy, three types of fluid inclusion were identified in the vein minerals: NaCl–H₂O (A-type), CO₂–H₂O–NaCl (AC-type), and pure CO₂ (PC-type). Quartz crystals in veinlets that formed during the first stage contain mainly AC-type fluid inclusions, with rare PC-type inclusions. These fluid inclusions homogenize at temperatures of 251°C–403°C and have low salinities of 2.2–9.4 wt% NaCl equivalent. Quartz crystals that formed in the second and third stages contain all three types of fluid inclusions, with total homogenization temperatures of 216°C–339°C and salinities of 1.8–13.8 wt% NaCl equivalent for the second stage and homogenization temperatures of 195°C–321°C and salinities of 1.4–13.3 wt% NaCl equivalent for the third stage. In contrast, quartz crystals that formed in the fourth stage contains mainly A-type fluid inclusions, with minor occurrences of AC-type inclusions; these inclusions have homogenization temperatures of 106°C–287°C and salinities of 0.5–7.7 wt% NaCl equivalent. Gold in the ore-forming fluids may have changed from Au(HS)⁰ as the dominant species under acidic conditions and at relatively high temperatures and *f*O₂ in the early stages, to Au(HS)²⁻ under neutral-pH conditions at lower temperatures and *f*O₂ in the later stages. The precipitation of gold and other metals is inferred to be caused by a combination of fluid immiscibility and water–rock interaction.

Key words: fluid inclusion, gold deposition, Dayingezhuang gold deposit, Jiaodong Peninsula

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1 Introduction

Jiaodong Peninsula, located in the eastern segment of the North China Craton (NCC; Fig. 1), is one of the most important gold-producing belts in China (Deng et al., 2008; Wang et al., 2015; Lei et al., 2016; Yu et al., 2016; Chai et al., 2017, 2019a, b). The belt hosts numerous gold deposits and is part of the Circum-Pacific metallogenic domain (Goldfarb et al., 2014; Hou et al., 2015). The majority of gold deposits in the region are controlled by NE-trending faults and are hosted in the contact zones between Mesozoic granitoids and Precambrian metamorphic rocks. The mineralization styles have been classified as Jiaojia-type and Linglong-type, with the former referring to a combination of disseminated and stockwork/veinlet gold mineralization, and the latter to auriferous quartz veins (Song et al., 2014, 2017; Yu et al., 2018).

Gold deposits are generally related to tectonic, geological and geochemical processes, in which the nature

of the hydrothermal fluids is of fundamental importance (Chen et al., 2007; Chai et al., 2016a, b, c). Gold mineralization in the region is generally considered to have occurred during the Early Cretaceous, with a peak age at 120±5 Ma (Zhai et al., 2004), although there are still controversies regarding the ore-forming age. Furthermore, several issues related to the nature and sources of the ore-forming fluids remain debated, and a number of hypotheses have been proposed. Initially, Zhang (1985) proposed that the ore-forming fluids were meteoric in origin. More recently, Fan et al. (2007) suggested that the ore-forming fluids originated from magmatic water, and Zeng et al. (2006) suggested that the gold mineralization resulted from magmatic–hydrothermal processes. Alternatively, the Jiaodong gold mineralization has been treated as orogenic type, and it has been proposed that the ore-forming fluids were derived from metamorphic water (Goldfarb and Santosh, 2014). In addition, because some of the orebodies within these deposits are accompanied by intermediate-mafic dikes,

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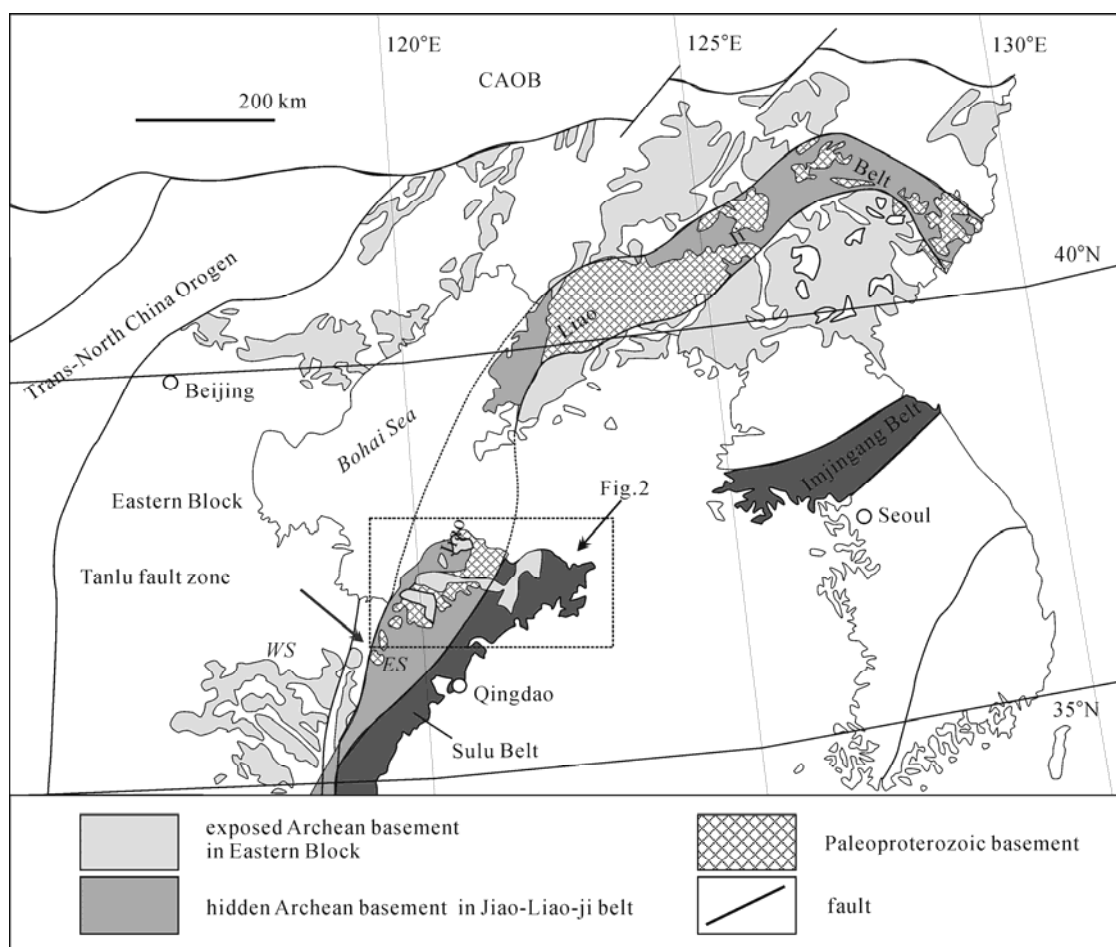


Fig. 1. Map of the Eastern Block of the North China Craton (after Li et al., 2011).

WS: Western Shandong Province; ES: Eastern Shandong Province.

therefore, the ore-forming fluids have been inferred to be derived from the mantle (Sun et al., 2001), although a combination of crustal and mantle components has also been proposed (Mao et al., 2005, 2008).

The Jiaodong gold belt is dominated by Jiaojia-type gold deposits, which make up more than 80% of its gold resources (Song et al., 2010, 2015). The Dayingezhuang deposit is a large representative Jiaojia-type gold deposit in the area, which contains a reserve of >100 t Au with an average grade of 3.10 g/t (Yang et al., 2014). Some chronological and geochemical studies have been undertaken with the aim of characterizing the nature of the Au mineralization (Dai, 2012; Guo, 1990; Jiang et al., 2012; Liu et al., 2014; Lu, 2012; Mao et al., 2005, 2008; Shen et al., 2000; Shi, 2013; Wang et al., 2010; Xu, 1999; Yang et al., 2009, 2014; Yu, 2014; Zhao, 2014). However, few studies have examined the metallogenic processes, and the mechanisms of gold transport and deposition (Yang et al., 2009), which limits our understanding of the nature of gold mineralization of the Dayingezhuang deposit. Besides, additional data are necessary to better characterize the mineralizing fluids and understand ore deposition in different stages of mineralization. In this study, based on previous geological information on the Dayingezhuang deposit, detailed petrographic,

microthermometric and Raman spectroscopic analysis for fluid inclusions contained within veinlets of different stages were conducted to examine the of gold transport and deposition mechanisms.

2 Geological Background

The North China Craton, which includes Jiaodong Peninsula, is bounded to the southeast by the Paleozoic–Triassic Qinling, Dabie, and Sulu orogenic belts, and to the north by the Central Asian Orogenic Belt (CAOB; Fig. 1). The craton consists of two Archean continental nuclei, namely the Eastern Block and Western Block, which are separated by a Paleoproterozoic orogenic belt (Zhao et al., 2001). However, unlike the majority of other Precambrian cratons worldwide, the NCC was reactivated along its margins by several younger orogenic events, and thus contains important records of secular variability in tectonics and metallogenic processes (Li et al., 2011).

Jiaodong Peninsula, located in Shandong Province, lies along the eastern margin of the Eastern Block of the NCC. It is situated within both the northeastern segment of the Qinling–Dabie–Sulu ultrahigh-pressure metamorphic zone, and the southern part of the Paleoproterozoic Jiao–Liao–Ji Belt (Figs. 1 and 2; Li et al., 2011). This region

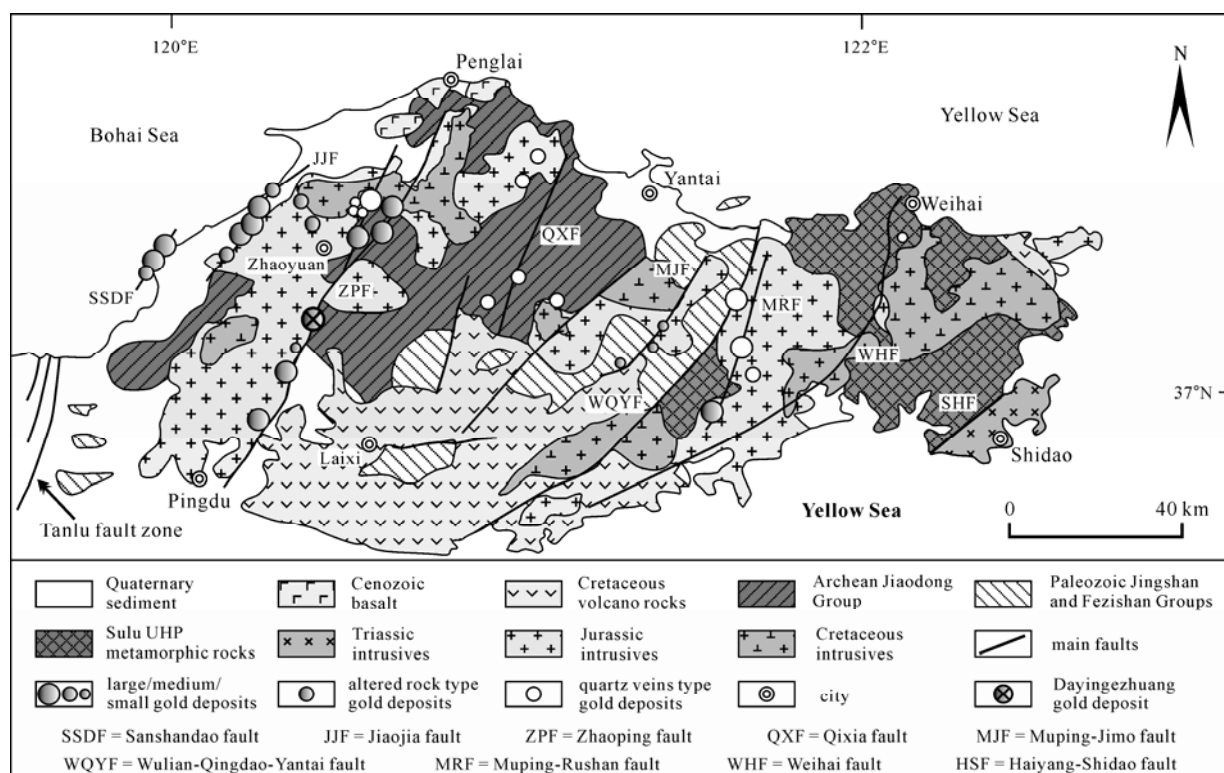


Fig. 2. Geology of the Jiaodong gold province showing locations of large (>20 t Au), medium (5–20 t Au), and small (<5 t Au) gold deposits (after Goldfarb and Santosh, 2014).

consists of two tectonic units, the Jiaobei Terrane in the west and the Sulu Terrane in the east, bordered by the Wulian–Mouping Fault (Fig. 2). The Sulu Terrane, located at the eastern edge of the Qinling–Dabie–Sulu Belt, developed along the southern side of the NCC during a period of ultrahigh-pressure metamorphism of Proterozoic rocks that was induced by collision between the Yangtze Craton and the NCC during the Late Triassic (Zhang et al., 2008).

The Jiaobei Terrane, in contrast to the Sulu Terrane, is the primary host of gold mineralization on Jiaodong Peninsula (Fig. 2). Exposed rocks in the Jiaobei Terrane include metamorphosed Precambrian basement sequences, as well as widespread Mesozoic intrusive and volcanic rocks (Fig. 2; Yu et al., 2012). The Precambrian sequences include the Neoproterozoic Jiaodong Group, the Paleoproterozoic Jingshan and Feizishan Groups, and the Neoproterozoic Penglai Group. The Jiaodong Group is characterized by widely distributed late-Archean tonalitic, trondhjemitic, and granodioritic gneisses, as well as supracrustal amphibolites and biotite-plagioclase gneisses that yield U–Pb zircon U–Pb ages of mainly between 2.9 and 2.5 Ga (Wan et al., 2012). The Jingshan and Feizishan groups contain widespread schist, marble, and amphibolite, plus minor amounts of mafic granulite. These groups yield metamorphic zircon ages of ca. 1.8 Ga and underwent amphibolite- to granulite-facies metamorphism and deformation (Wang et al., 1998). The Neoproterozoic Penglai Group, which is rarely exposed within the Jiaobei Terrane, consists mainly of marble and quartzite that were subjected to lower-greenschist facies metamorphism

(Faure et al., 2004). In addition to the above, there are numerous Mesozoic volcanic rocks and granitoids throughout the Jiaobei Terrane, including the Late Jurassic Linglong and Kunyushan batholiths, which are crustal remelting-type granitoids, and Early Cretaceous granitoids that contain a mixture of crustal and mantle components, such as the Guojialing and Weideshan plutons (Fig. 2; Zhang et al., 2006; Luo et al., 2014; Li et al., 2017). The southern part of the Jiaobei Terrane also includes a Cretaceous volcanic rock series with minor sediments, primarily within the Jiaolai Basin. Finally, a variety of dikes, including diabase, gabbro, and lamprophyre, are widespread in the area (Geng et al., 2015). The majority of these dikes strike NE–SW and are emplaced into Mesozoic granites and volcanic rocks, as well as Precambrian metamorphic rocks (Fig. 2).

The Dayingezhuang ore deposit is located in the center of the Zhaoping fracture zone at the eastern margin of the NCC, 18 km southwest of the city of Zhaoyuan in the Jiaobei Terrane (Fig. 2). The NE- to NNE-trending Zhaoping fracture zone, ~400 m wide and over 100 km long, is one of the most important structures controlling second-order ore-hosting shears and fractures in the Jiaobei Terrane (Lin et al., 2013; Tian et al., 2016). The Zhaoping fracture zone is part of the regional Tan–Lu Fault system, developed mainly at the contact between the Archean Jiaodong Group and Jurassic granites, and hosts about 50 percent of the gold deposits situated in the Jiaobei Terrane (Fig. 2). From northeast to southwest, in addition to the Dayingezhuang deposit examined in this paper, more important gold deposits in the fault zone

include the Taishang, Linglong, and Xiadian Au deposits.

The Dayingezhuang gold deposit is hosted in the Linglong detachment fault, which is part of the Zhaoping fracture zone, developed between Mesozoic intrusions and Precambrian rocks (Fig. 3). The metamorphosed Precambrian sequences (the hanging wall of the Zhaoping fracture zone) are mainly composed of the Archean Jiaodong Group with rare Proterozoic Jingshan Group, and distributed at the eastern part of the deposit area (Fig. 3). Several intrusive rocks, especially Jurassic granitoids with zircon U–Pb ages of 144–170 Ma (Wang et al., 2010; Jiang et al., 2012; Yu, 2014) occur in the western part of the mine, forming the footwall of the Linglong detachment fault (Fig. 3). Besides, many different kinds of dikes, such as diorite porphyrite (K–Ar age of 129 Ma, Guo, 1990; U–Pb age of 128.0 ± 8.5 Ma, Zhao, 2014) and aplite (K–Ar age of 114 Ma, Guo, 1990), are widespread in the deposit area. Structurally, the deposit area is characterized by the NE- to NNE-trending Linglong detachment fault, and the crosscutting NW–SE-trending high-angle post-mineralization Dayingezhuang Fault (Fig. 3). Second-order faults (ductile shear structures and brittle faults of different directions) associated with the Linglong detachment fault control the sizes, shapes and occurrences of orebodies, whereas the third-order joint fissures control the ore shoots (Wang et al., 2007). $^{40}\text{Ar}/^{39}\text{Ar}$ dating of hydrothermal sericite–muscovite gave ages from 126.8 ± 0.59 to 133.37 ± 0.56 Ma (Yang et al., 2014), suggesting that the gold mineralization of Dayingezhuang occurred in early Cretaceous.

3 Ore Deposit Geology

The Dayingezhuang deposit currently has a proven

reserve of >100 t of Au with at an average grade of 3.10 g/t (Yang et al., 2014); the total proven and estimated Au resource is 170 t of Au. Most of the orebodies are lenticular or irregular lodes. They are generally NE–SW-trending and parallel to one another, as controlled by the fault (Fig. 3). More than 90 orebodies have been identified in the deposit. The No. 2 orebody, which occurs to the north of the post-mineralization Dayingezhuang Fault (Fig. 3a), is the largest and most representative of the orebodies, containing 59% of the total proven gold reserve of the deposit. This orebody is composed of 73 ore lenses, is 930 m long and 10–30 m thick (maximum width about 100 m), dips at 18° – 51° to the SE, and has an average ore grade of 4.01 g/t Au. The No. 1 orebody, the second largest gold orebody and containing 34% of total proven gold reserve of the deposit, is composed of 18 ore lenses and situated to the southeast of the No. 2 orebody. The orebody is NE-trending and dips at 27° – 40° to the SE, with an average length of 740 m and thicknesses of 2–10 m, and an average ore grade of 4.03 g/t Au. The Dayingezhuang deposit is characterized by disseminated- and stockwork-style ores developed within altered granite, cataclastic granite and mylonitized granite. Similar to the other Jiaojia-type gold deposits in Jiaodong, auriferous quartz veins are not very well developed in this deposit.

Major ore minerals in the Dayingezhuang deposit include pyrite, galena, sphalerite, chalcopyrite (Fig. 4), along with minor magnetite, pyrrhotite and tetradymite. The gangue minerals include 80% quartz with amounts of K-feldspar, sericite, chlorite, albite, muscovite, calcite, and clay minerals. The most abundant sulfide is pyrite, which makes up $>75\%$ of the total metallic minerals. Au occurs mostly as native gold, followed by electrum. Native gold grains occur mainly in tiny fissures of pyrite,

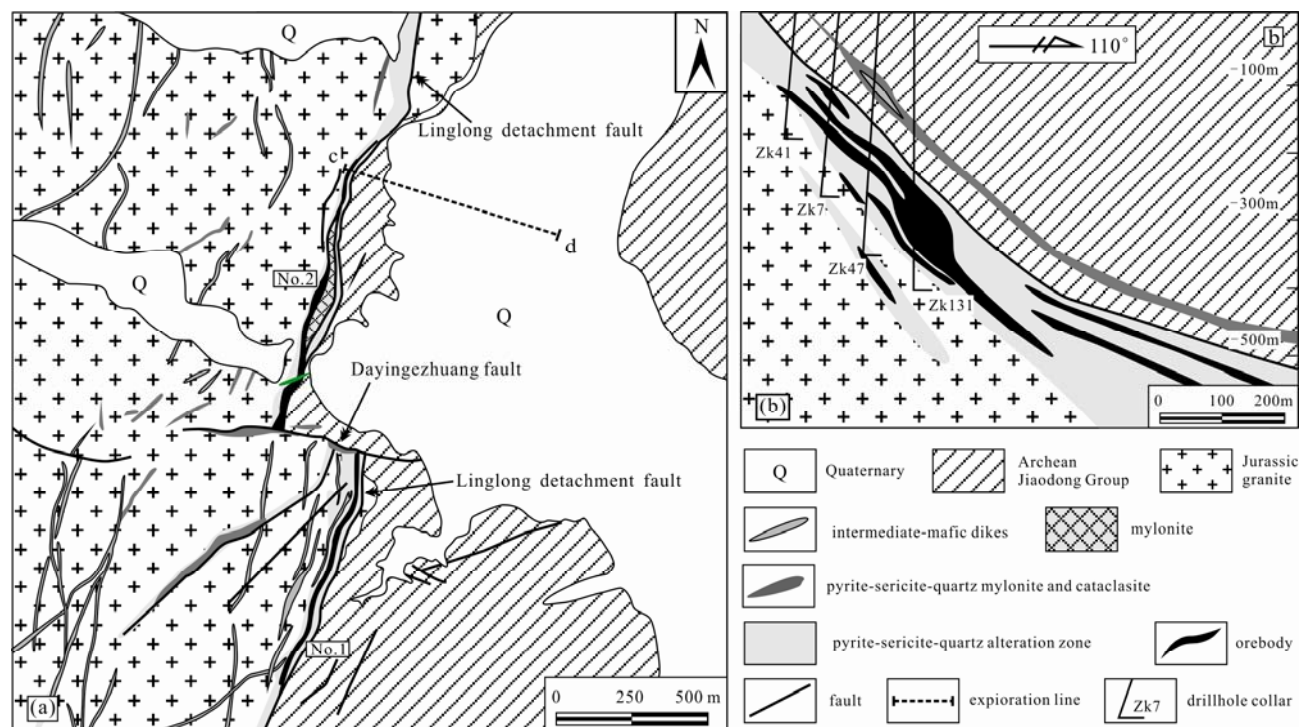


Fig. 3. (a) Geological sketch map of Dayingezhuang gold deposit; (b) Geological section of Dayingezhuang gold deposit (modified after Yang et al., 2014).

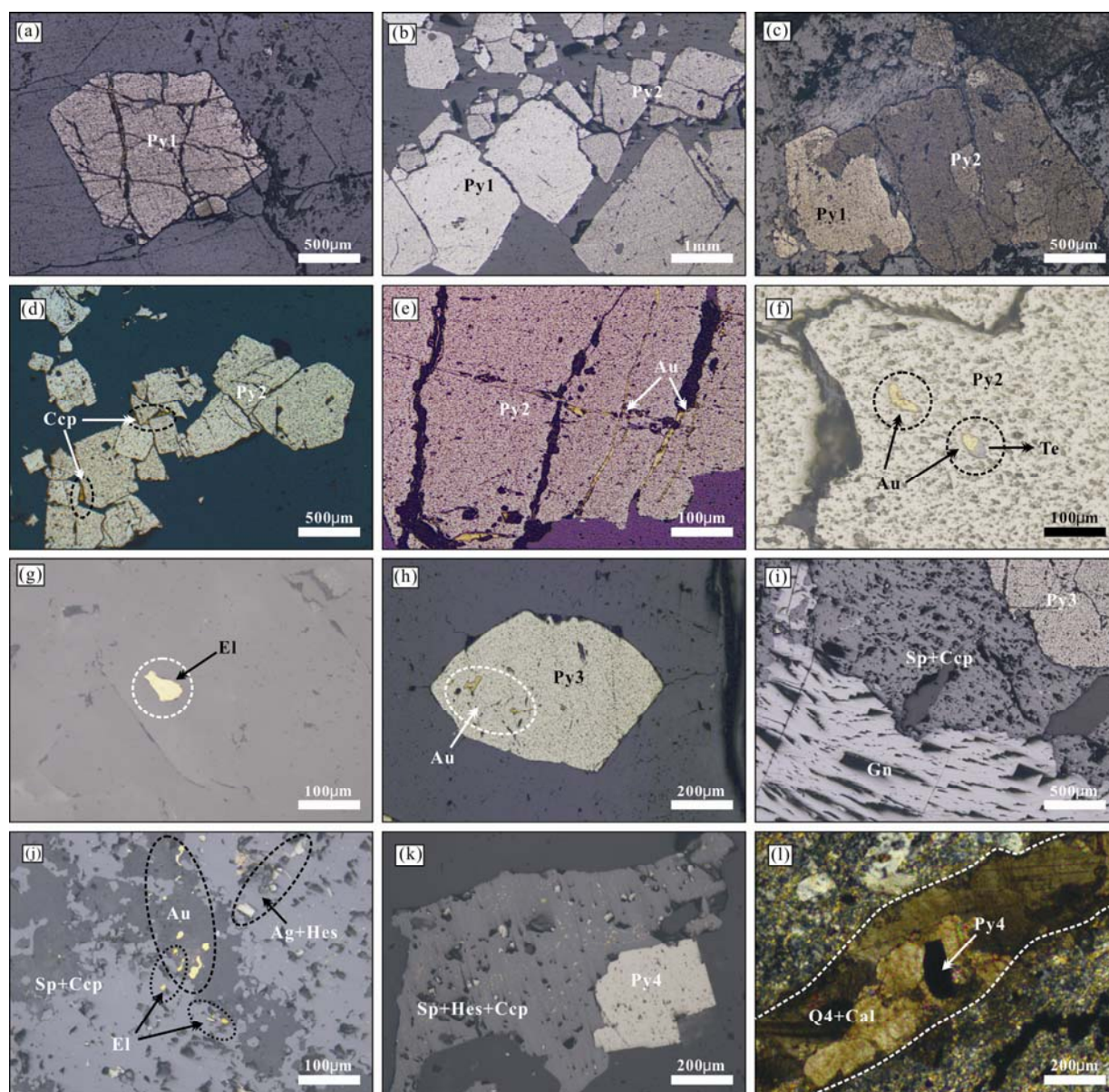


Fig. 4. Photographs showing the ore minerals of the Dayingezhuang gold deposit.

(a) Pyrite in first stage presents coarse-grained pentagonal dodecahedron with cataclastic texture; (b and c) euhedral cube pyrite in first stage is eroded by the pyrite in stage 2; (d) second stage pyrite occurs as subhedral aggregates with rare chalcopyrite; (e) native gold grains occurs in tiny fissures of second stage pyrite; (f) native gold occurs as inclusions in second stage pyrite crystals and intergrown with tetradymite; (g) electrum occurs as inclusion in second stage quartz crystals; (h) native gold occurs as inclusions in third stage pyrite crystals; (i) third stage subhedral galena coexists with sphalerite and pyrite; (j) native gold, electrum and hessite coexists with sphalerite and quartz of third stage; (k) fourth stage xenomorphic sphalerite coexisting with chalcopyrite crosscut by late-stage pyrite; (l) fourth stage pyrite in quartz-carbonate vein. Abbreviations: Sp, sphalerite; Gn, galena; Ccp, chalcopyrite; Au, native gold; Ag, native silver; Hes, hessite; Te, tetradymite; Py1, first stage pyrite; Py2, second stage pyrite; Py3, third stage pyrite; Py4, fourth stage pyrite; Q1, first stage quartz; Q2, second stage quartz; Q3, third stage quartz; Q4, fourth stage quartz; Cal, calcite.

less commonly as inclusions in pyrite crystals and gangue minerals, and rarely intergrown with tetradymite (Fig. 4e–g and j). Silver occurs as hessite, followed by native silver. The hessite occurs mainly as inclusions in sphalerite and galena (Fig. 4j and k). The native silver typically occurs as anhedral aggregates infilling voids between the base metal sulfides and gangue minerals, less commonly as inclusions in sphalerite and quartz, and rarely coexisting with electrum and native gold (Fig. 4j). Twenty alteration zones with different sizes of granitic wall rocks occur along the

Linglong detachment fault zone; among them, the No. 1 in the south and the No. 2 in the north, segregated by the post-ore NW-trending Dayingezhuang Fault, are the largest alteration zones. Extensive hydrothermal alteration, which is well developed in footwall and cataclastic zone of the Linglong detachment fault (Fig. 3b), is characterized by K-feldspar, albite, silica, sericite, pyrite, chlorite, carbonate and minor clay (Fig. 5a–i).

Extensive hydrothermal alteration, which is well developed in footwall and cataclastic zone of the Linglong

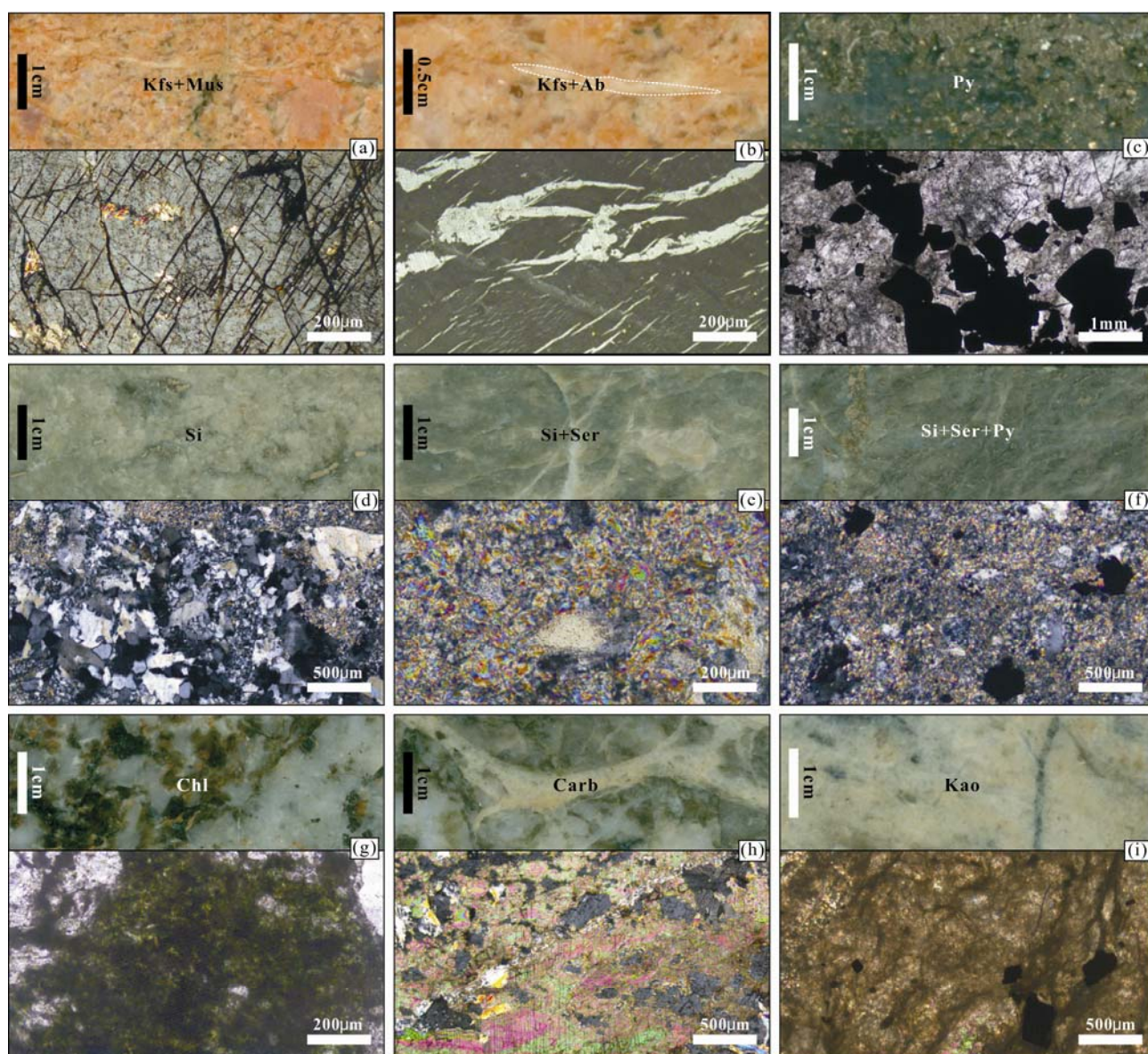


Fig. 5. Photographs showing the alteration assemblage at the Dayingezhuang gold deposit.

(a) Potassic and muscovitic alteration; (b) potassic and albitic alteration; (c) pyritic alteration; (d) silicified alteration; (e) silicified and Sericitic alteration; (f) silicified, sericitic and pyritic alteration; (g) chloritic alteration; (h) carbonate alteration; (i) kaolinic alteration. Abbreviations: Si, silicified alteration; Carb, carbonate alteration; Kao, kaolinic alteration; Kfs, K-feldspar; Mus, muscovite; Ab, albite; Ser, sericite; Chl, chlorite; Py, pyrite.

detachment fault (Fig. 3b), is characterized by K-feldspar, albite, silica, sericite, pyrite, chlorite, carbonate and minor clay (Fig. 5a–i). Twenty alteration zones with different sizes in granitic wall rocks occur along the Linglong detachment fault. Among them, the alteration zone associated with the No. 1 orebody in the south and the one associated with the No. 2 orebody in the north, separated by the post-ore NW-trending Dayingezhuang Fault, are the largest.

Four hydrothermal stages and a supergene stage have been identified in the Dayingezhuang ore system on the basis of mineralogical assemblage, textures, and cross-cutting relationships observed in hand specimens and thin sections (Figs. 4, 5 and 6). The hydrothermal stages include a pyrite–K-feldspar–sericite–quartz stage (stage I),

a quartz–gold–pyrite stage (stage II), a quartz–gold–silver–polymetallic sulfide stage (stage III), and a quartz–carbonate stage (stage IV). The gold mineralization occurred in stage 2 and stage 3.

Stage I is characterized by (K-feldspar)–pyrite–sericite–quartz altered rocks or, locally, (pyrite)–K-feldspar–quartz pods (Fig. 6a–c), forming K-feldspar–sericite–quartz altered zone which are mainly situated at the footwall of the Linglong detachment fault and extends for several hundred meters. The main mineral assemblage in this stage is gray white subhedral/anhydral quartz (Q1), sericite, K-feldspar, coarse euhedral disseminated pyrite, with variable amounts of albite and muscovite (Fig. 4 a–f). Quartz grains (Q1) surrounding the K-feldspar mainly occurs as polycrystalline crystals. Pyrite crystals (Py1) in

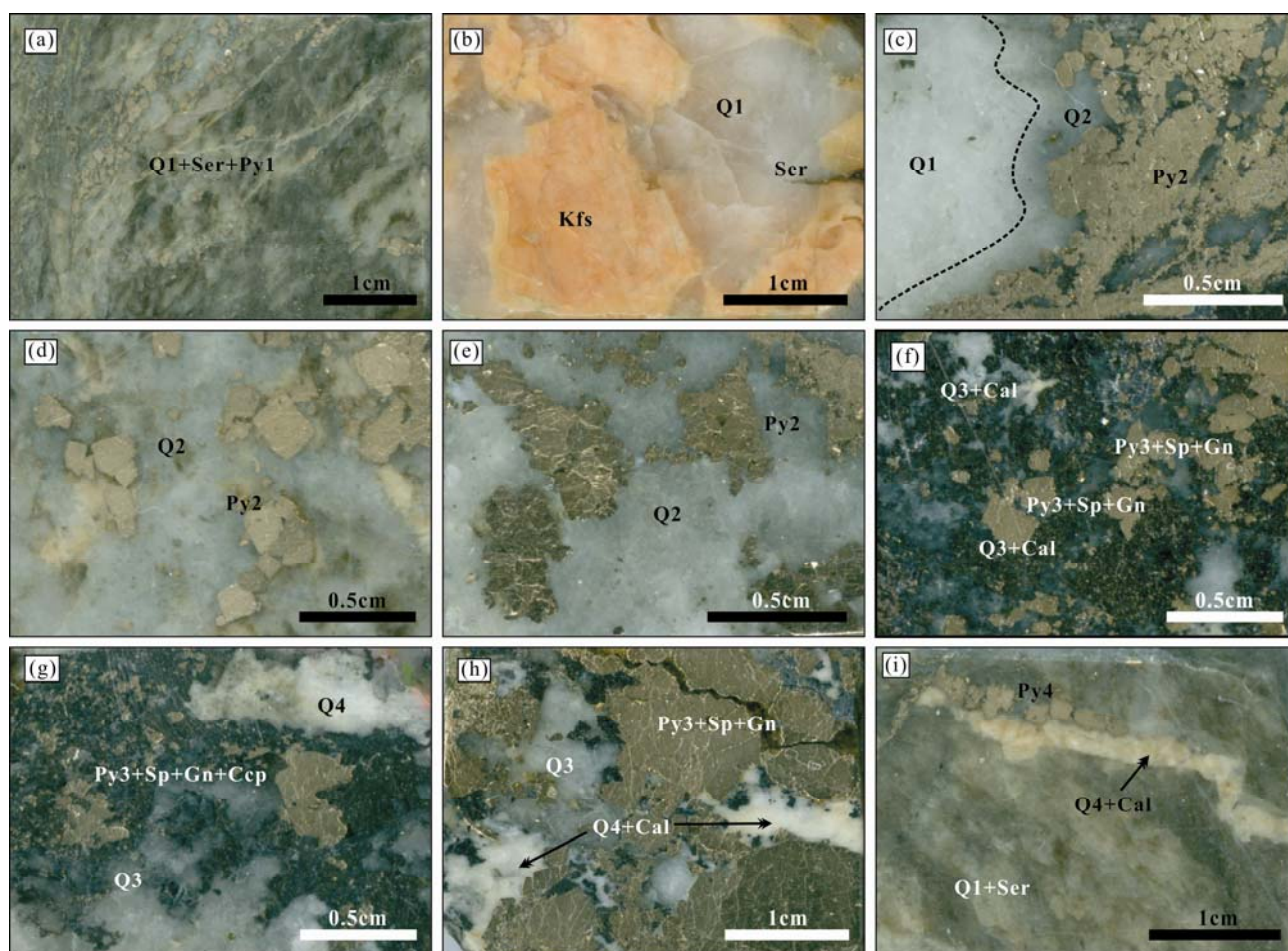


Fig. 6. Photographs showing hand specimens and cross-cutting relationships of different veins at the Dayingezhuang gold deposit. (a) First stage gray white quartz in pyrite-sericite-quartz altered rocks; (b) first stage gray white quartz coexisting with K-feldspar; (c) first stage gray white quartz infilled by second stage smoky gold-quartz-pyrite; (d and e) second stage smoky gold-pyrite-quartz; (f) third stage smoky gold-polymetallic sulfide quartz; (g and h) third stage smoky gold-polymetallic sulfide quartz crosscut by late quartz-carbonate vein; (i) pyrite-sericite-quartz altered rocks crosscut by late quartz-carbonate-pyrite vein.

this stage are present as coarse-grained euhedral cube and pentagonal dodecahedron with cataclastic texture, and are eroded by the pyrite in stage 2 (Fig. 4a–c). No gold was found in Py1 in our observation.

Stage II is characterized by auriferous quartz-pyrite veinlets and stockworks forming in the pyrite-sericite-quartz altered rocks, or in places as auriferous quartz-pyrite veinlets hosted in secondary faults. This stage constitutes one of the major gold mineralization periods. The mineral assemblage consists of white-gray anhedral quartz (Q2) and pyrite (Fig. 6c–e), with minor native gold, electrum, tetradymite, and chalcopyrite. Stage II pyrite (Py2) occurs as euhedral cubes or subhedral aggregates, and contains abundant native gold and electrum as irregular inclusions within it or in tiny fractures (Fig. 4a–f).

Stage III is characterized by the assemblage of pyrite, quartz, base metal sulfides, gold and silver minerals (Fig. 6f–h) that form veins/veinlets cutting the quartz-pyrite veinlets from stage II and fill fractures in early stage ore minerals, or occur as stockworks in disseminated ores. Large amounts of sulfide minerals were precipitated in this stage, including pyrite, galena, sphalerite, chalcopyrite,

and various gold and silver minerals (Fig. 4h–k). Quartz (Q3) is usually dark-gray in color and occurs as anhedral grains as in Stage II. Pyrite (Py3) occurs as fine-grained subhedral crystals, anhedral aggregates with minor pentagonal dodecahedron. The other sulfide minerals show anhedral aggregates.

Stage IV is characterized by quartz-carbonate veinlets. The veinlets show open-space filling textures in fissures that cross-cut the veins and replacement bodies that formed in the previous stages (Fig. 6i). This stage mainly contains calcite, quartz and siderite, with trace amounts of pyrite (Fig. 4l and Fig. 6i). No gold has been identified under reflected light in this stage.

4 Fluid Inclusion Characteristics

4.1 Sampling and analytical methodology

Samples for fluid inclusion study were collected from the No. 1 and No. 2 orebodies of the Dayingezhuang gold deposit (Figs. 3 and Fig. 4). Forty-two doubly polished thin sections (about 0.20 mm thick) were made from 35 hydrothermal quartz samples that were adjacent to sulfides

in ore from different stages (Fig. 4). Fluid inclusion petrography involved careful observation of the shapes, characteristics of spatial distribution, genetic and composition types, and vapor/liquid ratios. Thirty-one typical samples with abundant and representative fluid inclusions were selected for microthermometric measurements and laser Raman spectroscopy analyses.

Various inclusions in quartz were selected for microthermometry based on the distribution, size, types, and textural relationships of them. The microthermometric study was carried out at the Institute of Mineral Resources, Chinese Academy of Geological Sciences using a Linkam THMS-600 heating-freezing stage with a temperature range of -195°C to $+600^{\circ}\text{C}$. The equipment was calibrated with synthetic samples of fluid inclusions: pure water inclusions (0°C), pure CO_2 inclusions (-56.6°C), and potassium bichromate (398°C). The estimated precision of the measurements is $\pm 0.2^{\circ}\text{C}$ for temperatures lower than 31°C , $\pm 1^{\circ}\text{C}$ for the interval of 31 – 300°C , and $\pm 2^{\circ}\text{C}$ for temperatures higher than 300°C . The salinities of NaCl – H_2O inclusions were calculated using the final melting temperatures of ice (Bodnar, 1993). The salinities of CO_2 -bearing fluid inclusions were calculated using the melting temperatures of clathrate (Collins, 1979). Densities and pressure were calculated with Flnacor software (Brown, 1989) using the microthermometry data (Brown and Lamb, 1989). Compositions of individual fluid inclusions, including vapor and liquid phases, were analyzed using a

Renishaw System 2000 Raman Microspectrometer at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, with a blazing power of 20 mw and blazing wave length of 514.5 nm.

4.2 Petrography and classification

Fluid inclusions (FIs) are classified as follows: isolated FIs and randomly distributed groups of FIs hosted in intragranular quartz crystals are interpreted as primary in origin, and those aligned along micro-fractures in intragranular crystals trails are interpreted as pseudosecondary inclusions (Roedder, 1984; Goldstein and Reynolds, 1994; Lu et al., 2004; Chi and Lu, 2008). On the contrary, the secondary inclusions occur as intergranular arrays or aligned along micro-fractures in intergranular trails (Fig. 7a; Roedder, 1984). Three compositional types of fluid inclusions (Fig. 7b–g) are identified based on their phases at room temperature (i.e., liquid–vapor–solid; L–V–S), their observed phase transitions during heating and freezing runs, and from laser Raman spectroscopy. The FI types, in decreasing order of abundance, are aqueous–carbonic (CO_2 – H_2O – NaCl ; AC-type), aqueous (H_2O – NaCl ; A-type), and pure carbonic (CO_2 ; PC-type).

(1) Aqueous–carbonic fluid inclusions (AC-type)

AC-type fluid inclusions (Fig. 7b–d) are abundant in quartz grains formed in all the ore-forming stages. They can be further divided into tri-phase CO_2 -bearing fluid inclusions ($\text{L}_{\text{H}_2\text{O}} + \text{L}_{\text{CO}_2} + \text{V}_{\text{CO}_2}$) and two-phase CO_2 -bearing fluid inclusions ($\text{L}_{\text{H}_2\text{O}} + \text{L}_{\text{CO}_2}$ or $\text{L}_{\text{H}_2\text{O}} + \text{V}_{\text{CO}_2}$), which can be observed during freezing and heating. Vapor CO_2 or liquid CO_2 can also be observed in two-phase fluid inclusions through cooling down to 10°C or below. The CO_2 volumetric proportions (V_{CO_2} or $\text{V}_{\text{CO}_2} + \text{L}_{\text{CO}_2}$) of the inclusions at room temperature vary from 15% to 85%. AC-type FIs have ellipsoidal or irregular shapes, and sizes ranging from 5 to 18 μm (mainly 7–12 μm). The AC-type fluid inclusions account for up to 70% of the total FIs in ore-forming stages.

(2) Aqueous fluid inclusions (A-type)

The A-type FIs (Fig. 7e) are present in the second, third and last stage quartz crystals, and they account for 25% of the total FI population. These FIs are composed of aqueous liquid and vapor at room temperature, and they contain 5–85% vapor (generally 10–60%). However, a small number of single-phase aqueous inclusions contain only liquid water at room temperature; these inclusions are confined to the last stage and occur commonly in clusters with the two-phase aqueous fluid inclusions (Fig. 7e). A-type inclusions have negative crystal, elliptical, and irregular shapes, and range from 5 to 20 μm in size, with most measuring from 8 to 15 μm .

(3) Pure carbonic fluid inclusions (PC-type)

PC-type fluid inclusions (Fig. 7f and g) consist of almost pure carbonic fluid that contains little or no water at room temperature, and comprise two-phase CO_2 ($\text{V}_{\text{CO}_2} + \text{L}_{\text{CO}_2}$) or mono-phase CO_2 (vapor or liquid) that formed a CO_2 -rich vapor bubble during cooling. The PC-type FIs account for 5% of the total fluid inclusion population, and are generally 5–10 μm in size.

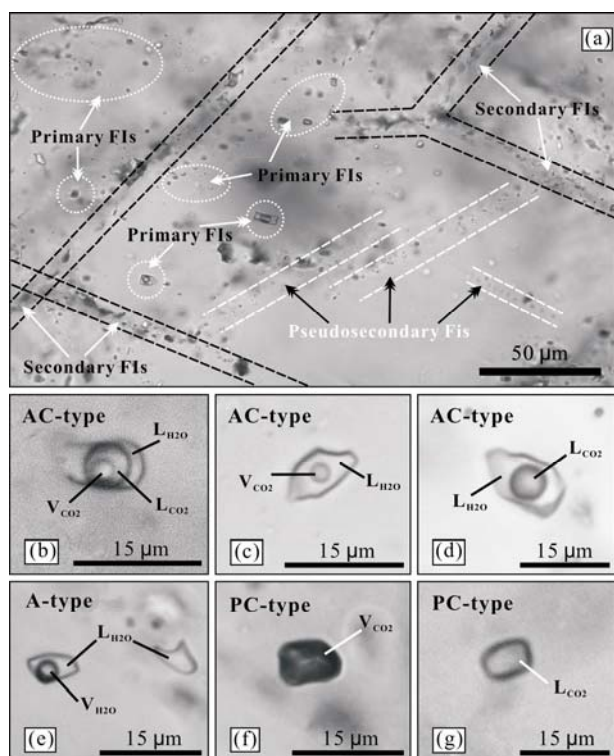


Fig. 7. Photomicrographs of typical fluid inclusions in the Dayingezhuang gold deposit.

(a) Primary, pseudosecondary and secondary fluid inclusions in same sample; (b) three phase AC-type fluid inclusion; (c and d) Two phase AC-type fluid inclusion; (e) A-type fluid inclusion; (f and g) PC-type fluid inclusion. Abbreviation: V_{CO_2} , vapor CO_2 ; L_{CO_2} , liquid CO_2 ; $\text{V}_{\text{H}_2\text{O}}$, vapor H_2O ; $\text{L}_{\text{H}_2\text{O}}$, liquid H_2O .

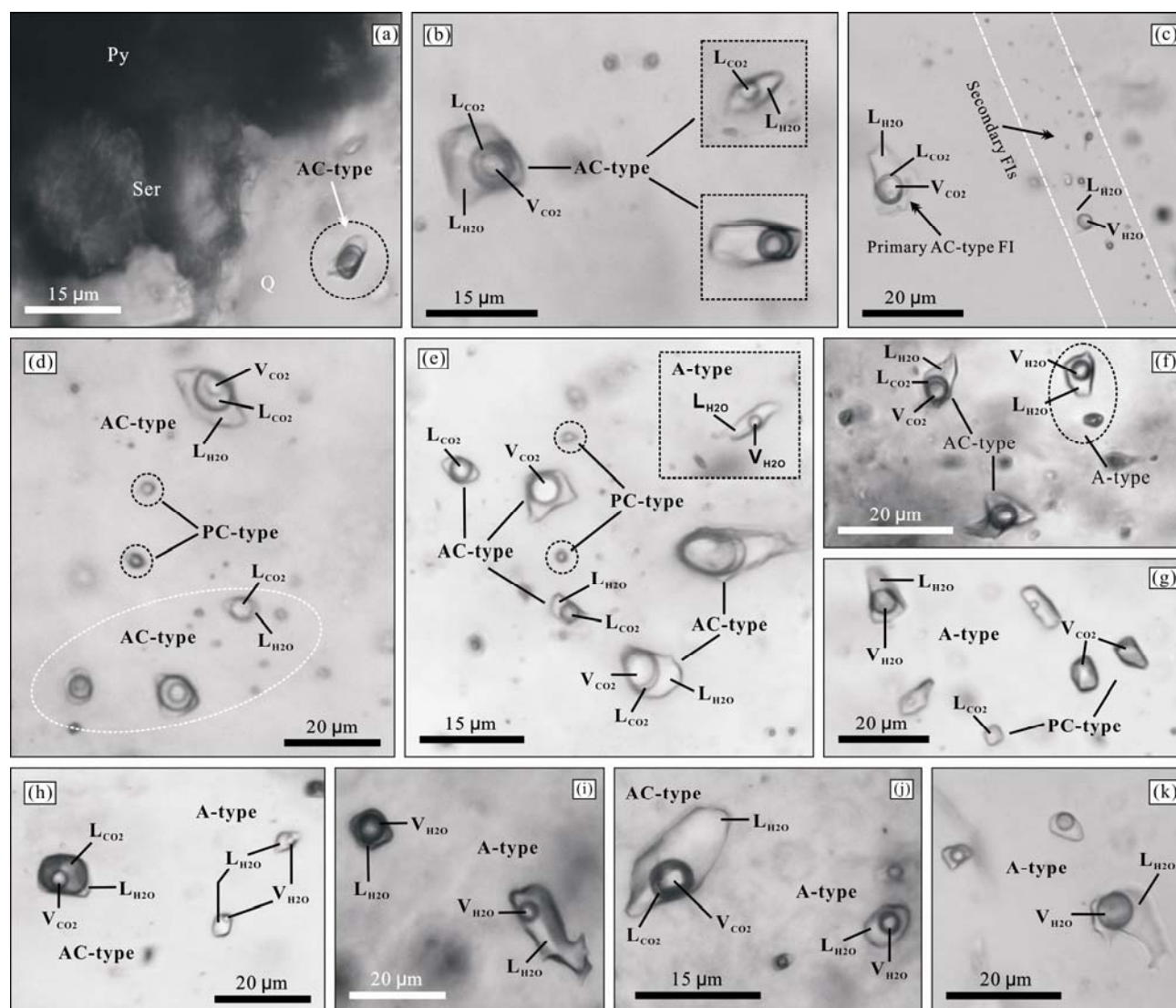


Fig. 8. Photomicrographs of fluid inclusion assemblages from different hydrothermal stages in the Dayingezhuang gold deposit.

(a and b) Primary AC-type fluid inclusions in first stage quartz; (c) primary AC-type and secondary FIs in first stage quartz; (d) primary AC-type fluid inclusions coexist with PC-type fluid inclusions in first stage quartz; (e) primary fluid inclusions (AC-type, A-type and PC-type FIs) in second stage quartz; (f and g) primary fluid inclusions (AC-type, A-type and PC-type FIs) in third stage quartz; (h) primary CO_2 extremely rich AC-type coexist with A-type FIs implying for fluid immiscibility in ore-forming stage quartz; (i) primary A-type Fluid inclusions with various vapor/liquid implying for fluid immiscibility in ore-forming stage quartz; (j) primary A-type fluid inclusions coexist with AC-type fluid inclusions in late stage quartz; (k) primary A-type fluid inclusions in late stage quartz.

4.3 Microthermometry

The microthermometric data in Table 1 were obtained from A-type, AC-type, and PC-type primary/pseudosecondary fluid inclusions from the four hydrothermal stages (Fig. 8). Secondary inclusions were excluded from this study. Microthermometric measurements were not possible for some FIs due to their small sizes (i.e., $T_{\text{h-}\text{CO}_2}$ for AC-type and PC-type, $T_{\text{m-cla}}$ for AC-type and $T_{\text{m-ice}}$ for A-type).

4.3.1 First hydrothermal stage

The first hydrothermal stage quartz crystals contain dominantly AC-type with rare PC-type primary/pseudosecondary fluid inclusions (Fig. 8a–d), and massive amounts of secondary FIs that are aligned along micro-

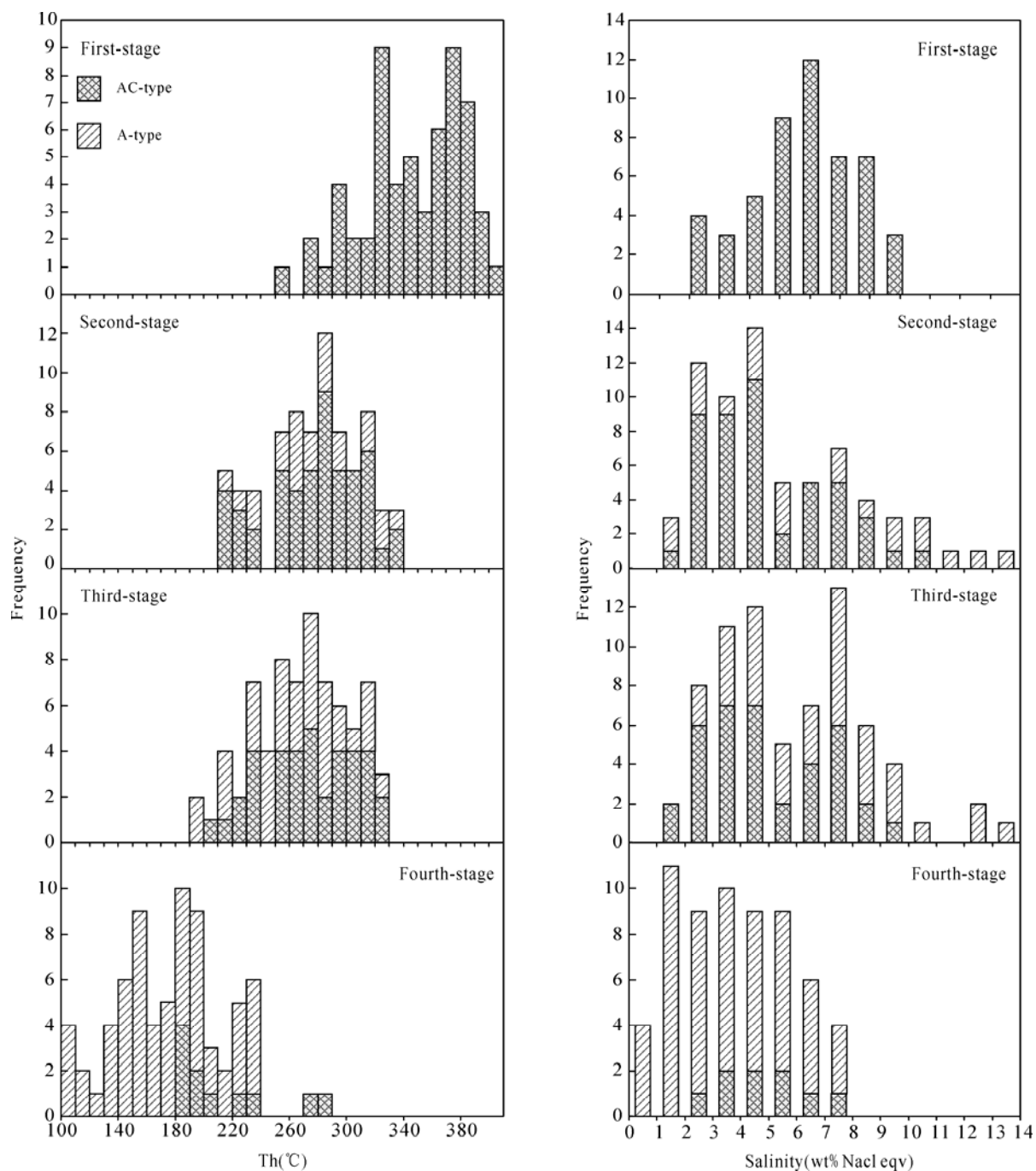
fractures in transgranular trails (Fig. 8c). AC-type fluid inclusions in this stage that occur in clusters and locally as isolated individual inclusions (Fig. 8a–c) were selected for study. AC-type inclusions locally occur with PC-type inclusions.

The first melting temperatures ($T_{\text{m-}\text{CO}_2}$) of solid CO_2 in the primary AC-type FIs range from -58.5°C to -56.6°C . These values are slightly lower than the triple point for pure CO_2 (-56.6°C), indicating the presence of minor amount of CH_4 or other components. Clathrate melting temperatures ($T_{\text{m-cla}}$) are from 4.7°C to 8.9°C . The CO_2 phase is totally homogenized to a liquid phase at temperatures ($T_{\text{h-}\text{CO}_2}$) from 12.1°C to 30.9°C . All AC-type FIs are homogenized to a liquid or vapour at temperatures ($T_{\text{m-hot}}$) of 357°C to 403°C (mean $344\pm 37^\circ\text{C}$; 1σ ; $n=54$);

Table 1 Microthermometric data for fluid inclusions of different stage from the Dayingezhuang deposit

Stage	Type	Number	T_{m-CO_2} (°C)	T_{m-cla} (°C)	T_{h-CO_2} (°C)	T_{m-ice} (°C)	T_h (°C)	Salinity (wt% NaCl equiv.)	CO ₂ density (g/cm ³)	Bulk density (g/cm ³)
First	AC	61	-58.5 to -56.6	4.7 to 8.9	12.1 to 30.9		251 to 403	2.2 to 9.4	0.50 to 0.85	0.63 – 0.93
	PC	15	-58.2 to -56.6		9.2 to 30.2				0.56 to 0.87	
Second	AC	51	-59.1 to -56.6	4.3 to 9.1	19.2 to 30.9		216 to 339	1.8 to 10.0	0.32 to 0.78	0.67 – 0.91
	A	22				-9.8 to -0.8	219 to 332	1.4 to 13.8		0.69 – 0.91
	PC	12	-60.1 to -56.6		17.3 to 30.9				0.50 to 0.81	
	AC	38	-59.6 to -56.6	4.5 to 9.3	20.1 to 30.8		207 to 328	1.4 to 9.8	0.33 to 0.77	0.64 – 0.92
Third	A	35				-9.4 to -1.6	195 to 321	2.7 to 13.3		0.76 – 0.91
	PC	9	-59.9 to -56.6		18.7 to 30.9				0.50 to 0.79	
Forth	AC	11	-57.2 to -56.6	5.9 to 8.5	25.8 to 30.4		181 to 287	3.0 to 7.5	0.34 to 0.70	0.80 – 0.91
	A	66				-4.9 to -0.3	106 to 237	0.5 to 7.7		0.84 – 0.98

Note: T_{m-CO_2} = melting temperature of solid CO₂; T_{m-cla} = temperature of CO₂-clathrate dissociation; T_{h-CO_2} = homogenization temperature of CO₂; T_{m-ice} = temperature of final ice melting; T_h = homogenization temperature; wt.% NaCl equiv. = weight percent NaCl equivalent.

Fig. 9. Histograms of total homogenization temperatures (T_h) and salinities of fluid inclusions in different stages.

however, some FIs decrepitated prior to homogenization during the heating process. The calculated salinities range from 2.2 to 9.4 wt% NaCl equivalent (Table 1; Fig. 9). The calculated CO₂ densities range from 0.50 to 0.85 g/cm³, and the bulk densities range from 0.63 to 0.93 g/cm³.

The PC-type FIs yield melting temperatures (T_{m-CO_2}) of -58.2°C to -56.6°C , which suggests the possible presence of minor amounts of other gases such as CH₄ or N₂. CO₂ generally homogenized to the liquid phase and homogenization temperatures of CO₂ (T_{h-CO_2}) range from 9.2°C to 30.2°C , corresponding to densities of 0.56 to 0.87 g/cm³.

4.3.2 Second hydrothermal stage

Quartz crystals from this hydrothermal stage contain abundant AC-, A-, and PC-type FIs. AC-type fluid inclusions in this stage occur in clusters or locally as isolated individual inclusions; they occasionally occur in an assemblage with PC-type inclusions (Fig. 8e). A-type fluid inclusions occur in clusters alone or occasionally occur in an assemblage with AC-type inclusions.

The solid CO₂ of the AC-type FIs yielded T_{m-CO_2} of -59.1°C to -56.6°C . These values are similar to or slightly lower than the triple point for pure CO₂ (-56.6°C), which indicates the presence of small amounts of CH₄ and H₂S (as identified using laser Raman spectroscopy). The T_{m-cla} range from 4.3 to 9.1°C , which correspond to salinities from 1.8 to 10.0 wt.% NaCl equivalent (Table 1; Fig. 9). The T_{h-CO_2} of CO₂ (mostly to liquid, and rarely to vapor phase) are from 19.2°C to 30.9°C . The calculated CO₂ densities are 0.32–0.78 g/cm³, and the densities of total fluids are 0.67–0.91 g/cm³. This type of FIs homogenized to liquid (for those rich in H₂O) or vapor (for those rich in CO₂) at temperatures (T_h) of 216°C – 339°C .

The A-type FIs yielded T_{m-ice} of -9.8°C to 0.8°C , and salinities of 1.4–13.8 wt% NaCl equivalent (Table 1; Fig. 9). This type of FIs homogenized to liquid phase (few homogenized to vapor) at temperatures (T_h) of 219°C – 332°C , and their calculated densities are 0.69–0.91 g/cm³.

The PC-type FIs yielded T_{m-CO_2} of -60.1°C to -56.6°C , which suggests the possible presence of small but remarkable amounts of other gases such as CH₄ (as identified using laser Raman spectroscopy). CO₂ generally homogenized to the liquid phase and T_{h-CO_2} range from 17.3°C to 30.9°C , and calculated densities vary from 0.50 to 0.81 g/cm³.

The T_h of all these FIs in the second stage range from 216°C to 339°C (mean $278\pm 32^{\circ}\text{C}$; 1σ ; $n=73$), peaking at 280°C – 290°C .

4.3.3 Third hydrothermal stage

All three types of FIs were identified in the third stage quartz, with the A-type FIs becoming much more common than the previous stage. A-type fluid inclusions in third stage occur in clusters or locally as isolated individual inclusions. They also occur in together with AC- and PC-type inclusions in some assemblages (Fig. 8f).

The AC-type FIs in this hydrothermal stage have T_{m-CO_2} values from -59.6°C to -56.6°C , which suggests the possible presence of other gases such as CH₄ (as identified using laser Raman spectroscopy). The homogenization

temperatures of CO₂ (T_{h-CO_2} ; mostly to liquid and rarely to vapor phase) vary between 20.1°C and 30.8°C . The temperatures of clathrate dissociation ($T_{m-cla}=4.5$ to 9.3°C) correspond to salinities from 1.4 to 9.8 wt.% NaCl equivalent (Table 1; Fig. 9). The final homogenization temperatures (T_h) are (some to the liquid and some to vapor) within the range of 207°C to 328°C . The calculated CO₂ densities range from 0.33 to 0.77 g/cm³, and bulk densities from 0.64 to 0.92 g/cm³.

The A-type FIs have T_h values ranging from 195°C to 321°C . Ice-melting temperature (T_{m-ice}) range from -9.4°C to -1.6°C , with the estimated salinities ranging from 2.7 to 13.3 wt.% NaCl equivalent (Table 1; Fig. 9), and their calculated densities are 0.76–0.91 g/cm³.

The PC-type FIs yield T_{m-CO_2} for solid CO₂ of -59.9°C to -56.6°C , which suggests the possible presence of minor amounts of other gases such as CH₄ or N₂. CO₂ generally homogenized to the liquid phase and T_{h-CO_2} range from 18.7°C to 30.9°C , corresponding to densities of 0.50 to 0.79 g/cm³.

The AC- and A-type FIs in this stage have an overall homogenization temperature (T_h) range of 195°C – 329°C (mean $269\pm 34^{\circ}\text{C}$; 1σ ; $n=76$), peaking at 270°C – 280°C .

4.3.4 Fourth hydrothermal stage

Only A- and a few AC-type fluid inclusions were observed in the last stage quartz and calcite crystals. A-type fluid inclusions in this stage occur in clusters or locally as isolated individual inclusions. They occasionally occur in an assemblage with AC-type inclusions (Fig. 8j–k).

The A-type FIs have T_h values from 106°C to 237°C , which are much lower than those from the former stages. The ice-melting temperatures (T_{m-ice}) range from -4.9°C to -0.3°C , with calculated salinities from 0.5 to 7.7 wt.% NaCl equivalent (Table 1; Fig. 9).

The AC-type FIs have first melting temperatures (T_{m-CO_2}) of -57.2°C to -56.6°C . These values are similar to or slightly lower than the triple point for pure CO₂ (-56.6°C), which indicates the presence of minor amounts of CH₄ or N₂. The T_{m-cla} range from 5.9°C to 8.5°C , which correspond to salinities between 3.0 and 7.5 wt.% NaCl equivalent (Table 1; Fig. 9). The homogenization temperatures (T_{h-CO_2}) of CO₂ (some to liquid and the other to gas phase) are between 25.8°C and 30.4°C . The calculated CO₂ densities are 0.34–0.70 g/cm³, and the densities of total fluids are 0.80–0.91 g/cm³. The AC-type FIs are completely homogenized to liquid at temperatures (T_{m-hot}) of 181°C – 287°C .

All the FIs in the last stage homogenized to liquid at temperatures (T_h) of 106°C – 287°C (mean $179\pm 38^{\circ}\text{C}$; 1σ ; $n=70$), peaking at 180°C – 190°C .

4.4 Laser Raman spectroscopy

To constrain the fluid inclusion compositions, representative fluid inclusions from the four different hydrothermal stages were examined using laser Raman microspectroscopy (Fig. 10). The AC-type inclusions from the different hydrothermal stages contain a vapor phase of CO₂ with minor amounts of CH₄ and N₂ (Fig. 10a, d, g and k), and a liquid phase dominated by water (Fig. 10b and h). The PC-type fluid inclusions hydrothermal stages 1–3

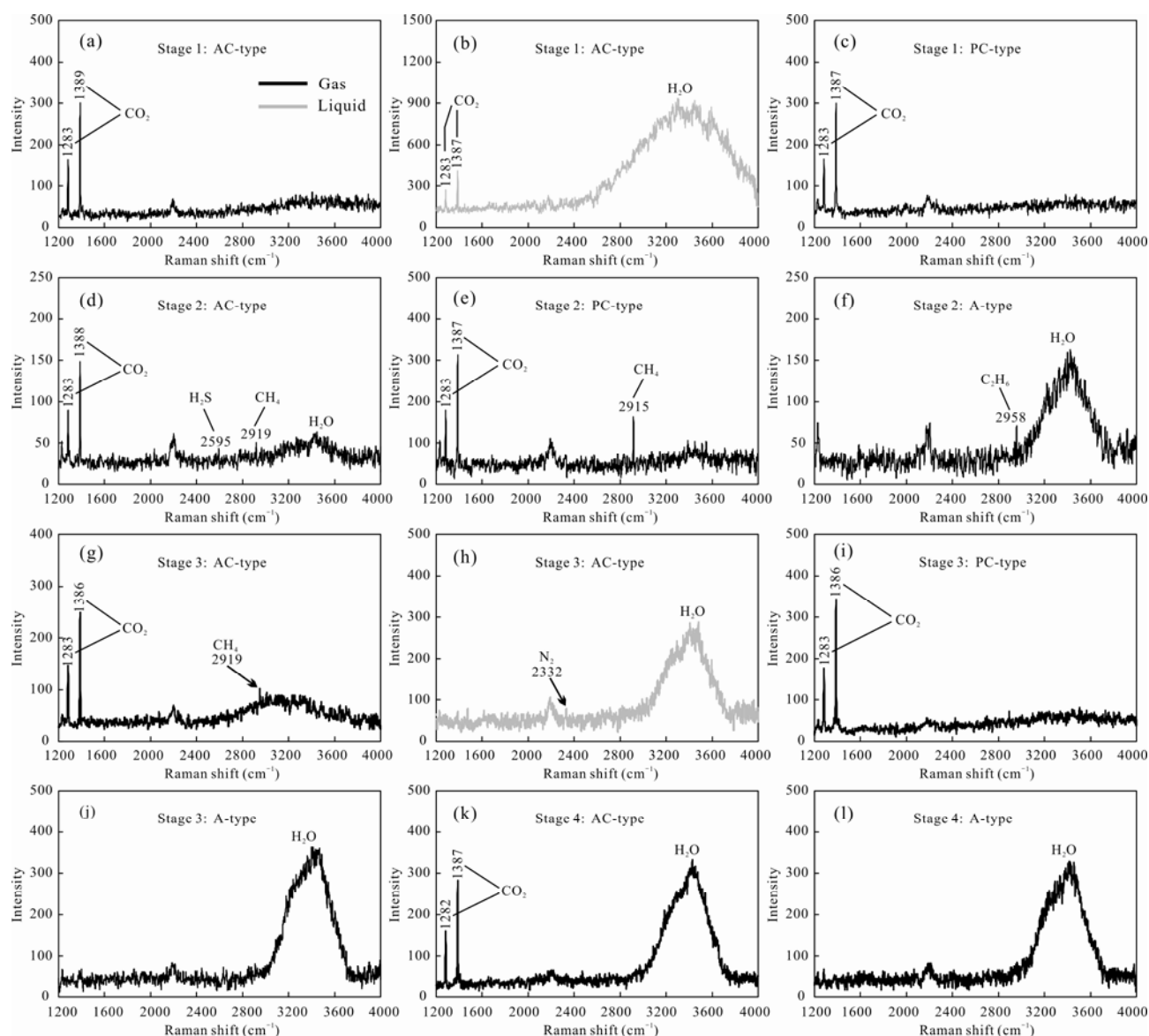


Fig. 10. Representative Laser Raman spectra of fluid inclusions.

(a) Spectrum for gas phase of AC-type FI in first stage; (b) spectrum for liquid phase of AC-type FI in first stage with few contents of CO₂; (c) spectrum for PC-type FI in early-stage; (d) spectrum for gas phase of AC-type FIs in second stage with few contents of H₂S, CH₄ and H₂O; (e) Spectrum for PC-type FI in second stage, showing variable contents of CH₄; (f) spectrum for gas phase of A-type FIs in second stage with few contents of C₂H₆; (g) spectrum for gas phase of AC-type FIs in third stage with few contents of CH₄; (h) spectrum for liquid phase of AC-type FIs in second stage with few contents of N₂; (i) spectrum for PC-type FI in second stage; (j) spectrum for gas phase of A-type FIs in second stage; (k) spectrum for gas phase of AC-type FIs in late stage with variable contents of H₂O; (l) spectrum for gas phase of A-type FIs in late stage.

show well-defined CO₂ peaks and minor CH₄ peaks (Fig. 10c, e and i). The main component of the A-type FIs for stages 2–4 is H₂O (Fig. 10f, j and l). In addition, AC-type inclusions from stage 2 contain traces of CH₄ and H₂S in the gas (Fig. 11d), and those from stage 3 contain traces of CH₄ in the vapor phase (Fig. 11g). A-type inclusions from stage 2 contain traces of CH₄ in the vapor phase (Fig. 11f and j).

5 Discussions

5.1 Evolution of mineralizing fluids

Fluid inclusions provide significant information on

mineralizing processes in hydrothermal systems (Lu et al., 2004), and in combination with ore geology, allow us to evaluate the evolution of the ore-forming system at the Dayingezhuang deposit (Chai et al., 2016a, b).

In this study, quartz crystals from the first stage of mineralization contain abundant AC- and rare PC-type fluid inclusions that exhibit relatively high homogenization temperatures (251°C–403°C) and low salinities (2.2–9.4 wt% NaCl equivalent). These factors indicate that the initial ore-forming fluids belonged to the CO₂–H₂O–NaCl system and was characterized by relatively elevated temperatures, low salinities, and enrichment in CO₂ (Figs. 9 and 11; Table 1). The

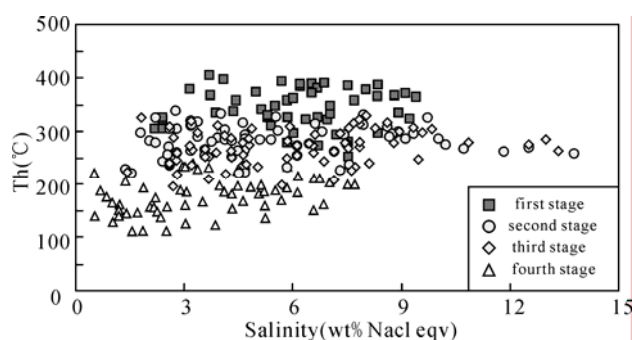


Fig. 11. Plots of homogenization temperature (Th) vs salinity of FIs from the Dayingezhuang deposit.

interaction of this primary fluid with wall rocks resulted in the precipitation of quartz, K-feldspar, sericite, pyrite, minor muscovite, and albite in early barren veins/veinlets, and formed the altered pyrite–K-feldspar–sericite–quartz rocks.

Quartz crystals that formed during the second stage of mineralization contain AC-, PC- and A-type FIs that yield moderate homogenization temperatures (216°C–339°C) and variable salinities (1.4–13.8 wt% NaCl equivalent) (Figs. 9 and 11; Table 1). These features indicate that the ore-forming fluids evolved into a H_2O – CO_2 –NaCl system at moderate temperatures and variable salinities, with small amounts of CH_4 . The fluids of the third stage are similar to those of the second, although with slightly lower CO_2 concentrations (i.e., larger A-type and smaller AC-type FI populations), lower homogenization temperatures (195°C–328°C).

The fluids in the final hydrothermal stage evolved towards a H_2O –NaCl system with medium–low temperatures (106°C–287°C), low salinity (0.5–7.7 wt% NaCl equivalent), and trace amounts of CO_2 (Figs. 9 and 11; Table 1). These suggest that the ore-forming fluids experienced cooling and diluting, probably due to mixing with circulating meteoric water (Shen et al., 2000; Mao et al., 2005, 2008; Dai, 2012).

5.2 Mechanisms of gold transport and deposition

As shown above, the main stage FIs contain H_2S (Fig. 10d), which may have been combined with gold to form Au–S complexes such as $\text{Au}(\text{HS})_2^-$ or $\text{Au}(\text{HS})^0$, and thereby increased the concentration of gold in solution (Benning and Seward, 1996). This view is in agreement with a previous study that revealed that HS^- is the most important ligand in gold complexes at temperatures of less than 400°C (Seward, 1973). It is also supported by the observation that gold is generally accompanied by pyrite and other sulfides in the Dayingezhuang deposit (Fig. 4d–j), as is typical in orogenic gold deposits worldwide, in which gold(I) sulfide complexes were considered the most likely species for transporting gold (Goldfarb et al., 2005).

The abundance of AC- and PC-type FIs in quartz from the first hydrothermal stage demonstrates that the initial ore-forming solution was enriched in CO_2 . It has been demonstrated that CO_2 may have played a critical role in the transport of gold by buffering the pH of the solution and thereby providing favorable conditions for migration of the Au–S complex (Phillips and Evans, 2004). On the other hand, the aqueous speciation of gold(I) sulfide complexes is also sensitive to temperature (Stefánsson and Seward, 2004). For example, when the temperature is below 400°C, $\text{Au}(\text{HS})^0$ dominates under acidic conditions with relatively high temperatures and oxygen fugacities, whereas $\text{Au}(\text{HS})_2^-$ is more likely to form under weakly acidic to neutral conditions at relatively low temperatures and oxygen fugacities (Stefánsson and Seward, 2004; Williams-Jones et al., 2009; Pokrovski et al., 2014; Fig. 12a and b). The fluid inclusion data documented in this study suggests an evolution of the hydrothermal fluids from relatively high temperature and low pH to relatively low temperature and high pH conditions, supporting gold dissolution as $\text{Au}(\text{HS})^0$ in the early stages and as $\text{Au}(\text{HS})_2^-$ in the late stages.

The earliest alteration mineral assemblages in the Dayingezhuang gold deposit consist of K-feldspar, albite, and muscovite (Fig. 5a and b; Fig. 7), which suggests a

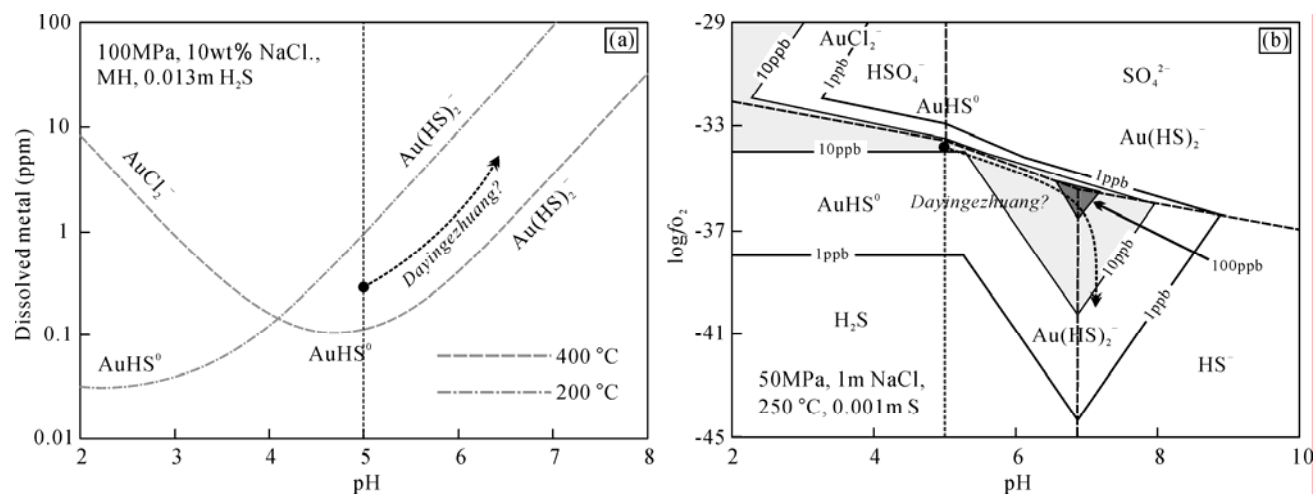
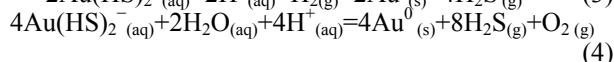
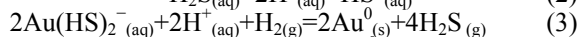
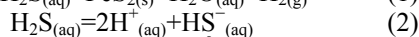
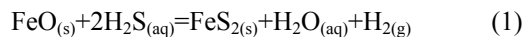


Fig. 12. (a) Solubility of native gold at 1000 bar and indicated temperatures in model 10 wt% NaCl equivalent aqueous as a function of pH in equilibrium with the magnetite-hematite assemblage (MH) and 0.013 m H_2S in solution (after Pokrovski et al., 2014); (b) Gold solubility and speciation at 500 bar and 250°C as a function of $\log f_{\text{O}_2}$ and pH in a solution containing 1 m NaCl with $\Sigma\text{S} = 0.01$ m (after Williams-Jones et al., 2009).

relatively acidic condition, with pH values possibly between 4.9 and 5.3 (Mikucki and Ridley, 1993; Xu et al. 2016). A change in alteration mineral assemblages to the quartz–sericite–chlorite–carbonate association (Fig. 5c–h) in the later stages suggest that the ore solution changed to a weakly acidic or near-neutral pH (McCuaig and Kerrich, 1998; Li et al., 2013), accompanied by a decrease in temperature as recorded by fluid inclusions. Furthermore, the mineralization stages are characterized by lower oxygen fugacity than the first stage, as indicated by the development of sulfides. We propose, therefore, that mineralization of the Dayingezhuang deposit is related to the change of physicochemical conditions of the hydrothermal system. Gold was initially dissolved in the solution predominantly as $\text{Au}(\text{HS})^0$, under acidic conditions with higher temperatures and $f\text{O}_2$, and was precipitated when the system became less acidic, cooler and more reducing (Fig. 12a and b), accompanied by shift of dissolved gold complexes to $\text{Au}(\text{HS})_2^-$. The possible mechanism for Au precipitation may be described by the equations as follow (Mikucki, 1998; Williams-Jones et al., 2009).



Consumption of H_2S through fluid-rock reaction, as shown in Eq. 1, may be the most direct cause of gold precipitation (Groves et al., 1985), as it will shift the reactions in Eqs. 3–5 to the right. Increase in pH values has two opposite effects on gold solubility: on one hand, it will move reactions 3 and 4 to the left, thus promoting gold dissolution, but on the other hand, it shifts reaction 2 to the right (thus decreasing H_2S), and so promoting gold precipitation. Similarly, $f\text{O}_2$ also has two opposite effects on gold dissolution versus precipitation: a decrease in $f\text{O}_2$ will move reactions 3–5 to the right, thus favoring gold precipitation, but it will move reaction 1 to the left, which increases H_2S and thus favors gold dissolution. Taking all these factors into consideration, it seems that an increase in pH and a decrease in $f\text{O}_2$ favor gold precipitation, with sulfide precipitation (through fluid-rock reactions) as the most important cause.

In addition to fluid-rock reactions, fluid immiscibility may have also played an important role in the formation of the Dayingezhuang gold deposit. Fluid immiscibility is commonly associated with gold and sulfide deposition in a variety of hydrothermal settings (Ramboz et al., 1982; Robert and Kelly 1987; Chi et al., 2006; Chi and Xue, 2011). Fluid immiscibility may result in significant loss of H_2S as well as increase in pH, which are favorable for gold precipitation as discussed above (Bowers and Helgeson, 1983). In the present study, the existence of the AC-, A- and PC-type FIs in the mineralization stages and their microthermometric attributes suggest that the fluid system may have experienced unmixing processes during mineralization. Although we have not documented concrete evidence for the contemporaneous entrapping of the different types of fluid inclusions as constrained from

the fluid inclusion assemblage approach (Reynolds and Goldstein, 1994; Chi and Lu, 2008), we believe that fluid immiscibility occurred during mineralization of the Dayingezhuang gold deposit based on the widespread coexistence of AC-, A- and PC- type FIs in the ore-stage quartz crystals.

6 Conclusions

(1) Three types of primary/pseudosecondary fluid inclusion were identified in the Dayingezhuang gold deposit: AC-type (aqueous–carbonic), A-type (aqueous), and PC-type (pure carbonic). AC- and minor PC-type FIs exist in quartz from the first stage of mineralization, whereas all three types of FIs were observed in quartz from the main period of mineralization (i.e., the second and third stages). In contrast, quartz from the final stage of mineralization contains abundant A-type FIs and only rare AC-type inclusions.

(2) The initial ore-forming fluids of the Dayingezhuang deposit are characterized by relatively high temperatures (with fluid inclusion homogenization temperatures of 251° C–403° C), CO_2 -rich composition, low salinity (2.2–9.4 wt% NaCl), and weakly acidic CO_2 – H_2O –NaCl system. During mineralization, the fluids evolved into a medium–low temperature NaCl– H_2O system, accompanied by an increase in pH and decrease in oxygen fugacity.

(3) Gold in the ore-forming fluids may have changed from $\text{Au}(\text{HS})^0$ as the dominant species under acidic conditions and at relatively high temperatures and $f\text{O}_2$ in the early stages, to $\text{Au}(\text{HS})_2^-$ under neutral-pH conditions at lower temperatures and $f\text{O}_2$ in the later stages. The precipitation of gold and other metals is inferred to be caused by a combination of fluid immiscibility and water–rock interaction.

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