On the origin of the PGE-enrichment in chromitites associated with ophiolite complexes: the case of Skyros island, Greece

Maria Economou-Eliopoulos,
Department of Geology & Geoenvironment, University of Athens, Athens 15784, e-mail: econom@geol.uoa.gr

ABSTRACT: Small massive and schlieren type chromite bodies hosted in the Skyros serpentinitized peridotites are dominated by high-Al variety in both PGE-poor and PGE-enriched (up to 3 ppm ΣPGE) chromitites, although both high-Cr and –Al type are found in the entire island. Detailed investigation, by SEM/EDS, showed that apart from laurite (RuS₂) occurring as small inclusions within unaltered chromite grains, Ru-Ir-Os- minerals were identified within silicate matrix as interstitial between chromite grains. Both Ru-Ir-Os alloys and sulfides exhibit significant Fe, Ni, Cr, Sb and As contents and a wide compositional variation. They are accompanied by serpentine, chlorite and Cr-garnet. The relatively high IPGE enrichment in chromitites may be related to post-magmatic processes during an extended period of deformation, including the ductile asthenospheric mantle flow and crustal brittle deformation. Metasomatic fluids have substantially modified the composition of primary laurite, generating Ru-Ir-Os-Fe-Cr-Co-Ni-bearing minerals.

KEYWORDS: PGE, PGM, chromite, PGE-enrichment, ophiolites, Skyros, Greece

1. INTRODUCTION

Commonly, the abundances of platinum-group elements (PGE) in large chromite deposits of Greece are generally low (few hundreds of ppb). A PGE-enrichment, in all PGE, only in Os, Ir and Ru (IPGE or refractory), or in Pt and/or Pd (PPGE), are a common feature of relatively small chromite occurrences. This enrichment seems to be local and independent of the major element composition of chromite (Economou-Eliopoulos, 1996; Zhou and Robinson, 1997; Economou-Eliopoulos et al., 1999; Tsoupas and Economou-Eliopoulos, 2005). Agiorgitis et al., (1978) and Economou-Eliopoulos (1996) investigated the PGE contents in chromitites from the Skyros ophiolitic massifs. Tarkian et al. (1992) gave compositions of PGE-minerals (PGM) the accompanying base metal-bearing and silicate minerals.

In the present contribution SEM/electron microprobe analyses of individual mineral phases are presented, documenting the compositional variation of chromite, PGM and accompanying silicates, and their evolutionary stages.

2. CHARACTERISTICS OF THE SKYROS OPHIOLITES

The ultramafic massifs of the Skyros island, belong to the EoHellenic Pre-Cretaceous nape. A tectonic melange and ophiolitic rocks compose the Skyros dismembered ophiolitic massifs, which overthrust on to the Pelagonian massif (Katsikatsos, et al., 1986). Serpentized harzburgites, and to a lesser extend lherzolites and dunites are the predominant petrological types. Broad mantle shear zones, are characterized by the presence of fish-shaped serpentinite bodies, commonly containing juxtaposed blocks with distinct compositional and microstructural characteristics. Small (a few thousand tons) massive and schlieren type chromite bodies are hosted within serpentinitized dunites (Economou-Eliopoulos, 1996).

3. METHODS OF INVESTIGATION

Polished sections prepared from the chromite occurrences of the Skyros area were examined by reflected light microscopy and scanning electron microscope. Quantitative analyses were carried out at the University of Athens, Department of Geology, using a JEOL JSM 5600 scanning electron microscope, equipped
with automated OXFORD ISIS 300 energy dispersive analysis system. Analytical conditions were 20 kV accelerating voltage, 0.5 nA beam current, <2 µm beam diameter and 50 second count times.

4. CHEMICAL COMPOSITION OF CHROMITE ORES AND PGE MINERALOGY

4.1 Chromite and silicates

The compositions of chromitites from the entire Skiros island area fall within both high-Cr and -Al types (Economou-Eliopoulos, 1996). Detailed investigation of numerous polished thin-sections from the area of Achладо̱nes (Skyros) showed a dominance of the high-Al variety in both PGE-poor and PGE-enriched chromitites. Although the composition of chromite is commonly homogeneous, dark gray and light colored phases can be distinguished (Fig. 1a,c) close to highly brecciated zones. A salient feature of PGE-enriched samples is the alteration of chromite (the average Cr/(Cr+Al) ratio of unaltered chromite is 0.56 and Mg/(Mg+Fe$^{2+}$) is 64) to ferrian chromite (the Cr/(Cr+Al) ratio ranging from 69 to 0.76 and Mg/(Mg+Fe$^{2+}$) from 57 to 51) even in the same polished section (Fig. 1c).

All silicate minerals occurring in interstices between chromite grains have been entirely altered to Fe-poor serpentine and chlorite. Cr-andradite (13-14 wt% Cr$_2$O$_3$ and 14 – 16 wt% FeO) as veinlets and interstitial secondary minerals are common (Fig 1a,b).

4.2 PGE contents and Ru-Ir-Os-minerals

Whole ore PGE analyses of massive chromitites in previous studies indicated that there is a local PGE-enrichment, mostly in refractory PGE in certain ophiolites of Greece (Table 1).

Table 2. Representative microprobe analyses of PGM (Figure 1) from PGE-rich chromitites of the Skyros (Achладо̱nes) island

<table>
<thead>
<tr>
<th>Location</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skyros (Achладо̱nes area)</td>
<td>14.1</td>
<td>5.88</td>
<td>7.96</td>
<td>15.49</td>
<td>44.8</td>
<td>38</td>
</tr>
<tr>
<td>Veria</td>
<td>38</td>
<td>80.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data from Economou-Eliopoulos &amp; Eliopoulos (1999); Tsoupas &amp; Economou-Eliopoulos (2007)</td>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Laurite (RuS$_2$) has been identified as small inclusions within unaltered chromeite grains in the Skyros (Achладо̱nes) chromitites (Tarkian et al., 1992; Table 2). Ru-Ir-Os- minerals were, however, identified within silicate matrix as interstitial secondary minerals (Fig. 1c,d,e). Both Ru-Ir-Os alloys and sulfides exhibit significant Fe, Ni and Cr contents and a wide compositional variation (Table 2; Fig. 1d,e). In addition sulfides contain Pt, Sb and As. Heazlewoodite (Ni$_3$S$_2$) occurs commonly within fractures and the serpentine-chlorite matrix.

5. DISCUSSION

It has been accepted that inclusions of laurite in unaltered chromite are early magmatic phases formed by direct crystallization from basaltic magmas (Auge, 1985; Brenan and Andrews, 2001; Peregoedova and Ohnenstetter, 2002; Mungall, 2005). Also, the presence of Os-, Ir, Ru- and Rh-bearing PGM within chromitites from some ophiolite complexes have been attributed in both in situ alteration or/and re-mobilization and re-deposition of PGE during post-magmatic processes, such as retrograde hydrothermal metamorphism (Tarkian and Prichard, 1987; Garutti and Zaccarini, 1997; Ahmad and Arai, 2003).

The mineralogical characteristics and textural relationships between PGM and hosting chromitites from the Skyros ophiolites are similar to those from Veria in terms of: (a) the IPGE enrichment, although it is much higher in the Veria chromitites (up to 25 ppm), (b) the association of the IPGE-enrichment with shearing zones, (c) the presence of laurite as inclusions within chromite, and Ir-group phases interstitial to strongly fragmented chromite grains, (d) the significant Ni, Cr, Fe As and Sb

| Table 1. Representative whole ore analyses of chromitites from Skyros (Achладо̱nes area) and Veria concentrations in ppb |
|-----------------|-----|-----|-----|-----|-----|-----|
| Location        | Os  | Ir  | Ru  | Rh  | Pt  | Pd  |
| Skyros          | 13-140 | 30-480 | 150-1200 | 7-160 | 20-280 | 20-40 |
| Veria           | 13-7400 | 26-6020 | 15-9700 | 11-310 | 2-760 | 3-750 |
| Data from Economou-Eliopoulos & Eliopoulos (1999); Tsoupas & Economou-Eliopoulos (2007) | 4.2 |

Symbols: n.d. = below detection limit; * = data from Tarkian et al. (1991).
Fig. 1. Back-scattered electron images of strongly fragmented chromite (chr) associated with garnet (grt) and serpentine (srp) (Fig. 1a,b), IPGM in a matrix of serpentine associated with chromite/Fe-chromite (Fe-chr) (Fig. 1c,d,e) and alloys along cracks of chromite and Fe-chromite (Fig. 1f) from Skyros island. Heazlewoodite (hz) is common (Fig. 1b).
contents in both Ru,Ir,Os-sulfides and alloys, and their wide compositional variation, (e) the association of IPGM with Cr-garnet and low-Fe serpentinite.

Thus, besides the typical laurite grains found as inclusions within chromite and the Pt and Pd enrichment in chromitite attributed to magmatic processes (Prichard et al., 1996; Economou-Eliopoulos, 1996) the mineralogical and texture characteristics of relatively high IPGE enrichment in chromitites may be related to post-magmatic processes. They may cover an extended period of deformation, including the ductile asthenospheric mantle flow and culminated in shallow crustal brittle deformation. Metasomatic fluids have substantially modified the composition of primary PGM, mostly laurite, generating Fe-Cr-Co-Ni-bearing Os-Ir-Ru minerals (Tsoupas and Economou-Eliopoulos, 2005, 2007). Furthermore, it seems likely that the most targeted locations for the chromitite-IPGM association are small chromite occurrences found along shear zones within ophiolite complexes.

ACKNOWLEDGEMENTS
The University of Athens is greatly acknowledged for the financial support of this work.

REFERENCES
