Research Article

Geology, Fluid Inclusion, and H–O–S–Pb Isotope Constraints on the Mineralization of the Xiejiagou Gold Deposit in the Jiaodong Peninsula

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The Xiejiagou deposit is a representative medium-sized gold deposit in Jiaodong the Peninsula, which contains gold reserves of 37.5 t. The orebodies are hosted in the Linglong biotite granite with a zircon LA-ICP-MS U–Pb age of 160 ± 3 Ma (N = 15, MSWD = 1.2) and are characterized by disseminated- or stockwork-style ores. Mineralization and alteration are structurally controlled by the NE-striking fault. Three stages of mineralization were identified with the early stage being represented by (K-feldspar) sericite quartz pyrite, the middle stage by quartz gold polymetallic sulfide, and the late stage by quartz carbonate. Ore minerals and gold mainly occurred in the middle stage. Three types of primary fluid inclusions were distinguished in the Xiejiagou deposit, including carbonic-aqueous, pure carbonic, and aqueous inclusions. The primary fluid inclusions of the three stages were mainly homogenized at temperatures of 262–386°C, 192–347°C, and 137–231°C, with salinities of 2.22–8.82, 1.02–11.60, and 1.22–7.72 wt% NaCl equivalent, respectively. These data indicate that the initial ore-forming fluids were a medium temperature, CO₂-rich, and low-salinity H₂O–CO₂–NaCl homogeneous system, and the ore-forming system evolved from a CO₂-rich mesothermal fluid into a CO₂-poor fluid. Considering the fluid inclusion characteristics, H–O–S–Pb isotopes, and regional geological events, the ore-forming fluid reservoir was likely metamorphic in origin. Trapping pressures of the first two hydrothermal stages estimated from the carbonic aqueous inclusion assemblages were ~224–302 MPa and ~191–258 MPa, respectively. This suggests that the gold mineralization of the Xiejiagou gold deposit occurred at a lithostatic depth of ~7.2–9.7 km. Au(HS)₂ was the most probable gold-transporting complex at the Xiejiagou deposit. Precipitation of gold was caused by a CO₂ effervescence of initial auriferous fluids.

1. Introduction

The Jiaodong Peninsula (Figure 1) is an important gold metallogenic belt in China hosting about 4000 t of gold reserves and also considered as one of the most famous gold mineralization belts in the world [1–11]. The majority of gold deposits in the region are temporally and spatially related to Mesozoic NE-trending faults, and the deposits have been classified as Jiaojia-type and Linglong-type mineralization, where the former refers to a combination of disseminated and stockwork/veinlet gold mineralization and the latter to auriferous quartz veins [1, 12–15]. The Jiaodong gold belt is dominated by Jiaojia-type gold deposits, which make up more than 80% of its gold resources [16, 17], and extensive research has been under taken on them ([14, 15, 18–22] and the references therein). Gold mineralization in the region is generally considered to have occurred during the Early Cretaceous, with a peak age at 120 ± 5 Ma [23], although there are still controversies regarding the ore-forming age [20].

Gold deposits are generally related to tectonic, geological, and geochemical processes, in which the nature of the hydrothermal fluids is of fundamental importance [24–26]. 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 [27] speculated that the ore-forming fluids were meteoric in origin. More recently, Fan et al. [16, 17] suggested that the ore-forming fluids originated from magmatic water, and Zeng et al. [28] suggested that the gold mineralization resulted from magmatic-hydrothermal processes. In addition, because some of the orebodies within these deposits are accompanied by intermediate-mafic dikes, therefore, the ore-forming fluids have been inferred to be derived from the mantle [28], although a combination of crustal and mantle components has also been proposed [16, 17]. Alternatively, based upon ore geological characteristics and mineralization style, the Jiaodong gold mineralization has been treated as an “orogenic type” and it has been proposed that the ore-forming fluids were derived from metamorphic water [21]. Although some geologists classified these as orogenic gold deposits, the nearly 1.7-billion-year gap between gold mineralization and the latest regional metamorphism, together with the tectonic settings, has raised doubt on the orogenic gold deposit model [5, 9, 18, 23]. Therefore, it is difficult to apply the conventional classification schemes for common ore deposit types (such as epithermal gold, orogenic gold, porphyry gold,...) to define the formation of the Jiaodong gold mineralization. The Xiejiagou deposit is a representative medium-sized Jiaobei-type gold deposit, which contains gold reserves of >35t. Given that this deposit is an important producer of gold, some geochemical studies have been undertaken with the aim of characterizing the nature of the Au mineralization (e.g., [29–34]). Nevertheless, the nature and evolution of the fluid associated with gold mineralization have not been well documented through petrographic, isotopic, and fluid inclusion studies, which limit our understanding of gold mineralization of the Xiejiagou deposit. Based on previous geological information on the Xiejiagou deposit, in particular, petrographic, microthermometric, and Raman spectroscopic analyses for inclusions contained within different stage veins were conducted to investigate the ore-forming P-T conditions and examine the mechanisms of gold transport and deposition. In addition, based on the geologic characteristics and isotopic compositions (H, O, S, and Pb) of the ores from the deposit, we try to trace the origin of ore-forming fluids. We hope that this study can further address the implications for the better understanding of the gold mineralization in the Jiaodong Peninsula.

2. Regional Geology

The Jiaodong Peninsula, located in east Shandong Province, occupies the southeastern margin of the North China Block (NCB) and is bounded by the Tanlu fault in the west (Figure 1). This region consists of two tectonic units, the Jiaobei terrane in the west and Sulu terrane in the east, bordered by the Wulian-Qingdao-Yantai fault (WQYF) (Figure 1). The Jiaobei terrane comprises the Jiaobei uplift in the north and the Jiaolai basin in the south (Figure 1). The Jiaobei uplift is the primary host of gold on the Jiaodong Peninsula with
gold reserves of more than 3600 t ([19], 90% of the proven gold resources). The main lithological units in the Jiaobei uplift include the metamorphosed Precambrian basement, as well as widespread Mesozoic intrusive rocks [35], Figure 1. The Precambrian basement includes the Neoarchean Jiaodong, Paleoproterozoic Jingshan, and Fenzishan groups [36], Figure 1. The Jiaodong group is characterized by widely distributed late Archean tonalitic, trondhjemitic, and granodioritic gneisses, as well as supracrustal amphibolites and gneisses that yield U–Pb zircon ages of mainly between 2.9 and 2.5 Ga [37]. The Paleoproterozoic Jingshan and Fenzishan groups contain widespread schist, marble, and amphibolite, plus minor amounts of mafic granulite. These groups yield metamorphic zircon ages of about 1.8 Ga and underwent amphibolite- to granulite-facies metamorphism and deformation [38]. Mesozoic granitoids that intruded into the Jiaobei uplift have been traditionally divided into the Late Jurassic Linglong granite and the Early Cretaceous Guojialing granite, with both of them being significant hosts for gold mineralization ([39–41], Figure 1). Mesozoic volcanic rocks were widespread in the Jiaolai basin (Figure 1). The volcanic sequences mainly include trachybasalt, trachyte, and rhyolite, forming at about 110–95 Ma [42]. The Sulu terrane is formed by the subduction of the Yangtze Block beneath the NCB in the Triassic [43] and is characterized by the presence of high and ultra-high-pressure (HP to UHP) metamorphic rocks as well as Late Triassic, Late Jurassic, and Early Cretaceous granitoids (Figure 1). Subsequently, these rocks were unconformably overlain by Cenozoic basalt and Quaternary sedimentary rocks (Figure 1).

Most of these gold deposits in the Jiaobei uplift are controlled by the NE- to NNE-trending fault systems ([39], Figure 1): from west to east, the Sanshandaofu fault (SSDF), Jiaojia fault (JJF), Zhaoping fault (ZPF), Muping-Jimo fault (MJJF), and Qixia fault (QXF). These faults are subsidiary faults to the continental-scale Tanlu fault zone [44]. Among them, the ZPF is one of the most important tectonic structures controlling second-order ore-hosting faults in the Jiaobei uplift [1, 44, 45].

3. Ore Deposit Geology

The Xiejiagou gold deposit is located about 5 km southwest of Zhaoyuan city in the northwestern part of the Jiaobei uplift and near the middle part of the ZPF (Figure 1). Structurally, the mineralization and hydrothermal alteration are controlled by a series of NE-trending secondary faults (ductile shear structures and brittle faults) located in the hanging wall of the ZPF fault zone (Figure 2). The principal lithologic unit in the Xiejiagou deposit is a pluton of biotite granite, the so-called Linglong granite. Numerous intermediate-mafic dikes are widespread in the Xiejiagou gold deposit. Among them, the lamprophyre dikes (pre-ore, Figure 2(b)) are cross-cut by orebodies or faults and display intense hydrothermal alteration with a whole rock K–Ar age of 123.6 Ma [29], whereas the orebodies are cut by the NW-trending diorite porphyrite, gabbro diorite, and dolerite dikes (post-ore, Figures 2(a) and 2(b)) with whole rock K–Ar ages of 98.6 to 115.2 Ma [29], 97.2 to 98.8 Ma [29], and 100.5 to 107.6 Ma [29], respectively. These geochronological data indicate that the age of Xiejiagou gold mineralization occurred at ~123.6–115.2 Ma, which is identical to 120 ± 5 Ma, the generally considered main mineralizing period of the major gold deposits within the Jiaodong Peninsula [46]. The formation of the Jiaodong gold mineralization including Xiejiagou deposit was closely related with subduction of the Paleo-Pacific Plate beneath the Eurasian continent accompanied by lithospheric delamination, asthenospheric upwelling, and intense craton destruction [4–9].

The Xiejiagou deposit currently has proven reserves of about 37.5 t of Au [33]. Most of the orebodies are lenticular or irregular lodes and are controlled by the NE-trending faults, which cut the granitoids (Figure 2). The ore-controlling faults are 200–1000 m long and 2–15 m in width with a strike of 20 to 35° and a dip of 60° to 85° (Figure 2). Four major orebodies have been identified in the ore district, and no. 3 is the largest and most representative (Figure 2), containing roughly 70% of the total proven gold reserves of the deposit [32]. The no. 3 orebody is 600 m in length with a gentle dip of 76° to 85° and contains an ore grade of 3.0 to 6.8 g/t Au [31]. We have focused on the no. 3 orebody, as it is the most productive for Au. The mineralization style of the Xiejiagou deposit appears associated with pyrite sericite silica-altered granites or fine pyrite veinlets, belonging to the disseminated- and stockwork-style gold mineralization. Extensive hydrothermal alteration also occurs in ore-controlling faults and is characterized by K-feldspar, quartz, sericite, pyrite, chlorite, and carbonate (Figures 3(a)–3(f)). Major ore minerals in the Xiejiagou deposit include pyrite, galena, sphalerite, and chalcopyrite, along with minor pyrrhotite (Figures 3(g)–3(l)). The gangue minerals include 80% quartz with amounts of K-feldspar, sericite, chlorite, calcite, and clay minerals (Figure 3). Au occurs mostly as native gold, followed by electrum. Native gold grains occur mainly as inclusions in pyrite crystals (Figure 3(k)) and less commonly in tiny fissures of pyrite. Electrum occurs mainly as inclusions in sphalerite or galena crystals (Figure 3(l)).

4. Hydrothermal Quartz Vein Sequences and Mineral Assemblages

Three hydrothermal stages and a supergene stage have been identified in the Xiejiagou deposit on the basis of mineralogical assemblage, textures, and cross-cutting relationships observed in hand specimens and thin sections (Figures 3 and 4). The hydrothermal ore-forming processes occurred during an early (K-feldspar) sericite quartz pyrite stage, a middle quartz gold polymetallic sulfide stage, and a late quartz carbonate stage (Figure 5). The gold mineralization occurred in the middle stage.

The early hydrothermal stage is characterized by (K-feldspar) sericite pyrite silica alteration granites (Figure 4(a)) or in ore-barren quartz veinlet places (Figure 4(b)). Minerals comprise milky quartz, sericite, K-feldspar, and sparsely distributed euhedral cube pyrite (Figures 3(a), 3(b), 3(g), 4(a), and 4(b)). The main mineral assemblage in this stage is milky subhedral/anhedral quartz (Qz1), sericite, K-feldspar, and sparsely distributed euhedral cube pyrite, with variables of
albite and muscovite (Figures 3(a), 3(b), 3(g), 4(a), 4(b), and 5). Not any gold was found in our observation. The early-stage ores were locally cut or cemented by middle- or late-stage veinlets (Figures 4(c) and 4(f)).

The middle stage is the main gold-producing stage and is characterized by the quartz gold polymetallic sulfide veinlets (Figures 4(c) and 4(d)). During this stage, large amounts of sulfide minerals were precipitated including pyrite, galena, sphalerite, chalcopyrite, and minor pyrrhotite (Figures 3(h)–3(j)). Quartz in the middle stage (Qz2) is commonly dark-gray (smoky) in color coexisting with sulfide minerals and minor calcite (Figures 4(c)–4(e)). Gold mainly occurs as native gold and that coexists with other sulfide minerals (Figures 4(e) and 4(f)).

The late stage is characterized by quartz carbonate veinlets. This stage mainly contains calcite, quartz, and siderite, with trace amounts of pyrite (Figures 4(e) and 4(f)). No gold has been identified under reflected light in this stage. The paragenetic sequence of the Xiejiagou gold deposit is summarized in Figure 5.

5. Sampling and Analytical Methodology

5.1. Zircon U–Pb Dating. Zircons were separated by an unaltered Linglong biotite granite sample (C156-13) from the south of the Xiejiagou gold deposit (Figure 2(a)). The main minerals of the medium-grained biotite granite sample (C156-13) are plagioclase (30%), K-feldspar (30%), quartz (35%), and biotite (5%) (Figure 6(a)), with accessory titanite, zircon and apatite. Zircon sample preparation, cathodoluminescence (CL), and back-scattered electron imaging were completed at the Nanjing Hongchuang Exploration Technology Service Company Limited. U–Pb dating was performed on a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for constraining the age of the wallrocks of the deposit.

LA-ICP-MS U–Pb isotope analyses were conducted using an Agilent 7500 mass spectrometer connected to a 193 nm ArF excimer laser ablation system at the Wuhan Sample Solution Analytical Technology Company Limited. The synthetic silicate glass standard reference material NIST
Figure 3: Continued.
SMR610 was used to calibrate the instrument, and the international reference standard zircon 91500 was used as the external standard for age calibration. During the analyses, high-purity He gas was used to transfer the ablated materials. The spot size was 32 mm. For detailed procedures and methods, as well as the instrument settings, see Yuan et al. [47]. The ICPMSDataCal [48, 49] and Isoplot 3.0 software [50] were used for data reduction. Common Pb corrections were undertaken using the approach of Andersen [51]. Fifteen zircon analyses were performed via LA-ICP-MS. Uncertainties on individual LA-ICP-MS analyses are quoted at the 1σ level, with results given in Table 1.

5.2. Fluid Inclusion Studies. Samples for the fluid inclusion study were collected from the main orebody (lode no. 3) of the Xiejiagou gold deposit to determine the nature of the fluids associated with mineralization. (Figure 4). Doubly polished thin sections (about 0.20 mm thick) were made from 45 quartz samples associated with different stages. Fluid inclusion petrography included careful observation of the shapes, characteristics of spatial distribution, genetic and composition types, and vapor/liquid ratios. Twenty-nine typical samples with abundant and representative inclusions were selected for microthermometric measurements with a temperature range of +45 to 100°C, and Institute of Geology, Chinese Academy of Geological Sciences, with a precision of the measurements was ±0.2°C for temperatures lower than 31°C, ±1°C for the interval of 31–300°C, and ±2°C for temperatures higher than 300°C. The salinities of NaCl–H₂O inclusions were calculated using the final melting temperatures of ice [52]. The salinities of CO₂-bearing fluid inclusions were calculated using the melting temperatures of clathrate [53]. Densities and pressure were calculated using FLINCOR software according to the microthermometry data [54, 55]. Representative fluid inclusion volatiles 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 a blazing wave length of 514.5 nm according to the method of Burke [56].

5.3. Oxygen Isotope and Hydrogen Isotope Analyses. Six quartz samples that were intergrown with ores during the different stages of mineralization were collected for detailed hydrogen and oxygen isotope analyses. All samples were handpicked and checked under a binocular microscope to achieve >95% purity. The isotopic compositions of oxygen and hydrogen were analyzed using a MAT-253 stable isotope ratio mass spectrometer in the analytical laboratory of the Beijing Research Institute of Uranium Geology. Oxygen was extracted for analysis using the BrF₅ technique [57], and hydrogen from H₂O was released from fluid inclusions [58]. The isotopic ratios are reported in standard δ notation (‰) relative to standard mean ocean water (SMOW) for oxygen and hydrogen. The analytical precision was better than ±0.2‰ for δ¹⁸O and ±2‰ for δD. The oxygen isotope ratios of water in equilibrium with quartz were calculated by the equation 1000Inε_{quartz-H₂O} = 3.38 × 10⁶T⁻² – 3.40 [59]. T is the average homogenization temperature of fluid inclusions from different stages.

5.4. Sulfur Isotope Analysis. Sulfur isotope analyses were carried out from 50 to 100 mg of sulfide minerals including pyrite, sphalerite, and galena. The sulfide grains were mixed with cuprous oxide and crushed into 200 mesh powder. SO₂ was produced through the reaction of sulfide and cuprous oxide at 980°C under a vacuum pressure of 2 × 10⁻³ Pa. The SO₂ was then measured by MAT-252 mass spectrometer for sulfur isotope. The sulfur isotope analysis
5.5. Lead Isotope Analysis. For lead isotope ratios, approximately 10 to 50 mg of five sulfide samples was first leached in acetone to remove surface contamination and then washed by distilled water and dried at 60°C in the oven. Washed sulfides were dissolved in dilute mix solution of nitric acid and hydrofluoric acid. Following ion exchange chemistry, the lead in the solution was loaded onto rhenium filaments using a phosphoric acid silica gel emitter. The lead isotopic compositions were measured on MAT-261 thermal ionization mass spectrometer with the standard sample NBS 981. The lead
isotope analysis was carried out at the analytical laboratory of the Beijing Research Institute of Uranium Geology. The analytical precision of Pb isotope is better than ±0.09‰.

6. Results

6.1. Zircon U–Pb Age of Biotite Granite. Zircons from the biotite granite (C156-13) are subhedral to euhedral, with a crystal length of 100 to 300 μm and aspect ratios of 2 : 1 to 4 : 1. Most of the grains display well-developed oscillatory zoning (Figure 6(b)), indicating a typical magmatic origin [60, 61]. The zircons contain variable moderate concentrations of U (1445–2493 ppm) and Th (125–971 ppm). The Th/U ratios range from 0.09 to 0.85. They have concordant 206Pb/238U ages of 156 ± 2 Ma to 164 ± 2 Ma, yielding a concordia age of 160 ± 0.6 Ma (MSWD = 2.9, probability = 0.09; Figure 6(c)) and a weighted mean 206Pb/238U age of 160.5 ± 1.3 Ma (MSWD = 1.2, probability = 0.24; Figure 6(d)). The weighted mean 206Pb/238U age with a low mean square of weighted deviation (MSWD) of 1.2 is interpreted as the crystallization age of the biotite granite.

6.2. Type and Occurrence of Fluid Inclusions. Fluid inclusions (FIs) occurring as isolated inclusions, randomly distributed groups, or in clusters were considered to be primary or pseudosecondary in origin, whereas those aligned along microfractures in transgranular trails were interpreted as secondary [62, 63]. Abundant primary, secondary, and pseudosecondary fluid inclusions are observed (Figure 7(a)).

Three compositional types of fluid inclusions (Figure 7) were identified based on their phases at room temperature, their observed phase transitions during heating and cooling runs, and laser Raman spectroscopy results. The FI types, in decreasing order of abundance, are aqueous carbonic (Figures 7(b)–7(d); CO2–H2O–NaCl; type I), pure carbonic (Figure 7(e); CO2; type II), and aqueous (Figures 7(f) and 7(g); H2O–NaCl; type III).

Type I inclusions are as follows: CO2-bearing aqueous solution inclusions comprise 60% of the total inclusions and are mainly three-phase CO2-bearing fluid inclusions (LH2O + LCO2 + VCO2) at room temperature (Figure 7(b)). Occasionally, two phases can be observed (LH2O + LCO2; LCO2 + VCO2) (Figure 7(c)). Besides, two subtypes of aqueous carbonic FIs were identified (type Ia and type Ib). The aqueous carbonic type Ia and type Ib inclusions contain two or three phases, but the volumes of the carbonic phases are 10–50% and 50–80%, respectively (Figures 7(b)–7(d)). These inclusions have ellipsoidal or irregular shapes with a long axis ranging from 5 to 20 μm (mainly 10–15 μm). Type Ia inclusions commonly coexist with type II inclusions in the early stage. Types Ia and Ib inclusions commonly coexist with type II and type III inclusions in the middle stage.

Type II inclusions are as follows: these types of inclusions consist of pure CO2 (Figure 7(e)). The pure CO2 inclusions are less than 5% of the total population and mainly occur in the early and middle stages. They are composed of single or two phases (LCO2 + VCO2 or LCO2 + VCO2). These types of inclusions are oval to negative crystal morphologies with a long axis of about 5–15 μm, with most measuring between 5 and 10 μm. Type II FIs are distributed in clusters with type I in quartz grains from the early stage and type I and type III FIs in quartz grains from the middle stage.

Type III inclusions are as follows: NaCl-H2O-type inclusions consist of H2O liquid and H2O vapor at room temperature and comprise 35% of total inclusions. Three subtypes of aqueous FIs were identified (type IIIa, type IIIb, and type IIIc). The aqueous type IIIa and type IIIb inclusions contain
two phases, but the volumes of the vapor phase are 10–50% and 50–80%, respectively (Figures 7(f) and 7(g)). Besides, a small number of one-phase aqueous inclusions (type IIIc) contain liquid water at room temperature; these inclusions are confined to the late stage and occur commonly in clusters with the two-phase type IIIa inclusions (Figure 8(g)). The type III inclusions are oval, nearly round, or irregular. The long axis of this type of inclusion ranges from 5 to 20 μm, with most measuring between 8 and 15 μm. Type III FIs commonly coexist with type I and type II inclusions in the middle stage.

6.3. Fluid Inclusion Microthermometry. Microthermometric data obtained from primary, pseudosecondary, and secondary type I, II, and III FIs of the three mineralization stages are summarized in Table 2 and presented in Figure 9. Microthermometric measurements were not possible for some FIs due to their small sizes (i.e., $T_{h, CO_2}$ for type I and type II, $T_{m, cla}$ for type I, and $T_{m, ice}$ for type III).

6.4. Laser Raman Microprobe Analysis. To constrain the fluid inclusion compositions, representative samples of the three different hydrothermal stages were examined using laser Raman microspectroscopy (Figure 10). The type I and II FIs from the early and middle hydrothermal stages contain a vapor phase of CO$_2$ with minor amounts of CH$_4$ (Figures 10(a)–10(d)). The main volatile component of the type III FIs for the last two stages is H$_2$O with minor amounts of CO$_2$ and H$_2$S (Figures 10(e) and 10(f)).

6.5. Oxygen and Hydrogen Isotopes. The oxygen and hydrogen isotopic results of Xiejiagou gold deposit are given in...
Table 1: Results of LA-ICP-MS zircon U-Pb analysis for the biotite granite (C156-13) in the Xiejiagou gold deposit.

<table>
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<tr>
<th>Sample no.</th>
<th>$T_b$ (ppm)</th>
<th>U (ppm)</th>
<th>$T_b$/U</th>
<th>$^{207}$Pb/$^{206}$Pb Ratio</th>
<th>$^{207}$Pb/$^{235}$U Ratio</th>
<th>$^{206}$Pb/$^{238}$U Ratio</th>
<th>Age (Ma) $^{207}$Pb/$^{235}$U Ratio</th>
<th>Age (Ma) $^{206}$Pb/$^{238}$U Ratio</th>
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<td>D01</td>
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</table>
Table 3, including the data from previous studies [30]. The measured δ18O values for quartz crystals from the gold mineralization at Xiejiagou have intervals between 3.1‰ and 13.2‰. The δ18Owater was calculated according to the oxygen isotopic compositions of quartz and the corresponding homogenization temperatures obtained from our fluid inclusion study (Table 3); average temperatures for early stage, middle stage, and late stage are estimated to be 327, 268, and 183°C, respectively. The calculated δ18Owater values of the fluid range from −9.7‰ to 5.7‰, and the δD values range from −101.8‰ to −83.1‰.

6.6. Sulfur Isotopes. The sulfur isotopic results of Xiejiagou gold deposit are given in Table 4, including the data from previous studies [34]. The sulfur isotope compositions of hydrothermal sulfide inclusions have a narrow range of δ34S between 4.7‰ and 7.8‰; the δ34S values of pyrite samples are between 5.9‰ and 7.8‰; the δ34S value of one sphalerite sample is 6.4‰; and the δ34S value of one galena sample is 4.7‰.

6.7. Lead Isotope. Lead isotope data were obtained for sulfides in ore samples from Xiejiagou deposit (Table 5). The 206Pb/204Pb (17.251 to 17.315), 207Pb/204Pb (15.486 to 15.519), and 208Pb/204Pb (37.904 to 38.029) ratios are relatively constant.

7. Discussion

7.1. Evolution of Ore-Forming Fluids. In this study, fluid inclusion microthermometry and laser Raman spectroscopy indicate that dominant type Ia and rare type II FIs are developed in the early-stage quartz crystals. The homogenization temperatures of the early-stage FIs are from 262 to 386°C with salinities of 2.22–8.82 wt% NaCl equivalent. These factors indicate that the initial ore-forming fluids were characterized by medium-high temperatures, low salinities, and enrichment in CO2 with minor CH4 (Table 1, Figures 9 and 11). Therefore, the initial ore fluids belonged to a homogeneous CO2–H2O–NaCl ± CH4 fluid system.

Quartz crystals formed during the middle stage of mineralization contain type I, II, and III FIs that yield moderate homogenization temperatures (192°C–347°C) and variable salinities (1.02–11.60 wt% NaCl equivalent) (Table 1, Figures 9 and 11). These features indicate that the ore-forming fluids evolved into a H2O–CO2–NaCl ± CH4 system at moderate temperatures and variable salinities. The ore-forming fluid then became an H2O–NaCl system at the end of mineralization as only type III FIs existed in the late stage. In addition, FIs trapped during the late stage of mineralization have low temperatures (137°C–231°C) and salinities (1.22–7.72 wt% NaCl equivalent) similar to that of meteoric water [7], which indicated that the ore-forming fluids experienced cooling and diluting (Figure 11).

In another way, the average δ18O value of ore-forming fluids slightly decreases from 4.8‰ to 4.2‰ and to −9.7‰ in stages 1–3, as well as the δD values for each stage (median, −86.3‰ to −96.2‰ to −101.8‰). Thus, the O–H isotopic compositions obviously have a shift towards meteoric water from the early to late hydrothermal stage (Figure 12), indicating that significant amount of meteoric water infiltrated into the fluid system during the late mineralization stage.

7.2. Source of Metallic and Hydrothermal Components of the Ore-Forming Fluids. Sulfur isotopic composition of sulfide minerals can be used to trace the source of sulfur in ore fluids [64, 65]. The δ34S values of the sulfides in Xiejiagou deposit display a narrow range (4.7‰–7.8‰, with an average of 6.6‰, Figure 13), suggesting an extremely homogeneous source; this is similar to the majority of gold deposits in Jiaodong [2, 3, 66]. The average δ34S values of those sulfide minerals from Xiejiagou deposit show a δ34Spyrite (6.7‰) > δ34Spbalerite (6.4‰) > δ34Sgalena (4.7‰) trend (Figure 13, Table 4), suggesting equilibrium fractionation of sulfur isotopes among the sulfide minerals. Based on the average homogenization temperatures of the corresponding fluid inclusions from the first two stages (327°C and 268°C), the δ34S values of the
mineralizing fluid are 4.5 to 6.9‰ using the equations of Ohmoto and Rye [67]. These δ^{34}S_H2S values are obviously higher than that of chondrite (δ^{34}S = ~0‰) indicating that the sulfur is unlikely to have originated from the mantle. In addition, the average δ^{34}S_H2S value is within the typical range of the orogenic gold deposits worldwide (Figure 13, 0 to 10‰) and also within the ranges of whole rocks and pyrite from the Archean Jiaodong group, the Mesozoic Linglong and Guojialing granites, and the Early Cretaceous mafic-intermediate dikes. Even though the average δ^{34}S_H2S value of the Xiejiagou deposit is close to that of the Late Jurassic Linglong granite (host rock, pre-ore), it is still difficult to establish whether the ore-forming fluids had a magmatic source or other sources.

Lead isotope compositions (particularly of sulfide minerals) are an excellent proxy for constraining the sources of lead in ore-forming fluids [68, 69]. Sulfide minerals in the Xiejiagou deposit show Pb isotope compositions of 206Pb/204Pb = 17.251 – 17.315, 207Pb/204Pb = 15.486 – 15.519, and 208Pb/204Pb = 37.904 – 38.029. In a similar manner to S isotope data, all of the Pb isotope data overlap with the compositions of whole rocks from Mesozoic granites and dikes, as well as Precambrian metamorphic rocks (Figure 14), and are consistent with the lead isotope compositions of most gold deposits in Jiaodong [19]. These values overlap the field of Late Jurassic Linglong granite, which is the main host rock of the Xiejiagou deposit. Thus, the lead isotopic compositions of sulfides can be interpreted to suggest that the host rocks may be one of the lead sources for sulfides but can not be used to trace the source of gold. In another way, on plumbotectonic diagrams (Figure 14, Table 5), the Pb isotope compositions of sulfide minerals fall within a range that spans within the orogenic and lower crust lead isotope evolution curves [70], indicating that the lead in ore-forming fluids may be originated from the lower crust reservoir in an orogenic regime. The Jiaodong gold mineralization had a genetic relationship...
Table 2: Microthermometric data for fluid inclusions of different stages from the Xiejiagou gold deposit.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type</th>
<th>Number</th>
<th>$T_{m-CO2}$ °C</th>
<th>$T_{m-cla}$ °C</th>
<th>$T_{h-CO2}$ °C</th>
<th>$T_{h-ice}$ °C</th>
<th>Salinity wt% NaCl equiv.</th>
<th>CO$_2$ density g/cm$^3$</th>
<th>Bulk density g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td>Ia</td>
<td>67</td>
<td>-59.4 to -56.6</td>
<td>5.1 – 8.9</td>
<td>21.3 – 30.6</td>
<td>262 – 386</td>
<td>2.22 – 8.82</td>
<td>0.562 – 0.760</td>
<td>0.773 – 0.912</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>6</td>
<td>-57.9 to -56.7</td>
<td>16.7 – 28.4</td>
<td></td>
<td></td>
<td></td>
<td>0.651 – 0.813</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sec Ia</td>
<td>4</td>
<td>-58.1 to -56.7</td>
<td>5.8 – 7.3</td>
<td>21.6 – 30.5</td>
<td>245 – 301</td>
<td>5.14 – 7.70</td>
<td>0.569 – 0.756</td>
<td>0.857 – 0.920</td>
</tr>
<tr>
<td></td>
<td>Sec Ib</td>
<td>1</td>
<td>-56.9</td>
<td>8.7</td>
<td>25.3</td>
<td>272</td>
<td>2.58</td>
<td>0.707</td>
<td>0.798</td>
</tr>
<tr>
<td></td>
<td>Sec II</td>
<td>2</td>
<td>-57.4 to -57.1</td>
<td>8.7</td>
<td>20.4 – 25.6</td>
<td></td>
<td></td>
<td>0.702 – 0.770</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sec IIIa</td>
<td>6</td>
<td></td>
<td>-1.3 to -3.6</td>
<td>165 – 233</td>
<td>2.23 – 5.85</td>
<td></td>
<td>0.845 – 0.939</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ia</td>
<td>53</td>
<td>-59.1 to -56.6</td>
<td>4.6 – 8.8</td>
<td>20.4 – 30.7</td>
<td>235 – 347</td>
<td>2.39 – 9.59</td>
<td>0.581 – 0.773</td>
<td>0.839 – 0.908</td>
</tr>
<tr>
<td></td>
<td>Ib</td>
<td>7</td>
<td>-57.8 to -56.6</td>
<td>6.0 – 9.5</td>
<td>25.0 – 30.2</td>
<td>251 – 302</td>
<td>1.02 – 7.48</td>
<td>0.586 – 0.734</td>
<td>0.779 – 0.846</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>9</td>
<td>-57.6 to -56.8</td>
<td></td>
<td>13.1 – 25.6</td>
<td></td>
<td></td>
<td>0.690 – 0.830</td>
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<tr>
<td>Middle</td>
<td>IIIa</td>
<td>61</td>
<td></td>
<td>-1.9 to -7.9</td>
<td>192 – 313</td>
<td>3.21 – 11.60</td>
<td></td>
<td>0.740 – 0.896</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IIIb</td>
<td>6</td>
<td></td>
<td>-1.5 to -1.6</td>
<td>242 – 266</td>
<td>2.56 – 2.73</td>
<td></td>
<td>0.800 – 0.828</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sec IIIa</td>
<td>10</td>
<td></td>
<td>-1.0 to -3.3</td>
<td>144 – 187</td>
<td>1.73 – 5.40</td>
<td></td>
<td>0.915 – 0.941</td>
<td></td>
</tr>
<tr>
<td>Late</td>
<td>IIIa</td>
<td>69</td>
<td></td>
<td>-0.7 to -4.9</td>
<td>137 – 231</td>
<td>1.22 – 7.72</td>
<td></td>
<td>0.850 – 0.950</td>
<td></td>
</tr>
</tbody>
</table>

Sec: secondary Fls; $T_{m-CO2}$: melting temperature of solid CO$_2$; $T_{m-cla}$: temperature of CO$_2$ clathrate dissociation; $T_{h-CO2}$: homogenization temperature of CO$_2$; $T_{h-ice}$: temperature of final ice melting; $T_h$: homogenization temperature; wt% NaCl equiv.: weight percent NaCl equivalent.
Figure 9: Histograms of total homogenization temperatures ($T_h$) and salinities of fluid inclusions in different stages of Xiejiagou gold deposit. (a) Homogenization temperatures for primary and secondary FIs in early-stage quartz; (b) salinity for primary and secondary FIs in early-stage quartz; (c) homogenization temperatures for primary and secondary FIs in middle-stage quartz; (d) salinity for primary and secondary FIs in FIs of middle-stage quartz; (e) homogenization temperatures for type IIIa FIs of late-stage quartz; (f) salinity for type IIIa FIs of late-stage quartz.
with continental extension that was induced by the upwelling of hot felsic magma during the Mesozoic [8, 71, 72]. Therefore, the lead in the ore-forming fluids, and included lead in the Mesozoic granites and dikes, may be originated from the Mesozoic orogenic lead reservoir.

The oxygen and hydrogen isotopic compositions of hydrothermal quartz crystals are useful tracers for determining the source of ore-forming fluids. Unlike hydrothermal minerals that form during the late stage of mineralization, those that form during the early and middle stages preserve O and H isotope ratios that should not have been significantly influenced by meteoric water and thus have the potential to accurately reflect the nature of the original ore-forming fluids [26, 73]. The O–H compositions of ore-forming fluids are shown in Figure 12. The calculated δ^{18}O_{H_{2}O} (1.9‰ to 5.7‰) and δD (–99.4‰ to –83.1‰) values for fluid of the
first two stages are slightly lower than the magmatic water composition ([74], −50‰ to −85‰ for δD; 5.5‰ to 9.0‰ for δ18O_H2O). As such, it is difficult to establish whether the ore-forming fluids had a magmatic source. Mesozoic granites are widespread on the Jiaodong Peninsula (Figure 1), and many researchers have therefore suggested that magmatic

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample no.</th>
<th>Mineral assemblages</th>
<th>δ18O_m</th>
<th>δD_H2O</th>
<th>Stage</th>
<th>T (°C)</th>
<th>δ18O_H2O</th>
<th>Data sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C156-07</td>
<td>Qz + Kfs + Ser + Py</td>
<td>11.2</td>
<td>-92.0</td>
<td>Early</td>
<td>327</td>
<td>5.2</td>
<td>This study</td>
</tr>
<tr>
<td>2</td>
<td>C156-12</td>
<td>Qz + Py</td>
<td>12.3</td>
<td>-99.7</td>
<td>Middle</td>
<td>268</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C156-28</td>
<td>Qz + Py</td>
<td>13.2</td>
<td>-95.4</td>
<td>Middle</td>
<td>268</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C156-36</td>
<td>Qz + Py + Gn + Sp</td>
<td>12.8</td>
<td>-99.4</td>
<td>Middle</td>
<td>268</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C156-201</td>
<td>Qz + Py + Gn + Sp</td>
<td>10.0</td>
<td>-94.6</td>
<td>Middle</td>
<td>268</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C156-29</td>
<td>Qz + Cc</td>
<td>3.1</td>
<td>-101.8</td>
<td>Late</td>
<td>183</td>
<td>-9.7</td>
<td></td>
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<tr>
<td>7</td>
<td>X-07</td>
<td>Qz + Ser + Py</td>
<td>120</td>
<td>-83.8</td>
<td>Early</td>
<td></td>
<td>5.7</td>
<td>Sun, 2006 [30]</td>
</tr>
<tr>
<td>8</td>
<td>X-73</td>
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<td>-83.1</td>
<td>Early</td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>05021</td>
<td>Qz + Py</td>
<td>12.3</td>
<td>-91.7</td>
<td>Middle</td>
<td></td>
<td>5.4</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4: Sulfur isotope compositions for sulfides from the Xiejiagou gold deposit.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample no.</th>
<th>Mineral assemblages</th>
<th>Stage</th>
<th>Mineral</th>
<th>δ34SCDT (‰)</th>
<th>δ34SH2S (‰)</th>
<th>Data sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C156-13</td>
<td>Qz + Kfs + Ser + Py</td>
<td>Early</td>
<td>Py</td>
<td>7.5</td>
<td>6.4</td>
<td>This study</td>
</tr>
<tr>
<td>2</td>
<td>C156-24</td>
<td>Qz + Py</td>
<td>Middle</td>
<td>Py</td>
<td>6.3</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C156-38</td>
<td>Qz + Py + Gn + Sp</td>
<td>Middle</td>
<td>Py</td>
<td>6.5</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C156-38</td>
<td>Qz + Py + Gn + Sp</td>
<td>Middle</td>
<td>Sp</td>
<td>6.4</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C156-38</td>
<td>Qz + Py + Gn + Sp</td>
<td>Middle</td>
<td>Gn</td>
<td>4.7</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>JT02</td>
<td>Qz + Ser + Py</td>
<td>Early</td>
<td>Py</td>
<td>7.1</td>
<td>6.0</td>
<td>Ding et al., 2017 [34]</td>
</tr>
<tr>
<td>7</td>
<td>JT09</td>
<td>Qz + Py</td>
<td>Middle</td>
<td>Py</td>
<td>6.2</td>
<td>4.8</td>
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<td>Py</td>
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<td>5.1</td>
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<tr>
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<td>Middle</td>
<td>Py</td>
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<td>5.3</td>
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<tr>
<td>11</td>
<td>JT43</td>
<td>Qz + Py</td>
<td>Middle</td>
<td>Py</td>
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<tr>
<td>12</td>
<td>JT65</td>
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<td>Py</td>
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<tr>
<td>13</td>
<td>JT68</td>
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<td>Py</td>
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<tr>
<td>14</td>
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<td>Py</td>
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<tr>
<td>15</td>
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<td>Py</td>
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<tr>
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<td>Early</td>
<td>Py</td>
<td>6.7</td>
<td>5.6</td>
<td></td>
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<td>Py</td>
<td>7.8</td>
<td>6.7</td>
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<td>18</td>
<td>JT95</td>
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<td>Early</td>
<td>Py</td>
<td>6.7</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5: Lead isotope compositions for sulfides from the Xiejiagou gold deposit.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample no.</th>
<th>Mineral assemblages</th>
<th>Mineral</th>
<th>206Pb/204Pb</th>
<th>2σ</th>
<th>207Pb/204Pb</th>
<th>2σ</th>
<th>208Pb/204Pb</th>
<th>2σ</th>
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<tbody>
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<td>C156-13</td>
<td>Qz + Kfs + Ser + Py</td>
<td>Py</td>
<td>17.271</td>
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<td>15.498</td>
<td>0.002</td>
<td>37.953</td>
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</tr>
<tr>
<td>2</td>
<td>C156-24</td>
<td>Qz + Py</td>
<td>Py</td>
<td>17.315</td>
<td>0.002</td>
<td>15.519</td>
<td>0.002</td>
<td>38.008</td>
<td>0.005</td>
</tr>
<tr>
<td>3</td>
<td>C156-38</td>
<td>Qz + Py + Gn + Sp</td>
<td>Py</td>
<td>17.285</td>
<td>0.004</td>
<td>15.486</td>
<td>0.004</td>
<td>37.904</td>
<td>0.009</td>
</tr>
<tr>
<td>4</td>
<td>C156-38</td>
<td>Qz + Py + Gn + Sp</td>
<td>Sp</td>
<td>17.280</td>
<td>0.002</td>
<td>15.509</td>
<td>0.002</td>
<td>37.993</td>
<td>0.004</td>
</tr>
<tr>
<td>5</td>
<td>C156-38</td>
<td>Qz + Py + Gn + Sp</td>
<td>Gn</td>
<td>17.251</td>
<td>0.005</td>
<td>15.517</td>
<td>0.005</td>
<td>38.029</td>
<td>0.005</td>
</tr>
</tbody>
</table>
water is likely to be the dominant source of the fluids that formed the Jiaodong gold deposits [16, 17, 28]. However, FIs of the Xiejiagou deposit are characteristic of low-salinity mesothermal CO$_2$-rich fluids, which are widely accepted to be of metamorphic origin and differ markedly from typical high-temperature, high-salinity exsolved magmatic fluids [73, 75]. Furthermore, because the mineralization of the Xiejiagou deposit occurred at about 123.6–115.2 Ma, it is reasonable to narrow the field of magmatic water compositions to include only those of Early Cretaceous Guojialing granite (132–126 Ma; [39]) in the Jiaodong Peninsula. None of the analyzed compositions fall within this narrower field ([76]; magmatic water of Guojialing granite: −50% to −85% for δD; 5.5% to 9.0% for δ$^{18}$O$_{H_2O}$), indicating that magmatic water may not to be the source of the fluids that formed the Xiejiagou deposit. On the other hand, it is worth noting that the ore-forming fluids of reduced intrusion-related gold deposit are also characterized by CO$_2$-rich fluids with variable temperature and salinity [77, 78]. This raises the possibility that the Xiejiagou deposit is a reduced intrusion-related gold deposit. Unfortunately, as with previous researchers, we were unable to find any syn-ore-reduced igneous rocks in the Jiaodong Peninsula and we did not observe any of the exsolved textures (e.g., unidirectional solidification textures and quartz eyes) that are typical of primary magmatic water [77]. There is also no evidence of sheet-formed gold-bearing veins ([78]; representative mineralization style of reduced intrusion-related gold deposit) in the Xiejiagou deposit or, for that matter, in any other gold deposits within the Jiaodong Peninsula. In combination, these factors indicate that Xiejiagou is not a reduced intrusion-related deposit.

Representatively, because the nature of ore-forming fluids of the gold deposits in the Jiaodong Peninsula was mesothermal, has low salinity, and enriched in CO$_2$, it has been suggested that the Jiaodong gold deposits including Xiejiagou might be orogenic gold deposit [21] and that the ore-forming fluids were of metamorphic origin. In addition, the secondary FIs within quartz crystals of the early and middle stages (Table 1; Figure 9) probably lead to inaccurate δD values for the hydrothermal fluids in each stage [22, 79–81], making the calculated O–H values slightly less than those of the typical range of the majority of orogenic gold deposit (Figure 12; [82]). Therefore, the true δD values for the hydrothermal fluids are higher than the δD values of FIs and may come to lie in the metamorphic water field.

In summary, we speculate that the most probable explanation is that the fluids that formed the Xiejiagou deposit were dominated by a metamorphic source. It is commonly believed that orogenic gold deposits, which are predominantly hosted by greenschist facies or low-amphibolite facies metamorphic terranes, have gold-forming ages that are either synchronous with, or slightly younger than, terrane metamorphism and deformational events [82]. However, the Jiaodong gold deposits including Xiejiagou are of the granite-hosted “gold-only” type [1], with only a limited number of metamorphic rocks within the vicinity of the ore deposit (Figure 2). In addition, the ages of mineralization at the Jiaodong Peninsula postdate peak at high amphibolite to granulite facies metamorphism in the area by at least 1.7 Ga, indicating that the source of ore-forming fluids can not come from the Neoarchean and Paleoproterozoic basement rocks [22]. Therefore, the original ore fluids may in fact have formed via metamorphic dehydration, decarbonization, and desulfidation of the subducting Paleo-Pacific slab within an accretionary orogeny [14, 15, 21, 22].
7.3. Trapping Pressure of FIs and Metallogenic Depth. The assemblage of the fluid inclusions from the different hydrothermal stages can estimate the pressure conditions of the fluid inclusions trapped during ore forming [25, 26]. Given that the type I FIs are common in the early and middle hydrothermal stages, these FIs exhibit $T_{m-CO_2}$ values of approximately -56.6°C; as such, the pressure can be estimated based on the CO$_2$–H$_2$O–NaCl system with a range of isochores calculated using FLINCOR software [54] and the formula of Burke [56].

Based on the homogenization temperatures and salinity of the type I FIs in the first two stages, a representative isochore calculated for the H$_2$O–CO$_2$–NaCl system containing 6 wt% NaCl equivalent and 15 mol% CO$_2$ ([55], Figure 15) was constructed to estimate the trapping pressures of type I FIs from the early and middle stages. Given that the homogenization temperatures of FIs from the first two stages have wide ranges and can not provide the accurate temperature and pressure of fluid entrapment, upper and lower quartiles are more suitable than the average values to reflect the data distribution [80, 83]. Therefore, intersections of isochores of FIs with the upper and lower quartiles of homogenization temperatures and bulk densities are used to constrain the trapping pressure range of the fluids.
The trapping pressure for FIs from quartz veinlets of the early hydrothermal stage were calculated to be 224–302 MPa using homogenization temperatures ranging from 305 to 359°C and CO₂ densities ranging from 0.574 to 0.751 g/cm³ (Figure 15(a)). The pressure of the gold polymetallic quartz veinlets from the middle hydrothermal stage was estimated ranging from 191 to 258 MPa by homogenization temperatures of 246 to 289°C and CO₂ densities ranging from 0.589 to 0.767 g/cm³ (Figure 15(b)). Applying an ancient ground pressure gradient of 0.0265 GPa/km (mean density of upper crust), the calculated trapping pressure for the gold polymetallic quartz veinlets corresponds to a depth of 7.2 to 9.7 km within a lithostatic fluid system. The thermochronologic study indicates that the erosion depth of the Jiaobei uplift has been calculated as about 3.0 to 7.0 km between the Early Cretaceous and the present [84]. Consequently, it is inferred that the Xiejiagou gold deposit has undergone very less total denudation since its formation. Accordingly, it can be predicted that large gold reserves could still exist at deep levels within the Xiejiagou deposit.

7.4. Mechanisms of Gold Transport and Deposition. Gold is commonly dissolved and transported in the form of gold bisulfide complexes (Au(HS)₀ and Au(HS)₂⁻) in hydrothermal solutions at temperatures of <400°C [85]. The aqueous speciation of gold(I) sulfide complexes is sensitive to physical and chemical conditions of solution [86]. For example, when the temperature is below 400°C, Au(HS)₀ dominates under acidic conditions, whereas Au(HS)₂⁻ is more likely to form under weakly acidic to neutral conditions [86–88]. The alteration mineral assemblages of the Xiejiagou deposit consist of quartz sericite K-feldspar chlorite association (Figures 3 and 4), indicating that the pH of the ore solution was near-neutral to weakly acidic [89, 90]. Thus, gold was most probably transported as the Au(HS)₂⁻ complex at the Xiejiagou deposit. It is also supported by the observation that gold is generally accompanied by pyrite and other sulfides in the Xiejiagou deposit (Figures 3(k) and 3(l)), as is typical in orogenic gold deposits worldwide, in which gold(I) sulfide complexes (especially Au(HS)₂⁻) were considered the most likely species for transporting gold [82]. Besides, the abundance of type I and II FIs in quartz from the early hydrothermal stage demonstrates that the ore-forming solution was enriched in CO₂. CO₂ can buffer or neutralize the fluid within the pH range in which the gold bisulfide complexes are stable and increase its solubility in the ore-forming fluids [91], which provides favorable conditions for gold bisulfide migration. Therefore, the initial auriferous hydrothermal fluids need changes of physical and chemical conditions to reduce solubility of Au(HS)₂⁻ so that gold can be precipitated.

In the pressure-temperature isochore diagram (Figure 15(b)), the P–T window with the yellow-shaded area of the middle stage is mainly below the solvus (6 wt% NaCl equivalent with 15 mol% CO₂), indicating that the initial homogeneous fluids entered the two-phase field and experienced phase separation process in this stage [55]. Besides, the existence of the types I, II and III FIs within a single thin-section of the middle stage with different compositions and densities is inferred to be caused by the CO₂ effervescence from an initial homogeneous CO₂ – H₂O – NaCl ± CH₄ fluid system [92, 93]. In addition, the homogenization temperatures of type III FIs are slightly lower than those of coexisting type I FIs within middle-stage samples, also because the homogenization temperatures of aqueous inclusions can thus be significantly lowered by CO₂ effervescence resulting from pressure fluctuations [94]. Such CO₂ effervescence in auriferous hydrothermal systems could have led to the exsolution of the volatiles such as H₂S (Figure 10(e)). The exsolution of carbon dioxide of the original ore fluid led to an increase in pH values and a decrease in temperature. This process, in conjunction with the exsolution of H₂S from the ore-forming fluid, which may have made gold bisulfide complexes unstable and reduced their solubility, resulted in the precipitation of abundant gold.
8. Conclusions

(1) Three types of primary fluid inclusion were identified in the Xiejiagou gold deposit: type I (aqueous carbonic), type II (pure carbonic), and type III (aqueous). Type I and minor type II inclusions exist in quartz from the early stage of mineralization, whereas all three types of inclusions are observed in quartz from the middle period of mineralization. In contrast, quartz from the late stage of mineralization only contains type III inclusions

(2) The initial ore-forming fluids of the Xiejiagou deposit belonged to a medium-high temperature (262–386°C), CO2-rich, low salinity (2.22–8.82 wt% NaCl), and homogeneous CO2 – H2O – NaCl ± CH4 fluid system. During mineralization, the fluid finally evolved into a medium-low temperature NaCl–H2O system as a result of an influx of meteoric water. Considering the fluid inclusion characteristics, H–O–S–Pb isotopes, and regional geological events, the ore-forming fluid reservoir of the Xiejiagou deposit was likely metamorphic in origin

(3) Trapping pressures of the first two hydrothermal stages estimated from the type I inclusion assemblages were ~224–302 MPa and ~191–258 MPa, respectively. The gold mineralization of the Xiejiagou gold deposit occurred at a lithostatic depth of ~7.2–9.7 km

(4) Au(HS)2− was the most probable gold-transporting complex at the Xiejiagou deposit. CO2 effervescence in auriferous hydrothermal systems resulted in the precipitation of gold

Data Availability

The manuscript is a data self-contained article, whose results were obtained from the laboratory analysis, and the entire data is presented within the article.

Conflicts of Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the submitted paper.

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