

# Phase Transformations and Genesis of Platinum-Group Minerals in Various Types of Platinum-Bearing Deposits

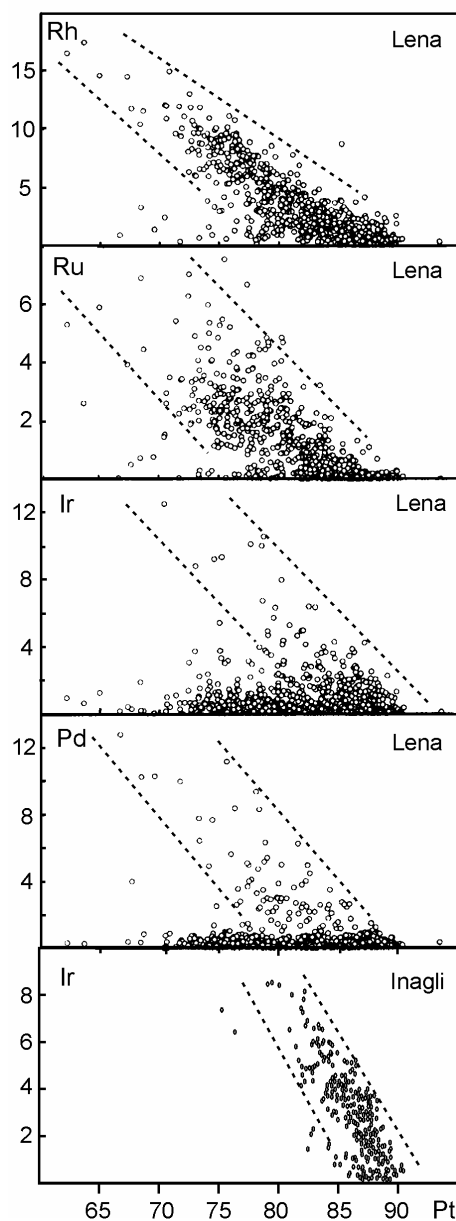
A. V. Okrugin

Institute of Diamond and Precious Metals Geology, SB RAS, Yakutsk, Russia

e-mail: a.v.okrugin@diamond.ysn.ru

Platinum-group element (PGE) mineralization in magmatogene deposits is formed in three ways. These are (1) fractional separation of PGE during magma crystallization; (2) PGE concentration in the oxide-ore phase forming segregations; (3) PGE extraction from magma into immiscible sulfide liquids. PGE concentration in mafic-ultramafic igneous rocks varies substantially from one to several tens of ppb and only rarely do Pt and Pd concentrations reach hundreds of ppb or more. Numerous experiments show that PGE solubility in silicate melts is exceptionally low. This is at the ppb level for Pt, Rh, Ir, Ru and Os, and at the ppm level for Pd. All this evidence suggests that ultrabasic and basic magmas may contain PGE (except Pd) within the limits of saturation, i.e. platinum-group minerals (PGM) formation begins with the subliquidus crystallization of refractory PGE and the subsequent fractional separation of metal liquids rich in Pt. Because of variation in the differentiation behaviour of different PGE, each type of basic-ultramafic rocks is characterized by the predominance of a particular PGM paragenesis.

Detailed mineralogical studies (Okrugin, 1998) show three basic trends of compositional variation of Fe-Pt alloys from different types of Pt-bearing placer deposits of the Siberian platform. These are the ruthenium-rhodium, iridium, and palladium trends. These trends appear as increases (up to 10% and more) of contents of trace-element and each is characteristic of certain genetic types. Each formational type, exhibits a main trend, but the other trends are also present (because of the presence of minor PGE). For instance, all three types of trends are observed within PGM from placer deposits of the Lena province in the east of the Siberian platform which we have distinguished as the unique "Vilyuyan" type of the PGM association (Fig. 1). In these placer deposits, where PGM are mainly represented by high-concentrations of ferroan platinum, the ruthenium-rhodium trend is typical (is the main trend). Rh concentrations in ferroan platinum reach 17.5% and the content of Ru admixtures in the mineral increases up to 7.6% correlating with increasing Rh



**Figure 1.** Correlation of typomorphic trace-elements in Fe-Pt alloys from placer deposits of the Lena platinum-bearing province and the Inagli placer.

concentration. Besides the predominating ferroan platinum grains belonging to the ruthenium-rhodium trend, these placer deposits contain some grains belonging to the iridium (to 12% Ir) and palladium (to 13% Pd) trends. Typically, Rh, Ir and Pd are concentrated in different minerals. For example, high Rh concentrations occur in minerals with low Ir and Pd contents and the latter two elements are also abundant in different minerals. Thus, we observe the opposite behaviours in Rh, Ir and Pd distribution. Concentrations of these elements in ferroan platinum indicate reflect different evolutionary paths for the ore-forming systems.

The iridium trend is most characteristic of Pt-bearing placers related to zonal mafic-ultramafic intrusives found in both platform (Inagli, Kondyor and others - Aldanian type) and orogenic (Urals, Columbia and others - Alaskan (Uralian) type) regions. The palladium trend is most weakly developed in nature, although Pd is the second (following Pt) in its abundance in mafic-ultramafic rocks. This fact is explained by the chalcophile character of Pd and its lower temperature of fusion resulting in Pd accumulation in less refractory sulfide phases. High-palladium varieties of ferroan platinum grains are generally poor in Ir, Os, Rh, Ru, and Ni.

Textures of natural polyphase aggregates are similar to those of artificial alloys. Hence, comparative analysis may be used for interpreting the formation of different paragenetic assemblages of PGM. Phase transformations in the multicomponent alloys can be traced using ternary diagrams. At present, ternary diagrams of phase equilibria are known only for a limited group of elements and PGE. In this connection, the ternary Os-Ru-Ir and Ir-Os-Pt diagrams with a projection of binary systems was constructed from binary systems of platinum metals (Hansen & Anderko, 1958; Shunk, 1969) using the interpolation graphic technique. On the ternary plots, liquidus isotherms, border-lines between liquidus surfaces, and solvus isotherms are schematically shown as thin dashed, dashed, and dotted lines, respectively. In the system Ir-Os-Pt, the Pt solubility contours in Ir and Os are given after Slansky et al. (1991). The author uses the ternary diagrams with a projection of binary systems for tracing and depicting the crystallization and subsequent solid-phase transformations of PGE rich metal liquids.

Temperatures in dry artificial systems are much higher in comparison with those of the ore-magmatic processes. The considerably lower temperatures during the crystallization of natural

metals are explained by the eutectic relationship of a silicate melt with polymetal PGE immiscible liquids. Some differences are also explained by the presence of impurities, including low-melting and volatile components in natural alloys. On the diagram, the Os and Fe contents are added to those of Ru and Pt, respectively, because these pairs have similar phase equilibrium diagrams with other PGE and their addition cannot substantially change the pattern of phase transformations.

The analysis of mineral associations from different types of deposits shows that first phases originating during the early stage of magmatogenic ore formation are the most refractory discrete grains of osmium, ruthenium, rutheniridosmine and iridium. These are idiomorphic crystal phases composed of Ru, Ir, and Os and associated sulfides of the laurite-erlichmanite series frequently occurring as accessory minerals in dunites from ophiolite complexes. The ideal crystal form of these phases and their occurrence in accessory chromites indicate their early magmatic genesis. The experimental data (Taylor, 1980; Distler et al., 1988) show the high affinity of Os, Ru, and Rh for sulphur which is confirmed by the early paragenetic assemblage (Ru-Ir-Os alloys +  $\text{OsS}_2$  +  $\text{RuS}_2$  ( $\pm \text{Rh}_{17}\text{S}_{15}$ ) + Pt-Fe solid solutions) in the Alpine-type ultramafic rocks.

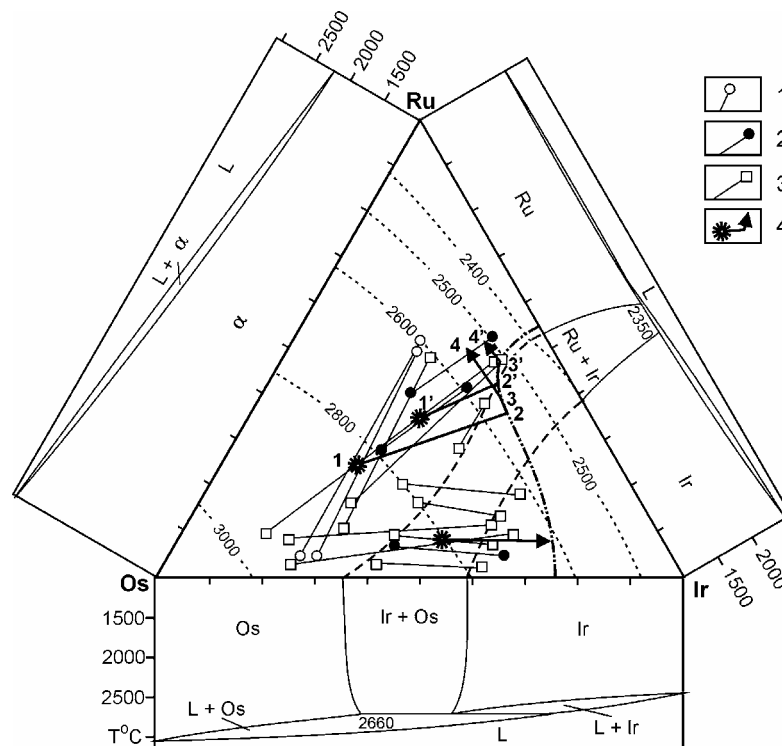
On the ternary plot, compositions of Ru-Ir-Os alloys usually lie in the field of hexagonal Ru-Os solid solutions and cubic iridium-alloys. Compositions of two-phase intergrowths of osmium and iridium are generally arranged along the lines bounding (as the experimental data show) the Os and Ir miscibility. This indicates the similarity between phase relationships of natural and artificial alloys (Fig. 2). However, there are rare cases of coexistence of two-phase osmium and ruthenium aggregates with compositions that lie within the field of complete solid solution. The formation of two-phase metal alloys generating complete solid solutions seems to be impossible. Therefore, high pressures should cause the immiscibility field between hexagonal and cubic solid solutions to shift towards the hexagonal alloys when osmium-ruthenium intergrowths are present (Bird & Bassett, 1980).

The Ru-Ir-Os diagram shows that osmium and iridium develop as a simple binary system of peritectic type when the system contains no more than 20 at.% Ru. In this case, pre-peritectic Os and Ir alloys form (straight arrowed line) zonal osmium grains rimmed with iridium. The grains sometimes occur in the deposits associated with the Alpine-type ultramafic rocks. If the Ru-Ir-Os metal liquid

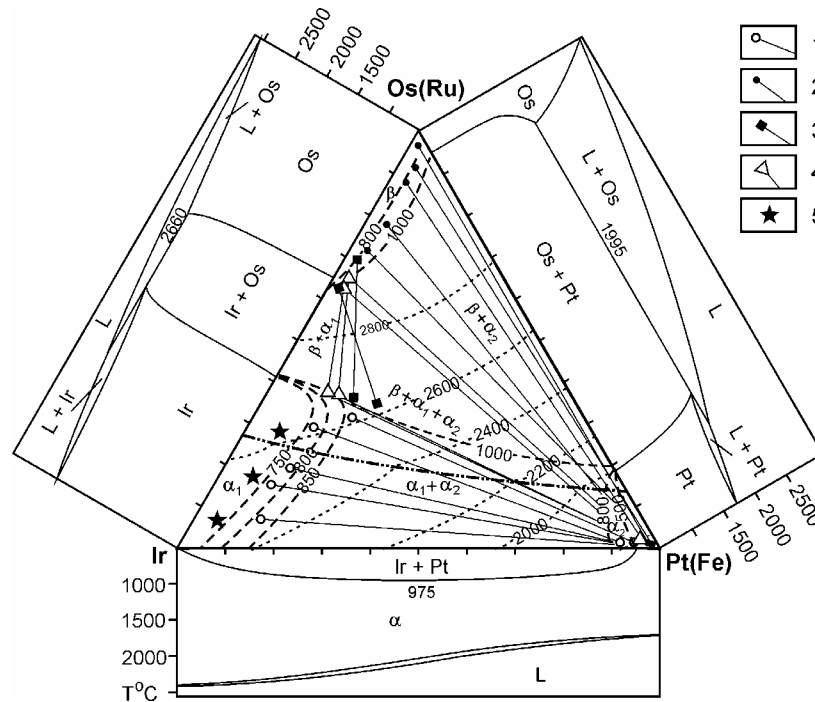
contains high amounts of Ru (more than 20%) its crystallization (points 1 and 1') begins with the appearance of osmium, and the residual melt is enriched in Ir and Ru. At peritectic temperatures, crystallization coincides with the peritectic line (lines 2-3 and 2'-3') when osmium and iridium solidification occurs and the liquid phase is enriched in Ru. In this case, the Os phase should be also enriched in Ru because it reacts peritectically with a residual melt. However, high-temperature Os crystals are probably more stable during rapid nonequilibrium crystallization of the system and are preserved as metastable phases. Since Ir is more refractory than Ru, the peritectic curve does not have a simple convex form but has a complex "S" configuration. Thus, the field of the initial iridium crystallization is expanded in the high-ruthenium section of the diagram resulting in the expansion of the Ir and Ru immiscibility field. At the final stage, the liquid crystallizes following a simple binary Ir-Ru system: iridium which separated earlier after the peritectic reaction is dissolved in the residual melt when Ru is present (lines 3-4 and 3'-4'). This mechanism explains the presence of two-phase

intergrowths of osmium and ruthenium, i.e. the metals producing a complete solid solution.

During fractional crystallization of the magmatic melt, the composition of separated liquid changes resulting in a decrease in refractory PGE amounts and substitution of more low-melting elements, i.e. Pt and Fe. The experiments show that in the Fe-Ni-Cu-S system high  $fS_2$  values result in a change of platinum mineralization, i.e. from tetraferroplatinum (PtFe) towards isoferroplatinum ( $Pt_3Fe$ ) and then to sulfide forms (Kolonin et al., 1993). In accordance with these data, tetraferroplatinum, rather than isoferroplatinum, should be associated with native forms of Os, Ru and Ir. However, isoferroplatinum predominates in natural associations with Ru-Ir-Os alloys. It seems that Fe activity is much lower in low-sulfide silicate systems and the Fe content of Fe-Pt solid solutions is generally estimated based on  $fO_2$ . With reference to the experimental data (Borisov & Palme, 2000), at a temperature of 1200°C isoferroplatinum crystallizes at  $fO_2 = QFM$  from the magmatic liquid containing FeO = 10 mol.% and tetraferroplatinum is generated under conditions close to IW equilibrium.



**Figure 2.** Ternary Ir-Os-Ru plot of compositions of coexisting phases of iridium, osmium and ruthenium. 1 - phases from placer occurrences of the Taas Eyeekit river of the Siberian platform; 2 - Josephine Creek, Oregon (Bird, Bassett, 1980); 3 - placer deposits of the Altai-Sayany region (Krivenko et al., 1990; Tolstykh et al., 1999); 4 - crystallization curves.



**Figure 3.** Ternary Ir-Os-Pt plot of compositions of paragenetic assemblages of iridium, osmium and isoferroplatinum from the Inagli placer deposit. 1 – isoferroplatinum + iridium; 2 – isoferroplatinum + osmium; 3 – iridium + osmium; 4 – isoferroplatinum + iridium+osmium; 5 – single grains of iridium. The lines connect coexisting phases.

The ternary Ir-Os-Pt diagram (Fig. 3) shows that if the initial platinum melts was enriched with osmium, then two-phase aggregates of Ir-Pt alloys with inclusions of native osmium were formed after the peritectic reaction. If the Pt liquid was enriched with Ir, two-phase intergrowths of isoferroplatinum and iridium were formed by exsolution of these solid solutions below 975°C. A three-phase field of coexisting Pt, Os and Ir occurs in the middle diagram. The crystallization of these alloys begins with osmium solidification above the peritectic field of the system. A reaction of Os with the residual liquid occurred during the crossing of a peritectic line. However, these conditions do not occur during the natural nonequilibrium processes. As a result, early Os crystals are cemented by platinum with a higher Ir content. The Ir-Pt alloy of the matrix exsolved isoferroplatinum and iridium below a critical point at 975°C. Textures of three-phase aggregates composed of corroded relics of lamella parent crystals of osmium, cemented by isoferroplatinum with myrmekitic intergrowths of iridium illustrate this crystallization trend of polycomponent Os-Ir-Fe-Pt melts.

Pd should be introduced into the Fe-Pt

melts only during the later stage of fractional crystallization of PGE in magmas. This is because Pd is the most highly soluble PGE (values of a few ppm and more) in silicates, and the initial Pd content in magmatic rocks is generally much lower. The experimental data show that most Pd is characterized by chalcophilic properties, i.e. sulfide melt separation from magma is the most effective mechanism for Pd extraction if its initial content is low. Therefore, Pd occurs generally only as an admixture or as small inclusions of Pd minerals in Fe-Pt melts in low-sulfide mafic-ultramafic rocks. Whereas in sulfide ores of differentiated and layered complexes Pd is the major component among PGE and generates the most abundant class of PGM.

Although PGE-metal liquids begin to solidify at an early magmatic stage, their final solidification tracks the crystallization of rock-forming minerals, i.e. olivine and chromite. At the postmagmatic evolutionary stage of ore-magmatic complexes, the rest of PGE, low-melting Pd and Pt in particular, transform into more mobile components and take part in metasomatic and hydrothermal processes as a wide variety of

minerals consisting of Pt and Pd with S, As, Te, Se, Hg, Sb, Sn, Bi, Pb, Au, Ag.

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