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Trace element and REE geochemistry of the Zhewang gold deposit, southeastern Guizhou Province, China

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Abstract The quartz vein-type gold deposits are widely hosted by the Neoproterozoic (Xiajiang Group) epimetamorphic clastic rock series in southeastern Guizhou Province, China. The Zhewang gold deposit studied in this paper occurs in the second lithological member of the Pinglue Formation of the Xiajiang Group. Trace element geochemistry of host rocks, quartz veins and arsenopyrite has revealed that ore-forming fluid was enriched in sulphophile elements such as Au, Ag, As, Sb, Pb and Zn, and simultaneously concentrated some magmaphile elements such as W and Mo, which probably provides some evidence for multi-stage mineralization or overprinting of magmatic hydrotherm. Quartz veins and arsenopyrite were characterized by depletion in HFSE and enrichment in LREE. Hf/Sm, Nb/La and Th/La imply that the ore-forming fluid was probably a NaCl-H_2O solution system enriched in more Cl than F; Th/U values reflect the strong reducibility of the ore-forming fluid, coincident with the sulfide assemblages. The values of Co/Ni reflect that magmatic fluids may have partly participated in the ore-forming process and Y/Ho values have proved that the ore-forming fluid was associated with metamorphism and exotic hydrotherm which has reformed former quartz veins during late mineralization. The concentrations of REE, Eu anomalies and Ce anomalies of this deposit display that ore-forming elements mainly were derived from host rocks and possibly from a mixed deep source, and the ore-forming fluid was mixed by dominant metamorphic fluid and minor other sources. The physical-chemical conditions of ore-forming fluid changed from the initial stage to the late stage. The metamorphic fluid is responsible for the mineralization. Therefore, the Zhewang gold deposit is classified as a quartz vein-type gold deposit which may have been reformed by magmatic fluids during the late stage.

Key words arsenopyrite; trace element; REE; Zhewang gold deposit; southeastern Guizhou Province

1 Introduction

The quartz vein-type gold deposits are widely hosted by the Neoproterozoic (Xiajiang Group) epimetamorphic clastic rock series in southeastern Guizhou Province. Those gold deposits are obviously controlled by faults and folds, and commonly occur in the secondary anticlinal cores, interformational faulted zone structures and shear fracture zones, forming the conformable quartz vein-type gold deposits and shear fracture zone-type gold deposits. In southeastern Guizhou Province, the quartz vein-type gold deposits are well known for the Bake gold deposit, the Jinjing gold deposit, the Pingqiu gold deposit and so on. Since the 1930s, a series of productive activities and scientific research have been carried out, mainly including the following aspects: the geology and geochemistry of ore deposits, the origin of metallogenic materials and ore-forming fluids, the physical-chemical conditions, metallogenic temperature of gold mineralization, evolution history of tectonics, metallogenic dynamics, metallogenetic epoch, ore genesis, metallogenetic model and so on, and great achievements have been acquired (He Lixian et al., 1993; Yu Dalong, 1997; Wu Pan and Yu Dalong, 1997, 1998; Wu Pan et al., 2005; Zhang Jie et al., 1997, 1998; Sun Shijun and Pan Wenmao, 2002; Yang Guangzhong, 2005, 2006, 2009; Lu Huanzhang et al., 2005, 2006; Fang Weixuan et al., 2006; Chen Wenyi et al., 2006; Wang Shangyan et al., 2006; Wu Xueyi et al., 2006; Zhu Xiaoqing et al., 2006; Ma Xiaowen et al., 2007; Yang Ruidong et al., 2009; Zheng Jie et al., 2010, 2011; Wang Jiasheng et al., 2011; Zhang Xiaodong et al., 2011).

The occurrences of gold in the Zhewang gold deposit are dominated by native gold which exists in quartz veins and fissured gold which occurs in different sulfides (arsenopyrite, pyrite and so on) or fractured alteration zone. Due to the transformation of physical-chemical conditions, sulfides were precipitated from the ore-forming fluid during the process of mineralization. So, trace element and REE compositions of sulfides objectively reflect trace element and REE characteristics of ore-forming fluid. By analyzing the characteristics of trace elements and REEs of auriferous quartz veins, host rocks and monomineral (arsenopyrite), this paper attempts to discuss the probable source of metallogenetic materials and ore-forming fluid for the Zhewang gold deposit.

2 General geological features

Schematic regional geology of the Zhewang gold deposit is shown in Fig. 1. The deposit is located approximately 6 km southeast of Jinping County. The mine is situated in the southwestern part of the transition zone (southeastern Guizhou Province) between the Yangtze Platform and the fold belt of South China (Chen Wenyi et al., 2006), and controlled by the territorial Wenjiang anticline and Zhongling fault. Auriferous quartz veins were hosted along the core of the secondary anticline, interformational fracture zones and altered fault zones. Exposed regional strata mainly consist of the Fanzhao, Qingshuijiang, Pinglue and Longli formations of the Neoproterozoic Xiajiang Group which have experienced low-grade metamorphism. In addition, the Sinian, Cambrian, Permian and Quaternary strata are partly exposed in the area (Wu Pan and Yu Dalong, 1997; Yang Ruidong et al., 2009).

The exposed layer in the ore district belongs to the Pinglue Formation which consists of light grey, light mignonette thin-thick bedded siliceous sericite slate, silty sericite slate, interleaved metasandstone or lens of glutenite, which can be divided into three units. Gold-bearing quartz veins are mainly hosted by the grey silty sericite slate of the second number of the Pinglue Formation.

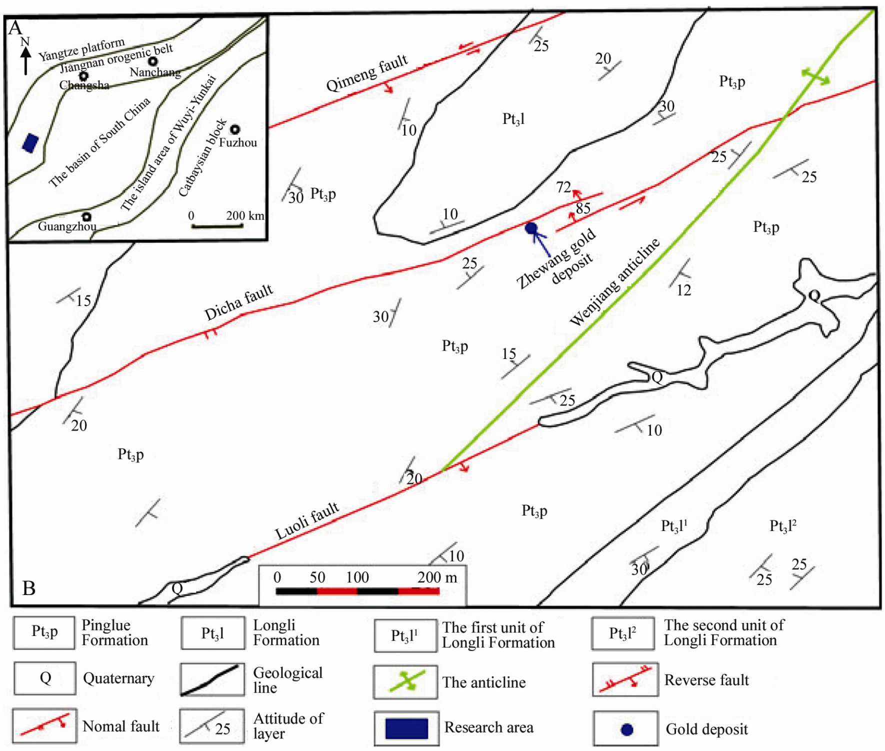

Fig. 1. Regionally geological map of the Zhewang gold deposit in southeastern Guizhou Province [A, B after Gu Xuexiang et al. (2003) and the regionally geological map of 1/200000 scale from the No. 108 Geological Team of the Bureau of Geology and Mineral Resources of Guizhou Province (1963), respectively].

Based on the occurrence characteristics of auriferous quartz veins, orebodies are obviously controlled by structures. Especially, high-grade orebodies occur in the convergence zone of polydirectional structures. The attitude of bedding quartz veins is consistent with that of the host rocks, and saddle orebodies occur in the core of the secondary anticline. At the same time, network and crumby quartz veins occur in the fractured zone, forming altered-type gold mineralization. Therefore, shear zones, folds and bedding quartz veins jointly constitute the "Trinity" metallogenetic model of auriferous quartz veins in southeastern Guizhou Province (Wu Xueyi et al., 2007).

Ore minerals include abundant arsenopyrite, and minor pyrite, galena, sphalerite, and gangue minerals include dominant quartz, minor chlorite and calcite. The Zhewang gold deposit exhibits idiomorph-hypautomorphic, xenomorphic, poikilitic, veiny interpenetration textures, and massive, disseminated, brecciform, saccharoidal, banded, mesh-vein structures. Based on the intersecting relationship of quartz veins and the textures and structures of ores and mineral assemblages, the mineralization can be divided into two stages: (1) native gold-arsenopyrite-pyrite-quartz stage, mainly with massive and disseminated textures. Ore minerals include native gold, arsenopyrite, pyrite, native gold independently occurs with visible gold, and quartz is commonly present as ivory macro-crystals; (2) native gold-sulfide-quartz stage, with mineralization occurring in the former quartz veins through supraposition metallogenesis. Quartz is smoky gray, arsenopyrite and pyrite are present as irregular strings. Besides, polymetallic sulfides of Cu, Pb and Zn were also precipitated from the fluids in this stage. Native gold was present in the form of micro-fine particles within the crystalline fractures of arsenopyrite, pyrite, galena and so on. Alterations observed in the deposit include silicification, sulphidation, argillization, carbonization, chloritization and brecciation. Gold mineralization of quartz veins is closely associated with silicification, sulphidation, argillization and brecciation. Especially, sulfidation is quite obvious at the contact site between host rocks and quartz veins, accompanied with strong gold concentration.

3 Sampling and analytical methods

In this paper, samples were collected from the ores (quartz veins) and altered host rocks from the dump, the mesh quartz veins and fractured rocks of altered shear zone, including four samples of gold-bearing quartz veins and three samples of host rocks. Sulfides closely associated with gold mineralization mainly contain arsenopyrite, and less pyrite, based on field petrographic observation and geochemical analysis. Arsenopyrite in quartz veins occurs with lumpy fine-grained aggregation. Arsenopyrite in altered host rocks is present as idiomorphic crystals. In addition, a lot of earthy limonite resulting from denudation and weathering from primary sulfides (e.g. arsenopyrite) can be found in this deposit. Single mineral samples of arsenopyrite [ZW-6(ds), ZW-7(ds), ZW-8 (ds)] were selected from quartz veins samples (ZW-6, ZW-7) and altered host rocks (ZW-8), respectively. All the samples were crushed into -200 meshes, and then sent to determine the concentrations of trace elements and rare-earth elements (REEs) by using ME-MS 61 and the contents of Au by using fire analysis (Au-AA23) at ALS-Chemex (Guangzhou) Co. Ltd.

4 Results and discussion

4.1 Geochemical characteristics of trace elements

The analytical results of trace elements for arsenopyrite, ores and host rocks from the Zhewang gold deposit are presented in Table 1 and the spider diagram normalized to upper crust average value (Taylor and McLennan, 1985) is shown in Fig. 2. As viewed from Table 1 and Fig. 2, arsenopyrites are characterized by obvious enrichment in common metallogenetic elements (Au, Ag, As, Sb, Pb, Zn, Co, Ni, W, and Mo) compared with the average values of the upper crust (Taylor and McLennan, 1985), and their enrichment coefficients vary from several to thousands of times, reflecting the geochemical affinity of trace elements (Mao Guangzhou et al., 2006). The contents of Au vary from 3.11×10^{-6} to 27.3×10^{-6}, averaging 12.71×10^{-6}, and the average enrichment coefficient is 7059; the contents of Ag change from 0.25×10^{-6} to 2.03×10^{-6}, averaging 0.973×10^{-6}, and the average enrichment coefficient is 19; the contents of Sb change from 365×10^{-6} to 442×10^{-6}, averaging 409×10^{-6}, and the average enrichment coefficient is 2050. Especially, the contents of W vary from 68.3×10^{-6} to 84.8×10^{-6}, and the average enrichment coefficient is up to 42.

Compared with arsenopyrite, in ores are concentrated metallogenetic elements such as Au, Ag, As, Sb, Co, and W, with lower contents of sulphophile elements, reflecting the geochemical affinity of trace elements. Host rocks are enriched in Au, Ag, As, Sb, Co, and W, but their enrichment strength is lower than that of arsenopyrite and ores in the mass, representing that mineralization gradually becomes exhausted after being far away from quartz veins. It is worthwhile to notice that the contents of Co, Ni, and W are higher than those reported or published results of quartz vein-type gold deposits in southeastern Guizhou Province, especially the contents of W are up to 760×10^{-6}. In this paper, the contents of Co, Ni, and W are similar to the data of trace elements from the Bake gold deposit (Zheng Jie et al., 2010).

Au, Ag, As, Sb, Pb, Zn, W, and Mo in arsenopyrite, ores and host rocks display great positive correlations which are obvious between Au and Ag, Pb, Zn, and Sb with Au, suggesting that the enrichment of Au, Ag, As, Sb, Pb, and Zn synchronously took place. In addition, high-temperature elements such as W and Mo show positive correlations with Au. Anomalies of W and Mo are often correlated with the activity of magmatic hydrothermal fluids (Yang Ruidong et al., 2009). Plentiful Caledonian, Indosinian and Yanshanian granites enriched in W and Mo were exposed in the adjacent areas, for instance, in northwestern Guangxi Province and western Hunan Province (Liu Yingjun and Ma Dongsheng, 1987; Lin Wenchuang, 1990; Kuang Wenlong et al., 2004; Li Wuwei et al., 2010; Wang Shangyan et al., 2006). W and Mo values of the epimetamorphic Xiajiang Group are close to the upper crust average value (Yang Ruidong et al., 2009; Zhang Xiaodong et al., 2011). Therefore, high positive anomalies of W and Mo indicate that magmatic hydrothermal fluids originated from the deep crust and W and Mo may have probably taken part in the mineralization or overprinted and interacted with primary quartz veins and sulfides. The trace element composition of arsenopyrite possibly reflects the element features of ore-forming fluids (Mao Guangzhou et al., 2006). It can be concluded that ore-forming fluids of this deposit were enriched in sulphophile elements such as Au, Ag, As, Sb, Pb and Zn and simultaneously concentrated high-temperature elements such as W and Mo. At the same time, enrichment in W and Mo reflects multi-stage mineralization or overprinting of magmatic hydrothermal fluids.

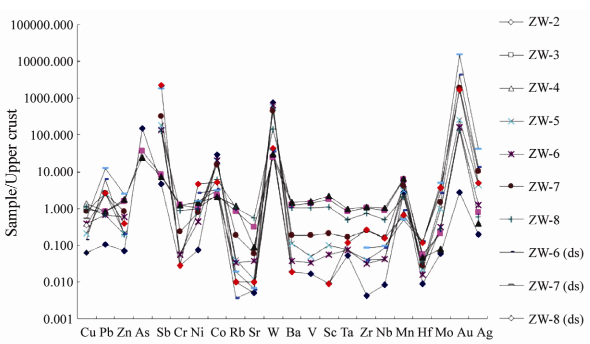

Fig. 2. The spider diagram of trace elements in arsenopyrites, ores and host rocks from the Zhewang gold deposit.

Recent studies suggest that hydrothermal fluids enriched in Cl can effectively concentrate light REE but deplete HFSE, whose values of Hf/Sm, Nb/La and Th/La are usually less than 1; and hydrothermal fluids enriched in F can synchronously concentrate light REE and HFSE, whose values of Hf/Sm, Nb/La and Th/La are usually more than 1 (Oreskes and Einaudi, 1990; Bi Xianwu et al., 2004; Mao Guangzhou et al., 2006). According to the analytical results (Tables 1 and 2), arsenopyrite, quartz veins and host rocks of the Zhewang gold deposit are obviously enriched in light REE and universally depleted in HFSE, with the values of Hf/Sm, Nb/La and Th/La being less than 1 except two of Hf/Sm values. Previous fluid inclusion studies (Yu Dalong, 1993, 1997) for the Bake, Kengtou and Xiada gold deposits located in the same metallogenetic belt around the Zhewang gold deposit suggested that the ore-forming fluids of those gold deposits belong to the $NaCl-H_2O$ hydrothermal system. Based on the above-mentioned evidence, it is inferred that ore-forming fluids of the Zhewang gold deposit belong to the $NaCl-H_2O$ hydrothermal system enriched in Cl instead of F.

The Th/U values of ores, minerals and host rocks reflect the oxidation-reduction features of the geological environment (Jones and Manning, 1994): (1) the Th/U value of the oxidizing environment is less than 0.75; (2) Th/U=0.75—1.25 represents a transitive anoxic environment; (3) the value of Th/U of the reductive environment is greater than 1.25. The Th/U values of arsenopyrite, ores and host rocks are greater than 1.2 and vary from 3.00 to 5.59, illustrating relatively strong reducibility of the metallogenetic environment. The Th/U value and mineral assemblage of sulfides jointly display the strong reducibility of ore-forming fluids.

The trace element composition of minerals reflects the forming conditions of auriferous quartz veins to some extent, being regarded as a tracer of genesis. The geochemical parameters of Co, Ni are similar to those of Fe, and Fe in arsenopyrite can be replaced by Co and Ni through isomorphism. A large number of Co/Ni distributions of pyrite and arsenopyrite from different gold deposits have been studied in order to constrain ore genesis (Mao Guangzhou et al., 2006; Zhou Jiayun et al., 2008; Zheng Jie et al., 2010). Generally, the Co/Ni value is positively correlated with the formation temperature of minerals (Sheng Jifu et al., 1999). In this paper, the Co/Ni values of ores and arsenopyrite are shown in Fig. 3. Co/Ni distribution spots of ores and arsenopyrites of the Zhewang gold deposit are located outside the margins of the volcanic area, hydrothermal area and sedimentary area, indicating that the metallogenetic process has experienced three stages. The discussion is similar to the three-stage metallogenetic model of gold deposits hosted by metamorphic clasolite (Wang Xiuzhang et al., 1995), namely, sedimentation stage, regional metamorphism stage and Au mineralization stage.

The magnitude of Co/Ni value represents pyrites and arsenopyrites of different geneses according to previous studies (Bralia et al., 1979). The Co/Ni values of arsenopyrite from the Zhewang gold deposit are less than 1, showing relatively low mineralization temperature, which is basically consistent with the study of fluid inclusions for metallogenetic temperature of the Zhewang gold deposit (Wu Pan and Yu Dalong, 1997). The Co/Ni values of arsenopyrite vary from 0.63 to 0.96, reflecting that medium-low temperature fluid has leached and inherited the metallogenetic elements from the host rocks. The Co/Ni value of arsenopyrite from host rocks is 0.54, having the characteristics of Co/Ni value of sedimentary gold deposits and also reflecting the inherited relationship between arsenopyrite and host rocks. The Co/Ni values of ores are far more than 1.5, showing relatively high metallogenetic temperature and the features of magmatic hydrothermal fluids (Zhao Hongjun et al., 2005; Wang Shangyan et al., 2006). So, the Co/Ni values of ores have revealed that the overprinting of magmatic hydrothermal fluids probably took place after mineralization. The Co/Ni values of host rocks ranging from 0.70 to 3.13 synthetically show the multi-genesis mineralization characteristics. Therefore, the Co/Ni values of this deposit suggest that the ore-forming fluid belongs to medium-low temperature hydrotherm, and the superposition of magmatic hydrothermal fluids probably took place during the late stage of mineralization.

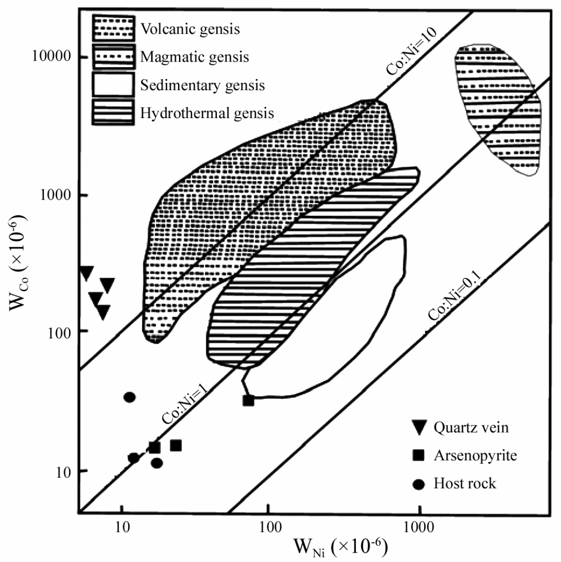

Fig. 3. Co/Ni distribution diagram of arsenopyrites, ores and host rocks from the Zhewang gold deposit (Boundaries of different geological settings are defined after Bajwah et al., 1987 and Brill, 1989).

Y and Ho generally have similar geochemical behaviors, and the Y/Ho ratio can keep relatively stable in many geological processes. So using Y/Ho to discuss the origin of ore-forming fluids has been proved effective, and numerous researches on Y/Ho values for ore-forming fluids and submarine hydrothermal fluids have been reported (Bau et al., 1997; Bau and Dulski, 1995, 1999; Douville et al., 1999; Bi Xianwu et al., 2004; Mao Guangzhou et al., 2006). In this paper, the Y/Ho values of arsenopyrite, ores and regional metamorphic rocks (Fig. 4) have been compared with those of modern submarine hydrothermal fluids to possibly constrain the genesis of this deposit.

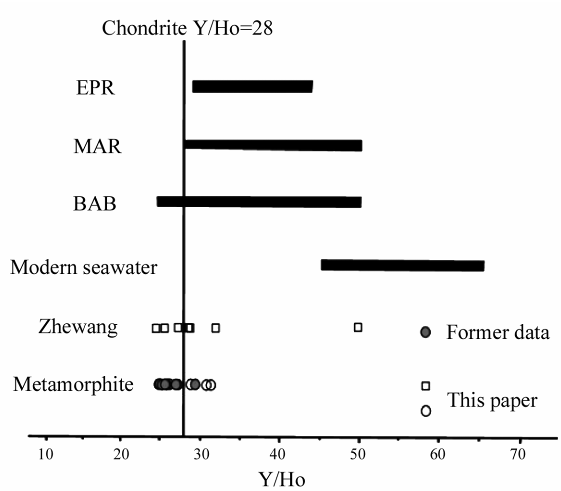

Fig. 4. Y/Ho ratios of arsenopyrites, ores and host rocks from the Zhewang gold deposit. Modern submarine hydrothermal fluids and seawater. Data of hydrothermal fluids and modern seawater, BAB (Back-Arc Basin), MAR (Middle-Atlantic Ridge) and EPR (East Pacific Ridge) from Bau et al., 1997; Bau and Dulski, 1999; Douville et al., 1999，the data of metamorphic rocks from Yang Ruidong et al., 2009.

According to Table 1 and Fig. 4, the Y/Ho values of arsenopyrite range from 27.50 to 28.18, and the Y/Ho value of arsenopyrite from host rocks is 24.52. The Y/Ho values of ores basically vary from 25.45 to 32.00 except ZW-2 (Y/Ho=50) whose Y/Ho value obviously differs from others' Y/Ho values. The Y/Ho values of arsenopyrite and ores are similar to those of the regional metamorphic rocks (Yang Ruidong et al., 2009; Zhang Xiaodong et al., 2011), reflecting the metamorphism is responsible for gold mineralization. Anomalous Y/Ho value of ZW-2 revealed that early quartz veins were probably overprinted and reformed by exotic hydrothermal fluids during late mineralization process. The Y/Ho values of the Zhewang gold deposit suggested that ore-forming fluids were closely associated with metamorphism and exotic hydrothermal fluids overprinted and reformed early quartz veins during late mineralization.

Table 1 The trace element concentrations ($\times10^{-6}$) and characteristic parameters for arsenopyrites, quartz veins and host rocks from the Zhewang gold deposit

Element	Ore				Arsenopyrite			Host rock		
	ZW-2	ZW-5	ZW-6	ZW-7	ZW-6(ds)	ZW-7(ds)	ZW-8(ds)	ZW-3	ZW-4	ZW-8
Cu	1.60	5.30	9.60	20.50	3.50	12.90	8.60	22.80	33.80	27.40
Pb	2.10	52.50	13.40	52.50	124.50	250.00	50.90	16.80	16.90	13.30
Zn	5.00	15.00	42.00	60.00	14.00	171.00	27.00	107.00	122.00	14.00
As	223.00	10000.00	>10000.00	>10000.00	>10000.00	>10000.00	>10000.00	55.80	36.70	>10000.00
Sb	0.92	36.00	27.70	65.10	422.00	363.00	442.00	1.65	1.45	25.20
Cr	1.00	2.00	2.00	8.00	<1.00	<1.00	1.00	43.00	44.00	30.00
Ni	1.50	16.50	8.70	15.50	52.10	31.40	92.60	20.50	29.60	19.90
Co	286.00	193.00	203.00	151.50	32.90	30.00	50.40	22.50	20.60	62.30
Rb	1.10	4.40	3.70	20.20	0.40	2.10	1.10	94.80	129.00	113.00
Sr	1.70	4.20	13.00	20.40	2.10	2.30	3.50	107.50	31.10	196.00
W	1520.00	1160.00	1250.00	910.00	68.30	78.90	84.80	47.80	61.80	289.00
Ba	10.00	60.00	20.00	100.00	10.00	10.00	10.00	660.00	790.00	570.00
V	1.00	3.00	2.00	11.00	<1.00	<1.00	<1.00	84.00	91.00	61.00
Sc	0.10	1.10	0.60	2.30	<0.10	0.10	0.10	19.40	23.80	12.40
Ta	0.05	0.07	0.07	0.16	<0.05	<0.05	0.11	0.80	0.93	0.46
Zr	0.80	7.30	5.90	46.90	7.40	15.40	49.20	192.00	208.00	139.00
Nb	0.10	0.50	0.50	1.90	1.00	1.10	1.90	10.30	12.30	5.80
Mn	169.00	187.00	269.00	241.00	53.00	30.00	40.00	359.00	390.00	123.00
Hf	0.05	0.13	0.09	0.16	0.70	0.66	0.66	0.32	0.27	0.19
Mo	0.09	1.44	0.47	2.16	3.98	7.12	5.45	0.31	0.12	0.42
Ho	0.01	0.11	0.10	0.24	0.04	0.11	0.73	1.53	0.98	0.95
La	0.50	2.20	1.10	7.80	1.30	3.30	18.30	84.60	51.90	49.40
Sm	0.06	0.60	0.55	1.66	0.29	0.56	3.39	14.45	8.18	8.44
Th	0.06	0.60	0.39	3.13	0.57	1.51	4.95	14.15	14.90	10.45
U	0.05	0.20	0.09	0.68	0.13	0.35	0.92	2.95	2.83	1.87
Y	0.50	2.80	3.20	6.80	1.10	3.10	17.90	43.00	30.80	29.00
Au	0.01	0.46	0.29	3.53	7.71	27.30	3.11	<0.01	<0.01	0.25
Ag	0.01	0.22	0.06	0.51	0.64	2.03	0.25	0.04	0.02	0.03
Co/Ni	190.67	11.70	23.33	9.77	0.63	0.96	0.54	1.10	0.70	3.13
Hf/Sm	0.83	0.22	0.16	0.10	2.41	1.18	0.19	0.02	0.03	0.02
Nb/La	0.20	0.23	0.45	0.24	0.77	0.33	0.10	0.12	0.24	0.12
Th/La	0.12	0.27	0.35	0.40	0.44	0.46	0.27	0.17	0.29	0.21
Y/Ho	50.00	25.45	32.00	28.33	27.50	28.18	24.52	28.10	31.43	30.53
Th/U	>1.20	3.00	4.33	4.60	4.38	4.31	5.38	4.80	5.27	5.59

Based on the above-mentioned geochemistry of trace elements, it is concluded that reductive ore-forming fluids are enriched in Cl and numerous metallogenetic elements such as Au, Ag, As, Sb, Pb, and Zn are associated with metamorphism. It is possible that magmatic hydrothermal fluids enriched in high-temperature elements such as W and Mo reformed early quartz veins during the late stage. During the migration of ore-forming fluids along faults, Si, Au, Ag, As, Sb, Pb and Zn were crystallized and precipitated from the fluids because of the decrease of temperature and pressure which would lead to the saturation of metal elements, forming auriferous quartz veins containing multiplex sulfides. Sulfides and quartz veins partly inherited the trace element characteristics of their host rocks. During the advanced stage, atmospheric water may have been involved in the fluids, but the nature of ore-forming fluids enriched in Cl did not change. Magmatic hydrothermal fluids enriched in magmaphile elements overprinted and reformed former quartz veins and sulfides, making early quartz veins and sulfides enriched in W and Mo and form extraordinary anomalies of Co/Ni and Y/Ho values. Of course, the factual metallogenetic process is more complicated than the above-mentioned process, the Zhewang gold deposit has probably overprinted more multi-stage mineralization. Therefore, the Zhewang gold deposit is classified as a quartz vein-type gold deposit, which may be reformed by magmatic fluids during the late stage, and gold mineralization is closely associated with metamorphism.

4.2 REE geochemical characteristics

The REE data of the Zhewang gold deposit are listed in Table 3 and the REE distribution patterns are shown in Fig. 5. The chondrite-normalized REE patterns of arsenopyrites, quartz veins and host rocks are obviously lightly oblique-type patterns except ZW-6, and the minerals are enriched in LREE, but depleted in HREE.

The total REE concentrations of host rocks are on the order of 232.78×10^{-6} to 356.87×10^{-6}, keeping uniform LREE-enrichment patterns (La_N/Yb_N=9.51 to 12.67, ∑LREE/∑HREE=9.91 to 11.27), flat HREE patterns (Gd_N/Yb_N=1.28 to 1.95), being greatly comparable with those of the Neoproterozoic Xiajiang Group (Yang Ruidong et al., 2009).

The REE characteristics of sulfides in auriferous quartz veins are controlled by the REE characteristics of fluid media, from which the minerals were crystallize and precipitated. So the REE composition of sulfides can greatly reflect the REE composition of ore-forming fluids. The total REE concentrations of arsenopyrites [ZW-6(ds), ZW-7(ds)] of quartz veins are relatively low, on the order of 7.77×10^{-6} to 18.01×10^{-6}, showing LREE enrichment (∑LREE/∑HREE=8.48 to 12.40, La_N/Yb_N=6.36 to 6.74) with flat HREE patterns (Gd_N/Yb_N=0.56 to 1.29). The total REE concentrations of arsenopyrites ZW-8(ds)] from host rocks are up to 91.49×10^{-6}, with LREE enrichment (∑LREE/∑HREE=12.33, La_N/Yb_N=7.05) with flat HREE patterns (Gd_N/Yb_N=4.15). The REE patterns of ZW-7(ds) and ZW-8(ds) are consistent with those of host rocks and regional metamorphic rocks (Yang Ruidong et al., 2009), suggesting metal elements were derived from epimetamorphic rocks (the Neoproterozoic Xiajiang Group). However, the REE pattern of ZW-6(ds) distinctly is different from other patterns, indicating that other fluids have probably participated in gold mineralization.

The total REE concentrations of quartz veins range from 2.14×10^{-6} to 40.03×10^{-6}. According to the REE patterns, two types can be distinguished: lightly oblique patterns and flat type. Lightly oblique patterns are characterized by relatively high LREE (∑LREE/∑HREE=6.38 to 7.41, La_N/Yb_N=5.30 to 6.74) with flat HREE patterns (Gd_N/Yb_N=1.29 to 1.64), similar to those of host rocks and regional epimetamorphic rocks, implying that metal elements were derived from the host rocks. ZW-6 is a typical example of the flat type, the total REE concentrations are 8.37×10^{-6}, ∑LREE/∑HREE=2.88, La_N/Yb_N=2.06, La_N/Sm_N=1.26, Gd_N/Yb_N=1.37, obviously differing from those of others samples and regional epimetamorphic rocks, being close to those of the upper mantle (∑HREE/∑REE=0.2528, ∑LREE/∑HREE=2.8) and lower crust (∑HREE/∑REE=0.2335, ∑LREE/∑HREE=3.28) (Tang Wenchun and Zhu Huipai, 2008). The REE characteristics of ZW-6 suggest the fluids derived from the deep crust possibly took part in the mineralization or reformed the deposit during late mineralization.

The REE concentrations and patterns imply that metallogenetic materials from this mine were derived from host rocks. Metamorphic fluids are dominant, and former quartz veins may have been overprinted and reformed by the fluids derived from the deep crust during late mineralization.

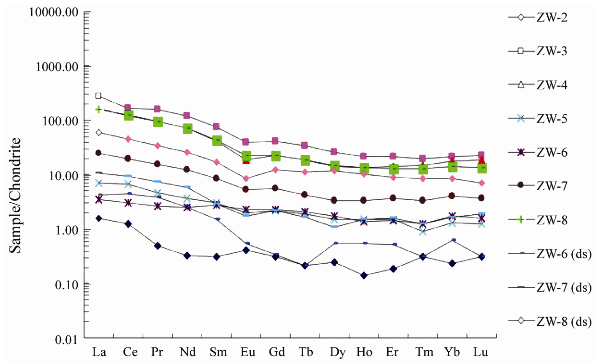

Fig. 5. The chondrite-normalized REE distribution patterns of arsenopyrite, ores and host rocks from the Zhewang gold deposit.

In general, Eu is a significantly multivalent element. Under relatively oxidizing conditions, Eu^{3+} can keep stable in the solution with other REEs, but it can be reduced to Eu^{2+} and separated from the REE system under a relatively reducing environment, and Ce displays an opposite trend. Therefore, the Eu-anomalies and Ce-anomalies are considered as the tracer of oxidation-reduction environment (Constantopoulos, 1999; Tang Wenchun and Zhu Huipai, 2008; Zheng Jie et al., 2011). The Eu and Ce anomalies of arsenopyrite and quartz veins from the Zhewang gold deposit can be divided into two types: (1) slightly positive Ce-anomaly (δCe=0.97 to 1.16) and moderately negative Eu-anomaly (δEu=0.58 to 0.89) type, indicating that arsenopyrite and quartz veins were formed under strongly reductive conditions during the early stage; (2) slightly positive Ce-anomaly (δCe=1.18) and significantly positive Eu-anomaly type (ZW-2), indicating that the ore-forming fluids display weak reducibility relative to the former type. The difference between the two types implies that the physical-chemical conditions of ore-bearing fluids changed from the initial stage to the late stage.

Gold deposits in southeastern Guizhou Province are hosted by the Neoproterozoic Xiajiang Group interleaving numerous tuffs where gold concentrations are relatively high (Li Yingshu et al., 2004; Lu Huanzhang et al., 2006). The REE contents, REE patterns and Eu-anomalies and Ce-anomalies of the Zhewang gold deposit imply that metallogenetic elements mainly come from host rocks and possibly a mixed deep source, and ore-forming fluids dominantly contain metamorphic fluids and minor amounts come from other sources. The physical-chemical conditions of ore-bearing fluids changed from the early stage to the late stage.

The analytial results of trace elements and REEs suggest mineralization of the Zhewang gold deposit is closely associated with metamorphism, probably overprinted and reformed by magmatic fluids after mineralization.

5 Conclusions

(1) It can be concluded that ore-forming fluids of this deposit are enriched in sulphophile elements (Au, Ag, As, Sb, Pb, and Zn) and simultaneously concentrated magmaphile elements (W and Mo). At the same time, W and Mo enrichment reflects multi-stage mineralization or overprinting and interaction of magmatic hydrothermal fluids.

(2) According to the analytical results, arsenopyrite, ores and host rocks of the Zhewang gold deposit are obviously enriched in light REEs and universally depleted in HFSE, the values of Hf/Sm, Nb/La and Th/La are less than 1 except two of the Hf/Sm values, showing that the ore-forming fluids of the Zhewang gold deposit belong to the NaCl-H_2O hydrothermal system enriched in Cl than F.

(3) The Th/U values and mineral association of sulfides jointly display the strong reducibility of ore-forming fluids.

(4) The high concentrations of W and Mo and the values of Co/Ni indicate that magmatic fluids may have participated in the ore-forming process. Y/Ho values have proved that metamorphic fluid is responsible for gold mineralization.

(5) The contents of REE, patterns and Eu-anomalies and Ce-anomalies imply that the metallogenetic elements are mainly derived from host rocks and a possibly mixed deep source. Ore-forming fluids contained dominantly metamorphic fluid and minor other sources. The physical-chemical conditions of ore-bearing fluids have changed from the early stage to the late stage.

Table 2 REE concentrations ($\times10^{-6}$) and characteristic parameters for arsenopyrites, quartz veins and host rocks from the Zhewang gold deposit

Element	Ore				Arsenopyrite			Host rock		
	ZW-2	ZW-5	ZW-6	ZW-7	ZW-6(ds)	ZW-7(ds)	ZW-8(ds)	ZW-3	ZW-4	ZW-8
La	0.50	2.20	1.10	7.80	1.30	3.30	18.30	84.60	51.90	49.40
Ce	1.00	5.50	2.50	16.10	3.60	7.70	36.70	132.00	96.90	99.90
Pr	0.06	0.56	0.32	1.91	0.46	0.92	4.24	19.25	11.80	11.40
Nd	0.20	2.20	1.50	7.40	1.50	3.50	15.90	71.00	44.10	43.00
Sm	0.06	0.60	0.55	1.66	0.29	0.56	3.39	14.45	8.18	8.44
Eu	0.03	0.15	0.17	0.40	0.04	0.13	0.63	2.86	1.38	1.67
Gd	0.08	0.57	0.61	1.44	0.09	0.56	3.14	10.85	5.86	5.87
Tb	0.01	0.09	0.10	0.20	0.01	0.08	0.54	1.66	0.90	0.90
Dy	0.08	0.48	0.56	1.06	0.18	0.36	3.77	8.33	4.63	4.75
Ho	0.01	0.11	0.10	0.24	0.04	0.11	0.73	1.53	0.98	0.95
Er	0.04	0.32	0.31	0.76	0.11	0.34	1.90	4.48	2.91	2.71
Tm	0.01	0.03	0.04	0.11	0.01	0.04	0.27	0.64	0.48	0.41
Yb	0.05	0.28	0.36	0.83	0.13	0.35	1.75	4.50	3.68	2.94
Lu	0.01	0.04	0.05	0.12	0.01	0.06	0.23	0.72	0.60	0.44
∑REE	2.14	13.13	8.27	40.03	7.77	18.01	91.49	356.87	234.30	232.78
∑LREE	1.85	11.21	6.14	35.27	7.19	16.11	79.16	324.16	214.26	213.81
∑HREE	0.29	1.92	2.13	4.76	0.58	1.90	12.33	32.71	20.04	18.97
∑LREE/∑HREE	6.38	5.84	2.88	7.41	12.40	8.48	6.42	9.91	10.69	11.27
δCe	1.18	0.76	0.91	1.16	1.00	0.98	0.98	1.12	1.05	0.97
δEu	1.32	0.67	0.58	0.77	0.89	0.77	0.69	0.59	0.70	0.58
$(La/Yb)_N$	6.74	12.67	9.51	5.30	2.06	6.34	11.33	6.74	6.36	7.05
$(La/Sm)_N$	5.24	3.68	3.99	2.31	1.26	2.96	3.68	2.82	3.71	3.40
$(Gd/Yb)_N$	1.29	1.95	1.28	1.64	1.37	1.40	1.61	0.56	1.29	1.45

(6) The analytical results of trace elements and REEs suggest mineralization of the Zhewang gold deposit is closely associated with metamorphism, probably overprinted and reformed by magmatic fluids after mineralization.

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