Platinum-group minerals in chromitites from the Pindos ophiolite complex, Greece

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With 4 figures and 6 tables in the text


Abstract: Chromitites from several localities in the Pindos ophiolite complex were studied for platinum-group minerals and base metal sulphides. The platinum-group element concentrations are generally low and exhibit chondrite-normalized patterns with negative slopes. However, a platinum and palladium enrichment (Pt 1460–3460 ppb, Pd 600–1660 ppb) was established in PGM-bearing chromitites hosted in strongly serpentinitized dunites in the area of Korydallos. They are characterized by positive slopes of chondrite-normalized PGE-patterns and high Pd/Ir ratios. The PGM consist of Os-rich laurite, sperrylite, and an unidentified phase, Pt(Ni,Fe)4, representing an intermediate composition between synthetic PtFe5 and PtNi5. In general, the chromitites from Pindos are extremely poor in base metal sulphides. Minute grains of pentlandite are found as inclusions in chromite and in the silicate matrix. They contain small amounts of Pt and Pd which also were recorded in secondary heazlewoodite and awaruite. Textural features and analytical results suggest that serpentinization is responsible for a local redistribution of Pt and Pd.

Keywords: PGM, PGE, ophiolite, chromitite, microprobe analysis.

Introduction

Platinum-group element (PGE) and gold concentrations in chromite ores from ophiolite complexes of Greece are generally low, ranging from less than 100 ppb to a few hundreds of ppb. However, some chromitite samples exhibit an enrichment (of a few ppm): (a) only in Os, Ir and Ru, (b) only in Pt and/or Pd and (c) all in PGE. This enrichment seems to be local and independent of the chromitite major element composition (Economou-Eliopoulos 1993). Also, a Pt and Pd enrichment is well-known in chromitites related to ophiolites of the Shetland islands (Pritchard et al. 1986), the Philippines (Bacuta et al. 1990), Albania (Ohnemstetter et al. 1991), Portugal (Bridges et al. 1994) and elsewhere.
A previous work on the Pindos chromite mineralization, with exception of
the Milia area, showed low PGE concentrations and chondrite-normalized
PGE-patterns with a negative slope (Economou-Eliopoulos & Vacondis
1990). In the present study some strongly serpentinized chromitites from
the Pindos ophiolite were investigated for platinum-group minerals (PGM) and a
few representative samples, which are enriched in Pt and Pd, were analyzed for
PGM. These results are given and the relative effects of metamagmatic processes
(deformation, serpentinization) on the primary composition are discussed.

Geological setting and location of the chromitites

The Pindos ophiolite complex, NW Greece, is part of a nappe which is tec-
tonically overthrusted on to the Eocene flysch of the Pindos zone (Fig. 1). It
constitutes a complete complex, although it is mainly comprised of large harz-
burgite–dunite masses. The degree of depletion in the mantle peridotites
(harzburgite and plagioclase–harzburgite) ranges from relatively low to ex-
treme depletion (Economou-Eliopoulos & Vacondis 1990). The magmatic

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Fig. 1. Simplified geological map of the Pindos ophiolite complex (after Magiros et al.
(1986) showing the sampling localities (present study and Economou-Eliopoulos &
Vacondis 1990). A = Ageladostalos; D = Dakos Mine, Kambos Despoti; K = Kory-
dallos (Gournes, Agios Taxarchis); M = Milia; N = Dramala; X = Kyra Kali. 1 = Terti-
iary and Quaternary; 2 = limestones, shales, cherts, sandstones and conglomerates
(Triassic-Jurassic); 3 = limestones with rudists (Cretaceous); 4 = cumulates (mainly
gabbros and werlites); 5 = gabbros and extrusives; 6 = tectonized ultramafics.
sequence of the complex includes cumulate rocks ranging from ultramafic to gabbros, diabase and a complete spectrum from MORB basalts through IAT tholeiites to boninite series volcanics (BSV) (Capek, 1980, 1985; Pearce, 1984). Thus, in the Pindos complex more than one mantle source and eruptive setting seems to be represented, all having a place in a supra-subduction zone environment (Pearce et al. 1984).

Small chromite occurrences, of all textural types (massive, schlieren, banded, nodular and disseminated) are found within elongate dunite bodies in harzburgite and in lower parts of the magmatic sequence. The maximum length of chromite lenses is a few tens of centimeters (Higoumenakis et al. 1977). Due to mantle and emplacement tectonics, a strong plastic and brittle deformation was superimposed of primary magmatic textures and this had an important influence on the present form and distribution of chromitites (Rassos 1990).

Representative samples of chromitites from the areas of Ageladostallos (Trygona, Pefki), Dako’s Mine, Dramala, Kampos Despoti, Korydallos, Milia, Kyra Kali and Koziakas, covering much of the Pindos ophiolite complex (Fig. 1), were investigated for PGM. Also, a few selected samples were analyzed for PGE.

Analytical techniques

Microprobe analyses were carried out with a Cameca Camebax microbeam wavelength-dispersive electron microprobe at the Department of Mineralogy and Petrology, University of Hamburg. The operating conditions were: 20–25 nA and 20 kV. The following X-ray lines were used: SiKα, FeKα, NiKα, CuKα, ZnKα, CoKα, AsKα, OsKα, IrLα, RuLα, RhLα, PtLα, PdLα, Pyrite, bornite, ZnS, synthetic GaAs, and pure elements were used as standards. The results were processed by the Cameca PAP program.

PGE were determined by neutron activation analysis after preconcentration from large samples, using the nickel fire-assay technique described by Hoffman et al. (1978), with minor modifications. The nickel sulphide button was dissolved in 12 M HCl. The residue was collected on filter paper and irradiated (together with standards) for 2 min, and then was allowed to decay for another 3 min, after which Rh and Pd were determined. Pt, Os, Ru, Ir, and Au were determined following the second irradiation. Samples and standards were irradiated for 16 hours and were allowed to decay for 9 days. Information on detection limits, precision and accuracy is given by Hoffman et al. (1978). Ni, Co, and Cu were determined by Atomic Absorption Spectroscopy (AAS); sulphur was obtained using a Leco CS-244, HF-100 analyzer.

PGE concentrations

The first study on the PGE concentrations in chromitites from several localities of the Pindos complex (Fig. 1) showed a wide variation, ranging between 8 and
150 ppb Os, 4–320 ppb Ir, 15–550 ppb Ru, 2–82 ppb Rh, 3–150 ppb Pt and 1.5–20 ppb Pd (ECONOMOU-ELIPOULOS & VACONDIOS 1990). The highest values were found at the area of Milia, while the PGE content in the majority of chromitites was very low. A typical feature of all of these chromitites, including the Milia area (total PGE = 1260 ppb) is an enrichment in Os, Ir, and Ru compared to Pt and Pd, resulting in chondrite-normalized PGE-patterns with a negative slope (Fig. 2).

Fig. 2. Average chondrite-normalized PGE+Au concentrations in chromitites from the Pindos ophiolite complex (after ECONOMOU-ELIPOULOS & VACONDIOS 1990).
These are similar to published data from other ophiolites (Page et al. 1982, 1984; Economou 1986, Konstantopoulos & Economou-Eliopoulos 1991).

In addition to the above chromitites, four representative samples, from the area of Korydallos, hosted also in dunites (which contain PGM), were analyzed for PGE, Au, Ni, Co, Cu and S. They are characterized by an enrichment in Pt and Pd and chondrite-normalized PGE-patterns with a positive slope (Table 2, Fig. 3) similar to those of chromitites from the uppermost part

Fig. 3. Chondrite-normalized PGE+Au concentrations in chromitites from Korydallos, Pindos (this study).
Table 1. Mineral assemblages in chromitites from the Pindos ophiolite complex.

<table>
<thead>
<tr>
<th>Sample</th>
<th>49A</th>
<th>49C</th>
<th>57B</th>
<th>N1A</th>
<th>165</th>
<th>17C</th>
<th>174</th>
<th>182</th>
<th>188</th>
<th>191</th>
<th>193</th>
<th>K3A</th>
<th>K3B</th>
<th>178</th>
<th>179</th>
<th>Koz</th>
<th>M2</th>
<th>D1A</th>
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</table>

Sample localities: 49A, 49C Dakos Mine (Kostaraki Hill); 57B, N1A Dramala; 165, 170, 174, 182, 188, 191, 193, K3A, K3B Korydallos (Gournes); 178, 179 Korydallos (Agios Taxiarchis); Koz Koziakas; M2 Milia; D1A Kambos Despoti.
of the mantle sequence and/or lower cumulate sequence of some ophiolite complexes (Prichard et al. 1986, Bacuta et al. 1992, Ohnenstetter et al. 1991, Bridges et al. 1994), and layered intrusions (Talkington & Watkinson 1986).

Mineralogy

A total of 18 samples of chromitites were systematically studied for PGM and base metal sulphides using reflected light microscopy and the electron microprobe. The mineral assemblages are listed in Table 1. In general all samples studied are extremely poor in sulphides. Primary minerals consist of PGM and pentlandite. More abundant are secondary minerals consisting of base metal alloys, heazlewoodite and millerite. All of these are found only in the serpentinized silicate matrix of chromite. The abundance of Ni-Fe alloys is pronounced evidence for reducing environment and very low sulphur concentration during serpentinization.

PGM

Laurite is the only PGM entirely enclosed by chromite. Its composition is Os-rich (Table 3). The crystals are euhedral or roundish and usually smaller than 10 μm in diameter (Fig. 4a).

Pt(Ni,Fe). Three grains of this mineral were found in two samples. It is located in cracks or along grain boundaries of chromite. The crystal size varies from 25 × 10 to 40 × 10 μm (Fig. 4b). In polished sections the mineral has a yellowish colour and is isotopic. The reflectance values (Table 4) differ insignificantly from those for ferronickelplatinum, PtFeNi, as reported by Rudashevsky et al. (1983). Results of microprobe analyses of the mineral correspond to (Pt0.9Fe0.1)(Ni0.35Fe0.65Cu0.10), or, ideally, Pt(Ni,Fe) or PtNiFe (Table 3). A phase of this composition is not known as a mineral, so far. It represents an intermediate composition between the synthetic phases, PtFe and PtNi (Hansen & Andersso 1958, Shunk 1969). Small grain size of the mineral has precluded X-ray study.

Sperdyrite exclusively occurs in the serpentinized matrix of chromite. The grain sizes do not exceed 15 μm in diameter (Fig. 4c). Small amounts of Rh and Ir were recorded in one of the analyses (Table 3).

Pentlandite

Pentlandite is located in three textural sites: A) euhedral-anhedral inclusions in chromite, B) inclusions in silicates enclosed by chromite, and C) small grains distributed in the serpentinized matrix. The modes A and B are thought to have formed early (during chromite crystallization). They are characterized by
higher Ni (40.8–46.8 wt %) and lower Co (0.16–0.34 wt %) contents than the mode C (Ni <38 wt %, Co 1.49–3.63 wt %) which is thought to be of post-magmatic formation. One of the mode C pentlandites exhibits extremely Co-rich composition (Table 5, 179-3) representing an intermediate member between (Ni,Fe)9S8 and Co9S8 (c.f. Kaneda et al. 1986). However, all three modes of pentlandite contain small amounts of Pt and Pd (Table 5).

Secondary Ni sulphides

Heazlewoodite and millerite are found in a few samples as minute grains distributed in the serpentinitized silicate matrix (Table 1). Traces of Pt and Pd were recorded in heazlewoodite (Table 6).

Base metal alloys

Awaruite occurs in most of the samples studied (Table 1). Textural features (relics of pentlandite) suggest that it was formed by alteration of pentlandite. Microprobe analyses gave Ni 73–76, Fe 23–25 wt % corresponding to Ni₅Fe

![Image of PtAs₂ crystal in chromite](image)

**Fig. 4.** Laurite (RuS₂) crystal in chromite (a), Pt(Ni,Fe)₁$_₂$ at the grain boundaries of chromite (b) and sperrylite (PtAs₂) in the serpentinitized silicate matrix (c).
Table 2. Platinum-group element concentrations in chromites from the area of Korydallos (Gournes) of the Pindos ophiolite complex.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample</th>
<th>ppm</th>
<th>ppb</th>
<th>Pt+Pd</th>
<th>Pd/Ir</th>
<th>Cr</th>
<th>Ref.</th>
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<td>K (G)</td>
<td>170</td>
<td>825</td>
<td>50</td>
<td>290</td>
<td>30</td>
<td>24</td>
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<td>K (G)</td>
<td>174</td>
<td>800</td>
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<td>30</td>
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<td>30</td>
<td>62</td>
<td>150.9</td>
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<td>K (G)</td>
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<td>1580</td>
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<td>190</td>
<td>50</td>
<td>62</td>
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<td>K (G)</td>
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<td>70</td>
<td>62</td>
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<td>N</td>
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<td>1350</td>
<td>35</td>
<td>110</td>
<td>70</td>
<td>62</td>
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<tr>
<td>M</td>
<td>M2</td>
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<td>750</td>
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<td>D</td>
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<td>67</td>
<td>290</td>
<td>60</td>
<td>62</td>
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</table>

Symbols: (1) = present study; (2) = Economou-Eliopoulos & Vakondios (1990); K (G) = Korydallos (Gournes); N = Dramala; M = Milia; D = Kampos Despoti.
Table 5. Microprobe analyses of pentlandite.

<table>
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<tr>
<th>Sample</th>
<th>182-3</th>
<th>K3B-1</th>
<th>165-1</th>
<th>188-1</th>
<th>188-3</th>
<th>188-4</th>
<th>188-5</th>
<th>188-7</th>
<th>179-3</th>
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<td>Ni</td>
<td>42.29</td>
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<td>40.82</td>
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<td>37.97</td>
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<td>Fe</td>
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<td>20.22</td>
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<td>26.97</td>
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<td>0.16</td>
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<td>33.74</td>
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<td>0.04</td>
<td>0.04</td>
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<td>97.52</td>
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<td>99.83</td>
<td>100.53</td>
<td>100.61</td>
<td>98.64</td>
<td>100.42</td>
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Formulae calculated on the basis of a total of 17 atoms:
182-3: (Ni$_{16.67}$Fe$_{3.11}$Co$_{0.05}$)$_{0.83}$(Si$_{8.13}$As$_{8.02}$)$_{0.17}$
K3B-1: (Ni$_{16.33}$Fe$_{3.89}$Co$_{0.03}$)$_{0.11}$(Si$_{8.17}$)
165-1: (Ni$_{16.33}$Fe$_{3.89}$Co$_{0.03}$)$_{0.11}$(Si$_{8.17}$)
188-1: (Ni$_{16.67}$Fe$_{3.11}$Co$_{0.05}$)$_{0.83}$(Si$_{8.13}$As$_{8.02}$)$_{0.17}$
188-3: (Ni$_{16.33}$Fe$_{3.89}$Co$_{0.03}$)$_{0.11}$(Si$_{8.17}$)
188-4: (Ni$_{16.67}$Fe$_{3.11}$Co$_{0.05}$)$_{0.83}$(Si$_{8.13}$As$_{8.02}$)$_{0.17}$
188-5: (Ni$_{16.67}$Fe$_{3.11}$Co$_{0.05}$)$_{0.83}$(Si$_{8.13}$As$_{8.02}$)$_{0.17}$
188-7: (Ni$_{16.67}$Fe$_{3.11}$Co$_{0.05}$)$_{0.83}$(Si$_{8.13}$As$_{8.02}$)$_{0.17}$
179-3: (Ni$_{16.67}$Fe$_{3.11}$Co$_{0.05}$)$_{0.83}$(Si$_{8.13}$As$_{8.02}$)$_{0.17}$

Table 6. Representative microprobe analyses of heazlewoodite (No. 1), millerite (No. 2) and awaruite (Nos. 3–7).

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<td>As</td>
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<td>Total</td>
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<td>99.73</td>
<td>98.30</td>
<td>99.77</td>
<td>98.77</td>
<td>99.23</td>
<td>98.56</td>
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</table>

plexes (BACUTA et al. 1990, KONSTANTOPOULOU & ECONOMOU-EIPOULOS 1991, OHENSTETER et al. 1991, ECONOMOU-EIPOULOS 1993, LORD et al. 1994, BRIDGES et al. 1994). Mineralogical textures and compositions of PGM and PGE-bearing sulphides provide evidence for either magmatic or hydrothermal concentration processes. The occurrence of laurite and Os–Ir–Ru alloys as inclusions in chromite grains, the lack of correlation between PGE and degree of serpentinization of host rocks in some ophiolite complexes, and Os
Platinum-group minerals from Pindos, Greece

isotopic data on PGM inclusions in chromite (Bacuta et al. 1990, Ohnenstetter et al. 1991, Tarkian et al. 1991, Hattori et al. 1992) suggest that the composition of parent magmas themselves derived by variable degree of partial melting and/or fractional crystallization is a main factor controlling the primary PGE distribution. On the other hand, the significant role of serpentinization by remobilization of PGE has been described by several authors (e.g. Orberger et al. 1987, Thalhammer & Stumpf 1988, Thalhammer et al. 1990, McElrudd & Stumpf 1990, Nilsson 1990, Leblanc & Fischer 1990, Tarkian et al. 1992).

The PGE mineralization in the area of Korydallos resembles Pt-and Pd-enriched chromites from the Bulqiza ophiolite complex in Albania, derived from the Pindos ocean, which is considered to reflect the PGE fractionation from a mineralizing system evolving from mantle to cumulates under different fO2 and fS2 conditions (Ohnenstetter et al. 1991). The platinum plus palladium content in the studied chromite samples reaches 5 ppm and Pt/Pd ratios range between 2 and 5. In contrast to many other chromite occurrences in the Pindos ophiolite complex, the chromites in the area of Korydallos are characterized by positive slopes of chondrite-normalized PGE-patterns and high (Pt+Pd)/(Os+Ir+Ru) and Pd/Ir ratios probably reflecting a relatively high degree of fractionation (Barnes et al. 1985). However, in general the chromites from Pindos are extremely poor in sulphides suggesting very low sulphur content in the silicate melt both during and after chromite formation. Thus a sulphide melt cannot account for the PGE concentration. Textural features and analytical results indicate PGM crystallization from the silicate melt. Lautite was formed first (prior or contemporaneously with chromite) followed by PtNi3Fe and sperrylite. The latter exclusively occurs in the serpentinized silicate matrix, where secondary minerals are more common. Pentlandites both of early (magmatic) and late (post-magmatic?) formation carry detectable amounts of Pt and Pd. Moreover, traces of Pt and Pd recorded in the secondary heazlewoodite and aawaruite suggest their remobilization and redistribution by decomposition of primary PGM and pentlandite during serpentinization. Furthermore, As, Sb and Te contents of the PGE-enriched chromitites from Korydallos are very low (2–3 ppm, 0.2–0.6 ppm and 0.02 ppm, respectively, unpubl. data), a feature that is considered to reflect a limited secondary alteration of primary processes (Lind et al. 1994). Thus, it seems likely that serpentinization is responsible for a local redistribution of only Pt and Pd.

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