

Supergene mobility of noble metal elements in black rock series

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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 [SO₄]²⁻ with pH value being about 2.4 at a temperature below 50 °C.

Keywords: supergene water, leaching process, gold-silver-platinum group elements, relative mobility, physiochemical 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[11]. 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 mechanisms 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 °C.

Some modeling and experiments have been conducted on the mobility of PGE at about 300 °C. 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
reach 1000 ppm. Under the condition of common Eh and pH, however, the solubility of the compounds of Pt and Pd with HS\textsuperscript{-} were much higher than that with Cl\textsuperscript{-}.

Few researches have been done on the chemical mobility of PGE at temperature below 200 °C. Up to now, in the studies of the mineralogy and geochemistry of the Lower Cambrian black rock series in South China, Li et al.\textsuperscript{[1],[15]} noticed the mobility of Au, Ag and PGE in sedimentation, diag enesis 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.\textsuperscript{[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 dolomite 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 “polylelement 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 “polylelement 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. “polylelement bed”; 3. chert; 4. phosphorite; 5. baritic rock; 6. paleoregolith; 7. dolomitite; 8. sampling location.](image)

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 CONMET\textsuperscript{1} portable conductivity meter and a YSI55 dissolved oxygen meter (Table 1).

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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 "polycation 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 Na2O2 in corundum crucible. After dissolving the fused disc with aqua regia and evaporating the solution to remove the SiO2, PGEs were concentrated by Te co-precipitation. 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 + HNO3 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 "polycation 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.

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 laterite 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 x 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 Jordsiste-rich ore. Li’s previous study\(^{[1]}\) 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>
<thead>
<tr>
<th>Sample No.</th>
<th>Description</th>
<th>Pd/Pt</th>
<th>Ag/Au</th>
<th>Au/Ir</th>
<th>Pd/Ru</th>
<th>Pd/Rh</th>
<th>Pt/Ir</th>
<th>(Pt + Pd)/(Ru + Rh + Ir)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZN-10</td>
<td>Jordsiste-rich ore</td>
<td>2.1</td>
<td>94.0</td>
<td>51.29</td>
<td>36.15</td>
<td>101.13</td>
<td>31.35</td>
<td>28.0</td>
</tr>
<tr>
<td>ZN-12</td>
<td>Leached jordsiste-rich ore</td>
<td>2.8</td>
<td>18.6</td>
<td>88.85</td>
<td>20.44</td>
<td>113.06</td>
<td>9.44</td>
<td>14.0</td>
</tr>
<tr>
<td>ZNW1A</td>
<td>Pit water, clean</td>
<td>0.81</td>
<td></td>
<td></td>
<td>798.33</td>
<td>1.3</td>
<td>2.6</td>
<td>1.33</td>
</tr>
<tr>
<td>ZNW1B</td>
<td>Pit water, milky</td>
<td>0.69</td>
<td></td>
<td></td>
<td>250.77</td>
<td>0.82</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>ZNW2</td>
<td>Well water</td>
<td>0.93</td>
<td></td>
<td></td>
<td>617.14</td>
<td>1.17</td>
<td>7</td>
<td>1.07</td>
</tr>
<tr>
<td>ZNW3</td>
<td>Stream water</td>
<td>0.80</td>
<td></td>
<td></td>
<td>297.5</td>
<td>0.73</td>
<td>8</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The ratios Ag/Au, Pd/Ru, Pt/Ir and \((\text{Pt + Pd})/(\text{Ru + Rh + Ir})\) are smaller and Pd/Rh, Pd/Pt and Au/Ir are greater for the leached jordsiste-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 jordsiste-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 °C. Because a large quantity of sulfides existed in the ore and their decomposition by water would form \([\text{SO}_4]^{2-}\), 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

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reached a quite high level (>1999uS). 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°C) 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 [SO₄]²⁻ at temperature below 50°C and pH of about 2.4 can mobilize 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 Zuren 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.

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