Supergene mobility of noble metal elements in black rock series*

LI Shengrong**, XIAO Qiyun, SHEN Junfeng, SUN Li, YAN Baikun and LIU Bo

(School of Geosciences and Land Resources, China University of Geosciences, Beijing 100083, China; Key Laboratory of Lithospheric Tectonics Deep-level Process and Exploration, Minsitry of Education, Beijing 100083, China)

Received August 31, 2001; revised December 24, 2001

Abstract In order to discuss the supergene mobility of noble metal elements in black rock series, measurements have been conducted with ICP-MS method for the contents of Ru, Rh, Pd, Ir, Pt, Au and Ag in the primary jordisite-rich black shale ore, in the supergene leached jordisite-rich black shale ore, in the pyrite-rich black shale ore and in the water of pit, well and stream of the mining area near Zhongnan Village, Zunyi District of Guizhou Province. The temperature, pH, electric conductivity, dissolved oxygen of the water were also measured. The pit water is acidic with high electrical conductivity and low dissolved oxygen. The total content of platinum group elements in the primary pyrite-rich black shale ore is only 1/13 of that in the primary jordisite-rich black shale ore. The Ag content in the former is only a half of that in the latter while the Au contents in the two kinds of ores are almost the same. Being leached under supergene condition, the contents of most of the noble metal elements except Au in the jordisite-rich black shale ore greatly decrease; the leaching rates of Rh, Pd, Pt, the total platinum group elements and Ag reach as high as 66.72%～74.79%, revealing that under supergene condition, platinum group elements and Ag can migrate along with water; the ratios of Ag/Au, Pd/Ru, Pt/Ir and(Pt + Pd)/(Ru + Rh + Ir) are remarkably decreased, displaying that Pt and Pd relative to Ru, Rh and Ir, Ag relative to Au bear more active mobility. The noble metal elements in the black rock series near Zhongnan Village might be mobilized and migrate under the procession of "cold water" rich in $[SO_4]^{2-}$ with pH value being about 2.4 at a temperature below 50 ℃.

Keywords: supergene water, leaching process, gold-silver-platinum group elements, relative mobility, physicochemical condition, black rock series, Guizhou.

The mobility of noble metal elements under supergene condition is an important research area in lower temperature geochemistry. In the past decade, much attention was paid to the supergene geochemical behaviors of gold and silver, and it has been found that gold placer in frigid zone at high latitude is characterized by its regeneration and the rate of regeneration goes greatly beyond the limit of general geological temporal and spatial scale[1]. Recently, the enrichment of gold and silver in the regolith of humid zone at low latitude has also been observed. Although a generally recognized enrichment mechanics has not been elucidated, the phenomena of migration and reorganization of gold and silver under this condition do exist[2~5]. From these observations, the chemical mobility of gold and silver, instead of their chemical inertia, has been deeply acknowledged[6].

As the major carrier of platinum group elements (PGE), traps (mafic-ultramafic rocks) have long been studied by geologists and geochemists. The high temperature magmatic fluid attribute of platinum group elements in traps has also been recognized. In studies of the PGE, the action of non-magmatic fluids on the enrichment of PGE in some traps was also noticed, and the function of hydrothermal fluids was emphasized in the studies on the Cu-Ni-PGE ore deposit in New Rambler Mine[7], the platiniferous Cu-Ni ore deposits[8], the (PGE)-Cu ore deposit in Salt Chunk of Alaska[9], the (PGE) -Cu-Ni ore deposit in the Duluth complex[10], and the Selukwe Subchamber PGE ore deposit in the Great Dyke of Zimbabwe[11]. It was generally accepted that temperatures of the hydrothermal fluids leading to the migration and enrichment of PGE were about 500 ℃.

Some modeling and experiments have been conducted on the mobility of PGE at about 300 ℃. The modeling by Mountain et al.[12] revealed that PGE could migrate along with fluid as complex compounds of OH^-, HS^- and Cl^- at this temperature. Gammons et al.[13,14] indicated that in the hydrothermal fluid with very high Eh and very low pH, the solubility of the compounds of Pt and Pd with Cl^- could

---

* Supported by the National Natural Science Foundation of China (Grant Nos. 49873013 and 40073012)

** To whom correspondence should be addressed. E-mail: lisr@cugb.edu.cn

reach 1 000 ppm. Under the condition of common Eh and pH, however, the solubility of the compounds of Pt and Pd with HS^- were much higher than that with Cl^-.

Few researches have been done on the chemical mobility of PGE at temperature below 200 ℃. Up to now, in the studies of the mineralogy and geochemistry of the Lower Cambrian black rock series in South China, Li et al.1)[15] noticed the mobility of Au, Ag and PGE in sedimentation, diagenesis and epigenesis. Recently we measured the contents of noble metal elements with ICP-MS method in the primary jordisite-rich black shale ore, in the supergene leached jordisite-rich black shale ore, and in the pit water within the pay bed, in the water of well and stream of the mining area at lower altitude near Zhongnan Village, Zunyi Prefecture of Guizhou Province. It was found that Au, Ag and PGE decreased in this geological body, which provides new data for the study on the mobility of noble metal elements.

1 Characteristics of samples and analytical results

1.1 Sampling and sample characters

Samples for experiment were collected from the bottom of the Lower Cambrian System near Zhongnan Village, Zunyi Prefecture of Guizhou Province. The lithological sequence of the Lower Cambrian System is almost the same as described by Li et al.[16] for the black rock series in Hunan-Guizhou region, and it is disconformably deposited on the Sinian (Upper Proterozoic) dolomitite, and its lithology from the bottom to the top is Sinian dolomitite and paleoregolith, Cambrian black baritic rock with hydroxylapatite dominated nodules (0~0.2 m thick), Cambrian black phosphorite (0.5~1 m thick), Cambrian black chert (0~0.2 m thick), Cambrian Ni-Mo-PGE-rich black shale ore—"polyelement bed" (0.2~0.3 m thick), Cambrian Ni-Mo-PGE poorly mineralized black shale (1~2 m thick), Cambrian black shale (>20 m thick), and modern regolith.

In order to discuss the supergene mobility of noble metal elements, samples were collected from the "polyelement bed" including one primary jordisite-rich ore sample, one strongly-leached jordisite-rich ore sample and one pyrite-rich ore sample. A water sample was collected from the bottom of a pit within the "polyelement bed", another two water samples were collected respectively from a well and a stream about 30 m away from and 50 m below the "polyelement bed" (Fig. 1). The relative density of the jordisite-rich ore sample and pyrite-rich ore sample were almost the same (about 3.5) whereas that of the strongly-leached jordisite-rich ore sample was only about 2.5. The primary ore showed compacted massive structure whereas the leached ore was a loosened massive but without the distinctive honeycomb structure. Both the water from the well and the water from the stream were colorless and limpid; and the water from the pit was milky white. After being laid aside at a standstill for 24 h the pit water was separated into two parts: the lower 1/4 part was thick milky white liquid and the upper 3/4 part was clean water. The samples were taken from the two parts. The contents of noble metal elements of these samples were all measured with ICP-MS.

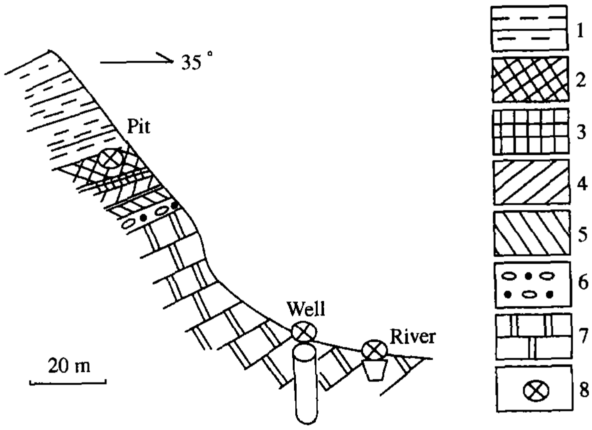

Fig. 1. Section of black rock series near Zhongnan Village and sampling locations. 1, black shale; 2, "polyelement bed"; 3, chert; 4, phosphorite; 5, baritic rock; 6, paleoregolith; 7, dolomitite; 8, sampling location.

1.2 Physicochemical parameters of the water samples

The temperature, pH, electric conductivity and dissolved oxygen of the water from the pit, the well and the stream were measured on location with a special thermometer, an HI9024 microcomputer pH meter, a CONMET1 portable conductivity meter and a YSI55 dissolved oxygen meter (Table 1).

---

1) Li, S. Geochemistry of gold, silver and platinum group elements in the Lower Cambrian black rock series of Guizhou-Hunan Provinces. Postdoctoral Scientific Report. Institute of Geochemistry, Chinese Academy of Sciences, 1994.

Table 1. Physicochemical parameters of the water samples from Zhongnan Village

Sample No.	Description	Temperature(℃)	pH	Electric conductivity (μS)	Dissolved oxygen ($mg \cdot L^{-1}$)
ZNW1A	Pit water, clean	18.2(27.9)1)	2.45(2.44)	>1999	3.02(3.55)
ZNW1B	Pit water, milky	18.2(27.9)	2.45(2.44)	>1999	3.02(3.55)
ZNW2	Well water	16.7	6.55	546	6.45
ZNW3	Stream water	20.9	7.60	455	8.04

1) The values in parentheses are from the water being laid 24 h at a standstill.

It is noticed from Table 1 that there is no big difference in temperatures of the water from different sources but the pH and dissolved oxygen values are obviously different. The water from the pit is acidic with much higher electric conductivity than that of the water from the well and stream, implying its dissolved ionic materials are far richer than those in well and stream waters. Although the pH values of both the water from the well and from the stream are close to medium, the former, which is spatially more close to the "polyelement bed", is somewhat acidic with a relatively higher electric conductivity. This implies that dissolved ionic materials are richer.

1.3 ICP-MS analyses of noble metal elements

The analyses (Table 2) were conducted in the Institute of Geochemistry, Chinese Academy of Sciences. The samples were decomposed with Na_2O_2 in corundum crucible. After dissolving the fused disc with aqua regia and evaporating the solution to remove the SiO_2, PGEs were concentrated by Te coprecipitation. Ru, Pd, Ir and Pt were determined by ID-ICP-MS; Rh and Au by internal standard ICP-MS. The samples were dissolved using distilled HF + HNO_3 in a microwave oven, then using internal standard ICP-MS to determine Ag. The detailed analytical condition and procedure were the same as described by Qi et al.[17] and Ma et al.[18].

The analyses of ores show that the major carrier of PGE in the "polyelement bed" is the primary jordisite-rich ore. The total contents of PGE and Ag in the pyrite-rich ore are only 1/13 and 1/2 respectively of those in the primary jordisite-rich ore. Their contents of Au are nearly the same. The present data also show that in natural waters, the content of Au can reach 10^{-9} order of magnitude, while the contents of Pt, Pd and Ru are equivalent to the contents of Ir and Rh, being lower than 10^{-9} order of magnitude.

Table 2. ICP-MS analyses of noble metal elements in different ores and waters

Sample No.	Description	Unit	Ru	Rh	Pd	Ir	Pt	ΣPGE	Ag	Au
ZN-10	Jordisite-rich ore	$ng \cdot g^{-1}$	4.98	1.78	180.02	2.71	84.96	274.45	13065	139
ZN-12	Leached jordisite-rich ore	$ng \cdot g^{-1}$	2.99	0.53	59.92	2.27	21.42	87.13	3750	201.7
ZN-02	Pyrite-rich ore	$ng \cdot g^{-1}$	2.8	0.24	6.69	2.47	8.66	20.86	4966	128.9
ZNW1A	Pit water, clean	$ng \cdot mL^{-1}$	0.010	0.005	0.013	0.012	0.016	0.056		9.58
ZNW1B	Pit water, milky	$ng \cdot mL^{-1}$	0.011	0.003	0.009	0.013	0.013	0.049		3.26
ZNW2	Well water	$ng \cdot mL^{-1}$	0.012	0.002	0.014	0.014	0.015	0.057		8.64
ZNW3	Stream water	$ng \cdot mL^{-1}$	0.011	0.001	0.008	0.012	0.010	0.042		3.57
Leaching rate a)		%	39.96	70.23	66.72	6.24	74.79	68.25	71.30	−45.11

a) Leaching rate = [(ZN10 − ZN12)/ZN10] × 100%

2 Discussion

2.1 Leaching rate of noble metal elements

From Table 2, it can be seen that the jordisite-rich ore (ZN-10), having been strongly leached (ZN-12), shows great deficit in noble metal elements except Au. The leaching rates of Rh, Pd, Pt, Ag and total PGE (ΣPGE, without Os) are as high as 66.72% ~ 74.79%. This reveals that in supergene environment PGE and Ag can migrate along with natural water.

Gray et al.[19] observed an upward steady increasing of PGE in a 40 ~ 60 m thick lateritic regolith, Ora Banda Sill, Western Australia. A total enrichment of 3 ~ 5 times in the lateritic, in the ferruginous zone even had maximum concentrations up to 2000×10^{-9} for total PGE in clay-rich duricrusts. They thought that the PGE accumulations appeared to be residual and the elements appeared to be immobile.

On the basis of studies of the stratigraphic distribution, environments and textures of the platinum group minerals, Coghill et al.[20] pointed out that the primary mineralizing events were due to orthomagmatic processes, but under the action of trapped interstitial hydromagmatic fluids PGE had remobilized in microscale.

After studies of the PGE in the soils on traps of the Freetown peninsula, Sierra Leone, Bowles et al. concluded that weathering processes could dissolve PGE and permit their transport and deposition as minerals in eluvial deposits and that organic compounds could provide potential means for PGE transportation in solution[21].

Above-mentioned are three representative viewpoints at present with regard to the mobility of PGE. As a matter of fact, whether an element migrates or not generally depends upon not only the element's chemical mobility, but also its occurrence mode. As mentioned in this paper, the major carrier of PGE in the "polyelement bed" is the primary Jordisite-rich ore. Li's previous study1) showed that the major carrier of PGE was sulfide. Although the exact occurrence mode of the PGE in the black rock series is not clear yet, the present study at least supports that when primarily carried by sulfide, PGE can transport in supergene leaching environment.

2.2 Relative mobility of noble metal elements

It is generally accepted that Pt and Pd relative to Os, Ru, Rh and Ir, Pd to Pt, Ag to Au, and Au to Os, Ru, Rh, Ir and Pt, bear more active mobility. Taking the relative active elements as numerators and the relative inert elements as denominators, the following related parameters were calculated as shown in Table 3.

Table 3. Parameters of noble metal elements in different ores and waters

Sample No.	Description	Pd/Pt	Ag/Au	Au/Ir	Pd/Ru	Pd/Rh	Pt/Ir	(Pt + Pd)/(Ru + Rh + Ir)
ZN-10	Jordisite-rich ore	2.1	94.0	51.29	36.15	101.13	31.35	28.0
ZN-12	Leached jordisite-rich ore	2.8	18.6	88.85	20.44	113.06	9.44	14.0
ZNW1A	Pit water, clean	0.81		798.33	1.3	2.6	1.33	1.1
ZNW1B	Pit water, milky	0.69		250.77	0.82	3	1	0.8
ZNW2	Well water	0.93		617.14	1.17	7	1.07	1.0
ZNW3	Stream water	0.80		297.5	0.73	8	0.83	0.8

The ratios Ag/Au, Pd/Ru, Pt/Ir and (Pt + Pd)/(Ru + Rh + Ir) are smaller and Pd/Rh, Pd/Pt and Au/Ir are greater for the leached jordisite-rich ore than for the primary one. Although the evaluation of the relative mobility of the elements is not efficient for statistical analysis from the present data, the more active characters of Ag relative to Au, and Pt and Pd to Ru, Rh and Ir in the present supergene environment are distinctive.

Suppose that all the noble metal elements in the water of different source near Zhongnan Village were from the mineralized black rock series, and consider the active order of the elements, the most active elements should be the first to enter the water and the parameters for the waters in Table 3 should be larger. Whether the elements are mobile or not, their contents in the water are around the detection limit. Therefore these parameters obtained are not very reliable for evaluating the mobility of the elements. Even so, the parameters for the clean and milky pit water suggest a preference for the relative active elements to enter the clean water, and the parameters for the well water, which is spatially more close to the "polyelement bed", are generally greater than those for the stream water far from the "polyelement bed".

2.3 Possible condition and mode of the element transportation

From the field geological setting and the ore characters, it is deduced that the medium leaching the jordisite-rich ore was mainly the supergene water with the characters similar to those of the pit water. Considering the solar radiation in summer, the temperature of the supergene water would not exceed 50 ℃. Because a large quantity of sulfides existed in the ore and their decomposition by water would form $[SO_4]^{2-}$, the pH of the water would be about 2.4. Since the supergene water absorbed a large quantity of metal ions from the ore, its electric conductivity

---

1) Li, S. *Geochemistry of gold, silver and platinum group elements in the Lower Cambrian black rock series of Guizhou-Hunan Provinces*. Postdoctoral Scientific Report. Institute of Geochemistry, CAS, 1994

reached a quite high level (>1999μS). When the supergene water migrated under the ground, its dissolved oxygen would be lower than that of the ground water (about 3 mg/L). When the supergene water carrying PGE and other metal ions further migrated away from the ores and mixed with other supergene water, its pH value would tend to medium, its electric conductivity and carried metal ions would tend to decrease.

3 Conclusions

(i) Gold, silver and PGE not only bear high mobility in the hydrothermal fluid with high temperature (>300 ℃) and can transport in diagenesis of sedimentary rocks, but also bear quite high mobility and can transport under the action of supergene water.

(ii) In supergene environment, Pt and Pd relative to(Os), Ru, Rh and Ir, Ag to Au are more active geochemically.

(iii) The "cold" water rich in $[SO_4]^{2-}$ at temperature below 50 ℃ and pH of about 2.4 can remobilize the so called "inertia" elements such as Au, Ag and PGE to transport along with the water.

Acknowledgements Authors are grateful to Professor Gao Zhenmin, Dr. Luo Taiyi and Dr. Yang Zusen for their support during the field work. The thanks also extend to Dr. Qi Liang, Institute of Geochemistry, Chinese Academy of Sciences, for his help in the ICP-MS measurement.

References

1 Tu, G. On the Forming Condition of Gold Placer and the Spatial Relation between Gold Placer and Primary Gold Deposit. Researchers of the Geology and Geochemistry of the Chinese Gold Deposits (Series 1) (in Chinese). Beijing: Science Press. 1993, 22.

2 Wilson, A. F. Origin of quartz-free gold nuggets and supergene gold found in laterites and soils—a review and some new observations. Australian Journal of Earth Sciences, 1984, 31: 303.

3 Mann, A. W. Mobility of gold and silver in lateritic weathering profiles: some observations from Western Australia. Economic Geology, 1984, 79: 38.

4 DaCosta, M. L. Gold distribution in lateritic profiles in South America, Africa, and Australia: applications to geochemical exploration in tropical regions. Journal of Geochemical Exploration, 1993, 47: 143.

5 Zang, W. et al. A three stage genetic model for the Igarape Bahia lateritic gold deposit, Carajas, Brazil. Economic Geology, 1993, 88: 1768.

6 Tu, G. et al. Lower Temperature Geochemistry. Beijing: Science Press. 1998, 1.

7 McCallun, M. E. et al., Platinum metals associated with hydrothermal copper ores of the New Rambler Mine, Medicine Bow Mountain, Wyoming. Economic Geology, 1976, 71: 1429.

8 Xiao, S. et al. Platinum group element geochemistry of the platiniferous sulfide Cu-Ni ore deposits. In: Institute of Geochemistry, Chinese Academy of Sciences (ed): Platinum Group Element Geochemistry and Platinum Group Minerals of the Chinese Platiniferous Geological Bodies (in Chinese). Beijing: Science Press. 1981: 39.

9 Watkinson, D. H. et al. Hydrothermal origin of platinum-group mineralization in low-temperature copper sulfide-rich assemblages, Salt Chunk intrusion, Alaska. Economic Geology, 1992, 87: 175.

10 Ripley, E. M. et al. Hydrothermal alteration in the Babbitt Cu-Ni deposit, Duluth complex: mineralogy and hydrogen isotope systematics. Economic Geology, 1993, 88: 679.

11 Bronwen, M. C. et al. Platinum-group minerals in the Selukwe Subchamber, Great Dyke, Zimbabwe: implications for PGE collection mechanisms and post-formational redistribution. Mineralogical Magazine, 1993, 57: 613.

12 Mountain, B. W. et al. Chemical controls on the solubility, transport and deposition of platinum and palladium in hydrothermal solutions. Economic Geology, 1988, 83: 492.

13 Gammons, C. H. et al. Experimental investigation of the hydrothermal geochemistry of platinum and palladium: 1. Solubility of platinum and palladium sulfide minerals in NaCl/H_2SO_4 solutions at 300 ℃. Geochim et Cosmochim Acta, 1992, 56: 3881.

14 Gammons, C. H. et al. Experimental investigation of the hydrothermal geochemistry of platinum and palladium: 3. The solubility of Ag-Pd alloy + AgCl in NaCl/HCl solutions at 300 ℃. Geochim et Cosmochim Acta, 1993, 57: 2469.

15 Li, S. et al. Element redistribution in the nucleation of calcareous nodules in the lower Cambrian black shales of Zunyi area, Guizhou, China. In: Research of Geology and Geochemistry (eds. Peng, R. et al.) (in Chinese with English abstract). Guiyang: Guizhou Science and Technology Press. 1996: 72.

16 Li, S. et al. Source tracing of noble metal elements in Lower Cambrian black rock series of Guizhou-Hunan Provinces, China. Science in China (Series D), 2000, 43(6): 625.

17 Qi, L. et al. Fast determination of platinum group elements and gold in geological samples by ICP-MS. Rock and Mineral Analysis, 1999, 18(4): 267.

18 Ma, Y. et al. Determination of rare earth elements in rock samples by ICP-MS using microwave digestion. Rock and Mineral Analysis, 1999, 18(3): 189.

19 Gray, D. J. et al. Mineral associations of platinum and palladium in lateritic regolith, Ora Banda Sill, Western Australia. Journal of Geochemical Exploration, 1996, 57: 245.

20 Coghill, B. M. et al. Platinum-group minerals in the Selukwe Subchamber, Great Dyke, Zimbabwe: implications for PGE collection mechanisms and post-formational redistribution. Mineralogical Magazine, 1993, 57: 613.

21 Bowles, J. F. W. et al. The mobility of the platinum-group elements in the soils of the Freetown peninsula, Sierra Leone. The Canadian Mineralogist, 1994, 32: 957.