Selenium Enrichment in Cambrian Stratabound Gold Deposits in the Western Qinling Mountains

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Abstract Stratabound gold deposits in the western Qinling Mountains occur in Cambrian chert formation composed of carbonaceous chert and carbonaceous slate. The distinctive chert formation provides important grounds for the mineralization and controls on the formation of gold deposits. Study shows that Se is exceptionally higher in both host rocks and gold orebodies. It may be recovered as a valuable component in ores for total utilization, and in some localities even independent Se orebodies (which are mined exclusively for Se) may be delineated. In gold ore Se mainly occurs as independent minerals or in the isomorphous form in sulphides and there is a positive correlation between Se and Au.

Key words: stratabound gold deposit, selenium, mineralization, enrichment, western Qinling Mountains

Cambrian gold deposits in the south subzone of the western Qinling Mountains, China, comprise the La' erma (Edu) and Qiongmo gold deposits and the Yaxiang gold occurrence (Fig. 1). They are distinctive stratabound gold deposits. In the middle 1980s, the Northwestern Sichuan Regional Geological Survey Party of the Sichuan Bureau of Geology and Mineral Resources (SBGMR) and the Third Geological Party of the Gansu Bureau of Geology and Mineral Resources (GBGMR) began to carry out gold prospecting and exploration in the gold districts. In the study of the mineral composition of these deposits, the

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authors found not only many Se–bearing minerals and independent selenium minerals but also the high degree of enrichment of selenium in gold ores, and outlined independent selenium orebodies ($Se \geqslant 0.05\%$) in some places. These discoveries have important significance for the total use of abundant mineral resources of the study region and the exploitation, utilization and study of selenium in the western Qinling Mountains and even other similar regions in China.

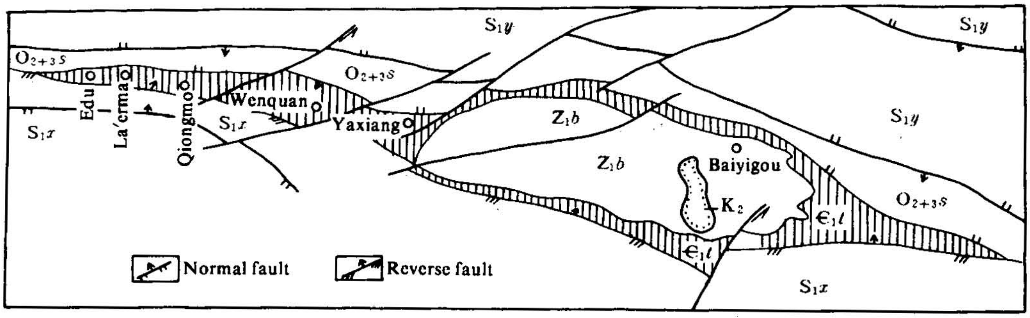

Fig. 1. Geological sketch map of Cambrian stratabound gold deposits in the western Qinling Mountains (modified after the Regional Geological Survey Party of northwestern Sichuan, SBGMR, 1990).

K_2–Upper Cretaceous; S_{1y}–Lower Silurian Yangchanggou Formation; S_{1x}–Lower Silurian Xiadi Formation; O_{2-3s}–Middle–Upper Ordovician Sulimutang Formation; ϵ_{1t}–Lower Cambrian Taiyangding Group; Z_{1by}–Lower Sinian Baiyigou Group; 1–reverse fault; 2–overthrust.

1 Geological Features of Gold Deposits

Gold deposits located in the Sichuan–Gansu border region in the south subzone of the western Qinling Mountains are the only stratabound gold deposits associated with submarine hydrothermal emanation ever found in China (Zheng et al., 1994). The deposits occur in the chert formation composed of carbonaceous chert and carbonaceous slate of the Cambrian Taiyangding Group and are controlled so obviously by the strata, lithology and structures that their stratabound nature is accepted by geologists.

More than 80% of the gold orebodies are localized in chert. They generally occur in stratified and lenticular forms along the bedding in a fractured zone, with their attitude largely coinciding with that of the host rocks. The ores have very complex mineral and element assemblages. Over 80 mineral species have been identified now. Besides pyrite, marcasite, stibnite and native gold, there are also a number of copper, uranium and selenium minerals. Independent Cu, U, Mo, Sb, V and Zn orebodies may be delineated in some localities.

According to the host rocks, three types of gold ore may be distinguished: (1) chert–type gold ore, (2) slate–type gold ore, and (3) dacite–porphyrite–type gold ore. Of the three types, chert–type gold ore is the principal ore of the deposits, accounting for over 80% of the total amount of ores; slate–type gold ore is present in small quantity and mostly noncommercial; dacite–porphyry–type gold ore is commonly found in the Qiongmo gold district.

The authors have conducted systematical studies of the trace elements and their characteristic ratios, rare earth element (REE) distribution patterns, fluid inclusions and

Table 1 Contents of selenium (10^{-6}) in the gold ore belts

Sampling locality	No. of samples	Range	Average	Remarks
Yaxiang section	10	0.52–36.30	10.999	Weakly mineralized area
Wenquan prospecting line 101	100	0.20–37.90	4.501	Unmineralized area
Qiongmo prospecting line 15	10	1.40–19.50	7.370	Weakly mineralized area
Qiongmo prospecting line 11	8	1.10–13.90	39.098	Strongly mineralized area
Qiongmo prospecting line 7	71	1.00–315.98	23.684	Strongly mineralized area
La' erma prospecting line 137	21	1.75–47.77	10.728	Weakly mineralized area
La' erma prospecting line 106	105	2.50–100.00	17.922	Strongly mineralized area
La' erma prospecting line 103	114	3.64–1994.0	63.56	Strongly mineralized area
Qiongmo OP1 tunnel	12	7.00–316.00	163.98	Strongly mineralized area
Qiongmo PD11 tunnel	60	1.30–279.00	43.424	Strongly mineralized area
Qiongmo Hole ZK3–1	2	2.10–2.60	2.350	Weakly mineralized area
Qiongmo Hole ZK7–1	46	3.40–125.00	22.437	Strongly mineralized area
Qiongmo Hole ZK7–2	39	6.60–232.00	31.097	Strongly mineralized area
Qiongmo Hole ZK7–3	54	2.90–67.00	12.009	Strongly mineralized area
Average	652	0.20–1994.0	29.436	

Note: Part of the data in the table are provided by Liu Xinhua and Mao Yunian.

sulphur, lead, carbon, oxygen, hydrogen and silicon isotopic compositions in the Cambrian chert formation and gold ores in the western Qinling Mountains. Through these studies, the authors (Zheng et al., 1994) consider that the formation of gold deposits progressed through two mineralization stages, i.e. the stage of hydrothermal emanation and precipitation and the stage of groundwater (meteoric water) hydrothermal activity. The former stage is represented by the appearance of high anomalies of many ore elements and formation of banded and laminated structures of pyrite etc., showing initial concentration of ore substances; the latter brought about remobilization and reconcentration of ore substances, thus leading to the formation of mineral deposits of commercial value.

2 Enrichment of Selenium in the Gold Deposits

2.1 Selenium content in rocks and ores and its relation to gold

High Se anomalies are prevalent in the gold deposits. Analyses of the element Se in 652 samples of carbonaceous chert and carbonaceous slate from eight geological sections, four drill holes and two mine workings in the ore–bearing chert formation (Table 1) indicated that Se is more or less enriched in both mineralized and unmineralized localities. The average Se content of 652 samples is 29.436×10^{-6}. In gold ores, the Se content generally ranges from 10×10^{-6} to 50×10^{-6} and may reach a maximum of 7700×10^{-6}, with the highest value in the Qiongmo deposit and the lowest in the Yaxiang gold district. In Qiongmo the average Se contents of chert–type ore and slate–type ore are close, being 42.3×10^{-6} and 43.0×10^{-6} respectively; while in La' erma the average Se content (33.9×10^{-6}) of chert–type ore is notably higher than that (18.6×10^{-6}) of slate–type ore. The Se content of dacite porphyrite–type ore in gold deposits is also relatively high, ranging from 14.1×10^{-6} to 57.5×10^{-6}. Se in gold ores is very high and can be recovered as a valuable by–product for the total use. In some localities even independent Se orebodies may be outlined.

Table 2 Enrichment coefficients of elements in various types of ores

Element \ Order / Ore type	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Au–Se	Se	As	Au	Sb	Hg	U	Cu	W	Ag	Mo	B	Ba	Zn	Bi	Pb	V	Cr	Ni
Au–U	As	Se	Au	Sb	Hg	U	W	Zn	Ag	B	Cu	Mo	Ba	Ni	V	Bi	Cr	Pb
Au–V	As	Sb	Au	Se	Hg	Mo	Ag	Ba	V	B	U	W	Cr	Bi	Zn	Pb	Cu	Ni
Au–W	As	Au	Sb	Se	Hg	U	W	Mo	Zn	B	Ag	Bi	Ba	Cu	V	Cr	Ni	Pb
Au–Cu	As	Se	Au	Sb	Hg	U	Cu	W	Ag	Zn	B	Mo	Bi	Cr	Ba	Ni	V	Pb
Au–Zn	As	Au	Sb	Se	Hg	U	Zn	W	B	Ag	Cu	Mo	Ba	Pb	Bi	Ni	Cr	V
Au–As	As	Au	Sb	Se	Hg	U	Zn	W	B	Mo	Ag	Cu	Bi	Ba	Cr	Ni	Pb	V
Au–Sb	Sb	As	Hg	Se	Au	Mo	Ag	Ba	W	U	B	V	Bi	Cr	Pb	Cu	Zn	Ni
Au–Hg	As	Hg	Sb	Au	Se	Ag	Mo	Ba	B	W	Mo	V	Bi	Zn	Cr	Pb	Cu	Ni
Au–Mo	Au	As	Se	Sb	Hg	Mo	Ag	Ba	W	B	V	U	Bi	Cr	Pb	Cu	Zn	Ni
Au–Ba	Sb	As	Hg	Se	Au	Ag	Mo	Ba	B	W	V	U	Bi	Cr	Zn	Pb	Cu	Ni
Au–As–Zn	As	Au	Sb	Se	Hg	U	Zn	W	Ag	B	Cu	Mo	Ni	Ba	Cr	Bi	Pb	V
Au–V–Mo	Au	As	Se	Sb	Hg	Mo	Ba	V	Ag	U	Cr	W	Bi	B	Pb	Cu	Zn	Ni
Au–Se–U	Se	As	Au	Sb	Hg	U	Ag	Cu	W	Mo	Zn	B	Ba	Cr	Ni	V	Bi	Pb
Au–Se–Cu	Se	Au	As	Sb	Hg	U	Cu	W	Ag	Mo	B	Zn	Ni	V	Ba	Cr	Bi	Pb

Notes: 1. The enrichment coefficient (Z) of an element = lg (element content in ore / aver·ge crustal abundance); 2. average crustal abundances of elements are after B. Mason et al., 1982.

The major elements and associated ore–forming elements are arranged in order of decreasing enrichment coefficients Z (Z = lg (content of the element M in ore / average crustal abundance of the element M)) in Table 2, which shows that Au, Se, Sb, Hg and As generally occupy the first five positions. If the major elements As, Sb and Hg are excluded, Au and Se show a much closer relation.

2.2 Spatial distribution of selenium enrichment

The authors have constructed selenium and gold enrichment patterns by using the bidimensional and tridimensional finite–element methods. The boundaries of the patterns are defined by actual sampling positions. This way is adopted for both bidimentsional and tridimensional cases.

(1) The planar patterns (Fig. 2) are mainly formed by surface samples of prospecting lines 106 and 137 of La' erma, prospecting line 7 of Qiongmo, Huangshuigou and uranium ore district 510–3, prospecting line 101 of Wenquangou and the Yaxiang mineralized section. There are 250 nodes in the patterns. Their X– and Y–coordinates are geographical

coordinates and the Z–coordinate (as far as the tri–dimensional pattern is concerned) stands for the content of the ore–forming elements. The bi–dimensional finite–element planar patterns of gold and selenium indicate that Au is enriched considerably in the La' erma and Qiongmo ore districts and slightly in Huangshuigou and Yaxiang. As is the case with Au, Se is also considerably enriched in La' erma and Qiongmo.

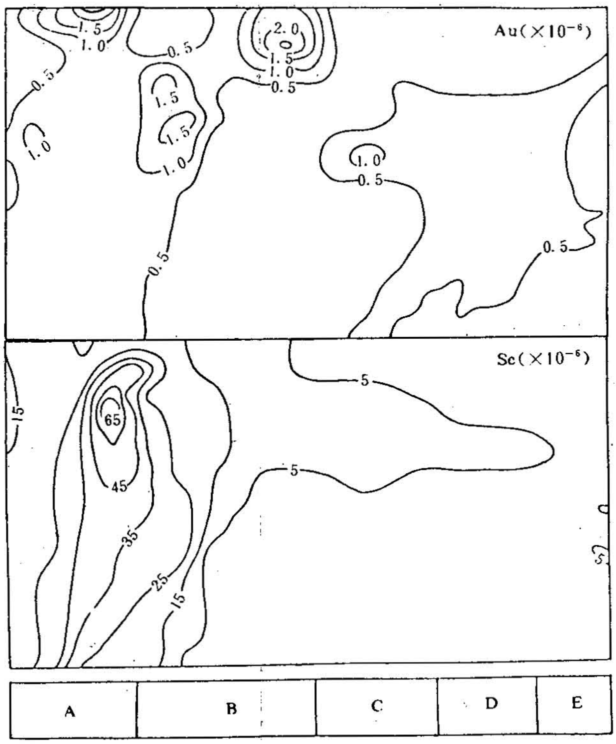

Fig. 2. Bi–dimensional finite–element planar patterns of gold and selenium.
A. La' erma gold district; B. Qiongmo gold district; C. Huangshuigou and uranium district 510–3;
D. Yaxiang gold occurrence.

(2) The sectional patterns (Fig. 3) are mainly constructed by samples from the surface, tunnels and drill holes of prospecting line of Qiongmo. There are 220 nodes. In the patterns the X–coordinate stands for the geographical coordinate, Y for the elevation above sea level, and Z for the content of the ore–forming elements. As shown in Fig. 3, Au and Se are enriched at shallow depths and become depleted gradually towards the deep levels.

2.3 Position of selenium in axial element zoning of the deposits

In the study of the characteristics of the axial zoning of elements in a mineral deposit, the linear productivity of an element is obtained by multiplying the weighted average content (%) of the element in the halo by the halo width (m) of the element. After the linear productivities at various elevations are known, the indices of element zoning can be obtained (Table 3). The elevation at which the maximum value of an element lies is just the position of the element in the zoning. Thus the axial zoning sequence of the elements from the surface downwards can be established as follows: (Ba, Hg, Ag, Se, Bi)→(Au, As, Cu) →(B, V, Ni)→(Sb, Cr) →(Zn, Pb, U, W, Mo). It is evident that there are many elements at all the levels. Their more exact positions in the zoning sequence should be determined by the variability index and variability index gradient (Ruan and Zhu, 1985; Wang, 1988). Through calculation, the authors obtained the following complete and exact zoning sequence of the elements on prospecting line 7 of the Qiongmo gold district: (Ba–Se–Hg–Ag–Bi) → (As–Cu–Au) →(B–Ni–V) →(Sb–Cr) →(Zn–Pb–Mo–U–W). By comparing the element zoning sequence of this case with that of S.V.Grigorian in hydrothermal deposits (Wang, 1988) it may be found that the positions of these elements are essentially consistent with the exception of a few elements such as Sb, Bi, Zn and Pb, whose positions are somewhat deviated, but the positions of Bi, Zn and Pb are consistent with what were described by E.M. Kaveyakovski (Wang, 1988).

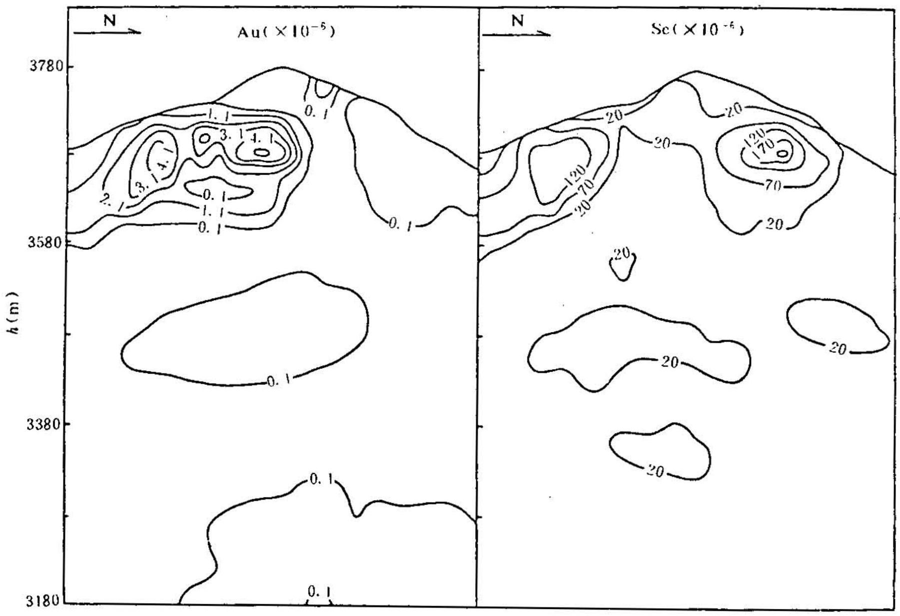

Fig. 3. Bidimensional finite–element section patterns of gold and selenium.

It may be ascertained from the sequence of element zoning that As and Cu should mainly exist in the form of tennantite rather than arsenopyrite and chalcopyrite. This is true of the deposits under study.

It is noteworthy that selenium is not mentioned by S.V. Grigorian in his element zoning sequence of hydrothermal deposits (Wang, 1988). In this study the authors consider that it is reasonable to place Se between Ba and Hg because Se in the mineral deposit mainly occurs in barite–quartz veins as tiemannite and other selenides.

3 Modes of Occurrence of Selenium

Se mainly has three modes of occurrence in gold ores.

3.1 Occurrence as independent minerals

Under the reflecting microscope the authors have identified such independent selenium minerals and selenium–bearing minerals (Liu Jiajun and Zheng, 1992, Liu Jiajun et al., 1992, 1993a, 1995, 1996) as tiemannite (HgSe), clausthalite (PbSe), sederholmite (NiSe), antimonselite (Sb_2Se_3), ferroselite ($FeSe_2$), berzelianite (Cu_2Se), Se–famatinite, selenio–skinnerite and one unnamed selenium mineral ($Ni_3As_3S_3Se$). The occurrence of large amounts of selenium minerals in sediment–hosted stratabound gold deposits has not been reported abroad.

Table 3 Indices of element zoning

Element	Surface–3700 m	3700–3600 m	3600–3500 m	3500–3400 m	3400–3300 m
Au	0.1056	0.1344	0.0271	0.0697	0.0196
Se	0.0887	0.0358	0.0411	0.0385	0.0433
Ba	0.0597	0.0368	0.0581	0.0432	0.0424
Hg	0.1396	0.1328	0.1393	0.1295	0.1269
Ag	0.0298	0.0135	0.0251	0.0213	0.0008
B	0.0472	0.0492	0.0689	0.0665	0.0565
Sb	0.0124	0.0189	0.0224	0.0245	0.0234
Zn	0.0005	0.0143	0.0123	0.0187	0.0499
Pb	0.0227	0.0197	0.0321	0.0320	0.0424
As	0.0362	0.0462	0.0181	0.0324	0.0119
U	0.0162	0.0442	0.0322	0.0496	0.0697
V	0.0298	0.0291	0.0410	0.0326	0.0295
W	0.0665	0.0614	0.0586	0.0424	0.1063
Cu	0.0663	0.0887	0.0411	0.0618	0.0509
Mo	0.0114	0.0218	0.0299	0.0338	0.0580
Ni	0.1583	0.1759	0.2208	0.2102	0.2117
Cr	0.0434	0.0388	0.0410	0.0471	0.0195
Bi	0.0618	0.0400	0.0309	0.0263	0.0303

In gold ores, selenium minerals are found in intergrowths with native gold, stibnite and other minerals, as fillings in the interstices of grains of quartz, barite, stibnite and other minerals, as 1–2 mm thick veinlets or networks in the fissures of chert, quartz and barite and enclosed within single grains of stibnite, barite, quartz and dickite.

3.2 Occurrence as isomorphs in sulphide minerals

Voluminous data of electron microscope analysis indicate that almost all sulphide minerals in the deposits contain a certain amount of selenium (Table 4). These minerals are pyrite, marcasite, tetrahedrite, sphalerite, stibnite, cinnabar etc., of which stibnite has the highest selenium content (up to 31.5%). A part of selenium occurs in dispersed or isomorphous forms in sulphides. X–ray scanning images show that selenium is evenly dispersed in these sulphides.

3.3 Occurrence in the state of adsorption

There are relatively high organic carbon (generally 0.5%–5.0% with a maximum of 22.0%) and selenium in rocks and ores of the Cambrian chert formation (Table 1). Study indicates that selenium is positively correlated with organic carbon, which is because a part of selenium is adsorped by organic carbon.

Table 4 Contents of selenium in hydrothermal minerals (%)

Mineral	Electron microprobe analysis (%)			Chemical analysis (10^{-6})		
	No. of samples	Range	Average	No. of samples	Range	Average
Se–bearing stibnite	71	1.20–31.5	12.5	2	320.0–625.0	472.5
Se–famatinite	5	5.11–9.57	7.73			
Pyrite	3	0.00–0.31	0.16	9	7.51–546.70	210.47
Marcasite	2	0.42–0.77	0.69	2	2.21–9.07	5.64
Tetrahedrite	5	0.47–2.01	1.18			
Sphalerite	3	0.54–1.89	1.21			
Cinnabar	2	1.21–2.37	1.79			
Native gold	1		0.26			
Vermiculite				1		4.91
Au–free quartz				5	0.89–25.53	8.75
Au–bearing quartz *				6	10.28–200.0	35.77
Barite				6	6.57–178.0	35.55
Dickite *				1		3.3

* After Zhou De' an (1992).

4 Discussion

Selenium is a rare and disperse element in nature. Although some independent selenium minerals may be found, no deposits are ever mined exclusively for selenium (Liu Yingjun et al., 1987). As selenium is close to sulphur in crystal chemical properties and some geochemical properties (e.g., the ion radius is 0.184 nm for S^{2-} and 0.191 nm for Se^{2-}, the lattice energy coefficient is 1.15 for S^{2-} and 1.10 for Se^{2-} and the ionic potential is −1.09 eV for S^{2-} and −1.05 eV for Se^{2-}), selenium usually replaces sulphur in the lattice of sulphides in the isomorphous form. Selenium minerals mainly occur in deposits which are obviously deficient in sulphur, especially in some low–temperature and low–sulphur fugacity hydrothermal deposits related to volcanism.

There are a lot of independent Se minerals and Se–bearing minerals and even selenium concentrated mineralizations in Cambrian stratabound gold deposits in the western Qinling Mountains (Liu Jiajun and Zheng Minghua, 1993). These demonstrated that the deposits were formed under special conditions. Studies (Zheng Minghua et al., 1994) show that the Se– and Au–bearing hydrothermal ore solutions are characterized by medium and low temperatures (142—270℃) and low pressure ($< 300 \times 10^5$). When the ore–forming elements were precipitated, the pH and Eh values were 3.69—5.88 and −0.5—+0.082 respectively. In hydrothermal ore solutions gold and selenium migrated mainly in the form of the complex $[Au(HS,HSe)_2]^-$. The decrease in sulphur fugacity, increase in oxygen fugacity and mixing of hydrothermal solutions with cold groundwater are the direct factors for promoting the precipitation of gold from the hydrothermal ore solutions.

This study suggests that under hydrothermal geochemical and physical–chemical conditions given in our deposits selenium can be transported and concentrated through hydrothermal solutions, thus forming independent selenium minerals and selenium concentrated mineralizations. Because selenium minerals indicate a very close relationship with gold, selenium probably plays an important role in gold remobilization and concentration.

In a word, with such a complex element assemblage of Au–Cu–U–Mo–Se–PGE, gold deposits hosted in the Cambrian chert formation are really unusual as compared with other gold deposits. As a matter of fact, this type of gold deposits has been reported for the first time in China and is worthy of further study (Liu Jiajun et al., 1993b).

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