

Article

Ore Genesis of the Toudaochuan Gold Deposit in Central Jilin Province, NE China: Constraints from Fluid Inclusions and C–H–O–S–Pb Isotopes

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Abstract: The Toudaochuan gold deposit is a recently discovered lode gold deposit in Central Jilin Province. Gold ore bodies are dominantly controlled by NE-trending fault. The major hydrothermal period can be further divided into the quartz–pyrite stage (stage I), quartz–gold–polymetallic sulfides stage (stage II, major gold mineralization stage), and quartz–carbonate stage (stage III). Primary fluid inclusions (FIs) identified in quartz at different hydrothermal stages include liquid-rich aqueous FIs (L-type), CO₂ FIs (C-type, including CO₂-bearing C1-type FIs and CO₂-rich C2-type FIs), and minor vapor-rich aqueous FIs (V-type). Microthermometry studies on different fluid inclusions indicate that the original ore-forming fluids belonged to the CO₂–H₂O–NaCl system characterized by a moderate–low temperature and low salinity in stages I and II, and they finally evolved into a H₂O–NaCl system characterized by low temperature and low salinity in stage III. Fluid immiscibility is considered to be the key ore-forming mechanism. The initial ore-forming fluid was originated from magmatic water and was mixed with meteoric water in the later stage. The S and Pb isotope data suggest that the ore metal materials were derived from the mixed source of mantle and crust. Based on all the above data, therefore, it can be proposed that the Toudaochuan gold deposit is a mesothermal magmatic–hydrothermal gold deposit.

Keywords: ore genesis; fluid inclusions; C–H–O–S–Pb isotopes; Toudaochuan gold deposit; Central Jilin province



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1. Introduction

Central Jilin Province in Northeast (NE) China is located at the intersection of the northern margin of the North China Craton (NCC) and the eastern segments of the Central Asian Orogenic Belt (CAOB). The multi-stage and intense tectonic and magmatic activities resulted in numerous deposits of various genetic and metal types in this area, including porphyry Mo deposits represented by Daheishan and Jidetun [1,2], magmatic Cu–Ni sulfide deposits represented by Hongqiling [3,4], and mesothermal magmatic–hydrothermal vein-type Pb–Zn–(Ag) represented by Xiaohongshilazi [5], as well as the gold deposits represented by Jiapigou [6], Haigou [7], and Toudaochuan involved in this study. Previous studies on representative gold deposits (e.g., Jiapigou, Haigou, Erdaogou, Xiaobeigou, etc. [6–11]) showed that these gold deposits almost belong to magmatic–hydrothermal gold deposits. The Toudaochuan gold deposit is geographically close to these deposits, being located to the northwest of them. However, it is unknown whether its genetic type is the same as these gold deposits, thus restricting the study of regional gold metallogenic regularity and further prospecting and exploration in this area.

The Toudaochuan gold deposit is a recent discovery located about 50 km southwest of Yongji County, Jilin Province. Up to now, some properties which are important for understanding of the ore genesis of this deposit are still unclear, for instance, the ore-forming geological conditions, the source and evolution of ore-forming fluid, and the ore-forming material source. There are still some disputable views on the ore genesis of this deposit. For example, Wang et al. [12] believed that gold mineralization was closely related to Yanshanian biotite granites in the mining area periphery. Li et al. [13] proposed that the formation of the gold deposit was associated with the ore-bearing metamorphic volcanic strata, and accordingly classified the genetic type of the deposit as a medium- and low-temperature metamorphic hydrothermal quartz-vein-type gold deposit. Moreover, Wang et al. [14] also considered the deposit to be a metamorphic hydrothermal gold deposit.

Considering the above disputes, this study, on the basis of field and petrographic observation, carried out some analytical research on fluid inclusions, C–H–O, S and Pb stable isotopes of the gold ore in the Toudaochuan gold deposit. Moreover, the source of the ore-forming fluid and ore material, genetic type, gold mineralization process, and mineralization mechanism of this deposit have been discussed. The conclusions can provide a basis for knowledge on regional metallogeny and exploration of gold resource in the study area.

2. Regional Geology

The Central Jilin Province is tectonically located in the southeast part of the NE China which lies between the Siberian Craton and the North China Craton (NCC), including the Xing'an-Mongolia Orogenic Belt (XMOB), which belongs to the eastern segment of the Central Asian Orogenic Belt (CAOB) [15], and the northernmost part of the NCC (NNCC) (Figure 1a). The XMOB is composed of the Erguna, Xing'an, Songnen–Zhangguangcai Range, Jiamusi, and Khanka blocks from northwest to southeast, as well as Liaoyuan terrane in the south [16,17] (Figure 1b).

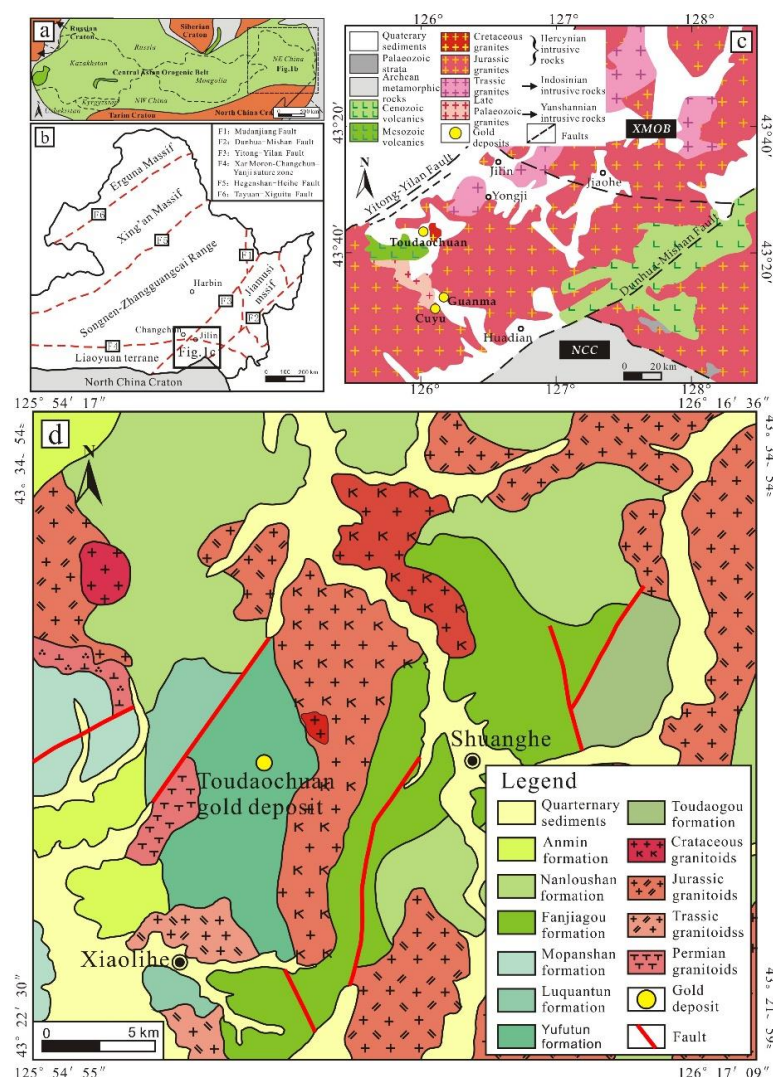


Figure 1. (a) Simplified tectonic map of the CAOB (after Safonova and Santosh [16]). (b) Tectonic divisions of the NE China (after Wu et al. [18]). (c) Geological map of the central Jilin Province, showing some representative gold deposits (after Yang et al. [19]). (d) Detailed geological map of the study area (after JBGMR [20]).

The NNCC comprises dominantly Mesoproterozoic to Paleoproterozoic basement [21–24] and Mesozoic igneous rocks [25–29]. This area has experienced the subduction and closure of the Paleo-Asian Ocean, the subduction of the Paleo-Pacific, and the superimposed conversion of the two tectonic systems [20,30–35], leading to extremely complex tectonic settings and large-scale magma intrusions. The interplay of tectonic and magmatic activities provided superior geological conditions for the various metallogenies and resulted in a large number of copper, gold, tungsten, molybdenum, lead, and zinc deposits.

Central Jilin Province is adjacent to Songnen–Zhangguangcai Range block in the north and NCC in the south, and bounded by Dunhua–Mishan fault and Yitong–Yilan fault to the east and west, respectively (Figure 1b,c). The outcropping strata in this area comprise the Cambrian–Ordovician Toudaochuan formation composed of quartz schist and marble; the Lower Carboniferous Yufutun formation composed of intermediate–basic volcanic rocks; metamorphosed tuff and tuffaceous slate and siltstone and Luquantun formation composed of tuffaceous sandstone and rhyolitic tuff; the Middle Carboniferous Mopanshan formation composed of limestone with chert intercalations; the Lower Permian Fanjiagou formation composed of limestone, siltstone and tuffaceous sandstone; the Lower Jurassic Nanloushan formation composed of andesite, dacite, and dacite tuff; and the

Lower Cretaceous An'min formation composed of rhyolite, rhyolitic tuff, and andesitic tuff [19] (Figure 1d). Affected by the evolution of multiphase tectonic system, many faults and folds striking E–W and NNE developed in the study area. The E–W faults were produced by N–S-trending compression in the Paleo Asian Ocean tectonic regime and reactivated by the Paleo Pacific regime in the Mesozoic. The NNE trending faults were formed under the influence of the NNW trending subduction of the Paleo Pacific plate beneath Eurasia [36,37]. Folds were represented by a large-scale synclinore striking NE in the study area. The two wings of the syncline extended to the NW and SE, formed some small-scale anticlines and thrust nappes under the influence of later tectonic activities [38]. The available geochronological data divided the widespread magmatic rocks in the study area into the following main periods: (1) Hercynian (362–250 Ma) intrusive rocks mainly consist of syenogranite, granodiorite, and monzogranite, as well as a small amount of mafic-ultramafic rocks as batholiths [39]; (2) Indosinian intrusive rocks (250–235 Ma) commonly have the characteristics of adakite, suggesting that they are related to the final closure of the paleo Asian Ocean [40–42]; (3) and Yanshanian intrusive rocks are mostly A/I-type granites, including diorite, tonalite, granodiorite, granite, etc. [20,43], which were spatially and temporally associated with the Mo mineralization in the region [1,2]. In addition, there are various dikes such as diorite porphyrite and granite porphyry intruded in the late Yanshanian period.

3. Toudaochuan Ore Deposit Geology

The lower Carboniferous Yufutun formation, composed of intermediate–basic volcanic rocks, metamorphosed tuff, and tuffaceous slate and siltstone, is developed in the mining area (Figure 2a). The intrusions in the mining area are mainly composed of granite porphyry dikes and diorite porphyrite dikes. Both the granite porphyry dikes and gold-bearing quartz vein are controlled by NE-trending faults and have a similar occurrence and close spatial relationship. The diorite porphyrite dikes intrude along NNE-trending faults and cut across ore bodies and granite porphyry (Figure 2b). Besides NE- and NNE-trending faults, an NNE-trending anticline which is subsidiary to the large-scale synclinore in Central Jilin developed in the east of the mining area. The intersection parts of the anticline and NE-trending faults provide favorable ore-hosting space for the emplacement of gold ore bodies and make mineralization more concentrated.

Fifteen gold orebodies containing about 2 t Au (average 1.01–52.36 g/t), 2.5 t Ag (average 15.64 g/t), and 5 t Cu (average 0.03%) have been identified in the Toudaochuan deposit. The orebodies consist mainly of irregular veined, stockwork, and lenticular-shape gold-bearing sulfide–quartz veins. They are intimately controlled by NE-trending faults and fractures and hosted within the Yufutun formation. The No. 1 and No. 14 are the two major orebodies in the deposit. The No. 1 orebody is about 40 m long and 6–7 m wide at most, dipping at 50°, and a maximum extension depth of about 60 m with the highest gold grade of 160.7 g/t. The No. 14 orebody is about 80 m long and 2 m wide with the highest gold grade of 19.5 g/t [44].

The mineral paragenesis and cross-cutting relationships in Toudaochuan deposit was clarified through field and specimen observations and microscopic studies. The metallic minerals in primary gold ores mainly include chalcopyrite, pyrite, sphalerite, galena, hes-site, petzite, and native gold. The non-metallic minerals include quartz, potassium feldspar, chlorite, epidote, plagioclase, and calcite. Ore structures mainly include massive, veinlet, and miarolitic structures. Ore textures include euhedral–subhedral–anhedral granular texture (Figure 3d) and metasomatic textures (Figure 3e). Such alterations as silicification (Figure 3h), chloritization, epidotization, sericitization (Figure 3i), and carbonation commonly developed in orebodies and granite porphyries. Silicification and epidotization are mainly distributed around the orebodies and are closely related to mineralization. Most chloritization was formed by regional metamorphism, and a small amount is distributed around the ore bodies, which is related to mineralization. Carbonation is mainly formed in the later stage, which cut across orebodies.

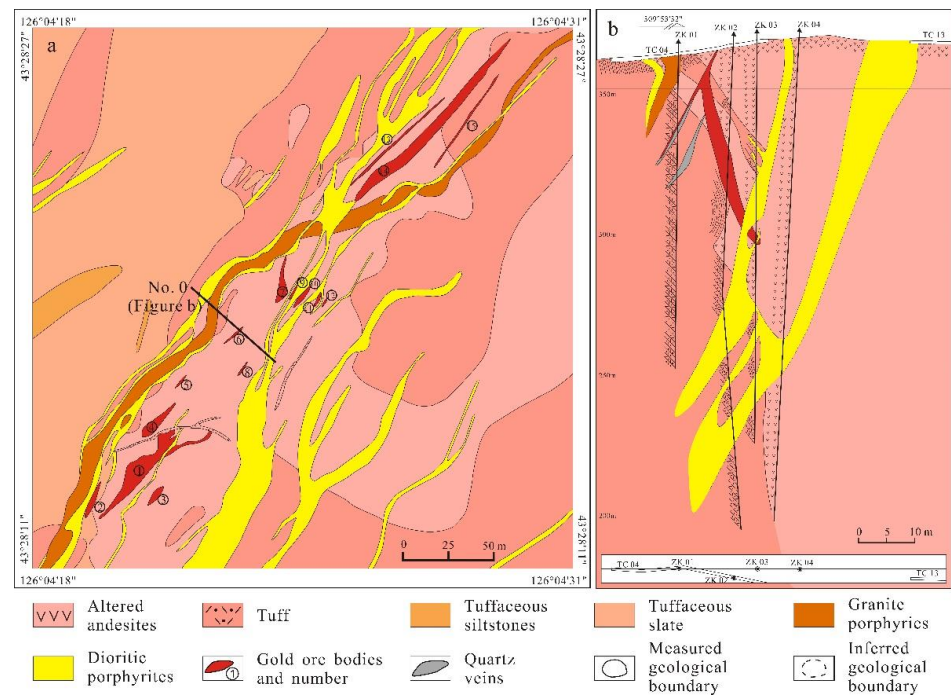


Figure 2. (a) Geologic map of the Toudaochuan deposit. (b) Geologic profile of Toudaochuan exploration line No. 0 (after JBGMR [44]).

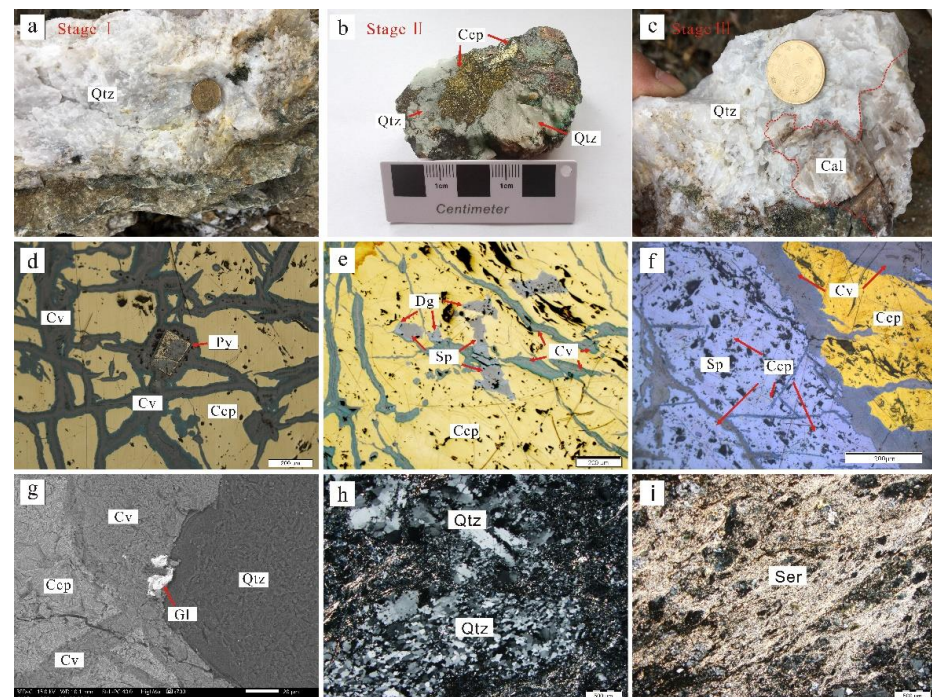


Figure 3. Ore hand specimens, mineralization, and alteration characteristics of the Toudaochuan deposit. (a) sulfide-poor quartz vein from stage I; (b) gold-bearing polymetallic sulfide-quartz vein from in stage II (c) quartz-calcite veins from stage III; (d) euhedral-subhedral granular pyrite from stage I was replaced by the stage II sulfides (reflected light); (e) the sulfides assemblages in stage II (reflected light); (f) minor chalcopyrite distributed in sphalerite with solid-solution separation texture (reflected light); (g) native gold in backscatter photographs; (h) silicification in the surrounding rock strata near the ore bodies (crossed light); (i) sericitization in granite porphyry (crossed light). Abbreviations: Cal = calcite; Ccp = chalcopyrite; Cv = covellite; Dg = digenite; Gl = native gold; Py = pyrite; Qtz = quartz; Ser = sericite; Sp = sphalerite.

According to cross-cutting relationship and mineral paragenesis, mineralization can be divided into two periods: earlier hydrothermal period and later supergene period (Figure 4). The hydrothermal period can be further subdivided into three stages: (1) the quartz–pyrite stage (stage I) is characterized by the occurrence of sulfide-poor white quartz vein (Figure 3a), and the main metal mineral is pyrite as euhedral–subhedral crystal (Figure 3d); (2) the quartz–gold–polymetallic sulfides stage (stage II) is the major gold mineralization stage (Figure 3b) and mainly includes abundant chalcopyrite (Figure 3e,f), sphalerite (Figure 3e,f), native gold (Figure 3g), minor galena, hessite, and petzite, as well as minor chalcopyrite distributed in sphalerite with solid-solution separation texture (Figure 3f); and (3) the quartz–carbonate stage (stage III) is defined by the coexistence of quartz, calcite (Figure 3c), and occasionally chalcopyrite. In the supergene period, covellite (Figure 3d–f), malachite mainly developed.

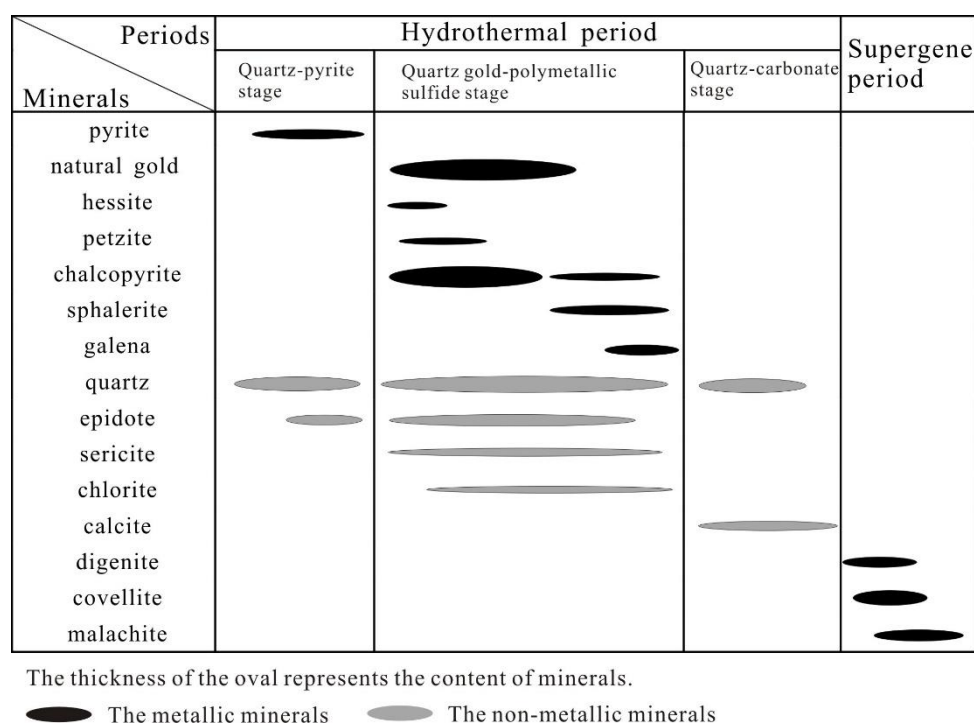


Figure 4. Paragenetic sequence of mineral deposition of the Toudaochuan gold deposit.

4. Samples Description and Analytical Methods

A total of 23 quartz samples were used for the fluid inclusion and C–H–O isotope studies. All quartz samples were selected from the exposed No. 1 orebody and open pit since No. 2–15 orebodies were inaccessible. These quartz samples were formed in different hydrothermal and mineralization stages recognized by observing intersection and overprinting relationships between various veins (veinlets), mineral assemblages, and alteration types. The average weight of each sample is about 3 to 5 kg. They were double-polished into thin sections and used for petrographically fluid inclusion studies, and 7 of them were further analyzed by microthermometry. Samples 7TDC-4–5, 8TDC-5–8, and 7TDC-6 represent the quartz–pyrite stage, quartz–gold–polymetallic sulfides stage, and quartz–carbonate stage, respectively. Four chalcopyrite samples selected from the quartz–gold–polymetallic sulfide stage were used for S and Pb measurement.

4.1. Fluid Inclusions

Microthermometry was carried out on a Linkam THMSG 600 (Linkam Scientific Instruments Ltd., Salfords, UK) heating–freezing stage within a temperature range of –196 to +600 °C at the Fluid Inclusion Laboratory of the Chinese Academy of Geological Sciences, Beijing, China. The accuracy of the stage was calibrated beforehand by using

standard of synthetic FIs produced by America FLUID Inc. (Elyria, OH, USA). The estimated accuracy of the freezing/heating measurements was ± 0.1 °C at temperatures of <30 °C, ± 1 °C at 31–300 °C, and ± 2 °C at temperatures of >300 °C. The heating/freezing rate was generally 2–5 °C/min, but less than 0.2 °C/min near the phase transition. The volatile compositions of single fluid inclusion were identified on a Renishaw RM2000 Raman microprobe (Renishaw, Wotton-under-Edge, UK), using an Ar ion laser with a surface power of 20 mW for exciting the radiation (514.53 nm); the scanning range for the spectra was set between 1000 and 4000 cm^{-1} , with an accumulation time of 60 s for each scan. The laser beam width was approximately 1 μm , and the spectral resolution is approximately 1–2 cm^{-1} .

4.2. C–H–O Isotope Analysis

The quartz samples for the C–H–O isotope analysis were collected together with those in use of fluid inclusions. Quartz grains were crushed into 40–80 mesh and further handpicked under a binocular microscope to ensure a purity of more than 99%. Analyses were measured at the Beijing Research Institute of Uranium Geology, China (BRIUG), using a MAT-253 gas isotope ratio mass spectrometer (Thermo Fisher Scientific, MA, USA). The purified quartzes were heated up to 400–500 °C in terms of an induction furnace, and a mixture of H_2O and CO_2 could be extracted, which were immediately separated by a sophisticated device. Oxygen isotopes were analyzed based on the BrF_5 extraction technique [45]. Hydrogen isotopes were measured for water released from fluid inclusions by thermal decrepitation and reaction with zinc powder. Carbon isotopes were obtained from the CO_2 extracted and separated from fluid inclusions. The δD and $\delta^{18}\text{O}$ were reported relative to the V-SMOW standard, with analytical precisions of approximately $\pm 2\text{‰}$ for δD values, and about $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ values. The oxygen isotope compositions of the fluid ($\delta^{18}\text{O}_{\text{fluid}}$) were calculated based on the following equation: $1000\ln\alpha_{\text{Qtz-H}_2\text{O}} = 3.38 \times 10^6/T^2 - 3.40$ [46]. The $\delta^{13}\text{C}$ values were reported relative to the V-PDB standard, with analytical precisions of approximately $\pm 0.2\text{‰}$.

4.3. S, Pb Isotope Analysis

The S and Pb isotope analyses were completed at the BRIUG. A MAT-251 mass spectrometer with analytical precisions of about $\pm 0.2\text{‰}$ was used for the sulfur isotopic test. The chalcopyrite grains mixed with CuO_2 were heated at 980 °C to produce SO_2 , which was then analyzed by a Delta V Plus gas isotope mass spectrometer. Sulfur isotopic compositions is reported as $\delta^{34}\text{S}$ relative to the CDT standard. Lead isotope analyses were carried out by Isoprobe-T Thermal Ionization Mass Spectrometer, using the standard sample NBS 981. The samples were dissolved by acids, and lead was purified with anion exchange resin. Analytical precision was better than 0.008%. The parameters related to lead isotopes such as μ are calculated with the Geokit software (College of resources and environment, Yangtze University, Jinzhou, China) developed by Lu [47].

5. Results

5.1. Fluid Inclusions Analysis

5.1.1. Petrographic Characteristics

Since the primary fluid inclusions (FIs) are trapped during crystal growth, and the secondary fluid inclusions are trapped after the growth of the host crystal [48,49], the analytical work is focused on the primary inclusions in quartz of all three hydrothermal stages. The microscopic petrographic observation of fluid inclusions shows that the primary fluid inclusions in the quartz veins of Toudaochuan gold deposit are generally distributed as isolated individuals or as random clusters. According to the phases composition at room temperature (25 °C) and phase transitions during heating and cooling, three types of fluid inclusions can be distinguished: liquid-rich aqueous FIs (L-type), CO_2 FIs (C-type), and vapor-rich aqueous FIs (V-type).

The liquid-rich aqueous FIs (L-type) consist of liquid water (L_{H_2O}) and vapor (V_{H_2O}), with 10%–40% vapor–liquid ratios (Figure 5a,c,e–h) at room temperature. They are abundant in quartz from all three hydrothermal stages, most of which are subcircular-, elliptical-, and strip-shaped with sizes ranging from 5 to 20 μm . During the heating process, these inclusions are completely homogenized to a liquid phase.

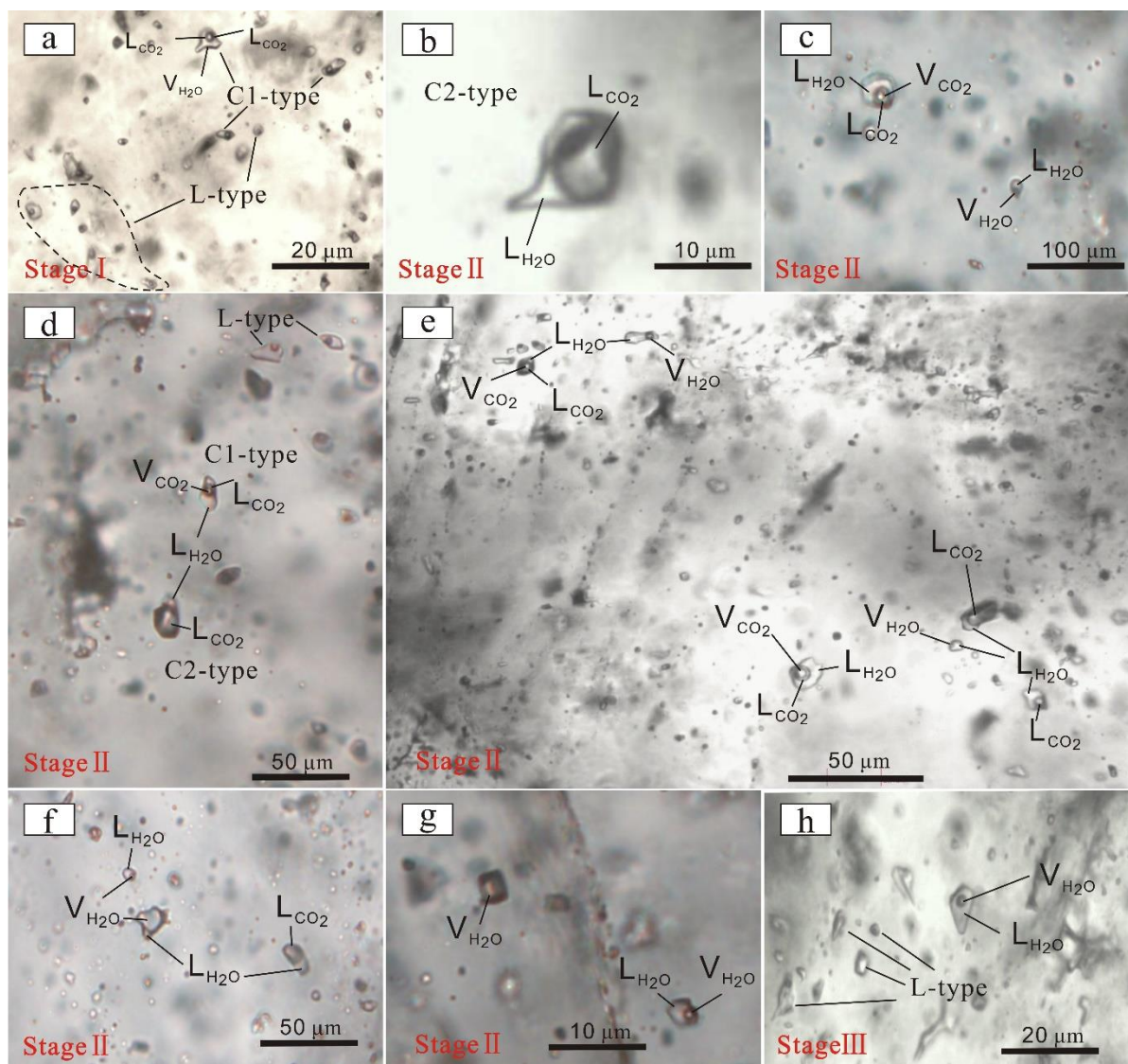


Figure 5. Photomicrographs of typical fluid inclusions in Toudaochuan deposit: (a) C1-type FIs coexisted with L-type FIs in stage I quartz; (b) C2-type FIs as two phases (liquid water + liquid CO_2) at room temperature in stage II quartz; (c) C1-type FIs coexisted with L-type FIs in stage II quartz; (d,e) L-type, C1-type, and C2-type FIs coexisted in stage II quartz; (f) L-type, V-type, and C2-type FIs coexisted in stage II quartz; (g) L-type and V-type FIs coexisted in stage II quartz; (h) L-type FIs assemblage in stage III quartz.

The vapor-rich aqueous FIs (V-type) consist of liquid water (L_{H_2O}) and vapor (V_{H_2O}), with >50% vapor–liquid ratios (few of them are close to pure vapor FIs) (Figure 5f,g). They have a small number and only exist in stage II, coexisting with L- and C-type FIs. They have subcircular and irregular shapes, with sizes ranging from 3 to 15 μm . During the heating process, these inclusions are completely homogenized to vapor phase.

The CO_2 FIs (C-type) consist of liquid H_2O + liquid CO_2 + vapor CO_2 (Figure 5a,c) or liquid water + liquid CO_2 phases (Figure 5b,d) at room temperature, and the latter can

change into the former, with the appearance of CO₂ bubbles when the temperature drops to 10 °C or below. They have negative crystal, ellipsoidal, or irregular shapes and can be further divided into two subtypes, named C1-type and C2-type based on their CO₂-phase volumetric proportions $[(L_{CO_2} \text{ or } V_{CO_2} + L_{CO_2}) / (V_{CO_2} + L_{CO_2} + L_{H_2O})]$. The C1-type is 7–20 µm in size, and their CO₂-phase volumetric proportions are mainly 30%–40% at room temperature (Figure 5a,c–e). This type of inclusion could be observed in stages I and II. They are finally homogenized to liquid H₂O phase. C2-type ones are 5–20 µm in size, and their CO₂-phase volumetric proportions are mainly 60%–85% at room temperature (Figure 5b,d,f). This type of inclusion can only be observed in stage II. They are finally homogenized to liquid CO₂ phase.

5.1.2. Microthermometry Results

The microthermometric data (e.g., T_{m-ice} , T_{m-cla} , T_{m-CO_2} , T_{h-CO_2} , and $T_{h-total}$) and calculated parameters (e.g., salinities and densities) of different types, primary FIs from the three hydrothermal stages, are listed in Table 1 and shown in Figure 6.

Table 1. Microthermometric data for fluid inclusions from the different hydrothermal stages in the Toudaochuan deposit.

Stages	Samples	Type	Quantity	T _{m-ice} (°C)	T _{m-CO2} (°C)	T _{m-cla} (°C)	T _{h-CO2} (°C)	T _{h-total} (°C)	Salinity (%)
Stage I	quartz	L-type C1-type	25 8	−7.9—−3.2	−58.0—−56.8	4.1–6.5	25.6–29.8	212.6–322.8 235.0–335.8	5.2–11.6 6.6–10.4
Stage II	quartz	L-type	30	−5.7—−1.2	−58.0—−57.0	6.0–9.1	26.7–30.0	195.7–282.0	2.1–8.8
		V-type	5	−5.3—−1.1				202.5–275.4	1.9–8.3
		C1-type	24	210.0–298.5				1.8–7.5	
		C2-type	10	212.5–286.2				1.2–7.3	
Stage III	quartz	L-type	24	−2.7—−0.3	−58.2—−56.9	6.1–9.4	26.8–30.0	154.0–229.4	0.5–4.5

Quartz–pyrite stage (stage I): L-type and C1-type FIs (Figure 5a) were dominantly observed in the stage I quartz grains. The initial melting of CO₂ solid (T_{m-CO_2}) in C1-type fluid inclusions ranged from −58.0 to −56.8 °C, while CO₂ clathrate melting temperatures (T_{m-cla}) were 4.1–6.5 °C, corresponding to the salinities ranging from 6.6 to 10.4 wt.% NaCl equivalent (Figure 6b). The partial homogenization of CO₂ phase to liquid phase happened at a temperature of (T_{h-CO_2}) 25.6–29.8 °C. All C1-type inclusions finally homogenized to the liquid water phase at temperatures ($T_{h-total}$) between 235 and 335.8 °C (Figure 6a). The coexisting L-type fluid inclusions yielded ice-melting temperatures (T_{m-ice}) from −7.9 to −3.2 °C, with calculated salinities ranging from 5.2 to 11.6 wt.% NaCl equivalent (Figure 6b). They were homogenized to the liquid phase at temperatures between 212.6 and 322.8 °C (Figure 6a).

Quartz–gold–polymetallic sulfide stage (stage II): In this stage, quartz grains contained all type of FIs, including the L-type, V-type, C1-type, and C2-type FIs (Figure 5c–g). The L-type FIs homogenized to the liquid phase at temperatures 195.7–282.0 °C (mainly 220–250 °C) during heating (Figure 6c). The ice-melting temperatures (T_{m-ice}) ranged from −5.7 to −1.2 °C, with corresponding salinities ranging from 2.1 to 8.8 wt.% NaCl equiv. (Figure 6d). The V-type FIs homogenized to vapor phase at temperatures 202.5–275.4 °C (Figure 6c), and their ice-melting temperatures (T_{m-ice}) ranged from −5.3 to −1.1 °C, with corresponding salinities ranging from 1.9 to 8.3 wt.% NaCl equiv. (Figure 6d). The C1-type FIs yielded initial melting temperatures (T_{m-CO_2}) in the range of solid CO₂ from −58.0 to −57.0 °C, and their clathrate melting temperatures (T_{m-cla}) were 6.0–9.1 °C, corresponding to salinities of 1.8–7.5 wt.% NaCl equiv. (Figure 6d). The CO₂ phase homogenized to the liquid phase at a temperature of 26.7–30.0 °C (T_{h-CO_2}). C1-type FIs were totally homogenized to liquid H₂O at 210.0–298.5 °C ($T_{h-total}$) (Figure 6c). The C2-type FIs yielded initial melting temperatures (T_{m-CO_2}) of solid CO₂ from −58.2 to −56.9 °C, and their clathrate melting temperatures (T_{m-cla}) were 6.1–9.4 °C, corresponding to salinities of 1.2–7.3 wt.%

NaCl equiv. (Figure 6d). The partial homogenization of CO₂ phase happened at 26.8–30.0 °C (T_{h-CO_2}). The C2-type FIs were finally homogenized to liquid CO₂ at 212.0–286.2 °C ($T_{h-total}$) (Figure 6c).

Quartz–carbonate stage (stage III): Only L-type inclusions occurred in this stage quartz grains. They completely homogenized to liquid phase with the homogenization temperature of 154.0–229.4 °C (Figure 6e). Their ice-melting temperatures (T_{m-ice}) were −2.7 to −0.3 °C, with corresponding salinities ranging from 0.5 to 4.5 wt.% NaCl equiv. (Figure 6f).

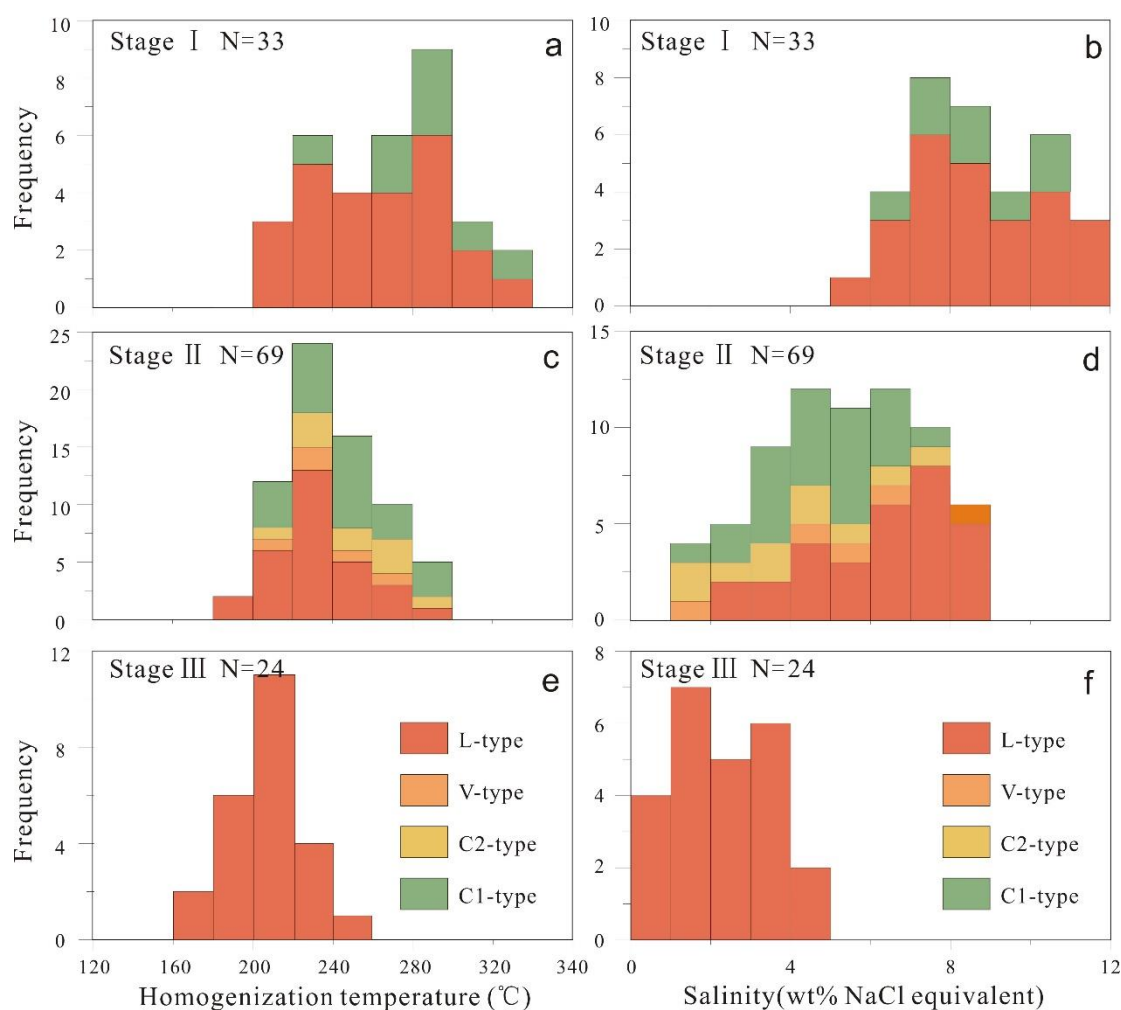


Figure 6. (a–f) Histograms of total homogenization temperatures (T_h) and salinities of FIs from three hydrothermal mineralization stages.

5.1.3. Laser Raman Spectroscopy

Different types of representative fluid inclusions within the quartz of the first two stages were measured by using laser Raman spectroscopy to determine their gas components, and representative spectra are shown in Figure 7. The results showed that only the CO₂ component was detected in the C-type FIs (C1- and C2-type) in the both stage I and II. L-type and V-type FIs were composed of nearly pure H₂O.

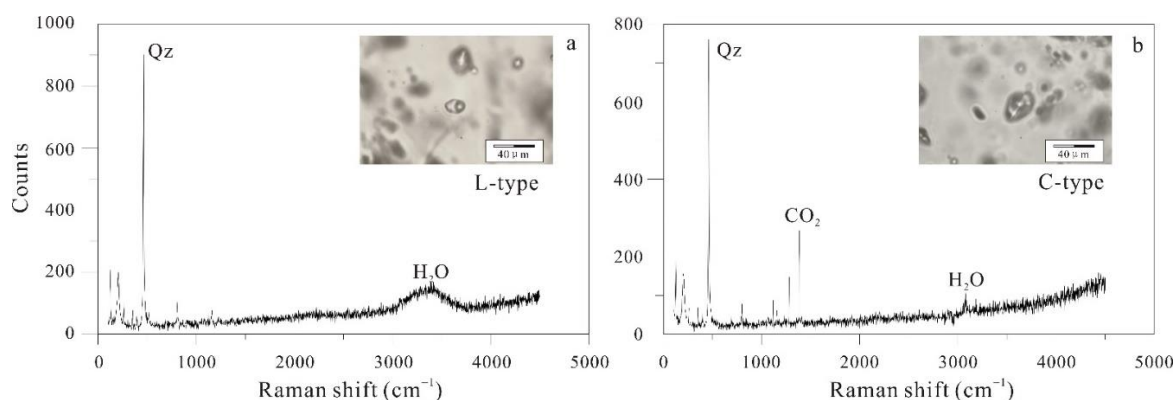


Figure 7. Representative Laser Raman spectra of fluid inclusions in the Toudaochuan deposit: (a) spectrum for C-type FIs and (b) spectrum for L-type FIs.

5.2. C–H–O Isotope Compositions

Hydrogen, oxygen, and carbon isotope data are listed in Table 2. The $\delta^{18}\text{O}_{\text{V-SMOW}}$ values in quartz samples of three hydrothermal stages were 10.9‰–11.9‰, 10.8‰–12.7‰, and 9.7‰–10.2‰, together with fluid inclusion $\delta\text{D}_{\text{V-SMOW}}$ values between −70.2 and −66.3‰, −84.7 and −80.8‰, and −89 and −84.3‰, respectively (Figure 8). The corresponding calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ for three stages were 3.64‰–4.64‰, 1.10‰–3.00‰, and −2.67 to −2.17‰, respectively. The $\delta^{13}\text{C}$ values of the CO_2 extracted from fluid inclusions in quartz range from −8.3 to −7.7‰ (stage I), −15.5 to −8.8‰ (stage II), and −15.6 to −14.5‰ (stage III) (Figure 9).

Table 2. Hydrogen, oxygen, and carbon isotope data of inclusion fluids from the different hydrothermal stages in the Toudaochuan deposit.

Stages	Sample Description	$\delta^{13}\text{C}_{\text{V-PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{V-SMOW}}$ (‰)	$\delta\text{D}_{\text{V-SMOW}}$ (‰)	Th (°C)	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)
Stage I	sulfide-poor quartz veins	−8.3	11.9	−70.2	290	4.64
		−7.7	10.9	−66.3	290	3.64
Stage II	Au-bearing quartz veins	−13.1	12.7	−84.7	235	3.00
		−15.5	11.4	−80.8	235	1.70
		−8.8	10.8	−83.4	235	1.10
Stage III	Quartz veins	−15.6	10.2	−84.3	190	−2.17
		−14.5	9.7	−89	190	−2.67

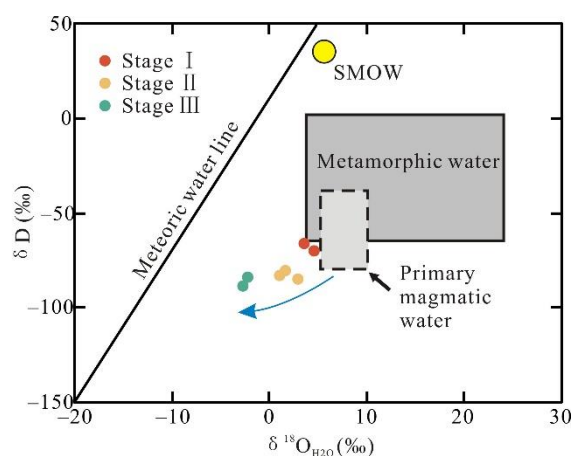


Figure 8. The diagram of hydrogen and oxygen isotopic compositions of the ore fluids for the Toudaochuan deposit. The magmatic, metamorphic water boxes and meteoric water line are from Taylor [50].

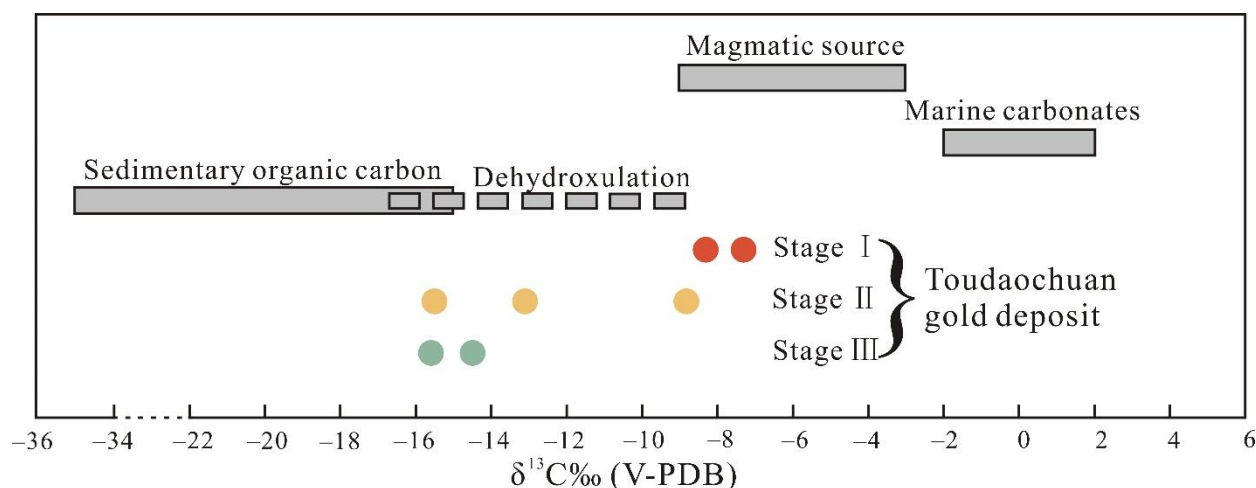


Figure 9. The diagram of carbon isotopic compositions of the ore fluids for the Toudaochuan deposit (after Niu et al. [51]).

5.3. S, Pb Isotope Compositions

The sulfur and lead isotopic analyses were performed on chalcopyrite samples coexisting with gold. Sulfur isotopic compositions are listed in Table 3 and shown in Figure 10. The $\delta^{34}\text{S}$ values of the four chalcopyrite samples were between -6.3 and -5.8 ‰, with an average of -6.0 ‰.

Table 3. The S and Pb isotope compositions of sulfides from the Toudaochuan deposit.

Sample Number	Sample Description	Samples	$\delta^{34}\text{S}$ (‰)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
8TDC-5-1	massive ores	chalcopyrite	-6.3	18.370	15.574	38.295
8TDC-5-2		chalcopyrite	-5.8	18.374	15.567	38.286
8TDC-8-1		chalcopyrite	-5.8	18.388	15.582	38.324
8TDC-8-2		chalcopyrite	-6.2	18.386	15.582	38.323

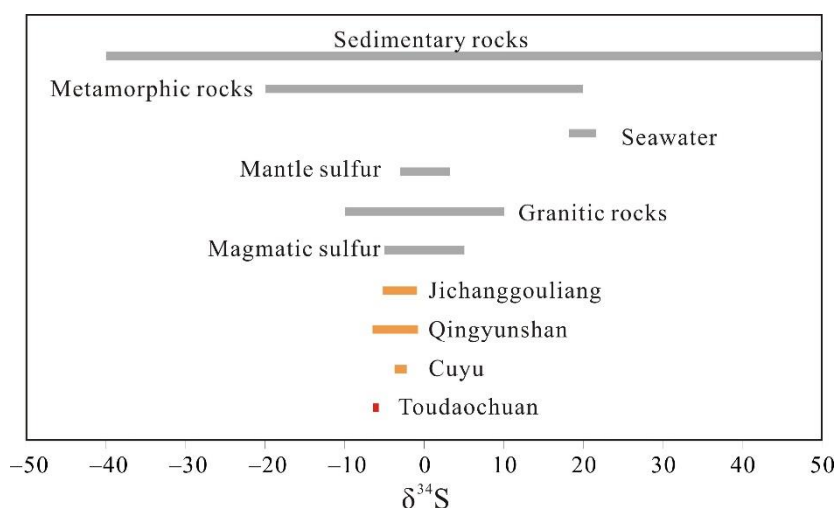


Figure 10. Ranges of the $\delta^{34}\text{S}$ values of selected geologically important sulfur reservoirs and comparison of $\delta^{34}\text{S}$ values between representative deposits and the Toudaochuan deposit (after Zhang et al. [52] and Hoefs et al. [53]).

Lead isotopic compositions are listed in Table 3 and shown in Figure 11. Four chalcopyrite samples gave Pb isotope ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.370–18.388, $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.567–15.582, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 38.286–38.324.

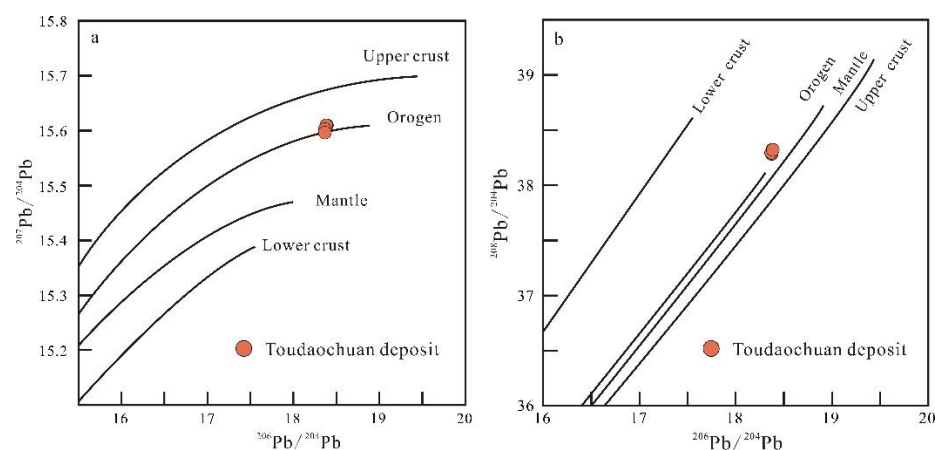


Figure 11. (a,b) Lead isotopic composition for the Toudaochuan deposit (after Zartman and Doe [54]).

6. Discussion

6.1. Sources of Ore-Forming Fluids and Materials

6.1.1. Ore-Forming Fluids

Hydrogen and oxygen isotope compositions, together with the homogenization temperatures of the corresponding FIs have been widely used to trace the source and evolution of ore-forming fluids [50,55,56]. The δD and calculated $\delta^{18}O_{H_2O}$ values of quartz samples in stage I of Toudaochuan deposit are -70.2 to -66.3‰ and 3.64 – 4.64‰ , respectively. These values are close to those of magmatic water (δD : -80 to -40‰ , $\delta^{18}O_{H_2O}$: 5.5‰ – 10‰), and different from those of metamorphic water (δD : -65 to -20‰ , $\delta^{18}O_{H_2O}$: 5‰ – 25‰) [57,58]. In the $\delta^{18}O_{H_2O}$ – δD diagram (Figure 8), the H–O isotopic compositions for the early stage (stage I) fluids are plotted close to the field of the primary magmatic water, indicating that the initial ore-forming fluids were primarily derived from a magmatic source. With fluid evolution, the δD and calculated $\delta^{18}O_{H_2O}$ values of fluid inclusions in quartz decrease from -70.2 to -66.3‰ , via -84.7 to -80.8‰ , to -89 to -84.3‰ , and from 3.64 to 4.64‰ , via 1.10‰ – 3.00‰ , to -2.67 to -2.17‰ , respectively. In Central Jilin Province, the ore-forming fluids of numerous typical deposits (e.g., Toudaoliuhe (Au), Benqu (Au), Erdaogou (Au), Xiaobeigou (Au), Jidetun (Mo), etc.) were mixed with meteoric water during the fluid evolution. Their H–O values after the mixing were concentrated in -105 to -85‰ and -6 to 4‰ , respectively [2,10,11,52,59]. The H–O values of stages II and III in Toudaochuan deposit are comparable to those of these deposits, and the sample gradually shifted toward the meteoric water evolution line in the $\delta^{18}O_{H_2O}$ – δD diagram, both of which indicate that the continuous influx of meteoric water in the process of fluid evolution.

Marine carbonate source ($\delta^{13}C$ mean value of 0‰ , [57]), mantle/magmatic source ($\delta^{13}C$ value of -9 to -3‰ , [60]), and sedimentary organic source ($\delta^{13}C$ value mean value of -25‰ , [61]) are interpreted as the three main carbon sources. The $\delta^{13}C$ values in hydrothermal quartz from the early to later stage in the Toudaochuan deposit are -8.3 to -7.7‰ (stage I), -15.5 to -8.8‰ (stage II), and -15.6 to -14.5‰ (stage III) (Figure 9), suggesting that carbon was mainly derived from a magmatic source and organic carbon source mixed in the later stage.

In general, the ore-forming fluids of the Toudaochuan gold deposit were mainly derived from magma, with continuous input of meteoric water during the evolution.

6.1.2. Ore-Forming Materials

The sulfur isotope composition of sulfide can trace the source of ore-forming materials well [57,62]. S sources are determined based on the total sulfur isotope compositions ($\delta^{34}S_{CS}$), which are impacted by parameters such as the pH value, oxygen fugacity, and temperature and not always equal to $\delta^{34}S$ values, in the ore-forming hydrothermal fluids during sulfide precipitation. However, when sulfur exists mainly in the forms of H_2S and S^{2-} under low oxygen fugacity and low pH circumstances [63], the $\delta^{34}S$ values are approximate to and

can represent the $\delta^{34}\text{S}_{\Sigma\text{S}}$ values of the ore-forming fluids [64,65]. The sulfide assemblages of the Toudaochuan deposit are mainly chalcopyrite, pyrite, and sphalerite, and no sulfate minerals are found. Therefore, the sulfur isotope compositions of sulfide are similar to the total sulfur isotope compositions of ore-forming fluids. The following are several common sources of sulfur in ore-forming fluids: (1) mantle or magma source ($\delta^{34}\text{S}$: $0 \pm 3\%$ and $0 \pm 5\%$, respectively; [56,66,67]); (2) seawater ($\delta^{34}\text{S}$: 20% ; [56]); (3) sedimentary source ($\delta^{34}\text{S}$: -40 to 50% ; [64]); (4) metamorphic source ($\delta^{34}\text{S}$: -20 to 20% ; [64]). Four chalcopyrite samples from the Toudaochuan deposit yielded $\delta^{34}\text{S}$ values of -6.3 to -5.8% , which are similar to Qingyunshan Cu–Au deposit ($\delta^{34}\text{S}$: -3.7 to -2.3% ; [68]), Cuyu gold deposit ($\delta^{34}\text{S}$: -6.5 to -0.9% ; [39]) and Jinchanggouliang gold deposit ($\delta^{34}\text{S}$: -5.2 to 0.9% ; [69]) (Figure 10), such sulfur isotope compositions are similar to but somewhat lower than $\delta^{34}\text{S}$ values of magmatic source, indicating that sulfur was primarily derived from magmatic source with contamination or assimilation by sulfur in the country rock strata.

Lead isotopes of sulfides can also be used to reflect the source of ore-forming metals. Zartman and Doe argued in 1979 that the lead with a μ value of 8.92 was derived from the mantle [70] and then proposed in 1981 that the lead with a μ value of more than 9.58 was derived from the upper crust [54]. The μ values of sulfides from the Toudaochuan deposit ranged from 9.40 to 9.43, indicating that lead was derived from the lower crust. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram (Figure 11b), the Pb isotope compositions of all four sulfides samples were plotted between the lower crust and orogenic belt evolution lines but close to the latter. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram (Figure 11a), they were projected between the upper crust and the mantle area and concentrated nearby orogenic belt evolution lines. Therefore, it is suggested that the metals in the Toudaochuan deposit were derived from a mixed source of mantle and crust.

6.2. Fluids Evolution and Gold Precipitation Mechanism

Petrography and microthermometry results of fluid inclusions showed that the L- and C1-type coexist in the quartz–pyrite stage (stage I). These FIs have similar homogenization temperatures and corresponding salinities which concentrated at $260\text{--}300\text{ }^{\circ}\text{C}$ and $7\text{--}11\text{ wt.}\%$ NaCl equivalent, respectively, indicating that they were captured simultaneously [49]. They have similar vapor–liquid ratios and homogenization behaviors, which both homogenized to liquid H_2O . Furthermore, laser Raman spectroscopy showed that the vapor phase components in different FIs were mainly H_2O and CO_2 . Therefore, the initial ore-forming fluids belonged to the $\text{CO}_2\text{--H}_2\text{O--NaCl}$ system characterized by moderate temperatures and moderate–low salinities.

The quartz–gold–polymetallic sulfides stage (stage II) contained all types FIs, with L-type, C1-type, and C2-type being the most developed. The peak total homogenization temperatures and corresponding salinities of all of these FIs concentrated at $220\text{--}260\text{ }^{\circ}\text{C}$ and $3\text{--}8\text{ wt.}\%$ NaCl equivalent, respectively. Laser Raman spectroscopy also showed that the vapor phase components in all FIs were mainly H_2O and CO_2 . These characteristics revealed that the ore-forming fluid at this stage belonged to a medium–low temperature and medium–low salinity $\text{H}_2\text{O--CO}_2\text{--NaCl}$ system.

The following petrographic and microthermometric characteristics of the FIs indicate that fluid immiscibility occurred during the quartz–gold–polymetallic sulfide stage (stage II). (1) Various types of FIs frequently coexisted in the same quartz grains, implying that they were captured at the same time [49]. (2) The C1- and C2-type FIs, as well as the L-type and a small number of V-type FIs had overlapping homogenization temperature ranges but different homogenization behaviors [48,49,71]. During heating, the C1- and C2-type FIs homogenized to liquid H_2O and liquid CO_2 phases, respectively; the L- and V-type FIs homogenized to liquid H_2O phase and vapor H_2O phase, respectively. (3) Distinct types of FIs showed comparable homogenization temperature ranges but varied salinity ranges. Previous studies of the solubility of Au in hydrothermal systems had shown that gold is most likely transported as $[\text{Au}(\text{HS})_2]^-$, $\text{Au}(\text{HS})$, and $[\text{AuCl}_2]^-$ [72–74]. In the Toudaochuan deposit, the widespread occurrence of CO_2 -rich FIs and the coexistence of gold and sulfides

suggested that $[\text{Au}(\text{HS})_2]^-$ was the likely agent responsible for Au transport [75,76]. During the migration and evolution of ore-forming fluids, the occurrence of fluid immiscibility made CO_2 in ore-forming fluids escape. The escape of CO_2 increased the pH values of the solution [76], destroyed the stability of Au-bisulfide complexes, and reduced the solubility of Au, resulting in the precipitation of gold and sulfides [77–82]. Gold accompanied by a large number of sulfides could be observed at stage II, while only a small amount of pyrite occurred at stage I. Therefore, fluid immiscibility is regarded as an important and plausible mechanism for gold precipitation in the Toudaochuan gold deposit.

The fluid immiscibility that occurred in stage II caused CO_2 to be eliminated from the ore-forming fluids and only L-type FIs to be developed in the quartz–carbonate stage (stage III). The FIs' homogenization temperatures dropped to 154.0–229.4 °C, and the salinities dropped to 0.5–4.5 wt.% NaCl equivalent compared to earlier stages. In addition, the H–O isotope compositions shifted dramatically toward the meteoric water line. The considerable fall in temperatures and salinities, as well as the features of H–O isotopic compositions, revealed that the ore-forming fluid had evolved into an H_2O –NaCl system with low temperatures and salinities at this stage, owing to the continual inflow of meteoric water.

6.3. Genetic Type and Ore-Forming Process

As mentioned above, there are controversies over the genetic type of the Toudaochuan gold deposit, and the arguable focus can be summarized as whether it is the metamorphic hydrothermal origin [13,14] or magmatic–hydrothermal origin [12]. This study showed that the Toudaochuan gold deposit has similar characteristics to the magmatic–hydrothermal gold deposit, as follows. The Au-bearing sulfide–quartz veins ore bodies hosted in the metamorphic volcanic rocks of the Yufutun formation were mainly controlled by the NE-trending faults and were accompanied by granite porphyry and diorite porphyrite dikes. The wall-rock alterations, such as silicification, sericitization, and chloritization, are similar to those found in mesothermal magmatic–hydrothermal deposits [83,84]. The ore-forming fluids belonged to an H_2O – CO_2 –NaCl system with medium–low temperatures and medium–low salinities at stages I and II and finally evolved into a low-temperature and low-salinity H_2O –NaCl system at stage III. Such characteristics of the ore-forming fluids were also similar to those of magmatic–hydrothermal gold deposits, such as the Shajingou (China) [85], Jinchanggouliang (China) [69], Liyuan (China) [86], Berezovsk (Urals), and Linares (Spain) [87]. The C–H–O isotope data showed that the ore-forming fluids were predominantly magmatic water. The S isotopic compositions ($\delta^{34}\text{S}$: −6.3 to −5.8‰) differed significantly from those of typical metamorphic hydrothermal gold deposits (orogenic gold deposits) ($\delta^{34}\text{S}$: 0–9‰; [88,89]). The Pb isotope compositions of sulfides implied that the ore-forming materials were derived from a mantle–crust mixed source. Moreover, the geological evidence also showed that the granite porphyry dikes in the Toudaochuan gold deposit may have a close genetic relationship with gold mineralization. Firstly, no other intrusions, except for granite porphyry dikes and diorite porphyrite dikes developed in and around the mining area, and no concealed granites and ore bodies had been found. Granite porphyry dikes and ore bodies had a close spatial relationship which occurred in parallel and had similar occurrences. Secondly, previous studies have shown that the content of Au in most of the surrounding rock strata was low, and only a small amount of Au (mostly 0.01–0.1 g/t) was contained in the sections with strong alterations of the surrounding rock strata, while the content of Au in most of the granite porphyry samples was high, up to 160 g/t in some cases [44]. In addition, according to field observation, although diorite porphyrite dikes were closely related to ore bodies spatially, they cut across granite porphyry dikes and gold ore bodies and had insignificant alteration and mineralization. Therefore, the diorite porphyrite dikes should be emplaced after mineralization. In summary, based on the above features of mineralization and alteration, characteristics of the ore-forming fluids, sources of the ore-forming fluids and materials, and the comparison with some typical magmatic–hydrothermal deposits (Table 4), the Toudaochuan can be classified as the mesothermal magmatic–hydrothermal gold deposit.

Table 4. Comparison between the Toudaochuan Au deposit and typical mesothermal magmatic–hydrothermal gold deposits.

Deposits	Ore-Hosting Rocks	Orebody Shape	Ores Structures and Textures	Metal Mineral Assemblies	Wall Rock Alterations	Fls Characteristics	Source of Ore-Forming Fluids	Source of Ore-Forming Materials	Ore Genesis	References
Toudaochuan	Intermediate–basic volcanic rocks, metamorphosed tuff and tuffaceous slate and siltstone of Yufutun formation	Irregular veined, stockwork and lens shape	Massive, veinlet, and miarolitic structures; euhedral–subhedral–anhedral granular texture and metasomatic texture	chalcopyrite, pyrite, sphalerite, galena, hessite, petzite, and native gold	Silicification, chloritization, sericitization, carbonation	Liquid-rich aqueous, vapor-rich aqueous, CO ₂ -rich and CO ₂ -bearing Fls; medium–low temperature, medium–low salinity H ₂ O–CO ₂ –NaCl fluids	Magmatic water and mixing of the meteoric water	A mixed source of mantle and crust	Mesothermal magmatic–hydrothermal deposit	This paper
Shajingou	Middle Jurassic diorite	Veined	Disseminated, vein, veinlet, taxitic and nodular structures; euhedral–subhedral granular, cataclastic, and metasomatic textures	Pyrrhotite, chalcopyrite, pyrite, native gold	Silicification, chloritization and sericitization	Liquid-rich aqueous, CO ₂ -pure, CO ₂ -rich and CO ₂ -bearing Fls; medium–high temperature, medium–low salinity H ₂ O–CO ₂ –NaCl fluids	Dominantly from magmatic fluid and mixed with meteoric water	-	Mesothermal magmatic–hydrothermal quartz-vein deposit	[85]
Jinchanggouliang	Xiaotazigou metamorphic rocks of the Archean Jianping Group, including biotite hornblende and plagioclase gneiss	Veined	Veinlet, banded, disseminated, brecciated and massive structures; metasomatic relict, anhedral granular, exsolution textures	Pyrite, chalcopyrite, galena, sphalerite, and native gold	Silicification, sericitization, pyritization, chloritization and carbonatization	halite-bearing inclusions, aqueous inclusions, and CO ₂ –H ₂ O inclusions; moderate–high temperature and great fluctuating salinity H ₂ O–CO ₂ –NaCl fluids	Magmatic water	derived from deep magma	Magmatic–hydrothermal deposit	[69]

Table 4. Cont.

Deposits	Ore-Hosting Rocks	Orebody Shape	Ore Structures and Textures	Metal Mineral Assemblies	Wall Rock Alterations	Fls Characteristics	Source of Ore-Forming Fluids	Source of Ore-Forming Materials	Ore Genesis	References
Heilongtan-Xiejiagou (China)	Middle–low grade metamorphosed volcanic rocks of Wudang group and low-grade metamorphic rocks of Yaolinghe group	Bedded, lentoid, and veined	-	Sphalerite, chalcopyrite, pyrite, galena, tetrahedrite	Potassic feldspathization, silicification, sericitization, carbonation	Aqueous, CO ₂ -pure and CO ₂ -bearing Fls; medium–low temperature, medium–low salinity H ₂ O-CO ₂ -NaCl fluids	dominantly from magmatic fluid and mixed with meteoric water	Mixture of magma and surrounding metamorphic rocks	Magmatic–hydrothermal vein-type deposit	[51]
Samhwanghak (Korea)	Precambrian metamorphic rock and granodiorite batholith	Veins	Massive and ribbon structures	Sphalerite, pyrrhotite, chalcopyrite, pyrite, galena, tetrahedrite	Silicification, chloritization, sericitization, carbonation, kaolinization, illitization	CO ₂ (±CH ₄)-rich, aqueous Fls; Medium–high temperature, low salinity H ₂ O-CO ₂ -NaCl fluids	Magmatic water	Magmatic sulfur	Mesothermal magmatic–hydrothermal deposit	[90]

Based on the above discussion results, the ore-forming processes for the Au mineralization of the Toudaochuan deposit are proposed below and illustrated in Figure 12. For the initial ore-bearing fluid exsolved from granitic magma, NE-trending faults provided ideal migration channels. The initial ore-forming fluid was mostly constituted of magmatic water rich in Au and other metals, as well as CO_2 during the early stage of mineralization. The ore-forming fluid largely developed rich-liquid (L-type) and CO_2 -bearing (C1 type) FIs and was characterized by medium temperatures and medium–low salinities. At this stage, just a limited amount of coarse euhedral–subhedral pyrite was deposited, and there was no gold mineralization. During the migration of ore-forming fluids, the CO_2 component can buffer the pH value of the solution, ensuring the steady and continuous migration of the gold–disulfide complex [76].

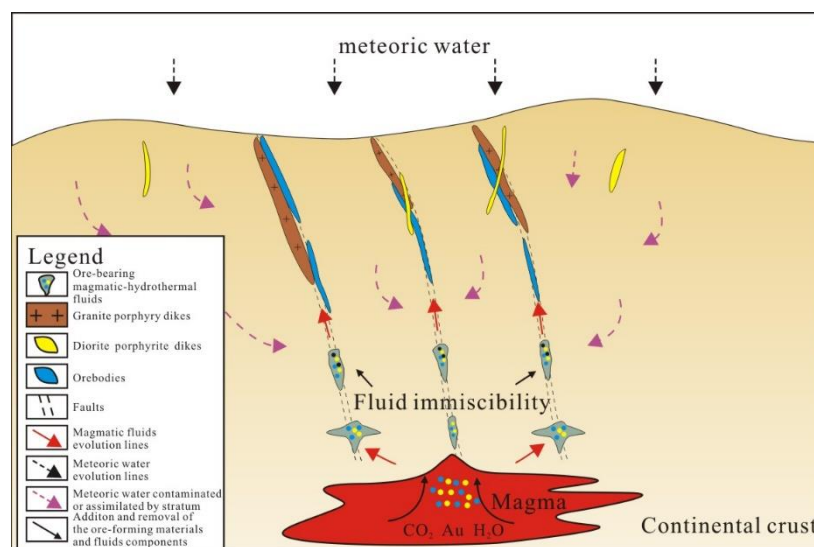


Figure 12. Simplified cartoon for the ore-forming model of the Toudaochuan deposit.

Subsequently, meteoric water carrying a small amount of organic carbon was mixed with the initial ore-forming fluid, resulting in the mixed source of carbon isotopes discussed above. Meanwhile, the inflow of meteoric water and the decreased fluid pressure induced fluid immiscibility. The immiscibility resulted in the release of CO_2 from the ore-forming fluids, thereby increasing the pH, which destroyed the stability of the gold–disulfide complex. These changes in physicochemical conditions caused the precipitation of a large number of gold and polymetallic sulfides at stage II (the main mineralization stage), leading to the formation of abundant quartz–polymetallic sulfide veins accompanied by silicification, chloritization, epidotization, and sericitization. The quartz–polymetallic sulfide veins were finally filled, enriched, and precipitated at the NE-trending structural faults or structural intersections.

With the continuous addition of meteoric water, the late ore-forming fluid gradually evolved into the $\text{NaCl-H}_2\text{O}$ system, which is characterized by a low temperature and low salinity. At this stage, some calcite veinlets were formed and cut through the ore body, indicating that the hydrothermal mineralization was basically over.

7. Conclusions

The Toudaochuan gold deposit, in light of the received examination results, is a mesothermal magmatic–hydrothermal gold deposit. It is likely related to the granite porphyry dikes developed in the mining area. The mineralization process can be divided into the primary hydrothermal and supergene period, and the hydrothermal period can be further divided into the quartz–pyrite stage, quartz–gold–polymetallic sulfide stage, and quartz–carbonate stage, in which the gold–polymetallic sulfide stage is the major gold mineralization stage.

The primary fluid FIs in ore-bearing quartz in the Toudaochuan gold deposit mainly included liquid-rich aqueous FIs (L-type), CO₂ FIs (C-type, including CO₂-bearing C1-type FIs and CO₂-rich C2-type FIs), and minor vapor-rich aqueous FIs (V-type). The ore-forming fluids evolved from a medium-temperature, medium-low salinity CO₂-H₂O-NaCl system to a low-temperature, low-salinity H₂O-NaCl system.

The C-H-O isotope compositions suggest that ore-forming fluids were derived mainly from a magmatic source, with the inflow of meteoric water and organic carbon source in the later stage. The S isotope compositions show that sulfur was primarily derived from magmatic source with contamination or assimilation by sulfur in the country rock strata. The Pb isotope compositions indicate that the metals were derived from a mixed source of mantle and crust.

The fluid immiscibility in stage II is the key mechanism of gold mineralization. Fluid immiscibility caused CO₂ to escape from the ore-forming fluid, increased the pH value of the solution, reduced the stability and solubility of gold-sulfur complexes, and finally lead to the precipitation of gold and sulfides (e.g., chalcopyrite and sphalerite).

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