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On the Mechanism of Transformation from Primary Ores into Oxidized Ores in Finely Disseminated Gold Deposits

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Abstract This paper, taking the finely disseminated gold deposits in southwestern Guizhou and northwestern Guangxi as examples, discusses the difference between the occurrence of primary ores and that of oxidized ores, analyzes the occurrence mechanism in terms of crystallochemistry and geochemistry, and especially studies the chemical model for supergene leaching transformation of clay minerals in the two types of ores. This study proposes a new idea for dressing and smelting technology for primary gold ores.

Key words: occurrence of gold ore, clay minerals, supergene leaching transformation, chemical model

1 Introduction

At present, mining, dressing and smelting for fine-disseminated gold deposits are mainly restricted to oxidized ores. In order to meet the needs of the national economy, a research project was launched during the ninth Five-Year Plan period as one of the major application researches in the exploitation and utilization of primary ores of this type of deposits. Therefore, it is of great theoretical and economic significance to study the difference of occurrence between primary and oxidized ores and the mechanism of the transformation for occurrence.

The previous researches related to the transformation from primary ores into oxidized ores for this type of deposits have been limited to the case of sulphides (Wang and Guan, 1993) and never touched upon the transformation in the course of supergene oxidation of clay minerals.

2 Difference of Occurrence between Primary and Oxidized Ores

2.1 Difference of occurrence

Existing data indicate that gold in primary ores of fine-disseminated gold deposits occur mainly in sulphides and clay minerals; while oxidized ores in limonite and clay minerals (Wu, 1992; Zhu and Zhang, 1994). From Tables 1, 2 and 3 one can see that the occurrence

of gold will be changed as primary ores are transformed into oxidized ores, that is, the gold in the former exists primarily as micro-inclusion gold; while that in the latter as free gold. The gold which occurs in mineral textures usually has a rather uneven distribution, hence it is generally called micro-inclusion gold; whereas the gold which is related to surface adsorption other than mineral texture is generally called free gold.

Table 1 Results of chemical phase analysis of gold in primary ores (after Zhu and Zhang, 1994)

Ore district	Sample No.	Free gold (μg)	Inclusion gold (μg)						Residue
			In carbonate		In sulphide		In clay minerals		
			Soluble (< 1μm)	Grain (> 1μm)	Soluble (< 1μm)	Grain (> 1μm)	Soluble (< 1μm)	Grain (> 1μm)	
Getang	Y63	0.03	0.00	0.00	0.00	2.00	0.02	1.60	0.50
	Y66	0.15	0.00	0.01	0.01	1.50	0.02	1.50	0.12
	Y71	0.12	0.00	0.01	0.29	0.74	0.06	0.48	0.72
Zimu-dang	X70-A	0.48	0.00	0.03	30.00	2.50	0.19	0.58	0.13
	X91	0.06	0.00	0.04	25.00	2.50	0.38	2.30	1.35

Table 2 Results of chemical phase analysis of gold in oxidized ores (after Zhu and Zhang, 1994)

Ore district in SW Guizhou	Sample No.	Free gold (μg)	Inclusion gold (μg)				Hardly soluble substance
			Limonite		Clay mineral		
			Soluble (< 1μm)	Grain (> 1μm)	Soluble (< 1μm)	Grain (> 1μm)	
Getang	Y96	10.62	0.40	0.14	0.21	0.01	0.05
	Y117	45.00	2.50	0.40	2.31	0.12	0.01
Zimudang	X67	20.00	1.75	0.17	0.10	0.05	0.11

Table 3 Contents of gold of different forms in primary ores and oxidized ores (after Zhu and Zhang, 1994)

Ore district in SW Guizhou	Oxidized ore		Primary ore	
	Free gold	Inclusion gold	Free gold	Inclusion gold
Getang	91.15	8.84	3.04	96.95
Zimudang	90.17	9.82	0.82	99.18

2.2 Mechanism of occurrence

Previous work has given ample evidence for the fact that the micro-inclusion gold occurring in sulphides and clay minerals is mainly nano-level native gold, namely the soluble gold listed in Tables 1 and 2, and there are some gold grains that are larger than $1\mu\text{m}$ in size, which is grain gold shown in Tables 1 and 2 (Zhang and Jiang, 1993; Wu, 1992; Liu et al., 1991; Ye et al. 1994). Study by Cheng Feng and Yang Keyou revealed^① that part of the large-sized grains appear as fine pyrite grains enriched in nano-sized native gold and

^① Chen Feng and Yang Keyou, 1992. On the occurrence and associated components of fine-grained gold in southwestern Guizhou, Research report of the Institute of Geochemistry (Guiyang), Chinese Academy of Sciences.

that this grain gold or gold-rich pyrite grains occur mainly in clay minerals. Then it is interesting to know whether nano-sized micro-inclusion gold is able to enter the crystal lattices of sulphides and clay minerals.

As is known to all, limited isomorphous replacement is prone to occur between $[S_2]^{2-}$ and $[AsS]^{2-}$ in pyrite and arsenopyrite crystals. These two anions are different in size with the latter being larger than the former, thus bringing about lattice defect. According to diffusion dynamics of crystal growth, these defect positions are most attractive to particles and the filling particles are most likely impurities outside the crystal textures. As a sequence, nano-level native gold will enter the defect positions of the crystal lattices in the form of micro-inclusion gold.

Clay minerals have a layered texture with fairly large space between the layers and relatively large specific surface compared with other minerals. Besides, the charges in the interlayer space of different minerals are different in quantity. As a rule, negative charges become smaller as the clay mineral changes in the following sequence: sericite \rightarrow hydromica \rightarrow illite \rightarrow montmorillonite \rightarrow kaolinite, and the capacity of the corresponding texture to receive micro-inclusion gold becomes smaller accordingly; on the other hand, a small amount of gold gains of comparatively large sizes might remain in the intergranular fissures of clay minerals or sulphide crystals. In principle, these gold grains can be extracted by means of extra-fine processing.

The occurrence form of nano-level microgranular gold existing commonly in primary minerals is related to its source and special migration form. Previous study (Liu Xianfan, 1996) revealed that the ore-forming substances came directly from ore-bearing siliceous fluids resulting from the differentiation of the upper mantle and that the gold migrated as nano-level native gold grains. This was proved by REE geochemistry (Liu Xianfan, Jin Jingfu and Ni Shijun, 1996) and geochemistry of stable isotopes (Liu Xianfan, Ni Shijun and Su Wenchao, 1996; Liu Xianfan et al., 1997) and was especially supported by researches on geochemistry of silicon isotope and siliceous cathodo-luminescence as well as physico-chemical conditions of fluids. It can thus be seen that special occurrence of the gold in primary ores of fine-disseminated gold deposits reflects the unique metallogeny of the deposits. Further study and discussion are worthwhile in this aspect.

Clearly, free gold in oxidized ores is nothing but the one which is free from the mineral textures and assumes only a surface adsorption state. It can be easily understood that the micro-inclusion gold in sulphides can be freed out of textures as it becomes oxides and sulphates due to oxidation and decomposition by means of mineral carriers. The difference between primary and oxidized ores in regard to gold occurrence indirectly indicates that primary ore was formed through a one-step process without activation-migration-concentration following an earlier concentration. Then, how can micro-inclusion gold be freed in the case of clay minerals?

3 Supergene Leaching Transformation and Chemical Model of Clay Minerals

3.1 Transformation of clay minerals

The above tables show that clay minerals are a gold-carrier for both primary and oxidized ores, but there is a sharp contrast in type and quantity of clay minerals between these two cases. The major clay minerals can be separated from other minerals by repeated floatation. Siliceous and organic substances can be removed from the separated clay minerals by ad-

ding an appropriate amount of HCl and H₂O followed by repeated rinse and precipitation to produce a mixing sample consisting mainly of clay, for which phase and quantitative analyses were performed by X-ray diffraction. The results are given in Table 4. Under

Table 4 X-ray diffraction phase and quantitative analysis of clay minerals in the ores of Carlin-type gold deposits

Ser. No.	Sample No.	Ore district	Ore type	Clay minerals			Quartz	Other minerals
				Illite	Kaolinite	Montmorillonite		
1	XGL-1	Longhuo in NW Guizhou	Carbonaceous mudstone primary ore	91			8	Anatase
2	XGL4-10		Oxidized ore	80			19	feldspar
3	XGL-5		Altered tuff	57	3	1	38	goethite
4	XQG-24	Getang in SW Guizhou	Gypsum-bearing oxidized ore	3	66		30	Anatase
5	XQG-17		Oxidized ore	8	70		22	Anatase
6	XQG-23		Pyrite-bearing clayrock	32	63		4	Gibbsite, anatase
7	XGS-6	Shijia in NW Guizhou	Jarosite-bearing oxidized ore	11	53	28	8	Svanbergite
8	XGS-11		Leached oxidized ore	23	58	!	18	svanbergite anhydrite
9	XQL-20	Lannigou in SW Guizhou	Primary ore	74	3		22	
10	XQL-23		Oxidized ore	90	5		5	Goethite
11	XQD-20	Qinglong in SW Guizhou	Weakly altered basalt		23	11	9	Feldspar 57%

Notes: Analyzed by the X-ray Lab of the Test and Analysis Centre, Chengdu Institute of Technology; Unit: %.

supergene conditions, primary ores that even do not have clear supergene leaching alteration were still subjected to post-ore hydrothermal alteration of varying degrees. This kind of alteration is indicated by the following facts: primary sericite was hydrated in varying degrees to become hydromica or illite while primary ores were turned into oxidized ones; the clay minerals are characterized by transformation from hydromica or illite into kaolinite and from montmorillonite to illite or kaolinite. To obtain the crystallochemical formulae listed in Table 5, we first named the minerals according to the formulae calculated based on microprobe analytic data of 27 ore samples, and then applied the weighted arithmetical average to the samples of the same name to yield the final results. One can see the following facts from this table: the measured hydromica and illite have markedly higher contents of Al₂O₃ and K₂O but lower contents of Fe₂O₃, MgO and CaO compared with the standard illite (D-28); in the measured montmorillonite K₂O is higher but MgO and CaO are lower in contents compared with the standard montmorillonite (D-29); absolute values of the surface charges decrease successively from hydromica through illite to montmorillonite, indicating an increase of leaching alteration; absolute values of the surface charges of the measured hydromica and illite are higher than that of the standard illite, indicating the measure objects are close to sericite; and absolute values of the surface charges of the measured montmorillonite are lower than that of the standard montmorillonite, indicating the former was subjected to leaching against the latter.

Table 5 Calculation for crystallochemical formulae of average chemical compositions of three clay minerals in the ores of Carlin-type gold deposits

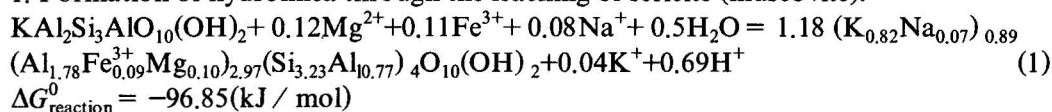
Mineral	Average composition (%)										Crystallochemical site occupation						Surface charge
											Interlayer space		Octahedral plane (O)		Tetrahedral plane (T)		
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Ca ²⁺	Na ⁺	K ⁺	Al ³⁺	Fe ³⁺	Mg ²⁺	Si ⁴⁺	Al ³⁺	
Hydro-mica	47.36	31.69	1.82	0.96	0.04	0.56	9.38	0.28	0.003	0.073	0.816	1.78	0.094	0.098	3.231	0.769	-0.94
	Crystallochemical formula: (K _{0.82} Na _{0.07}) _{0.89} (Al _{1.78} Fe _{0.09} ³⁺ Mg _{0.10}) _{2.97} (Si _{3.23} Al _{0.77}) _{4.0} O ₁₀ (OH) ₂																
Illite	51.19	32.15	1.64	1.63	0.16	0.19	9.79	0.17	0.011	0.023	0.806	1.753	0.079	0.157	3.306	0.694	-0.88
	Crystallochemical formula: (K _{0.81} Na _{0.02} Ca _{0.01}) _{0.84} (Al _{1.75} Mg _{0.16} Fe _{0.08} ³⁺) _{1.99} (Si _{3.31} Al _{0.69}) _{4.0} O ₁₀ (OH) ₂																
Montmorillonite	60.97	25.25	0.84	0.80	0.12	0.14	6.41	0.10	0.008	0.017	0.519	1.762	0.040	0.076	3.872	0.128	-0.57
	Crystallochemical formula: (K _{0.52} Na _{0.02} Ca _{0.01}) _{0.55} (Al _{1.76} Mg _{0.08} Fe _{0.04} ³⁺) _{1.88} (Si _{3.87} Al _{0.13}) _{4.0} O ₁₀ (OH) ₂																
Illite (D-28)	50.30	25.58	4.85	2.44	0.38	0.20	7.99	0.49	0.028	0.026	0.695	1.484	0.249	0.248	3.428	0.572	-0.85
	Crystallochemical formula: (K _{0.70} Na _{0.03} Ca _{0.03}) _{0.76} (Al _{1.48} Mg _{0.25} Fe _{0.25} ³⁺) _{1.98} (Si _{3.43} Al _{0.57}) _{4.0} O ₁₀ (OH) ₂																
Montmorillonite (D-29)	57.69	24.68	0.85	3.52	1.93	0.17	5.26	0.12	0.133	0.021	0.432	1.583	0.041	0.338	3.711	0.289	-0.74
	Crystallochemical formula: (K _{0.43} Ca _{0.13} Na _{0.02}) _{0.58} (Al _{1.53} Mg _{0.34} Fe _{0.04} ³⁺) _{1.96} (Si _{3.71} Al _{0.29}) _{4.0} O ₁₀ (OH) ₂																

Notes: Data of microprobe analysis were provided by Zhang Xingchun and calculation and mineral denomination were done in this study; D-28 and D-29 obtained average values after C.E. Weaver (1989).

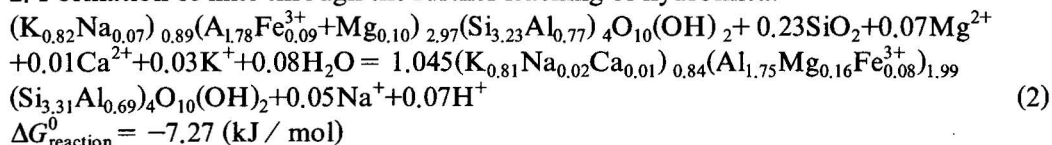
3.2 Chemical model for the transformation of clay minerals

We used the calculated average chemical formulae for hydromica, illite and montmorillonite listed in Table 5 as approximate ones for the three clay minerals in the gold ores. Based on the above discussion the following model can be formulated for the transformation of clay minerals due to leaching of supergene solutions upon primary ores. (Relevant thermodynamic data are mainly referred to Helgeson, 1969.).

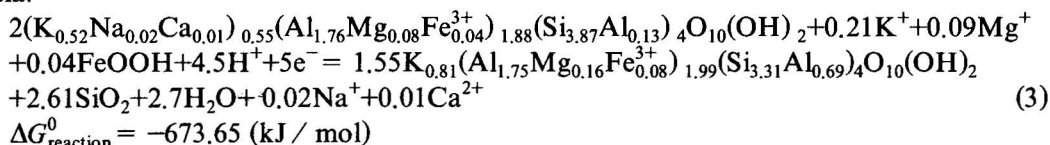
1. Formation of hydromica through the leaching of sericite (muscovite):



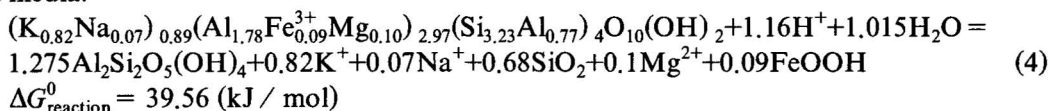
2. Formation of illite through the further leaching of hydromica:



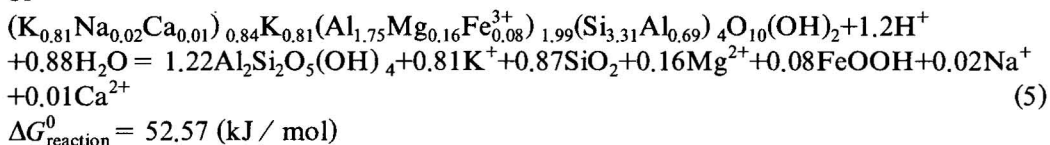
3. Montmorillonite transforming into illite in the midst of intermediate-weakly acid media:



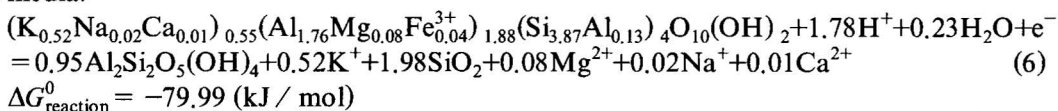
4. Formation of kaolinite through the alteration of hydromica (or illite) in the midst of acid media:



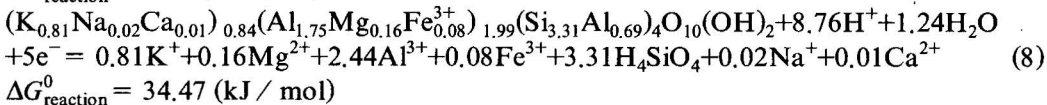
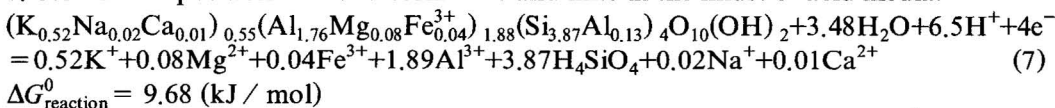
or



5. Formation of kaolinite through the alteration of montmorillonite in the midst of acid media:



6. Self-decomposition of montmorillonite and illite in the midst of acid media:



We can infer according to the above standard free energy of reaction that reactions (4), (5), (7) and (8) can hardly occur, which means that either the transformation from hydromica

or illite into kaolinite through direct alteration in acid media or the self-decomposition of illite and montmorillonite is unlikely to proceed spontaneously under the supergene conditions; whereas such hydrated alteration as sericite \rightarrow hydromica \rightarrow illite and the transformation from montmorillonite into illite and kaolinite are apt to occur. The possible transformations mentioned above indicate the following. Intermediate or weakly acid media are favourable for the transformation from montmorillonite into illite (reaction (3)); weakly alkaline and alkaline media are favourable for the transformation from sericite and hydromica into illite (reactions (1) and (2)); acid media are favourable for the transformation from montmorillonite into kaolinite (reaction (6)). Moreover, the transformation of clay minerals in primary ores by supergene oxidation can be achieved mainly through leaching and mutual replacement of K^+ , Na^+ and Mg^{2+} in the interlayer space and further decomposition of part of OH^- along with supergene silicification. Since the above processes were completed through the gradual replacement of solutions for solid minerals without recrystallization after the resolution of minerals, this gradual replacement will directly cause the micro-inclusion gold to be released out of the interlayer space of the primary minerals to become gold free from mineral textures.

4 Conclusions

It is the sulphides and clay minerals in primary ores that are either altered and transformed in the presence of supergene solutions to release micro-inclusion gold originally enclosed in mineral textures to become invisible free gold and then adsorbed between particles and on the surface of the transformed limonite and clay minerals; or oxidized by thiosulphates to become Au^+ and the resultant thiosulphate complexes migrate (Zheng Dazhong, 1994a, 1994b) to form invisible free gold by decomposition and redox under favourable conditions or in favourable positions and then adsorbed between particles and on the surface of the transformed limonite and clay minerals, so that gold in oxidized ores is enriched and ready for leaching.

Based on the principle we have discussed with respect to the occurrence of micro-inclusion gold and its transformation into free gold, the authors consider that with a view to achieving a high leaching rate of primary gold ores emphasis should be placed on developing economic and efficient chemical processes for the oxidation of primary ores in the study of dressing and smelting technology. This task can not be fulfilled without combining various disciplines or fields such as geology, textural analysis and chemical engineering.

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