Composition and Origin of Ir-Os-Ru-Pt Alloys from the Zolotaya River Gold Placer, Southwestern Primorye, Russia

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Geological setting

Platinum-group minerals (PGM) have been discovered in gold placers of the Laoelin-Grodekovskaya foldbelt, Primorye. The foldbelt has E-W strike and stretches along the China-Russia borderline, southwest of Khanka Lake. This area represents a marginal basin, which formed at the southwestern margin of the Sino-Korean craton as a result of late Paleozoic extensional tectonics. The stratigraphic sequence of the rift margins consists of Permian carbonaceous and volcanic rocks (spilite-keratophyre association); the central part is filled by clastic rocks (black shales). Late Permian folding/thrusting was accompanied by basic-ultrabasic magmatism, followed by intensive granitic magmatism. The granites are discordantly overlain by early Triassic sedimentary rocks. The Permian black shales are intruded by the differentiated Odnorechenskiy dunite-hornblendite-gabbro complex with magmatic copper-nickel sulfide mineralisation. This complex has a concentrically-zoned structure and is regarded as of Uralian (Alaskan)-type. The basic-ultrabasic intrusion is thought to be the source of the primary PGM mineralisation, as suggested by the close spatial association and intergrowths of PGM and chromite with composition typical of Uralian-type deposits. A large part of these Alaskan-type intrusions was flooded by late Permian granites, which carry xenoliths and large blocks (roof pendants) of the basic-ultrabasic rocks.

Ir-Os-Ru-Pt alloy assemblages

About 40 grains of PGM from the Zolotaya river gold placer have been studied by electron microprobe (Cameca SX 100 at Institute of Mineralogy and Mineral Resources of Technical University of Clausthal). Ninety percent of the grains are ferroan platinum alloys; the remainder are alloys of Os-Ir-Ru-Pt. The latter form extremely inhomogeneous textures and consist of up to four different mineral phases reflecting different stages of exsolution of the primary solid solution.

Sample ZL-22 was found to be the most interesting because it allowed to define and to correlate the primary grain composition and the composition of its decay products. The grain matrix consists of a micrographic intergrowth aggregate of iridium isoferroplatinum $(Pt,Ir,Rh)_{2.71}Fe$ and an alloy phase of $Ir_{0.52}Ru_{0.18}Pt_{0.16}Fe_{0.06}Rh_{0.05}Pd_{0.02}Os_{0.02}$ (Fig. 1a) with disordered submicron-sized elongated inclusions of native osmium. It appears likely that exsolution occurred in two stages: the paragenesis of iridium ferroplatinum with an Ir, Os, Pt alloy formed first, and native osmium appeared later on cooling. Numerous inclusions of cherepanovite (RhAs) and iridarsenite ($IrAs_2$) are located in the matrix. The grain has a homogeneous rim of $Pt_{0.46}Ir_{0.25}Fe_{0.18}Ru_{0.08}Os_{0.02}Rh_{0.02}Cu_{0.05}$ with graphic inclusions of cherepanovite with high Ru (up to the 20 wt.%) content, in association with irarsite [(Ir,Rh,Pt)(AsS)] (Fig. 1b). Cherepanovite shows a compositional trend towards rithenarsenide [(Rh,Ru,Ir,Pt)As].

We analysed the micrographic grain matrix by defocussed beam (∅50 μm) in oder to find out its bulk composition. The composition obtained of $Pt_{0.48}Ir_{0.22}Fe_{0.17}Ru_{0.07}Rh_{0.02}Os_{0.01}Pd_{0.01}$ is nearly identical to the rim composition, suggesting variable degree of exsolution from a homogeneous primary phase for both rim and core as a consequence of quenching.

Other samples consist of (i) zonal ruthenosmiride $Ir_{0.40}Ru_{0.22}Os_{0.20}Pt_{0.11}Rh_{0.04}Fe_{0.03}$ intergrowth aggregates with ruthenosmiride $Ir_{0.38}Ru_{0.29}Os_{0.27}Rh_{0.02}Pt_{0.01}$, rutheniridosmine $Os_{0.42}Ir_{0.29}Ru_{0.23}Pt_{0.02}Rh_{0.02}$, and iridium isoferroplatinum $(Pt,Ir,Rh)_{2.3}(Fe,Ni,Cu)$ (Fig. 2, sample ZL-1/6), (ii) platosmiride $Ir_{0.41}Os_{0.28}Pt_{0.11}Rh_{0.09}Ru_{0.07}Pd_{0.03}$ filled by numerous spotted inclusions of iridium platinum $(Pt,Rh,Ir,Pd)_{2.9}Fe$ and ribbon-like iridosmine $Os_{0.57}Ir_{0.30}Ru_{0.08}Rh_{0.03}$ (Fig. 1c; Fig. 2, sample ZL-2), and (iii) iridium isoferroplatinum $(Pt, Ir, Rh)_{2.7}Fe$ with isometric inclusions of platosmiride $Ir_{0.57}Os_{0.26}Pt_{0.08}Rh_{0.06}Ru_{0.02}$ (Fig. 1d; Fig. 2, sample ZL-14).

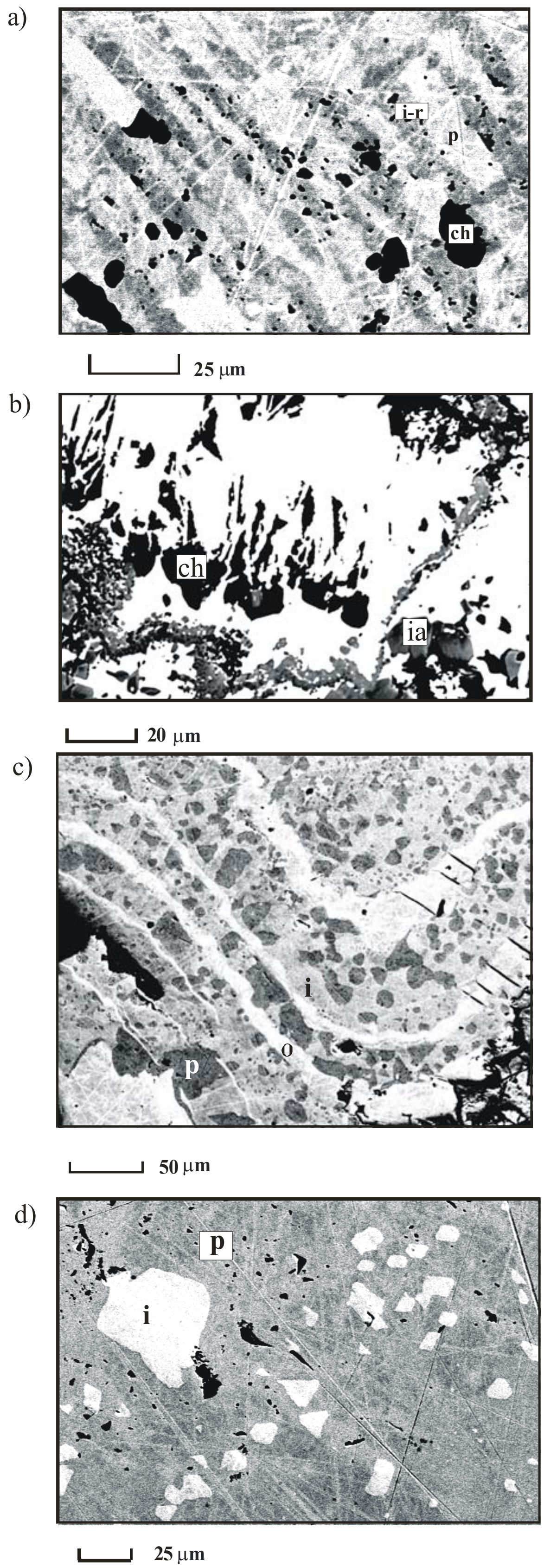

Figure 1. *Examples of different exsolution fabrics of the Ir-Os-Ru-Pt alloys of the Zoplotaya River, Primorye, Russia. BSE images, Cameca SX100. a) Sample ZL-22 – matrix: micrographic intergrowth of iridium isoferroplatinum (p) with Ir-Ru-Pt alloy (i-r) and cherepanovite inclusions (ch). b) Sample ZL-22 – homogeneous rim with inclusions of the middle member of the solid solution cherepanovite-ruthenarsenite (ch) and irarsite (ia). c) Sample ZL-2 – spotted inclusions of iridium isoferroplatinum (p) in platosmiride matrix (i) and ribbon-like iridosmine. d)Sample ZL-14 – isometric inclusions of platosmiridium (i) in the iridium ferroplatinum (p).*

We have found just one homogeneous iridium grain with composition of $Ir_{0.56}Os_{0.32}Ru_{0.06}Pt_{0.05}Rh_{0.01}$. Besides of these mineral associations there are intergrowths of isoferroplatinum with osmium plates $Os_{0.71}Ir_{0.26}Rh_{0.02}Pt_{0.01}$ (Fig. 2, sample ZL-30), and submicron-sized inclusions of native osmium $Os_{0.96}Pt_{0.04}$ in ferroan platinum alloys (Fig. 2, sample ZL-34).

Discussion

As a rule, alloys of the refractory PGE from the Zolotaya river placer are inhomogeneous. It is likely that they have undergone two-phase solid solution decay. The paragenesis with iridium isoferroplatinum has formed first. Native osmium and iridosmine have formed later. Iridium isoferroplatinum forms three different morphological structures: lattice (Fig. 1a), interstitial (Fig. 1c) and matrix (Fig. 1d). According to Shashkin and Botova (1989), the morphology of exsolution structures depends on primary composition, in particular on the Ir-content of associated isoferroplatinum. Our samples show that the Ir content changed from 25-30 wt.% Ir (Fig. 1a) to 15-17 wt.% Ir (Fig. 1d). It is likely that this reflects changing temperature. In order to estimate the formation temperature we used the pseudoternary Pt+(Fe)-Os+(Ru)-Ir+(Rh) diagram of Slanskiy et al. (1991) employed to Alaskan-type intrusions (Fifield, Nizhniy Tagil and Durance River), as applied later by Tolstykh and Krivenko (1997) to the Inagli massif. The composition of multiphase assemblages is plotted in relation to formation temperature (Fig. 2). Grain ZL-22 shows the highest temperature (>850^{o}C). The Ir content of associated isoferroplatinum is 5.50 wt.%. The projection of the rim and primary matrix compositions on the diagram shows a high temperature of the primary melt. Four-phase mineral associations plot inside of the miscibility gap. They indicate temperature decreasing from formation of Ir-rich members to Os –rich members. The Ir content in associated iridium isoferroplatium is 5.94 wt.%. Exsolution in sample ZL-2 occurred in two stages. At 800°C, iridium isoferroplatinum (4.40 wt.% Ir) with platosmiride were formed. Iridosmine formed during cooling. The formation of platosmiride from iridian feroplatinum (3.72 wt.%) took place at a temperature slightly below 750°C.

Conclusions

1. The detailed study of the morphological features of the multiphase mineral associations and the interpretation of the compositional data by help of the Slanskiy diagrams (Slanskiy et al., 1991) point to a high-temperature formation of the Ir-Os-Ru-Pt alloys of the Zolotaya River placer contemporary with the formation of the forsteritic dunite host rocks (based on Shashkin and Botova, 1989).

2. Applying the estimation of the level of erosion of Shashkin and Botova, 1989 and Nekrasov et al.,1991 the PGM-bearing intrusion of the Zolotaya River can be estimated as moderate eroded.

3. There is also a correlation of Ir content in isoferroplatinum with formation temperature. The higher the temperature the higher the Ir content in iridian isoferroplatinum in paragenesises with Ir-Os-Ru-Pt alloys.

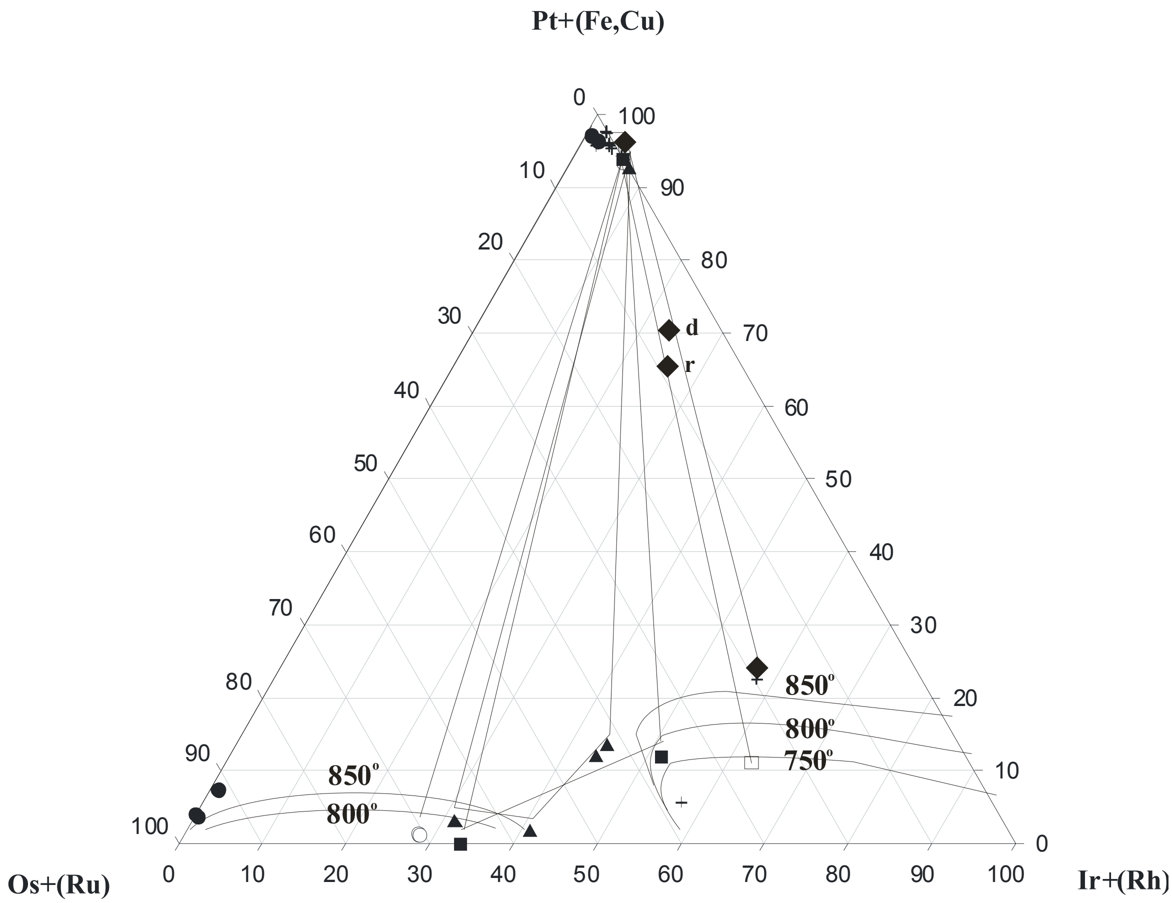

__Figure 2.__ Pseudoternary phase diagram of the Pt+(Fe) – Os+(Ru) – Ir+(Rh) system by Slanskiy et al., 1991. Filled diamonds – sample ZL-22: d – matrix composition by defocussed beam, r – rim composition; filled triangles – sample ZL-1/6; filled squares – sample ZL-2; open square – sample ZL-14; open circle – sample ZL-30; solid dots – sample ZL-34; crosses – monophase sample.

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