Geochemistry of Platinum Group Elements in Chromitites from The Rhodope Massif (Bulgaria)

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INTRODUCTION.

Ophiolite chromitites are usually enriched in platinum-group elements (PGE) with respect to other mantle rocks. The origin of such enrichment is still controversial, and not completely understood. It is widely accepted that concentration of PGE depends on the degree of partial melting, the nature of the source rock, and the sulphur content of the parent partial melt. All these parameters are closely linked to the geotectonic setting where chromitite forms. Thus, Cr-rich chromitites formed in suprasubduction zones are rich in PGE, while Al-rich chromitites formed in spreading zones are usually poor in PGE (Prichard et al., 1986; Proenza et al., 1999; Ahmed & Arai 2002, 2003; Proenza et al., 2004; Gervilla et al., 2005). Furthermore, some mechanisms, such as hydrothermal activity (Prichard et al., 1986), serpentinization (Thalhammer et al., 1990), metamorphism (Zaccarini et al., 2005), or weathering (Augé & Legendre 1994) can modify the concentration of PGE in chromitites.

In the current communication, we report whole rock PGE analyses of a set of chromitites from three metamorphosed meta-ophiolite bodies, scattered in the Rhodope Massif (Southern Bulgaria). The degree of metamorphic alteration varies among these bodies as well as their PGE contents and their distribution among the different chromitites. This will allow us to discuss the origin of the geochemical distribution of PGE in the chromitites of the Rhodopean massif, its geodynamic implications and the role played by metamorphism.

GEOTECTONIC SETTING.

The studied meta-ophiolite bodies (Dobromirtsi, Jakovitsa and Golyamo Kamenyane) occur scattered within the easternmost part of central Rhodopes which is a crystalline nappe, composed of granitic and metamorphic rocks, extending along south Bulgaria and north Greece (Marchev et al., 2005).
At Dobromirtsi and Jakovitsa massifs, the ophiolite sequence is dominated by mantle rocks (harzburgites and dunites) metamorphosed up to lower-temperature amphibolite facies. These rocks are strongly serpentinized although in some areas they also show chloritization, carbonatization and talcization (González-Jiménez et al., 2008). At Golyamo Kamenyane the sequence comprises harzburgites and dunites, grading upward to alternating dunite-pyroxenite. Rodingite bodies are also recognized at the top of the sequence. This massif is spatially associated with amphibolitized gabbros. All these rocks are highly metamorphosed. The alteration includes, serpentinization, tremolitization, chloritization, talcization, carbonatization, phlogopitization and listvenitization (Zhelyaskova-Panayotova & Economou-Eliopoulous 1994). In fact, the studied chromitites occur scattered in a wide area mined for asbestos.

PLATINUM-GROUP ELEMENTS.

All the studied chromitites are of podiform-type, hosted by mantle rocks (dunites in harzburgites). The PGE contents are low, mainly below 2 ppm. The highest values are recorded in chromitites from Dobromirtsi (up to 1.6 ppm). As expected in ophiolite chromitites, they are enriched in Ir-subgroup PGE (IPGE: Os, Ir, Ru) relative to Pt-subgroup (PPGE: Rh, Pt, Pd) (Table 1). The Pd/Ir ratio is consequently low (0.04-1). Their chondrite-normalized PGE patterns plot between 0.002 and 1.10 times the chondritic values showing variable, negative-sloped patterns. These are relatively flat from Os to Ir, with Ru anomalies, followed by strong negative slopes from Ru to Pt. Most samples show significant enrichment in Pd relative to Pt.

Total PGE contents in chromitites from Jakovitsa are lower than those from Dobromirtsi (<0.5 ppm). Their chondrite-normalized PGE patterns plot between 0.013 and 0.33 times the chrondritic values and show variable shapes, with slight positive anomalies in Ru. The patterns of the samples with the lower PGE content show a nearly flat, horizontal shape. Nevertheless, two samples show a Pd positive anomaly relative to Pt. These variations of PGE contents causes strong variation of Pd/Ir ratios (0.1-2.5).

The studied chromitites from Golyamo Kamenyane have the lowest PGE contents (<0.2 ppm) (Table 1). Their chondrite-normalized PGE patterns plot between 0.004 and 0.08 times the chondritic values and show relatively flat horizontal shape. Most samples show negative slope from Os to Ir, positive anomalies in Ru relative Os and Ir, and smooth negative slope from Ru to Pt. Some samples also show a relative enrichment in Pd compared with Pt, and one sample shows a smooth positve-sloped pattern from Os to Pd, with a slight, positive anomaly in Ru.

PGE	Dobromirtsi	Jakovitsa	Golyamo Kamen.
Os	6-299	7-84	6-34
Ir	9-370	10-97	5-32
Ru	33-765	35-229	18-58
Rh	4-94	6-19	2-10
Pt	2-42	14-51	5-36
Pd	2-7	8-42	6-17

Table1. PGE contents (in ppb) of the analyzed chromitites.

palabras clave: Elementos del grupo del platino, Metamorfismo, Cromitítas | *key words:* Platinum-group elements, Metamorphism, Chromitites.

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CONCLUDING REMARKS.

The features of chromitites from the Rhodope Massif suggest that these bodies are typical ophiolite chromitites. The high PGE concentrations are found in Cr-rich chromitites from Dobromirtsi, whereas the lower PGE contents are found in Al-rich chromitites from Jakovitsa and Golyamo Kamenyane. This correlation between PGE (mainly IPGE) and Cr# observed in the chromitites from the Rhodope Massif is in agreement with previous results elsewhere (Zhou et al., 1998; Ahmed & Arai 2002, 2003; Proenza et al., 2003; Gervilla et a., 2005). These authors stress that PGE contents of chromitites tend to increase with the increase of Cr content in chromitite. Thus, coexistence of PGE-rich and PGE-poor chromitites along the Rhodope Massif also suggests that different parental melts were involved in the formation of the chromitites. Since that nature of parental melts is strongly dependent on the mantle source and the geotectonic setting, the spectrum of chromite chemistry and PGE geochemistry of the chromitites is probably the consequence of the progressive change (in time and space) of the composition of parental melts (Zhou y Robinson 1997 ; Proenza et al., 1999; Gervilla et al 2005). According to these authors Cr-rich chromitites form from magmas of boninitic affinity, whereas those from which Al-rich chromitites form have a composition close to that of back-arc basin basalts (BABB). Thus, it can be suggested that the Dobromirtsi Massif would represent a piece of suprasubduction mantle located close to an arc environmet a the time of chromite formation, whereas Jakovtisa and Golyamo Kamenyane, would represent mantle portions located in a nascent spreading center, such as back arc basin.

As noted above, metamorphism can modify the original PGE distribution in chromitites. As expected for ophiolite chromtities, those from the Rhodope Massif generally show typical low PGE contents and negative-sloped, chondrite-normalized patterns. The preservation of PGM within chromite crystals prevents any modification of PGE distribution. Nevertheless, some morphological features of the patters suggest local redistribution of the more mobile PGE (Rh, Pt and, mainly, Pd). Thus, the observed positive Pd anomaly could suggest partial remobilization of this element during alteration. Source of Pd during alteration could be provided by PGM located in the interstitial altered silicate matrix (González-Jiménez et al., 2007). Our preliminary mineralogical investigations reveal the presence of minute Pd-bearing minerals associated with metamorphic minerals or the alteration products of chromite. The positive-sloped chondrite-normalized patterns shown by some samples from Jakovitsa and Golyamo Kamenyane suggest that PPGE remobilization during metamorphism is not homogeneous but has variable spatial intensity.

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