

Generation of Polyphase Assemblage of the Platinum-Group Minerals in the Inagli Dunite-Shonkinite Massif of the Aldan Shield of the Siberian Platform

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Abstract

The Inagli massif is a concentric-zonal ring massif consisting of a dunite core bordered by a sequential series of peridotites, pyroxenites and shonkinites. In dunites, there are densely disseminated accumulations of chromspinelides, as well as schlieren and veined particles of massive chromitites, to which polyphase growths of platinum-group minerals (PGM) are confined. The Inagli intrusive, like the well-known Konder massif, belongs to an independent "Aldan" type of platinum-bearing deposits. The Aldan type of ring intrusions is a platform analogue of the "Ural-Alaskan" zonal dunite-gabbro massifs of orogenic regions. In placers, dunites and chromitites of the Inagli massif, PGM are mainly represented by isoferroplatinum (Pt3Fe) with an admixture of iridium up to 8 wt %. In isoferroplatinum, symplektitic iridium particles and small inclusions of osmium, laurite, ehrlichmanite, malanite, as well as other sulfides and arsenides of platinum-group elements (PGE) are often observed. The bulk composition of such polymineral aggregates can be calculated based on the volume ratios and chemical composition of *individual phases. The results obtained in this way show that the compositions of the initial polycomponent solid solutions vary from Pt-Ir-Fe to Ir-Os-Ru-Rh-Pt-Pd-Fe alloys. Polycomponent homogeneous solid solutions, which composition gradually changes from Ru-Rh-Ir-Os minerals to Fe-Pt alloys, are known in the Witwatersrand placers. A similar series of solid solutions of PGE is identified in the placers of the Guli massif on the Siberian platform. Unlike the placers of the Witwatersrand and Guli massif, where PGM are mainly represented by Os-Ir alloys, Inagli minerals have mainly a Pt-Ir-Fe composition with a low proportion of Os. The structures of most natural polyphase PGM aggregates are similar to those of artificial alloys, therefore, the former are also products of crystallization of multicomponent metal melts and their subsequent solid-phase transformations. The limits of solubility between PGE differ significantly, therefore, depending on the initial composition of metal alloys, both polycomponent solid solutions and polymineral aggregates can be formed. Based on the analysis of combined double and triple diagrams of PGE systems, the author considers possible ways of evolution of phase transformations of alloys of different composition.*

Keywords: polyphase assemblage, platinum-group minerals, inagli dunite-shonkinite massif, aldan shield, siberian platform

Introduction

The Inagli massif is located in the northern part of the Aldan shield, and like the well-known Konder intrusive, it belongs to the concentric-zonal ring massifs. These platinum-bearing massifs have been distinguished as an independent platform Aldan type of platinum deposits, which differ from the orogenic platinum-bearing zonal ultramafic massifs by their geological position [1]. In 1951, a platinum placer was discovered on the Inagli massif, which was developed by the Inagli prospector artel from 1992 to 2004. In 1958, platinum grains up to 0.1 mm in size in growth with olivine and chromite were found in ore samples from dunites [2, 3]. Later, platinum minerals from this placer were studied by many researchers [4-8 etc]. The author studied PGMs and associated minerals from placers and chromite-containing dunites of the Inagli massif [9, 10], and further proposed a hypothesis regarding the early magmatic concentration of PGE as a result of separation from the silicate melt of a chromium-enriched ore liquid that can concentrate a significant amount of PGE [11]. Resulted from such immiscibility between ore liquid and silicate magma, polyphase associations of PGM are formed in close coalescence with chromite and other minerals. This paper focuses on the mineralogical, geochemical and structural features of polymineral growths and explains their crystallization mechanism.

Paragenesis of PGM of the Inagli massif

In placers and in dunites with chromite mineralization, PGM is represented primarily by isoferroplatinum 'Figure 1'. The composition of minerals was determined using a Camebax-Micro microprobe analyzer, and their microstructural relationships were studied using a scanning microscope JSM-6480LV JEOL. X-ray studies on determining the structure and parameters of the elementary lattices of minerals were carried out at the URS-0.3 facility at DPMGI SB RAS. According to microprobe analysis, the iron content in isoferroplatinum varies mostly in the range of 7-11 wt. % (20-30 at. %) at a maximum of 25 at. %. X-ray studies reveal that Inagli iron-platinum alloys have an ordered primitive cubic structure, i.e. they belong to isoferroplatinum Pt3Fe. Isoferroplatinum is characterized by a high content of iridium, which varies in the range of 1-4 %, less often up to 8-12 % with an average content of 2.9 wt. %. The matrix of isoferroplatinum grains with a high Ir content comprises symplectic or emulsion intergrowths of iridium. Occasionally, in some grains, the iridium phase predominates over isoferroplatinum, and such aggregates consist of iridium with small inclusions of isoferroplatinum. Monomineralic iridium grains are rarely observed. Osmium inclusions are observed in individual grains of isoferroplatinum, which, in contrast to iridium, have thinly bedded or small tabular forms. Less

commonly observed are three-phase grains consisting of intergrowths of tabular osmium lamellae cemented by an iridiumisoferroplatinum aggregate 'Figure 1, D'. In contrast to iridium, osmium was never detected in the form of single grains in the Inagli placer. The compositions of the most common PGM of the Inagli placer are shown in 'Table 1'.

Fig. 1. Chromitite veinlets (black) in dunites (A) of the Inagli massif; isoferroplatinum nuggets (B) with abundant chromite dissemination from the Inagli placer and backscatter electron images (C-F) intergrowths of PGM and chromite: Pt3Fe – isoferroplatinum; Chr – chromite; Ir – iridium; Os – osmium; Mla – malanite (Pt, Ir, Rh) ₂CuS₄; OsS₂ – erlichmanite; IrAsS – irarsite.

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Tab. 1. Representative analyses of PGM from the Inagli plaser, wt. %.

Note: $* - (001m)$ is grain matrix analysis, and $(001i)$ - analysis of inclusion in this grain.

In the Inagli placer, rare PGMs include tetraferroplatinum, tulameenite and hongshiite, and single grains of sperrylite, сooperite and mertieite are also occasionally observed. Sperrylite typically composes cuboctahedral and octahedral crystals, in which minor admixtures of Rh (up to 0.28%), Os (up to 0.22%) and S (up to 1.26%) are continuously recorded. In sperrilite, hongshiite, irarsite, laurite, covellite, chalcopyrite and pyrrhotite are identified as inclusions. In addition to the above minerals, small phases containing As, Bi, Sb, Te, Sn, Pd, Au were found in the isoferroplatinum of the Inagli placer, which are difficult to diagnose precisely. The compositions of the main sulfide, arsenide and sulfoarsenide minerals of PGE, often associated with PGM, are given in 'Table 2'.

In growth with PGMs and in the inclusion forms, chromspinelides $(44-62\% \text{ Cr}_2\text{O}_3)$, chromium-containing diopside (up to 6%) Cr2O3), olivine (Fa2-5), serpentine, phlogopite, Ni-containing vermiculite (up to 5% NiO), potassium feldspar, pectolite, apatite etc. Chromian spinel are the most common accessory minerals of PGM in the Inagli placer and are frequently found as inclusions or growths in the grains of isoferroplatinum. Practically all isoferroplatin nuggets larger than 5 mm in size are chromian spinel isoferroplatinum aggregates 'Figure 1 B, C'. Chromian spinel in dunites of the Inagli massif occur in the form of accessory minerals represented by octahedral crystals or rounded grains. The amount of minerals usually does not exceed 1 % of the rock volume with their sizes varying mainly in the range of 0.1 - 1 mm. Occasionally, in local areas there are densely disseminated accumulations (50-90 volume%) of chromian spinel, which form irregularly isometric segregation of up to 4-5 cm in size or, less

often, several tens of centimeters. In such areas, 2-3 cm thick veins of massive chromitites occur, which often have unusually curved shapes 'Figure 1 A'.

In accessory chromian spinel of dunites, the content of Cr₂O₃ decreases from 58 to 35 wt. %, while the triple $AI - Ct$ (Fe3++2Ti) diagram 'Figure 2' shows a typical chromite-magnetite crystallization trend for igneous rocks. Minerals from segregated and vein bodies of chromitites contain 48-58% Cr₂O₃, whereas those in chromian spinel coalescing with isoferroplatinum have Cr2O3 concentrations varying in the range of 44-62%. In comparison with accessory chromian spinel, they are more magnesian, which is clearly evident on the $Fe^{2+}/(Mg+Fe^{2+})$ – Cr binary system. As accessory chromespinelides from dunites reach primarily the upper field of ferruginous spinelides above the dividing line of $Fe^{2+}/(Mg+Fe^{2+}) = 0.5$, chromian spinel coalescing with isoferroplatinum, as well as chromitites, gravitate to the lower magnesian part. The complete overlap of the fields of chromian spinel from schlieren formations and PGM placers indicates that chromitite segregations in dunites are one of the primary sources of platinum metals in the Inagli placer.

Fig. 2. The Al-Cr-Fe⁺³-Mg/(Mg + Fe⁺²) diagram of spinelides from the Inagli massif. 1, chromite intergrown with isoferroplatinum from the placer; 2, schlieren-veinlets chromitites in dunite; 3, the field of accessory chromian spinel (n=101 analyses) from dunite.

Olivine composition in dunites of the Inagli massif varies from Fo⁹⁵ to Fo⁸⁶ and correlates well with the magnesia value of the host dunites. Further, in peridotites, pyroxenites and shonkinites, olivine varies from Fo₈₂ to Fo₇₀ and also directly correlates with a decrease in the MgO content in rocks [12]. Olivines from massive chromitite ores or inclusions of large chromite crystals from dunites are characterized by a magnesian composition of Fo92-95. Forsterites that are in close coalescence with isoferroplatinum or in the form of inclusions, are characterized by even higher magnesia value of Fo94-96. All this once again confirms the close genetic connection of the platinum-chromite mineralization of the Inagli massif with the early magmatic crystallization history of the dunites formation [13].

Due to the similarity of physicochemical properties, most PGE form solid solutions with each other that have a wide range of solubility. However, only Os and Ru, as well as Pt and Pd, can produce a continuous series of solid solutions, whereas other PGE pairs that form high-temperature unlimited solid solutions, for example, Pt-Ir, Pt-Rh and Ir-Rh, decompose into independent phases with limited solubility when the temperature decreases. Most pairs of Os-Ir, Ru-Ir, Ru-Pt, Os-Pt, Ru-Rh, Ru-Pd and Pd-Os interact with each other peritectically with different solubility ranges. Due to these differences, PGE usually form binary, rarely triple solid solutions represented by PGM. These include Pt-Fe alloys and intermediate intermetallic compounds [14], minerals of the Os-Ru-Ir system [15], as well as hexagonal Fe compounds with Ru, Os and Ir [16].

Besides these widespread PGM, however, polycomponent solid solutions of more than three PGE and Fe are found occasionally, in which the thinnest lamellar decay products are detected. These alloys were first discovered and described in the Witwatersrand placers [17, 18], then similar solid solutions were found in the placers of the Guli massif [19]. In the placers of the Inagli massif, in addition to these widespread PGM, multicomponent alloys consisting of three or more comparable amounts of metals are also found occasionally 'Table 3'. They occupy a large area in the middle part of the diagram and, therefore, present problems regarding their classification. Here the author considers the compositions of PGM that are present in close growths on two combined triple diagrams: (Pt+Pd+Rh+Fe+Ni+Cu)–(Os+Ru)–Ir and (Pt+Pd)–(Os+Ir+Ru+Rh)–(Fe+Ni+Cu) 'Figure 3'. In the first (upper right) diagram, PGM components are divided into three groups: Os-Ru – high-temperature hexagonal alloys, Ir – hightemperature cubic metal and (Pt, Pd, Rh, Fe) - mainly Pt alloys. The lower left diagram is plotted in (Pt+Pd)–(Os+Ru+Ir+Rh)– (Fe+Ni+Cu) coordinates to demonstrate the function of iron in PGM formation.

Fig. 3. Composition of PGM: 1 – Inagli placer: а – isoferroplatinum, b – polycomponent Ir-Os-Pt-Ru-Rh-Fe alloys, с – osmium and ruthenium; 2 – placer of the Guli massif [19]: а-с – same from 1; 3 – paragenetic assemblages of PGM from chromitites in zonal massifs of the Middle Urals [20]; 4 – chromitites of the Chirynai massif, Koryak Highland, Russia [21]; 5 – Witwatersrand placers [17, 18]. Dotted lines are the borders of Pt, Pt-Fe, Os-Ru and Ir mineral fields.

In multicomponent solid solutions of metals, in which the content of admixtures exceeds the limits of their solubility, as a rule, protophases and exsolution products occur, represented by an excess component. The structures of most natural polyphase PGM aggregates are similar to those of artificial alloys, therefore, the former are also products of crystallization of multicomponent metal melts. A large set of minerals, wide variations in the content of admixture elements in them and the presence of various inclusions of protocrystals and decomposition products allow us to establish the mechanisms of formation of paragenetic associations of PGM and trace the pathways of their evolution.

Triple diagrams illustrate the evolution of phase transformations of complex alloys most prominently. Regrettably, currently triple diagrams of phase equilibria are constructed only for an extremely limited range of systems involving PGE. Therefore, the author applied the method of graphical interpolation of data on binary systems of platinum metals to construct triple diagrams Ir-Os-Ir with expanded binary state systems 'Figure 4'. The binary state diagrams are adopted from the reference literature on metal systems (e.g. Diagrams Handbook, Laykishev N ed., Moscow. 2000). On the triple diagrams, liquidus isotherms, peritectic lines, and solvus isotherms are schematically shown as thin dashed, dash-dotted, and dotted lines, respectively. The Pt solubility contours in Ir and Os are given after [22].

Fig. 4. Ternary Ir-(Os+Ru)-(Pt+Rh+Fe+…) plot of compositions of PGM modified after [11]: 1-3 – Inagli: single grains of polycomponent alloys (1), co-existing two (2) and three (3) phases; $4 -$ Guli [5]; $5 -$ Urals [6]; $6 -$ Chirynai massif [7]; $7 -$ Witwatersrand [8, 9]. Liquidus isotherms, peritectic lines, and solvus isotherms are schematically shown as thin dashed, dashed, and dotted lines, respectively. The Pt solubility contours in Ir and Os are given after [12].

The diagrams given by the author can only be applied to characterize the fundamental course of phase transformations in platinum-metal systems, without absolutization of temperature values that are incomparably higher in dry artificial systems compared to the temperatures of the development of natural ore-magmatic processes. The presence of admixtures of Fe, Cu and other elements slightly reduce the melting temperatures of platinum metals. A significant decrease in the temperature of PGE crystallization can result in the occurrence of low-melting and volatile elements, such as Sb, As, S, etc. Based on the high content of sulfide and arsenide minerals in the growths with PGM, the content of low-melting elements in primary polycomponent metallic liquids was rather high and probably reached several percent. For example, in the Pt-S system platinum and cuperite crystallization occurs at S content of 7.5 wt. % and T=1240°C, while in the Pt-As system the eutectic crystallization of platinum and sperrylite completes at As content of approximately 13 wt. % and $T=600^{\circ}C$ [23].

Pt-Ir-Os-Ru-Rh-Fe solid solutions are preserved as high-temperature metastable phases with rapid consolidation of host bodies, while long-term formation of the massif leads to the exsolution of such alloys into simple components with normally oriented lamellar (widmanstatten) structure 'Figure' 1 E' characteristic of solid-phase transformations. This is due to the high crystallization temperatures of PGE, as long-term natural annealing is required for the solid-phase exsolution of polycomponent alloys, which can be fulfilled during the crystallization of large zonal and differentiated massifs.

Conclusion

Thus, the polycomponent solid solutions of PGE found in placer and bedrock deposits of different areas are primary hightemperature protophases that represent PGE separations from deep mafic magmas. The structures of most natural polyphase PGM aggregates are similar to those of artificial alloys, therefore, the former are also products of crystallization of multicomponent metal melts and their subsequent solid-phase transformations. Despite the different formation accessories and geodynamic conditions of the formation of the initial platinum-bearing magmas, they are all characterized by a complex composition, including all PGEs of different proportions. In general, the final total composition of PGM varies from high-temperature Os-Ru-Ir alloys in ophiolite complexes through Ir-Pt-Fe associations in zonal dunite-gabbroid massifs of the Uralian-Alaskan and Aldanian types to Pt-Pd-Cu-Ni-sulfide ores in mafic differentiated intrusive.

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