Platinum-group minerals in metapyroxenite from Jasov, Meliatic Unit, Slovakia

Martin Radvanec & Pavel Uher

Abstract: The platinum-group minerals (PGM) occur in Triassic-Jurassic metapyroxenite from allochthonous serpentinite body near Jasov village, Meliatic Unit, Inner Western Carpathians, eastern Slovakia. The PGM assemblage originated during two genetic stages. The primary magmatic stage 1, formed under very low $P_O_2$; it comprises older generation of PGM: laurite ($RuS_3$), erlichmanite? ($OsS_3$), sperrylite ($PtAs_3$), iridium, and osmium. The younger generation of PGM formed during post-magmatic, hydrothermal-metamorphic stage 2, including irarsite [(Ir,Rh)AsS], hollingworthite [(Rh,Ir)AsS], possibly part of sperrylite ($PtAs_3$), temagamite ($Pd_HgTe_2$), vasilite-like mineral [$Pd_3(S,Tes)]$, and unnamed phases of [IrOsAs$_3$]$_2$(Pd,Ni)$_3$Sb$_2$ and Pd$_3$Ni$_3$Sb$_2$ (? stoichiometry. Minerals of the magmatic stage were derived from the deep mantle source under highly reductive conditions, and the primary rock was probably transported by a plume to shallower upper mantle depth. The hydrothermal-metamorphic stage originated by partial hydration and serpentinization of the metapyroxenite under the blueschists facies metamorphism. The Jasov metapyroxenite represents the first reported occurrence of PGM in the Western Carpathians.

Keywords: platinum-group minerals; awaruite; metapyroxenite; serpentinization; Western Carpathians; Meliatic Unit

1. INTRODUCTION

Platinum-group minerals (PGM) represent rare natural phases stable under very reductive and commonly high P-T conditions, which are characteristic for ultramafic mantle rocks. For example, magmatic PGM + Fe-Ni-Cu sulfide deposits were formed in sulfide saturated mafic or ultramafic magmas due to segregation of immiscible sulfide liquid (e.g., Norilsk area, Russia; Arndt et al., 2005, and references therein). However, PGM accumulations are presented also in layered intrusions and could be connected with silicate minerals, chromite or independent mineralization (e.g., Bushveld Complex, South Africa; Cawthorn et al., 2005). Moreover, the PGM in association with Fe-Ni-Cr alloys and Fe silicides occur in podiform chromitites (e.g., in the Luobusa ophiolites, Tibet, China (Bai et al., 2000, 2002, 2003; Shi et al., 2012).

However, textural relationships and composition of many occurrences indicate post-magmatic origin of PGM, associated with late metamorphic-hydrothermal overprint of primary magmatic ultramafic rocks, especially during their serpentinization (e.g., Prichard et al., 1994; Bai et al., 2000; Barkov & Fleet, 2004; Seabrook et al., 2004; Augé et al., 2005; Melcher et al., 2005; Economou-Eliopoulos, 2010; Fedortchouk et al., 2010).

In this study, we describe a unique assemblage of PGM and associated minerals in metapyroxenite from Jasov, Meliatic Unit, eastern Slovakia, the first occurrence of PGM in the Western Carpathians. The textural and compositional variations of this peculiar mineral association allow recognizing a successive evolution of PGM from the lower to upper mantle magmatic stage to post-magmatic, hydrothermal-metamorphic overprint.

2. GEOLOGICAL SETTING

Studied metapyroxenite represents the major part of tectonically brecciated and segmented serpentinite body (~200 to 500 m in size), ca. 1 km east from Jasov village in the south-eastern part of the Spišsko-Gemerské Rudohorie Mts., which belongs to the Meliatic Unit of the Inner Western Carpathians, eastern Slovakia (Fig. 1a,b). The geographic coordinates of the occurrence are following: N 48°41.0' and E 20°59.2'. The serpentinite forms allochthonous, plate-like body of slightly synclinal shape with average thickness of 25 to 75 m, striking to NE–SW and gently dipping (5 to 20°) to the S (Zlocha & Hovorka, 1971; Hovorka et al., 1985). Lower to Middle Triassic variegated marly shales and limestones form the tectonic mélange in the footwall of the serpentinite body, whereas the original overlying part has been denuded.

On the basic of relationships to analogous ultramafic rocks of the Meliata Unit, Triassic to Jurassic age is proposed for primary magmatic crystallization and later metamorphic overprint of the Jasov metapyroxenite. The Jasov serpentinite body is considered to be an isolated Alpine-nappe fragment of the Meliatic Unit, situated in allochthonous tectonic position on Paleozoic crystalline basement of the Gemeric Unit (Bajaník et al., 1984; Mello et al., 2000; Grecula et al., 2009; Németh & Radvanec, 2012) and represents a part of tectonic mélangé, considered to be exhumed from the subduction channel during Jurassic period. Prior the exhumation, various rock types of the mélangé were overprinted by high-pressure metamorphic event, including glaucohpae-bearing blueschists (Kozur & Mock, 1973, 1985; Faryad, 1997; Faryad et al., 2005; Grecula...
et al., 2009; Ivan & Méres, 2009; Radvanec & Putiš, 2011; Putiš et al., 2015, 2016). Moreover, the serpentinite body now forms a megaolistolite in Miocene (Pliocene) clastic sediments (gravels and sands) of the Poltár Formation (Grecula et al., 2009).

3. ANALYTICAL METHODS

The investigated metapyroxenite rocks were studied in polished thin sections. The platinum-group minerals were identified using a JEOL JSM-7001F field-emission scanning electron microprobe in electron dispersion mode (EDS) at the Kyoto University, Japan, using accelerating voltage of 7 kV. Following standards were used: FeS₂ (S), Fe₂O₃ (Fe), NiO (Ni), NiAs (As) HgTe (Hg and Te), metallic Co, Ru, Rh, Pd, Os, Ir and Pt (for Co and platinum-group elements). Unfortunately, size of studied PGM is usually only 0.2 to 2 μm, thus it is too small for correct analysing by the electron microprobe. Therefore, mixed PGM + host millerite or silicate compositions were commonly obtained. In such cases, after calculation from weight to atomic proportions, stoichiometric amount of host Ni + S (millerite) or Mg + Si (silicate minerals) were subtracted from the raw analyses and residual amounts of platinum-group elements, S, As, Sb, Te, Hg, Ni, and Co were recalculated to expected formulae (for example 3 atoms Pd + 1 atom Hg + 3 atoms Te in temagamite, Pd₃Hg₄Te₃) and weight amounts of elements based on 100 %. Such procedure was successful in the majority of cases and enabled us to reconstruct approximate, more or less real compositions of PGM.

Chemical analyses of associated silicate and oxide minerals were carried out in the State Geological Institute of Dionýz Štúr (Geological Survey) in Bratislava, using a Cameca SX-100 electron microprobe in wave-length dispersion mode (WDS). Accelerating voltage of 15 kV, beam current of 20 nA, beam diameter of 1 to 5 μm, natural and synthetic standards were used for measuring of silicate and oxide minerals.

4. RESULTS

4.1. Mineral composition of metapyroxenite

The investigated metapyroxenite is mainly composed of different, chemically zoned porphyroblasts of clinopyroxenes, up to 2 cm in size (Figs. 1b, 2a,c,d). The Al,Cr-rich diopside-1 (Wo₄₈₋₅₀En₄₆₋₄₈Fs₄₋₅Jd₀₉₋₁₀; ~ 7 wt.% Al₂O₃, ~ 1 wt.% Cr₂O₃, ~ 0.5 wt.% TiO₂) forms a core to intermediate zones whereas younger diopside-2 (Wo₄₃₋₄₉En₄₇₋₅₂Fs₃₋₅Jd₅₋₁₂, 4–7 wt.% Al₂O₃; 0.5–1.4 wt.% Cr₂O₃; 0.2–0.5 wt.% TiO₂) occurs in the inner rim of the porphyroblasts (Fig. 2a). The outer rim of diopside porphyroblasts (Di1 and Di2) is covered by diopside-3 (Wo₄₈₋₅₀En₄₈₋₅₁Fs₁₋₃Jd₀₋₂; 0–1.4 wt.% Al₂O₃, 0–0.5 wt.% Cr₂O₃) and the final and chemically pure diopside-4 forms a dot neoblasts in matrix and commonly fills cavities and cracks in the former porphyroblasts of Di1 and Di2 (Fig. 2a). The diopsides occupy ~ 70 vol.% of the metapyroxenite. Awaruite forms tiny inclusions (~ 4 to 10 µm in size) and always in diopside-2 (Fig. 2c–d); its composition ranges from Ni₂.7Fe to Ni₃.1Fe.

The groundmass consists mainly of chrysotile, Ni,Fe-rich serpentine mineral and chlorite (~ 25 vol.%). Millerite (NiS), siegenite (CoNi₂S₄) and Ti-bearing andradite are usually enclosed by the chrysotile and rarely were found in diopside-3 and 4. Other minerals include sporadic remnants of forsterite (Fo₉₉₋₉₁) in association with very rare occurrence of enstatite (W₀₄₋₅₀En₅₀₋₅₁; ~ 6 wt.% Al₂O₃; 0.7 wt.% Cr₂O₃; both of them ~ 2 vol.%), spinel-group minerals (Fig. 2b), ilmenite, grossular, andradite, anthophyllite, edenite, Cr-rich clinohlorite, hematite, perovskite, goethite, Cu-Ni-Fe sulfides, and titanite (~ 3 vol.% of metapyroxenite). The late calcite forms small fracture fillings.

4.2. Platinum-group minerals

The platinum-group minerals (PGM) commonly occur in millerite and chrysotile as very small anhedral to subhedral...
inclusions, usually only ~0.2 to 1 µm, and rarely up to 3 µm in size (Figs. 3–4). According to the EDS analyses made by the field-emission microprobe, following PGM were distinguished: (1) native elements and alloys of PGM: Os-bearing iron, osmium, iridium; and (2) S,As,Sb,Te,Hg-bearing PGM: laurite (RuS₂), erlichmanite (OsS₂), vasilite-like phase [Pd₂(S,Te)], sperrylite (PtAs₂), irarsite [(Ir,Rh)AsS], hollingworthite [(Rh,Ir)AsS], temagamite (Pd₃HgTe₃), and unnamed phases of (Ir,Os)As₃, (Pd,Ni)₃Sb, and Pd₆Ni₃Sb₂ stoichiometry. Representative compositions and calculated formulae of PGM are summarized in Tab. 1 (see also note in the Analytical methods chapter).

The native iron represents an alloy with 85 wt.% Fe and 15 wt.% Os and native iridium contains 10 wt.% Fe, 7 wt.% Co and 5 wt.% As, whereas native osmium and erlichmanite (?) don’t show any measurable admixtures, probably due to very small size of their inclusions (~1 µm). Laurite analyses reveal a relatively high content of iron (7 to 12 wt.%; 0.22 to 0.33 apfu Fe), 12 to 16 wt.% Os (0.10–0.14 apfu) and locally ~4 wt.% Ir and ~6 wt.% As (Tab. 1). The vasilite-like mineral shows 74 wt.% Pd, 19 wt.% Te and 7 wt.% S and Pd₃S₀.₁₅Te₀.₅₂ composition, close to Pd₃(S,Te) formula. This composition indicates a rough similarity to vasilite, a mineral with (Pd,Cu)₁₆(S,Te)₁₆ or ~ (Pd,Cu)₁₆(S,Te) stoichiometry and 77 wt.% Pd, 8 to 10 wt.% Cu, 11 wt.% S and 2.5 to 4 wt.% Te (Atanasov, 1990), however, our composition does not contain Cu and reveals lower metal/(S+Te) ratio (1.85) in comparison with vasilite (2.29). Such divergences are probably a result of our measurement inaccuracy or there are two different minerals. Sperrylite analyse shows end-member composition without measured admixtures. Irregular inclusions of irarsite to hollingworthite solid-solution series (IrAsS – RhAsS; Fig. 4a) reveal 26 to 37 wt.% Ir, 15 to 27 wt.% Rh, ~2 wt.% Co, 26 to 30 wt.% As and ~3 to 6 wt.% Sb; the atomic Rh/(Rh+Ir) ratio varies between 0.44 and 0.66 from irarsite to hollingworthite (Tab. 1). Temagamite displays end-member composition very close to Pd₃HgTe₃ formula. Three PGM show compositions of unknown (possibly new) mineral species close to (Ir,Os)As₃, (Pd,Ni)₃Sb, and Pd₆Ni₃Sb₂ formulae (Tab. 1). The (Pd,Ni)₃Sb or Pd₂.₆₇Ni₀.₃₃Sb mineral shows a stoichiometry close to mertieite-II, Pd₃Sb, or Pd₂.₆₇Sb (Cabri et al., 1975), if we subtract Ni content (~4 wt.%) as a possible impurity from host millerite.
5. DISCUSSION AND CONCLUSION

The Jasov metapyroxenite represents the first reported occurrence of PGM in the Western Carpathians. Generally, origin of PGM is a subject of controversy: they are considered as products of high-temperature primary magmatic crystallization but also post-magmatic metamorphic or hydrothermal, relatively low-temperature overprint of the host-rocks, mainly during serpentinization or oxidation. The primary magmatic PGM usually occur as microscopic inclusions in chrome spinels or chromitite layers (Prichard et al., 1994; Melcher et al., 1997; Garuti et al., 1999; Ahmed & Arai 2003; Zaccarini et al., 2008; Fedortchouk et al., 2010). On the other hand, secondary PGM originated in many places as a result of hydrothermal-metamorphic and relatively low-temperature overprint, especially during serpentinization or oxidation of the host ultramafic rocks; such secondary PGM commonly associate with serpentine-group minerals, chlorite and other late silicate or sulphide minerals (e.g., Prichard et al., 1994; Melcher et al., 1997; Bai et al., 2000; Barkov & Fleet 2004; Seabrook et al., 2004; Zaccarini et al., 2008).

Origin of PGM from the investigated Jasov metapyroxenite is also not obvious. Based on the above mentioned references and textural relationships, a part of the minerals, especially Os-rich iron, laurite (RuS₂) and erlichmanite? (OsS₂) and possibly also sperrylite (PtAs₂), iridium and osmium, could represent remnants of the primary magmatic stage at very low fO₂ and high temperature. These PGM minerals of the magmatic stage were firstly derived from the deep mantle source under highly reductive conditions, and the primary rock was probably transported by a plume to shallower upper mantle depth. In the upper mantle, the deep mantle magma was equilibrated at P-T conditions where the spinel is the stable phase (Fig. 2b). On the contrary, PGM with As, Sb, Te, and Hg, including vasilite-like mineral [Pd₃(S,Te)], irarsite [(Ir,Rh)AsS], hollingworthite [(Rh,Ir)AsS], possibly part of sperrylite (PtAs₂), temagamite (Pd₃HgTe₃), and unnamed phases of (Ir,Os)As₃, (Pd,Ni)₃Sb, and Pd₆Ni₃Sb₂ stoichiometry indicate their secondary origin during post-magmatic, hydrothermal-metamorphic stage more likely. The source of Hg, As, Sb, and Te in the younger generation of PGM is unclear; the presence

Fig. 3. Back-scattered electron images of PGM and associated minerals in the Jasov metapyroxenite: a) inclusion of osmium-rich native iron (FeOs) in millerite (NiS); b) inclusions of iridium (Ir) in millerite (NiS); c) sperrylite (Spr) and native arsenic (As) in millerite (NiS), all minerals in chrysotile (Ctl); d) sperrylite (Spr) with millerite (NiS), both in chrysotile (Ctl).
of such highly mobile elements probably indicates their external origin in late hydrothermal-metamorphic fluids in the stability field of blueschists and or greenschist-facies for the final metamorphism.

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References


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