Hydrothermal alteration associated with Mesozoic granite-hosted gold mineralization at the Sanshandao deposit, Jiaodong Gold Province, China

Xiao-Chun Li a, Hong-Rui Fan a,⁎, M. Santosh b, Fang-Fang Hu a, Kui-Feng Yang a, Ting-Guang Lan a

a Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
b China University of Geosciences (Beijing), Beijing 100083, China

A R T I C L E   I N F O

Article history:
Received 15 July 2012
Received in revised form 31 January 2013
Accepted 31 January 2013
Available online 17 February 2013

Keywords:
Alteration geochemistry
Physicochemical condition
Fluid source
Sanshandao deposit
Jiaodong gold province

A B S T R A C T

The Sanshandao gold deposit (reserves of more than 200 t Au and average grade of 3.96 g/t), located at northwestern edge of the Jiaodong Peninsula, eastern North China Craton, is one of the largest gold deposits in the Jiaodong gold province. In this deposit, disseminated- and stockwork-style ores are hosted in Mesozoic granitoids; mineralization and alteration are largely controlled by the regional Sanshandao–Cangshang fault. Host granitic rocks for the deposit display a complex paragenetic sequence of alteration and mineralization. Activities of the Sanshandao–Cangshang fault created structurally controlled permeability allowing for infiltration of hydrothermal fluids, leading to diffusive K-feldspar alteration on the two fault planes. Later, large scale diffusive sericitization symmetrically developed across the main fault, and partially overprinted the earlier K-feldspar alteration. Following the sericitization, relatively small scale silicification occurred, but now it is only retained in the hanging wall of the main fault. Subsequently, the fault gouge formed as a "barrier layer", which is impermeable for later fluids to move upward. After that, strong pyrite–sericite–quartz alteration occurred only in the footwall of the main fault, and was accompanied by gold precipitation. The last stage carbonation and quartz-carbonate veins marked the waning of gold-related hydrothermal activity. Mass-balance calculations indicate complex behaviors of different types of elements during fluid–rock interaction. Most major elements were affected by intensive mineral replacement reactions. As expected, the fluid-mobile elements, LILE and LREE, generally show moderate to high mobility. It is notable that even the commonly assumed fluid-immobile elements, such as HREE and HFSE, tend to be changed to various degrees. In addition, Y–Ho, Zr–Hf and Nb–Ta fractionations are observed in altered domains. Studies on alteration assemblages and fluid inclusions suggest that the ore-forming fluids were characterized by low salinity (≤8.4 wt.% NaCl equiv.), moderate temperature (300–400 °C), weakly acidic (pH: 3–5), and relatively reducing (log fO2: −28) characteristics. In this type of fluids, gold was most likely transported as Au(HS)2 complex. With alteration going on, log (αK+/αH+) of fluids generally decreased due to significant formation of secondary K-bearing minerals. In addition, there might be a decrease of fO2 from pre-gold alteration stage to the main gold mineralization stage, and decrease of fO2 was probably one of the factors controlling gold precipitation. The Sr and Nd isotopic compositions of hydrothermal minerals, combined with previous H–O and He–Ar isotopic studies, indicate that the hydrothermal fluids were mainly derived from crustal sources (e.g., degassing of felsic magmas and metevic rock), but with involvement of mantle derived components. The gold mineralization event just coincided with reactivation of the North China Craton, as marked by asthenosphere upwelling, voluminous igneous rocks, and high crustal heat flow, which may have provided sufficient heat energy and fluid input required for the formation of the gold deposits.

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1. Introduction

The Jiaodong Peninsula is currently the most important gold province in China, with a total gold ore reserve of 1300 t (Li et al., 2007). It is located along the southeastern margin of the North China Craton (NCC), which is the largest and oldest (2.5–3.8 Ga) craton in China, with a total gold ore reserve of 1300 t (Li et al., 2007). It is notable that even the commonly assumed fluid-immobile elements, such as HREE and HFSE, tend to be changed to various degrees. In addition, Y–Ho, Zr–Hf and Nb–Ta fractionations are observed in altered domains. Studies on alteration assemblages and fluid inclusions suggest that the ore-forming fluids were characterized by low salinity (≤8.4 wt.% NaCl equiv.), moderate temperature (300–400 °C), weakly acidic (pH: 3–5), and relatively reducing (log fO2: −28) characteristics. In this type of fluids, gold was most likely transported as Au(HS)2 complex. With alteration going on, log (αK+/αH+) of fluids generally decreased due to significant formation of secondary K-bearing minerals. In addition, there might be a decrease of fO2 from pre-gold alteration stage to the main gold mineralization stage, and decrease of fO2 was probably one of the factors controlling gold precipitation. The Sr and Nd isotopic compositions of hydrothermal minerals, combined with previous H–O and He–Ar isotopic studies, indicate that the hydrothermal fluids were mainly derived from crustal sources (e.g., degassing of felsic magmas and metevic rock), but with involvement of mantle derived components. The gold mineralization event just coincided with reactivation of the North China Craton, as marked by asthenosphere upwelling, voluminous igneous rocks, and high crustal heat flow, which may have provided sufficient heat energy and fluid input required for the formation of the gold deposits.
Mesozoic granitoids, whereas the jiaojia-type mineralization consists of disseminated- and stockwork-style ores located in regional faults, which are enveloped by broad alteration halos. Many papers, mostly in Chinese, have been published on the Jiaodong gold deposits and related igneous rocks (e.g., Chen et al., 1989, 2005; Fan et al., 2003, 2005; Goldfarb et al., 2007; Li and Yang, 1993; Li et al., 2004, 2006; Lu and Kong, 1993; Luo and Wu, 1987; Mao et al., 2008; Qiu et al., 2002; Wang et al., 1998; Yang and Lu, 1996; Yang and Zhou, 2001; Yang et al., 1998), mainly focusing on the geological features, age, fluid characteristics and geodynamic mechanism of the ore deposits. These investigations have shown that deposit mineralogy, hydrothermal fluid compositions, stable isotope compositions and ore-forming P–T conditions of the Jiaodong gold deposits are similar to those of typical orogenic gold deposits (Goldfarb et al., 2001; Qiu et al., 2002).

However, relatively few comprehensive studies have been published on gold-related wall rock alterations, especially for the Jiaojia-type gold deposit. Qiu et al. (2002) briefly summarized the spatial zonation, petrography and geochemistry of alteration assemblages for both Linglong-type and Jiaojia-type mineralization. Ling et al. (2002) studied the alteration geochemistry of the Dayingezhuang gold deposit and Jinqingding gold deposit in detail. Most other works only briefly introduced the spatial zonation, mineralogy and petrography of alteration assemblages.

The Sanshandao gold deposit is located at the northwestern edge of the Jiaodong Peninsula, and is one of the largest gold deposits (with reserves of more than 200 t Au and average grade of 3.96 g/t) in the Jiaodong gold province (personal communication with Mr. Xiannian Jin). This deposit is a typical Jiaojia-style gold occurrence. It is associated with the Sanshandao–Cangshang fault zone (Figs. 1 and 2), which also structurally controls the large Cangshang gold deposit located 4 km south of the Sanshandao deposit. Wide alteration zones are developed along the fault zone. In the past five years, several drill holes were made in this area under the “Deep Ore Exploration” programs, exposing excellent geological features and providing important specimen for investigations on hydrothermal alteration.

In this paper, we provide a comprehensive description of the alteration assemblages and veins of the Sanshandao gold deposit, documenting their paragenesis, spatial zonation, petrography, geochemistry and Sr–Nd isotopes of hydrothermal minerals. Based on the data, we (1) illustrate mobility of elements associated with the hydrothermal alteration; (2) more tightly constrain the physicochemical conditions of the ore fluid system and (3) better define the sources of hydrothermal fluids.

2. Regional geology

The North China Craton, with an Archean core of 2.5–3.8 Ga, comprises three major crustal blocks: the Eastern Block (Yanliao Block), the Ordos Block and the Yinshan Block (together defining the Western Block) (Zhao et al., 2001). The Jiaodong Peninsula occupies the easternmost edge of the Eastern Block of the NCC and is geologically divided into the southeastern Ludong terrane and the northwestern Jiaobei terrane by the Mishan fault (Fig. 1). The Ludong terrane petrotectonically belongs to the northern margin of the South China Block which records a subduction history associated with the Triassic collisional event (Zheng et al., 2009).

The Jiaobei terrane petrotectonically belongs to the southern margin of the NCC. Almost all gold deposits are hosted in the Jiaobei terrane (Zhai et al., 2004), and more than 80% of the gold reserves are concentrated in the Zhaoyuan–Laizhou gold belt (Fig. 1). The Precambrian basement in the Jiaobei terrane is principally defined by the Archean Jiaodong Group and the Paleoproterozoic Fenzishan and Jingshan Groups (e.g., Tam et al., 2011; Tang et al., 2007). Mesozoic magmatic rocks are widely exposed in the Jiaobei terrane and two
main periods of magmatism are recognized: Jurassic and Early Cretaceous. The Jurassic magmatic activity is represented by the crustally-derived Linglong and Luanjiahe granitoids, emplaced during 158 to 160 Ma (Hou et al., 2007; Wang et al., 1998; Yang et al., 2012). In the Early Cretaceous, extensive magmatism took place through strong crust–mantle interaction, including widespread granitoids (113–130 Ma), mafic to felsic volcanic rocks in Jiaolai Basin (110–130 Ma), and numerous mafic dikes (122–124 Ma) (Fan et al., 2001; Goss et al., 2010; Li et al., 2012; Yang et al., 2004; Yang et al., 2012). The Mesozoic granitoids are potential hosts of gold deposits.

Two main phases of deformation were identified in this region during the Mesozoic. The first phase is characterized by northwest–southeast oblique compression, presumably related to the subduction of the Izanagi–Pacific plate (Wang et al., 1998), which induced prominent NNE- to NE-trending brittle-ductile shear zones with sinistral oblique reverse movements. The second phase involved the development of NNE- and NE-trending extensional brittle structures and half-graben basins, accompanied by intrusion of mafic dikes and hydrothermal gold mineralization. These structures are commonly thought to be subsidiary to the Tan–Lu fault (Yang and Lu, 1996).

3. Geology of the Sanshandao gold deposit

The Sanshandao gold deposit is located about 30 km north to the Laizhou city and occupies an area of 0.3 km². This deposit, first discovered in 1967 and originally developed by local prospectors for the first few years, is now being worked by the Shandong Gold Group Co. Ltd. By 2010, the known reserves were more than 200 t, the grade ranges from 3.04 to 14.56 g/t (with an average grade of 3.96 g/t), and the annual production is more than 3 t Au (personal communication with Mr. Xiannian Jin).

Four major lithological groups can be identified in the Sanshandao deposit as follows (Fig. 2): (1) Archean Jiaodong Group; (2) Jurassic Linglong granite; (3) Cretaceous Guojialing granodiorite and (4) Cretaceous mafic dikes. The Linglong granite intruded into the TTG gneiss and amphibolite of the Late Archean Jiaodong Group during 158–160 Ma. The gray granite shows a fine- to medium-grained, equigranular texture. The main mineral assemblage is plagioclase (25–30%), K-feldspar (35–40%), quartz (20–30%) and biotite (5–10%), with accessory minerals such as garnet, titanite, ilmenite, zircon and apatite. Early studies demonstrated that the Linglong granite was mainly derived from partial melting of the ancient crust in the NCC (Hou et al., 2007; Yang et al., 2012). The Guojialing granodiorite was emplaced during 126–130 Ma, and is pale red in hand specimen with porphyritic texture. The main minerals are plagioclase (35–55%), K-feldspar (10–25%), quartz (15–30%), biotite (4–6%). Titanite is the main accessory mineral, with subordinate magnetite, zircon, apatite and monazite. K-feldspar appears mainly as euhedral phenocryst, with the largest crystal measuring up to 10 cm in length. Geochemical and isotopic studies indicated the Guojialing granodiorite was derived mainly from a crustal source, but with the involvement of mantle components (Yang et al., 2012). Mafic dikes intruded between 122 and 124 Ma (Yang et al., 2004). Most of the mafic dikes are fault controlled and share similar strikes with the gold orebodies or gold-bearing quartz veins. They are mainly composed of dolerite, hornblende dolerite and lamprophyre, and show ophitic and/or porphyritic-seriate textures, with phenocryst contents of 10–30%. The phenocrysts consist dominantly of clinopyroxene with subordinate plagioclase and plagioclase. The mineral assemblage of the matrix is similar to that of the phenocrysts but has a higher population of plagioclase. Previous studies suggested that the mafic dikes were derived from an enriched lithosphere mantle source (Yang et al., 2004).

The Sanshandao gold deposit is controlled by the Sanshandao–Cangshang fault zone, with the Linglong granite in the hanging wall and the Linglong granite/Guojialing granodiorite in the footwall (Fig. 2). This fault zone generally trends 35°, dips 35–40° southeast and extends to the northeast and southwest into the Bohai Sea. Structures along the fault zone are mainly characterized by brittle fracturing, throughout a zone of 50–200 m in width.

The alteration halos and orebodies generally trend northeast (20–40°), dip (35–70°) southeast, and extend offshore into the Bohai Sea (Fig. 2). Six orebodies, which are tabular or lenticular in shape and parallel to the main fault plane, have been identified. The No. 1 orebody accounts for 69% of the proven reserves, and lies within the middle to upper part of the pyrite-sericite-quartz alteration zone in the footwall of the main fault. This orebody is up to 1020 m in length, averages 6.4
Samples for analysis in this study were collected mainly from Borehole 56-4, 96-2 and 96-3. These three boreholes are about 1500 m, 2100 m and 2200 m to the east of the Sanshandao gold deposit (Fig. 2), and have a drilling depth of 2050 m, 2030 m and 2025 m, respectively. Borehole 56-4 reveals that both hanging wall and footwall of the Sanshandao–Cangshang fault are occupied by the Linglong granite. The other two boreholes reveal that the hanging wall of the fault are the Linglong granite, whereas the footwall of the fault are the Guojialing granodiorite.

4. Methodology

Thin sections and polished blocks were prepared for petrographic study, and both optical and scanning electron microscopy observations were performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS).

The whole rock major and trace elements were determined for 20 samples from Borehole 56-4 at IGGCAS. For major element analyses, mixtures of whole-rock powder (0.5 g) and Li2B4O7 + LiBO2 (5 g) were heated and fused into glass disks and analyzed by X-ray fluorescence spectroscopy (XRF) with an AXIOS-Miners spectrometer. The analytical uncertainties were generally within 0.1–1% (RSD). Loss on ignition (LOI) was obtained using 0.5 g powder heated up to 1100 °C for 1 h. For trace element analyses, whole-rock powders (40 mg) were dissolved in distilled HF + HNO3 in Teflon screw-cap capsules at 200 °C for 5 days, dried, and then digested with HNO3 at 150 °C for 1 day, and the final step was repeated. Dissolved samples were diluted to 49 ml with 1% HNO3 and 1 ml 500 ppb indium was added to the solution as an internal standard. Trace element abundances were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Finnigan MAT ELEMENT spectrometer, which has analytical uncertainties within 5% for most elements.

Secondary K-feldspar, sericite and pyrite from the alteration and mineralization zones of Borehole 56-4 were selected for Sr–Nd isotopic analysis. The Rb–Sr and Sm–Nd isotopic analysis followed procedures similar to those described by Chiu et al. (2009). Crushed samples were dissolved in a HF–HClO4–HNO3 mixture and spiked with appropriate amounts of mixed 87Rb–84Sr, 149Sm–150Nd tracer solution in Teflon bombs. Rb and Sr were separated using standard ion-exchange resins, and Sm and Nd were separated using Eichrom LN (LN-C-50B, 100–150 μm, 2 ml) chromatographic columns. They were analyzed on an IsoProbe-T thermal ionization mass spectrometer (GV Instruments, England), installed at the IGGCAS. The isotopic ratios were corrected for mass fractionation by normalizing to 86Sr/88Sr = 0.1191 and 146Nd/144Nd = 0.7219, respectively. The measured value for NBS987 Sr standard and JNd-1 Nd standard were 0.710245 ± 10 (2σ, n = 12) and 0.512120 ± 11 (2σ, n = 12), respectively. Total procedural blanks are <40 pg for Rb, <300 pg for Sr, <25 pg for Sm, and <70 pg for Nd. USGS reference material BCR-2 was measured to monitor the accuracy of the analytical procedures, with the following results: 87Sr/86Sr = 0.704996 ± 10 (2σ, n = 12) and 147Nd/144Nd = 0.512636 ± 11 (2σ, n = 12).

The fault gouge from Borehole 56-4 was separated for XRD analysis at IGGCAS. XRD measurement was carried out on a D/MAX-2400 X-ray diffractometer, with CuKα radiation at 60 mA and 40 kV. The goniometer was equipped with a graphite monochromator in the diffracted beam. Data was collected in the angular range 3°–70° in 2θ, with 8°/min.

Phase-equilibrium calculation was carried out using the SUPCRT92 software package (Johnson et al., 1992), with an upgraded version of the database (slop98.dat). The thermodynamic properties for Au(HS)2— are from Akinfiev and Zotov (2010). All other data are from the slop98.dat database. All the thermodynamic parameters for the thermal dynamic modeling were incorporated into SUPCRT92.
5. Gold-related hydrothermal alteration, vein types and mineralization

Broad hydrothermal alteration halos of granitic wall rocks occur along the Sanshandao–Cangshang fault zone (Fig. 2), and regular spatial zonation of alteration and vein minerals can be observed (Fig. 3). Our petrographic studies reveal five major types of mineral assemblages. A fault gouge layer, which separates the hanging wall and footwall of the main fault, occurs in the innermost alteration zone. Below this layer, pyrite–sericite–quartz alteration occurs as the most intense alteration zone, and it is closely related to the gold mineralization. A relatively narrow silicification zone occurs above fault...
Both pyrite—sericite—quartz alteration in the footwall and silicification in the hanging wall are enveloped by variable intensities of diffusive sericitization. K-feldspar alteration typically occupies the outermost part of alteration halos, but a few relatively narrow discrete sericitization zones develop along fractures in K-feldspar alteration zone. Minor amounts of sodic (albite) alteration, carbonation and argillic alteration are also observed. Because of the scarcity of their distribution, they are not described in detail.
in this paper. Similar to the other typical Jiaojia-type gold deposits, quartz-sulfide veins/veinlets are less developed in the Sanshandao deposit, and occur mainly in alteration halos in the footwall.

5.1. K-feldspar alteration

K-feldspar alteration occurs in the outermost part of the alteration zone, and generally developed along brittle fractures in the granitic wall rocks. The alteration is well developed (50–60 m in thickness) in Borehole 56-4, whereas it is only locally noticed in the other two boreholes and the Sanshandao deposit itself. K-feldspar alteration usually gives the rocks a pinkish appearance (Fig. 4a), which is commonly believed to be due to hematitic dusting (Plümper and Putnis, 2009; Putnis et al., 2007).

K-feldspar alteration is irregular in intensity and generally diffuse. Weakly altered rocks are characterized by relict plagioclase within secondary K-feldspar (Fig. 4c), partial or total transformation of biotite to muscovite and magnetite. With strong K-feldspar alteration, the original igneous texture was largely obliterated, with secondary K-feldspars totally replacing plagioclase (Fig. 4d), biotite disappeared, and minor secondary albite and muscovite occurred together with the secondary K-feldspar crystals (Fig. 4d). The secondary K-feldspar crystals are anhedral and large (1–4 cm in size) (Fig. 4a). Patch or vermicular albite crystals are included in the K-feldspar (Fig. 4d). Secondary quartz, replacing plagioclase, is also a very common part of both weak and strong K-feldspar alteration assemblage. Quartz grains mainly occur as polycrystalline quartz ribbons surrounding the K-feldspar crystals, indicating that they have experienced ductile deformation (Fig. 4e). Only limited sulfide minerals are associated with K-feldspar alteration. With increasing alteration intensity, the accessory minerals, such as apatite and titanite, are also gradually replaced by quartz (Fig. 4f and g). Most of these minerals show a decrease in grain size and become increasingly anhedral. Zircons, which are traditionally assumed to be resilient to hydrothermal alteration, also become smaller and anhedral. As seen from CL images, the inner textures of zircons were largely altered by hydrothermal fluids (Fig. 4h).

A very small portion of the K-feldspar alteration is related to quartz±muscovite veins (Fig. 4b). These veins have halos of K-feldspar crystals, which are anhedral, relatively large (0.5–2 cm in size) and contain some vermicular albite. Quartz crystals in the vein occur as recrystallized sub-grains. Very minor amounts of muscovite aggregates also occur in the vein. No clear timing relationships have been observed between vein related and diffusive K-feldspar alteration, but similar mineral assemblages and petrographic characteristics of K-feldspar suggest that they were probably contemporaneous.

5.2. Sericitization

Large scale (about 100 m in thickness) diffusive sericitization symmetrically developed across the fault zone, and is marked by green to white colors (Fig. 5a). The intensity of the diffusive sericitization generally decreases from inner to outer parts of the alteration zone. Towards the outer part, the sericitization generally took place along brittle fractures. Borehole 56-4, 96-2 and the Sanshandao deposit itself reveal that rocks in the footwall experienced stronger sericitization than those in the hanging wall. However, the samples from Borehole 96-3 show that wall rocks in the hanging wall also underwent strong diffusive sericitization.

With weak diffusive alteration, biotite was partly or totally replaced by sericite, and plagioclase crystals were converted to sericite along
Hairline cracks or polysynthetic twinning, although the twinning and zoning are still visible (Fig. 5d and e). K-feldspar crystals underwent little alteration. With strong diffusive sericitization, sericite replaced all the plagioclase and biotite, retaining pseudomorphs of plagioclase (Fig. 5f, g and h). Minor portion of the K-feldspar crystals were converted into sericite (Fig. 5f and g). In both weakly and strongly altered rocks, sericite...
not only replaced feldspars locally, but also formed as thin veinlets filling in micro-fractures (Figs. 4e and 5e). A small amount of sulfide minerals, mainly pyrite, as disseminated grains are also a ubiquitous part of the diffusive sericitization assemblages (Fig. 5h). Quartz crystals in this alteration zone also display features of ductile deformation (Fig. 5f and g). A minor portion of sericitization was quartz-vein related, and is mainly composed of sericite, with subordinate pyrite. Adjacent to the quartz-vein, sericite locally replaced plagioclase, or appeared as thin veinlets among other crystals, and pyrite occur as euhedral cubes or subhedral aggregates (Fig. 5b). Quartz in the vein appears as elongated sub-grains. Vein-related sericitization shares similar alteration mineral assemblage with diffusive sericitization, indicating that they were broadly contemporaneous.

In macro-scale, it is clear that sericitization overprints K-feldspar alteration (Fig. 5c), especially along fractures in the K-feldspar alteration zone. In micro-scale, sericite appears as thin veinlets filling micro-fractures in secondary K-feldspar crystals (Fig. 4e). Therefore, sericitization is inferred to be later than K-feldspar alteration.

5.3. Silification

The three boreholes (56-4, 96-2 and 96-3) reveal that a relatively narrow silification zone (5–20 m in thickness) occurs above the fault gouge layer in the hanging wall, and varies from white to green in color (Fig. 6a). As with sericitization, the intensity of silification generally decreases away from the center of the main fault. With weak silification, parts of former altered rocks were replaced by quartz, with remnant K-feldspar, sericite, plagioclase and sulfide surrounded by newly formed quartz (Fig. 6b). Strong silification replaced most former minerals by quartz. Small amounts of sericite and sulfide precipitated together with secondary quartz. Most silified rocks, especially those near the main fault, sustained strong brittle deformation. Angular quartz ± feldspar fragments of variable size are present (Fig. 6c). It is noted that most single quartz porphyroclast consist of elongated quartz sub-grains (Fig. 6d), indicating that ductile deformation of quartz had occurred before strong brittle deformation.

The contact between the silification and sericitization zones is gradational, but in both macro- and micro-scale it is clear that silification overprinted sericitization (Fig. 6a and b). Therefore, the timing of silification may have overlapped with, or more probably largely postdated, that of sericitization.

5.4. Pyrite–sericite–quartz alteration, veins and gold mineralization

Boreholes expose that a ca. 5–15 m thick pyrite–sericite–quartz alteration zone occurs nearest to the fault gouge in the footwall of the main fault, and is characterized by black to dark green in color (Fig. 7a). As with silified rocks mentioned above, rocks in this zone are also cataclastic breccias formed during brittle deformation. Strong pyrite alteration, sericitization and silification, which heavily overprinted former sericitization and silification, developed along cracks or other open spaces of breccias (Fig. 7a, b and c). This zone mainly comprises quartz, sercite and pyrite. Most quartz grains are porphyroclasts, exhibiting irregular shapes and various sizes (Fig. 7a, b and d). Most single quartz porphyroclasts are aggregates of former dynamically recrystallized sub-grains (Fig. 7c). A small portion of quartz, especially those fine grained crystals, may have been derived from hydrothermal alteration. Sericite generally appears as veinlets filling

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Fig. 9. Paragenetic sequence for the hydrothermal minerals of the Sanshandao gold deposit. The widths of the solid lines denote relative abundance of minerals.
fissures (Fig. 7c), or as disseminated grains coexisted with fine-grained quartz (Fig. 7d). Pyrite is the most common sulfide mineral in this zone, and occurs as euhedral to subhedral grain ranging from 10 to 500 μm in size (Fig. 7d). They are disseminated within the rocks, or occur as pyrite±sericite±quartz stockworks. In addition to pyrite, minor amounts of chalcopyrite (Fig. 7f) and little galena, sphalerite, arsenopyrite, chalcocite and pyrrhotite can also be found, typically as micro-crack fillings or inclusions in pyrite. They probably precipitated contemporaneously with disseminated pyrite and pyrite stockworks.

The gold mineralization is closely associated with pyrite–sericite–quartz alteration. Gold occurs mostly as electrum, with minor amounts of native gold. Gold grains are anhedral and range from 10 to 100 μm in size. Most of the electrum and native gold grains are spatially associated with pyrite, occurring as inclusions or fillings in pyrite (Fig. 7ea and f). Less commonly, gold also occurs as small inclusions in quartz or as individual grains along cleavage planes in sericite.

Quartz-sulfide veins/veinlets, which were largely contemporaneous with pyrite–sericite–quartz alteration, can be observed in alteration halos, especially in the footwall. It is noted that the Sanshandao deposit itself contains more veins/veinlets than the three other observed boreholes (56-4, 96-2 and 96-3). Based on mineral assemblages, two types of veins can be distinguished: quartz–pyrite veins and quartz–base metal sulfide veins. The quartz–pyrite veins consist of quartz and pyrite, with minor chalcopyrite and arsenopyrite (Fig. 7g). Quartz occurs as white–gray aggregates, and pyrite occurs as coarse euhedral cubes and subhedral aggregates. The quartz–base metal sulfide veins are characterized by precipitation of gray quartz and different types of fine-grained anhedral sulfide minerals (e.g. pyrite, chalcopyrite, arsenopyrite, galena, sphalerite and so on) (Fig. 7h). Gold occurs as inclusions or crack fillings within sulfide minerals.

Late stage quartz-carbonate veins cut all other stages. They are composed mainly of quartz, calcite and siderite, with subordinate pyrite

| Table 1 |

Major oxides (wt.% and trace elements (ppm) for the Linglong granite and altered samples.

<table>
<thead>
<tr>
<th>Rock-type</th>
<th>Linglong granite</th>
<th>K-feldspar alteration</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-1545 m</td>
<td>L-1899 m</td>
<td>K-1805 m</td>
</tr>
<tr>
<td>SiO₂</td>
<td>72.24</td>
<td>70.72</td>
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<tr>
<td>TiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<td>FeO</td>
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<td>MgO</td>
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<tr>
<td>CaO</td>
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<td>1.57</td>
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<tr>
<td>Na₂O</td>
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<tr>
<td>K₂O</td>
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<tr>
<td>P₂O₅</td>
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<tr>
<td>LOI</td>
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<tr>
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<td>99.61</td>
</tr>
<tr>
<td>Sc</td>
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<tr>
<td>V</td>
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<td>6.6</td>
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<tr>
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<tr>
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<tr>
<td>Ni</td>
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<td>Gd</td>
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<td>1.71</td>
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<tr>
<td>Dy</td>
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<tr>
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<tr>
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<td>0.06</td>
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<td>Yb</td>
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<tr>
<td>Lu</td>
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<td>5.8</td>
<td>3.6</td>
</tr>
<tr>
<td>U</td>
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<td>1.10</td>
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<td>30.14</td>
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<tr>
<td>Y/Ho</td>
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<tr>
<td>δEu</td>
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<td>0.53</td>
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<tr>
<td>∑Ree</td>
<td>73.17</td>
<td>59.80</td>
</tr>
</tbody>
</table>
5.5. Fault gouge

The black-colored fault gouge with a thickness of 10–30 cm mainly consists of very fine grained quartz, illite, kaolinite, with minor pyrite (Fig. 8). Besides, amorphous phases are also detected assemblages have been identified by XRD analysis. The fault gouge may largely form in response to the movements along the Sanshandao Cangshang fault, which also created permeability which allows hydrothermal fluids from moving upward. After the formation of fault gouges, pyrite–sericite–quartz alteration occurred, acting as a “barrier layer” that is impermeable to in-fertile ore-forming fluid, leading to diffusive K-feldspar alteration on wall rocks, leading to diffusive K-feldspar alteration on...

5.6. Summary on paragenetic sequence of alteration, veins and mineralization

Based on field and microscopic investigations, five stages of alteration assemblages have been identified (Fig. 9). Activities of the Sanshandao–Cangshang fault created permeability which allows hydrothermal fluids to infiltrate wall rocks, leading to diffusive K-feldspar alteration on the fault planes. Pervasive sericitization followed, and overprinted K-feldspar alteration. Subsequently, small scale silicification occurred, mainly overprinting sericitization. Later, reactivation of the main fault led to strong brittle deformation and the formation of fault gouges, which prevented later fluids from moving upward. After the formation of fault gouges, pyrite–sericite–quartz alteration occurred during the most intense phase of hydrothermal alteration, strongly overprinting...
former sericitization and silicification in the footwall of the main fault. Gold mineralization was closely related to pyrite–sericite–quartz alteration. Quartz–pyrite and quartz–base metal sulfide veins/veinlets also developed during pyrite–sericite–quartz alteration stage. The latest stage quartz-carbonate/carbonate veins mark the waning of gold-related hydrothermal activity.

6. Bulk-rock geochemistry and mobilization of elements

To estimate the chemical changes associated with the main alteration assemblages, the major elements (Si, Al, Fe, Mg, Ca, Na, K and P), rare-earth elements (REEs), light-lithophile elements (LILEs; e.g., Cs, Rb, Sr, Ba, Pb and U; Schilling, 1973), high-field strength elements (HFSEs; e.g., Nb, Ta, Ti, Zr, Hf, Th and Ga; Panahi et al., 2000) and trans-transition elements (TRTEs; e.g., Sc, V, Cr, Co, Ni, Cu, Zn and Bi; Jenner, 1996) were analyzed in representative samples of altered rocks and their equivalent, least altered “protoliths” (Table 1). Our sample selection for geochemical analysis ensured representation of a specific alteration assemblage and without any obvious open-space filling veins to overcome the problem of alteration overprinting.

The iscon method of Grant (1986) was used to demonstrate potential chemical changes between altered wall rocks and their corresponding “protoliths” (Fig. 10a, b and c). In this paper, we choose Al₂O₃ as the most immobile reference element during construction of iscons. Element gains and losses on a weight basis have been calculated following Grant’s approach (Grant, 1986) and using Al₂O₃ as the immobile element:

\[ \Delta C = \left( \frac{C_{\text{immobile}}^F}{C_{\text{immobile}}^A} \right) \cdot \left( C_{\text{A}}^F - C_{\text{A}}^F \right) \]

where \( C_{\text{A}}^F \) and \( C_{\text{A}}^A \) are the concentrations in the fresh (F) and altered (A) sample, respectively, and \( \Delta C \) denotes the gain or loss in grams per 100 g of rock for major elements or in parts per million for trace elements. The results are presented in Table 2.

6.1. K-feldspar alteration

Typical K-feldspar altered rocks from both hanging wall and footwall of the main fault in Borehole 56-4 were selected for analysis, and they were compared with the igneous compositions of the Linglong granite in the isocon diagram (Fig. 10a). The data show a decreasing trend of Na₂O and CaO and a large increase of K₂O, as expected from the replacement of plagioclase by K-feldspar. During the consumption of biotite, FeO and MgO are removed. The obvious loss of P₂O₅ mainly reflects the breakdown of P-rich accessory minerals (such as apatite and monazite). LILEs exhibit high mobility during K-feldspar alteration. Rb and Pb are enriched due to their preference of substitution for K in the lattice of K-feldspar, whereas Sr and Ba are depleted, reflecting the breakdown of former Sr- and Ba-rich igneous feldspars (K-feldspar within the fresh granitic wall rocks can contain up to 2.90 wt.% BaO and 0.40 wt.% SrO, our unpublished data). The K-feldspar alteration is also characterized by a large gain of U, which is proven to be fluid mobile in many cases.

K-feldspar alteration is also accompanied by marked modifications of REEs concentrations and patterns. The total REEs contents of altered rocks are much lower than those of granitic wall rocks (Table 1). REEs are usually hosted in accessory zircon, apatite, titanite or monazite. Petrographic observation shows that with increasing alteration intensity the accessory minerals were gradually consumed.

Fig. 10. Isocon diagrams in which the “protolith” (the Linglong granite and, in the case of silicification, samples undergone sericitization) versus the altered samples are plotted. Various elements are multiplied or divided by a constant to improve the graphical effects; this process would not affect the validity in illustrating the mass transfer characters (Grant, 1986). Black lines (iscons) are defined by the constant ratios of immobile element (Al₂O₃), which were used for the calculation of the gains and losses. Elements above these lines are enriched in the altered rock, whereas elements below the lines are depleted during alteration.
This is also supported by the obvious decrease of P2O5, Ti and Zr (Table 1 and Fig. 10a). Therefore, the decrease of REE contents may be associated with the breakdown of REE-rich accessory minerals. It is also noted that there was much larger loss in LREEs (from La to Eu) than in HREEs (from Gd to Lu) (Fig. 10a and Table 2), indicating with higher mobility of LREEs during fluid–rock interactions, in con- formity with similar observations in former studies (Guo et al., 2012; Küpeli, 2010; Panahi et al., 2000; Zhao et al., 2007).

Three altered K-feldspar samples (K-1995, K-2047, K-2048) display pronounced positive Eu anomalies (ΣEu = 8.46–14.67), and they are also characterized by very low total REE contents (1.19–2.68 ppm) (Fig. 11a). As mentioned above, along with the increased alteration intensity, relatively REE-rich minerals (e.g., monazite, zircon and apatite) gradually broke down. The major rock-forming minerals (e.g. K-feldspar and albite), which are commonly REE-poor, probably became the most important REE budget for the whole rock. In this case, the total REEs concentrations of altered rocks should be low, and the whole-rock chondrite-normalized REE patterns are similar to those of feldspar minerals, which have been shown to be very compatible with Eu by previous studies (Bédard, 2006; White, 2003).

Heavy chemical leaching of Nb, Ta, Zr and Hf is also observed. Zr and Hf tend to reside in zircon, and Nb and Ta are contained in titanium minerals (e.g., titanaite and ilmenite). Losses of the HFSE should result from the consumption of related accessory minerals. Strong Zr–Hf, Nb–Ta and Y–Ho fractionations are observed in some altered samples, with deviations of Zr/Hf, Nb/Ta and Y/Ho values from corresponding magmatic ratios (Table 1). Ga displays much lower mobility than the other HFSE mentioned above. The ionic radii of Al and Ga are very similar that most of the Ga is present in Al-bearing minerals, and therefore Ga maintains similar immobility with Al.

6.2. Sericitization

Representative sericitization assemblages from both hanging wall and footwall of the main fault in Borehole 56–4 were analyzed, with the Linglong granite as their precursor.

Sericitization is characterized by strong gains of K2O and LOI and loss of Na2O, due to the replacement of plagioclase by sericite. CaO should also be lost in response to the consumption of plagioclase, but there is a gain of CaO shown in the isocron diagram (Fig. 10b), which may be caused by the presence of quartz-carbonate veinlets. As expected, the breakdown of biotite led to the depletion of FeO.

In the sericitization zone, Rb and Pb show gain due to their substitution of K in the lattice of sericite and K-feldspar. Sr was lost due to the consumption of igneous plagioclase, whereas Ba shows immobility, which is probably related to the conservation of K-feldspar during sericitization. U and Cs display slight to moderate loss.

During the sericitization stage, REEs and HFSEs show relatively low mobility (Fig. 10b). LREEs (except for Sm) display minor gain, whereas Sm and HREEs show slight loss. The altered rocks display similar chondrite-normalized REE patterns with the Linglong granite (Fig. 11b). Most HFSEs were retained in the rocks, except for Nb and Ta which were moderately decreased. Zr–Hf, Nb–Ta and Y–Ho fractionations are also observed in sericitization domains (Table 1).

Some TRTEs (e.g. Cu, Zn and Bi) were largely enriched, probably resulting from the presence of disseminated sulfide.

6.3. Silicification

Typical silicification assemblages were analyzed from the hanging wall of the Borehole 56–4. As mentioned above, silicification overprinted earlier sericitization, so gains and losses of elements are tested by plotting average element concentrations of altered rocks in the silicification zone versus those in sericitization zone in the isocron diagram (Fig. 10c).

Silicification is characterized by a strong addition of SiO2 and losses of K2O, CaO, P2O5 and LOI, resulting from the fact that quartz replaced the former igneous and secondary minerals. Na2O shows increase, which contradicts the consumption of plagioclase. Considering that there are many fluid inclusions within the secondary quartz, we infer that the Na2O reside in fluid inclusions in quartz. FeO also shows gain, due to the presence of disseminated pyrite.

Along with the consumption of former K-feldspar, plagioclase and sericite, Sr and Ba were lost. Pb and U were gained, which may also be related to the common presence of fluid inclusions within the secondary quartz. Compared with the LILEs mentioned above, Rb and Cs show very slight mobility (Fig. 10c).

As with K-feldspar alteration, all the REEs were lost from former altered rocks, and the LREEs generally display higher mobility than the HREE (Fig. 10c and Table 2). The chondrite-normalized REE patterns were changed: two analyzed samples have low total REE contents (7.80–10.18 ppm) and moderately positive Eu anomalies (Fig. 11a). This might also have resulted from the marked consumption of REE-rich accessory minerals and presence of feldspars in silicification zone.

The behavior of HFSEs is complex in the silicification zone. Zr, Hf, Ti and Th were moderately to largely lost, whereas Ga shows large enrichment. Nb and Ta show minor mobility. The Nb/Ta, Zr/Hf and Y/Ho values deviate from those of the Linglong granite (Table 1).

Silicification is also marked by addition of most TRTEs (e.g. Sc, V, Cr, Co, Ni and Cu) due to the precipitation of sulfide.

| Table 2 |
| Calculated gains and losses for the different alteration zones. |
| K-feldspar alteration | Sericitization | Silicification |
| SiO2 | 1.69 | 3.24 | 41.83 |
| TiO2 | -0.11 | -0.01 | -0.10 |
| FeO | -0.75 | -0.45 | -0.25 |
| MgO | -0.12 | 0.03 | 0.20 |
| CaO | -0.55 | 0.80 | -1.27 |
| Na2O | 1.57 | -4.74 | -4.27 |
| K2O | 3.80 | 1.19 | -0.94 |
| P2O5 | -0.02 | 0.00 | -0.02 |
| LOI | 0.26 | 3.07 | -1.57 |
| Sc | -0.44 | -0.05 | 1.73 |
| V | -3.05 | -1.22 | 21.65 |
| Cr | -61.20 | -46.75 | 200.09 |
| Co | -0.63 | -0.31 | 1.04 |
| Ni | -1.62 | -0.56 | 5.43 |
| Cu | 1.15 | 11.44 | 129.81 |
| Zn | -18.07 | 68.09 | -77.93 |
| Ga | 2.49 | -0.43 | 24.69 |
| Rb | 109.28 | 14.24 | 17.80 |
| Sr | -284.62 | -209.68 | -206.65 |
| Y | -3.12 | -2.42 | -1.31 |
| Zr | -85.23 | 14.29 | -70.64 |
| Nb | -5.46 | -4.44 | -0.04 |
| Cs | 0.07 | -0.50 | 0.05 |
| Ba | -754.40 | -37.15 | -1178.66 |
| La | -13.48 | 4.53 | -17.42 |
| Ce | -21.85 | 5.70 | -27.53 |
| Pr | -2.62 | 0.52 | -3.16 |
| Nd | -8.84 | 1.07 | -10.56 |
| Sm | -1.35 | -0.26 | -1.53 |
| Eu | -0.12 | 0.21 | -0.36 |
| Gd | -0.93 | -0.42 | -0.90 |
| Tb | -0.13 | -0.08 | -0.09 |
| Dy | -0.52 | -0.25 | -0.38 |
| Ho | -0.09 | -0.03 | -0.06 |
| Er | -0.22 | -0.06 | -0.14 |
| Tm | -0.04 | -0.01 | -0.02 |
| Yb | -0.24 | -0.04 | -0.19 |
| Lu | -0.04 | 0.00 | -0.04 |
| Hf | -2.07 | 0.37 | -2.02 |
| Ta | -0.26 | -0.34 | -0.05 |
| Pb | 15.12 | 26.21 | 46.84 |
| Bi | 0.00 | 0.01 | 0.51 |
| Th | 0.68 | 0.02 | -1.21 |
| U | 3.07 | -0.75 | 1.32 |
6.4. Pyrite-sericite-quartz alteration

For rocks in the pyrite-sericite-quartz alteration zone, it is inevitable to include some samples with a few veins/stockworks. In addition, pyrite-sericite-quartz alteration may have overprinted either sericitization or silicification, so it is hard to define the "protoliths" of pyrite-sericite-quartz alteration. Therefore, we presented only the whole-rock major and trace element data for pyrite-sericite-quartz altered rocks in Table 1, and do not attempt to compare them with any precursors.

Due to the common presence of sulfide minerals, which are spatially close to gold as mentioned above, this zone is characterized by obvious addition of S and Au. Along with the addition of gold, other metal elements (e.g. Cu, Pb and Bi) are also enriched (Table 1). Former studies found that at relatively lower temperatures (<400 °C), HS⁻ is the most important ligand complexed with gold (Seward, 1973), with Au(HS)₂⁻ predominating at acidic condition and Au(HS)₂⁻ at weakly acidic to neutral conditions (Stefánsson and Seward, 2004); whereas at a high temperature, high salinity and H₂S-poor systems, AuCl⁻ will predominate (Mikucki, 1998; Stefánsson and Seward, 2004). The close association of gold with sulfides in the pyrite-sericite-quartz alteration zone supports that gold was most likely complexed with HS⁻ during transportation.

6.5. Summary

The presence of large mineralized bodies, wide alteration halos and strong modification of igneous textures and mineral assemblages indicate large scale and intense fluid-rock interaction. Such hydrothermal processes should have the potential to mobilize most elements when fluids flowed through granitic wall rocks.

As shown in the previous section, major element concentrations are affected by various mineral replacement reactions. Most fluid-mobile elements, LILEs and LREEs, show relatively high mobility. The traditionally assumed fluid-immobile elements (e.g. HREEs and HFSEs) could also be changed, especially during the K-feldspar alteration and silicification stages. In fact, mobilization of HREEs and HFSEs owing to hydrothermal alteration has been reported by several authors (e.g. Dongen et al., 2010; Hynes, 1980; Jiang, 2000; Jiang et al., 2005; Salvi and Williams-Jones, 1996; Salvi et al., 2000). These observations are noteworthy because these elements, especially the REEs and HFSEs, are widely used for petrogenetic studies; therefore, caution must be taken with samples which are hydrothermally altered.

7. Physicochemical conditions of ore fluid system

In this section, previous fluid inclusion data and newly computed log [aNa⁺/aH⁺]-log [aAl³⁺/aH⁺] and logfO2-pH diagrams are employed to derive the principal physicochemical parameters (e.g. temperature, pressure, pH, fO2 and fluid compositions) that potentially controlled the hydrothermal alteration and gold mineralization.

Coeexistence of ductile deformation of quartz and slight brittle deformation of the feldspar in the altered rocks (Figs. 4e and 5f) indicates that deformation, and thus gold mineralization, occurred under temperature conditions of 300–400 °C (Scholz, 1988). As mentioned above, rocks adjacent to the main fault underwent strong brittle deformation (Figs. 6c, 7a and b), and before that quartz in the alteration halos had experienced slight to moderate ductile deformation. These facts suggest that the Sanshandao–Cangshang fault is a brittle-ductile transitional deformation zone, but it is dominantly characterized by cataclastic deformation. Therefore, it is deduced that the deformation occurred at depth of about 10 km (Sibson, 1977), corresponding to pressure of about 300 MPa. The deduced temperature and pressure are broadly consistent with those obtained by Fan et al. (2003) from fluid inclusions in mineralization stage. Therefore, we chose 350 °C and 300 MPa for phase equilibria calculations.

Stability relationships of Na–K alteration phases were determined as a function of fluid composition and an isothermal–isobaric abridged activity diagram [log (aAl³⁺/aH⁺)] versus log (aNa⁺/aH⁺)] was constructed in the system Na–K–Al–Si–H–O (Fig. 12a). The phases considered are K-feldspar [KAlSi₃O₈], albite [NaAlSi₃O₈], sericite [KAl₂(AlSi₃)O₁₀(OH)₂], paragonite [NaAl₂(AlSi₃)O₁₀(OH)₂] and kaolinite [Al₂Si₂O₅(OH)₄]. End-member reactions used for the construction of the log (aAl³⁺/aH⁺)] versus log (aNa⁺/aH⁺)] diagram and the computed log K values are given in Table 3 (A1–A7). LogfO2-pH diagram for the system Fe–S–O–H was also constructed to depict phase relationships of Fe-bearing minerals and fields of predominance of aqueous sulfur species (Fig. 12b). The species boundaries between H₂S, HS⁻, SO₄²⁻ and SO₂⁻ were determined using log K values of A8 through A12 (Table 3). Mineral stability fields were plotted based on log K values of A13 through A19 (Table 3). The concentration of total dissolved sulfur in solution was on the order of Au(HS)₂⁻.
Contour lines of Au(HS)$_2$ are from the slop98.dat database. Narrow and bold lines represent the boundaries between aqueous sulfur species and Fe-bearing minerals, respectively. Calculated solubility K-feldspar could lead to a decrease of log ($a_{\text{K-feldspar}}$) with alteration going on (thermodynamic data used are from slop98.dat database). (b) Log $a_{\text{H}_2\text{O}}$-pH diagram at 350 °C, 300 MPa and $\Sigma S=0.1$ mol/kg (the thermodynamic properties for Au(HS)$_2$ are from Akiniev and Zotov [2010]; other data are from the slop98.dat database). Narrow and bold lines, represent the boundaries between aqueous sulfur species and Fe-bearing minerals, respectively. Calculated solubility contours of Au(HS)$_2$ at 10, 100 and 1000 ppm (thin continuous lines) are shown in the predominance fields of various aqueous sulfur species. The arrow represents the possible decrease of $f_{\text{CO}_2}$ with marginal drop in pH, caused gold precipitation. Abbreviations: Hm—hematite, Mt—magnetite, Py—pyrite, Po—pyrrhotite, Bn—bornite, Ccp—chalcopyrite.

$\Sigma S=0.1$ mol/kg, which is within the $\Sigma S$ range (10–10$^{-3.3}$ mol/kg) compiled by Mikucki [1998] for the orogenic gold deposits.

In K-feldspar alteration stage, replacement of plagioclase by K-feldspar could lead to a decrease of $a_{\text{K-feldspar}}$ and an increase of $a_{\text{K}}$ in aqueous solutions, and the fluid compositions locate in the stability field of K-feldspar in log $(a_{\text{K}-}\text{feldspar})$-$log (a_{\text{K}})$ diagram (Fig. 12a). During sericitization and silicification stages, plagioclase was transformed into sericite, but K-feldspar experienced little alteration. Thus, log ($a_{\text{K}}$/$a_{\text{K-feldspar}}$) of the fluid is constrained on the equilibrium line between K-feldspar and sericite (Fig. 12a). Pyrite-sericite-quartz alteration is marked by the common presence of sericite and disappearance of both plagioclase and K-feldspar, so the fluid compositions should be confined in the stability field of sericite, and the formation of sericite would lead to a decrease of $a_{\text{K}}$ in the fluid (Fig. 12a). In general, the hydrothermal fluids were marked by decreases of log ($a_{\text{K}}$/$a_{\text{K-feldspar}}$) from early to late alteration stages, which can be caused by a decrease of $a_{\text{K}}$ and/or an increase of $a_{\text{K-feldspar}}$. Generally kept constant due to weak acid buffering by H$_2$CO$_3$ utilizing the common presence of CO$_2$ in the fluid (Phillips and Evans, 2004), but formation of secondary K-feldspar and sericite would largely consume K$^+$ in the fluid. Thus, decrease of $a_{\text{K}}$ was probably responsible for the decreases of log ($a_{\text{K}}$/$a_{\text{K-feldspar}}$) of the fluids.

In relatively acid solutions, feldspar tends to be transformed into sericite (Sverjensky et al., 1991; A2 and A3 in Table 3). However, sericite is not stable if the acidity is strong, under which sericite can be replaced by kaolinite (Sverjensky et al., 1991; A4 in Table 3). Therefore, the common presence of sericite in ore-bodies can be effectively used to constrain pH of ore-forming fluids. If activity coefficients are ignored ($\gamma =1$), temperature was 350 °C, pressure was 300 MPa, sodium ion concentrations of the fluid were assumed to be 1 mol/kg (~6 wt.% NaCl equiv) based on the calculated salinities of fluid inclusions and the potassium concentration was assumed to be 0.1 m/kg, which corresponds to a Na/K ratio of 10, an estimate that is similar to that of other mesothermal gold deposits (Diamond et al., 1991; Robert and Kelly, 1987; Yardley, 2005), PH is calculated to be between 2.9 and 5.0 in order for sericite to be stable. This is consistent with the weak acidity suggested by the presence of CO$_2$ in the mineralizing fluids.

The $f_{\text{CO}_2}$ of ore-forming fluid can be constrained based on the phase relationships of Fe-bearing minerals in Fig. 12b. Pyrite is the predominant Fe-bearing mineral in ore-bodies, which assigns log $f_{\text{CO}_2}$ between −25.08 and −32.22, assuming pH = 4, T = 350 °C and P = 300 MPa. In addition, chalcopyrite is the most important accessory sulfide mineral, which usually coexists with pyrite (Fig. 7f). The coexistence of these minerals during the main mineralizing stage further constrains log $f_{\text{CO}_2}$ near −28 (Fig. 12b). This paper does not cover fluid inclusion studies for specimen from deep boreholes, but it is notable that through fluid inclusion studies Fan et al. (2003) found that CH$_4$ was almost absent in the fluids of pre-gold alteration stages, whereas it was commonly present in fluid inclusions in the main gold mineralization stage at Sanchandao. This might indicate a decrease of $f_{\text{CO}_2}$ from pre-metallagenic stage to the main gold

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**Table 3**

<table>
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<tr>
<th>Reaction no.</th>
<th>Reaction</th>
<th>LogK</th>
</tr>
</thead>
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<tr>
<td>A1</td>
<td>Na(AlSi$_3$O$_8$) + K$^+$ = K(AlSi$_3$O$_8$) + Na$^+$</td>
<td>0.929</td>
</tr>
<tr>
<td>A2</td>
<td>3K(AlSi$_3$O$_8$) + 2H$^+$ = K(AlSi$_3$O$_8$O$_3$)(OH)$_2$ + 6SiO$_2$ + 2K$^+$</td>
<td>7.951</td>
</tr>
<tr>
<td>A3</td>
<td>3Na(AlSi$_3$O$_8$) + 2H$^+$ + K$^+$ = NaAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + 6SiO$_2$ + 3Na$^+$</td>
<td>10.739</td>
</tr>
<tr>
<td>A4</td>
<td>2KAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + 2H$^+$ + 3H$_2$O = 3Al$_2$Si$_2$O$_5$(OH)$_4$ + 2K$^+$</td>
<td>3.705</td>
</tr>
<tr>
<td>A5</td>
<td>NaAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + Na$^+$ = NaAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + K$^+$</td>
<td>−1.511</td>
</tr>
<tr>
<td>A6</td>
<td>3NaAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + 2H$^+$ = NaAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + 6SiO$_2$ + 2Na$^+$</td>
<td>9.228</td>
</tr>
<tr>
<td>A7</td>
<td>2NaAl$_2$(AlSi$_3$O$_10$(OH)$_2$) + 2H$^+$ + 3H$_2$O = 3Al$_2$Si$_2$O$_5$(OH)$_4$ + 2Na$^+$</td>
<td>6.727</td>
</tr>
<tr>
<td>A8</td>
<td>H$_2$Saq = HS$^-$ + H$^+$</td>
<td>−6.768</td>
</tr>
<tr>
<td>A9</td>
<td>HSO$_3^-$ = SO$_2^{2-}$ + H$^+$</td>
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</tr>
<tr>
<td>A10</td>
<td>HS$^-$ + 2O$_2$aq = SO$_2^{2-}$ + H$^+$</td>
<td>49.204</td>
</tr>
<tr>
<td>A11</td>
<td>H$_2$SO$_4$ + 2O$_2$aq = HS$^-$ + H$^+$</td>
<td>47.947</td>
</tr>
<tr>
<td>A12</td>
<td>H$_2$SO$_4$ + 2O$_2$aq = SO$_2^{2-}$ + H$^+$</td>
<td>42.436</td>
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<tr>
<td>A13</td>
<td>2Fe$^{2+}$ + 2O$_2$aq + 2H$^+$ = 2Fe$^{3+}$ + 2H$_2$Oaq</td>
<td>34.218</td>
</tr>
<tr>
<td>A14</td>
<td>2Fe$^{2+}$ + 2O$_2$aq + 2H$^+$ = 2Fe$^{3+}$ + 2H$_2$Oaq</td>
<td>47.754</td>
</tr>
<tr>
<td>A15</td>
<td>6Fe$^{2+}$ + 6H$_2$Oaq + 2O$_2$ = 2Fe$_3$O$_4$ + 6H$^+$ + H$^+$</td>
<td>−22.634</td>
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<tr>
<td>A16</td>
<td>3Fe$^{2+}$ + 6H$_2$Oaq + Fe$_2$O$_3$ + 6HS$^-$ + 6H$^+$</td>
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<td>A17</td>
<td>3Fe$^{2+}$ + 6H$_2$Oaq + 11O$_2$ = Fe$_3$O$_4$ + 6SO$_4^{2-}$ + 12H$^+$</td>
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<td>A18</td>
<td>4Fe$^{2+}$ + 8H$_2$Oaq + 15O$_2$ = 2Fe$_3$O$_4$ + 8SO$_4^{2-}$ + 16H$^+$</td>
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<td>4Fe$^{2+}$ + 8H$_2$Oaq + 15O$_2$ = 2Fe$_3$O$_4$ + 8HSO$_4^-$ + 8H$^+$</td>
<td>336.226</td>
</tr>
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<td>A20</td>
<td>4Au + 8H$^+$ + O$_2$ = 4Au(AlSi$_3$O$_8$)+ + 2H$_2$Oaq</td>
<td>−4.636</td>
</tr>
<tr>
<td>A21</td>
<td>4Au + 8H$^+$ + O$_2$ = 4Au(AlSi$_3$O$_8$)+ + 2H$_2$Oaq</td>
<td>50.284</td>
</tr>
<tr>
<td>A22</td>
<td>4Au + 8SO$_4^{2-}$ + 12H$^+$ = 4Au(AlSi$_3$O$_8$)+ + 8HSO$_4^-$ + 12H$^+$</td>
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</tr>
<tr>
<td>A23</td>
<td>4Au + 8SO$_4^{2-}$ + 4H$^+$ = 4Au(AlSi$_3$O$_8$)+ + 2H$_2$Oaq + 15O$_2$g</td>
<td>−387.512</td>
</tr>
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</table>
showed that oxygen isotope ratios for auriferous quartz samples from crustal rocks were 6.6 to 10.9‰, and the hydrogen isotopes measured for inclusion fluids extracted from auriferous quartz range from -48 to -81‰ (Fan et al., 2003; Mao et al., 2008). These data locate within or adjacent to the magmatic water region in the plot of δD vs. δ18O, suggesting that a magmatic fluid might have dominated at the Sanshandao deposit. Nevertheless, the ore fluids may also contain a portion of meteoric waters, as some δD values are lighter than typical values of primary magmatic waters. Furthermore, typical exsolved magmatic fluid is characterized by high temperatures and relatively high salinity (Audétat et al., 2008), so external, largely meteoric, fluids were needed to mix with the magmatic fluid to produce the moderate-temperature and low salinity ore-forming fluids as suggested by fluid inclusions in the Sanshandao deposit. This lends additional support for the involvement of meteoric water in the ore-forming system.

It is possible that during fluid generation and migration, Sr and Nd entered the ore fluids, and during large scale and intense fluid–rock interactions, the isotopic signature of the fluids was recorded in the newly formed hydrothermal minerals. Investigations by Bell et al. (1989), Frei et al. (1998) and Yang and Zhou (2001) have shown that the sources of hydrothermal fluids can be determined by Rb–Sr, and Sm–Nd isotopic studies of hydrothermal minerals. In this paper, the isotopic data of the hydrothermal minerals (secondary K-feldspar, sericite and pyrite) from alteration and mineralization zone are employed to provide further constraints on the source of the hydrothermal fluids.

The εNd values of hydrothermal minerals at 120 Ma are within the range −17.7 to −25.2, and the initial 87Sr/86Sr ratios at 120 Ma range from 0.7088 to 0.7143, with most values higher than 0.7110 (Fig. 13 and Table 4). Previous studies yielded similar Sr ([87Sr/86Sr]0) = 117 Ma: 0.7103 to 0.7119 and Nd [εNd(t = 117Ma): −16.1 to −20.0] isotopic compositions for mineralized rocks in the Xincheng gold deposit, another large Jiaodong-type deposit near the Sanshandao gold deposit (Yang, 2000). The high initial 87Sr/86Sr ratios of hydrothermal minerals generally overlap with those of crustally-derived granitoids (Fig. 13), which suggests that Sr in the mineralizing fluids was mainly derived from a crustal source. The low diffusion rate of Nd isotope in minerals (Cherniak, 2003; Michard, 1989) suggests that there might be limited fluid–wall rock Nd isotopic exchange during fluid migration and thus, Nd isotopic composition can largely reflect the nature of the fluid source. The strongly negative εNd(t) values for hydrothermal minerals suggest that Nd isotopic composition of the hydrothermal fluids mainly derived from crustal source. Early Cretaceous granitoids contemporaneous with the gold deposits crop out widely in the Jiaobei terrane, which indicate widespread crust reactivation and melting (Zhai, 2008). Post-magmatic fluids of felsic magmas may have easily ascended along a regional fault and largely participated in the gold-forming event. In
addition, meteoric water which had equilibrated with crustal rocks can also be induced by widespread intrusions to participate in the ore-forming event. It should also be noted that some 0 values of hydrothermal minerals are relatively higher than published crustal values for the North China Craton (Jahn et al., 1999) and those of the crustally-derived granitic wall rocks, but can be compared with those of mafic dikes (Fig. 13), which suggests the possibility that fluids derived from an enriched lithospheric mantle might have also participated in the ore-forming process. Given the close spatial and temporal relationship between gold deposits and the 122 years of ore-forming activity waned, as represented by the late quartz-carbonate veins.

Collectively, stable, radiogenic and noble gas isotope compositions are consistent with multiple sources of the ore-forming fluids in the Sanshandao deposit. Crustally-derived fluids (degassing of felsic magmas and meteoric water) may constitute a major portion of the ore fluids, but mantle derived fluids, most probably degassing of the parental magmas which generated the mafic dikes, were also involved in gold mineralization. This is in accord with the regional background of strong crust–mantle interactions in the Early Cretaceous.

9. Conclusion

Intense fluid–rock interaction, over a zone of hundreds of meters around the regional Sanshandao–Cangshang fault zone, is a typical feature of the Sanshandao gold deposit. Relatively early K-feldspar alteration, sericitization and silicification were generally symmetrically developed on both hanging wall and footwall of the fault. The subsequent formed layer of fault gouge function as an impermeable horizon for the later fertile ore-forming fluid to move upward and thus, the intense pyrite–sericite–quartz alteration and related gold mineralization developed only in the footwall of the main fault. Finally, gold related fluid activity waned, as represented by the late quartz-carbonate veins.

Although the hydrothermal fluids were characterized by moderate temperature, low to moderate salinity and weak acidity, they still had the potential to mobilize most elements, including the commonly fluid-immobile HREE and HFSE, during intense fluid–rock interactions. With alteration going on, log (aS/aH) of fluids generally decreased due to the formation of secondary K-bearing minerals, and there might be a decrease of fO2 from pre-gold alteration stage to the main gold mineralization stage. Gold, most likely transported as Au(HS)2 complex, was probably deposited in response to fO2 decrease of the ore-forming fluids.

Sr–Nd isotopes of hydrothermal minerals and H–O and He–Ar data of ore fluids, combined with the regional background of strong crust–mantle interaction, favor a mixed source of the ore-forming fluids. Although crustally-derived magmatic and meteoric water constitute the dominant portion of the ore fluids, the signature of mantle-derived fluids was also identified to participate in the gold mineralization. The gold metallurgy occurred within the tectonic framework of lithospheric thinning and reactivation in the North China Craton, which not only provided the heat and fluid input, but also generated favorable structural sites for fluid flow and gold deposition.

<table>
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<tr>
<th>Sample no.</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>87Rb/86Sr</th>
<th>87Sr/86Sr</th>
<th>86Sr/87Sr</th>
<th>±2σ</th>
<th>Sm (ppm)</th>
<th>Nd (ppm)</th>
<th>147Sm/144Nd</th>
<th>147Nd/144Nd</th>
<th>εNd (0)</th>
<th>εNd (f)</th>
<th>±2σ</th>
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<td>1800-kf</td>
<td>276.35</td>
<td>372.87</td>
<td>2.15</td>
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<td>0.711706</td>
<td>0.000013</td>
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<td>0.08</td>
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<td>120.81</td>
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<td>0.000111</td>
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<td>1976-py</td>
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Table 4
Sr and Nd isotopic compositions for hydrothermal minerals. Note: Chondrite Uniform Reservoir (CHUR) values (87Rb/86Sr = 0.8547, 87Sr/86Sr = 0.7045, 147Sm/144Nd = 0.1967, 146Nd/144Nd = 0.512838) are used for the calculation. λsm = 1.42 × 10−12 year−1, λsm = 6.54 × 10−12 year−1 (Lugmair and Hart, 1978).

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Acknowledgment

Dr. Richen Zhong from Peking University is greatly appreciated for his assistance with the phase equilibrium calculation by means of SUPCRT92 software. Sincere thanks are extended to Xiannian Jin from the Shandong Gold Group Co. Ltd. for his help during the fieldwork. Two anonymous referees and the editor Dr. Olga Potinskaya are thanked for their constructive and valuable comments which greatly contributed to the improvement of the manuscript. This study was financially supported by the Natural Science Foundation of China (41173056), 100 Talents Programme of the Chinese Academy of Sciences and the Crisis Mines Continued Resources Exploration Project of China Geological Survey (20089930).

References


