

# Hydrothermal remobilization platinum group elements and their secondary minerals in chromitite deposits of the Eastern Sayan ophiolites (Russia)

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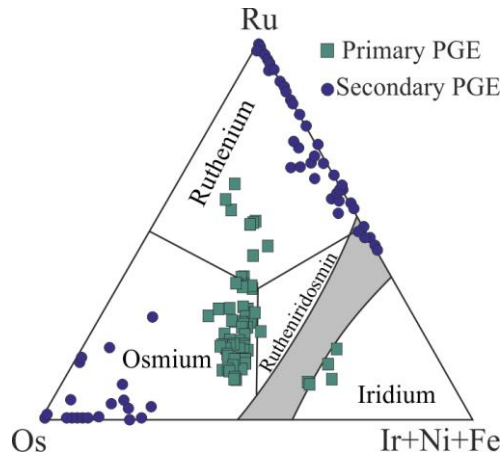
**Abstract.** Serpentinization is an important post-magmatic process in spreading and subducted zones. This process is the cause of the remobilization and redistribution of highly mobile elements, platinum group elements (PGE) and base metals. Secondary platinum group minerals (PGMs) formed because of PGE remobilization under the action of mantle and crustal fluid on the rocks. The formation of the secondary PGMs can occur in several stages. Under the effect on the chromitites of reduced mantle fluids, native PGE alloys were formed during early serpentinization. Under dehydrating subducted slab fluid phase was caused in serpentinization mantle peridotites and have been dissolved magmatic high-temperature platinum group minerals. During the obduction of ophiolites, an inversion from reducing to oxidizing condition took place with the formation of nickel arsenides and As, Sb – bearing PGMs.

## 1 Introduction

Ophiolites of Eastern Sayan have been formed at supra-subduction conditions of ensimatic island arcs. However, they have a heterogeneous composition corresponds to spreading and subduction settings of different geologic age [1-3]. Ultramafic sequences (massifs) of ophiolite bodies consist of highly deformed partially serpentinised peridotites with podiform chromitite bodies cut by few- centimetre thick, veins of pyroxenites and altered rocks of cumulate sequence. Serpentinization is an important post-magmatic process at the temperature lower than 650-700 °C [5] in spreading and subducted zones, which is the cause of the remobilization and redistribution of highly mobile elements, PGE and base metals. Platinum metal mineralization in ophiolitic complexes is localized mainly in podiform chromitites. In chromitites there are primary and secondary platinum group minerals (PGM), in the Os-Ir-Ru system, formed at various stages of formation and transformation of rocks of the ophiolite complex from the mantle stage to the metamorphogenic-hydrothermal one [3, 6].

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**Fig. 1.** Classification diagram for (Os,Ir,Ru) alloys. Field according to [4].

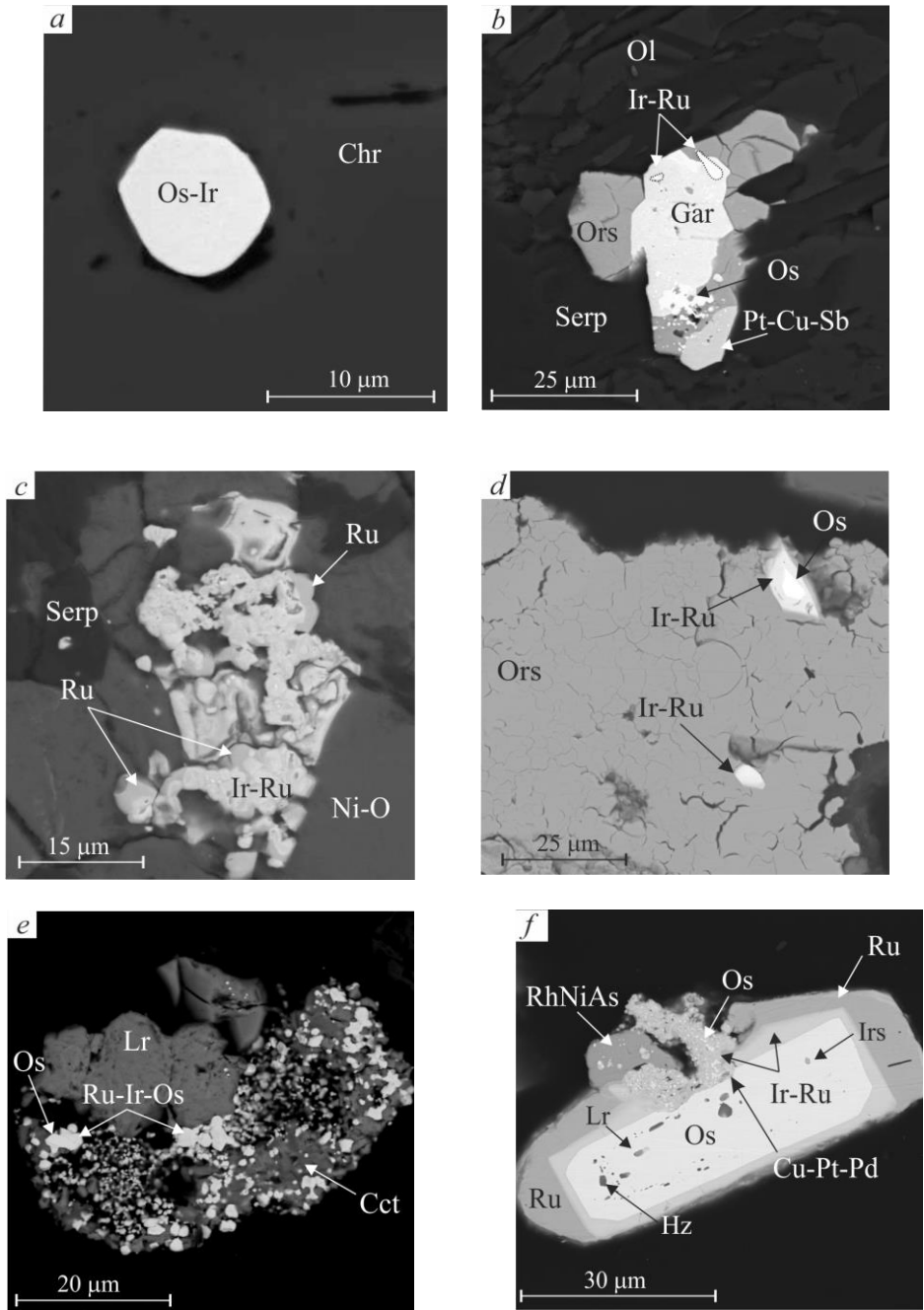
## 2 Methodology

The chemical composition of the platinum group minerals minerals and microstructural features were analyzed by Tescan-MIRA 3 LMU electron scanning microscope with an INCA Energy EDS for quantitative analysis at Analytical Center in the Laboratory of X-Ray Microanalysis, Sobolev Institute of Geology and Mineralogy.

## 3 Platinum group minerals

The primary PGM within the mantle are solid solutions of the Os-Ir-Ru alloys (Fig. 1), formed at high temperatures above 2600 °C, according to phase diagrams, up to 1200 °C in association with RuS<sub>2</sub>, according to experimental data [7, 8]. Primary PGMs are usually enclosed in the chrome-spinel crystals (Fig. 2a), or in their aggregates [6].

Secondary PGMs within low-temperature base metal sulfides are enclosed by serpentine or chlorite. The formation of secondary PGM occurs when the primary magmatic platinum minerals dissolve under the influence of the fluid phase and/or hydrothermal solutions. Secondary PGMs are native Os<sup>0</sup>, Ru<sup>0</sup>, alloys of Ir-Ru (Fig. 1), garutiite (Ir, Ni, Fe), zaccarinite (RhNiAs), newly-formed laurite RuS<sub>2</sub>. In addition there are PGE – bearing minerals such as nickel cuproiridsite ([Cu, Ni]Ir<sub>2</sub>)S<sub>4</sub> and unidentified grains containing PGE with base chalcophile elements, for example (Cu, Rh, Sb). These phases are usually located in the rime of polyphase aggregates or as inclusion in pores. The phase composition and microstructural features of remobilized PGMs are very diverse (Fig. 2). Native osmium, ruthenium and (Ir-Ru) alloys are present as tiny (5-15 μm) emulsion-shape micro-inclusion, disseminated in the awaruite and sulfides and sulfoarsenides of nickel (Fig. 2b). In the some cases, awaruite contains Ir up to 8 wt. % and (Pt, Ir)-containing awaruite. Another common occurrence of secondary PGMs are polyphase aggregates with sulfides, sulfoarsenides, arsenides of nickel in serpentine-chlorite matrix (Fig. 2 c, d, e). Often secondary PGMs consist of elevated impurity contents, relative to primary PGMs, of Ni, Fe, Cu, Co, As, Sb. New-formed laurite has homogeneous microtexture and «ideal» stoichiometric composition (Ru = 61.2 wt. %, S = 38,2 wt. %). It forms individual grain in chlorite and serpentine with irarsite, nickel and copper sulfides, and in the edging around primary (Os,Ru)S<sub>2</sub>. Garutiite often occurs growing with orselite (Fig. 2d).



**Fig. 2.** (a) Inclusion of primary PGM in chrome-spinel; secondary PGMs; (b) Polyphase aggregate Gar, Ors, (Ir-Ru); (c) Pore aggregate Ru, (Ir-Ru) in serpentine and (Ni-O); (d) Zonal micro-inclusion (Os, Ir, Ru) composition in the orselite with colloidal microtexture; (e) Polyphase aggregate; (f) Micro-inclusions of  $Ni_3S_2$  on the growth zones. Legend: Chr – chrome-spinel, Ol – olivine, Serp – serpentine, Ors – orselite, Hz – hzlewoodite, Cct – chalcocite  $Cu_2S$ , Lr – laurite, Gar – garutiite, Os – native osmium, Ru – native ruthenium.

In chromitites that have an abnormally high concentration of PGE (8 ppm) and high concentrations of Ni, Cu, Zn in the rock, relatively large, zoned PGE crystals (up to 50  $\mu\text{m}$ ) occur in close association with micro-inclusions of  $\text{Ni}_3\text{S}_2$  on the growth zones (Fig. 2f). Polyphase aggregate of secondary PGM with base metal sulfides often have an emulsion-shaped, colloidal, and sponger texture.

## 4 Discussion

Subduction processes are the major driving force of hydrothermal remobilization of PGE in ophiolite complexes of Eastern Sayan. This is indicated by the geochemical features of the rocks of the ophiolite complex - mantle peridotites, podiform chromitites and volcanic rocks [2, 3], although there are also subordinate indicators of a spreading geodynamic setting.

Several sources are assumed for the fluid phase: a first stage of S- and As-bearing) residual magmatic fluids; a second stage fluid formed during dehydration of the subducting slab containing anions/or anion complexes such as S, As, and mantle fluid flowing through tectonically weakened fault zones; and a third stage of metamorphic fluid within crustal environments [3, 6].

The secondary PGMs are characterized by the absence of miscibility between Os and Ir, which indicates low formation temperatures. The combined presence of PGMs with Ni sulfides and the presence of such impurities as Ni, Fe, Cu, Co, As, Sb in the PGM reflect mobility of PGEs during the hydrothermal process. The processes of redistribution and concentration of Os, Ir, Ru and formation of secondary (Os, Ir, Ru) alloys occur at sufficiently low temperatures, corresponding to the temperature of formation of nickel sulfides, and serpentinization process. Present research in the PGE remobilization field testifies to the mobility of refractory PGE in the course of metasomatic (serpentinization) processes, fluid-rock interaction, with the participation of reduced fluids ( $\text{H}_2$ ,  $\text{CH}_4$ ) of mantle origin. The results of these processes are observed in altered chromitites [9, 10]. Remobilization of IPGE by fluids was proposed based on theoretical calculations. The effect of fluid on Pt-containing rocks (chromitites) under certain conditions leads to the formation of bisulfide complexes such as  $\text{Os}(\text{HS}_6)^{2-}$ ,  $\text{Ru}(\text{HS}_6)^{3-}$ ,  $\text{Ir}(\text{HS}_6)^{3-}$  [11, 12] and their remobilization occurs with the formation of late 'secondary' PGM compounds. By serpentinization and chloritization at a temperature of about 300  $^\circ\text{C}$ , fluid penetrated through the permeable zones into the PGE sulfides, which led to desulfurization of sulfides, deviation from stoichiometry, the appearance of microdefects in the crystal lattice, and the appearance of nanopores on the surface of the grain [13, 14, 15]. According to the experimental data, congruent decomposition of  $\text{RuS}_2$  to  $\text{Ru}^0$  occurs at  $T = 300^\circ\text{C}$ ,  $f\text{S}_2 = (-20)$ ,  $P = 0.5$  kbar [16]. During of these processes, native  $\text{Os}^0$  and  $\text{Ru}^0$  formed [17, 18]. Fluids or/and hydrothermal solutions can affect on the boundaries or cracks of high-temperature PGM grains and they will change their composition according to their primary solubility [19, 20]. During the alteration (desulphurisation or after) of the primary PGE phases, with high activity of metallic Fe, Ni, [16] this metals begins to enter platinum group phases with the formation of garutiite, zaccarinite. The close association of secondary PGM with awaruite, which is formed in reducing conditions at  $\log f\text{S}_2$  is from (-17) to -20,  $T = 400$  to 500  $^\circ\text{C}$  [16, 21] also indicates the low-temperature origin of secondary PGMs. Minute emulsion-shape inclusion  $\text{Os}^0$ ,  $\text{Ru}^0$  in garutiite indicates the PGE transfer in the fluid phase. When Os is deposited in the solid phase at low temperatures, it cannot enter the structure of the newly formed phase with Ir, and even more so with Ni, Fe, and as a result the phase is formed -  $(\text{Ni}, \text{Ir}, \text{Fe}) + \text{Os}^0$ . During the obduction of ophiolites, an inversion from reducing to oxidizing conditions occurred that resulted in the formation of nickel arsenides and As, Sb - bearing PGMs [3, 6].

## 5 Conclusion

Subduction processes are the major driving force of hydrothermal remobilization of PGE in the Eastern Sayan ophiolite complexes. The formation of the secondary PGMs can occur in several stage and mechanism. The variable composition and microstructural features of the remobilized PGMs are due to the influence of fluids of different composition, multistage tectonic processes, and the overprint of metamorphic processes in crustal environments.

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