

Study on the evolution of ore-formation fluids for Au-Sb ore deposits and the mechanism of Au-Sb paragenesis and differentiation in the southwestern part of Guizhou Province, China

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Abstract Ore deposits (occurrences) of Au, As, Sb, Hg, etc. distributed in Southwest Guizhou constitute the important portion of the low-temperature metallogenic domain covering a large area in Southwest China, with the Carlin-type Au and Sb deposits being the most typical ones. In this paper the Au and Sb ore deposits are taken as the objects of study. Through the petrographic analysis, microthermometric measurement and Raman spectroscopic analysis of fluid inclusions in gangue minerals and research on the S and C isotopic compositions in the gold ore deposits we can reveal the sources of ore-forming materials and ore-forming fluids and the rules of ore fluid evolution. Ore deposits of Au, Sb, etc. are regionally classified as the products of ore fluid evolution, and their ore-forming materials and ore fluids were probably derived mainly from the deep interior of the Earth. Fluid inclusion studies have shown that the temperatures of Au mineralization are within the range of 170–361 °C, the salinities are 0.35 wt%–8 wt% NaCl eq.; the temperatures of Sb mineralization are 129.4–214 °C and the salinities are 0.18 wt%–3.23 wt% NaCl eq.; the ore-forming fluid temperatures and salinities tend to decrease progressively. In the early stage (Au metallogenic stage) the ore-forming fluids contained large amounts of volatile components such as CO₂, CH₄, N₂ and H₂S, belonging to the H₂O–CO₂–NaCl fluid system; in the late stage (Sb metallogenic stage) the ore-forming fluids belong to the Sb-bearing H₂O–NaCl system. The primitive ore-forming fluids may have experienced at least two processes of immiscibility: (1) when early ore-bearing hydrothermal solutions passed through rock strata of larger porosity or fault broken zones, CO₂, CH₄, N₂ would escape from them, followed by the release of pressure, resulting in pressure release and boiling of primitive homogenous fluids, thereafter giving rise to their phase separation, thus leading to Au unloading and mineralization; and (2) in the late stage (Sb metallogenic stage) a large volume of meteoric water was involved in the ore-forming fluids, leading to fluid boiling as a result of their encounter, followed by the drop of fluid temperature. As a result, the dissolubility of Sb decreased so greatly that Sb was enriched and precipitated as ores. Due to differences in physic-chemical conditions between Au and Sb precipitates, Au and Sb were respectively precipitated in different structural positions, thus creating such a phenomenon of Au/Sb paragenesis and differentiation in space.

Key words Au-Sb ore deposit; fluid inclusion; ore-forming fluid evolution; Au-Sb paragenesis; differentiation; Guizhou Province

1 Introduction

Lying on the southwestern margins of the Yangtze Platform is an important constituent part of the vast low-temperature metallogenic domain in Southwest China (Hu Ruizhong et al., 2007), and regionally are developed the typical Carlin-type Au and Sb ore

deposits. So it is also an area where the Carlin-type Au deposits were first discovered in China, and those Au deposits seem to have all been found in the known As, Sb and Hg ore deposits (occurrences) or their surroundings. In the Au deposits are usually observed different degrees of As, Sb and Hg mineralization (Zhu Laimin and Hu Ruizhong, 1999). Previous re-

search workers had made some research on the relationship among the Au, As, Sb and Hg ore deposits in this region, holding that there must be a close relation in occurrence between the strata-bound Carlin-type Au deposits in Southwest Guizhou and the Dachang strata-bound Sb deposit in Qinglong, Guizhou (Cao Hongshui, 1991; Tan Yunjin, 1994; Han Zhijun et al., 1999; Liu Jianzhong, 2001; Gao Zhenmin et al., 2002; Tao Ping et al., 2002; Xia Yong et al., 2006). However, some scholars considered that the Getang Au deposit and the Dachang Sb deposit occurring in the interlayered broken zone at the karst interrupted surface between the Upper and Lower Permian series are of unique metallogenic significance (Fan Jun and Xiao Rongge, 1997; Zhuang Hanping et al., 1998). As for the phenomenon of Au-Sb paragenesis and differentiation, some scholars made some studies on the thermodynamics of Au-Sb paragenesis and differentiation (Zhu Laimin and Hu Ruizhong, 1999), the mechanism of transport and precipitation of ore-forming materials for Au ore deposits (Wang Xiaochun, 1998) and the rules of Au transport in the “Fe-Au-Sb-S” system (Li Jiuling et al., 1997) and some achievements were made. However, no overall comparative and systematic research has been made on the evolution of Au, As and Sb hydrothermal system on a regional scale. In the paper a comparative study has been conducted on the petrography, micro-thermometry, laser Raman spectroscopy of fluid inclusions and isotope geochemistry in the Au and Sb ore deposits in the region of Southwest Guizhou, and this paper, in combination with the geological conditions, fully revealed the sources, properties and evolution rules of ore-forming fluids for the Au, Sb ore deposits in this region and also analyzed the mechanism of Au/Sb differentiation in the hydrothermal system, thus providing the basis for the exploration of the interaction mechanism of fluids in association with Au and Sb mineralization, as well as for the metallogenic prediction there.

2 Regional background and the geology of ore deposits

Southwest Guizhou Province is the important region where the Carlin-type Au, Sb, Hg ore deposits and other mineral resources are distributed (Fig. 1), and it is located at the juncture of the southwestern margin of the Yangtze Platform and the westward extension of the Youjiang fold zone of the South China fold system. The regionally exposed strata are dominated by the Devonian to Triassic ones, with the Triassic system being distributed most widely, followed by the Permian system; the Carboniferous and Devonian strata are seen in the cores of a few anticlines. The total thickness of the exposed strata reach 10000

meters or more, showing the characteristics of alternative sedimentation of a suite of shallow sea-continental shelf platforms and basins. Development of the Devonian to Permian strata displays the distinguishing features of alternative sedimentation of shallow sea-continental shelf platform and basin. The regionally tectonic outline came into being during the Yanshanian period and its tectonical deformation assemblage is complex and diverse in form, featuring the tight closeness of anticline and the gentle and wide extension of syncline. Regional magmatic rocks are not developed, mainly including the Permian Emeishan basalts overlying the Maokou Formation and scattered diabase, alkaline ultramafic rocks, etc. Due to a great disparity between diagenetic age (Song Xieyan et al., 2001; Liu Shen et al., 2010) and metallogenic age (Peng Jiantang et al., 2003; Chen Mao-hong et al., 2007, 2009; Su Wenchao et al., 2009), the Emeishan basalts and alkaline ultramafic rocks have a relatively small impact on Au and Sb metallogenesis or have no direct genetic relation to Au and Sb ore deposits.

Gold and Sb ore deposits are distributed mainly in the “triangular terrain” confined by the regionally N-E extending Mile-Shizong deep fault, the N-W extending Ziyun-Yadu deep fault and the nearly E-W extending Kaiyuan-Pingtang deep fault. At present, several hundreds of Au ore deposits (occurrences) have been discovered, of which there are two super-large Au deposits, four large-sized Au deposits, while the Dachang is one of the most typical Sb ore deposits in this area. The Carlin-type Au deposits are hosted mainly in the Permian and Triassic strata, the strata-bound-type orebodies are dominated in the Permian Longtan Formation and the “Dachang Bed” and the fault-bound-type orebodies are dominated in the Permian Changxing and Dalong formations and the Triassic Yelang Formation. Antimony ore deposits occur mainly in a suite of hydrothermally altered, strongly silicified limestones and brecciated claystones and siltstones near the unconformable boundary between the Permian Maokou Formation (P_{2m}) and the Permian Longtan Formation (P_{3l}). Antimony orebodies are stratiform and stratoid in shape. In space Au and Sb are of paragenesis or differentiation. Although a certain amount of Sb is tested in the Au ore deposits, gold mineralization can also be observed in Sb orebodies, but only few Au-Sb associated ore deposits have been found.

Ore minerals in the Carling-type Au deposits include pyrite, arsenopyrite, realgar (orpiment), stibnite, and cinnabar (occasionally seen). Pyrite is distributed in the disseminated manner, realgar is distributed in the massive and stockwork forms. Gangue minerals are quartz, dolomite, calcite, fluorite, clay minerals, etc. These minerals form the following paragenic as-

sociations: quartz-dolomite, quartz-fine-grained pyrite-arsenopyrite, quartz-calcite-realgar-orpiment-stibnite-cinnabar, coarse-grained pyrite-marcasite, etc. and these associations respectively represent the minerals which crystallized at different stages of hydrothermal metallogenesis (Table 1). However, the mineral associations are relatively simple in Sb ore deposits. Metallic minerals are dominated by stibnite and subordinated by the sedimentation-type pyrite which was reworked by late-stage hydrothermal solutions. Non-metallic minerals include mainly quartz, fluorite, calcite, kaolinite and minor barite. Hydrothermal alterations in the Au, Sb ore deposits include silicification, decarbonation, sulfidization, fluoritization, clayization and minor baritization.

Table 1 Forming sequence of minerals in the hydrothermal system in Southwest Guizhou Province

| Stage Mineral | Gold/antimony hydrothermal system | | |
|------------------|-----------------------------------|---|---|
| | Quartz-dolomite-pyrite stage | Arsenopyrite-pyrite-quartz-clay mineral stage | Quartz-orpiment-stibnite-realgar-fluorite-calcite |
| Quartz | ————— | | |
| Dolomite | ————— | | |
| Marcasite | | ————— | |
| Arsenic pyrite | | ————— | |
| Native gold | | ————— | |
| Arsenopyrite | | ————— | |
| Clay mineral | | ————— | |
| Orpiment | | | ————— |
| Stibnite | | | ————— |
| Realgar | | | ————— |
| Fluorite | | | ————— |
| Calcite | | | ————— |

3 Study of fluid inclusions

The phenomenon that Au and Sb in the ore deposits distributed in the region of Southwest Guizhou are both of paragenesis and differentiation may be related to the properties and evolution of ore-forming fluids for the Au and Sb ore deposits in that region, and the fluid inclusions do preserve the basic information about primitive ore-forming fluids. Quartz and fluorite samples used in this fluid inclusion study were collected from the Taipingdong, Zimudang and Ni-baoka Carlin-type Au ore deposits and the Dachang Sb ore deposit. Quartz was taken from the three Au ore deposits and it was the product of silicification in the process of Au mineralization. Such quartz coexists with Au-bearing pyrite and arsenopyrite, while fluorite in the Sb ore deposit usually coexists with stibnite. Therefore, research on fluid inclusions in the gangue minerals quartz and fluorite in the Au and Sb ore de-

posits can effectively reveal the properties and evolution rules of fluids in the Au and Sb hydrothermal system.

The micro-thermometric experiments on fluid inclusions were accomplished at the Laboratory of Fluid Inclusions, Institute of Geochemistry, Chinese Academy of Sciences, on the Linkam THMSG600 Model heating-freezing stage (made in UK). Please refer to Leng Chengbiao et al. (2008) for the procedure of concrete measurement.

As for both liquid and gaseous inclusions, their salinities were converted from table looking-up of ice-point temperatures (Bodnar, 1993). This table is based on the following formula: $W_{NaCl}=0.00+1.78X-4.42\times 10^{-2}X^2+5.57\times 10^{-4}X^3$, where X is the absolute value of ice-point temperature (Hall et al., 1988).

The laser Raman spectroscopic experimental study of individual fluid inclusions was conducted on the Renishaw in Via Reflex Model laser Raman spectroscope at the State Key Lab. of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The testing conditions are: light source: Spectra-Physics argon ion laser (Ar^+ laser); laser wavelength: 514.5 nm; laser power: 20 mW, sample surface laser power: 5 mW; optical grating: 1800 grooves/mm; spectral line resolution: 2 cm^{-1} ; spatial resolution: $11\text{ }\mu\text{m}$ ($\times 100$ objective lens); scanning time: 10, 30, and 60 sec; and scan area: $150\text{--}4500\text{ cm}^{-1}$.

3.1 Fluid inclusion types

Abundant fluid inclusions were developed in quartz and fluorite (Fig. 2). The fluid inclusions are $3\text{--}70\text{ }\mu\text{m}$ in diameter, generally within the range of $10\text{--}40\text{ }\mu\text{m}$. There are two types of fluid inclusions, including primary and secondary ones. The primary fluid inclusions are scattered like the stars, showing a zonal distribution pattern along the crystal faces, while the secondary fluid inclusions are distributed in the linear form along cracks. According to their compositions and phase states at room temperature (21°C) (Lu Huanzhang et al., 2004), the fluid inclusions can be divided into four types:

3.1.1 Aqueous solution inclusions

Fluid inclusions of this type are commonly seen in the Sb ore deposits, but less in the Carlin-type Au ore deposits. Fluid inclusions of this type in the Sb ore deposits vary in volume over a large range. They are generally $6\text{--}70\text{ }\mu\text{m}$ in long-axis length, with the gas/liquid ratios of 3%–25%. The inclusions are mostly elongated, elliptical and irregular in shape (Fig. 2e, g). The aqueous solution inclusions can be divided into gas/liquid two-phase and pure liquid-phase aque-

ous solution inclusions.

According to gas/liquid ratios, the aqueous solution inclusions can be divided into liquid-rich phase, gas-rich phase and pure liquid phase aqueous solution inclusions. The liquid-rich two-phase aqueous solution inclusions occupy a relatively large proportion, and they are mostly negatively crystalline, elliptical, elongated and irregular in form, with the long axis length generally being 8–60 μm and the gas/liquid ratio generally being 3%–30%; gas-rich two-phase aqueous solution inclusions are relatively rare, mostly elliptical but subordinately negatively crystalline in form, with the gas/liquid ratio generally being 52%–80%; pure liquid aqueous solution phase inclusions are commonly seen in the Sb ore deposits, distributed in groups or coexisting with the two-phase aqueous solution inclusions (Fig. 2e). Inclusions of this type are light in color and vary over a relatively large range in

volume, with the long axis length generally being 3–40 μm. Inclusions of this type are mostly irregular and elliptical in form. In the process of temperature rising, liquid-rich phase inclusions are homogenized to liquid phase while gas-rich phase inclusions are homogenized to gas phase.

3.1.2 CO₂-H₂O inclusions (type C)

CO₂-H₂O inclusions are commonly seen in the Carlin-type Au ore deposits, but no in the Sb ore deposits. At room temperature the inclusions are present as two-phase ones (Fig. 2a, b, c), with gas/liquid ratios mostly being within the range of 20%–70%. Inclusions of this type are mostly elliptical and nearly elliptical in form, with the long axis length varying between 8–30 μm. Only a small number of CO₂-H₂O inclusions are present as three-phase ones at normal

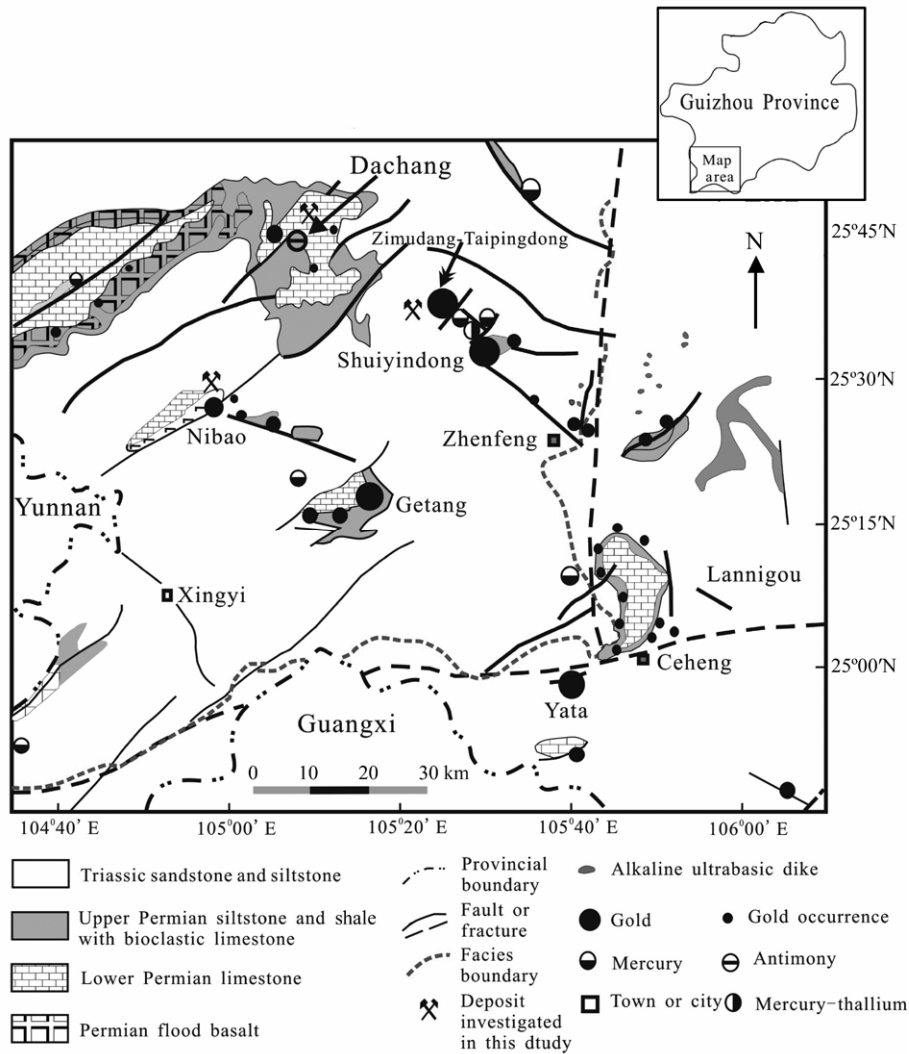


Fig. 1. Geological sketch map showing the distribution of Au, Sb and Hg ore deposits in Southwest Guizhou Province (Modified by Su Wentao et al., 2009).

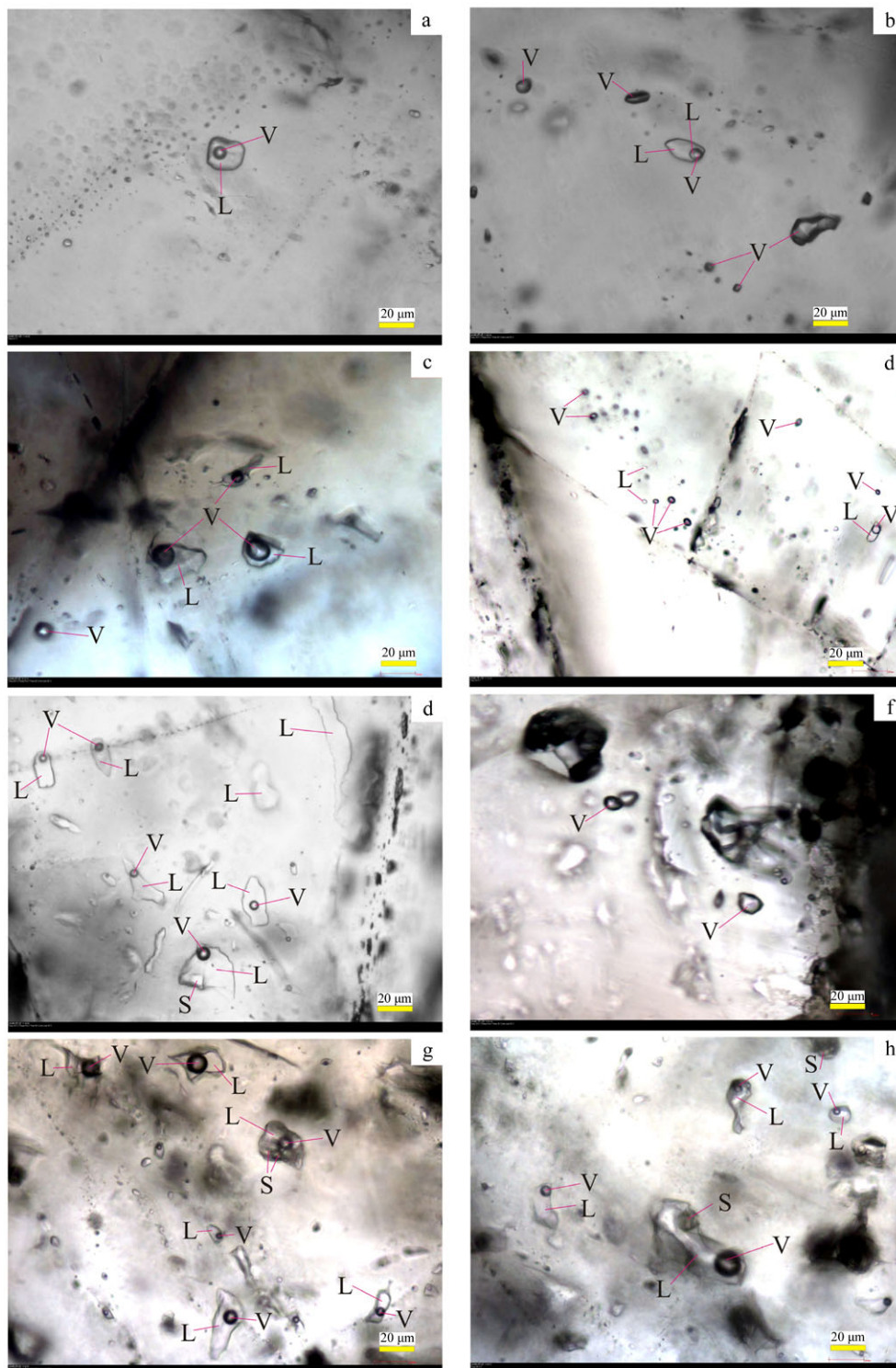


Fig. 2. The types of fluid inclusions in gangue minerals (quartz, fluorite) in the Au and Sb ore deposits in Southwest Guizhou Province. a. CO₂-bearing two-phase inclusions in the Au ore deposits; b. CO₂-rich three-phase and pure gas-phase inclusions in the Au ore deposits; c. pure CO₂ two-phase inclusions and gas/liquid two-phase inclusions in the Au ore deposits; d. pure gas-phase and gas/liquid two-phase inclusions in the Au ore deposits; e. gas/liquid two-phase and pure liquid-phase inclusions in the Sb ore deposits; f. pure gas-phase inclusions in the Sb ore deposits; g and h. gas/liquid two-phase and daughter crystal-bearing inclusions in the Sb ore deposits. Note: V. Gas phase; L. liquid phase; S. solid phase.

temperature (Fig. 2b). The color at the phase boundary is deep. Usually the two-phase CO₂-H₂O inclusions exhibit three-phase structure in the process of temperature dropping, some inclusions show no obvious phase change when the temperature drops to -90°C, which may be attributed to the fact that the inclusions contain CH₄, etc. (van Denkerkhof and Thiery, 2001).

3.1.3 Pure CO₂ inclusions (type PC)

The Au ore deposits contain a minor amount of pure CO₂ inclusions, which occur mainly as single-phase ones (Fig. 2d). Two-phase pure CO₂ inclusions do exist but are relatively rare (Fig. 2c). In the freezing process T_{mco_2} value of this type of inclusions is generally close to or slightly lower than -56.5°C, indicating that the major component in the inclusions is CO₂. The inclusions are usually elliptical and nearly rounded in form, with the long axis length lying between 2–15 μm. The color at the inclusion boundary is relatively deep. In the same quartz crystal one can usually observe the CO₂-type and CO₂-H₂O-type inclusions, and the filling percentage of the CO₂-H₂O-type inclusions shows a great variation trend (Fig. 2b), probably owing to phase separation during gold metallogenesis (Lu Huanzhang et al., 2004; Diamond, 2001).

3.1.4 Daughter crystal-bearing inclusions

Inclusions of this type exist as gas/liquid two-phases in fluorite from the Sb ore deposits. The inclusions are irregular, elliptical and elongated in form, with the long axis length generally being 8–60 μm. The daughter crystals vary greatly in color, which are divided into transparent and opaque minerals (Fig. 2g, h).

3.2 Micro-thermometry of fluid inclusions

Gas and liquid inclusions in quartz and fluorite were determined for their homogenization temperatures (T_h) and ice-point temperatures (T_m) (Table 2). As shown in Table 2, the homogenization temperatures of gas/liquid two-phase and three-phase inclusions in quartz from the Carlin-type Au deposits are 170–361°C and 190.4–241°C, respectively, both of which are basically consistent with each other. The homogenization temperatures vary over a large range with the peak values within the range of 200–220°C; the homogenization temperatures of gas/liquid two-phase inclusions in fluorite from the Sb ore deposits are 129.4–214°C, with peak values within the range

of 140–160°C.

Table 2 shows that the ice-point temperatures of fluid inclusions in quartz from the Carlin-type Au ore deposits vary over the range of -5.1– -0.2°C and the corresponding salinities vary over the range of 0.35 wt%–8 wt% NaCl eq., with the peak values being 3.0 wt%–5.0 wt% NaCl eq. The ice-point temperatures of gas/liquid two-phase inclusions in fluorite from the Sb ore deposits vary over the range of -1.9– -0.1°C and the corresponding salinities vary over the range of 0.18 wt%–3.23 wt% NaCl eq., with the peak values being 1.0 wt%–2.0 wt% NaCl eq. As shown in the salinity-homogenization temperature diagram (Fig. 3), the open dots in the elliptical area delineated by the dashed line represent the salinity-homogenization temperature points of fluid inclusions in the Au ore deposits and the open triangles in the rectangular area delineated by the dashed line represent the salinity-homogenization temperature points of fluid inclusions in the Sb ore deposits. As can be seen in Fig. 3, the salinity-homogenization temperature points of fluid inclusions in the Au ore deposits are relatively scattered, mainly distributed on the upper right corner of the diagram, while those of fluid inclusions in the Sb ore deposits are relatively concentrated, mainly distributed on the lower left corner. The salinity-homogenization temperature points of fluid inclusions in the Au and Sb ore deposits show a trend of continuous variation.

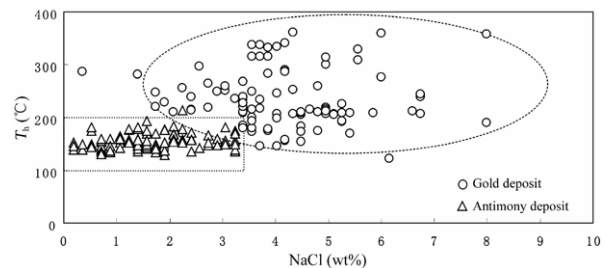


Fig. 3. Salinity-homogenization temperature diagram of fluid inclusions in the Au and Sb ore deposits in Southwest Guizhou Province.

3.3 Composition analysis of fluid inclusions

The laser Raman probe analysis is an approach of non-destructive qualitative measurement and by using this method one can quickly determine the composition of major covalent compounds in the gas phase of fluid inclusions. By using laser to scan the gas, liquid and solid phases of individual inclusions, one can determine the sites of characteristic Raman peaks corresponding to different components, so as to judge their compositions (Lu Huanzhang et al., 2004).

From the laser Raman comparative analysis of inclusions in the gangue minerals selected from the

Taipingdong, Zimudang and Nibao Carlin-type Au ore deposits and the Dachang Sb ore deposit it can be seen clearly that there exist significant differences in the composition of fluid inclusions from the Au and Sb ore deposits. Fluid inclusions in the Carlin-type Au ore deposits are relatively complicated in composition, whereas those in the Sb ore deposits are relatively simple in composition (Fig. 4).

The analyses of gas/liquid two-phase inclusions in quartz from the Carlin-type Au deposits indicate that the liquid phase is dominated by the salt-water system, with a minor amount of CO₂, etc. The gas-phase is relatively complicated in composition, and the gaseous components are CO₂, CH₄, N₂, H₂S, etc. (Fig. 4a, b, c, d, e). On the whole, the composition of gas/liquid two-phase fluid inclusions possesses the following rules of variation. Generally, in the gas/liquid two-phase inclusions with relatively small gas/liquid ratios the gas-phase components are mainly CO₂ or CO₂ and CH₄ with minor N₂, while in the gas/liquid two-phase fluid inclusions with relatively large gas/liquid ratios the gas-phase components are mainly CH₄ or CH₄, CO₂, with minor N₂ (Fig. 4d). Meanwhile, pure gas-phase CO₂ inclusions have also been discovered in quartz, which are characterized by small volume. The main component is CO₂, with minor CH₄ and N₂ (Fig. 4a). All these may indicate that the ore-forming fluids once experienced phase separation, representing the major characteristic features of the main-stage Au metallogenesis. Found in fluorite from the Sb ore deposits are gas/liquid two-phase, pure liquid-phase, pure gas-phase and daughter crystal-bearing inclusions. The composition of fluid inclusions is dominated by a simple salt-water system (Fig. 4f, g, h) and the solid components of solid inclusions are mainly organic matter and REE minerals (Fig. 4i, j), showing the characteristics of late-stage hydrothermal metallogenesis.

4 Sulfur and carbon isotope geochemistry

The sulfur isotopic composition can be used as the most direct and most effective approach to trace the source of sulfur in ore-forming fluids (Ohmoto and Goldhaber, 1997). Different geological bodies in nature show great differences in carbon isotopic composition, so variations in their $\delta^{13}\text{C}_{\text{V-PDB}}$ values can reflect the source of carbon to a certain extent. Therefore, research on S and C isotopes in the Carlin-type Au deposits can provide much information about the source of early ore-forming fluids. Sulfides are commonly developed in the Carlin-type Au deposits, including As-bearing pyrite, arsenopyrite, realgar (orpiment), stibnite, cinnabar, etc. The sulfides are closely related to the formation of Au ore deposits,

responsible for the formation of the unique Au-As-Sb-Hg element association in the Carlin-type Au deposits. Ohmoto (1972) pointed out that the sulfur isotopic composition of sulfides in the hydrothermal ore deposits is the function of the isotopic composition of total sulfur in ore-forming fluids, oxygen fugacity (f_{O_2}), pH, ionic intensity and temperature. Therefore, the S isotopic composition of hydrothermal sulfides is not only dependent on the $\delta^{34}\text{S}$ of source-region materials, but also related to the physico-chemical conditions of the evolution of ore-forming fluids (Wu Nanping et al., 2003). As the Au ores studied in this paper almost contain no sulfate, pyrrhotite, magnetite, etc, the sulfur isotopic composition of sulfides can approximately represent the sulfur isotopic composition of ore-forming fluids. The main Au-carrier minerals in the Carlin-type Au deposits are As-bearing pyrite and arsenopyrite. Arsenopyrite particles are generally fine in size and low in content, so mono-mineral selection is very difficult. Pyrite of hydrothermal origin is generally extremely fine in size as well (1–30 μm), and larger grain-sized Au-bearing pyrite is generally resultant from the superposition of pyrite of hydrothermal origin on the surface of sedimentary pyrite, with obviously zonal texture (including pyrites crystallized at the sedimentary and hydrothermal stages). And in Au ores is contained more sedimentation-type pyrite which usually occurs in sedimentary strata and by way of mono-mineral selection it is still hard to separate such pyrite from the sedimentary strata. Therefore, the sulfur isotopic composition of pyrite mono-minerals can represent the outcome of mixing of sedimentary sulfur and hydrothermal sulfur, but can not reflect the realistic information about the sulfur isotopic composition of ore-forming fluids. As reported previously, the $\delta^{34}\text{S}$ values of pyrite vary over a large range of -8.41‰–27.17‰ (Xia Yong, 2009; Wang Chenghui et al., 2010). Realgar in close association with the formation of Au ore deposits can be taken as an ideal candidate for sulfur isotopic analysis. Analysis showed that the $\delta^{34}\text{S}$ values of realgar vary over the range of +0.81‰–+3.03‰ (Fig. 5), with a range of 2.22‰ and a mean value of 1.6‰. As can be seen, the data vary over a relatively narrow range and the homogenization degree is relatively high, indicating the isotopic characteristics of mantle-source sulfur ($\delta^{34}\text{S}$ values of mantle-source sulfur are 0‰–3‰, Chaussidon and Lorand, 1990). In their studies of sulfur isotopes in the Carlin-type Au deposits in the central-western parts of the United States, Kesler et al. (2005) also indicated that the sulfur isotopic composition of hydrothermal overgrowths in pyrite is consistent with that in realgar, which may reflect that both the minerals were derived from the same source and they would come from the deep interior.

Table 2 Results of micro-thermometric measurement and some characteristic parameters for fluid inclusions in the Au and Sb ore deposits in Southwest Guizhou Province

| Hydrothermal stage | Mineral | Type | Number | Homogenization temperature ($T_h/^\circ\text{C}$) (Peak value) | Ice-point temperature ($T_m/^\circ\text{C}$) | Salinity $\omega(\text{NaCl eq.})$ 140–160 (%) (Peak value) |
|---|----------|-------------|--------|--|--|---|
| Metallogenic stage of the Carlin-type Au deposits | Quartz | Gas-liquid | 171 | 170–361 200–220 | -5.1–-0.2 | 0.35–8.0 3.0–5.0 |
| | | Three-phase | 9 | 190.4–241 | -2.9–-2.6 | 4.34–4.8 |
| Metallogenic stage of Sb ore deposits | Fluorite | Gas-liquid | 179 | 129.4–214 140–160 | -1.9–-0.1 | 0.18–3.23 1.0–2.0 |

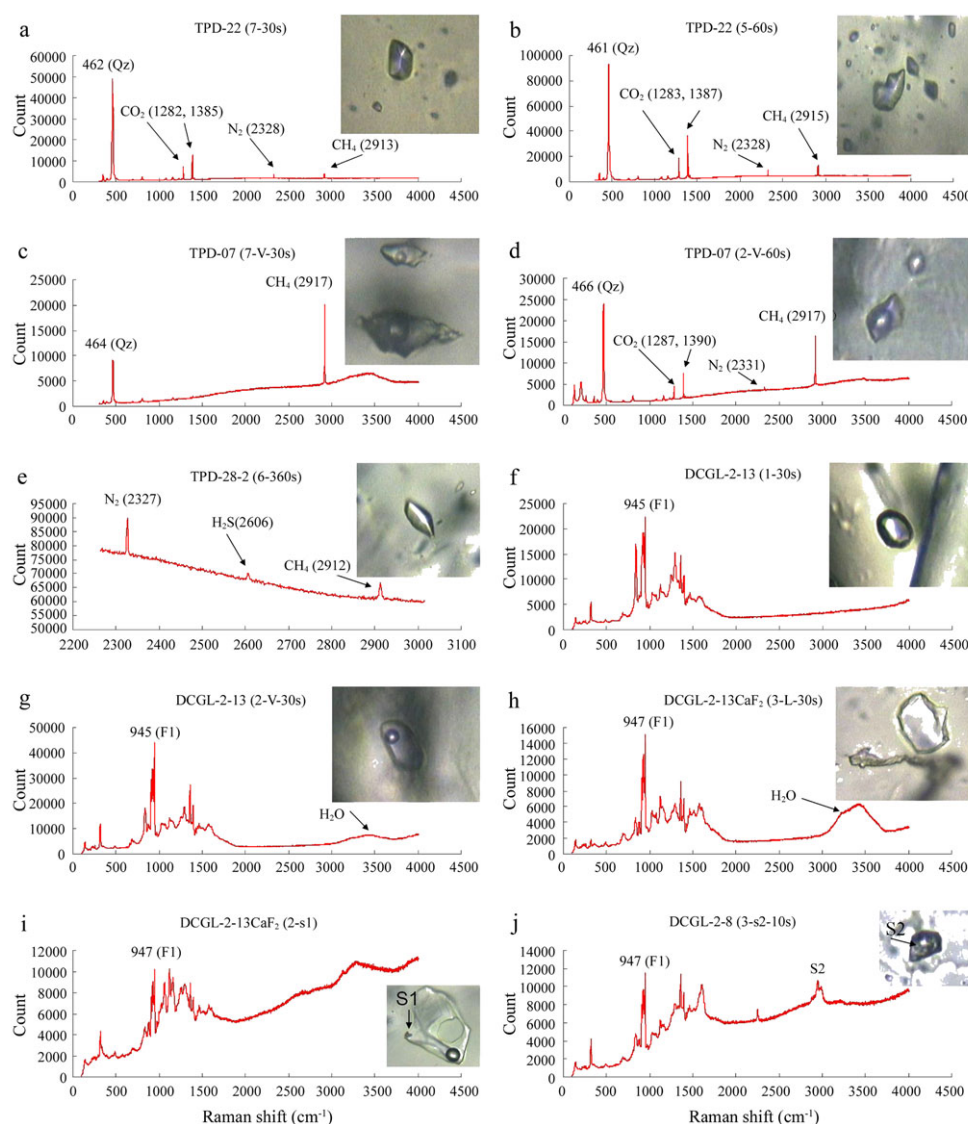


Fig. 4. The laser Raman (LRM) spectra of fluid inclusions in the Au and Sb ore deposits in the region of Southwest Guizhou. a. CO₂-rich gas-phase inclusions in Au ores; b. CO₂-, CH₄-, N₂-rich gas-phase inclusions in Au ores; c. gas/liquid two-phase inclusions in Au ores, with CH₄ as the main gas-phase component; d. gas/liquid two-phase inclusions in Au ores, with CO₂, CH₄ as the main gas-phase components; e. H₂S-bearing inclusions in Au ores; f. the composition of pure gas-phase inclusions in Sb ores; g. the gas-phase composition of gas/liquid two-phase inclusions in Sb ores (containing a minor amount of H₂O); h. the composition of pure liquid-phase inclusions in Sb ores (mainly H₂O); i, j. the composition of daughter minerals (S1, S2) in gas/liquid two-phase inclusions in Sb ores. Qz. Quartz; Fl. fluorite; S. daughter mineral or organic matter.

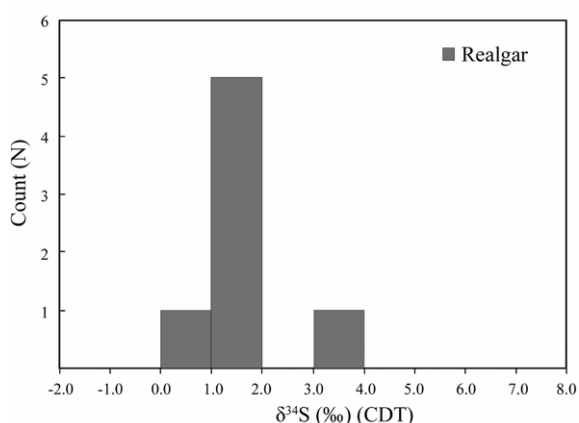


Fig. 5. Frequency histogram of sulfur isotopes in realgar from the Carlin-type Au deposits.

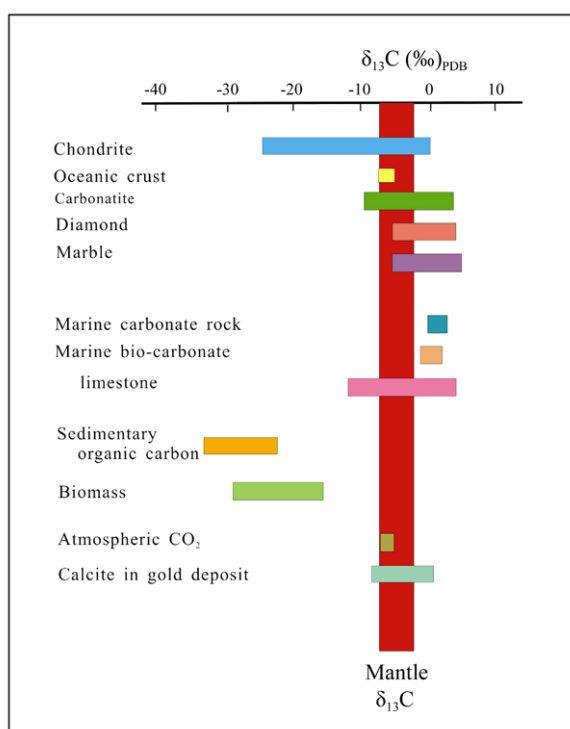


Fig. 6. Comparison of the carbon isotopic values of calcite ($\delta^{13}\text{C}_{\text{V-PDB}}$) in the Carlin-type Au deposits with those of other relevant materials (Modified by Mao Jingwen et al., 2003).

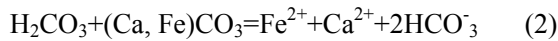
At the metallogenic state calcite is the product of decarbonation in the process of metallogensis and also one of the important gangue minerals in the Au ore deposits. The $\delta^{13}\text{C}_{\text{V-PDB}}$ values of calcite vary over the range of -4% – -9% (Fig. 6), partly near 0% . Carbon isotopes also display the characteristics of deep-source carbon (the average $\delta^{13}\text{C}_{\text{V-PDB}}$ values of deep-source carbon are within the range of -5% – -8% , Hoefs J., 1980), showing that the carbon in ore-forming fluids may have been brought about by mantle-source magmas in the deep interior of the Earth.

5 Properties and evolution of ore-forming fluids and mechanism of Au/Sb paragenesis-differentiation

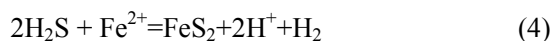
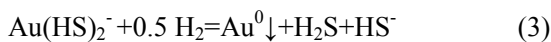
Southwest Guizhou is an important region where the Carlin-type Au and Sb ore deposits are distributed in China, and their tempo-spatial distribution is related to the unique regionally geological background. During the Late Yanshanian period there occurred unified large-scale fluid activity and transport in the Yunnan-Guizhou-Guangxi regions, which are closely associated with vast epithermal metallogenesis (Wang Guozhi et al., 2002). Both ore-forming materials and fluids seem to have come predominantly from the deep interior of the Earth. Tectonic activities occurring from the Late Indosinian to the Early Yanshanian mark the end of evolution history of the basin in in this region. The development of strata folds, faults, deep giant faults and magmatic activity, abnormally high ground temperature, and relatively deep burial were responsible for the formation of super-pressure ore-forming fluids enriched in volatile mobile elements (Zhang Xingchun et al., 2004; Zhang Yu et al., 2010). And these fluids also extracted the ore-forming elements in the Au-, Hg-, Sb-, As- and Tl-enriched strata and rocks both in the basement and at the deep levels (Hu Ruizhong et al., 2002), forming ore-forming fluids. The Au-, As-, Sb-, and Hg-bearing ore-forming fluids constituted the ore-forming hydrothermal system in this region. Fluid inclusions in the Carlin-type Au ore deposits contain large amounts of volatile components such as CO_2 , CH_4 , N_2 and H_2S , with the homogenization temperatures of $170\text{--}361^\circ\text{C}$ and the salinities within the range of $0.35\text{ wt}\%$ – $8\text{ wt}\%$ NaCl eq. (Table 1), displaying that the Au ore-forming fluids belong to the $\text{H}_2\text{O-CO}_2\text{-NaC-(Au)}$ system. The temperatures and salinities of ore-forming fluids are relatively high and their oxygen fugacities are relatively low (Li Baohua et al., 2011). CO_2 may act as a pH buffering agent in Au ore fluids. Because of the condition of weak acidity, the solubility of Au-bearing complexes is highest (Lu Huanzhang, 2008), favorable to the transport of Au in ore-forming fluids. And H_2S has an important impact on the transport and precipitation of sulfides in the Au ore deposits. Studies showed that gold in ore-forming hydrothermal solutions may be present mainly in the form of complexes such as $\text{Au}(\text{HS})_2^-$, $\text{Au}_2(\text{HS})_2\text{S}^{2-}$, etc. (Rytuba, 1988; Benedetti and Bouleque, 1991; Benning and Seward, 1996; Seward, 1973; Wang Xiaochun, 1998; Zhu Laimin and Hu Ruizhong, 1999). When hydrothermal solutions passed through rocks (carbonate rocks) with a large porosity or fault broken zones, the pressure would be released suddenly, leading to hydrothermal solution boiling due to pressure

release. In this process there may occur phase separation and the NaCl-H₂O-CO₂-(Au) system was divided into the H₂O-NaCl and CO₂-(Au) systems (Lu Huanzhang, 2008), accompanied with the escape of CO₂, CH₄, N₂, etc. As a result, the ore-forming fluids showed a decrease in temperature and pressure and an increase in pH. In this process considerable amounts of Au and Sb were unloaded. In fact, both liquid phase-rich and gas phase-rich fluid inclusions in quartz often coexist in the same plane or in micro-cracks, providing evidence suggesting that there occurred fluid immiscibility in the process of Au metallogenesis, and the oversaturation and precipitation of a small amount of Au in ore-forming fluids led to the formation of native gold grains that were accumulated on the surface of As-bearing pyrite grains or on their edges, forming natural Au grains (Su et al., 2008). Gold in the hydrothermal solutions may find its way into pyrite, arsenopyrite and other sulfides mainly in the form of chemically bonded gold, and Ca²⁺ and CO₃²⁻ took part in the formation of calcite with changes in physico-chemical conditions of ore-forming fluids. The chemical reaction formula in the process is presented as follows (Su Wenchao et al., 2008):

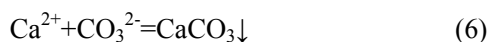
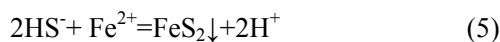
Decarbonation:



Gold and sulfide precipitation:

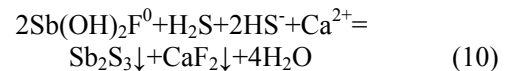
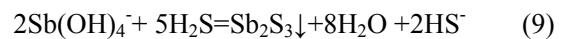
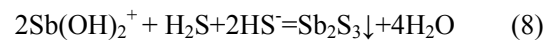
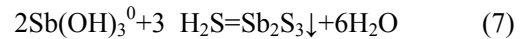


Formation of carbonate veins:



In the case of relatively high temperature, antimony in hydrothermal solutions may be transported as such oxyhydrogen complexes as Sb(OH)₃⁰, Sb(OH)₂⁺, Sb(OH)₄⁻, Sb(OH)₂F⁰, etc. in fluids (Rytuba, 1988; Spycher and Reed, 1989; Tossell, 1994; Williams-Jones and Normand, 1997), and the separation of early ore-forming hydrothermal solutions caused the escape of volatile components such as CO₂, CH₄, N₂, etc. The ore-forming hydrothermal solutions progressively evolved as a H₂O-NaCl system, accompanied by the increase of pH and the rise of oxygen fugacity (Peng Jiantang et al., 2002). At the same time,

antimony found its way into the H₂O-NaCl system. Inclusions of different types in fluorite coexist in the same plane or fissures (Fig. 2e, g), and the existence of organic matter in fluid inclusions indicates that meteoric waters would have been involved in ore-bearing hydrothermal solutions, and the encounter of ore-forming fluids with meteoric waters resulted in boiling of fluids, thus leading to the drop of temperature of the ore-forming hydrothermal solutions and the increase of oxygen fugacity. The reduction of Sb solubility led to the precipitation and enrichment of Sb (Zhu Laimin and Hu Ruizhong, 1999). That is to say, the oxyhydrogen complexes of Sb in the ore-forming hydrothermal solutions reacted with H₂S to form stibnite [reactions (7), (8), (9), (10)], while F⁻ and Ca²⁺ crystallized as fluorite with the change of conditions such as hydrothermal temperature [reaction (10)]. The relevant equations are presented as follows:



So the late-stage ore-bearing fluids with Au- and Sb-bearing ore-forming elements become simple in composition due to phase separation, late meteoric water involvement, successive precipitation of various kinds of materials in ore-forming hydrothermal solutions, and escape of volatile components. At the early stage (Au metallogenic stage) the primitive ore-forming fluids contained such volatile components as CO₂, CH₄, N₂, H₂S, etc. So, at that time, the pressure was relatively high and temperature and sulfur fugacity were relatively high as well. At the late stage (Sb metallogenic stage), volatiles in fluids escaped, meteoric water was involved, pressure and temperature decreased, thus leading to successive precipitation of Au and Sb in different structural locations, thereafter forming the unique Au and Sb ore deposits in the region of Southwest Guizhou, even in Yunnan and Guizhou provinces and Guangxi Zhuang Autonomous Region. In space there appears the phenomenon of Au/Sb paragenesis and differentiation. Therefore, in the practice of prospecting Au and Sb ore deposits in the region of Southwest Guizhou what should be taken into consideration is that Au-enriched locations are always not favorable to Sb ore prospecting, whereas in the Sb-enriched locations there would not appear Au enrichment.

6 Conclusions

Through fluid inclusion of gangue minerals and isotope geochemical studies in the Au and Sb ore deposits from the Au and Sb hydrothermal system in Southwest Guizhou the following conclusions can be drawn as follows:

(1) The Au and Sb ore deposits in the region of Southwest Guizhou are the result of regionally unified, large-scale fluid mobility and fluid migration. The ore-forming materials and fluids may both have been derived mainly from the deep interior of the Earth.

(2) Fluid inclusion studies have shown that the temperatures of Au metallogenesis are 170–361 °C and the salinities vary over the range of 0.35 wt%–8 wt% NaCl eq., while the temperatures of Sb metallogenesis are 129.4–214 °C and the salinities vary over the range of 0.18 wt%–3.23 wt% NaCl eq., displaying that the temperature and salinity of the hydrothermal system tend to decrease progressively. The early-stage ore-forming fluids contain large amounts of CO₂, CH₄, N₂, H₂S, etc., belonging to the H₂O-CO₂-NaCl-(Au) fluid system. At the late stage, the Sb-bearing H₂O-NaCl system was dominant.

(3) Gold and Sb in the primitive hydrothermal system were transported in different forms. The ore-forming fluids may have experienced at least twice immiscibility. One is that at the early stage (Au metallogenesis stage), when ore-bearing hydrothermal solutions passed through significantly porous strata or fault broken zones, large amounts of CO₂, CH₄, N₂ and other gases would escape from the solutions, accompanied by pressure relief. All this led to boiling of the primitive homogenous fluids due to pressure relief, as well as phase separation, resulting in the unloading and precipitation of ore-forming materials such as Au and Sb as ores. The other is that at the late stage (Sb metallogenesis stage) meteoric water was involved in the ore-forming fluids, the encounter of ore-forming fluids with meteoric water resulted in fluid boiling and temperature decrease. The decrease of Sb solubility led to Sb precipitation and enrichment as ores. Differences in physico-chemical conditions of Au and Sb precipitation led to their respective precipitation in different structural locations, forming the unique Au and Sb ore deposits in Southwest Guizhou, even in Yunnan and Guizhou provinces and Guangxi Zhuang Autonomous Region, in which the phenomenon of Au/Sb paragenesis and differentiation in space has been observed.

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