GEOCHEMISTRY STUDY OF GOLD-SILVER DEPOSITS IN THE MIDDLE-UPPER PROTEROZOIC SUBERATHEM IN SOUTHERN QINLING METALLOGENETIC ZONE①

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ABSTRACT

According to the combinations of metallogenetic elements and minerals assemblages, the Au–Ag deposits in the Middle-Upper Proterozoic Suberathem of the middle of northern margin of Yangtze Platform could be classified into four types: (1)Au–Ag–Pb–Zn type; (2)Au–Ag–Te type; (3)Au–quartz vein type; (4)Au–Ag–Pb–Zn–Ba type. The Yangpin formation and the upper Dangyuhe subformation, which belong to Wudangshan group, are regarded as favorable strata for Au–Ag mineralization by systematic assessments for Au–Ag bearing ability of the strata, as well as the felsic rocks of Bikou group. The metallogenetic physicochemical conditions and the stable isotopic compositions (S, Pb, H, O, C) have been studied in this paper. The sources of metallogenetic materials, origins of fluids and genesis of various deposits have also been studied.

Key words: Yangtze Platform Middle–Upper Proterozoic Suberathem Au–Ag deposit assessment physico-chemical stable condition isotopic geochemistry

1 INTRODUCTION OF REGIONAL GEOLOGIC BACKGROUND

The Middle-Upper Proterozoic Suberathem (Pt_{2+3}) is distributed widely in the region of northern margin of Yangtze Platform, as well as the Paleozoic Erathem (Pz) and the Mesozoic Erathem (Mz). The Pt_{2+3} is called respectively Wudangshan group (Pt_{2+3w}) in Wudangshan area, Yunxi group (Pt_{2+3y}) in Ankang area and Bikou group (Pt_{2+3b}) in Mianlue area[1]. The Upper Proterozoic Suberathem (Pt_3) is called Yaolinhe group (Pt_{3y}) in Wudangshan area. From bottom to top, Pt_{2+3w} consists of Loutai formation ($Pt_{2+3w_1^l}$), Dangyu formation ($Pt_{2+3w_2^d}$) and Yangpin formation ($Pt_{2+3w_3^y}$). $Pt_{2+3w_1^l}$ is mainly composed of metamorphic quartz-keratophyic-tuff, meta-tuffaceous feldspathic quartz and meta-arkose sandstone. The lower $Pt_{2+3w_2^d}$ is composed of metamorphic basic volcanic rocks, and the upper $Pt_{2+3w_2^d}$ is a series of rocks from the metamorphic quartz-keratophyre-crystall tuff. $Pt_{2+3w_3^y}$ is a set of minus metamorphic rocks that enrich S, P, and C. Pt_{2+3y} is mainly composed of metamorphic quartz-keratophyrebreccia, tuff and fragment tuff which show obvious characters of cyclic eruption. Pt_{2+3b} is mainly composed of mafic-intermediale-felsic volcanic rocks and normal sedimentary rocks. Pt_{3y}

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mainly consists of mafic volcanic rocks which contain moraine-conglomerate and splite in Wudangshan area, and of a series of Na-bearing basic lava which contain breccia and tuff in Ankang area.

In the region, magma activity was very strong so that a system of sea facies volcanic sedimentary rocks was formed by the magma eruptions during Pt_{2+3} Era. From Jinninian to Yanshanian, magma intrusion movements brought up a series of instrusion bodies from selsicmafic to ultramafic rocks, especially in Caledonian.

Regional tectonic grain are very complex. The major fault control the magmatic activities and metallizations in the region, which have NE, NW or near EW trends.

The metamorphic grades of Pt_{2+3} in the region are very low, they only get to green schist facies.

The regional mineral resources are very plentiful. There are many deposits of Hg, Sb, Fe, Cu, Co, Ni and non-metalliferrous ores have been found in the region besides Au–Ag deposits. According to the combinations of metallogenetic elements and minerals, the Au–Ag deposits could be classified into four types (Table 1).

2 ASSESSMENTS OF Pt_{2+3} FOR Au–Ag BEARING ABILITY

Table 1 shows the obvious differences of the Au–Ag deposits in Pt_{2+3}. In order to find out the differences of metallogenetic types and mineralize intensity in different areas, and systematic appraise for field and lab of the stratum, the author has analysed and counted the abundances of Au–Ag geometrical average X_g, arithmetic averages X_a in different strata of Pt_{2+3} and X_g / X_a. Based on the field and lab work, the ratios of accessible Au–Ag (absorptive Au–Ag, Au–Ag in sulfides and organic matters) in various strata as well as the ratio have been deduced, while the element combinations with Au–Ag in various stratum have also been given by statistical analysis (Table 2). The Au-quartz vein type deposits have not been studied further more in this paper because of their lower research extents.

From table 2 some conclusions could be deduced: (1) Abundances of Au–Ag in various strata are lower than the Clark values (Li, To-

Table 1 Types and characteristics of Au–Ag deposits in Pt_{2+3}

Type	Au–Ag–Pb–Zn	Au–Ag–Te	Au–quartz vein	Au–Ag–Pb–Zn–Ba
Host rock	$Pt_{2+3w_2^d}$	$Pt_{2+3w_3^y}$	Pt_{3y}	Pt_{2+3b}
Occurrence	vein, lens	layeroid, vein, lens	veinlet	layer, layeroid, vein, lens
Ore minerals	silver, electrum küstelite, galena sphalerite, acanthite pyrite	hessite, silver, küstelite, jalpaite, proustite	gold, pyrite, specularite, chalcopyrite	barite, electrum, küstelite, galena salenite, sphalerite pyrite
Gangue minerals	quartz, sericite muscovite ankerite chlorite	quartz, ollite, tremolite, muscovite, chlorite	quartz, sericite, epidote chlorite	quartz, sericite, albite, actinolite calcite, chlorite
Elements combination	Au, Ag, Pb, Zn, Cu (As, Sb, Bi, Mo, Cd)	Au, Ag, Te(Pb, Zn, Cu, Sb, Mo)	Au	Au, Ag, Pb, Ba (Cu, As)
Ag / Au (strata)	50	45	>10	55~65
Ag / Au (ore)	100	58	>10	12~52
Scale	large	middle, small	small	middle
Example	Yindonggou	Xujapo	Baiyangou	Donggouba

ng *et al*, 1990). $Pt_{2+3w_3^y}$ and the upper $Pt_{2+3w_2^d}$, in which there are higher abundances, higher ratios of accessible Au–Ag, lower X_g / X_a, (2) The felsic volcanic rocks of Pt_{2+3b} are thought to be favorable strata for Au–Ag mineraliza- tion because of their higher abundances and accessible ratios of accessible Au– Ag, lower X_g / X_a, compared with the mafic volcanic rocks of Pt_{2+3b}; (3) Pt_{3y} in Ankang area is similar to the strata such as $Pt_{2+3w_3^y}$ and the upper $Pt_{2+3w_2^d}$, so that they should be paid more attention in the future.

As mentioned above, the geochemical rules of assessment for Au–Ag bearing ability of favorable strata could be summed up as: higher abundances and accessible ratios of Au–Ag, lower X_g / X_a and especial element combinations[1].

3 METALLOGENETIC PHYSICO-CHEMICAL CONDITION OF Au–Ag DEPOSITS IN Pt_{2+3}

In order to learn the metallogenetic physico-chemical conditions of various Au–Ag deposits, the author has done the research work of fluid inclusion geochemistry, mineralogy, stable isotopic geochemistry and thermodynamic computation. Based on fetched analytic values, thermodynamic parameters, diagrams and reaction equations etc.[2–4], the metallogenetic physico-chemical conditions of three types of Au–Ag deposits excepted Baiyangou Au–quartz vein type deposit have been given (Table 3).

The wide variable ranges of metallogenetic temperatures is thought due to the multistage mineralization of various deposits in Table 3. The main mineralization temperatures vary in a range of 160～270 ℃, the salinities generally vary in a range of 4.0～8.0 (wt–% NaCl), except the one of the early mineralization of Au–Ag–Pb–Zn type deposit (9.3～12.1 wt–% NaCl). The pH values of mineralization fluids have not a wide variable range compared to the neutral pH value (pH_n), they vary in a range of pHn–1～pHn+1 and have a trend from acid to base varied with time[1,5–6]. The sulfur fugacities vary in a very close range as well as the oxygen fugacities, but the oxygen fugacity of Au–Ag–Pb– Zn–Ba type deposit is a little higher because of the appearance of sulfate minerals (e. g. barite). Although the

Table 2 Abundance of Au–Ag (ppb), X_g / X_a, ratio of accessible Au–Ag and element combination with Au–Ag in various stratum

Area	Wudangshan				Ankang			Mianlue	
Stratum*	1	2	3	4	5	6	7	8	9
X_a (Au)	0.84	1.05	1.17	0.73	0.59	1.08	0.95	0.80	0.85
X_g (Au)	0.73	0.76	0.76	0.52	0.54	0.90	0.81	0.70	0.80
N**	59	73	65	46	33	68	77	29	19
X_g / X_a (Au)	0.87	0.72	0.66	0.71	0.92	0.83	0.85	0.88	0.91
X_a (Ag)	10	47	53	26	/	<10	<10	50	29
X_g (Ag)	/	40	34	24	/	(37)***	(49)	40	26
N	93	58	68	73		68–490	40–200	29	12
X_g / X_a (Ag)	/	0.85	0.64	0.92	/	(32)	(5)	0.80	0.90
Accessible ratio	low	high	high	low	low	high	low	high	low
Elements	Au, Sb	Au, Ag, F	Au	Ag	/	Au, Ba, Ag,	As	Au, Ni	Au, Cu
combination		Sb, Hg, Bi	Ag	Cu		Bi, Cu, Zn,	Ag	Cr, P	Li, Al
		Cu, SiO_2	B			Cr, As, V,	Pb	Mg	Ca, Sr

* 1 = Pt_{3y}, 2 = $Pt_{2+3w_3^y}$, 3 = upper $Pt_{2+3w_2^d}$, 4 = lower $Pt_{2+3w_2^d}$, 5 = $Pt_{2+3w_1^l}$, 6 = Pt_{3y}, 7 = Pt_{2+3y}, 8 = Pt_{2+3b} (felsic volcanic rock), 9 = Pt_{2+3b} (mafic volcanic rock); ** Numbers of samples

Table 3 The parameter of metallogeneticly physico-chemical condition of Au-Ag deposits in Pt_{2+3}

Type	Au-Ag-Pb-Zn	Au-Ag-Te	Au-Ag-Pb-Zn-Ba
T_1 / ℃ *	290~330	220~320	124~312
T_2 / ℃ *	150~320	135~230	98~325
T_3 / ℃ *			116~206
T_4 / ℃ *	160~380	175~290	176~263
P / MPa	20~150	50~70	50~100
Salinity / wt-%Nacl	9.3~12.1	4.9~8.1	4.2~6.6
Density / g · cm^{-3}	0.85~0.98		0.85~0.94
pH * *	pHn ± 1	pHn ± 1	4.7~6.0
f_{O_2} / Pa	10^{-25}~10^{-36}	10^{-36}~10^{-42}	10^{-26}~10^{-32}
f_{S_2} / Pa	10^{-7}~$10^{-11.5}$	10^{-8}~10^{-10}	$10^{-6.56}$~$10^{-10.7}$
Composition	Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, $HS^-(S^{2-})$, Cl^-, F^-, CO_2, CO	Mg^{2+}, Na^+, K^+, Ca^+, HCO_3^-, $HS^-(S^{2-})$, Cl^-, F^-, CO_2, C, CH_4	Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, HCO_3^-, HS^-, SO_4^{2-}, CO_2, CO, CH_4

* T_1 — Temperature (℃) of=decrepitation method; T_2 — Temp. of homogenization method; T_3 — Temp. of isotopic geothermometer; T_4 — Temp. of metallogenetic Y condition and under correction pressure. * * neutral pH value of water under metallogenetic temperatures

compositions of anions are almost similar to each other in metallogenetic fluids of various deposits. The composition of cations are very different, so the correspondent alterations except silicification are also different. The major alteration of Au-Ag-Pb-Zn type, Au-Ag-Te type, and Au-Ag-Pb-Zn-Ba type are respectively ankeritization, talcization, baritization and pyritization. Using deduced physicochemical conditions of matallogenetic fluids and thermodynamic parameters[2-3,8,10], the author has calculated the solubilities of thio-Au (Ag) coordinate compounds and chloride-Au (Ag) coordinate compounds respectively in the matallogenetic fluids of various Au-Ag deposits. The calculated results show that the solubilities of thio-Au(Ag) complexes are about 10^5 times higher than those of choride-Au (Ag) complexes; therefore, the thio-Au(Ag) complexes have much stronger transport ability than chloride-Au(Ag) complexes in the matallogenetic fluids of three major Au-Ag deposits in the area. In addition, Au-Ag could be transported as other Au-Ag coordinate compounds, in which CO_2, HCO_3^-, HSO_4^-, HTe^-, Te^{2-}, probably play the role of coordinate anions.

4 STABLE ISOTOPIC GEOCHEMISTRY STUDY OF Au-Ag DEPOSITS IN Pt_{2+3}

The stable isotopie compositions have been studied by the author so as to bring forward metallogenetic mechanism of three major types of the Au-Ag deposits in Pt_{2+3}.

Fig. 1 shows with the compositions of sulfur isotope of various deposits including Au-Ag-Pb-Zn type, Au-Ag-Te type and Au-Ag-Pb-Zn-Ba type. As a whole, the $\delta^{34}S‰$ (CDT) values of different sulfide minerals of Au-Ag-Pb-Zn type deposit vary in a close range of 4~6. With the help of the δ^{34} S values of galena and sphalerite, the $\delta^{34}S_{\Sigma S}$ value of metallogenetic fluid is caught out as 2.5‰ by using the high-temperature balanced extrapolation (Pinckney, O. M. 1972), which demonstrate the characteristics of mantle source sulfur. The variable range of $\delta^{34}S‰$ (CDT) values of different sulfide minerals of Au-Ag-Te type deposit is similar to the one of Au-Ag-Pb-Zn type deposit. Because two types of

Au–Ag deposit are located in the same metallogenetic belt and have close mineral assemblage, the $\delta^{34}S_{\Sigma S}$ of them ought to be similar to each other. The Au–Ag–Pb–Zn–Ba type deposit is different to them. Its $\delta^{34}S$‰ (CDT) value of pyrite varies in a range of 5.3~ 10.5 and the one of barite varies in a range of 16.9 ~ 20.3. According to the isotope fractionation mechanism[7–9], $\delta^{34}S_{\Sigma S}$ is higher than the $\delta^{34}S$ of pyrite and lower than the one of barite when the two minerals are coexisting. Based on above, the $\delta^{34}S_{\Sigma S}$ has been estimated at 12–15‰, which was perhaps a mixture of volcanic reduction sulfur (enrich ^{32}S) and marine facies sulfate-sulfur (enrich ^{34}S) . From the $\delta^{34}S_{\Sigma S}$, We can find the sulfar to have multi-source and to drift away the compositon of mantle sulfur.

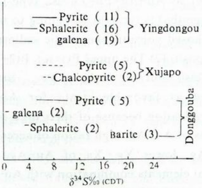

Fig. 1 Composition of Sulfur Isotope of Different Types of Au–Ag Deposits

References: 1— this paper; 2— Liu Chongqiang (1984); 3— Chendu College of Geology *et al* (1987); 4— Mineral Resources and Geologic Survey of North-westen Hubei province.The number of samples are in the parentheses.

The $\delta^{13}C$‰ (PBD) value of enkerite of Au–Ag–Pb–Zn type deposit varies in a range of −1.11~ −2.86. Based on the metallogenetic physico-chemical conditions, the isotopic composition of carbon ($\delta^{13}C_{\Sigma C}$) in the metallogenetic fluid is estimated at −2~ −7‰, which shows the characteristics of the primary carbon.

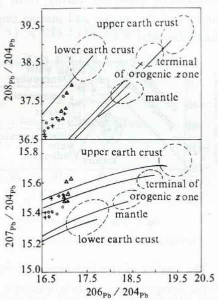

Fig. 2 Plots of ^{208}Pb / ^{204}Pb VS ^{206}Pb / ^{204}Pb vs and ^{207}Pb / ^{204}Pb VS ^{206}Pb / ^{204}Pb (simplified from ([9])

+—Yindonggon; ○—Xujiapo; △—Donggonba

References of the Fig. are the same as Fig.1

The isotopic compositions of lead of Au–Ag–Pb–Zn type deposit and Au–Ag–Te type deposit scatter between the two evolutional curves of oroganic zone and lower earth crust[9] on $^{208}Pb / ^{204}Pb \sim ^{206}Pb / ^{204}Pb$ plot (Fig. 2), and scatter between the two ones of mantle and orogenic zone on $^{207}Pb / ^{204}Pb \sim ^{206}Pb / ^{204}Pb$ plot (Fig. 2), which demonstrate that the metallogenetic materials (including pb, Au, Ag, Ba) probably of Au–Ag– Pb–Zn–Ba type deposit fall down between the evolutional curves of lower crust on $^{208}Pb / ^{204}Pb \sim ^{206}Pb / ^{204}Pb$ plot, and distribute over the upper evolutional curves on $^{207}Pb / ^{204}Pb \sim ^{206}Pb / ^{204}Pb$ plot which is a little higher in this kind of deposit, and also demonstrates that the metallogenetic materials cheifly came from bi-sources of the mantle and marine simultaneous Sediments.

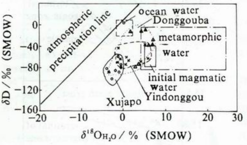

Fig. 3 Plot of δ18O vs.δD

References of the Fig. are the same as Fig. 1

The studies of the hydrogen and oxygen isotopic compositions of metallogenetic fluid show that $\delta^{18}O_{H_2O}$ of Au–Ag–Pb–Zn type deposit varies in a range of $-3\sim7$‰ and δD varies in a range of $-40\sim-80$‰, which take on the double property of magmatic water and metamorphic water; In view of the shifting $\delta^{18}O_{H_2O}$ and the stationary δD, there could be a few meteoric water joining in it (Fig. 3). δD of Au–Ag–Te type deposit varies in range of $-55\sim-12$‰ and $\delta^{18}O_{H_2O}$ of it varies in a range of $-1\sim-5$‰. Their compositions fall down between the two domains of metamorphic water and meteoric water on Fig. 3, which demonstrate that the metallogenetic fluid could be derived from sugenetic formation water and meteoric water by metamorphy. Since the wall rock of Xujiapo deposit is a serious of negative metamophic rock, the metallogenetic fluid shows more obvious characteristics of meteoric water. The variable ranges of $\delta^{18}O_{H_2O}$ and δD of Au–Ag–Pb–Zn–Ba type deposit are very wide, the major variable range of $\delta^{18}O_{H_2O}$ is $-4\sim+8$‰ and the one of $\delta^{18}O_{H_2O}$ is $-20\sim-100$‰ which shows the multi-sources characteristics of metallogenetic fluid. The water in the fluid were mixed with magmatic water, meteoric water, ocean water and metamorphic water, most of the fluid came from magmatic water and ocean water which is in line with the geologic fact that this type deposits are found in the marine facies volcanic rocks.

5 CONCLUSION

From the information and discussion mentioned above, the results could be concluded as: (1) The Au–Ag deposits of Au–Ag–Pb–Zn type and Au–Ag–Te type were mainly found in the strata of the upper $Pt_{2+3w_2^d}$ and $Pt_{2+3w_3^y}$ in Wudangshan area (e. g. Yindongou), which are thought to belong to metamorphic low-to-moderate-temperature hydrothermal deposits. The deposit of Au–Ag–Pb–Zn–Ba type (e. g. Donggouba) is thought to belong to metamorphosed volcanic syngenetic sedimentary deposit; (2) The upper $Pt_{2+3w_2^d}$, $Pt2+3w_3^y$ and felsic volcanic rocks of Pt_{2+3b} are regarded as favorable strata for Au–Ag mineralization because of their high abundances of Au–Ag, high ration of accessible Au–Ag, lower Xg / Xa of Au–Ag, and special elements combination with Au–Ag. (3) Au and Ag mainly are transported as $Au(HS)_2^-$ and $Ag(HS)_2^-$ in the metallogenetic fluid; (4) The compositions of stable isotope show the metallogenetic materials of Au–Ag–Pb–Zn type and Au–Ag–Te type deposits were mainly derived from the deep socerce, meanwhile the metallogenetic materials of Au–Ag–Pb–Zn–Ba type deposit probably came from the mantle and marine sediments.

(*To be continued on page* 29)