

Article

Element Migration of Mineralization-Alteration Zones and Its Geological Implication in the Beiya Porphyry–Skarn Deposit, Northwestern Yunnan, China

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Abstract: Porphyry and the associated skarn-type deposit is one of the most important types of ore deposits worldwide, which usually exhibit significant zoning of mineralization-alteration, but the research on element migration in these mineralization-alteration zones is relatively weak. The Beiya porphyry–skarn gold-polymetallic deposit is a super-large Cenozoic deposit located in the Sanjiang metallogenic belt, northwestern Yunnan, China. In this paper, through a detailed analysis of mineralization and alteration zoning and its element migration regularity, the findings are as follows: (1) Three types of hydrothermal alteration—porphyry alteration, contact alteration, and wall-rock alteration—are developed, and porphyry alteration includes potassic, phyllic, propylitic, and argillic alteration; (2) five types of mineralization—porphyry-type Cu–Au–(Mo), skarn-type Au–Fe–(Cu), hydrothermal vein-type Au–Fe, distal hydrothermal-type Pb–polymetallic, and oxidizing-leaching enriched-type Au—occur in a diversity of forms, which are dominantly controlled by structures and lithologies; (3) concentric-banded mineralization-alteration zones are exhibited centrally from the alkaline porphyry outward or upward, namely [porphyry alteration] potassic → phyllic → propylitic → argillic → [contact alteration] skarnitization–marbleization → [wall-rock alteration] marbleization–silicification–calcitization; (4) porphyry-type mineralization predominantly forms within potassic and phyllic zones, while skarn-type mineralization occurs in contact alteration zones, and proximal and distal hydrothermal (vein)-type mineralization are commonly distributed in marbleization–silicification–calcitization alteration zones; and (5) element migration analysis demonstrates a significantly lateral and vertical zoning in the metallogenic element association of Cu–Mo → Cu–Au → Au–Fe–Cu → Au–Fe → Pb–Zn–Au–Ag–Fe from alkaline porphyry outward to the wall-rock. The mineralization-alteration zoning model indicates the Beiya deposit has similar mineralization and alteration zone characteristics to the typical porphyry copper system; and element migration within mineralization-alteration zones provides new scientific information for understanding the metallogenic regularity and prospecting at Beiya, as well as the similar types of deposits in the Sanjiang metallogenic belt and elsewhere in the world.

Keywords: element migration; mineralization-alteration zone; porphyry copper system; Beiya porphyry–skarn deposit; Sanjiang metallogenic belt



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1. Introduction

Porphyry deposits are important sources of the metals Cu, Mo, Au, Ag, and Re [1–3]; they are formed as a result of dynamic interactions between magmatic, hydrothermal, and tectonic processes [4,5]. These deposits exhibit a particular mineralization and alteration

zoning that commonly comprises sodic–calcic, potassic, phyllic (sericitic), propylitic (chloritic–epidotic–carbonation), and (advanced) argillic, as well as greisen and skarn [2,6–9]. Hydrothermal alteration minerals and assemblages are zoned spatially, temporally, and thermally [2,9]: (1) sodic–calcic alteration usually occurs at the deepest level but is poorly preserved or uncommon [2]; potassic alteration is centrally located and deeper and is overlain by phyllic alteration, while (advanced) argillic alteration forms near the surface and generally overlaps the potassic and phyllic zones; propylitic alteration can develop at deep to shallow parts surrounding the central zones of potassic, phyllic, and argillic alteration—it may also grade downward into deeper zones of sodic–calcic alteration or upward into the argillic zone; skarn is commonly generated in contact with wall-rocks; (2) in general, these alteration types form progressively younger upward or outward [2]; and (3) these alterations are the result of the declining temperature of hydrothermal fluids [2]. These hydrothermal alterations record important information of ore-forming processes and provide the basis for the exploration of porphyry deposits [10–12]. For instance, potassic and phyllic alteration are predominantly associated with sulfide mineralization, whereas propylitic and argillic alteration are sulfide-free or contain minor amounts of sulfides [2,6,9]. Hydrothermal alteration is characterized by ionic metasomatism that consists of alkali metasomatism, hydrolytic (or acidic) reactions, oxidation/reduction reactions, and hydration–carbonation reactions, among others [9]. Moreover, element gains and losses always occur during metasomatic processes. Investigating the element migration associated with hydrothermal alteration has crucial significance for the establishment of mineralization and alteration zoning and for a deep understanding of the ore-forming process [13–15]. However, the element migration characteristics in distinctive mineralization and alteration zones of porphyry deposits are relatively unclear and lack a detailed case study.

The Beiya gold-polymetallic deposit is typical and representative of Cenozoic porphyry–skarn-type deposits in the Sanjiang metallogenic belt, northwestern Yunnan, China, with gold reserves of more than 200 tonnes and a gold grade of about 2.45 g/t [16]. Three stages of magmatic activities are mainly developed at Beiya: (1) quartz albite porphyry (QBP) and lamprophyre are formed in 65–60 Ma [17,18]; (2) quartz syenite porphyry (QSP) or monzogranitic porphyry (MGP) are formed at about 37–34 Ma [19–22]; and (3) there is 3.78–3.66 Ma of biotite syenite porphyry (BSP) [17]. The Re–Os isotope ages of molybdenite are 36–34 Ma [21,22], indicating that mineralization is closely related to QSP or MGP in the late Paleogene, and the sources of ore-forming fluids and materials are mainly derived from magma [23–26]. Five types of mineralization—porphyry, skarn, hydrothermal vein, stratabound, and supergene-enriched—are well developed in the Beiya deposit [16,25–30] and are intensely controlled by various structures and lithologies [16,27,30]. There are three main types of hydrothermal alteration—porphyry alteration, contact zone alteration, and wall-rock alteration—that occur in the Beiya deposit [16,19], and He et al. [16] proposed the characteristics of a metallogenic element zone. Nevertheless, the element migration of these mineralization–alteration zones has not been discussed.

In this paper, we identify the various types of mineralization and alteration and their occurrence features, carry out element migration regularity of different mineralization–alteration zones, and then establish the model of mineralization and alteration zoning, which provides new understandings of metallogenic regularity and a scientific basis for prospecting prediction of the Beiya deposit (Figure 1), as well as the similar porphyry deposits in the region and elsewhere in the world.

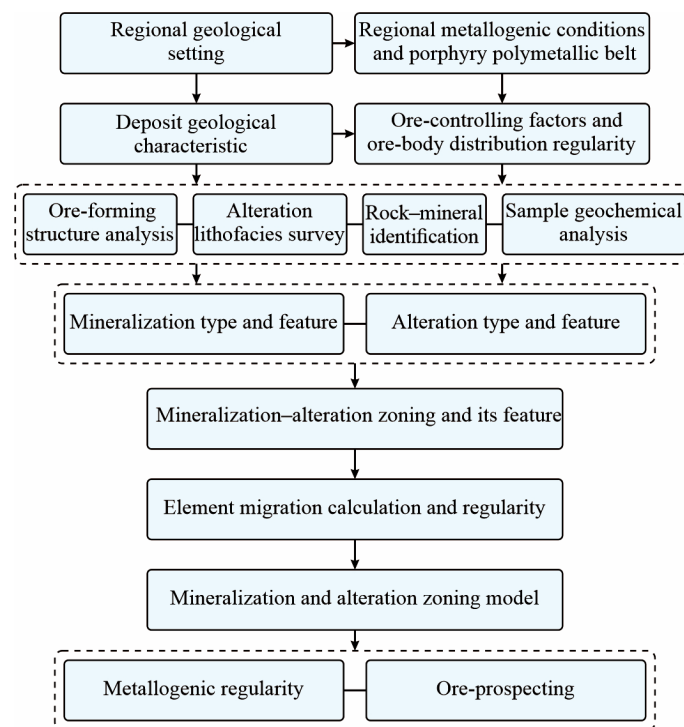


Figure 1. The framework plot of the study in the Beiya deposit.

2. Regional and Deposit Geology

The Beiya porphyry–skarn gold-polymetallic deposit is located in the middle part of Jinshajiang–Ailaoshan alkaline porphyry belt, on the western margin of the Yangtze Plate, where there is a combination of several geotectonic units (Figure 2a). The Jinshajiang–Ailaoshan Fault, the Honghe Fault, the Chenghai Fault, and the Lijiang–Muli Fault are a few examples of regional deep faults dispersed in neighboring areas (Figure 2a). These faults restrict the evolution of geological structures, magmatic activities, and mineralization in the area, particularly the formation and distribution of the Cenozoic alkaline porphyry and its genetically related porphyry-type polymetallic deposits.

The exposed strata at Beiya are composed of the Permian Emeishan Formation ($P_3\beta$) of dark-green basalts, the Early Triassic Qingtianbao Formation (T_1q) of amaranth sandstones, the Middle Triassic Beiya Formation (T_2b), and the Quaternary sediments (Q_1s , Q_p , and Q_h) (Figure 2b). The primary wall-rock of magmatic rocks and ore-bodies is the Beiya Formation, which is composed mainly of light-grey to dark-grey limestones and dolomites.

Structural activities are intense in the Beiya deposit. The SN-trending Beiya syncline, along with the dominant SN- and EW-trending faults, form the structural framework (Figure 2b). In addition, the secondary faults and fractures in various directions are developed. These structures together constitute a fold-fault-joint rock- and ore-controlling structural system [27,31,32], which controls the emplacement of alkaline porphyries and the formation and distribution of ore-bodies [16,30,31].

The Beiya deposit has three stages of alkaline porphyries, as previously mentioned. Most of these alkaline porphyries have a small scale, and their extended direction is primarily in the SN and EW orientations (Figure 2b). The geochemical characteristics of these porphyries indicate that they are silicon-supersaturation and high-K alkali-rich porphyries, which originated from the deep crust-mantle interaction caused by the intense tectonic deformation in the collision and orogeny of the Indo-Eurasian plates [17–19,21].

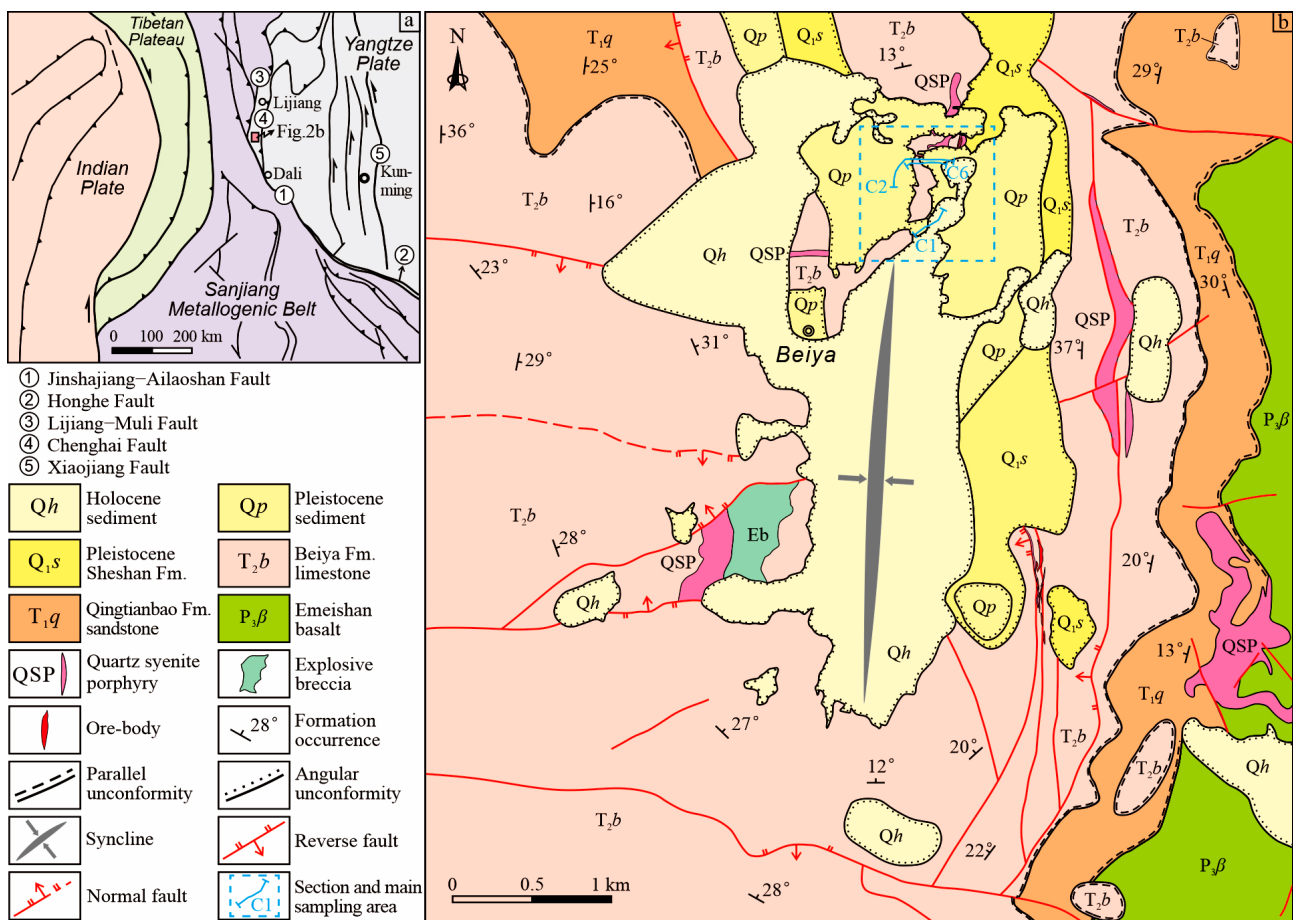


Figure 2. The regional geological setting (a) and geology of the Beiya deposit (b) (modified after Liu et al. [27]).

3. Samples Selected and Analytical Methods

The analysis of whole-rock major and trace elements was performed on 77 samples mostly collected from the measured geological sections (Figures 3 and 4) to study the element migration in different mineralization-alteration zones. These samples include the fresh and altered/mineralized limestones from the Beiya Formation, the exoskarns (protoliths are limestones), the unaltered quartz syenite porphyries, the altered quartz syenite porphyries (from potassic, phyllic, propylitic, and argillic alteration, respectively), and the endoskarns (protoliths are quartz syenite porphyries) (Table 1). To ensure the initial chemical compositions of the fresh limestone and the unaltered quartz syenite porphyry, these samples were collected from the periphery of the mining area to avoid the effects of hydrothermal alteration or mineralization. The altered samples were subjected to extensive macroscopic and microscopic rock-mineral identification, as well as electron probe microanalysis of typical minerals [33] to determine the types and characteristics of alteration and/or mineralization.

Table 1. The average geochemical characteristics of selected samples from the Beiya deposit.

Elements (10 ^{−6})/ Oxides (wt.%)	Al ₂ O ₃	CaO	Fe ₂ O ₃ [*]	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	W	Sn	Mo	Bi	Cu	Au	Ag	
UL (<i>n</i> = 6)	0.60	34.64	0.43	0.12	17.67	0.02	0.08	0.050	0.72	0.04	0.90	1.30	1.00	0.10	3.60	0.01	0.02	
AML (<i>n</i> = 14)	2.29	19.50	16.21	0.44	5.02	1.28	0.04	0.053	6.79	0.20	21.69	6.80	6.17	99.32	1540.00	3.45	15.70	
EXS (<i>n</i> = 2)	1.53	14.10	30.24	0.75	9.92	0.26	0.01	0.040	8.48	0.12	158.50	11.50	8.04	30.40	615.00	0.57	5.73	
UQSP (<i>n</i> = 3)	16.98	0.18	2.70	7.11	0.33	0.04	0.33	0.060	67.78	0.33	2.50	1.83	0.73	0.27	14.27	0.01	0.66	
PZ (<i>n</i> = 13)	8.60	0.10	10.53	7.68	0.34	0.03	0.33	0.061	61.01	0.15	15.00	12.70	81.50	477.31	20,770.00	5.88	84.84	
PLZ (<i>n</i> = 16)	8.68	0.09	9.67	4.63	0.24	0.02	0.63	0.064	69.80	0.16	31.94	8.00	93.60	207.70	16,647.00	3.68	57.50	
PTZ (<i>n</i> = 6)	12.12	0.23	8.88	5.17	1.38	0.03	0.92	0.033	57.40	0.41	23.83	7.50	56.80	207.37	3394.00	3.82	26.82	
AZ (<i>n</i> = 13)	15.04	0.26	5.13	6.91	0.34	0.04	0.42	0.067	63.40	0.17	32.31	3.40	53.30	37.51	1497.00	1.10	21.22	
ENS (<i>n</i> = 4)	4.31	2.98	26.66	2.18	10.98	0.49	0.18	0.073	45.80	0.19	39.88	12.70	16.37	2.43	64.90	0.02	5.32	
Elements (10 ^{−6})/ Oxides (wt.%)	Pb	Zn	As	Sb	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
UL (<i>n</i> = 6)	10.40	17.00	2.70	0.80	1.90	3.40	0.64	1.97	0.36	0.13	0.38	0.11	0.32	0.12	0.21	0.10	0.18	0.10
AML (<i>n</i> = 14)	17,190.00	7234.00	400.00	30.59	7.00	12.60	1.53	6.10	1.32	0.60	1.29	0.20	1.05	0.22	0.60	0.12	0.51	0.11
EXS (<i>n</i> = 2)	172.15	335.00	361.00	15.20	2.00	3.60	0.48	1.95	0.45	0.27	0.47	0.07	0.42	0.09	0.26	0.05	0.29	0.06
UQSP (<i>n</i> = 3)	103.40	82.90	6.47	2.68	21.47	42.83	3.94	14.67	2.64	0.66	2.11	0.30	1.60	0.30	0.83	0.14	0.75	0.14
PZ (<i>n</i> = 13)	219.70	111.00	283.10	61.45	14.30	29.50	3.28	12.90	2.76	0.52	2.42	0.33	1.67	0.31	0.80	0.12	0.66	0.11
PLZ (<i>n</i> = 16)	514.00	209.00	745.00	73.80	16.70	35.50	3.84	14.40	2.69	0.62	2.07	0.27	1.40	0.26	0.67	0.10	0.58	0.09
PTZ (<i>n</i> = 6)	320.70	118.00	285.40	42.80	27.90	51.00	5.21	19.50	3.92	0.83	3.10	0.41	2.02	0.37	0.97	0.15	0.87	0.14
AZ (<i>n</i> = 13)	422.50	148.00	286.80	35.37	23.00	37.00	3.97	14.30	2.74	0.68	2.24	0.31	1.56	0.29	0.79	0.13	0.71	0.13
ENS (<i>n</i> = 4)	1110.00	814.00	27.20	9.22	17.80	29.90	3.58	13.00	2.22	0.51	1.88	0.25	1.21	0.22	0.56	0.08	0.48	0.08

UL—Unaltered limestone (Beiya Fm.); AML—Altered/mineralized limestone (Beiya Fm.); EXS—Exoskarn (protolith is limestone); UQSP—Unaltered quartz syenite porphyry; PZ—Potassic zone; PLZ—Phyllic zone; PTZ—Propylitic zone; AZ—Argillic zone; ENS—Endoskarn (protolith is quartz syenite porphyry). Fe₂O₃^{*} = Fe₂O₃ + FeO. *n* represents the number of samples.

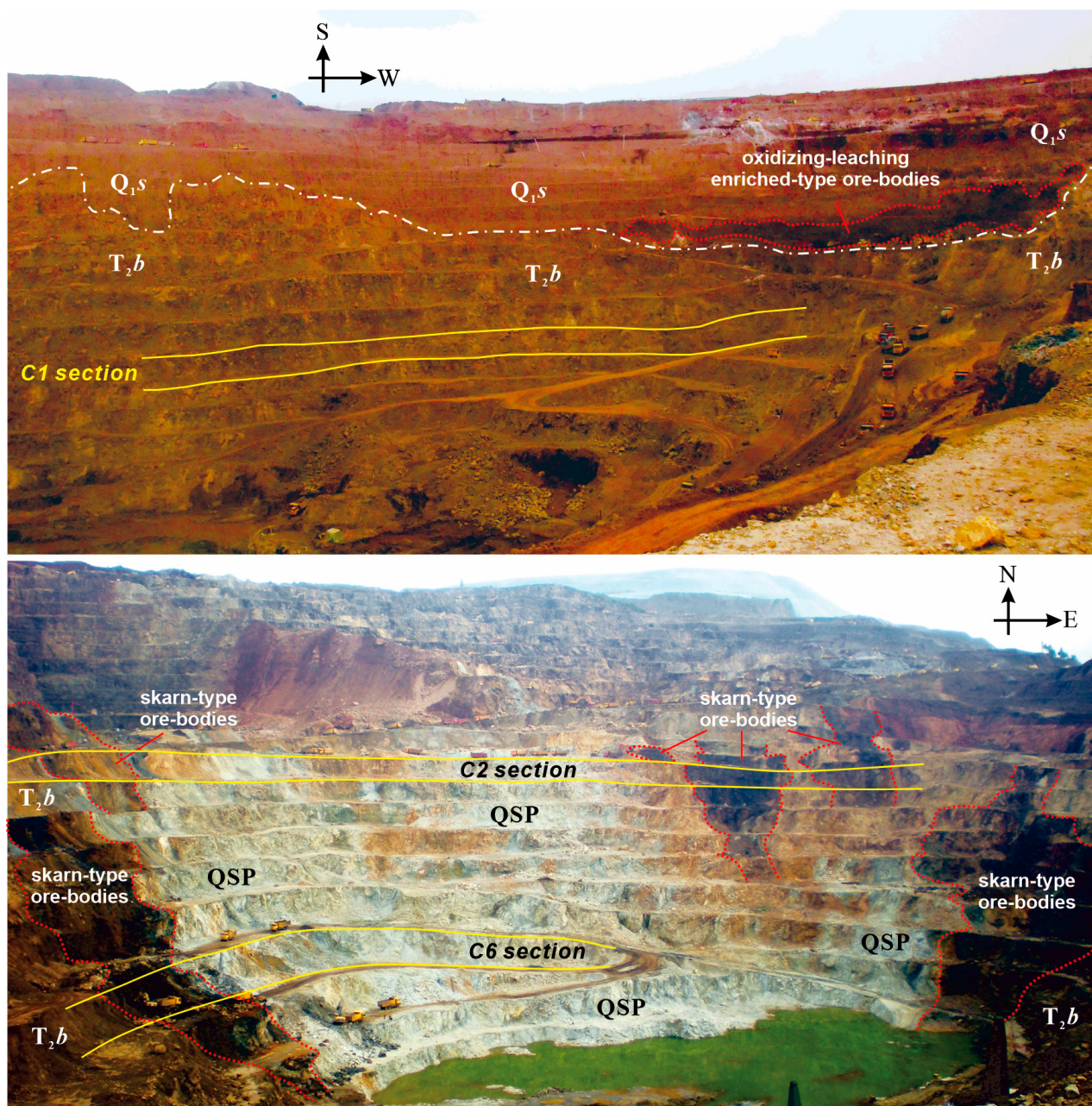


Figure 3. The location of geological sections in the Beiya deposit (modified after Liu et al. [31]).

The analysis of whole-rock major and trace elements was conducted at ALS Chemex (Guangzhou, China) Co., Ltd. The samples were cleaned and crushed to <200 mesh using an agate mill. The whole-rock major elements were analyzed by using X-ray fluorescence spectrometry (XRF), and the analysis precision was better than $1\% \pm 2\%$. The trace elements were analyzed by using inductively coupled plasma-mass spectrometry (ICP-MS) with analytical uncertainties of <5%.

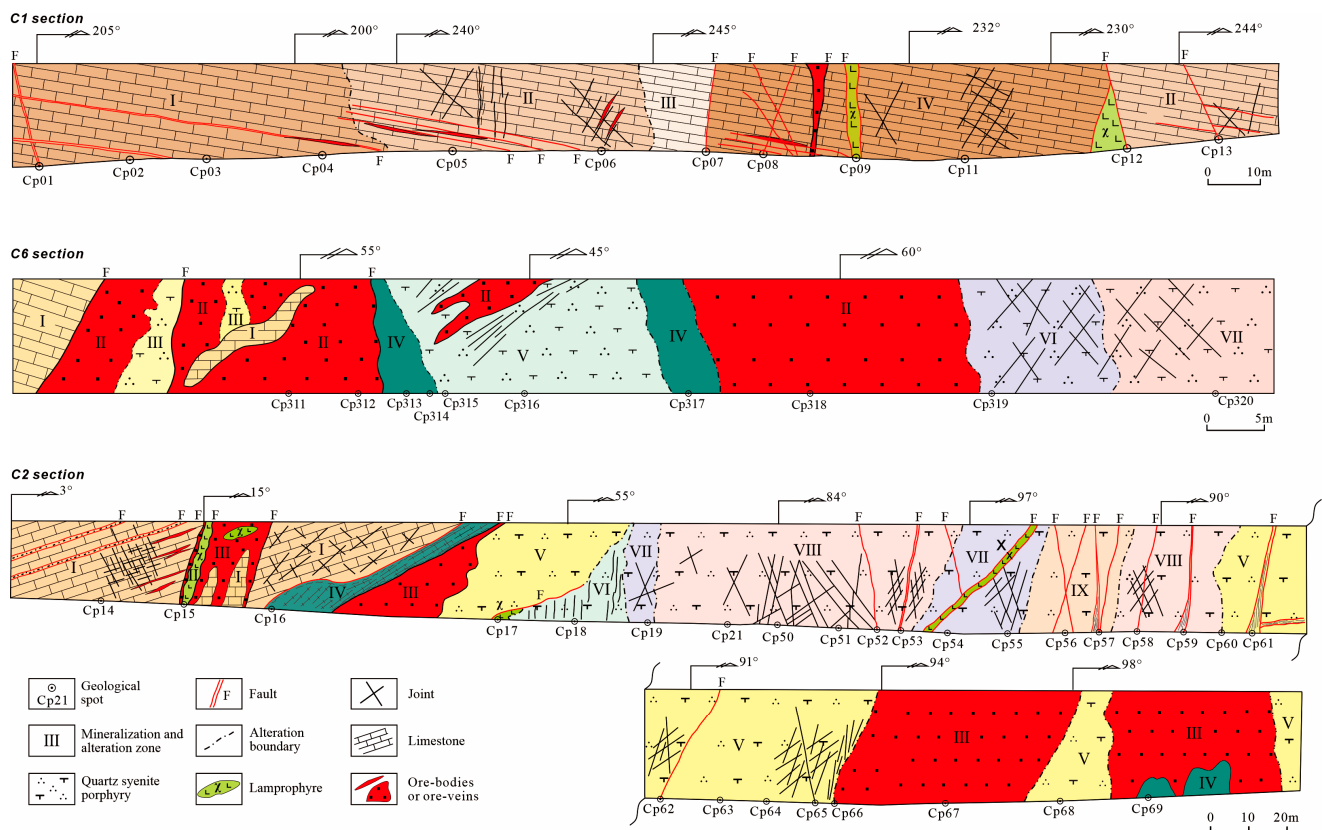


Figure 4. The mineralization-alteration zones of selected geological sections in the Beiya deposit. The description of the mineralization and alteration zones identified numerically is given in the text (C1 and C2 sections are modified after Liu et al. [31]).

4. Result

4.1. Alteration Types

Multi-stage magmatic and hydrothermal activities are developed in the Beiya deposit, resulting in significant hydrothermal alteration in the porphyries, wall-rocks, and their contact zones.

4.1.1. Porphyry Alteration

Potassic Alteration

Potassic alteration usually occurs in the central part of alkaline porphyry (Figure 4), which typically displays a pale red color (Figure 5A) and mainly contains hydrothermal orthoclase (K-feldspar) and hydrothermal biotite (Figure 5B,C), as well as a small amount of quartz, sericite (Figure 5B,C) and some metal minerals such as pyrite, chalcopyrite, molybdenite, native gold, etc. The potassic alteration has certain characteristics: (1) plagioclase or orthoclase phenocrysts are replaced by hydrothermal orthoclase or hydrothermal biotite, forming a ring edge of hydrothermal orthoclase (Figure 5B) and even replacing them completely; (2) hydrothermal orthoclase or hydrothermal biotite replace groundmass; (3) hydrothermal orthoclase or hydrothermal biotite fill in fractures (Figure 5C); (4) a small degree of sericitic and pyritic alteration telescopes on potassic alteration.

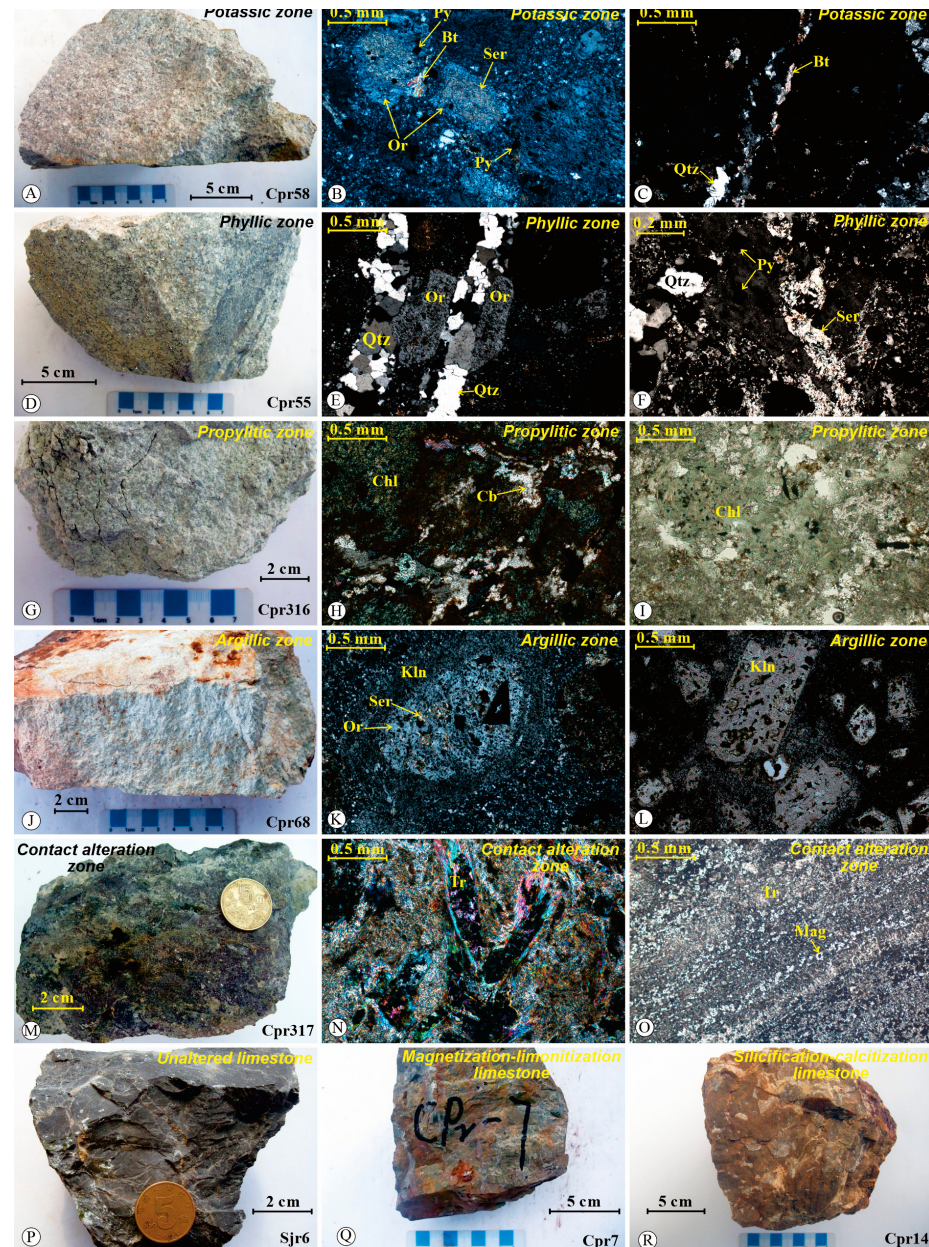


Figure 5. Alteration characteristics in the Beiya deposit. (A)—potassic alteration QSP, with light red to pink in color; (B)—hydrothermal orthoclase (K-feldspar) and hydrothermal biotite occur, and the hydrothermal orthoclase are replaced by the later sericites; (C)—hydrothermal biotite fill in fracture; (D)—phyllic alteration QSP; (E)—quartz occur in fracture and cut the previous orthoclase; (F)—quartz, sericite, and pyrite are developed in phyllic zone; (G)—propylitic alteration QSP, with light greenish in color; (H)—chlorite and some carbonate minerals are developed in propylitic zone; (I)—chlorite replace groundmass; (J)—argillic alteration QSP; (K)—kaolinite metasomatize orthoclase along the edge; (L)—kaolinite completely metasomatize plagioclase; (M)—endoskarn, with greenish-gray in color; (N)—tremolite are developed in skarn; (O)—tremolite and magnetite are developed in skarn; (P)—unaltered limestone of the Beiya Fm.; (Q)—magnetization and limonitization limestone of the Beiya Fm.; (R)—silicification and calcitization limestone of the Beiya Fm. Bt = Biotite, Or = Orthoclase, Ser = Sericite, Qtz = Quartz, Chl = Chlorite, Cb = Carbonate mineral, Kln = kaolinite, Tr = Tremolite, Py = Pyrite, Mag = Magnetite.

Phyllic Alteration

Phyllic alteration commonly occurs outside of potassic alteration (Figure 4), mostly including quartz, sericite, and pyrite (Figure 5D), and a small amount of K-feldspar, chal-

copyrite, bornite, native gold, etc. The phyllic alteration is characterized by (1) lots of sericite and quartz occurring, replacing mineral phenocryst and groundmass; (2) sericite or quartz in veins or veinlet fillings (Figure 5E,F); (3) large amounts of pyrite disseminated or in quartz sulfide veins or veinlets. Phyllic alteration is later than potassic alteration, in which the new hydrothermal alteration minerals are cut by those of the former. For instance, the quartz vein that formed in the fracture cut the previous hydrothermal orthoclase (Figure 5E).

Propylitic Alteration

Propylitic alteration usually occurs on the outside of phyllic alteration (Figure 4). These propylitic rocks are characterized by a light green color (Figure 5G), mainly containing epidote and chlorite (Figure 5H,I), with a small amount of carbonate minerals (Figure 5H), sericite, quartz, pyrite, etc. The propylitic alteration has the following characteristics: (1) many chlorites and epidotes are generated, replacing mineral phenocryst and groundmass (Figure 5H,I); (2) some carbonate minerals such as siderite and calcite occurred; (3) the content and variety of metal minerals are reduced, while pyrite veins or veinlets are dominant.

Argillic Alteration

Argillic alteration occurs on the outside and upside of porphyry alteration (Figure 4). The argillic rocks are predominantly light white (Figure 5J) and contain mainly kaolinite (Figure 5K,L), as well as a little sericite and quartz. The argillic alteration zone in the Beiya deposit has a relatively narrow range and is mainly distributed near the surface, with strong ferritization accompanying it.

4.1.2. Contact Alteration

The contact zone between alkaline porphyry and the wall-rock is primarily where calcareous skarn develops. The skarn rocks are dark green to greyish green (Figure 5M). Altered residues of limestone and alkaline porphyry can be observed in the skarn alteration zone. Two sub-types of tremolite–diopside skarn and apatite–grossularite–diopside skarn can be divided according to mineral association. The former mainly contains garnet, tremolite, diopside, epidote, chlorite, quartz, pyrite, magnetite, and arsenopyrite (Figure 5N,O), etc. The latter commonly contains apatite, grossularite, diopside, diopside, epidote, quartz, and a small amount of pyrite and magnetite.

4.1.3. Wall-Rock Alteration

Compared with the fresh limestones (Figure 5P) of the Beiya Fm., the altered wall-rocks mainly include marbleization, silicification, and calcitization, with some pyritization and magnetization (Figure 5Q,R). The wall-rock alteration is characterized by the recrystallization of calcite and the formation of calcite veins or clumps, as well as quartz–carbonate–(pyrite or magnetite) veinlets.

4.2. Mineralization Types

In consideration of the close relationship with the alkaline porphyry and structure, five types of mineralization are classified according to ore-controlling structures by Liu et al. [27]: (1) porphyry-type Cu–Au–(Mo), controlled by faults, fractures, and breccia pipes within the alkaline porphyries, while the metal minerals are mainly molybdenite, chalcopyrite, bornite, pyrite, and native gold (Figure 6A,E–G); (2) skarn-type Au–Fe–(Cu), controlled by contact zone structures between alkaline porphyries and wall-rocks (Figure 3), while the metal minerals are mainly magnetite, chalcopyrite, bornite, pyrite, and native gold (Figure 6B,H); (3) hydrothermal vein-type Au–Fe, controlled by interlayer fracture zones, faults, and fractures in the wall-rocks, while the metal minerals are mainly magnetite, pyrite, and native gold (Figure 6C,I); (4) distal low- to medium-temperature hydrothermal-type Pb–polymetallic, controlled by interlayer fracture zones between the Beiya Fm. and the Qingtianbao Fm. and interlayer faults within the Beiya Fm. limestone, while the metal

minerals are mainly galena, sphalerite, and pyrite; (5) oxidizing-leaching enriched-type Au, controlled by paleo-karst caves and angular unconformity between the Beiya Fm. and the Q₁s Fm. (Figure 3), while the metal minerals mainly contain magnetite, hematite, pyrite, and native gold (Figure 6D,J).

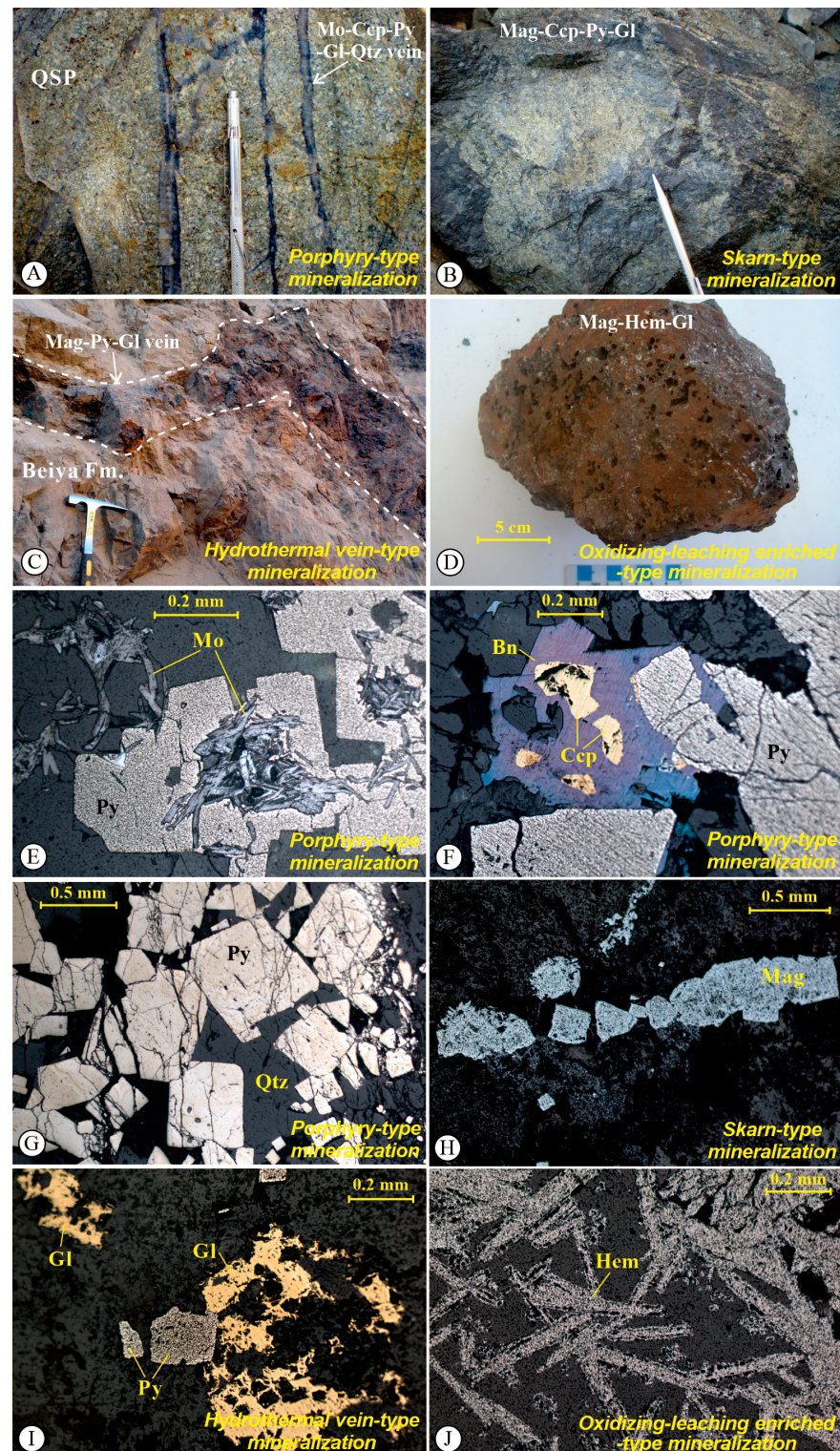


Figure 6. Mineralization characteristics in the Beiya deposit. (A)—porphyry-type mineralization, Au-containing molybdenite, chalcopyrite, pyrite and quartz occur in veins or veinlets; (B)—skarn-type

mineralization, Au-containing magnetite, chalcopyrite and pyrite occur in massive structure; (C)—hydrothermal vein-type mineralization, Au-containing magnetite and pyrite occur within fracture in the Beiya Fm. limestone; (D)—oxidizing-leaching enriched-type mineralization, Au-containing magnetite and hematite generate in honeycomb structure; (E)—porphyry-type mineralization, molybdenite coexist with pyrite; (F)—porphyry-type mineralization, bornite coexist with chalcopyrite and pyrite; (G)—porphyry-type mineralization, pyrite coexist with quartz; (H)—skarn-type mineralization, magnetite occur in vein; (I)—hydrothermal vein-type mineralization, gold coexist with pyrite; (J)—oxidizing-leaching enriched-type mineralization, hematite are developed. Mo = Molybdenite, Ccp = Chalcopyrite, Py = Pyrite, Gl = Gold, Mag = Magnetite, Hem = Hematite, Bn = Bornite, Qtz = Quartz, QSP = Quartz syenite porphyry, Beiya Fm. = Beiya Formation limestone.

4.3. Mineralization and Alteration Zone

Three representative measured sections show the characteristics of mineralization and alteration zoning at Beiya in Figure 3.

4.3.1. C1 Section

The elevation of the C1 section is about 1707 m and it is located within the limestone of the Beiya Fm. (Figure 3). From NE to SW, the mineralization and alteration zones successively are (Figure 4) (I) s cataclastic intense magnetization limestone zone, with Au-bearing magnetite–limonite veins occurring in the interlayer faults; (II) s weak magnetization limestone zone, with a few Au-bearing magnetite–limonite veins filling within interlayer faults or fractures; (III) no mineralized or altered limestone zones; (IV) a cataclastic intense magnetization–limonitization limestone zone, with abundant Au-bearing magnetite–limonite veins or ore-bodies occurring in interlayer faults or fractures. Marbleization, silicification, and calcitization usually develop around ore-bodies or ore-veins, which mainly contain metal minerals such as magnetite, hematite, pyrite, chalcopyrite, bornite, and native gold.

4.3.2. C2 Section

The elevation of the C2 section is about 1758 m and it is located in the limestone of the Beiya Fm. and QSP (Figure 3). From S to E, the mineralization and alteration zones successively are (I) a weak magnetization–limonitization–carbonation limestone zone, with Au-bearing magnetite–limonite veins occurring in the interlayer faults; (II) lamprophyre vein, with weak chloritization and epidotization; (III) skarn-type Au-bearing magnetite–limonite ore-bodies; (IV) skarn zone, formed in the contact zone structure; (V) argillic zone, mainly kaolinization QSP and commonly presenting a degree of limonitization; (VI) propylitic zone, mainly chloritization and epidotization QSP, with weak calcitization, sericitization, and silicification; (VII) phyllic zone, mainly sericitization and silicification QSP; (VIII) potassic zone, mainly potassium feldspathization and biotitization QSP, with weak sericitization and silicification; (IX) telescoped zone of phyllic and potassic alteration.

4.3.3. C6 Section

The elevation of the C6 section is about 1690 m and it is located in the limestone of the Beiya Fm. and QSP (Figure 3). From SW to NE, the mineralization and alteration zones successively are (I) a cataclastic magnetization–limonitization limestone zone; (II) Au-bearing magnetite–limonite ore-bodies; (III) argillic zone, mainly kaolinization QSP, with a few limonitizations; (IV) skarn zone, mainly tremolite–diopside skarn, with an amount of pyrite, magnetite, and arsenopyrite; (V) propylitic zone, mainly chloritization and epidotization QSP, with weak calcitization, sericitization, and silicification; (VI) phyllic zone, mainly sericitization and silicification QSP; (VII) potassic zone, mainly potassium feldspathization and biotitization QSP, with weak sericitization and silicification.

Metallogenic element associations also exhibit a significant zone. From alkaline porphyry outward to the wall-rock in the C2 section, the content of high-temperature met-

allogenic element associations of Cu–Au–Fe tends to gradually decrease, whereas the content of low-temperature metallogenic element associations of Pb–Zn tends to increase. From the C2 section to the C1 section, the ratios of Cu + Au/Cu + Mo, Au + Fe/Cu + Au, Pb + Zn + Ag/Au + Fe increase from 0.90, 0.01, and 103.53 to 0.99, 0.04, and 835.58, respectively (Table 2). These reflect that the metallogenic element associations have a lateral zoning of Cu–Mo → Cu–Au → Au–Fe–Cu → Au–Fe → Pb–Zn–Au–Ag–Fe from alkaline porphyry outward to the wall-rock. From the C6 section to the C2 section, the ratios of Cu + Au/Cu + Mo and Pb + Zn + Ag/Au + Fe increase from 0.88 and 34.04 to 0.90 and 103.53, respectively (Table 2), indicating that the metallogenic element associations have a similar zoning to the lateral zoning from the deep to the shallow surface.

Table 2. Characteristics of major mineralization elements at C1, C2, and C6 section in the Beiya deposit (10^{-6}).

Sections	Sample No.	Mo	Cu	Au	Fe	Pb	Zn	Ag	Ratios of Element Association		
									Cu + Au/ Cu + Mo	Au + Fe/ Cu + Au	Pb + Zn + Ag/Au + Fe
C1	Cp01	3.49	381.00	0.06	3.74	2740.00	838.00	5.72	0.991	0.010	942.588
	Cp03	2.92	251.00	0.57	47.30	2710.00	101.00	26.50	0.991	0.190	59.273
	Cp04	17.15	945.00	2.16	41.20	48,600.00	2390.00	40.70	0.984	0.046	1176.907
	Cp05	5.70	524.00	0.68	12.35	3960.00	829.00	13.20	0.991	0.025	368.578
	Cp07	6.66	1300.00	0.78	36.40	41,900.00	35,000.00	41.30	0.995	0.029	2069.427
	Cp08-1	6.62	3740.00	2.67	40.10	34,300.00	15,000.00	23.10	0.999	0.011	1153.217
	Cp08-2	4.86	1985.00	17.85	19.40	14,050.00	8440.00	17.30	1.006	0.019	604.223
	Cp11	4.89	7630.00	16.00	41.80	27,600.00	3930.00	17.40	1.001	0.008	545.803
	Cp13-1	10.45	914.00	2.35	17.95	7180.00	8260.00	12.30	0.991	0.022	761.197
	Cp13-3	1.49	126.50	0.05	4.79	425.00	2980.00	6.67	0.989	0.038	704.599
mean value		6.42	1779.70	4.32	26.50	18,346.50	7776.80	20.42	0.99	0.04	835.58
C2	Cp14	2.17	29.50	0.01	0.55	214.00	204.00	0.52	0.932	0.019	752.734
	Cp15-1	28.50	180.50	0.02	2.61	673.00	670.00	2.80	0.864	0.015	510.934
	Cp16-3	9.60	1040.00	0.09	5.32	256.00	592.00	7.99	0.991	0.005	158.311
	Cp17-2	165.50	919.00	0.08	7.56	102.50	132.00	7.46	0.847	0.008	31.674
	Cp18-2	94.70	9400.00	16.95	19.8	771.00	52.00	92.20	0.992	0.004	24.903
	Cp21-2	64.60	27,400.00	7.88	23.4	1020.00	84.00	123.00	0.998	0.001	39.226
	Cp50-3	236.00	9100.00	40.8.0	22.3	1310.00	96.00	550.00	0.979	0.007	30.998
	Cp52	86.50	160,500.00	4.24	17.65	119.50	61.00	606.00	0.999	0.0001	35.930
	Cp53-1	51.80	11,350.00	10.10	38.7	1350.00	169.00	129.00	0.996	0.004	33.770
	Cp54-2	54.10	5320.00	4.53	14.4	233.00	256.00	42.20	0.991	0.004	28.061
	Cp56-1	6.87	17,550.00	10.25	32.5	1860.00	26.00	58.60	1.000	0.002	45.488
	Cp57-2	16.35	168,500.00	4.92	18.7	904.00	135.00	442.00	0.100	0.0001	62.701
	Cp58-1	14.55	5650.00	19.25	23.7	1380.00	115.00	63.60	1.001	0.008	36.289
	Cp59-2	70.20	26,400.00	46.60	45	787.00	436.00	285.00	0.999	0.003	16.463
	Cp61-1	196.50	620.00	0.09	1.35	70.30	20.00	2.00	0.759	0.002	64.231
	Cp62	49.10	1540.00	8.42	23.7	302.00	71.00	69.80	0.974	0.021	13.786
	Cp63	115.5	907.00	6.67	22.5	2750.00	141.00	22.70	0.894	0.032	99.887
	Cp65	143.00	2680.00	0.71	34.1	435.00	279.00	5.94	0.950	0.013	20.681
	Cp66-1	482.00	2540.00	17.50	20.8	1570.00	176.00	98.40	0.846	0.015	48.157
	Cp67	62.60	4330.00	0.17	46.20	5160.00	369.00	31.30	0.986	0.011	119.925
mean value		93.00	21,712.00	9.00	20.00	1013.00	194.00	126.00	0.90	0.01	103.53
C6	Cp311	10.45	937.00	0.21	50.00	1135.00	207.00	3.74	0.989	0.054	26.801
	Cp314	2.96	111.50	0.02	16.60	141.50	279.00	1.16	0.974	0.149	25.375
	Cp315	7.92	89.70	0.01	12.20	213.00	377.00	0.91	0.919	0.136	48.384
	Cp316	6.50	180.50	0.01	2.19	46.20	108.00	0.63	0.965	0.012	70.281
	Cp317-1	55.7	46.30	0.02	23.30	31.80	637.00	0.56	0.454	0.503	28.708
	Cp318-1	6.48	190.00	1.05	35.10	88.30	78.00	3.46	0.972	0.189	4.696
mean value		15.00	259.20	0.20	23.20	276.00	281.00	1.70	0.88	0.17	34.04

4.4. Geochemical Characteristics of Mineralization and Alteration Zone

The mean compositions of major and trace elements of the analyzed samples are listed in Table 1. For six unaltered limestones from the Beiya Fm., they have a high content of CaO (34.64 wt.%) and MgO (17.67 wt.%), and a low content of Fe₂O₃^{*} (0.43 wt.%), Al₂O₃ (0.60 wt.%), SiO₂ (0.72 wt.%), MnO, K₂O, Na₂O, and TiO₂ (Table 1). The contents of metallogenic and rare earth elements in unaltered limestones are relatively low, with Cu,

Pb, and Zn contents of 3.60, 10.40, and 17.00×10^{-6} , respectively, while the content of Au and Ag is between 0.01 and 0.02×10^{-6} (Table 1).

While for fourteen altered or mineralized limestones in the wall-rock alteration zone, the abundances of CaO and MgO are 19.50 and 5.02 wt.%, respectively, there is also a high content of Fe_2O_3^* (16.21 wt.%), SiO_2 (6.79 wt.%), Al_2O_3 (2.29 wt.%), and MnO (1.28 wt.%) (Table 1). The contents of major metallogenic and rare earth elements from altered or mineralized limestones are high, with Cu, Pb, and Zn contents of 1540.00, 17,190.00, and 7234.00×10^{-6} , respectively, and Au (3.45×10^{-6}) and Ag (15.70×10^{-6}) also showing a high content (Table 1). Significantly, the content of P_2O_5 between unaltered limestones (0.050 wt.%, $n = 6$) and altered or mineralized limestones (0.053 wt.%, $n = 14$) is almost consistent (Table 1).

Unaltered quartz syenite porphyry has a high content of Al_2O_3 and SiO_2 (16.98 and 67.78 wt.%, respectively, $n = 3$), and a low content of Fe_2O_3^* (2.70 wt.%, $n = 3$), CaO, MgO, MnO, Na_2O , and TiO_2 , with the content of K_2O and P_2O_5 being about 7.11 and 0.060 wt.%, respectively (Table 1). The Cu, Pb, Zn, Au, and Ag contents of unaltered quartz syenite porphyry are about 14.27, 103.40, 82.90, 0.01, and 0.66×10^{-6} , respectively, showing the characteristics of low content.

With regard to the altered quartz syenite porphyry from four different porphyry alteration zones, they have various content and compositions of major and trace elements (Table 1). For instance, the altered quartz syenite porphyries in the potassic zone contain the highest amounts of Fe_2O_3^* (10.53 wt.%), K_2O (7.68 wt.%), Cu ($20,770.00 \times 10^{-6}$), Au (5.88×10^{-6}), and Ag (84.84×10^{-6}) (Table 1), while they have the highest amounts of SiO_2 (69.80 wt.%) and the lowest amounts of K_2O (4.63 wt.%) in the phyllic zone (Table 1). The content of P_2O_5 of altered quartz syenite porphyries, in addition to that in the propylitic zone ($\text{P}_2\text{O}_5 = 0.033$ wt.%), is about 0.061, 0.064, and 0.067 wt.% in the potassic, phyllic, and argillic zones (Table 1), respectively, which is consistent with that of unaltered quartz syenite porphyry.

In the contact alteration zone, exoskarn and endoskarn show different element compositions due to the difference of protoliths. Altered rocks in the exoskarn zone have a relatively high content of CaO (14.10 wt.%) and MgO (9.92 wt.%), while they have a high content of SiO_2 (45.80 wt.%) in the endoskarn zone, which is preferred to the compositional features of the respective protoliths. Both exoskarn and endoskarn have a high content of Fe_2O_3^* (Table 1). The P_2O_5 content varies greatly in the exoskarn zone (0.040 wt.%) and endoskarn zone (0.073 wt.%) (Table 1).

4.5. Element Migration of Mineralization and Alteration Zone

We adopting the equation of rock composition changing with volume change in the process of hydrothermal alteration proposed by Gresens [34] and Grant [35,36], to estimate the introduction and removal of elemental components from different alteration zone. Gresens [34] considered that some components in the rock were stable during the process of hydrothermal alteration, and Grant [35,36] established the corresponding equation of rock volume change, i.e., Equation (1):

$$C_i^A = M^O / M^A (C_i^O + \Delta C_i) \quad (1)$$

For the immobile component, M^O / M^A ratio is constant and $\Delta C_i = 0$, so it can obtain Equation (2):

$$C_i^A = (M^O / M^A) C_i^O \quad (2)$$

C_i^A and C_i^O represent the concentration of a component in the rock after and before alteration, respectively; M^A and M^O represent the equivalent mass of rock after and before alteration, respectively; ΔC_i represents the change in concentration of a component in the rock after alteration. Assuming that the volume and mass of rock remain constant before and after hydrothermal alteration and immobile components in the rock do not vary in concentration, by plotting the values of the bivariable C_i^A and C_i^O , we can create a straight

line of the immobile component through the origin with a slope of M^O/M^A and $\Delta C_i = 0$, i.e., the Isocon line [35,36].

As mentioned above, with the exception of propylitic, exoskarn, and endoskarn zones, the content of P_2O_5 is essentially constant between fresh rocks and altered rocks. For instance, the contents of P_2O_5 from unaltered and altered or mineralized limestones are 0.050 wt.% ($n = 6$) and 0.053 wt.% ($n = 14$), respectively; the same features are also shown between unaltered and altered quartz syenite porphyry, showing 0.060 wt.% ($n = 3$) of P_2O_5 in the former and 0.061–0.067 wt.% in the potassic, phyllic, and argillic zones. Therefore, P_2O_5 is selected as the immobile component by comparing unaltered samples with altered samples. The element migrations of six mineralization and alteration zones, including the wall-rock alteration zone, contact alteration zone, potassic zone, phyllic zone, propylitic zone, and argillic zone, are plotted by the Isocon method in Figure 7.

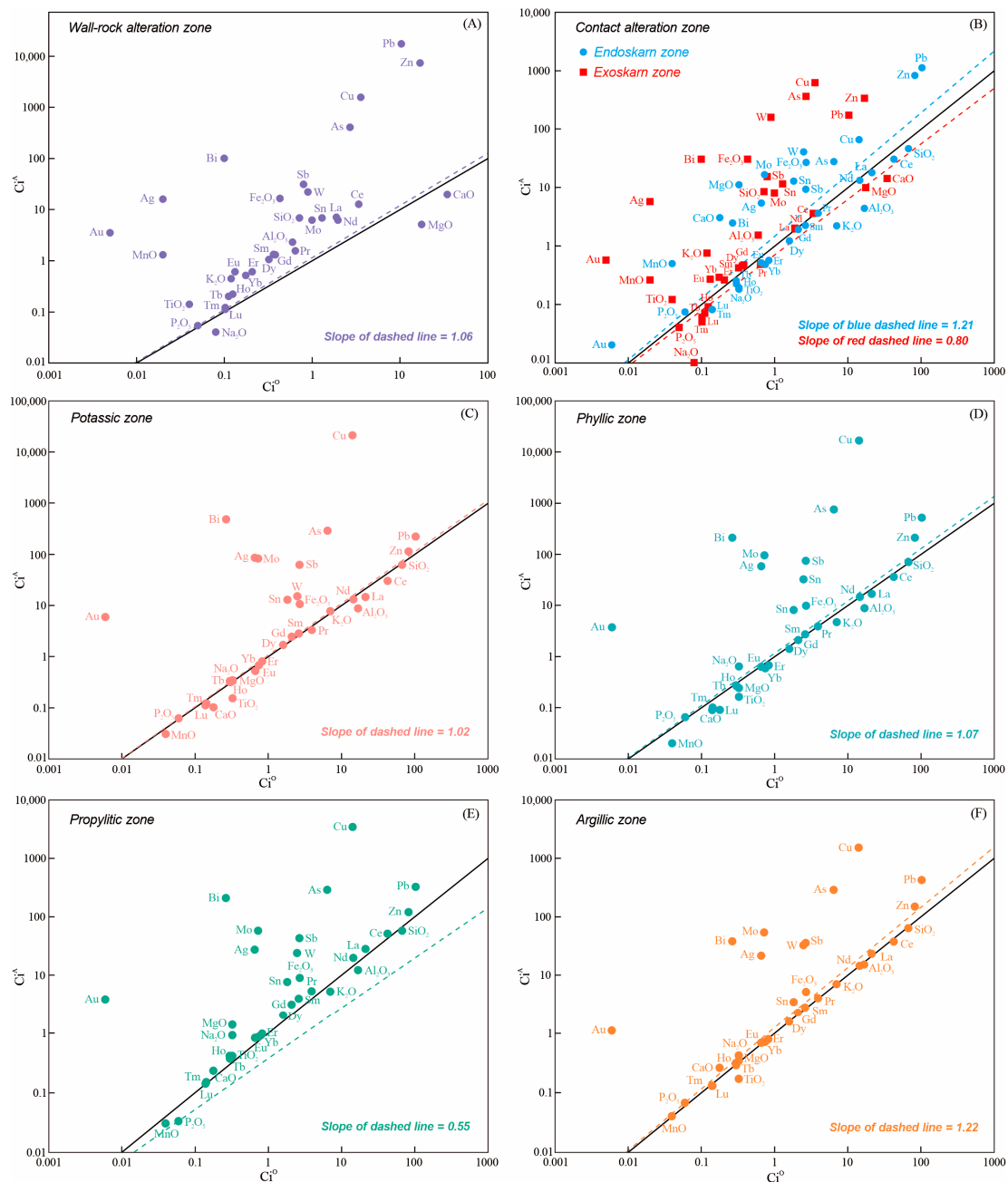


Figure 7. Element migration characteristics of different alteration zones in the Beiya deposit. The slope of the solid line is 1, and the slope of the dashed line is seen in each diagram (A–F).

In the wall-rock alteration zone, the Na_2O , MgO , and CaO contents significantly decrease, while Fe_2O_3^* , SiO_2 , K_2O , and Al_2O_3 increase. Compared to unaltered limestone, the content of metallogenic elements from altered or mineralized limestones increases, particularly for Pb and Zn, as well as rare earth elements.

In the potassic zone, K_2O , MgO , and Fe_2O_3^* are slightly enriched, while SiO_2 , Al_2O_3 , and CaO slightly decrease; the Cu, Mo, and Bi contents significantly increase, whereas Pb and Zn slightly increase; there is little change in the content of Na_2O and rare earth elements.

In the phyllic zone, Na_2O , SiO_2 , and Fe_2O_3^* are enriched; however, K_2O , Al_2O_3 , CaO and MgO decrease; it is similar to the potassic zone in that the Cu, Mo, and Bi contents significantly increase, while Pb and Zn slightly increase, as well as rare earth elements.

In the argillic zone, Na_2O , CaO , and Fe_2O_3^* are enriched, but K_2O , Al_2O_3 , and SiO_2 decrease; Au predominates even though the amount of metallogenic elements increases; the contents of MgO and rare earth elements have a minimal change.

In the contact zone and propylitic zone, probably due to the small number of samples, the slope of the Isocon line deviates greatly from 1. However, it can still provide some information about element migration; for instance, CaO and MgO decrease in the exoskarn zone, but they increase in the endoskarn zone; SiO_2 , Al_2O_3 , and K_2O increase in the exoskarn zone, while decreasing in the endoskarn zone. In a word, the element migration in these two zones is for reference only.

5. Discussion

5.1. Regularity of Mineralization and Alteration Zoning

The typically lateral and vertical alteration zone of porphyry copper deposits was first proposed by Lowell and Guibert [6], including concentric-banded alteration zones of potassic, phyllic, argillic, and propylitic zones, with typical hydrothermal mineral associations within each zone, as well as metal sulfide minerals and related mineralization zones displayed in various occurrences. Sillitoe [2] and John et al. [9] summarized the consistent mineralization and alteration zoning pattern in porphyry copper systems, which comprises sodic–calcic, potassic, chlorite–sericite, sericitic, and advanced argillic zones centrally from the bottom upward or outward. Similar to that of typical porphyry deposits, the Beiya deposit exhibits mineralization–alteration zoning of potassic, phyllic (pyritic–sericitic), propylitic, and argillic alteration from the center outward or upward (Figure 4). However, the propylitic zone is not fully developed and is absent or overprinted by the argillic zone in some areas (Figure 4). Wall-rocks, especially the Beiya Fm. limestones, have an influential impact on mineralization and alteration in the Beiya deposit, just as they do in other porphyry copper deposits worldwide [2], which results in contact and wall-rock alteration and the corresponding hydrothermal vein-type mineralization.

Additionally, it displays mineralization occurrence zoning at Beiya. Porphyry-type mineralization commonly occurs in veins and veinlets; skarn-type mineralization appears as long and thick veins or irregular-shaped veins; hydrothermal vein-type and distal hydrothermal-type mineralization occur in veins, bedded, near bedded, and lenticular shapes; oxidizing-leaching enriched mineralizations are mainly sack-like or irregular in shape. These various occurrences are dominantly controlled by structures and lithologies, which are generally observed in many porphyry and associated deposits [2,4,37,38].

The element migrations of different zones further reflect their alteration and mineralization characteristics. In the potassic and phyllic zone, the high temperature metallogenic element associations of Cu, Mo, Bi, and Au are significantly enriched, while the low temperature metallogenic element association of Pb, Zn, and Au significantly increases outward in wall-rock alteration zone (Table 1; Figure 7), demonstrating an obvious metallogenic element association zoning that consistent with the spatial interrelationships of mineralization in the porphyry copper system [2] and confirming a recent study that the alteration zones in the porphyry deposit result from gradual cooling of a single magma–hydrothermal continuous interaction with porphyry intrusion [12]. The gain and/or loss of oxides in

different zones reflects the primary generation or replacement of hydrothermal minerals. In the wall-rock mineralization-alteration zone, there is a decrease in Na_2O , MgO , and CaO with an increase in Fe_2O_3^* , SiO_2 , K_2O , and Al_2O_3 , reflecting the development of an amount of pyrite, magnetite, quartz, and some clay minerals and the replacement of calcite and dolomite. In the potassic zone, K_2O , MgO , and Fe_2O_3^* are slightly enriched, while SiO_2 , Al_2O_3 , and CaO slightly decrease, indicating the formation of K-feldspar, hydrothermal biotite, and pyrite and the replacement of plagioclase. In the phyllic zone, Na_2O , SiO_2 , and Fe_2O_3 are enriched, with K_2O , Al_2O_3 , CaO , and MgO decrease, reflecting the formation of some quartz, sericite, and pyrite and the replacement of plagioclase or mafic minerals.

5.2. Mechanism of the Mineralization-Alteration Zone

The temperature, sulfur fugacity, and solution pH are the principal controls of sulfide assemblages and the alteration type [2]. And the evolution of ore-forming fluids is not only a crucial component in the formation of various alterations but also a reflection of the ore-forming process [39–42].

Fluid inclusions and isotopes studies indicate that the ore-forming fluids and materials of the Beiya gold-polymetallic deposit originate from the magmatic–hydrothermal system related to alkaline porphyry [23–26,43]. In the early stage of the magmatic–hydrothermal system, the ore-forming fluid is at a high temperature (400–560 °C) and high salinity (38–67 wt.% NaCl equiv.) fluid [24,26]. This early-stage high temperature and salinity ore-forming fluid, on the one hand, causes osmotic potassium metasomatism in the alkaline porphyry [44], resulting in the formation of potassium silicate minerals of K-feldspar and hydrothermal biotite, along with enrichments of K_2O , MgO , and Fe_2O_3^* and losses of SiO_2 , Al_2O_3 , and CaO ; the early garnet-containing skarn alteration-mineralization occurs synchronously [45], which is predominantly induced by fluids with high temperature and salinity of 360–575 °C and 36–69 wt.% NaCl equiv., respectively, as well as a low to moderate salinity of 2–25 wt.% NaCl equiv. conducted in epidotes or garnets within the skarn [26,46]. On the other hand, the early-stage ore-forming fluid extracts metallogenic elements such as Au, Cu, and Mo from the alkaline porphyry, generating Cu–Au–Mo mineralization in the potassic zone and initial Au mineralization in the wall-rocks [44,45].

With the processes of cooling, boiling, and/or mixing with meteoric waters, the ore-forming fluid at Beiya transforms to a predominant low to moderate temperature (310–440 °C) and low salinity (1–15 wt.% NaCl equiv.) fluid [26,46], creating a general phyllic and propylitic alteration, which is similar to sericitic alteration occurring at temperatures between 370 and 450 °C in the Butte porphyry copper–molybdenum deposit [39]. The early garnet-containing skarn undergoes retrograde alteration as well, producing epidote, chlorite, and quartz through fluid metasomatism [45]. In addition, the diffusion and migration ability of Au and Cu decreases at this stage in the thermodynamics state; when the hydrothermal fluid migrates to the lithologic and structural discontinuity interface, Au, Cu, and other metallogenic elements precipitate in these special locations, mostly in phyllic and contact alteration zones (Figures 4 and 6).

In the late-stage evolution of ore-forming fluid, cooling and meteoric water mixing are the main processes to form a low temperature (160–340 °C) and low salinity (1–12 wt.% NaCl equiv.) of the hydrothermal fluid [26,46], which promotes the formation of argillic alteration and migrates Au, Ag, Pb, and Zn outward to form low- to medium-temperature hydrothermal vein- and distal hydrothermal-type mineralization in the wall-rocks (Figures 4 and 6).

5.3. Geological Implication of Element Migration for the Beiya Deposit

Element migration of different mineralization-alteration zones roughly describes the ore-forming process at Beiya; meanwhile, a reasonably inferred mineralization and alteration zoning model of the Beiya gold-polymetallic deposit is established as well (Figure 8). In Figure 8, along with the continuous evolution of ore-forming fluids, it generates concentric-banded alteration zone from the center of the alkaline porphyry outward

or upward, i.e., [porphyry alteration] potassic zone → phyllic zone → propylitic zone → argillic zone → [contact alteration] skarnitization-marbleization zone → [wall-rock alteration] marbleization-silicification-calcitization zone. In potassic and phyllic zones, it develops porphyry-type native gold–chalcopyrite–bornite–molybdenite–pyrite mineralization. Skarn-type native gold–pyrite–magnetite–chalcopyrite–bornite–siderite mineralization occurs outward in the contact alteration zone. Proximal hydrothermal vein-type native gold–pyrite–magnetite mineralization mainly distributes in the marbleization Beiya Fm. limestone, while distal hydrothermal-type galena–sphalerite–native gold–native silver mineralization predominantly forms in silicification and calcitization alteration zones. Metallogenic element association also exhibits a significant zone, laterally and vertically, of Cu–Mo → Cu–Au → Au–Fe–Cu → Au–Fe → Pb–Zn–Au–Ag–Fe from alkaline porphyry outward to the wall-rock.

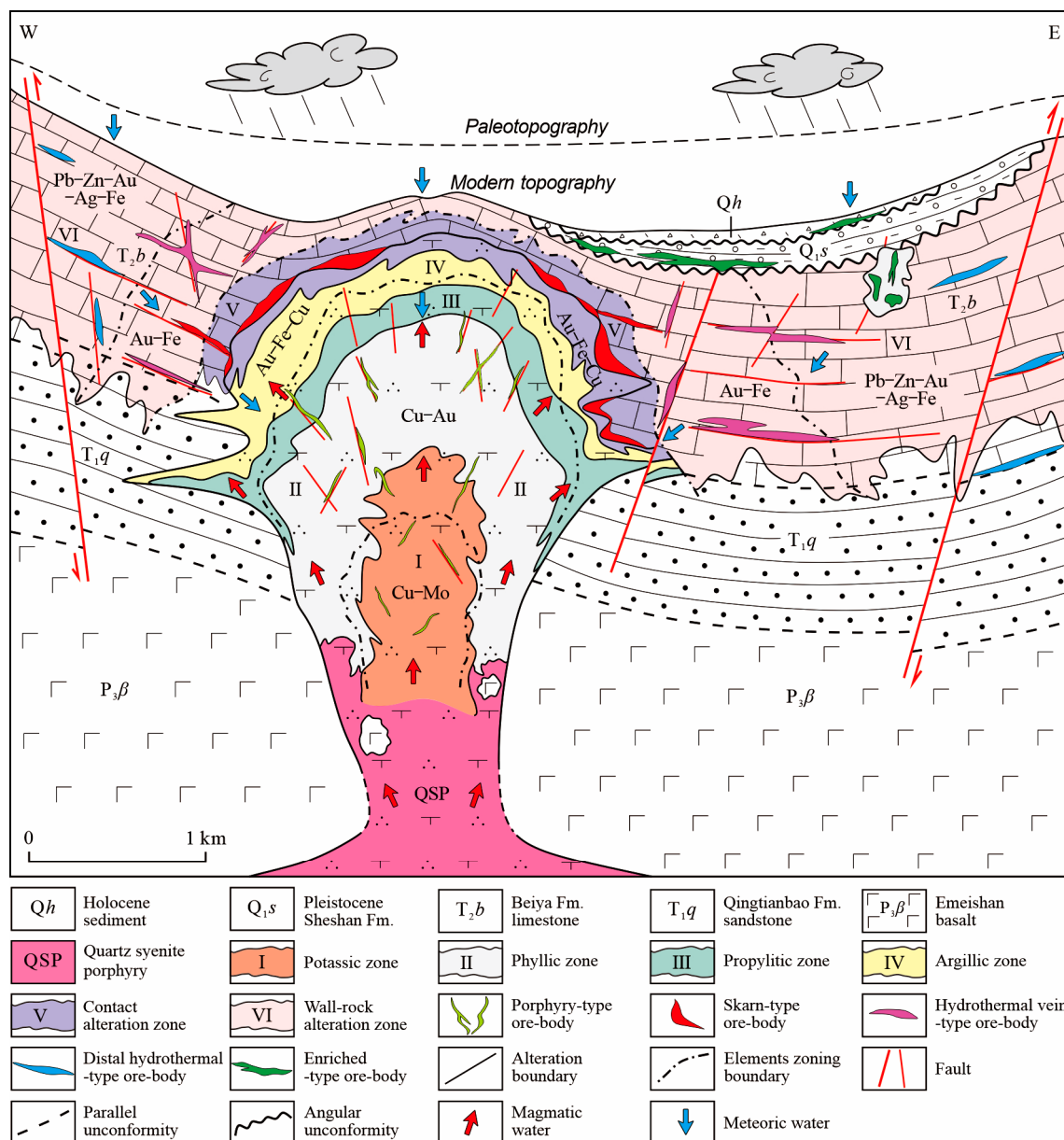


Figure 8. Mineralization and alteration zoning model of the Beiya deposit.

This provides a new basis for exploration in the Beiya deposit from the element migration and its related mineralization and alteration zoning model (Table 3). In the deep area and center of the porphyry that associated with mineralization, it is beneficial to find

the porphyry-type Cu–Mo–Au ore-bodies or deposits. In the space between wall-rock and ore-forming porphyry, skarn-type Au–Fe–Cu ore-bodies or deposits are the most favorable prospecting object. Distal to the ore-forming porphyry, the hydrothermal vein-type Au–Fe and Pb–Zn–Au–Ag–Fe ore-bodies or deposits are formed and distributed; moreover, the Pb-polymetallic deposit found at Luping [47,48] located 2 km north of the Beiya deposit is a good example.

Table 3. The brief information for prospecting prediction of the Beiya deposit.

Metallogenic System/Space	Ore-Controlling Structure	Mineralization and Alteration Type	Metallogenic Element Association	Mineralization Occurrence
oxidizing-leaching metallogenic system	angular unconformity interface, paleo-karst cave	calcitization silicification limonitization	Au–(Fe)	capsule-like irregular-shaped
porphyry metallogenic system	wall-rock (distal)	interlayer fracture zone, interlayer fault	Pb–Ag–Zn–(Au)–(Fe)	layered banded
	wall-rock (proximal)	interlayer fault, fracture and joint	Au–Fe	vein lenticular
	contact zone	contact zone structure	Au–Fe–(Cu)	irregular-shaped
	porphyry	fault, fracture and joint, breccia pipe	Cu–Au–(Mo)	stockwork veinlet

6. Conclusions

Based on the identification of types and features of mineralization and alteration, with a detailed study on the element migration of mineralization-alteration zones, allowing us to establish the mineralization and alteration zoning model at Beiya, we draw the following conclusions.

- (1) Three types of porphyry alteration, contact alteration, and wall-rock alteration are developed; and the porphyry alteration comprises four alteration zones of potassic, phyllic, propylitic, and argillic.
- (2) Five types of mineralization with various occurrence characteristics and distinctive metallogenic element associations are dominantly controlled by structures and lithologies.
- (3) Concentric-banded mineralization-alteration zones occur centrally from alkaline porphyry outward or upward, presenting common alteration zones of potassic → phyllic → propylitic → argillic → skarn alteration → wall-rock alteration, accompanying with individual elements gains and losses in different zones.
- (4) An inferred mineralization and alteration zoning model indicates the Beiya deposit is similar to the typical porphyry copper systems, and it also deepens the understanding of metallogenic regularity and provides scientific information for prospecting at Beiya, as well as at the same type of deposits in the Sanjiang metallogenic belt and elsewhere worldwide.

In addition, we suggest that in conjunction with the study of the properties and evolution of ore-forming fluids, isotopes and alteration minerals' microanalysis, among

others, studies will obtain a more reliable research results with respect to the element migration of mineralization-alteration zones.

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