

Article

Process and Mechanism of Gold Mineralization at the Zhengchong Gold Deposit, Jiangnan Orogenic Belt: Evidence from the Arsenopyrite and Chlorite Mineral Thermometers

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Abstract: The Zhengchong gold deposit, with a proven gold reserve of 19 t, is located in the central part of Jiangnan Orogenic Belt (JOB), South China. The orebodies are dominated by NNE- and NW- trending auriferous pyrite-arsenopyrite-quartz veins and disseminated pyrite-arsenopyrite-sericite-quartz alteration zone, structurally hosted in the Neoproterozoic epimetamorphic terranes. Three stages of hydrothermal alteration and mineralization have been defined at the Zhengchong deposit: (i) Quartz–auriferous arsenopyrite and pyrite; (ii) Quartz–polymetallic sulfides–native gold–minor chlorite; (iii) Barren quartz–calcite vein. Both invisible and native gold occurred at the deposit. Disseminated arsenopyrite and pyrite with invisible gold in them formed at an early stage in the alteration zones have generally undergone syn-mineralization plastic-brittle deformation. This resulted in the generation of hydrothermal quartz, chlorite and sulfides in pressure shadows around the arsenopyrite and the formation of fractures of the arsenopyrite. Meanwhile, the infiltration of the ore-forming fluid carrying Sb, Cu, Zn, As and Au resulted in the precipitation of polymetallic sulfides and free gold. The X-ray elements mapping of arsenopyrite and spot composition analysis of arsenopyrite and chlorite were carried out to constrain the ore-forming physicochemical conditions. The results show that the early arsenopyrite and invisible gold formed at 322–397 °C with $\lg f(\text{S}_2)$ ranging from -10.5 to -6.7 . The crack-seal structure of the ores indicates cyclic pressure fluctuations controlled by fault-valve behavior. The dramatic drop of pressure resulted in the phase separation of ore-forming fluids. During the phase separation, the escape of H_2S gas caused the decomposition of the gold-hydrosulfide complex, which further resulted in the deposition of the native gold. With the weakening of the gold mineralization, the chlorite formed at 258–274 °C with $\lg f(\text{O}_2)$ of -50.9 to -40.1 , as constrained by the results from mineral thermometer.

Keywords: orogenic-gold deposit; mineral geo-thermometry; physicochemical condition of mineralization; Zhengchong gold deposit; Jiangnan orogenic belt

1. Introduction

The process and mechanism of gold mineralization are essential for understanding the genesis of the deposit [1–4]. The evolution of P-T-X conditions of the ore-forming fluids provides unique insights into the process and mechanism of the mineralization [5–8]. The major and trace elements of hydrothermal minerals formed during mineralization contain important information on the ore-forming physicochemical conditions [9,10]. Many lode-gold deposits have been investigated in order to obtain the distribution of elements in the gold-bearing fluids by in-situ analysis [11–13]. The principal elements, Fe, S and As, in the hydrothermal arsenopyrite can be used to constrain its temperature and sulfur fugacity combined with mineral assemblages [11,14]. Compared with the microthermometry of fluid inclusions commonly used in research on ore-forming P-T conditions of the orogenic gold deposit [15–22], the mineral thermometers can constrain a more accurate forming temperature of gold-bearing sulfides, such as arsenopyrite, resulting in more detailed analysis of the gold mineralization.

Jiangnan Orogenic Belt (JOB) is situated in the collisional and subduction zone between the Yangtze and Cathaysian Blocks (Figure 1a) [23], which have undergone long-term and multiple deformations and magmatism [24]. The belt is defined as a significant Neoproterozoic to Late Mesozoic polymetallic metallogenic zone in China, which hosts more than 250 deposits with ~970 t gold in total [25,26].

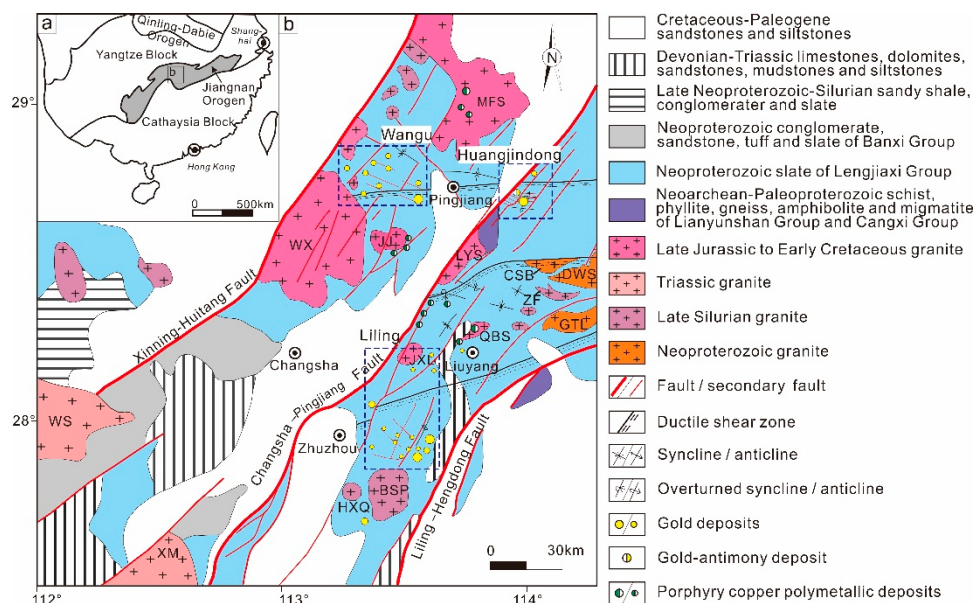


Figure 1. (a) Location of Jiangnan Orogenic Belt (JOB); (b) Geological map of the Changsha-Pingjiang metallogenic belt showing the distributions of gold deposits. Abbreviations for granites: BSP, Banshanpu; CSB, Changsanbei; DWS, Daweishan; GTL, Getengling; HXQ, Hongxiaqiao; JJ, Jinjing; JXL, Jiaoxiling; LYS, Lianyungshan; MFS, Mufushan; QBS, Qibaoshan; WS, Weishan; WX, Wangxiang; XM, Xiema; ZF, Zhangfang. Modified from references [26,27].

The Zhengchong gold deposit, with a proven gold reserve of 19 t and an average grade of 3.21 g/t [28], is located in the central part of JOB, South China. The gold deposit is defined as an orogenic gold deposit based upon mineral paragenesis, in-situ geochemistry of pyrites [29] and the characteristics of ore-forming fluids [28]. The lower limit of the ore-forming temperatures of the deposit were previously constrained by fluid inclusion microthermometer to 312–406 °C, 252–324 °C and 193–296 °C for a three-stage hydrothermal alteration and mineralization [28]. The deposition of gold was believed to result from the fluid-rock reaction [28]. However, the observations on the relationship

of hydrothermal minerals with gold and constraints on the ore-forming chemical conditions are still lacking. Thus, the process and individual mechanism of the invisible and free gold are still unclear.

In this study, detailed field and laboratory works, including petrography and microstructural studies and electro probe micro-analyses (EPMA) on arsenopyrite and chlorite, spatially and temporally associated with gold have been carried out to constrain the evolution of the ore-forming physicochemical conditions. Finally, the process and individual mechanism of the invisible and free gold are summarized based on the ore-forming physicochemical data.

2. Regional and Local Geology

2.1. Regional Geology

The NE-NNE-trending Changsha-Pingjiang metallogenic belt, bounded by the Xinning-Huitang and Liling-Hengdong faults, is located in the central part of JOB, with 125 Au and polymetallic occurrences and deposits, and an estimated ~300 t of gold resources [26] (Figure 1b). Sedimentary rock successions mainly consist of Neoproterozoic schist, phyllite, gneiss, amphibolite and migmatite of Lianyunshan Group and Cangxi Group; Neoproterozoic slate of Lengjiaxi Group; Neoproterozoic conglomerate sandstone, tuff and slate of Banxi Group; Silurian-Sinian sandy shale conglomerate and slate; Devonian-Triassic limestones, dolomites, sandstones, mudstones and siltstones and Cretaceous-Paleogene sandstones and siltstones [27].

Three goldfields including Huangjindong, Liling and Wangu are aligned along the first-order NNE- to NE- trending long-live Chang-Ping Fault. The orebodies in these goldfields are mostly directly controlled by EW- to NW- trending faults [26,30], while a few thin orebodies are controlled by NNE-trending faults in the Liling gold field. Multiple intrusions are exposed in this belt, including the Neoproterozoic, Late Silurian, Triassic and Late Jurassic-Early Cretaceous granitoids.

2.2. Deposit Geology

The Zhengchong gold deposit, which is located in the Liling goldfield, is hosted by Neoproterozoic low-metamorphic sedimentary rock of Lengjiaxi Group (Figure 1b). The Lengjiaxi Group, whose protolith is mainly turbidite, is composed of greywacke and silty slate of Lower Huanghudong Formation, sandstone, siltstone and slate of Upper Huanghudong Formation and sandstone and silty slate of Lower Xiaomuping Formation. All these strata strike NE and dip to NW with dip angles of 26°~65° [31] (Figure 2a). Only small granitoid intrusion has been revealed by both geological mapping and drilling at the deposit [31] (Figure 2).

The dominated thick and less important thin orebodies are controlled by NW- and NE-NNE-trending faults, respectively. The NNE-trending orebodies have strike lengths of 1400 m and dip lengths of ~200 m with thicknesses of 0.38–5.4 m [28]. In plane graph, the orebodies and related hydrothermal alteration are lens-shaped with thickness changing greatly in a short distance. The alterations are mainly composed of the significant muscovite alteration, silicification and arsenopyrite, pyrite and other sulfide alterations with minor chloritization. The main orebodies can be divided into two types: (1) auriferous arsenopyrite-pyrite-quartz vein; (2) altered slates with disseminated pyrite, arsenopyrite, muscovite and quartz (Figure 3). Crack-seal, a typical structure at this deposit, developed in the laminated quartz vein (Figure 3d). This structural vein formed during the cyclic episodes of co-seismic extension fractures [32,33]. These cyclic processes typically result in high-grade ores with gold in the fractures of the veins [34].

2.3. Mineral Association and Paragenesis

Ore minerals are mainly composed of native gold, arsenopyrite and pyrite with minor galena, sphalerite, chalcopyrite, tetrahedrite and pyrrhotite. Based on detailed field mapping and observation under microscope, three mineralization stages were recognized at the Zhengchong deposit (Figure 4): (i) Quartz–auriferous arsenopyrite–pyrite; (ii) Quartz–polymetallic sulfides–native gold–minor chlorite;

and (iii) Barren quartz–calcite vein. Compared with a previous description [26], early quartz vein is barren including no sulfides. The gold content of ore-bearing quartz vein is more than 10 g/t. We observed both invisible gold evenly dispersed in arsenopyrite and pyrite in this type of deposit in NEHP [10,35,36], and native gold in fractures and curved dissolution edges of arsenopyrite and pyrite.

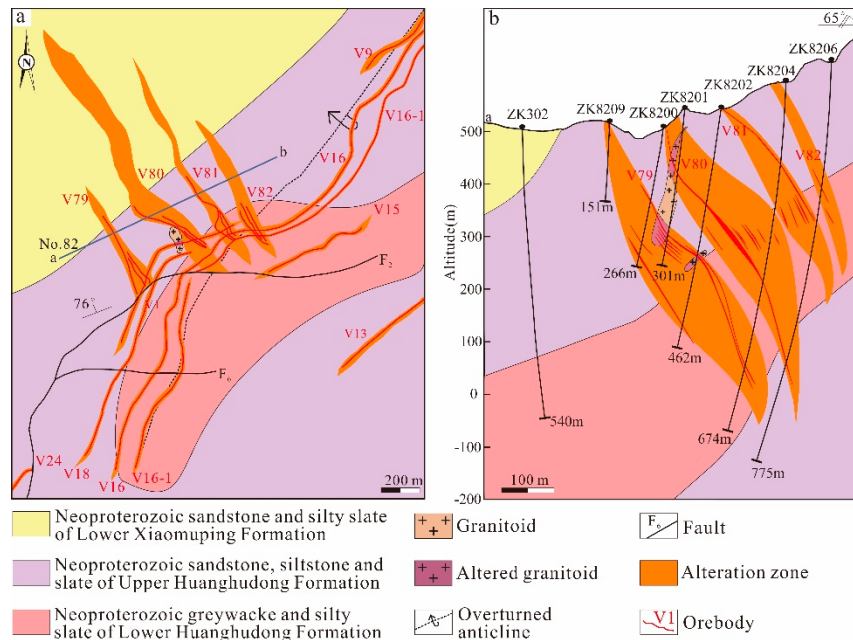


Figure 2. (a) Simplified geological map of Zhengchong gold deposit showing the major host rocks, orebodies and alteration zones; (b) Profile of the No. 82 cross section of the Zhengchong gold deposit.

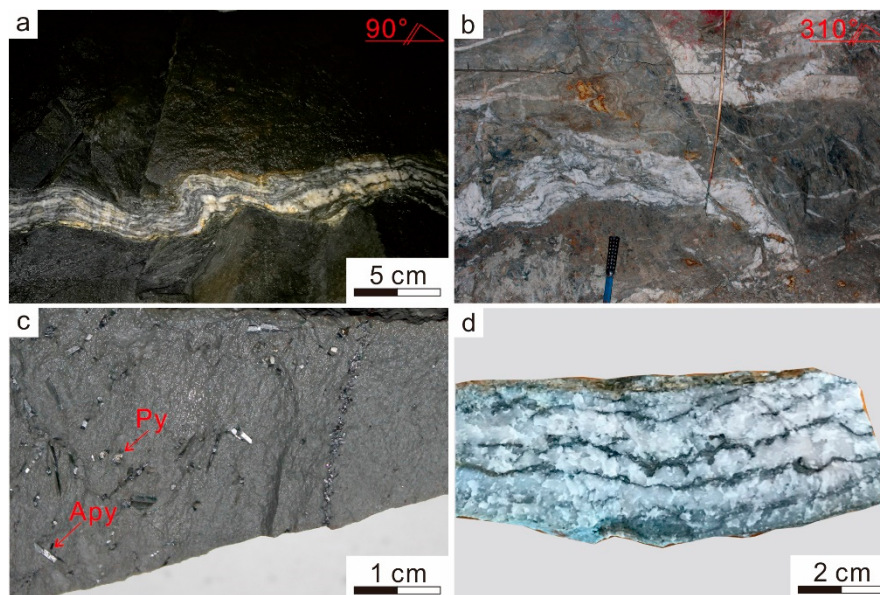


Figure 3. Photographs of representative ore styles at the Zhengchong gold deposit. (a) Auriferous arsenopyrite-pyrite-quartz vein folded in disseminated mineralized slate adjacent to the fault; (b) Auriferous arsenopyrite-pyrite-quartz vein cut by the post-fault; (c) Altered slate with disseminated arsenopyrite and pyrite; (d) A typical crack-seal structure showing white barren quartz vein with fractures infilled by the sulfides with fine-grained quartz and muscovite. Py-pyrite; Apy-arsenopyrite.

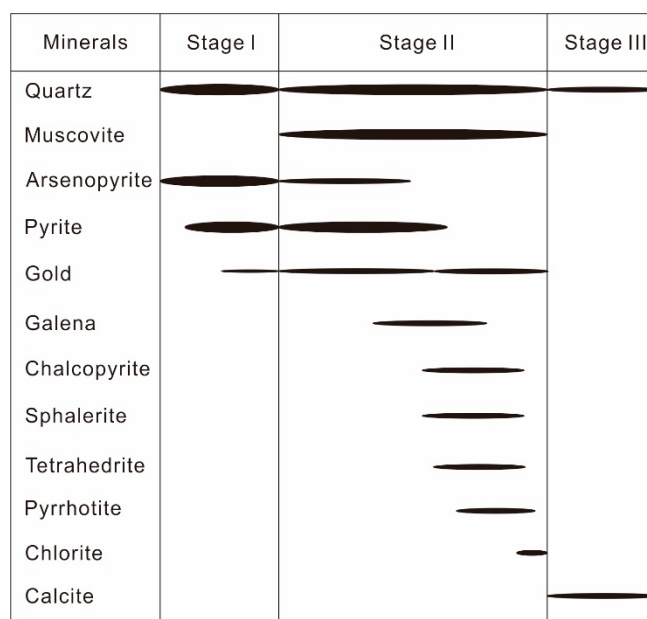


Figure 4. Paragenetic assemblages and sequences of minerals at the Zhengchong gold deposit.

In the altered slate with ~2 g/t gold, pressure shadows with gangue and metallic minerals around rigid arsenopyrite and pyrite in relatively weak matrix composed of fine-grained sericite and quartz are well developed (Figure 5b–e). The quartz fibers and chlorite are the major gangue minerals in the pressure shadow around the rigid sulfide grains (Figure 5b,d). Besides, polymetallic sulfides, such as sphalerite, chalcopyrite and tetrahedrite, which mainly occur in fractures of the pyrite and arsenopyrite, are also observed in these pressure shadows (Figure 5c,e). This indicates that the base metal sulfides formed contemporarily with the adjacent quartz fibers. In some cases, fractures of arsenopyrite were also filled with the fiber-shaped quartz (Figure 5d).

2.3.1. Arsenopyrite

Arsenopyrite is a significant and ubiquitous gold-bearing sulfide both in veins and altered rocks at the Zhengchong gold deposit. Disseminated euhedral arsenopyrite in an altered slate, generally, has acicular and granulous shapes, grain size of 100–600 μm , and straight boundaries (Figure 5a). Generally, the arsenopyrites disseminated in the altered rocks have been ductile-brittlely deformed, forming many cracks and a pressure shadow microstructure in low-stress areas (Figure 5a,b). The fractures of arsenopyrites have been filled by polymetallic sulfides (Figure 5c) and native gold (Figure 5h). The euhedral arsenopyrite in the veins is totally minor without deformation.

2.3.2. Polymetallic Sulfides

Polymetallic sulfides, such as galena, sphalerite, chalcopyrite, tetrahedrite and pyrrhotite, are the most relevant minerals associated with the native gold (Figure 5h). These sulfides formed at the second stage could be divided into several sub-stages. Chalcopyrite formed simultaneously with sphalerite on account of their exsolution-texture (Figure 5f). In places, the chalcopyrite was replaced by tetrahedrite in the fractures of the arsenopyrite (Figure 5c) and pressure shadows of arsenopyrite and pyrite (Figure 5e), or included by the late pyrrhotite. Galena predated the other polymetallic sulfides because of being cut by sphalerite (Figure 5i).

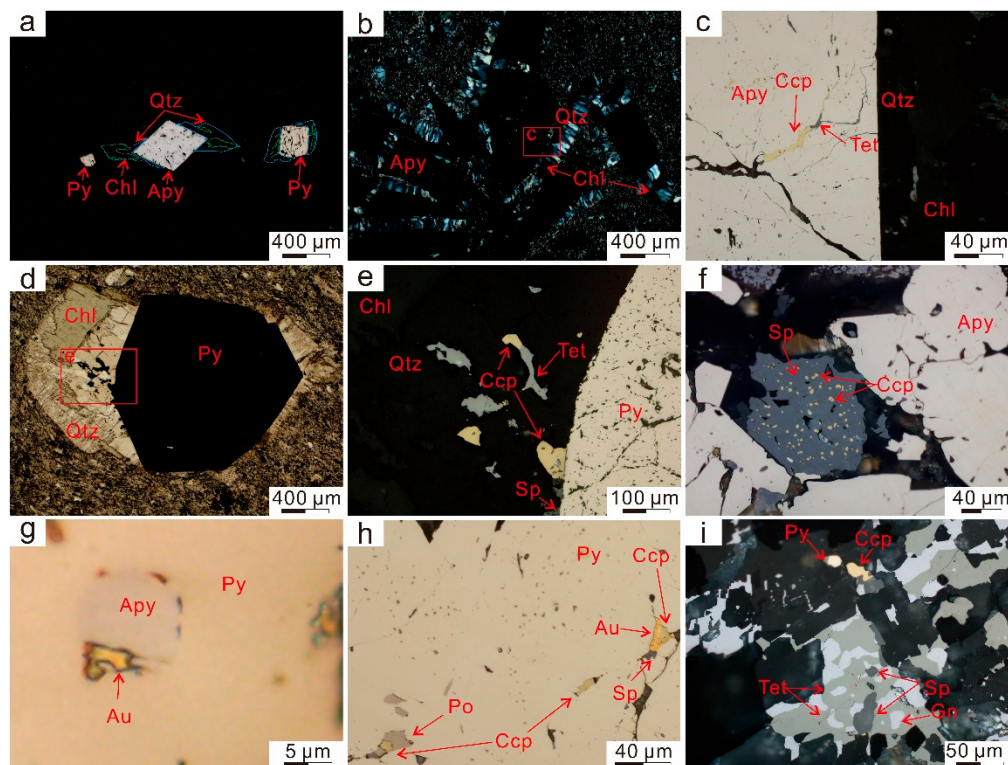


Figure 5. Photomicrographs showing the mineral assemblage. (a) Arsenopyrite and pyrite disseminated in the altered slates with pressure shadows infilling by the chlorite; (b) Typical pressure shadows filled by quartz and chlorite around the generation of arsenopyrite; (c) The fractures of arsenopyrite disseminated in the host-rock filled with the chalcopyrite, sphalerite and tetrahedrite, and later chlorite in the pressure shadows of the arsenopyrite; (d) Pyrite with the bulky pressure shadows filled by late quartz, sulfides, and chlorite; (e) Chalcopyrite, sphalerite and tetrahedrite in the pressure shadows; the tetrahedrite replaced the chalcopyrite; (f) Chalcopyrite and sphalerite exsolution-texture; (g) Gold along the grain edge between the pyrite and arsenopyrite; (h) Electrum, chalcopyrite, sphalerite and pyrrhotite in the healed and unhealed cracks of pyrite; chalcopyrite is included by the pyrrhotite; (i) The occurrence of polymetallic sulfides, where galena is cut by the sphalerite. Py—pyrite; Apy—arsenopyrite; Ccp—chalcopyrite; Gn—galena; Sp—sphalerite; Po—pyrrhotite; Tet—tetrahedrite; Au—native gold; Qtz—quartz; Chl—chlorite.

2.3.3. Chlorite

Late-stage chlorite is typically observed in the pressure shadows of early gold-bearing arsenopyrite and pyrite. Different from the fiber-shaped quartz in the pressure shadows, the chlorite is anhedral without specified shape.

3. Analytical Methods and Results

3.1. Sample Selection and Analytical Methods

Six gold-bearing sulfide-quartz veins and five altered slate samples were collected from the underground tunnel at 290 m level at the Zhengchong deposit. Elements-mapping for a deformed gold-bearing arsenopyrite, and spot element analysis on arsenopyrite, and chlorite in the pressure shadows were carried out by an Electron Probe Micro-Analyzer (EPMA).

Electron Probe Micro-Analyzer test was performed at the Laboratory of Isotope Geology, Tianjin Institute of Geology and Mineral Resources, Tian-jin, China. The operating conditions for the sulfide analysis were 15 kV acceleration voltages and 20 nA beam currents with 5 μm beam diameter.

The chemical compositions of chlorite were measured under the same operating condition but with a different beam diameter of 1–5 μm .

Content of major elements and its mineral association can indicate the forming environment of arsenopyrite. Its forming temperature and $\lg f(\text{S}_2)$ would be defined owing to the As content distribution in the diagram of sulfide symbiosis.

Chlorite is an important gangue mineral in the gold deposit, whose chemical formula is $(\text{R}_x^{2+}\text{R}_y^{3+}\square_{6-x-y})_6^{\text{VI}}(\text{Si}_z\text{R}_{4-z}^{3+})_4^{\text{IV}}\text{O}_{10}(\text{OH})^8$, where R^{2+} and R^{3+} represent the divalent and trivalent cations, respectively, such as Fe^{2+} , Mg^{2+} and Al^{3+} , Fe^{3+} . The octahedral vacancy is expressed by $\square$. The chemical compositions of chlorite are controlled by the substitution between Fe^{2+} and Mg^{2+} , the Tschermak substitution between $\text{Al}^{\text{IV}}\text{--Al}^{\text{VI}}$ and $\text{Si--(Mg, Fe}^{2+})}$, as well as $3(\text{Mg, Fe}^{2+})$ replacing $\square 2 \text{ Al}^{\text{VI}}$, which is due to the complexity of the formation environments. Analysis of the chemical compositions assists in deducing the temperature and oxygen fugacity of chlorites.

3.2. Results

The major and trace elements are not conformably distributed in the arsenopyrite deformed as shown in the elements map (Figure 6). Sulfur is a major element of the arsenopyrite with slightly higher content in the internal zone (Figure 6b), but this trending of value difference of other major and trace elements has not been observed. Cobalt, nickel, antimony and gold contents are uniformly distributed in the arsenopyrite with low values (Figure 6c,d,h,i). Similarly, copper and zinc also have uniform distribution in the arsenopyrite, but the contents of both elements are slightly high in the fractures and cracks (Figure 6e,f). Arsenic, a major element with high content, is homogeneously distributed in this kind of arsenopyrite (Figure 6g).

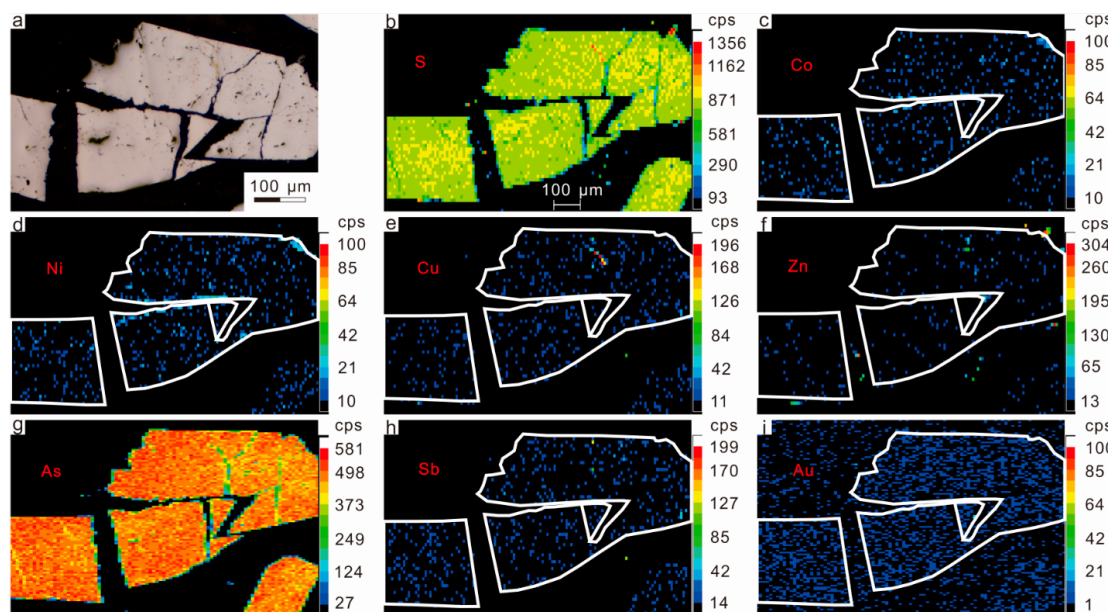


Figure 6. (a) Photomicrographs showing mineralogical features of the arsenopyrite selected to measure; (b–i) X-ray elements distribution maps of S, Co, Ni, Cu, Zn, As, Sb and Au.

Arsenic is the principal element in reflecting the forming temperature of different generations of arsenopyrite [37]. Twenty pieces of data of the core of ore-bearing arsenopyrite from the Zhengchong gold deposit yielded arsenic atomic percentages of 29.71%–31.66%, showing wide systematic variation within the same generation (Table 1). The yielded sulfur atomic percentages were 35.35%–37.44%. Moreover, the sulfur content has a negative correlation with arsenic values, with a regression coefficient of -0.97 and R^2 of 0.89 (Figure 7).

Table 1. Chemical compositions of arsenopyrite at the Zhengchong gold deposit.

Spot No.	Elements (wt %)										Total	Chemical Formula
	As	Au	S	Ag	Sb	Fe	Co	Ni	Cu	Zn		
ZC17D01B1-1	43.07	0	22.24	0	0	34.80	0.05	0.02	0	0	100.18	FeAs _{0.92} S _{1.11}
ZC17D01B1-2	42.43	0.04	22.80	0.01	0	34.64	0.01	0.07	0	0	99.99	FeAs _{0.91} S _{1.15}
ZC17D01B1-3	41.52	0	22.24	0.01	0.04	34.37	0.07	0.01	0.02	0	98.28	FeAs _{0.90} S _{1.13}
ZC17D01B1-4	43.22	0	22.43	0	0.05	34.45	0.02	0.01	0.01	0.12	100.30	FeAs _{0.94} S _{1.13}
ZC17D01B1-5	43.39	0.08	22.05	0.01	0.01	34.84	0.07	0.01	0.01	0.06	100.54	FeAs _{0.93} S _{1.10}
ZC17D01B1-6	43.85	0.01	22.02	0	0	35.03	0.06	0	0	0.03	100.99	FeAs _{0.93} S _{1.10}
ZC17D01B1-7	42.77	0.01	22.26	0	0.02	34.60	0.01	0.05	0.04	0	99.75	FeAs _{0.92} S _{1.12}
ZC17D01B1-8	44.72	0.07	21.37	0	0	34.65	0.01	0.02	0.01	0.04	100.89	FeAs _{0.96} S _{1.07}
ZC17D01B1-9	43.91	0.01	21.38	0	0	34.72	0.05	0	0.03	0.01	100.11	FeAs _{0.94} S _{1.07}
ZC17D01B1-10	44.04	0	21.66	0	0	34.58	0.02	0	0.07	0.01	100.37	FeAs _{0.95} S _{1.09}
ZC17D01B1-11	43.89	0	21.94	0.03	0	34.21	0.01	0	0	0	100.07	FeAs _{0.96} S _{1.12}
ZC17D01B1-12	44.21	0.09	21.88	0.02	0	34.71	0.01	0.05	0.06	0	101.02	FeAs _{0.95} S _{1.10}
ZC17D01B1-13	44.12	0	21.41	0.02	0	33.84	0.03	0	0.01	0	99.42	FeAs _{0.97} S _{1.10}
ZC17D01B1-14	43.91	0.01	21.46	0	0.01	34.29	0.02	0.03	0.08	0.02	99.82	FeAs _{0.96} S _{1.09}
ZC17D01B2-15	43.22	0	21.52	0	0	34.09	0.03	0.04	0.03	0	98.94	FeAs _{0.95} S _{1.10}
ZC17D01B2-16	43.40	0.06	21.60	0.03	0.01	34.67	0.07	0.05	0.06	0.05	100.00	FeAs _{0.93} S _{1.09}
ZC17D01B2-17	43.42	0.07	21.72	0	0.01	34.10	0.03	0.04	0	0	99.38	FeAs _{0.95} S _{1.11}
ZC17D01B2-18	42.20	0.03	22.42	0	0.02	34.55	0.04	0.01	0	0.04	99.29	FeAs _{0.91} S _{1.13}
ZC17D01B2-19	43.11	0.02	21.56	0	0.03	33.98	0.05	0.05	0.01	0.05	98.86	FeAs _{0.95} S _{1.11}
ZC17D01B2-20	43.44	0.01	21.29	0	0.03	34.28	0.03	9	0.07	0	99.14	FeAs _{0.95} S _{1.08}

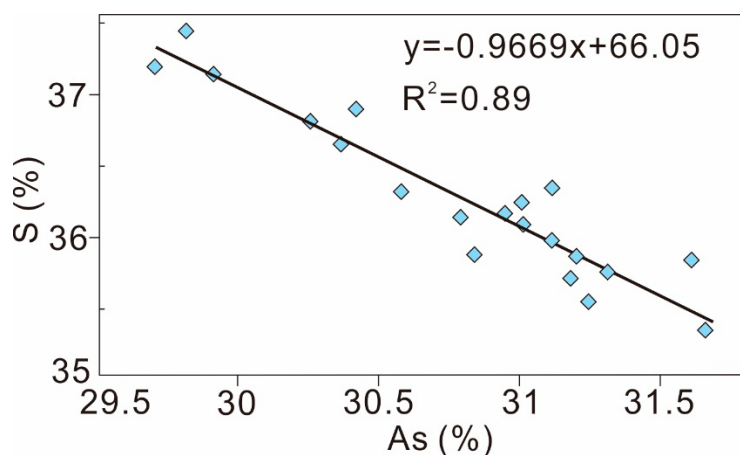


Figure 7. Distributions and relationship of As and S atomic percentages in the arsenopyrite [10].

Chlorite is widely distributed in the pressure shadows around rigid arsenopyrite and pyrite in ores at the Zhengchong deposit. Chlorite samples from different sites of the pressure shadows have similar compositions, such as SiO_2 (21.51–23.16 wt %), MgO (11.56–13.26 wt %), FeO (25.90–28.37 wt %) and Al_2O_3 (21.84–23.13 wt %) (Table 2). The contents of Cr_2O_3 , CaO , K_2O and Na_2O are low. The total values of the $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios range from 0.52 to 0.58. Owing to the extremely small amount of MnO in the chlorite, $\text{Fe}/(\text{Fe} + \text{Mg} + \text{Mn})$ is approximately equal to $\text{Fe}/(\text{Fe} + \text{Mg})$. Silicon values vary from 2.43 to 2.55 a.p.f.u. Hence, the chlorites in the pressure shadows were defined as ripidolite type (Figure 8), a kind of chlorite with relatively high Fe irons according to the classification of chlorites [38].

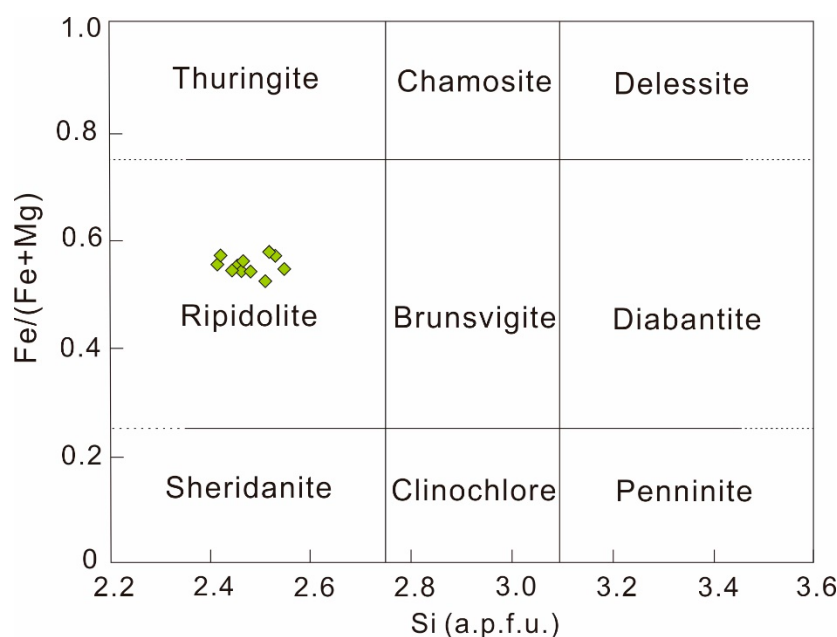


Figure 8. Chemical compositions of chlorite in the pressure shadows of arsenopyrite and pyrite at the Zhengchong gold deposit. Nomenclature and classification of chlorite [38].

4. Discussion

4.1. The Physicochemical Environment of Mineral Precipitations

Precipitation of minerals from the gold-bearing fluids is controlled by physicochemical conditions, including temperature and redox conditions. These conditions change with the evolution of the ore-forming fluids. Previous studies show that the major and trace elements of minerals provide

important information of their forming physicochemical conditions which in turn could be used to constrain the P-T-X evolution of the fluids [9,10].

4.1.1. Physicochemical Conditions of Arsenopyrite

As shown above, arsenopyrites formed earlier than the polymetallic sulfides in the fractures or pressure shadows of arsenopyrite and pyrite (Figure 5a,b,d). Thus, the sulfide associated with arsenopyrites is only pyrite (Figure 4). Hence, the arsenic values from both internal and external zones of arsenopyrite fall in the “pyrite + arsenopyrite” zone of the buffered assemblages involving arsenopyrite in the Fe-S-As system [14,39]. The temperatures and $\lg f(S_2)$ of arsenopyrite are almost successive due to their similar arsenic contents (Figure 7). The temperature is constrained from 322 °C to 397 °C, and the yielded $\lg f(S_2)$ of the disseminated arsenopyrites is from -10.5 to -6.7 (Figure 9).

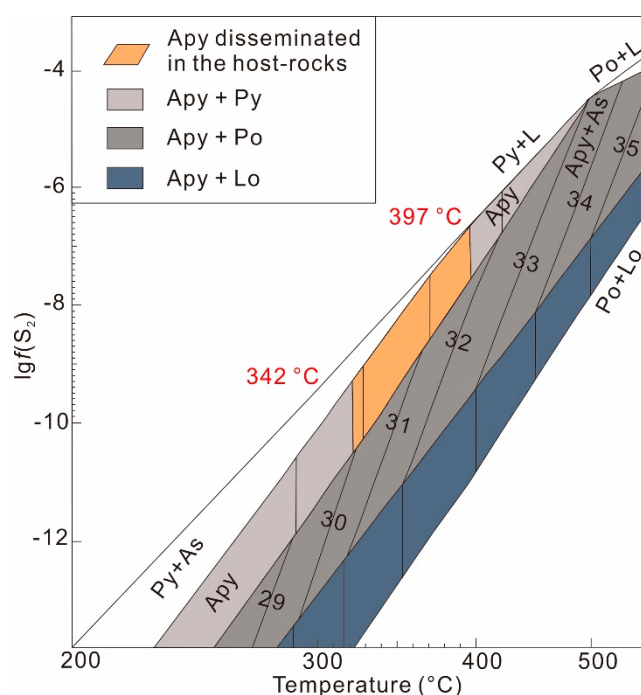


Figure 9. Activity of $\lg f(S_2)$ and temperature (T) projection of the stability field of arsenopyrite [14,39].

Table 2. Chemical compositions of chlorite in pressure shadows at the Zhengchong gold deposit.

Samples No.	zc17d01b1-1	zc17d01b1-2	zc17d01b1-3	zc17d01b1-4	zc17d01b1-5	zc17d01b1-6	zc17d01b1-7	zc17d01b1-8	zc17d01b1-9	zc17d01b1-10	zc17d01b1-11
W(B)/%											
Na ₂ O	0.08	0.05	0.09	0.06	0.00	0.05	0.07	0.03	0.03	0.02	0.04
MgO	12.11	12.47	12.57	12.30	12.61	11.56	11.85	13.26	11.84	12.06	12.58
Al ₂ O ₃	22.61	23.09	23.13	22.92	22.16	21.97	22.50	22.37	22.74	22.96	21.84
SiO ₂	22.22	22.07	22.39	22.15	23.16	22.57	23.02	22.79	21.74	21.51	21.96
K ₂ O	0.03	0.02	0.03	0.02	0.02	0.03	0.04	0.02	0.01	0.00	0.02
CaO	0.00	0.01	0.01	0.02	0.01	0.01	0.02	0.00	0.02	0.01	0.01
P ₂ O ₅	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.00	0.01	0.00	0.01
FeO	27.59	26.65	26.70	25.90	27.19	28.37	28.18	26.06	28.14	26.86	27.29
V ₂ O ₃	0.00	0.02	0.04	0.03	0.00	0.01	0.02	0.01	0.04	0.03	0.00
MnO	0.00	0.00	0.01	0.02	0.02	0.00	0.03	0.02	0.00	0.00	0.01
Cr ₂ O ₃	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cations											
Si	2.48	2.45	2.47	2.48	2.55	2.53	2.53	2.52	2.43	2.43	2.48
Al ^{IV}	1.52	1.55	1.53	1.52	1.45	1.47	1.47	1.48	1.57	1.57	1.52
ΣR _t	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	
Fe ³⁺	0.02	0.01	0.02	0.02	0.01	0.03	0.03	0.01	0.01	0.00	0.01
Fe ²⁺	2.55	2.46	2.44	2.41	2.50	2.63	2.57	2.40	2.62	2.53	2.56
Al ^{VI}	1.45	1.48	1.48	1.51	1.43	1.42	1.45	1.43	1.44	1.48	1.38
Mg	2.01	2.07	2.07	2.05	2.07	1.93	1.94	2.18	1.98	2.03	2.11
ΣR _o	6.03	6.03	6.01	5.99	6.01	6.02	6.01	6.03	6.06	6.05	6.08
Component Activity											
Fe/(Fe + Mg)	0.56	0.55	0.54	0.54	0.55	0.58	0.57	0.52	0.57	0.56	0.55
Fe/(Fe + Mg + Mn)	0.56	0.55	0.54	0.54	0.55	0.58	0.57	0.52	0.57	0.56	0.55
<i>d</i> ₀₀₁	14.1118	14.1109	14.1132	14.1152	14.1215	14.1159	14.1180	14.1195	14.1055	14.1063	14.1115
<i>t</i> /°C	267.23	268.13	265.79	263.84	257.54	263.10	261.04	259.48	273.52	272.65	267.54
lga ₃	−1.34	−1.40	−1.42	−1.43	−1.39	−1.29	−1.32	−1.48	−1.29	−1.35	−1.37
lga ₆	−2.32	−2.58	−2.34	−2.49	−2.83	−2.14	−2.24	−2.82	−2.52	−2.98	−2.54
lgK ₁	9.77	9.74	9.81	9.87	10.05	9.89	9.95	10.00	9.58	9.61	9.76
Lgf(O ₂)	−43.00	−43.66	−42.93	−43.71	−45.95	−42.98	−43.45	−45.32	−43.25	−44.97	−43.70

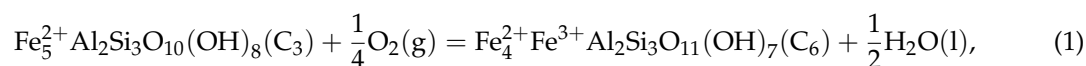
Calculations of Si, Al^{IV}, Al^{VI} and Mg were based on the fourteen oxygen atoms and on the assumption that iron was totally Fe²⁺. ΣR_t and ΣR_o are applied to the total number of the tetrahedral and octahedral coordination, respectively. The a₃ and a₆ in the table are the activity coefficient of the reaction between the C₃ and C₆ end members [40]. The K₁ and K₂ are the equilibrium coefficients of the reaction equation. $a_3 = 59.72(X_{Fe^{2+},o})^5(X_{Al,o})(X_{Si,t})(X_{Al,t})$, $a_6 = 729(X_{Fe^{2+},o})(X_{Fe^{3+},o})(X_{Al,o})(X_{Si,t})(X_{Al,t})$. X_{i,j} stands for the mole fraction of the “i” ion in the “j” coordination.

4.1.2. Physicochemical Conditions of Chlorite

Chlorite thermometer was used in gold deposits to assist the constraints on the metallogenic temperature [9,10,41]. Typically, basal spacing d_{001} of chlorite shows a positive correlation with its crystallographic temperature [42]. The value of d_{001} can be calculated through chemical compositions of chlorite using EPMA. After that, calculation for the temperature was proceeded by empirical equation having a positive r-squared ($r = 0.95$) [43,44]. The results show that the forming temperatures of chlorite ranged from 258 °C to 274 °C, with an average of 265 °C.

Oxygen fugacity of chlorite was also calculated through its chemical compositions, in which six groups of chlorite solid solution models were divided into six thermodynamic end-members. Reactions of various end-members were established to deduce not only the temperature but also the $\lg f(\text{O}_2)$ through the calculation of activity quotient a_i and equilibrium coefficient of chemical equation K_j according to the paragenesis with chlorite [40].

The $\lg f(\text{O}_2)$ of chlorite can be calculated by the chemical reaction between C_3 and C_6 thermodynamic end-members [40],



and the $\lg f(\text{O}_2)$ is also inferred [45],

$$\lg f(\text{O}_2) = 4(\lg a_6 - \lg a_3 - \lg K_1). \quad (2)$$

The K_1 in Equation (2) represents the equilibrium coefficient of Equation (1), the correlation between equilibrium and temperature was refitted after all $\lg K_1$ under the different temperatures were calculated by mathematical induction [46].

$$\lg K_1 = 21.77e^{-0.003t} \quad (3)$$

The t and e represent the temperature and natural logarithm. Therefore, the temperature obtained is 258–274 °C using Equation (3). The yielded $\lg f(\text{O}_2)$ is -50.9 – -40.1 .

4.2. Process and Mechanism of the Gold Precipitation

At the Zhengchong gold deposit, uniform invisible gold distributions in the arsenopyrite and visible gold related to the polymetallic sulfides locating in the fractures of early sulfides were observed by microscope and elements mapping. The process and physicochemical conditions of the two-stage gold mineralization are constrained by geological evidences and results from mineral geothermometer.

At the early stage, free elements sulfur, arsenic and gold precipitated from the gold-bearing fluids when fluid-rock reaction occurred [28], which promoted the deposition of arsenopyrite and pyrite with the invisible gold, disseminated in the altered slates at a temperature of 322–397 °C and the $\lg f(\text{S}_2)$ from -8.5 to -6.7 (Figure 10a). Arsenic of the arsenopyrite has negative correlation with sulfur (Figure 7), indicating that S could be substituted by As [47]; therefore, Au could enter into the arsenopyrite by substituting Fe to maintain the electric balance [10,48,49]. Subsequently, because of shortening event, the euhedral arsenopyrite underwent minor crystal plastic deformation (Figure 10b). As the compressional deformation grew, the microfractures propagated in the arsenopyrite (Figure 10c). Then, the cracks generated due to the significant brittle deformation of the arsenopyrite [50–53]. This indicates that the hydrothermal alteration and mineralization occurred during the brittle-ductile transition [54]. The pressure shadow microstructures and quartz fibers in the fractures and adjacent extensional zones of arsenopyrite and pyrite (Figure 5b,d) indicate an ongoing shortening event [51].

With or following the brittle deformation of the arsenopyrite and pyrite, gold-, copper-, zinc- and antimony-bearing fluids filled the fractures forming gold, chalcopyrite, sphalerite and tetrahedrite (Figure 10d). The absence of late arsenopyrite and pyrite in the cracks of early arsenopyrite and pyrite reveal that fluid-rock reaction was not the major mechanism which induced the deposition of gold at this stage. Although gold precipitation associated with some low temperature polymetallic sulfides, temperature reduction is typically not the main factor for orogenic-gold deposits [3].

The low-pressure extensional fractures and pressure shadows of early sulfides (Figure 3d) indicate that the dilational site is an important control on gold precipitation [55]. Crack-seal structure formed by fault-valve behavior [33] also indicates a cyclic pressure drop which could result in phase separation of the ore-forming fluids [18,56]. Early fractures of the early veins and other dilational sites from arsenopyrite deformation will be sealed by the successive deposition of hydrothermal minerals [34,57,58]. A renewed period of incremental fluid pressure built up the new fractures with favorable orientation. Minor native gold deposited with the chlorite precipitated, following the quartz, in the pressure shadow microstructure (Figure 10e) at 258–274 °C and $-50.9 \sim -40.1$ for $\lg f(\text{O}_2)$. The presence of quartz-calcite veins marked the termination of the gold mineralization.

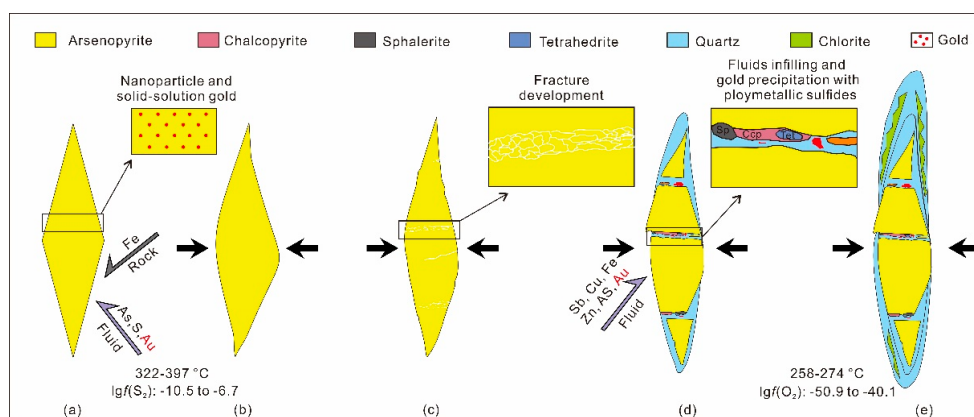


Figure 10. Simplified model interpreting the process and mechanism of deposition of minerals including gold. (a) Euhedral arsenopyrite with invisible gold disseminated in the altered slates; (b) Arsenopyrite underwent initial crystal plastic deformation; (c) Fractures development in arsenopyrite; (d) Fluids containing Sb, Cu, Zn, As and Au filled in the fractures and other dilational sites of arsenopyrite leading to gold and polymetallic sulfides precipitation. (e) Chlorite precipitated in the pressure shadow microstructure with minor gold.

5. Conclusions

Field and microscopic observations define three stages of hydrothermal alteration and mineralization at the Zhengchong gold deposit: (i) Quartz–auriferous arsenopyrite–pyrite; (ii) Quartz–polymetallic sulfides–native gold–minor chlorite; (iii) Barren quartz–calcite vein. Invisible and native gold both occurred in the deposit.

The invisible gold was distributed of the arsenopyrite generated from the fluid–rock reaction at about 322–397 °C and the $\lg f(\text{S}_2)$ from -8.5 to -6.7 . Successively after crystal plastic and brittle deformations, the later fluid carrying gold, copper, zinc, antimony and sulfide was injected into the fractures and extensional zones. The fault–valve behavior of the ore–controlling fault resulted in cyclic pressure fluctuation. The dramatic drop in pressure induced the fluid phase separation, decomposition of gold–hydrosulfide complex and deposition of native gold. With the weakening of the gold mineralization, chlorite deposited in the pressure shadow microstructure following the quartz around arsenopyrite and pyrite at 258–274 °C and $-50.9 \sim -40.1$ for $\lg f(\text{O}_2)$. The formation of quartz–calcite veins indicates the end of the gold mineralization.

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