PGE geochemistry of carbonatites in Maoniuping REE deposit, Sichuan Province, China: Preliminary study

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Concentrations of PGE and Au of seven carbonatite samples from the Maoniuping REE deposit in China are reported (ppb): Ir 0.50~0.78, Ru 1.61~6.75, Rh 0.08~0.14, Pt 2.62~12.15, Pd 1.11~3.65 and Au 1.24~8.61, respectively. The primary mantle-normalized PGE distribution patterns reveal “swallow type” curve, with enrichment in Ru, Pt, Pd in comparison with Ir, Rh, and are similar to those of harzburgite in Dazhuka, Tibet, China. Nobles-metals reveal different trend with increase of Zr/Hf ratios. The preliminary study indicates that the overall PGE abundances of carbonatites are higher than the averages of MORB and OIB; the PGE of carbonatites underwent multi-source evolution. Fluids derived by metasomatism and subduction may transport PGE into carbonatite magmas. We suspect that besides the role of sulfides, volatile and alloys may modify PGE distribution patterns in carbonatite magma.

INTRODUCTION

The platinum-group elements (PGE) and gold are highly siderophile and chalcophile elements that can be used to document processes of mantle evolution as well as in the differentiation of a magma series that the lithophile elements do not. The geochemical behavior of PGE in the mantle, however, is presently only poorly understood. Present insights are derived mainly from studies of sulfide ore bodies, chromitites, mantle peridotites, and komatiites, because such rocks are characterized by relatively high PGE abundance (Watkinson and Melling, 1992; Zhou et al., 1998; Schmidt et al., 2000; Puchtel and Humayun, 2001).

Carbonatites are one of the rare mantle-derived rocks in the world. The investigations of the rock play an important role both in theory and practice to discuss mantle metasomatism, source and evolution of magma and mineralization. Carbonatites, distributed worldwide, have been well documented in the aspect of geology, petrology, mineralogy, geochemistry, high temperature and high pressure experiment (Nielsen, 1980; Horgarth, 1989; Doboson and Jones, 1996; Xu et al., 2002). Investigations of the PGE geochemistry of carbonatites are few. In recent years, the platinum group minerals have been found in the carbonatite deposits of East-Africa and Russia, indicating that sulphide liquid can be fractionated from carbonatite magma. The sulphide liquid plays a role as a carrier of heavy and precious metals in carbonatite complexes (Rudashevsky et al., 2001). So the PGE geochemistry may be used to discuss the evolution of carbonatite magmas. We analyzed the PGE contents of carbonatites from the Maoniuping REE deposit, and preliminarily discussed the origin of PGE and cause of the PGE distribution patterns of carbonatites.

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GEOLOGICAL SETTING AND SAMPLING

The Maoniuping REE deposit is the second largest light REE deposit in China, subsequent to the Baiyun’ebo Fe-Nb-REE deposit in Inner Mongolia Autonomous Region. It is located on the north margin of the Panxi rift. The area is divided into the east rift zone, the middle transitional zone and the west geosynclinal fold zone by the NE-trending Nanhe fault and the Jingpingshan fault, and the Maoniuping REE deposit is located in the middle transitional zone (Fig. 1). The strata exposed in the area are the Middle Devonian siltclasolite, carbonate and Quaternary proluvium and talus. The main structure is the NE-trending fault. Igneous rocks are distributed extensively in the area, including Yansanian granites (Mianxi granite), Himalayan syenites and minor basalts and rhyolites (Yuan et al., 1995).

Vein-like carbonatites intruded into the center of syenites, with the attitude generally in consistence with the NE-trending fault. Veinlets on both sides of the main vein also intruded the syenites (Fig. 1). The carbonatite veins (90–200 m wide) extend 400 m with no sign of pinching out. Carbonatites are composed mostly of calcite (>90%), with minor amounts of biotite, aegirine, arfvedsonite and orthoclase (<10%), and accessory minerals such as apatite and arpidelite (<1%). At the margins of carbonatite veins are developed fenitization and arfvedsonitization. According to Pu (2001), the K-Ar age of carbonatites is about 31.7 ± 0.7 Ma.
ANALYTICAL METHODS

Fresh calcites were selected from carbonatites and crushed to 0.45–0.90 mm in size, washed and then hand-picked for analyses. The PGE data were obtained using ICP-MS, with the isotope dilution method at the Institute of Geochemistry, Chinese Academy of Sciences. The isotopes in spike include $^{195}$Pt, $^{194}$Pt, $^{106}$Pd, $^{105}$Pd, $^{99}$Ru, $^{101}$Ru, $^{191}$Ir and $^{193}$Ir (US Services Inc.). The mono-isotope elements Rh and Au were determined by external calibration method with Lu as the internal standard. Following sample dissolution, the PGE were concentrated using a Te-coprecipitation method, modified from Qi and Hu (1999). The reagents HCl and SnCl$_2$ were also purified twice by Te-coprecipitation. The limits of detection are 0.02 (Ir), 0.045 (Ru), 0.024 (Rh), 0.23 (Pt), 0.11 (Pd), 0.32 (Au) ppb. The total procedural blanks for PGE are less than 0.02 ppb. The PGE and Au contents of standard samples WGB-1, UMT-1 and WPR-1 are listed in Table 1.

Table 1. Analytical data and reference values for the standard samples (ppb)

<table>
<thead>
<tr>
<th></th>
<th>WGB-1</th>
<th></th>
<th>UMT-1</th>
<th></th>
<th>WPR-1</th>
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<tbody>
<tr>
<td></td>
<td>D</td>
<td>S</td>
<td>D</td>
<td>S</td>
<td>D</td>
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<tr>
<td>Ir</td>
<td>0.35±0.04</td>
<td>0.33</td>
<td>9.1±0.5</td>
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<td>12.7±0.6</td>
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<tr>
<td>Ru</td>
<td>0.28±0.04</td>
<td>0.30</td>
<td>10.2±0.9</td>
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<td>20.6±2.1</td>
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<tr>
<td>Rh</td>
<td>0.34±0.04</td>
<td>0.32</td>
<td>9.1±0.5</td>
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<td>12.8±0.9</td>
</tr>
<tr>
<td>Pt</td>
<td>6.5±0.5</td>
<td>6.1</td>
<td>121±7</td>
<td>128</td>
<td>294±11</td>
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<tr>
<td>Pd</td>
<td>14.5±0.9</td>
<td>13.9</td>
<td>112±8</td>
<td>106</td>
<td>242±8</td>
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<tr>
<td>Au</td>
<td>3.4±0.6</td>
<td>2.9</td>
<td>54±7</td>
<td>48</td>
<td>45±5</td>
</tr>
</tbody>
</table>

$D$ = determined data by repeated analyses ($n = 5$), $S$ = standard data (Govindaraju, 1994).

Table 2. PGE and Au data for carbonatites in the Maoniuping REE deposit (ppb)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>MNP-6</th>
<th>MNP-13</th>
<th>MNP-122</th>
<th>MNP-125</th>
<th>MNP-10</th>
<th>MNP-11</th>
<th>MNP-142</th>
<th>Mean</th>
<th>Origin mantle (A)</th>
<th>Chondrite (A)</th>
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<td>0.65</td>
<td>0.72</td>
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<td>0.61</td>
<td>0.50</td>
<td>3.2</td>
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<td>Ru</td>
<td>2.11</td>
<td>1.61</td>
<td>2.58</td>
<td>2.83</td>
<td>3.34</td>
<td>6.75</td>
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<td>5.0</td>
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<tr>
<td>Rh</td>
<td>0.12</td>
<td>0.09</td>
<td>0.08</td>
<td>0.12</td>
<td>0.14</td>
<td>0.13</td>
<td>0.12</td>
<td>1.0</td>
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<tr>
<td>Pt</td>
<td>2.62</td>
<td>2.97</td>
<td>4.93</td>
<td>5.77</td>
<td>9.06</td>
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<td>Pd</td>
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<td>1.11</td>
<td>1.57</td>
<td>2.74</td>
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<td>3.23</td>
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<tr>
<td>Au</td>
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<td>1.42</td>
<td>2.86</td>
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<td>1.31</td>
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<td>$\Sigma$PGE</td>
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<td>6.44</td>
<td>9.88</td>
<td>12.22</td>
<td>15.37</td>
<td>22.87</td>
<td>12.95</td>
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<td>Pd/Ir</td>
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<td>3.63</td>
<td>3.28</td>
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<tr>
<td>Pd/Ru</td>
<td>0.57</td>
<td>0.68</td>
<td>0.61</td>
<td>0.97</td>
<td>0.65</td>
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<tr>
<td>Pd/Rh</td>
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<td>11.88</td>
<td>19.26</td>
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<td>Pt/Pd</td>
<td>0.46</td>
<td>0.37</td>
<td>0.32</td>
<td>0.47</td>
<td>0.24</td>
<td>0.26</td>
<td>0.56</td>
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<tr>
<td>Pd/Rh</td>
<td>1.24</td>
<td>1.48</td>
<td>1.91</td>
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<td>2.71</td>
<td>1.80</td>
<td>2.91</td>
<td>2.06</td>
<td>1.42</td>
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<tr>
<td>Pd/Rh</td>
<td>2.50</td>
<td>2.35</td>
<td>3.81</td>
<td>3.35</td>
<td>3.93</td>
<td>8.57</td>
<td>3.24</td>
<td>3.96</td>
<td>1.0</td>
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<tr>
<td>Rh*</td>
<td>0.29</td>
<td>0.25</td>
<td>0.14</td>
<td>0.18</td>
<td>0.15</td>
<td>0.09</td>
<td>0.19</td>
<td>0.18</td>
<td>1.0</td>
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</tr>
<tr>
<td>Pt*</td>
<td>1.95</td>
<td>2.58</td>
<td>3.84</td>
<td>2.78</td>
<td>4.57</td>
<td>5.21</td>
<td>2.71</td>
<td>3.38</td>
<td>1.0</td>
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</tbody>
</table>

$Ru^* = (Ru)/((Ir)_{n} \times (Rh)_{n})^{1/2}, Rh^* = (Rh)/((Ru)_{n} \times (Pt)_{n})^{1/2}, Pt^* = (Pt)/((Rh)_{n} \times (Pd)_{n})^{1/2}$ (Garuti et al., 1997).

The $n$ represents the normalized mantle values. A, McDonough and Sun (1995).
**PGE AND Au CONTENTS AND DISTRIBUTION PATTERNS OF CARBONATITES**

The concentrations of PGE and Au are listed in Table 2. Data normalized to the primary mantle are illustrated in Fig. 2. The PGE characteristics of calcites can represent those of the carbonatite magmas, because the carbonatites are composed mostly of calcites (>90%).

1. The $\Sigma$PGE ($\text{Ir} + \text{Ru} + \text{Rh} + \text{Pt} + \text{Pd}$) of carbonatites range from 6.44 to 22.87 ppb with a mean of 12.37 ppb, and are higher than the means of alkali basalts ($\leq 1$ ppb; Rehkamper et al., 1999), Mid-ocean ridge basalts (MORB; $\leq 0.74$ ppb; Hertogen et al., 1980; Fryer and Greenough, 1992) and ocean-island basalts (OIB; $\approx 3.25$ ppb; Tatsumi et al., 2000). Except sample MNP-142, the other samples are characterized by Pt-Ru type (Pt > Ru > Pd > Ir > Rh).

2. The ratios of Pd/Ir, Pd/Ru, Pd/Rh, Pd/Pt and Pt/Ru range from 1.53 to 7.30, 0.48 to 1.64, 10.32 to 30.42, 0.24 to 0.56 and 1.24 to 2.91, respectively. Except Pd/Pt ratio, the others are generally higher than those in chondrite and original mantle (Table 2). All samples show positive Pt* and negative Rh* anomalies. The Pt anomaly provides a measure of the deviation of Pt concentration from the general trend of the primitive mantle-normalized pattern of a sample, whereas investigations describing the behavior of Rh are extremely rare in the literature.

3. The PGE distribution patterns of carbonatites show “swallow type” (Fig. 2), with enrichment in Ru, Pt and Pd relative to Ir and Rh. The enrichment extent of Pt is more than that of Pd. They differ from the flat, positive slope, and negative slope type rocks resulting from partial melting or crystal fractionation of the primitive mantle, but are similar to the harzburgite in Dazhuka, Tibet, China (Yu et al., 2001).

4. In Fig. 3., nobles-metals reveal different trend with Zr/Hf ratios. With the increase of Zr/Hf ratio, Ir tends to decrease, and Ru, Rh, Pt and Pd tend to increase. However, the correlation factors of Pt ($r = 0.59$) and Pd (0.66) are better than those of Ru (0.29) and Rh (0.48). This observation implies that there exist different evolutionary processes between Ir and Pt, Pd (possibly Ru, Rh).
DISCUSSION AND CONCLUSIONS

Origin of PGE in carbonatites

The carbonatites from Maoniuping REE deposit are enriched in the incompatible elements LREE (1922~3508 ppm), Sr (10530~15017 ppm) and Ba (426~1629 ppm; Xu et al., 2002). This shows that the carbonatite magma was the product of low-degree partial melting of mantle rocks. Nelson et al. (1988) invoked very small degrees of melting (<1%) from eclogitic source to generate primary carbonatite melt with extreme LREE-enrichment. Experimental studies in mantle peridotite-CO$_2$-H$_2$O systems have revealed a $P$-$T$ window (Falloon and Green, 1989; Meen et al., 1989) in which low degree partial melting of lherzolites can generate primary carbonatite melts. Low degree (8~25%) partial melting of primitive mantle generates primary melts that are S-saturated (Hamlyn et al., 1985; Sun et al., 1991; Fryer and Greenough, 1992; Keays, 1995), leaving behind sulfides in the residual peridotites (Mitchell and Keays, 1981; Hamlyn et al., 1985; Lorand et al., 1993). Because of their very high sulfide/silicate liquid partition coefficients ($10^3$~$10^4$; Fleet et al., 1991; Bezmen et al., 1994), the PGE are retained in residual sulfides in the upper mantle, and the primary magmas are strong depleted in the PGE (Hamlyn et al., 1985), e.g., alkali basalts, MORB and OIB (Hertogen et al., 1980; Fryer and Greenough, 1992; Rehkamper et al., 1999; Tatsumi et al., 2000). According to mantle melting model (Fryer and Greenough, 1992; Rehkamper et al., 1999), as percentages of melting increase, the sulphides enter the melt. Mantle is not able to generate magmas with Pd abundances > 1 ppb for F < 1%. The PGE concentrations of carbonatites, however, are higher than the averages of the MORB and OIB (Fig. 2). Although there has been much debate as to whether carbonatite magmas are formed by exsolution of an immiscible CO$_2$-rich silicate magmas derived from low degree parting melting (Baker and Wyllie, 1990; Bell and Simonetti, 1996), the carbonatite parental magmas (CO$_2$-rich silicate magmas) should be poor PGE. So PGE systematics of carbonatites are not determined by parting melting process only. More complex interaction process cannot be ruled out.

Carbonate-rich fluids/melts are effective agents in the upper mantle, and cause redistribution of trace elements in the mantle rocks (Green and Wallace, 1988; Hauri et al., 1993). Dalton and Wood (1993) pointed out that calcio-carbonatites can be generated by reaction between primary magnesian carbonatite melts and harzburgite in the upper mantle, and several such reactions have been proposed (Brey et al., 1983; Green and Wallace, 1988). Although there are different views about PGE mobility during mantle metasomatism (Wilson et al., 1996; Zhou et al., 1998; Handler and Bennett, 1999; Schmidt et al., 2000), recent studies (Schmidt et al., 2000; Kepezhinskas et al., 2002) suggest that PGE can be mobile in a metasomatized mantle. The relatively high over-
all PGE concentrations in carbonatite may be generated from metasomatized environment. As seen from Fig. 2, the PGE distribution patterns of carbonatites are similar to those of harzburgite from Dazhuka, Tibet. The PGE distribution patterns of Dazhuka harzburgite are different from those of mantle peridotites of parting melting relict origin, which are of the negative-slope type or the flat type as observed commonly. Yu et al. (2001) pointed out that the Dazhuka harzburgite had undergone mantle metasomatism.

Carbonatite magmas are characterized by low density (2.2) and rich volatile (Treiman, 1989). Brandon (1996) studied osmium recycling in subduction zones, and pointed out that PGE can be partitioned into oxidized and chlorine-rich fluids or melts. These results place new constrain on the behavior of PGE during subduction of crust by showing that PGE can be transported into the mantle. Although the Maoniuping carbonatites occur in the Panxi rift, they were emplaced during the Himalayan period when the Panxi rift closed (Zhang et al., 1988). Affected by collision between the Indian plate and the Yangtze plate, strongly orogenic movement was expected in this area during the Himalayan period. The Sr (0.706074–0.706149) and Nd (0.512383–0.512406) isotopic compositions of carbonatites from the Maoniuping are close to EM1, deviating from the East African Carbonatites Line (EACL) (Bell and Blenkinsop, 1987; Xu et al., 2002). They are characterized by high initial $^{87}$Sr/$^{86}$Sr ratios, and low $\varepsilon_{Nd}$ values. Xu et al.’ study (2002) shows that carbonatites were formed in subduction environment. According to Woodland et al. (2002), the Pt and Pd may have lightly greater transport efficiency in subduction-derived fluids or melts than do the Ir and Ru. The correlation factors in Fig. 3 show there exist different evolutional trend between Ir and Pt, Pd. This implies that fluids/melts generated by subduction carried PGE, and were transported into mantle source of carbonatites.

**Cause of PGE distribution patterns of carbonatites**

Since the study by Mitchell and Keays (1981), sulphides have been regarded as the main host phase for PGE in the mantle. This assumption has been confirmed by in situ proton microprobe analysis (Bulanova et al., 1996; Guo et al., 1999), and by analyses of separated sulphide fractions (Pattou et al., 1996). Alard et al. (2000) discovered the two types of sulphide that are characterized by different, or rather complementary, signatures of noble-metal abundances; sulphides enclosed in silicate mineral grains have low proportions of platinum and palladium relative to osmium, iridium and ruthenium ($(Pd/Ir)_{PM} = 0.01$). The interstitial sulphides, which occur only along grain boundaries, have high Pd contents and low concentrations of osmium, iridium and ruthenium ($(Pd/Ir)_{PM} = 1–20$). The analytical samples are fresh calcites and are crushed to 0.45–0.9 mm. Moreover, microscopic analysis reveal that calcite minerals enclose sulphiders, with grain size about 2 µm, and interstitial sulfides were not found. The carbonatites, however, show supra-chondritic Pd/Ir ratios, different from Alard et al.’ study (2000). It is possible that PGE-carrying fluids or melts came from different source. As shown above, besides the carbonatite metasomatism, the subduction took place at carbonatite source. The PPGE (mainly Pt, Pd) can be partitioned into subduction-derived fluids/melts and have lightly greater transport efficiency than do the IPGE (mainly Ir, Ru) (Brandon et al., 1996; Woodlant et al., 2002), which leads to PPGE relatively enrichment in carbonatite magma.

In Table 2 and Fig. 4, Ru shows better positive correlation ($r = 0.90$) with Pt than with Ir ($r = 0.21$); Pd concentrations are higher than Ir, but lower than Ru. These cannot be account for by the role of sulfides alone. Some microcrystalline may occur as discrete mineral unrelated to the sulfides. A number of studies also suggest that the PGE may be concentrated in non-sulfide minerals, such as chlorides or alloys (Boudreau and McCallum, 1986; Ballhaus et al., 1994; Rehkamper et al., 1997; Lorand et al., 1999). Carbonatite magmas enrich volatile (Treiman, 1989). Experiments have demonstrated the PGE may be transported as volatiles as fluoride and chloride (Wood, 1987; Fleet and Wu, 1993). In
addition, Pt concentrations are higher than other noble metals in carbonatites. The possibility exists that formation of Pt alloys is related with the positive Pt-anomaly (Garuti et al., 1997). Borisov and Palme (1997) suspect that formation of Pt nugget leads to very inhomogeneous distribution of Pt in the melt. But the mechanism by which fluid becomes trapped in the course of an experiment is poorly understood. The PGE geochemical studies of carbonatites are few. Our assumption needs more evidences.

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