Au-Sb association and fractionation in micro-disseminated gold deposits, southwestern Guizhou——geochemistry and thermodynamics

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Abstract The dual geochemical character of paragenesis and fractionation between gold, arsenic and antimony in micro-disseminated gold deposits in southwestern Guizhou is discussed in terms of spatial distribution of independent deposits, lateral and vertical enrichment, mineralization stage and factor and correlation analyses. Thermodynamic calculations of solubility and speciation of gold and antimony minerals indicate that gold is transported in hydrothermal solution as $Au(HS)_2^-$ and antimony is mainly as $Sb(OH)_3^0$ although $HSb_2S_4^-$ may be of increasing importance in acid environment at low temperatures during the late stage of mineralization. Changes in physicochemical conditions hold the key to the association and fractionation between gold and antimony. Gold and antimony response differently to physicochemical variations because they are distinct from each other in soluble speciation and mineral solubility, leading to precipitation at different times and localities during hydrothermal evolution.

Keywords: micro-disseminated gold deposits, association and fractionation of ore metals, thermodynamics, southwestern Guizhou.

A number of major micro-disseminated gold deposits have been discovered in recent years in the Yunnan-Guizhou-Guangxi region along the southwest margin of the Yangtze Block. On a large scale, most of these gold deposits are localized in or near deposits or prospects of arsenic, antimony and mercury while within each individual deposit mineralizations of these elements can be observed to varying extent[1—7]. For this reason it is generally accepted that gold is in close association with arsenic, antimony and mercury. With increasing study, however, apparent differences have been noticed in the mineralization of gold from those of As, Sb and Hg with resect to time and space. In other words, gold demonstrates a dual geochemical character of either association or fractionation with arsenic, antimony and mercury [1,4,6]. To reveal the mechanism of this phenomenon, the geochemistry of gold and antimony, taking the micro-disseminated gold deposits in southwest Guizhou as examples, is discussed from a thermodynamic approach.

1 Geological setting

The micro-disseminated gold deposits in southwest Guizhou are found along the southwest margin of Yangtze Craton in Ceheng, Anlong, Wangmo, Xingyi, Xingren and Qinglong (fig. 1).

Major host strata are clay siltstone, fine sandstone, clay rocks and marls of the Middle Triassic Xuman and Bianyang Formation and the Upper Permian Longtan Formation. The deposits are of two types. One type, for example, the gold deposits at Banqi and Getang, has layered or lenticular orebodies extended persistently along unconformity or bedding fractures associated with short anticlines or domes. The orebodies are in sharp contact with the bottom wall (limestone, siliceous limestone) but are transitional to the top wall of pelitic siltstone and carbonaceous shales. Orebodies of the other type, as exemplified by the gold deposits in Zimudang, Yata and Lannigou, are complex in form, commonly occurring as steep or dendritic veins, controlled by oblique fault systems. Their host strata are composed mostly of pelitic limestone, argillaceous rocks and siltstones. Major ore minerals of both of the two types of deposits are pyrite, arsenopyrite, stibnite, realgar and orpiment and common gangue minerals include quartz, calcite and dolomite. Gold is mostly contained in pyrite and arsenopyrite in the primary ore.
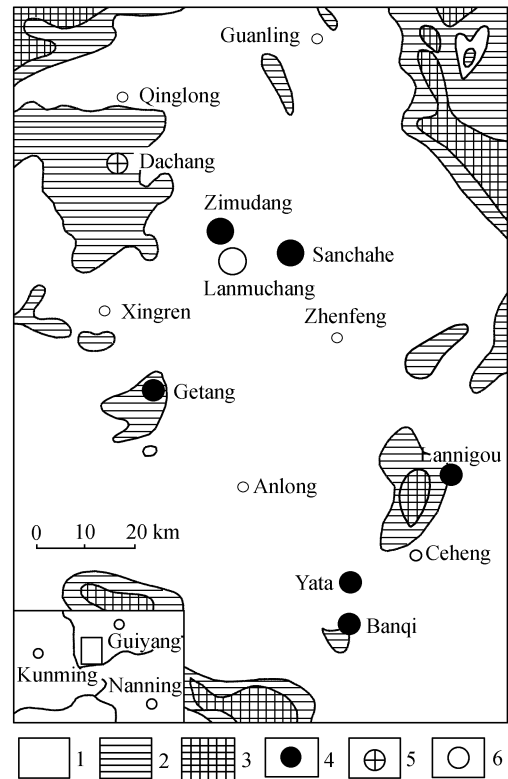

Fig. 1. Sketch geologic map of micro-disseminated gold mineralization region, southwest Guizhou (modified after ref. [7]). 1, Triassic; 2, Permian; 3, Carboniferous and Devonian; 4, gold deposits.

2 Association and fractionation between gold and antimony

It may be interesting to note that gold and antimony are incompatible in terms of independent deposits[1,6]. In other words, a deposit of gold is unlikely a deposit of antimony at the same time and vice versa. For example, gold enrichment is hardly recognizable in Dachang Sb deposit and antimony mineralization in micro-disseminated deposits in southwest Guizhou (Banqi, Yata, Getang, Zimudang and Lannigou), although developed to varying extent, is too poor to be treated also as a deposit of antimony.

In the same deposit, mineralizations of gold and antimony rarely coincide in space but shift from each other both laterally and vertically, resulting in a zoning distribution. The lateral variations of gold and antimony are shown in fig. 2 based on systematic sampling in every 5 meters across the primary halo in Banqi deposit. As may be seen: (i) The abnormal peaks of gold do not correspond to those of antimony. In most cases, antimony may be enriched to varying but insignificant extent around the peak value of gold (4×10^{-6}). This suggests that grade of gold is not
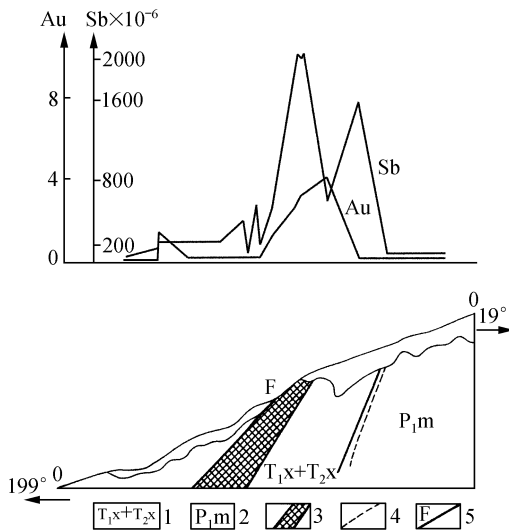
Fig. 2. Plane section of the primary halo, Banqi deposit (simplified after ref. [4]). 1, Middle and Lower Triassic; 2, Lower Triassic Maokou Formation; 3, gold orebody; 4, boundary of alteration; 5, faults and number.

dependent completely on antimony variation. (ii) In the left part of the primary halo, antimony is significantly enriched without apparent concentration of gold (the peak value of gold is only 1.2×10^{-6}), indicating fractionation between the two metals.

Such fractionation is also appreciable in vertical sections as shown by ICP MS analyses of drill cores from Zimudang deposit (table 1, fig. 3). It is evident from fig. 3 that antimony shows three peaks at depths of 216, 190 and 110 m, while only one peak is noticed of gold at the depth of 195 m. The deviations are remarkable and sometimes the enrichment of gold even seems to be accompanied by impov-
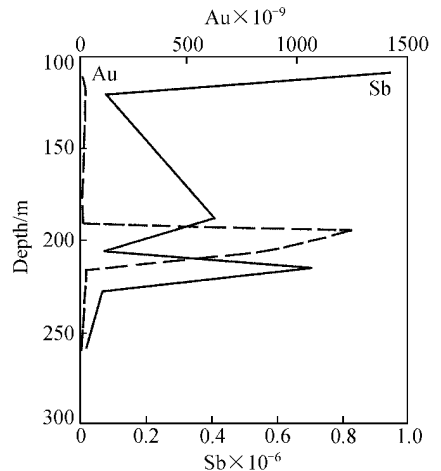
erish of antimony, indicating strongly a tendency of fractionation. Similar variation patterns are observed in drill core of No. 851. In addition, fractionation between gold and mercury is also noticed in Shuiyinchang deposit, Danzhai, where gold orebodies are in the middle lower level of the mercury zone[1].

Au-Sb fractionation can be also noticed with respect to time. In the same deposit, stibnite as the principal mineral of antimony is precipitated later than gold, and the evolution of the hydrothermal fluid can be divided into three stages with respect to Au-Sb relationship[6]: (i) The stage of Au-Sb paragenesis corresponding to the early stage of gold mineralization; (ii) the stage of initial fractionation between Au and

Fig. 3. Au and Sb variation in drilling core (No. 717), Zimudang deposit.

Table 1   Drilling core (Drill No. 717) analyses, Zimudang deposit

Depth / m	Au ($\times 10^{-9}$)	As	Sb	Hg
110	8.4	4 728	0.95	0.34
120	30.1	1 921	0.08	5.01
190	11.3	1 377	0.41	5.95
195	1 240	3 234	0.26	9.18
206	884	1 427	0.07	14.1
215.5	25.7	2 143	0.70	9.61
228	14.5	573	0.05	3.27
240	5	93.2	0.05	2.38
260	2.9	179	0.01	2.45

Analyst: ICP-MS Laboratory, Institute of Geochemistry, Chinese Academy of Sciences.

Sb corresponding to the major stage of gold mineralization; (iii) the stage of Au- Sb fractionation in the late stage of gold mineralization.

As a reflection of Au-Sb fractionation in both spatial and temporal frameworks, the correlation between gold and antimony in either ores and surrounding rocks is generally very poor. Regression analyses based on 116 samples of ore and mineralized rocks in the region show that gold and antimony are very poorly correlated, with a correlation coefficient as low as 0.051.

R-factor analyses based on INAA results of trace elements in 32 samples from Getang, Banqi and Yata deposits show that only arsenic is found in the same major factor with gold and antimony generally falls to different major factors from those of gold. This is consistent with the close association of gold and arsenic in the early stage when arsenic is precipitated as As-pyrite and arseno-pyrite as the major gold carriers, as well as with the fractionation between gold and antimony as mentioned above.

3 Thermodynamic analyses

3.1 Characters of the ore-forming solution

Studies of quartz inclusion fluids suggest that the ore-forming solution belongs to the type of Na-Ca-HS(Cl), with Na^+, K^+, Ca^{2+}, Mg^{2+} as the major cations ($K^+ / Na^+=0.07$- 1.19, $Ca^{2+} / Mg^{2+}=0.13$–14.50) and F^-, Cl^- and HS^- the major anions. With the ascending of the solution from deep to shallow depth, the temperature, oxygen fugacity and pH decreased gradually during the evolution of the hydrothermal system from the early to the late stage (table 2). Such changes in physicochemical conditions, as will be shown later, may have played a major role in controlling the geochemical behaviors of gold and antimony regarding to their paragenesis and fractionation.

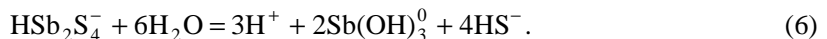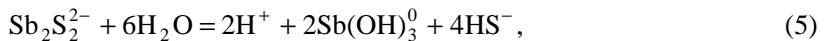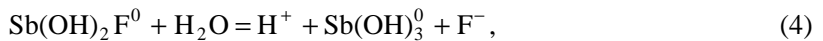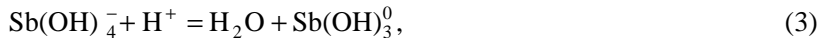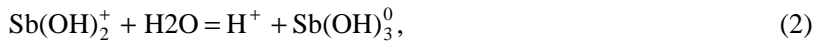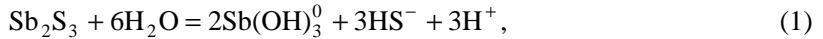Table 2   Physicochemical variation during hydrothermal evolution

Physico-chemical parameter	Early stage of mineralization ——Au-Sb paragenesis	Main stage of mineralization—— initial ractionation be-tween Au and Sb	Late stage of mineralization—— Au-Sb fractionation	Evolution tendency
$T / ℃$	300—250	250—200 （225）	200—100 （175）	decreasing temperature
$P (\times 10^{-5})$	500—300	227—199	117—144	decreasing pressure
pH	>7.50	7.00—6.00	6.00—4.70	increasing acidity
f_{O_2} /bar	1.0×10^{-27}—	1.80×10^{-39}—	1.23×10^{-40}—	decreasing f_{O_2}
	1.0×10^{-33}	1.25×10^{-33}	6.94×10^{-46}	
Depth/km	3.2—2.2	0.66—0.76	0.39—0.48	depth/km decreasing

Numbers in parentheses are averages.

3.2 Transport of gold and antimony

Available studies show that gold solubility can be significantly enhanced by complexing with sulfur and chlorine, in the form of either $Au(HS)^-_2$, $Au_2 (HS)_2 S^{2-}$ or $AuCl^-_2$[8–11]. On the other hand, antimony is mainly transported as hydroxy or sulfur complexes[8, 12—15], while chloride complex is only important in chlorine-rich, extremely acid solutions[15].

Based on the physicochemical characters of inclusion fluids it is reasonable to expect that $Au(HS)^-_2$, $Au_2(HS)_2S^{2-}$, $AuCl^-_2$, Au^+, $Sb(OH)_3$, $Sb(OH)^+_2$, $Sb(OH)^-_4$, $Sb(OH)_2F^0$, $Sb_2S^{2-}_4$ and $HSb_2S^-_4$ are among the major species of gold and antimony in the ore solutions in the micro-disseminated gold deposits in southwest Guizhou. The solubilities of gold and antimony can be calculated from relevant data in refs. [12, 14, 16]. For example, the solubility of antimony in the ore solution is controlled by the following reactions:

$$Sb_2S_3 + 6H_2O = 2Sb(OH)^0_3 + 3HS^- + 3H^+, \tag{1}$$

$$Sb(OH)^+_2 + H2O = H^+ + Sb(OH)^0_3, \tag{2}$$

$$Sb(OH)^-_4 + H^+ = H_2O + Sb(OH)^0_3, \tag{3}$$

$$Sb(OH)_2F^0 + H_2O = H^+ + Sb(OH)^0_3 + F^-, \tag{4}$$

$$Sb_2S^{2-}_2 + 6H_2O = 2H^+ + 2Sb(OH)^0_3 + 4HS^-, \tag{5}$$

$$HSb_2S^-_4 + 6H_2O = 3H^+ + 2Sb(OH)^0_3 + 4HS^-. \tag{6}$$

The total amount of dissolved antimony can be expressed as

$$\sum m_{Sb} = m_{SB(OH)^0_3} + m_{Sb(OH)^+_2} + m_{Sb(OH)^-_4} + m_{Sb(OH)_2F^0} + m_{Sb_2S^{2-}_2} + m_{HSb_2S^-_4}, \tag{7}$$

where the solubility of each of the species, m_i, can be calculated from relevant equation. For example, the solubility contributed by $Sb(OH)^0_3$ can be obtained from the following calculation acording to eq. (1):

$$\lg m_{Sb(OH)^0_3} = 1/2\lg K + 3/2pH - 3/2\lg m_{HS^-} - 3/2\lg \boldsymbol{g}_{HS^-} - \lg \boldsymbol{g}_{Sb(OH)^0_3},$$

where the equilibrium constant K_i can be obtained from refs. [12, 14, 16]，and the activity coefficients ($\boldsymbol{g}_i$), pH and m_{HS^-} are calculated following the procedures given in ref. [17]. In this study, the program SOLVEQ, in which mass and electric balance is taken into account[18], was used in dealing with the nonlinear equation sets to calculate the total amount of dissolved gold and antimony. The average composition of 25 inclusion fluid samples (i.e. Cl^-=0.66, F^-=0.052, SO^{2-}_4=0.066, Ca^{2+}=0.208, Mg^{2+}=0.055 and ΣS=0.001 mol/kg) from six deposits (Banqi, Yata, Getang, Zimudang, Baidi and Lannigou) was assumed to be representative of the ore-forming solution. The calculations were carried out in the ranges of f_{O_2} =10^{-27}—10^{-46} bar, T=100—300℃ and pH=3—8. Only a part of the results are given in fig. 4 owing to space limitations.

The results show that (i) gold is dissolved mainly as $Au(HS)^-_2$ and, to a lesser extent, $Au(HS)_2S^{2-}$ between 100 and 350℃. In comparison with the sulfur complexes, Au^+ and $AuCl^-_2$ are present in negligible concentrations although may be increased with increasing acidity as the hydrothermal system evolved. (ii) In the early and intermediate stages between 200 and 250℃ when the solution is alkaline antimony occurs mainly as $Sb(OH)^0_3$ which will give way to $HSb_2S^-_4$ and $Sb(OH)_2F^0$ in the late stage (100—150℃) as the solution became intermediate to acidic. The cal-
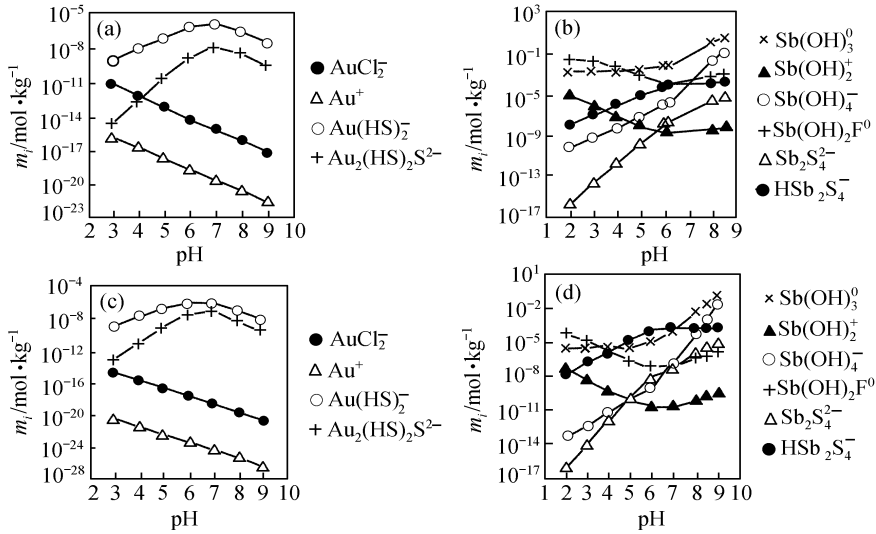
Fig. 4. Speciation of Au and Sb as a function of pH in the ore-forming solution under different physicochemical conditions. (a) Au speciation (250℃, lg f_{O_2} =-38 bar); (b) Sb speciation (250℃, lg f_{O_2} =-38 bar); (c) Au speciation (150℃, lg f_{O_2} =-47 bar); (d) Sb speciation (150℃, lg f_{O_2} =-47 bar).

culated total amounts of dissolved gold and antimony under various physicochemical conditions are given in table 3.

Table 3　　Total amounts of dissolved Au and Sb in the ore-forming fluid

Temperature	250℃		200℃		150℃	
pH	$m_{\Sigma Sb}$	$m_{\Sigma Au}$	$m_{\Sigma Sb}$	$m_{\Sigma Au}$	$m_{\Sigma Sb}$	$m_{\Sigma Au}$
4	7.34×10^{-3}	1.93×10^{-6}	2.60×10^{-4}	4.61×10^{-8}	9.35×10^{-6}	2.47×10^{-8}
5	3.61×10^{-3}	3.22×10^{-6}	1.98×10^{-4}	4.35×10^{-7}	3.84×10^{-5}	5.07×10^{-8}
6	5.31×10^{-3}	9.56×10^{-6}	5.57×10^{-4}	2.61×10^{-6}	1.82×10^{-4}	1.22×10^{-7}
7	6.80×10^{-3}	7.29×10^{-5}	5.33×10^{-3}	2.33×10^{-6}	3.59×10^{-4}	4.28×10^{-6}
8	1.18×10^{-3}	3.63×10^{-5}	1.44×10^{-1}	3.03×10^{-7}	4.90×10^{-3}	4.48×10^{-10}

3.3　Thermodynamics of Au-Sb paragenesis and fractionation

3.3.1　Relative solubilities of ore-metals in hydrothermal solution. As shown in table 3, the solubility of antimony is higher than that of gold by several orders of magnitude over a wide range of pH from acidic to alkaline. If a concentration of 10^{-5} mol/kg in the solution is taken to be the lower limit for ore metal to give rise to deposit of any economic interest, as generally accep- ted[19—21], it is logical to think that an ore forming fluid in which gold can be transported in concentrations above this threshold would surely be capable to transport effectively antimony, but the reverse is not necessarily valid. On the other hand, if the formation temperature of deposits is taken into consideration, i.e. gold deposits are formed at higher temperatures (140—260℃) than antimony (145—190℃), it is not hard to understand that gold and antimony are incompatible in terms of independent deposits as discussed above.
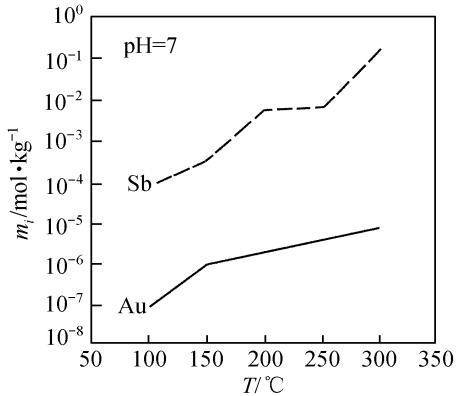
Fig. 5. Solubility of Au and Sb as a function of temperature.

3.3.2 Temperature. The paragenesis between gold and antimony should be dependent on a common mechanism of not only transportation but also precipitation. Fractionation between the two elements would be expected whenever there is any difference in details involved in these mechanisms. It is clear from fig. 5 that the effect of decreasing temperature is different on the precipitation of gold and antimony although precipitation is favored in a general way. The solubility of gold is lowered apparently with decreasing temperature from 100 to 300℃, while the solubility variation of antimony as a function of temperature is much more complicated. Antimony solubility is lowered from 300 to 250℃, but is much less variable with further decrease in temperature between 250 and 200℃. Obviously, fractionation between the two elements is expected as gold is precipitated continuously while antimony is remained in the solution. With further decrease in temperature, the solubility of antimony is significantly lowered from 200 to 100℃, leading to significant deposition at the late stage of mineralization. In the same stage, however, no gold mineralization can be expected because most of it had been precipitated earlier and the solution is impoverished with gold. This accounts for the fractionation between gold and antimony observed in the late stage of hydrothermal evolution.

3.3.3 pH. The solubility variation is also different between gold and antimony as a function of pH (fig. 6). From alkaline to neutral pH the solubility of antimony decreases but that of gold increases. With further decrease in pH from intermediate to acid range, gold solubility decreases while the solubility of antimony varies little between pH 7—5 and even tends to increase as pH is lower than 5. It is therefore apparent that fractionation would take place between gold and antimony with decreasing pH during the evolution of the hydrothermal system with most of the gold precipitated in the main stage of mineralization while antimony would still be carried in the solution and transport continuously.

Fig. 6. Solubility of Au and Sb as a function of pH.

3.3.4 Oxygen fugacity. Association-fractionation of gold and antimony can be also understood in terms of solubility as a function of oxygen fugacity (fig. 7). Under the condition of high f_{O_2} in the early st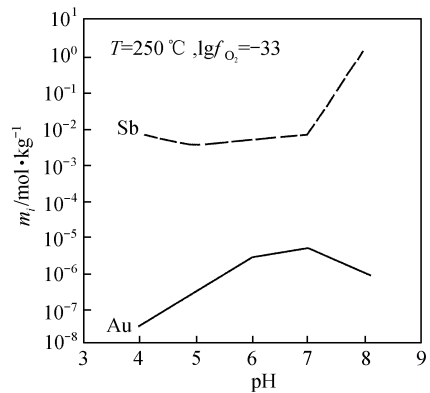age of mineralization ($\lg f_{O_2} = -33$— -27), the solubility of either gold or antimony increases with increasing f_{O_2}, favoring simultaneous transport

of both of them. With the evolution of the hy-drothermal system gold would first be precipitat-ed as its solubility decreased with decreasing f_{O_2} (lg f_{O_2} = -39—-33), while no precipitation is expected for antimony because in this circum-stance its solubility remains nearly constant or even tends to increase. Further fractionation between gold and antimony is inevitable with further decreasing temperature (table 2) as gold is largely impoverished in the solution.

Fig. 7. Solubility of Au and Sb as a function of oxygen fugacity.

4   Conclusions

1) Association-fractionation can be ob-served between gold and antimony in either tem-poral or spatial framework in the micro-disseminated gold deposits in southwest Guizhou.

2) Gold is transported mainly as Au(HS)$_2^-$ while the major soluble species of antimony is Sb(OH)$_3^0$, although HSb$_2$S$_4^-$ may be of increasing importance in acid environment at low tem-peratures during the late stage of mineralization.

3) Changes in physicochemical condition are the critical factor of the association-fractionation relationship between gold and antimony. The difference in soluble species and solu-bility behavior between gold and antimony decides that they would react differently to physico-chemical changes during hydrothermal evolution, thus leading to precipitation at different time and space.

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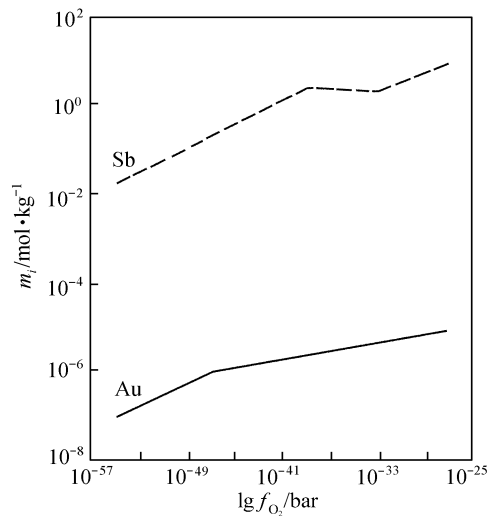
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