Research Article

The Au-Hosting Minerals and Process of Formation of the Carlin-Type Bojitian Deposit, Southwestern China

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Received 26 February 2017; Accepted 24 May 2017; Published 9 July 2017

Academic Editor: Weidong Sun

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The recently discovered middle-sized Bojitian Carlin-type Au deposit is located in southwestern Guizhou Province, China, near the well-known Shuiyindong super-large-sized deposit. To improve the understanding on this deposit, here we investigate the minerals that host Au and the occurrence of Au in the deposit, using a combination of microscopic work and electron probe microanalysis (EPMA). Based on the results, the formation of the deposit was addressed. Results indicate that the dominant minerals that host Au include arsenian pyrite and arsenopyrite. Au in the cores of zoned pyrite exists mainly as natural nanoscale Au (Au^0), while Au in the rims exists mainly as solid solution Au (Au^+), but it likely also exists in the rims as natural nanoscale Au. The framboidal, coarse-grained, and banded pyrite types contain both natural nanoscale Au^0 and solid solution Au^+ . The arsenopyrite is of hydrothermal origin, and Au within the arsenopyrite exists as gold solution Au^+ . The Bojitian deposit was formed from As-bearing, H_2S -rich, low-to-medium-temperature fluids that migrated along faults and other channels. Au that was already present in the strata or source beds migrated with the fluids in the form of $\text{Au}(\text{HS})^-$ and ore-forming fluids were then formed in the reducing environment. The ore-forming fluids interacted with Fe-rich carbonates to form an abundance of Au-hosting arsenian sulfides.

1. Introduction

The Carlin-type Au model, named after the deposits developed along the Carlin Trend in Nevada, USA, is widely used in exploration since the discovery of mineralization in 1962 [1]. This type of deposit is responsible for the largest known Au deposits and is the subject of a wealth of scientific and technical investigations [2–4]. One of the most important characteristics of the Carlin-type gold deposit is the fact that Au almost always occurs as visible gold in association with sulfides [5]. Study on the Au-bearing minerals and the occurrence of Au in the sulfides is important as it provides information on the ore-forming process (Zhao et al., 2011; [6, 7]; Cook et al., 2013). Whereas some studies suggest

that the occurrences of Au mainly occur as a solid solution (Au^+) and/or nanoparticles of native gold (Au^0), other studies suggest that Au can appear as Au^- and Au^{3+} in the crystal structure of the sulfide [8–11]. Notwithstanding, we also note that visible gold is observed in some Chinese gold deposits that are considered to belong to the Carlin-type [12].

In the 1970s, a Carlin-type deposit was discovered in southwestern Guizhou Province [13]. The deposit forms the main part of the renowned Dian-Qian-Gui Au ore district, and the other ores in this district include those in the nearby Yunnan and Guangxi provinces [14, 15]. Recent ore exploration in this area has resulted in a number of significant findings, including the Shuiyindong super-large deposit, which has an average Au grade of 9.05 g/t and

FIGURE 1: Geological sketch map showing the occurrence of Carlin-type gold deposits in the Dian-Qian-Gui gold-rich district (modified after Su et al., 2002). A, Triassic; B, Paleozoic; C, Proterozoic; D, late Yanshanian granite porphyry; E, late Yanshanian quartz porphyry; F, late Yanshanian alkaline ultrabasic rock; G, fault; H, gold deposit; I, towns, including (1) Lannigou, (2) Shuiyindong, (3) Zimudang, (4) Getang, (5) Yata, (6) Nibao, (7) Xiongwu, (8) Lubuge, (9) Banqi, (10) Gaolong, (11) Badu, (12) Gedang, (13) Maxiong, (14) Longhuo, (15) Nage, (16) Lekang, (17) Langquan, (18) Baidi, (19) Jinya, and (20) Linbu.

a proven reserve of over 50 t [16, 17]. One recently discovered Au deposit in this district, named the Bojitian deposit, is located close to Shuiyindong and has a proven Au reserve of ~18 t. To date, there have been few studies of the Bojitian deposit because it has only recently been discovered, and the nature of the ore-forming process is poorly understood [18, 19].

Therefore, to improve our understanding of the Bojitian deposit, we have used electron probe microanalyses to investigate the Au-hosting minerals and the occurrence of Au. The results will contribute to our understanding of the general processes of ore formation in this district, as well as the origins of the Carlin-type gold deposits in South China.

2. Geological Setting

The Bojitian Au deposit occurs in the Dian-Qian-Gui Au-rich district, which occurs in the Youjiang Basin at the

southwestern margin of the Yangtz Craton (Figure 1). The basin is bordered by the regional Mile-Shizong deep fault in the northwest, the Nanpanjiang Fault in the south, and the Shuicheng-Ziyun-Bama Fault in the northeast [20–23]. Many Au ores and deposits have been found in this area (Figure 1).

The Bojitian Au deposit is tectonically located on the southwestern margin of the Yangtz Craton [20, 21]. The deposit is located in the eastern part of the Huijiabao anticline (Figure 2) and together with other ore deposits makes up the E-W-trending Huijiabao Au–(Hg) field (Figure 2) [24, 25].

Huijiabao is an important anticline, hosting eight Au deposits, five Ag deposits, and one Ag-Tl deposit. The renowned super-large Shuiyindong Carlin-type Au deposit and the large-sized Zimudang Au deposit are both hosted in this anticline. Devonian to Triassic strata are prominent in this area and have a total thickness of >10,000 m. Triassic strata occupy roughly two-thirds of the total area, and Permian

FIGURE 2: Geological sketch map of the Huijiabao gold field in southwestern Guizhou Province (modified after [40]).

strata are the second most important in terms of outcrop area. Carboniferous and Devonian strata are only exposed locally in the cores of several anticlines and domes (Figure 2). The main strata in the district, from bottom to top, are the middle Permian Maokou Formation (P_2m), the upper Permian Longtan (P_3l) and Changxing (or equivalent Dalong) formations (P_3ch or P_3d), the Lower Triassic Yelang (T_1y) and Yongningzhen (T_1y^n) formations, and scattered Quaternary deposits. Magmatic rocks are found only to the NW, outside the mine area, and they consist of alkaline ultrabasic rocks and the Emeishan basalt [20, 26–28].

The dominant strata that host Au in the Bojitian deposit are the upper Permian Dachang layer, the Longtan Formation, and the first member of the Yelang Formation [18]. The Dachang layer is located along an unconformity between the Maokou and Longtan formations, and it commonly signals the presence of an altered rock association that formed during regional tectonism and hydrothermal activity [29]. The Maokou Formation consists predominantly of light-gray thick-layered bioclastic limestone. The Longtan Formation consists of gray layered siliceous limestone, calcareous clay rock, brecciated clay rock, siltstone, and fine sandstone. The Yelang Formation contains clay rock, siltstone, marl, limestone, and oolitic limestone.

Three structural trends can be recognized in the area (Figure 2): the NW-SE-trending Huijiabao anticline and

reverse faults along the anticlinal axis and NE-SW and N-S-trending anticlines, faults, and interlayer structures, such as the decollement between the lower Permian Maokou Formation and the upper Permian Longtan Formation. The surficial structures were formed during the Indosinian-Yanshanian orogeny, and the tectonic features are complex [20, 24, 30]. In general, the location of the Au deposits in this area is controlled by the E-W-trending Huijiabao anticline and to a lesser degree by E-W and N-S-trending faults [18].

The ore bodies of the Bojitian Au deposit can be divided into two types: strata-bound and fault-controlled, based on the occurrence, shape, and structure [31, 32]. The strata-bound ore bodies are the dominant type, and they can be subdivided into carbonate and silicified breccia types based on the nature of the ore-bearing rocks. The layered and stratiform-like carbonate-type ore bodies are found within 300 m of the Huijiabao anticlinal axis. In contrast, the silicified breccia ore bodies are found in the Dachang layer, parallel to the plane of the unconformity. The fault-controlled ore bodies occur only in fracture zones that formed along a gently dipping reverse fault that produced a small displacement along the axis of the anticline [18, 33].

These rocks contain a range of ore minerals, including pyrite, arsenopyrite, marcasite, realgar, orpiment, cinnabar, and stibnite. The gangue minerals are mainly calcite, dolomite, quartz, clay, and hydromica. These minerals form

FIGURE 3: Generalized lithological column of well G2 in the Bojitian gold deposit.

various paragenetic associations, including quartz-dolomite, quartz-pyrite-arsenopyrite, quartz-calcite-realgar-orpiment-stibnite-cinnabar, and pyrite-marcasite (Pan, 2012). Ore structures have multiple types, including disseminated, laminated, vein-like, lumpy, drusy, and brecciated. Ore textures are mainly euhedral and subhedral, framboidal, globular, metasomatic, and cataclastic.

Many types of hydrothermal alteration have been observed in the deposit, including silicification, dolomitization, pyritization, arsenopyrite mineralization, realgar (orpiment) mineralization, calcitization, stibnite mineralization,

talc mineralization, fluorite mineralization, and cinnabarite mineralization. The Au mineralization seems to have a close relationship with the silicification, dolomitization, and pyritization [28, 30].

3. Samples and Methods

We collected 48 samples from depths of 243.00 to 522.90 m in well G2 (total depth 796.65 m) (Figure 3). The samples were made into polished sections for observation under an optical microscope (Nikon E600POL). Thirty samples were then

chosen for measurements of Au content (Table 1; Figure 3). Three samples (G2-10, G2-32, and G2-35) with relatively high Au contents (2.54, 8.71, and 1.13 ppm, resp.) and different lithologies and occurrences were then chosen for further detailed electron probe microanalysis (EPMA). Five ore and 12 wall-rock samples were selected for trace element and REE analysis.

The contents of Au and trace elements were measured by ALS Chemex, Guangzhou, China. The Au analyses were conducted using the fire assay enrichment separation method and an atomic absorption spectrometer, with a detection limit of 0.005 ppm. The REEs and trace elements were detected by ICP-MS.

The EPMA analyses included backscattered electron (BSE) imaging and point analyses of minerals that host Au. Based on the EPMA results, representative minerals were chosen for elemental mapping (Au, As, S, and Fe). The EPMA analyses were conducted with a JEOL JXA-8100 instrument at the State Key Laboratory for Mineral Deposits Research of Nanjing University, China. The analyses employed an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam width of 1 μm . Basic analytical conditions for EPMA are given in Table 2.

4. Results

4.1. Minerals That Host Au. The analytical results indicate that the main minerals that host Au in the Bojitian Au deposit are arsenian pyrite and arsenopyrite. This is also the case in the nearby Shuiyindong Au deposit and in other typical Carlin-type Au deposits worldwide [11, 34–38]. Our analytical data and previous studies testified that the other minerals, such as quartz, calcite, clay, and carbonaceous, do not host Au in this deposit (Li and Ye et al., 2003 [19]).

4.1.1. Arsenian Pyrite

1. EPMA Backscattered Imaging and Point Analyses. The main types of arsenian pyrite in the present study are zoned pyrite and fine-grained pyrite, but we also observed framboidal, coarse-grained, and banded pyrite. In addition, some pyrite is present as filling in charcoal debris that forms a screen pipe or a conduit for plant rubble. The specific EPMA detection points and analytical results are given in Figure 4 and Table 3.

(a) Zoned Pyrite. The zoned pyrite is generally 10–30 μm across, rarely over 50 μm . The grains all have single rims occurring as cubes and/or pentagonal dodecahedrons.

Sixteen points on zoned pyrite were chosen for EPMA analysis (points z-1 to z-16, Figure 4), with 8 points each in cores and rims. The cores commonly have relatively low contents of As and high contents of S and Fe (average contents of 0.06, 53.66 and 45.64 wt%, resp.). We converted the EPMA analysis values to numbers of atoms and found that the Fe:S ratio is close to the theoretical value (1:2) of pyrite (FeS_2) (Table 4). Thus, we suggest that the cores of the zoned pyrite are typical pyrite. Au was detected in three of the eight core points at 0.03–0.05 wt%, indicating that these cores contain

Au. The average contents of other elements are 0.03 wt% Cu, 0.08 wt% Co, 0.02 wt% Ni, and 0.01 wt% Sb.

The elemental compositions of the rims of the zoned pyrite are quite different from the cores, being characterized by relatively high contents of As and low contents of S and Fe. The average As content in the rims is 6.60 wt%, two orders of magnitude higher than that in the cores. The average rim contents of S and Fe are 49.67 wt% and 43.36 wt%, respectively; both values are lower than those in the cores. Calculation of the numbers of atoms suggests that the numbers of S atoms in the rims are lower than that in the cores, but Fe atom numbers show little variation from core to rim. This result may indicate that some of the S was replaced by As. The Au content in the rims varies from 0.07 to 0.10 wt%, higher than that in the cores. The average contents of other elements in the rims are 0.23 wt% Cu, 0.01 wt% Ag, 0.05 wt% Co, 0.02 wt% Ni, and 0.01 wt% Sb.

(b) Fine-Grained Pyrite. The fine-grained pyrite is smaller than the zoned pyrite, typically <10 μm across. This type of pyrite is disseminated, individual grains are unzoned, and the textures are homogeneous. Five points on fine-grained pyrite were chosen for EPMA analysis (points f-1 to f-5; Figure 4). The average contents of As, S, and Fe are 7.28, 48.87, and 43.20 wt%, respectively. Calculating the numbers of atoms shows that most of the Fe:S values in the fine-grained pyrite are lower than 1:2. The numbers of Fe atoms are relatively constant from core to rim, whereas the numbers of S atoms are lower than in the cores and rims of the zoned pyrite. The numbers of As atoms are relatively high, indicating that some of the S was replaced by As. Au was detected at two points where the contents are 0.07 wt% and 0.14 wt%, and clearly the fine-grained pyrite also hosts Au. The average contents of other elements are 0.20 wt% Cu, 0.05 wt% Co, 0.03 wt% Ni, and 0.01 wt% Sb. In general, the elemental compositions are similar to those in the rims of the zoned pyrite, reflecting relatively high Au and As contents and low S and Fe contents.

(c) Framboidal Pyrite. The framboidal pyrite grains are generally 5–20 μm across, rarely 25 μm . The framboidal pyrite occurs as disseminated single grains or aggregates. Three points on framboidal pyrite were analyzed (points fb-1 to fb-5; Figure 4). The average contents of As, S, and Fe are 0.87, 51.89, and 44.39 wt%, respectively. Calculations of the numbers of atoms show that the value of Fe:S is close to the theoretical value (1:2) of pyrite (Table 4). This indicates that the framboidal pyrite is typical pyrite. The framboidal pyrite contains 0.03–0.07 wt% Au, suggesting that some of this pyrite is rich in Au; however, it is not the main type of pyrite that hosts Au. The average contents of other elements are 0.03 wt% Cu, 0.01 wt% Ag, 0.33 wt% Co, 0.06 wt% Ni, and 0.03 wt% Sb. The elemental compositions of the framboidal pyrite are generally similar to those in the cores of the zoned pyrite, being characterized by relatively low contents of Au and As and high S and Fe.

(d) Coarse-Grained Pyrite. The coarse-grained pyrite is generally 50–300 μm across, and it is unzoned. Four points on the coarse-grained pyrite were chosen for EPMA analysis (points

TABLE 1: Gold contents of analyzed samples.

Sample	G2-01	G2-03	G2-05	G2-06	G2-08	G2-10	G2-11	G2-14	G2-17	G2-19	G2-20	G2-22	G2-24	G2-25	G2-26
Depth (m)	243.00	259.30	275.15	281.50	295.40	306.95	310.10	315.30	329.9	336.30	342.20	353.09	367.45	372.46	374.96
Au (ppm)	0.013	0.006	<0.005	0.016	0.006	2.54	0.894	0.013	0.009	0.008	0.005	0.013	0.048	0.056	0.848
Sample	G2-28	G2-29	G2-31	G2-32	G2-33	G2-34	G2-35	G2-36	G2-37	G2-39	G2-41	G2-43	G2-45	G2-47	G2-48
Depth (m)	396.92	397.72	406.25	411.73	418.63	421.14	427.34	429.47	436.15	459.63	480.34	498.44	508.00	518.00	522.9
Au (ppm)	0.147	0.076	0.172	8.71	3.12	0.619	1.13	0.889	1.05	0.012	0.203	<0.005	<0.005	<0.005	<0.005

TABLE 2: Detection limits of EPMA analyses of minerals that host gold and that occur with gold.

Elements	Peak count time (s)	Background count time (s)	Detection limit (wt.%)
Au	40	20	0.03
As	30	15	0.02
S	10	5	0.01
Fe	10	5	0.03
Se	30	15	0.02
Ag	30	15	0.01
Cu	10	5	0.05
Te	30	15	0.02
Co	40	20	0.03
Pb	20	10	0.03
Ni	40	20	0.02
Bi	20	10	0.02
Zn	10	5	0.04
Sb	20	10	0.02

c-1 to c-4; Figure 4), yielding average contents of As, S, and Fe of 4.76, 49.88, and 44.48 wt%, respectively. Conversion to numbers of atoms indicates that the value of Fe:S in the coarse-grained pyrite varies slightly around 1:2, implying that As may have replaced some of S. The Au contents are higher than the detection limit of 0.05–0.08 wt%. Thus, the coarse-grained pyrite hosts Au. The average contents of other elements are 0.11 wt% Cu, 0.13 wt% Co, and 0.03 wt% Sb. The elemental compositions in the coarse-grained pyrite are similar to those in the rims of the zoned pyrite and in the fine-grained pyrite, with relatively high Au and As contents and low S and Fe.

(e) *Banded Pyrite*. Two points on banded pyrite were analyzed (points b-1 and b-2; Figure 3). The average contents of the three main elements, As, S, and Fe are 0.38, 52.38, and 45.52 wt%, respectively. The conversion to numbers of atoms shows that the value of Fe:S is close to 1:2. One of the two points contains relatively low amounts of Au (0.03 wt%), indicating that the banded pyrite is not the main host of Au. The average contents of other elements in the banded pyrite are 0.08 wt% Co, 0.10 wt% Ni, and 0.04 wt% Sb. The elemental compositions are generally characterized by relatively low As and Au contents and high S and Fe.

(f) *Pyrite in Charcoal Debris*. The charcoal debris (point cd-1; Figure 4) was formed by a plant screen or by rubble in a conduit, and pyrite fills holes in the debris. The average contents of the three main elements As, S, and Fe in this pyrite are 5.87, 50.72, and 43.53 wt%, respectively. The Fe:S value is 1:2.03, close to the theoretical value (1:2) of pyrite. Thus, the charcoal debris pyrite appears to be normal pyrite. The Au content at the analytical point is lower than the detection limit, indicating that this pyrite is not one of the main Au-hosting minerals. The average contents of other elements in this pyrite are 0.24 wt% Cu and 0.03 wt% Co.

2. *EPMA Mapping*. To further understand the distribution of different elements in typical zoned pyrite, one sample (G2-10-03 with points z-1 and z-2 in Figure 4) was chosen for mapping the elements Au, As, S, and Fe (Figure 5). The results further support the findings of the point analysis in general.

The distribution of Au does not show the predicted zonal structure, and there is instead a roughly heterogeneous distribution of light areas (Au-rich) and dark areas (less Au-rich) in Figure 5. However, the light areas are more concentrated in the rims of the zoned pyrite. Thus, while both the cores and rims of the zoned pyrite contain Au, the Au contents of the rims are slightly higher than those of the cores. This finding is generally consistent with the results of the EPMA point analyses.

With respect to the distribution of As, the rims of the zoned pyrite show bright colors, while the cores show relatively dark colors in Figure 5. This reflects a much higher As content in the rims than in the cores. The distribution of S shows the opposite trend, with bright colors in the cores and less bright colors in the rims. In general, the distribution of Fe is similar to that of S, but with a less obvious difference between rims and cores.

Overall, the above characteristics are similar to the results of the point analysis.

4.1.2. *Arsenopyrite*. In addition to arsenian pyrite, another Au-hosting mineral is arsenopyrite. Grains of arsenopyrite are 10–130 μm long and 2–15 μm wide. Eleven points on arsenopyrite were chosen for EPMA point analysis (Figure 6), and the analytical results (Table 5) indicate that the average contents of the three main elements, As, S, and Fe are 40.15, 23.64, and 34.97 wt%, respectively. The conversion to numbers of atoms (Table 6) shows that the Fe:As:S ratio is not the theoretical value of 1:1:1. The numbers of As and S atoms are approximately 1:2 in relation to Fe, implying that As has replaced some of S. Au was detected at two points (0.09–0.122 wt%; average 0.02 wt%). This indicates that the arsenopyrite is Au-hosting. The contents of Au in the arsenopyrite are commonly lower than in the rims of the zoned pyrite. The average contents of the other elements in the arsenopyrite are 0.02 wt% Cu, 0.08 wt% Co, 0.15 wt% Ni, and 0.01 wt% Sb.

The results of EPMA point analyses show that Au in the arsenopyrite exists as “invisible” ultramicroscopic packages of Au (nanoscale Au, Au^0) [6, 11]. In agreement with previous studies, we infer that Au occurs in the arsenopyrite in a relatively simple way [38], and for this reason we did not undertake EPMA mapping of Au.

4.2. *REEs and Trace Elements*. The REE and trace element analyses were conducted on 17 samples from the ores and wall rocks of the Bojitian gold deposit (Table 7).

4.2.1. *REEs*. The total REE contents of the five ore samples vary from 100 to 269 ppm, with an average of 199 ppm. Chondrite-normalized REE patterns (normalizing values from [39]) are shown in Figure 8. It is showed that almost all the ore samples have similar REE patterns (Figure 8(a)), and

FIGURE 4: Microphotographs showing the structures of arsenian pyrite. EPMA analysis points are marked by red dots and the data are given in Table 3. The black-and-white images are EPMA BSE images, while the color images were taken under reflected light. Z, zoned pyrite; F, fine-grained pyrite; C, coarse-grained pyrite; B, banded pyrite; Fb, framboidal pyrite; and Cd, charcoal debris pyrite.

TABLE 3: Results of EPMA analyses of arsenian pyrite (wt%).

Samples and location of measured points	Points	Au	As	S	Fe	Ag	Se	Pb	Cu	Zn	Sb	Co	Te	Ni	Bi	Total	Co/Ni
Zoned pyrite																	
G2-10-03-core	z-1	bdl	0.02	52.87	46.75	bdl	bdl	bdl	bdl	bdl	bdl	0.05	bdl	bdl	0.35	100.04	>1
G2-10-03-rim	z-2	bdl	5.33	50.56	43.71	bdl	0.02	bdl	0.10	bdl	bdl	0.03	bdl	0.14	0.35	100.24	0.22
G2-10-03-core	z-3	bdl	0.04	54.64	45.74	bdl	bdl	0.08	0.12	bdl	bdl	0.09	bdl	0.09	0.35	101.14	1.00
G2-10-03-rim	z-4	bdl	5.26	50.73	44.05	bdl	0.03	0.09	0.18	bdl	bdl	0.12	bdl	0.03	0.35	100.84	4.62
G2-10-05-core	z-5	0.05	0.28	53.81	45.32	bdl	bdl	bdl	bdl	bdl	bdl	0.14	0.02	0.05	0.35	100.02	2.64
G2-10-05-rim	z-6	0.09	6.81	49.83	44.03	0.02	0.03	0.07	0.24	bdl	bdl	0.03	bdl	0.02	0.35	101.51	2.00
G2-10-09-core	z-7	0.03	bdl	54.06	45.34	bdl	bdl	0.07	bdl	bdl	0.03	0.04	bdl	bdl	0.35	99.92	>1
G2-10-09-rim	z-8	0.10	5.04	51.59	43.48	0.02	0.06	bdl	0.21	bdl	bdl	0.03	bdl	bdl	0.35	100.88	>1
G2-10-10a-core	z-9	bdl	bdl	54.15	45.55	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.35	100.05	—
G2-10-10a-rim	z-10	bdl	7.75	47.12	43.31	0.01	0.09	bdl	0.13	bdl	bdl	0.04	bdl	bdl	0.35	98.80	>1
G2-10-10b-core	z-11	bdl	0.09	53.89	44.88	0.02	bdl	0.08	0.06	bdl	0.02	0.12	bdl	bdl	0.35	99.50	>1
G2-10-10b-rim	z-12	0.10	5.55	51.24	42.99	0.01	0.04	bdl	0.31	bdl	0.05	0.03	bdl	bdl	0.35	100.67	>1
G2-32-08a-core	z-13	bdl	0.02	52.54	46.05	bdl	bdl	bdl	0.08	bdl	bdl	0.13	bdl	bdl	0.32	99.13	>1
G2-32-08a-rim	z-14	bdl	7.90	48.23	43.13	bdl	0.10	0.07	0.35	0.04	bdl	0.05	bdl	bdl	0.30	100.16	>1
G2-32-09-core	z-15	0.03	0.03	53.30	45.49	bdl	bdl	bdl	bdl	bdl	bdl	0.06	bdl	0.06	0.37	99.33	1.07
G2-32-09-rim	z-16	0.07	9.15	48.03	42.19	bdl	0.04	bdl	0.31	bdl	0.02	0.05	bdl	bdl	0.28	100.14	>1
Fine-grained pyrite																	
G2-10-03	f-1	bdl	7.83	48.77	43.72	0.01	0.05	0.09	0.09	bdl	bdl	0.11	bdl	bdl	0.35	101.02	>1
G2-10-03	f-2	bdl	6.81	49.34	43.76	bdl	bdl	0.09	0.16	0.04	bdl	0.07	bdl	0.05	0.35	100.68	1.30
G2-10-09	f-3	bdl	5.72	50.78	43.21	bdl	bdl	0.07	0.27	bdl	0.02	bdl	bdl	0.02	0.35	100.43	<1
G2-32-09	f-4	0.14	7.86	46.91	42.22	bdl	0.05	bdl	0.16	bdl	bdl	0.03	bdl	bdl	0.26	97.63	>1
G2-35-02	f-5	0.07	8.17	48.56	43.07	bdl	0.03	bdl	0.31	bdl	0.02	0.03	bdl	0.07	0.27	100.59	0.44
Frambooidal pyrite																	
G2-10-05	fb-1	bdl	0.36	53.15	43.61	bdl	0.02	0.11	bdl	bdl	0.03	1.14	bdl	0.19	0.35	98.95	6.16
G2-32-08a	fb-2	0.07	1.52	51.27	44.61	bdl	0.02	bdl	bdl	bdl	0.03	0.15	bdl	bdl	0.32	97.99	>1
G2-35-02	fb-3	bdl	1.73	49.78	42.80	bdl	bdl	bdl	0.11	bdl	0.04	0.15	bdl	0.05	0.34	94.99	2.88
G2-10-02a	fb-4	0.03	0.10	53.82	45.65	0.03	bdl	0.09	0.05	bdl	0.03	0.13	bdl	bdl	0.35	100.27	>1
G2-32-08b	fb-5	0.07	0.67	51.41	45.27	bdl	bdl	0.06	bdl	bdl	bdl	0.08	bdl	0.05	0.31	97.92	1.48
Coarse-grained pyrite																	
G2-32-06	c-1	0.05	6.74	49.09	44.21	bdl	0.06	bdl	0.07	bdl	bdl	0.19	bdl	bdl	0.33	100.73	>1
G2-32-06	c-2	0.08	0.16	52.88	45.89	bdl	bdl	0.29	0.08	bdl	0.10	0.14	bdl	bdl	0.48	100.09	>1
G2-32-04	c-3	0.05	7.96	47.96	42.56	bdl	0.09	0.06	0.21	bdl	bdl	0.12	bdl	bdl	0.32	99.32	>1
G2-32-03	c-4	bdl	4.19	49.57	45.25	bdl	0.06	bdl	0.07	bdl	bdl	0.08	bdl	bdl	0.30	99.53	>1
Banded pyrite																	
G2-10-03	b-1	bdl	0.69	52.17	46.24	bdl	bdl	0.05	bdl	bdl	0.04	0.05	bdl	0.21	0.35	99.78	0.24
G2-32-11	b-2	0.03	0.07	52.58	44.80	bdl	0.03	0.06	bdl	bdl	0.04	0.10	bdl	bdl	0.32	98.03	>1
Charcoal detritus pyrite																	
G2-10-02b	cd-1	bdl	5.87	50.72	43.53	bdl	0.03	0.12	0.24	bdl	bdl	0.03	bdl	bdl	0.35	100.88	>1

Note. "bdl": below the detection limit.

TABLE 4: Results of conversion to numbers of atoms for arsenian pyrite.

Samples and location of measured points	Points	Au	As	S	Fe	Ag	Se	Pb	Cu	Zn	Sb	Co	Te	Ni	Bi	Total	Fe:S
Zoned pyrite																	
G2-10-03-core	z-1	bdl	0.011	66.295	33.660	bdl	bdl	bdl	bdl	bdl	0.003	0.032	bdl	bdl	0.067	100	1.970
G2-10-03-rim	z-2	0.004	2.922	64.735	32.135	0.002	0.012	bdl	0.067	bdl	0.004	0.024	0.001	0.094	0.068	100	2.014
G2-10-03-core	z-3	bdl	0.019	67.384	32.389	bdl	0.001	0.015	0.073	0.001	bdl	0.057	bdl	0.061	0.066	100	2.080
G2-10-03-rim	z-4	0.002	2.870	64.640	32.229	bdl	0.018	0.018	0.114	0.004	0.004	0.080	0.002	0.018	0.068	100	2.006
G2-10-05-core	z-5	0.010	0.151	67.203	32.499	0.000	bdl	bdl	bdl	bdl	0.002	0.092	0.007	0.036	0.066	100	2.068
G2-10-05-rim	z-6	0.019	3.727	63.704	32.321	0.007	0.017	0.015	0.152	0.006	bdl	0.022	bdl	0.010	0.068	100	1.971
G2-10-09-core	z-7	0.007	bdl	67.456	32.485	bdl	0.004	0.014	bdl	bdl	0.009	0.026	bdl	bdl	0.066	100	2.077
G2-10-09-rim	z-8	0.020	2.734	65.397	31.648	0.007	0.030	bdl	0.137	bdl	0.004	0.021	bdl	0.002	0.067	100	2.066
G2-10-10a-core	z-9	bdl	bdl	67.410	32.559	bdl	bdl	bdl	bdl	0.004	0.004	0.016	bdl	0.007	0.066	100	2.070
G2-10-10a-rim	z-10	0.003	4.397	62.452	32.960	0.004	0.050	0.009	0.089	bdl	0.004	0.031	bdl	0.002	0.071	100	1.895
G2-10-10b-core	z-11	bdl	0.046	67.515	32.285	0.007	bdl	0.015	0.037	0.004	0.006	0.084	bdl	bdl	0.067	100	2.091
G2-10-10b-rim	z-12	0.020	3.025	65.253	31.435	0.003	0.020	0.001	0.202	bdl	0.018	0.023	bdl	bdl	0.068	100	2.076
G2-32-08a-core	z-13	bdl	0.010	66.403	33.418	bdl	0.004	0.007	0.048	0.020	0.000	0.086	bdl	0.003	0.061	100	1.987
G2-32-08a-rim	z-14	0.002	4.410	62.924	32.310	bdl	0.050	0.013	0.230	0.025	bdl	0.036	bdl	bdl	0.060	100	1.947
G2-32-09-core	z-15	0.005	0.018	67.038	32.852	bdl	0.001	bdl	bdl	0.009	0.001	0.038	bdl	0.038	0.071	100	2.041
G2-32-09-rim	z-16	0.015	5.129	62.874	31.712	bdl	0.023	bdl	0.204	bdl	0.006	0.032	bdl	0.006	0.056	100	1.983
Fine-grained pyrite																	
G2-10-03	f-1	bdl	4.329	63.038	32.448	0.003	0.027	0.018	0.060	bdl	0.002	0.075	bdl	bdl	0.069	100	1.943
G2-10-03	f-2	0.002	3.758	63.609	32.394	bdl	0.006	0.019	0.104	0.023	0.002	0.046	0.000	0.038	0.069	100	1.964
G2-10-09	f-3	0.001	3.130	64.926	31.723	bdl	bdl	0.014	0.174	bdl	0.005	0.015	bdl	0.012	0.068	100	2.047
G2-32-09	f-4	0.031	4.507	62.819	32.464	bdl	0.027	0.004	0.108	0.020	bdl	0.020	bdl	bdl	0.053	100	1.935
G2-35-02	f-5	0.016	4.537	63.046	32.108	bdl	0.013	bdl	0.204	bdl	0.006	0.022	bdl	0.048	0.053	100	1.964
Frambooidal pyrite																	
G2-10-05	fb-1	bdl	0.192	67.198	31.659	bdl	0.008	0.022	bdl	0.002	0.008	0.783	bdl	0.128	0.067	100	2.123
G2-32-08a	fb-2	0.014	0.367	66.202	33.473	bdl	0.000	0.013	bdl	0.001	0.003	0.057	bdl	bdl	0.061	100	1.978
G2-35-02	fb-3	bdl	0.863	68.111	34.029	bdl	bdl	0.004	0.000	0.013	0.009	0.111	bdl	0.000	0.065	100	2.002
G2-10-02a	fb-4	0.007	0.053	67.107	32.683	0.009	bdl	0.017	0.030	bdl	0.009	0.085	bdl	0.001	0.066	100	2.053
G2-32-08b	fb-5	0.000	0.949	63.989	31.590	bdl	bdl	0.003	0.070	0.003	0.014	0.106	bdl	0.037	0.067	100	2.026
Coarse-grained pyrite																	
G2-32-06	c-1	0.011	3.719	63.315	32.741	bdl	0.034	bdl	0.044	bdl	bdl	0.133	0.002	bdl	0.064	100	1.934
G2-32-06	c-2	0.016	0.088	66.514	33.143	bdl	0.002	0.056	0.050	bdl	0.033	0.099	bdl	bdl	0.092	100	2.007
G2-32-04	c-3	0.011	4.481	63.084	32.144	bdl	0.049	0.012	0.136	bdl	bdl	0.083	bdl	bdl	0.064	100	1.963
G2-32-03	c-4	bdl	2.315	64.004	33.548	bdl	0.031	bdl	0.048	bdl	bdl	0.053	bdl	bdl	0.060	100	1.908
Banded pyrite																	
G2-10-03	b-1	0.005	0.371	65.884	33.530	bdl	bdl	0.009	0.013	bdl	0.013	0.034	bdl	0.142	0.067	100	1.965
G2-32-11	b-2	0.006	0.038	67.039	32.798	bdl	0.013	0.012	bdl	0.009	0.014	0.071	0.001	bdl	0.062	100	2.044
Charcoal detritus pyrite																	
G2-10-02b	cd-1	bdl	3.206	64.699	31.884	bdl	0.014	0.023	0.153	bdl	bdl	0.022	bdl	bdl	0.068	100	2.029

Note. "bdl": below the detection limit.

FIGURE 6: Microphotographs showing the structures of arsenopyrite. EPMA analysis points are marked by red dots and the data are given in Table 3. The black-and-white images are EPMA BSE images, while the color images were taken under reflected light.

is much more abundant in the ore bodies than in the wall rocks also suggests that the pyrite has various origins, because a simple sedimentary origin may not have provided all the pyrite cores that now exist. Thus, the origin of the cores in the zoned pyrite is complex. The rims yield Co/Ni values that are usually greater than 1.0, again suggesting a hydrothermal origin.

The other types of pyrite (i.e., the fine-grained, framboidal, coarse-grained, banded, and charcoal debris pyrite) have Co/Ni values that are higher than 1.0, also suggesting a hydrothermal origin or at least indicating the effects of hydrothermal activity. We conclude, therefore, that hydrothermal activity was commonplace during the period of ore formation.

5.1.2. Arsenopyrite. The arsenopyrite occurs mainly in ore samples from close to a hydrothermal channel (samples G2-32 and G2-35 from the T_1Y^{1-2} layer under the fault fracture zone; Figure 3). Only one generation of arsenopyrite was found, and the crystals are euhedral or subhedral and acicular or fibrous. In some cases the crystals form aggregates with a radiating pattern. EPMA analyses show that Au has a heterogeneous distribution, with local areas of enrichment. Generally, the Au content of the arsenopyrite is lower than that in the rims of the zoned pyrite.

5.1.3. Elemental Composition of Arsenian Pyrite and Arsenopyrite. Figure 7 shows the typical elemental compositions of

the Au-hosting arsenian pyrite and arsenopyrite. The data show no obvious relationship between Au and Fe in either the arsenian pyrite or the arsenopyrite (Figure 7(a)), but there is a negative correlation between As and S (Figure 7(b)) which suggests that the As in the structure of the arsenian pyrite has replaced S [10, 11, 47]. A similar negative correlation between As and S characterizes the arsenopyrite (Figure 7(b)). We found a relationship between Au and As contents in the arsenopyrite, although not a simple linear positive correlation as found for the arsenian pyrite (Figure 7(c)). In general, the pyrite with a high content of As also has more Au. For example, the Au content of the As-rich rims of arsenian pyrite (0.05 wt%) is roughly three times that of the cores (0.014 wt%), which lack As. In contrast, there is no obvious correlation between Au and As in the arsenopyrite (Figure 7(c)), and the arsenopyrite with low and high As contents shows little difference in terms of hosting Au.

These results, in combination with the EPMA analyses, suggest that different types of sulfide can display different Au-hosting abilities. Overall, the Au contents of arsenian pyrite are slightly higher than those of arsenopyrite, and the Au-hosting ability within different types of arsenian pyrite follows the order of (from highest to lowest ability) zoned pyrite rims, fine-grained pyrite, coarse-grained pyrite, framboidal pyrite, banded pyrite, zoned pyrite cores, and pyrite in charcoal detritus. In general, there is a close relationship between Au and As content. The zoned pyrite and fine-grained pyrite are the two main Au-hosting minerals, and the

TABLE 5: Results of EPMA analyses of arsenopyrite (wt%).

Samples and location of measured points	Points	Au	As	S	Fe	Ag	Se	Pb	Cu	Zn	Sb	Co	Te	Ni	Bi	Total	Co/Ni
<i>Arsenopyrite</i>																	
G2-32-01	21	bdl	39.731	24.61	35.69	bdl	0.240	0.124	bdl	0.103	0.028	0.096	bdl	bdl	0.159	100.78	>1
G2-32-01	22	0.122	41.736	22.54	33.27	0.006	0.272	bdl	0.027	0.012	0.016	0.078	bdl	bdl	0.111	98.19	>1
G2-32-01	23	bdl	37.544	25.19	35.64	bdl	0.270	bdl	bdl	0.056	0.019	0.097	bdl	bdl	0.153	98.96	>1
G2-32-01	24	bdl	37.487	25.36	35.84	0.001	0.318	bdl	bdl	0.031	bdl	0.087	bdl	0.001	0.157	99.28	87.0
G2-32-02	25	bdl	41.324	21.77	34.98	bdl	0.375	0.048	0.060	0.001	0.005	0.067	bdl	0.021	0.122	98.77	3.2
G2-32-02	26	bdl	42.138	22.65	35.64	bdl	0.274	bdl	bdl	0.054	bdl	bdl	0.006	0.037	0.116	100.91	<1
G2-32-05	27	bdl	39.921	23.04	34.24	bdl	0.313	bdl	0.076	bdl	bdl	0.174	bdl	0.803	0.144	98.71	0.2
G2-32-05	28	0.015	40.170	22.39	35.10	0.001	0.259	0.003	0.071	0.009	bdl	0.093	0.002	0.789	0.171	99.07	0.1
G2-35-01	4	0.017	40.336	25.00	34.94	bdl	0.297	bdl	0.020	0.009	0.024	0.088	bdl	0.027	0.149	100.91	3.3
G2-35-01	5	0.085	41.952	22.63	34.81	bdl	0.327	0.012	0.016	0.048	0.050	0.052	bdl	bdl	0.101	100.08	>1
G2-35-01	6	bdl	39.260	24.82	34.52	bdl	0.328	0.074	bdl	bdl	bdl	0.095	bdl	bdl	0.125	99.22	>1

Note. "bdl": below the detection limit.

TABLE 6: Results of conversion to numbers of atoms for arsenopyrite.

Samples and location of measured points	Points	Au	As	S	Fe	Ag	Se	Pb	Cu	Zn	Sb	Co	Te	Ni	Bi	Total
<i>Arsenopyrite</i>																
G2-32-01	21	bdl	27.27	39.47	32.86	bdl	0.156	0.031	bdl	0.081	0.012	0.084	bdl	bdl	0.039	100
G2-32-01	22	0.033	29.91	37.74	31.99	0.003	0.185	bdl	0.023	0.01	0.007	0.071	bdl	bdl	0.029	100
G2-32-01	23	bdl	25.94	40.67	33.04	bdl	0.177	bdl	bdl	0.044	0.008	0.085	bdl	bdl	0.038	100
G2-32-01	24	bdl	25.79	40.77	33.09	5E-04	0.208	bdl	bdl	0.024	bdl	0.076	bdl	9E-04	0.039	100
G2-32-02	25	bdl	29.58	36.4	33.59	bdl	0.255	0.012	0.051	8E-04	0.002	0.061	bdl	0.019	0.031	100
G2-32-02	26	bdl	29.41	36.93	33.37	bdl	0.181	bdl	bdl	0.043	bdl	bdl	0.002	0.033	0.029	100
G2-32-05	27	bdl	28.24	38.08	32.49	bdl	0.21	bdl	0.063	bdl	bdl	0.156	bdl	0.725	0.037	100
G2-32-05	28	0.004	28.47	37.07	33.37	5E-04	0.174	8E-04	0.059	0.007	bdl	0.084	8E-04	0.714	0.043	100
G2-35-01	4	0.004	27.6	39.96	32.07	bdl	0.193	bdl	0.016	0.007	0.01	0.077	bdl	0.024	0.037	100
G2-35-01	5	0.023	29.53	37.21	32.87	bdl	0.218	0.003	0.013	0.039	0.022	0.047	bdl	bdl	0.025	100
G2-35-01	6	bdl	27.25	40.25	32.15	bdl	0.216	0.019	bdl	bdl	bdl	0.084	bdl	bdl	0.031	100

Note. "bdl": below the detection limit.

TABLE 7: Contents (ppm) of REEs and trace elements for ore and wall rock samples.

Sample	Lithology	Type	Strata	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Mo	Sn	Cs	Ba	Hf	Ta	W	Tl	Pb	Th	U
G2-05	Marlstone	Wall rock	T ₁ y ¹⁻¹	214	80	33.5	59	138	154	24.6	144	822	34.6	339	40.3	2	3	15.2	368	8.8	2.8	4	1	8	11.4	2.68
G2-08	Calcareous clay rock	Wall rock	P ₃ d	152	60	24	62	55	109	15.8	84.8	670	24.9	247	30.7	3	2	10.9	223	6.5	2.1	16	0.7	16	8.67	1.65
G2-10	Calcareous clay rock	Ore	P ₃ d	137	60	26.5	73	49	131	16	79.4	1155	20	244	30.9	3	3	8.96	251	6.6	2.1	41	1.1	7	7.72	2.03
G2-11	Bioclastic limestone	Wall rock	P ₃ c	38	20	5.4	28	12	38	5.2	27.8	1635	24.8	80	8.4	2	1	2.93	105	2.1	0.6	9	bdl	bdl	3.77	1.69
G2-17	Bioclastic limestone	Wall rock	P ₃ c	161	60	25.7	83	50	151	18.8	87.9	1050	26.6	307	38.2	3	3	12.75	550	7.9	2.5	11	0.9	13	10.05	2.03
G2-26	Breccia	Wall rock	T ₁ y ¹⁻²	72	40	11.6	33	33	76	11.7	50.3	911	18.6	148	12.6	3	2	4.62	99.6	3.7	0.9	12	1	7	5.16	3.18
G2-31	Limestone	Wall rock	T ₁ y ¹⁻²	60	40	13.1	29	30	48	7.4	35	1695	13.4	100	12.8	2	1	2.26	72.1	2.5	0.8	14	bdl	bdl	3.27	0.91
G2-32	Marlstone	Ore	T ₁ y ¹⁻²	148	100	28.2	62	44	100	15.9	89	700	23.1	232	31.2	2	2	6.31	172	5.9	2.1	25	0.8	6	7.53	1.48
G2-33	Marlstone	Ore	T ₁ y ¹⁻²	192	100	37.6	79	101	144	21.2	115.5	580	29.6	322	39.1	3	3	10.15	223	8.5	2.6	6	1.8	14	10	2
G2-34	Limestone	Wall rock	T ₁ y ¹⁻²	31	20	4.6	10	12	21	3.4	15.5	2190	8.4	46	5.2	2	1	1.4	58.1	1.2	0.3	3	bdl	bdl	1.5	0.63
G2-35	Limestone	Ore	T ₁ y ¹⁻²	78	50	14.1	31	28	56	8.1	37	1575	13.9	105	13.9	2	1	3.4	100	2.8	0.9	14	0.6	bdl	3.32	0.83
G2-36	Limestone	Wall rock	T ₁ y ¹⁻²	47	30	11.6	22	24	32	5.1	21.2	1840	11.8	67	8.4	2	1	2.24	52.3	1.7	0.5	4	0.5	bdl	2.14	0.6
G2-37	Marlstone	Ore	T ₁ y ¹⁻²	222	90	36.2	69	131	122	23	105	537	34.7	350	40.4	2	3	13.3	263	8.9	2.7	10	1.2	8	9.92	1.82
G2-39	Marlstone	Wall rock	T ₁ y ¹⁻²	107	50	15.9	32	39	69	10.1	49.9	1185	15.7	142	18.2	5	1	6.91	105	3.5	1.1	5	bdl	bdl	3.95	0.93
G2-43	Limestone	Wall rock	T ₁ y ¹⁻¹	44	20	7.9	16	20	29	5.1	18.9	2120	10.1	70	7.8	3	1	2.18	81.3	1.7	0.5	1	bdl	bdl	2.1	0.95
G2-45	Marlstone	Wall rock	T ₁ y ¹⁻¹	207	90	34.8	79	138	148	27.1	86	1285	41.4	415	49.5	2	4	13.2	156	10.7	3.4	15	0.5	6	12.75	2.31
G2-48	Marlstone	Wall rock	T ₁ y ¹⁻¹	108	40	14.6	27	46	71	10.6	31.6	1220	21.1	166	19.9	2	1	4.16	85.3	4.1	1.3	12	bdl	bdl	5.12	1.31
Sample	Lithology	Type	Strata	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	LREE	HREE	LREE/HREE	δEu	δCe			
G2-05	Marlstone	Wall rock	T ₁ y ¹⁻¹	50	106	13.6	51	10	2.5	9.52	1.38	6.56	1.27	3.5	0.52	3.1	0.49	260	233	26.4	8.85	0.85	0.87			9.55
G2-08	Calcareous clay rock	Wall rock	P ₃ d	42	92	11	41	8.4	2	7.85	1.07	4.72	0.89	2.4	0.34	2	0.32	215	196	19.6	9.96	0.82	0.92			12.29
G2-10	Calcareous clay rock	Ore	P ₃ d	40	82	9.46	34	6	1.5	5.74	0.77	3.68	0.73	2.1	0.29	1.8	0.27	188	173	15.3	11.26	0.82	0.89			13.27
G2-11	Bioclastic limestone	Wall rock	P ₃ c	24	42	5.36	20	4.1	1.3	4.27	0.65	3.36	0.72	2.1	0.32	2.1	0.33	111	96.7	13.8	6.99	1.00	0.76			7.00
G2-17	Bioclastic limestone	Wall rock	P ₃ c	48	101	12.6	46	9.5	2.3	8.82	1.18	5.44	0.99	2.8	0.39	2.3	0.35	242	220	22.3	9.86	0.82	0.88			12.18
G2-26	Breccia	Wall rock	T ₁ y ¹⁻²	20	39	5.08	20	6.2	2	6.24	0.88	3.72	0.67	1.7	0.25	1.6	0.24	108	92.5	15.3	6.05	1.07	0.82			7.52
G2-31	Limestone	Wall rock	T ₁ y ¹⁻²	21	43	5.17	19	3.7	0.8	3.58	0.5	2.34	0.45	1.2	0.17	1.1	0.16	102	92.7	9.5	9.76	0.76	0.88			11.71
G2-32	Marlstone	Ore	T ₁ y ¹⁻²	39	81	10.1	37	6.9	1.7	6.58	0.91	4.26	0.83	2.4	0.33	2.1	0.32	193	175	17.6	9.94	0.83	0.87			11.35
G2-33	Marlstone	Ore	T ₁ y ¹⁻²	48	102	13.3	49	9.2	2.4	8.74	1.2	5.58	1.12	3.1	0.43	2.7	0.40	247	224	23.3	9.62	0.88	0.87			10.66
G2-34	Limestone	Wall rock	T ₁ y ¹⁻²	11	20	2.62	10	2	0.5	2.01	0.29	1.37	0.27	0.8	0.11	0.6	0.1	50.9	45.4	5.5	8.25	0.84	0.82			10.39
G2-35	Limestone	Ore	T ₁ y ¹⁻²	20	41	5.07	19	3.8	1.1	3.82	0.53	2.53	0.49	1.3	0.19	1.1	0.18	100	90.1	10.2	8.83	0.97	0.88			10.4
G2-36	Limestone	Wall rock	T ₁ y ¹⁻²	18	35	4.29	16	3.1	0.9	3.02	0.41	1.94	0.37	1.1	0.15	0.9	0.13	84.8	76.9	7.95	9.67	0.94	0.84			12.35
G2-37	Marlstone	Ore	T ₁ y ¹⁻²	52	110	14.2	53	11	2.8	9.75	1.38	6.46	1.27	3.5	0.5	3.1	0.46	269	243	26.4	9.20	0.90	0.87			10.15
G2-39	Marlstone	Wall rock	T ₁ y ¹⁻²	22	46	5.86	22	4.4	1.1	4.25	0.6	2.84	0.56	1.6	0.22	1.3	0.2	113	102	11.5	8.83	0.87	0.87			10.11
G2-43	Limestone	Wall rock	T ₁ y ¹⁻¹	12	25	3.12	12	2.4	0.6	2.39	0.35	1.71	0.33	0.9	0.13	0.8	0.12	60.9	54.2	6.77	8.00	0.84	0.87			8.65
G2-45	Marlstone	Wall rock	T ₁ y ¹⁻¹	64	134	16.9	62	12	3	11.1	1.53	7.54	1.48	4.3	0.61	3.7	0.57	322	291	30.8	9.47	0.85	0.87			10.3
G2-48	Marlstone	Wall rock	T ₁ y ¹⁻¹	34	66	7.69	27	5.4	1.6	5.25	0.78	3.67	0.7	2	0.27	1.7	0.26	157	142	14.5	9.78	0.98	0.86			12.2

Note. "bdl": below the detection limit.

FIGURE 7: Relationships between selected elements in the arsenian pyrite and arsenopyrite, including (a) Au-Fe, (b) As-S, (c) Au-As, and (d) lgAu-lgAs. The red line in (d) denotes the solubility limit of Au in arsenian pyrite. The equation of the curve is $C_{Au} = 0.02C_{As} + 4 \times 10^{-5}$ [11].

Au contents of the As-rich rims of zoned pyrite are much higher than in the As-poor cores. The average contents of As in the fine-grained pyrite can reach 7.3 wt%, and this pyrite also has a relatively high Au content.

Previous studies have indicated that the ore-forming fluids in the study area were rich in H_2S [40] and that $Au(HS)^-$ was the main material migrating in these H_2S -rich fluids [48]. Interaction between As-rich hydrothermal fluids and $Au(HS)^-$ and Fe^{2+} produced by decarbonation resulted in the formation of arsenian pyrite and Au^+ [6, 26, 27]. The

more that As contributes to the ore-forming process, the more that Au^+ enters the structure of arsenian pyrite, forming pyrite with a high Au content.

With regard to the arsenopyrite, Au was not detected at some analytical points, and it seems to be distributed heterogeneously. As a consequence, Au does not show a good correlation with As. Previous studies suggested that the iron in sulfide minerals was probably derived from the dissolution of ferroan carbonate minerals [6, 12]. Therefore, the migration of ore-forming fluids may promote the dissolution of

FIGURE 8: REE and trace element patterns of ore and wall rock in the Bojitian gold deposit. (a), (b) REE patterns of ore and wall-rock samples, respectively. (c), (d) Trace element patterns of ore and wall-rock samples, respectively.

Fe-rich carbonates, releasing more Fe^{2+} , thus accelerating the formation of sulfide minerals. During this process, Au^+ may be oversaturated and form natural Au (Au^0) [6, 26, 27, 40], and this may explain why Au is distributed heterogeneously in the arsenopyrite. For example, in the nearby Shuiyindong deposit, the sulfides contain visible natural Au (Au^0) and show a heterogeneous distribution of Au [12].

5.2. Occurrences of Au. Using the results of the EPMA point and mapping analyses, we discuss here the Au occurrences in

the Bojitian deposit. Using the methods of X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), EPMA, and SHRIMP II, Reich et al. [11] studied the arsenian pyrite in Carlin-type and epithermal Au deposits and suggested a figure for the limit of Au solubility in the arsenian pyrite. The figure is given by the equation $C_{\text{Au}} = 0.02C_{\text{As}} + 4 \times 10^{-5}$, where C_{Au} and C_{As} represent the molar percentages of Au and As, respectively. In a diagram of $\lg \text{As}$ versus $\lg \text{Au}$, the data that fall above the line (the limit of Au solubility) may indicate Au that exists in the form of natural nanoscale Au (Au^0), while the data below the

line may indicate Au that exists in the form of solid solution Au (Au^+) in the structure of arsenian pyrite.

We plotted our EPMA data for As and Au on the lgAs versus lgAu diagram (Figure 7(d)), and it shows that the data falling above the line are from the cores of zoned pyrite, framboidal pyrite, banded pyrite, and coarse-grained pyrite. Thus, Au in these pyrites may exist in the form of natural nanoscale Au (Au^0). In contrast, the data falling below the line are from the rims of the zoned pyrite, the fine-grained pyrite, framboidal pyrite, banded pyrite, and coarse-grained pyrite. This suggests that Au in these arsenian pyrites may exist in the form of solid solution Au (Au^+).

The EPMA mapping analysis yields contrasting results. As discussed above, Au in the zoned pyrite does not show the same obvious zonal structure as As, S, and Fe (Figure 5). The map shows few clear Au-rich points, indicating that Au exists in the form of “invisible” ultramicroscopic Au (natural nanoscale Au, Au^0).

In summary, Au in the cores of the zoned pyrite may exist mainly in the form of natural nanoscale Au (Au^0), while the rims of the zoned pyrite mainly contain solid solution Au (Au^+) and probably also natural nanoscale Au (Au^0). The framboidal, banded, and coarse-grained pyrites contain both natural nanoscale Au (Au^0) and solid solution Au (Au^+).

With regard to the arsenopyrite, Au was detected at some analytical points for both single grains and aggregates of arsenopyrite and pyrite. This result may suggest that Au is distributed heterogeneously and that there are Au-rich areas that were incorporated into the structure of the arsenopyrite in the form of gold solution (Au^+).

5.3. Implications of the REE and Trace Element Data. REEs are widely used for determining the genesis, source, evolution, and formation of rocks. REEs can migrate within fluids, such as seawater, groundwater, and metasomatic and hydrothermal fluids, during alteration (e.g., [49–55]), and the REEs in the ores of hydrothermal deposits can be affected by the REEs in the fluids (e.g., [56–59]). Therefore, comparing the REE patterns in the ores and wall rocks may provide information on the nature of the ore-forming fluids.

The ores and wall rocks in the Bojitian deposit show similar REE patterns (Figures 8(a) and 8(b)), and both are richer in the LREEs than the HREEs, implying that the fluids that influenced the ores and wall rocks changed little over time.

Ce and Eu are commonly used to assess the sedimentary environment [60–62], and most studies indicate that if $\text{Ce}/\text{Ce}^* > 1$, there is Ce enrichment that possibly reflects an oxidation environment in seawater. Values of $\text{Ce}/\text{Ce}^* < 1$ may represent Ce loss at the time of precipitation of metallic oxides, indicating an anoxic reducing environment [63–65]. Eu is a multivalent element, occurring as Eu^{2+} and Eu^{3+} . Under relatively oxidizing conditions, Eu can exist as Eu^{3+} , and this can persist in solution for a long time. Eu^{2+} can be precipitated in a reducing environment, which leads to negative Eu anomalies [7, 66, 67]. In the Bojitian gold deposit,

both the ore and wall-rock samples show slightly negative Eu anomalies, suggesting that the ore-forming fluids were from a reducing environment. However, Ce shows no apparent anomalies in the ore samples, whereas the slightly negative Ce anomalies that characterize the wall-rock samples reflect a slightly reducing environment.

Sr and W are highly enriched in both the ore and wall rock. Previous studies have suggested that Sr is typically enriched in hydrothermal fluids, especially in low-to-medium-temperature fluids, whereas W is considered to indicate magmatic hydrothermal activity [7, 68]. In the Bojitian deposit, the enrichment in Sr and W implies that the deposit was affected by low-to-medium-temperature hydrothermal fluids, but it also indicates that magmatic hydrothermal fluids played a role in the ore-forming process. Fluid inclusions and isotopic data also testified that the ore-forming fluids of the Au deposits in the Huijiabao anticline show low-to-medium-temperature, low salinity, and medium density with certain incorporation of magmatic hydrothermal fluids [69, 70].

5.4. Implications for Ore-Forming Processes. It is widely accepted that studies of Au occurrences and minerals that host Au in Carlin-type deposits provide not only information on the levels of Au-enrichment in different types of minerals, but also data on the distribution and content of Au in individual minerals, or even within one specific mineral grain. All such studies are important if we are to understand ore-forming processes. In this study we found that arsenian pyrite and arsenopyrite host Au and that Au exists mainly in the sulfides in the form of solid solution Au (Au^+) and natural nanoscale Au (Au^0). These features also characterize the nearby Shuiyindong ultra-large Au deposit and are similar to features in other Carlin-type Au deposits, such as those in Nevada and in the “Au triangle” Shan-Gan-Chuan area of China [11, 34–38].

The similarities in the geology of these ore deposits and their gold-bearing minerals may indicate that similar ore-forming processes were responsible for all Carlin-type gold deposits in this area, including the nearby Shuiyindong deposit (Figure 9). Many studies have examined the ore-forming processes of the Shuiyindong deposit. Su et al. [6] argued that Au migrated dominantly in the form of $\text{Au}(\text{HS})^{2-}$ and $\text{AuHS}(\text{aq})^0$ and that the dominant As species in the Shuiyindong deposit was $\text{H}_3\text{AsO}_3(\text{aq})^0$. They related the formation of this deposit mainly to metamorphic fluids, but a deep magmatic component could not be excluded [6]. Chen et al. [69] suggested that the ore-forming fluids originated mainly from subsurface hydrothermal water but that some magmatic water may have been involved. Our REE and trace element data also support this inference. The most recent research also supports the idea that the formation of the Shuiyindong deposit was related to basinal fluids that migrated along faults at around 235 ± 33 Ma [71–73]. Comparing Shuiyindong and Bojitian, it can be seen that the occurrence of Au in both of these deposits is similar (dominantly as Au^+ in arsenian pyrite). Both deposits were also produced in the same tectonic context and in similar

FIGURE 9: Sketch map showing the ore-forming processes in the Bojitian Carlin-type Au deposit.

strata. We infer, therefore, that the Bojitian deposit was formed via the same processes as the Shuiyindong gold deposit. The Bojitian deposit was formed from As-bearing, H_2S -rich, low-to-medium-temperature fluids that migrated along faults and other channels under the influence of regional stress. Au that was already present in the strata or source beds migrated with the fluids in the form of $\text{Au}(\text{HS})^-$ and ore-forming fluids were then formed in the reducing environment. The ore-forming fluids would have interacted with Fe-rich carbonates to release large amounts of Fe^{2+} ; subsequently, As, $\text{Au}(\text{HS})^-$, and Fe^{2+} all interacted with each other to form an abundance of arsenian sulfides. This process was accompanied by the precipitation of solid solution Au (Au^+) and natural nanoscale Au (Au^0) [40].

6. Conclusions

- (1) Arsenian pyrite and arsenopyrite are the main Au-hosting minerals in the Bojitian Carlin-type Au deposit. Zoned pyrite and fine-grained pyrite are the two major types of arsenian pyrite, followed by framboidal, coarse-grained, and banded pyrite. In addition, some pyrites fill spaces in charcoal debris that consisted of plant screen pipes or conduit rubble. All the pyrites have complex origins, and all have been affected by hydrothermal activity.
- (2) Au is present in all five types of arsenian pyrite, but the zoned pyrite and the fine-grained pyrite are the main Au-hosting types. Both the cores and rims of the zoned pyrite contain Au, but the rims are the main host. Individual arsenopyrite grains and aggregates of arsenopyrite and arsenian pyrite also contain Au, with the former being the main type to host Au.
- (3) Au in the cores of the zoned pyrite probably exists mainly in the form of natural nanoscale Au (Au^0). In contrast, in the rims Au exists as solid solution

Au (Au^+), but also probably as natural nanoscale Au (Au^0). Au in the framboidal, banded, and coarse-grained varieties of pyrite exists both as natural nanoscale Au (Au^0) and as solid solution Au (Au^+). Au in the arsenopyrite exists in the form of gold solution (Au^+).

- (4) The Bojitian deposit was formed by As-bearing, H_2S -rich, low-to-medium-temperature fluids in a reducing environment. A theoretical model for the ore-forming process was developed.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank Drs. Wenchao Su and Yuping Liu from the Institute of Geochemistry, Chinese Academy of Sciences, China (Guiyang), for field work, and acknowledge the kind help of Engineer Wei Chen from the Guizhou Zijin Mining Co., Ltd., when collecting samples. This research project is supported jointly by the Natural Science Foundation of China (Grant no. 41373044), the Doctoral Program of the Ministry of Education of China (Grant no. 20130091130007), and the Independent Research Subject of State Key Laboratory for Mineral Deposits Research, Nanjing University (Grant no. ZZKT-201308).

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