Physicochemical Conditions of Differential Mineralization of Au and As in Gold Deposits, Southwest Guizhou Province, China*

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Abstract: The conditions under which gold and arsenic are enriched separately during mineralization in gold deposits in southwestern Guizhou Province were described and the thermodynamic calculations gave: 200 - 150°C at $400 \times 10^{-6} - 300 \times 10^{-6}$ Pa (corresponding to a depth between 1.6 km and 1.2 km); $\lg f_{0_2} = 40$ to -35 Pa; $\lg f_{S_2} = 20$ to -16 Pa; pH 5.0 -4.2 and Eh = 0.53 V

Key words: Carlin-type gold deposit; gold; arsenic; differential mineralization; physicochemical condition

The spatial zonation of Au and As is strikingly notable in gold deposits in southwestern Guizhou with arsenic anomalies being commonly located 30 - 50 m (sometimes up to 60 m) above gold orebodies. Also, the contents of Au and As are found varying in a regular way in the ores. Particularly, a linear variation can be seen between the two elements in the ores formed in the early stage and higher Au is also shown in arsenic minerals (such as arsenopyrite). This linearity is less apparent in ores of the main mineralization stage during which ores with high Au were always depleted in As and vice versa. The late-stage ores are generally impoverished in As and, on the other hand, arsenic minerals (realgar and orpiment) contain very low or no gold. As a generalization, arsenic is very closely associated with gold in gold deposits, particularly those of hydrothermal types, in the area, giving rise to As-bearing or As-rich gold deposits. In fact, this observation has been used successfully in gold exploration in the area by taking arsenic as an indicator.

However, there is very little information about the differential mineralization of arsenic and gold in the literature. Although the observation was mentioned in the book "Papers on Regional Metallogenesis Conditions of Major Types of Gold Deposits in China" (edited by the Shenyang Institute of Geology and Mineral Resources) that the sympathetic variation of gold and arsenic exists as Au is lower than 2×10^{-6} and As is lower than 2000×10^{-6} and that this relationship becomes poor below these thresholds, but no further details are given.

This problem is studied in this paper, from a physicochemical approach, based on the geology of some major gold deposits in this area (Banqi, Yata, Getang and Lannigou). The author has come to the conclusion that the separation of gold and arsenic is controlled by the changing physicochemical character of the ore-forming hydrothermal system and the pertinent parameters were specified through calculation for the process of differential mineralization.

The Differential Mineralization of Gold and Arsenic

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Vertical zonation

As can be seen from Table 1, the vertical zonation of gold and arsenic is reflected by a reverse relationship of the contents of these two elements in the deposits. Arsenic is enriched at the upper levels near the surface and decreases markedly with increasing depth while gold tends to increase before it is lowered at the base of the deposits.

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Element (× 10 ⁻⁶)	No. of samples	Level I ^{a)}	Level 🛿	Level 👖	Level IV	Level V ^{EJ}
Au	3	0.041	12.125	0.266	5.525	0 303
As	3	5550	2350	1000	1300	500
Sb	4	13.10	33.30	7.85	98.10	4.80
Hg	4	7.055	52.64	16.29	42.12	11.50
Ag	5	0.4555	0.686	0.3995	0.4345	0.5185

 Table 1. The Au and As contents of ores from

 different levels, Lannigou gold deposit

Table 2. Anomalies of As, 50 and Ag and
their positions in terms of shift distance
with reference with gold orebody,
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Element (× 10 ⁻⁶)	Upper level	Int er mediate level	Lower Jevel	Shift (m) distance				
Au	0.42	4.24	0.35					
As	6000	920	150	52				
Sb	200	4000	120	73				
Ag	0.25	0.58	0.06	10				

a: Top level; b: bottom level.

Lateral zonation

As is clear from Table 2, the arsenic anomalies show an obvious shift, in most cases 30 - 50 m, sometimes up to more than 60 m, away from gold mineralization. Generally, the arsenic anomalies are found in the hanging walls of faults above the gold orebodies which are strictly confined in the fault system.

Gold-arsenic correlation coefficients

As shown in Tables 3-5, the contents of gold and arsenic in gold ores from the Getang, Banqi and Yata deposits exhibit a systematic variation during the process of mineralization. The correlation coefficients of gold and arsenic are above 0.5 in the co-precipitation stage, but drop to 0.5 as the separation started and then to as low as 0.4 during the main stage of separation.

Table 3. The Au and As contents of ores of various stages, Getang gold deposit ($\times 10^{-6}$)					Table 4. The Au and As contents of ores of various stages, Banqi gold deposit (× 10 ⁻⁶)						
Mineralization stage	Sample No.	Au	As	Ag	Sb	Mineralization stage	Sample No.	Au	As	Ag	Sb
Сь-	GK02	3.248	498.8	109.4	13011	Co- precipitation	BY1	2.19	2130	2.4	17.5
precipitation	GK08	4.198	120.0	57.0	5136		BK2	1.68	1276	5.6	50
Initial	GK07	7.910	349.8	0.5	1105	Initial separation	BK06	2.699	3701	2.8	34
separation	GK06	9.466	18100	0.6	2401		BD08	9.649	2140	9.4	48
Separation	GS2	0.335	2276	90.4	11950		BY	3.81	6035	6.2	57
	GP1	0.143	116.9	1.4	213	Separation	BK5	0.78	3701	21.6	75

Physicochemical Parameters for Au-As Separation

The process of mineralization is divided into three stages, i.e., the co-precipitation, initial separation and main separation stages based on the temperature at which bulk gold was deposited

Mineralization stage	Sample No.	Au	As	Ag	\mathbf{Sb}
<u>С</u> о-	YS2	0.566	301.5	15.6	2960
precipitation	YK1	0.902	2420	42.3	1478
Initial	YK03	1.261	1667	0.1	1010
separation	Y04	1.570	2410	14.9	134.5
C	YS1	0.346	36180	45.4	4470
Separation	Y104	0.055	1173	0.4	17.1

from hydrothermal fluids and on the Au-As correlation coefficients given above.

The three stages are characterized by changing physicochemical conditions in terms of T, P, $\lg f_{O_s}$, $\lg f_{S_s}$, pH and Eh as presented in Table 6.

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Physicochemical parameter	Co-precipita- tion stage	Initial separa- tion stage -	Separation stage	Evolution trend		
T (U)	350 - 200	200 - 150	< 150	Temperature decreas- ing		
$P (< 10^5 \text{Pa})$	800 - 500	400 - 300	< 150	Pressure decreasing		
$\lg f_{\Omega_2}(\operatorname{Pa})$	< - 40	- 40 35	> 25	Fugacity of O ₂ in- creasing		
$\lg f_{S_2}(\operatorname{Pa})$	< - 26	- 20 16	> -12	Fugacity of S ₂ in- creasing		
рН	6.7-5.4	5.0-4.2	< 4	Acidity increasing		
Eh (V)	- 0.65	- 0.53	- 0.27	More oxidizing		
Depth (km)	3.2-2.0	1.6-1.2	< 0.6	Depth decreasing		

Table 6. Physicochemical parameters during the various stages of Au-As separation

The co-precipitation stage

The ore-bearing solutions at this stage range from 350°C to 200°C in temperature at a pressure between 800×10^5 Pa and 500×10^5 Pa (or an equivalent depth between 3.2 km and 2.0 km), with $\lg f_{0_2} < -40$ Pa, $\lg f_{S_2} < -26$ Pa, pH between 6.7 - 5.4 and a redox potential of -0.65 V. Under this condition gold and arsenic would be precipitated simultaneously. The contents of gold and arsenic in the precipitates are linearly correlated with each other and gold can be commonly found in appreciable amounts in arsenic minerals such as arsenopyrite.

The initial separation stage

Corresponding to the main episode of mineralization, this stage is characterized by a temperature of $200 - 150^{\circ}$ C under a pressure of $400 \times 10^5 - 300 \times 10^5$ Pa (or 1.6 - 1.2 km in depth), with lg f_{0_2} between -40 Pa and -35 Pa, lg f_{S_2} between -20 Pa and -16 Pa, pH 5.0 -4.2 and Eh -0.53 V. The separation of gold and arsenic starts in this stage and goes to an increasing extent with evolution, resulting in highly variable contents of Au and As in the precipitated minerals. Arsenic minerals usually carry very low or no gold.

The separation stage

Prevailed by a condition of $T < 150^{\circ}$ C, $P < 150 \times 10^{5}$ Pa (above a depth of 0.6 km), $\lg f_{O_2} > -25$ Pa, $\lg f_{S_2} > -12$ Pa, pH < 4, Eh = -0.27 V, this stage is a typical low-temperature, low-pressure hydrothermal process, during which gold and arsenic are expected to be highly separated from each other, as indicated by the observation that the arsenic minerals (realgar and orpiment) formed in this stage are greatly depleted in, or completely free from, gold.

Conclusions

1. The differential enrichment of gold and arsenic can be attributed to the changing physicochemical conditions during hydrothermal evolution.

2. From the co-precipitation stage to the separation stage, the ore-bearing solution undergoes a geochemical process during which the temperature and pressure decrease while the fugacities of oxygen and sulfur, acidity and redox potential increase.

3. The coexistence of gold and arsenic as seen in the co-precipitation stage may be due to the miscibility of gas and liquid phases at elevated temperatures and pressures. As the temperature and pressure decrease, the gas phase is expected to escape, carrying arsenic, from the hydrothermal system and drop its arsenic content at the upper parts of the deposits.

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