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ASSOCIATIONS OF PLATINUM-GROUP MINERALS FROM THE ZOLOTAYA GOLD PLACER, PRIMORYE, RUSSIAN FAR EAST

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ABSTRACT

The platinum-group minerals (PGM) and chromite composition of the Zolotaya River gold placer, in the Russian Far East, indicate a genetic relationship to poorly exposed Late Permian dunite – hornblendite – gabbro intrusions of Uralian–Alaskan type. Ninety percent of the PGM grains studied consist of Pt–Fe alloy, typically with a rhodium content in the 1–2 wt.% range. Pt-bearing Os–Ir–Ru alloy occurs in three variants: (1) heterogeneous grains with an exsolution texture, (2) intergrowths of Os–Ir alloy with Pt–Fe alloy, and (3) homogeneous grains. Minerals of the erlichmanite–laurite series are relatively rare. Their composition varies from pure laurite through Os-bearing laurite to erlichmanite. Cooperite occurs in multiphase inclusions (in association with cuprorhodsite and chalcopyrite) in Pt–Fe alloy, and as a secondary rim (occasionally intergrown with platarsite and sperrylite) around Pt–Fe grains. Heterogeneous aggregates of Pt–Fe and Ru–Pt–Ir alloy have inclusions of arsenides of rhodium, iridium and ruthenium (cherepanovite, iridarsenite, ruthenarsenite) and a sulfarsenide-rich rim (irarsite).

Keywords: Pt–Fe alloy, platinum-group minerals, Uralian–Alaskan-type complex, gold-bearing placers, platinum-group elements, Primorye, Russia.

SOMMAIRE

D'après les minéraux du groupe du platine (MGP) et la composition du spinelle chromifère présents dans les placers aurifères de la rivière Zolotaya, dans la partie extrême orientale de la Russie, il y aurait un lien génétique avec des massifs intrusifs permiens tardifs à piètre affleurement de dunite – hornblendite – gabbro du type Ourale–Alaska. Quatre-vingt dix pour cent des grains de MGP que nous avons étudié sont un alliage Pt–Fe, typiquement avec une teneur en rhodium de 1–2% (poids). Un alliage Os–Ir–Ru platinifère y figure en trois variantes: (1) grains hétérogènes ayant une texture d'exsolution, (2) intercroissances d'un alliage Os–Ir avec l'alliage Pt–Fe, et (3) grains homogènes. Les minéraux de la série erlichmanite–laurite semblent relativement rares. Leur composition varie de laurite pure, passant par laurite osmifère, jusqu'à erlichmanite. La cooperite se présente en inclusions multiphasées (en association avec cuprorhodsite et chalcopyrite) dans l'alliage Pt–Fe, et en liseré secondaire en bordure (ici et là en intercroissance avec platarsite et sperrylite) autour des grains de l'alliage Pt–Fe. Des aggrégats hétérogènes des alliages Pt–Fe et Ru–Pt–Ir contiennent des inclusions d'arséniures de rhodium, iridium et ruthénium (cherepanovite, iridarsenite, ruthenarsenite) et une bordure riche en sulfarséniure (irarsite).

(Traduit par la Rédaction)

Mots-clés: alliage Pt–Fe, minéraux du groupe du platine, complexe de type Ourale–Alaska, placers aurifères, éléments du groupe du platine, Primorye, Russie.

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Introduction

Platinum-group minerals (PGM) in southwestern Primorye, in the Russian Far-East (Fig. 1), were discovered at the end of the 19th century during gold placer mining on the territory of the Sof'e–Alexeevskoe Cossacks. Over the interval 1900–1912, exploration for gold was carried out at four fields: Zolotaya and Baykal river (former Dzhunikha) valleys and their northern tributaries (Annert 1928). In 1931, S.G. Vaulin, mining engineer with the "Dal'zoloto" company, evaluated the platinum potential. He confirmed the presence of small amounts of PGM in the gold placers (up to 3 mg PGE/m^3) and noted the occasional occurrence of nuggets with a weight of more than 50 mg. Only about sixty years later, the composition and secondary transformation of the PGM from the Fadeevka placer were studied by researchers from the Far East Geological Institute in Vladivostok (Shcheka *et al.* 1991).

In the present study, we give a description of the primary and secondary PGM mineralization, on the basis of sample material from a heavy-mineral concentrate taken from the Zolotaya River. Grains of chromian spinel were analyzed from the Zolotaya and Fadeevka River placers.

Geological Setting

The Zolotaya and Fadeevka rivers are located in the Pogranichnaya gold belt, which is part of the southern Laoelin–Grodekov fold belt, Primorye (Figs. 1, 2). The fold belt strikes N–S and stretches along the China–Russia border, southwest of Lake Khanka. This area represents an island-arc terrane that accreted to the west of the Sino-Korean platform during the Late Paleozoic (Khanchuk *et al.* 1996). The stratigraphic sequence of the study area consists of an Early Paleozoic basement of muscovite–chlorite schist overlain by Permian black shale. Late Permian folding and thrusting were accompanied by basic to ultrabasic magmatism, followed by extensive granitic magmatism. Shallow gabbroic sills and stocks and granitic rocks with dominantly albitized granophyric granites (granodiorite–granite complex) are comagmatic with metabasaltic volcanism (spilite–keratophyre series). A differentiated dunite – hornblendite – gabbro complex, associated with magmatic copper–nickel sulfide mineralization, intrudes the Permian black shale. Cortlandite and hornblendite (with orthopyroxene) rich in high-aluminum hornblende (replacing orthopyroxene and clinopyroxene) are the most common rock-units. This complex is concentrically zoned and is regarded as of Uralian–Alaskan-type (Shcheka *et al.* 1990). A large part of it was intruded by Late Permian granites and now occurs as xenoliths and large blocks (roof pendants) within the granitic rocks. Larger occurrences are in the upper Baykal valley and in the upper reaches of the Kamenuska River west of Veranda Mountain (Fig. 2).

The hornblendite suite of the dunite – hornblendite – gabbro complex has a composition similar to peridotites and hornblende-rich pyroxenites of the zoned ultrabasic intrusions of southwestern Alaska (Taylor & Noble 1969, Himmelberg & Loney 1995). A minor amount of hornblendite also is present in some concentrically zoned massifs of the Uralian Platinum Belt (Ivanov 1997). All massifs mentioned above have similar petrochemical and mineralogical characteristics, although the proportion of hornblende-bearing ultrabasic rocks in individual intrusive complexes is highly variable.

The Permian black shale hosts a number of quartz veins with pyrite – arsenopyrite – gold; they formed in connection with the felsic intrusions, and are considered to be the source of the alluvial gold placers (Shcheka *et al*. 1991). The alluvial gold from the Zolotaya River consists of dominantly (1) low-silver Au–Ag alloy with <8 wt.% Ag, and (2) high-silver Au–Ag alloy with up to 25 wt.% Ag. Occasionally, a complex Au–Ag–Hg–Pd alloy occurs, with up to 8 wt.% Pd and 4 wt.% Hg. The palladium component in this variant is considered to be related to remobilization from dunitic rocks during the widespread felsic magmatism (Molchanov *et al.* 2001).

Analytical Methods

Both quantitative electron-microprobe analysis with wavelength-dispersion spectrometers (WDS) and energy-dispersion X-ray spectrometry (EDS) were done with a CAMECA SX100 electron microprobe at the Institute of Mineralogy and Mineral Resources of Technical University of Clausthal (Germany). The PGM were analyzed with a voltage of 20 kV and a beam current of 20 nA, with a beam 1 μm in diameter. The duration of the analyses varied from 10 to 30 s. Nineteen elements were determined using the following standards: FeS_2, PbTe, SnO_2, InAs and pure osmium, bismuth, ruthenium, rhodium, palladium, silver, antimony, gold, platinum, iridium, nickel, cobalt, iron and copper. The X-ray $K\alpha$ lines were used for Ni, Co, Fe; $L\alpha$ for Ru, Rh, Sn, Sb, Te, Au, Pt, Ir, Cu; $L\beta_1$ for Pd and Ag, and $M\alpha$ for Os, Pb, Bi. The following detection-limits were obtained (in wt.%): 0.15 for Os, 0.15 for Ir, 0.16 for Ru, 0.12 for Rh, 0.24 for Pd, 0.27 for Pt, 0.27 for Au, 0.32 for Ag, 0.23 for Pb, 0.04 for Fe, 0.02 for Ni, 0.09 for Cu, 0.03 for Co, 0.18 for Bi, 0.08 for Sb, 0.08 Sn, 0.09 for Te, 0.05 for As, and 0.06 for S.

Oxides and silicates were analyzed for twelve elements using the following standards and spectral lines: kaersutite, Cr_2O_3 (synthetic), rutile, sphalerite, Fe_2O_3 (synthetic), rhodonite, forsterite, albite. The Si$K\alpha$, K$K\alpha$, Ca$K\alpha$, Cr$K\alpha$, Ti$K\alpha$, S$K\alpha$, Fe$K\alpha$, Mn$K\alpha$, Zn$K\alpha$, Na$K\alpha$, Mg$K\alpha$, and Al$K\alpha$ lines were used. For the data reduction, we employed the approach of Pouchou & Pichoir (1984).

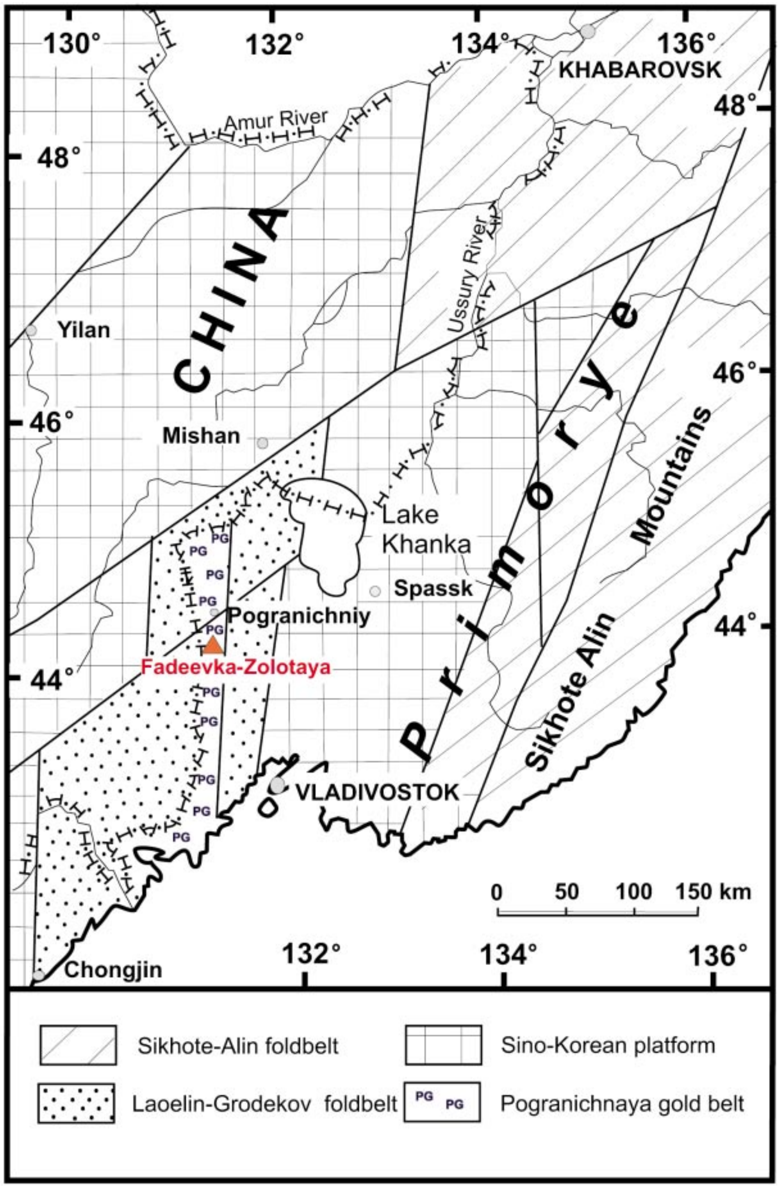


FIG. 1. Location map of the PGE-bearing gold placers of Zolotaya and Fadeevka in Primorye, Russian Far East. Map simplified after Shcheka *et al.* (2001).

SOURCE OF THE PGM

In an earlier study of the PGM and associated minerals from the Fadeevka River placer, Shcheka *et al.* (1991) suggested that the PGM mineralization is related to the dunite – hornblendite – gabbro complex. Since then, black shale was found that also could be a source of the platinum-group elements. The chemical composition of chromian spinel is often used for both the petrogenetic characterization of basic-ultrabasic igneous complexes and their related mineralization (*e.g.*, Barnes & Roeder 2001). We studied the chromian spinel from the Fadeevka and Zolotaya placers both as inclusions in PGM and in individual grains of chromian spinel in heavy-mineral concentrates, and compared it to chromian spinel from the Late Permian dunite –

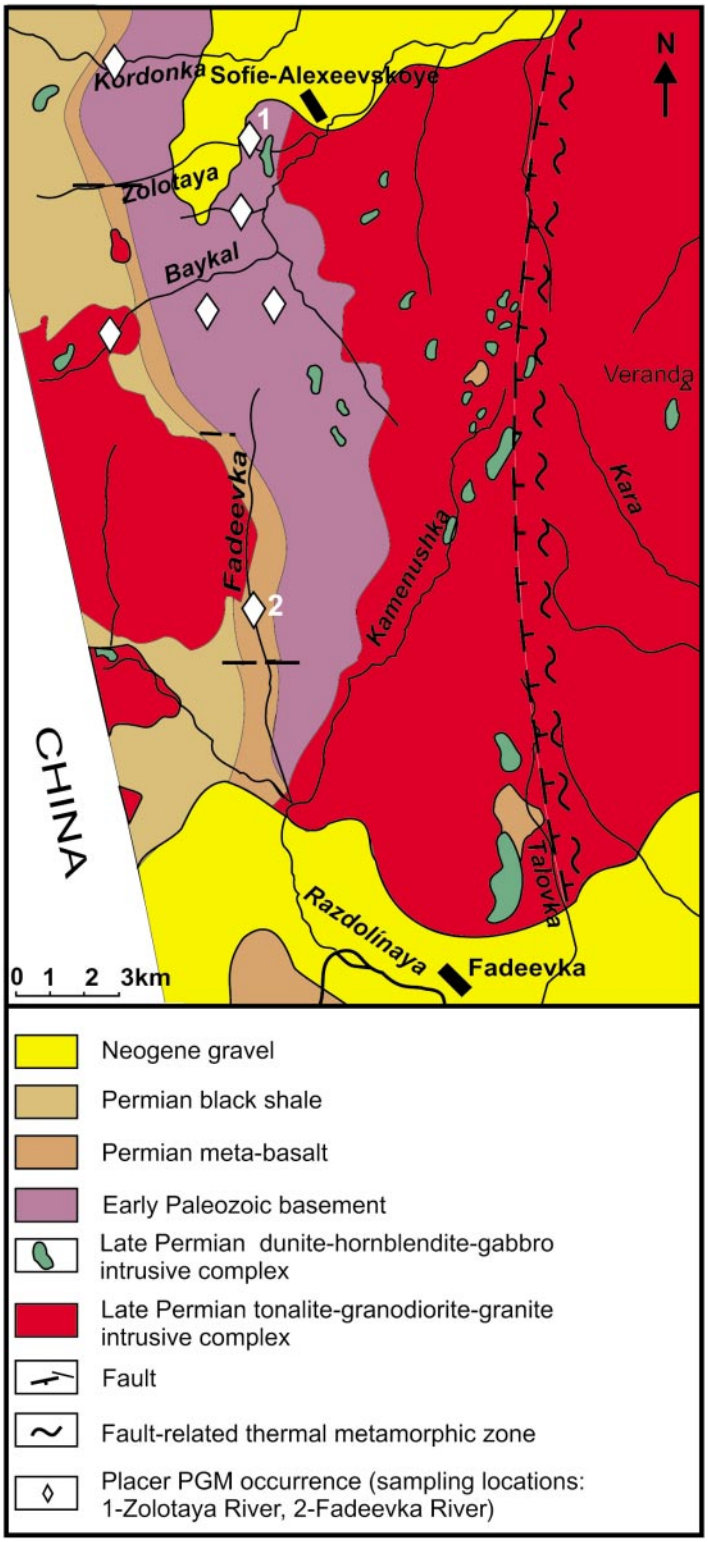


FIG. 2. Geological sketch-map of the study area.

TABLE 1. CHEMICAL COMPOSITION OF CHROMIAN SPINEL, ZOLOTAYA AND FADEEVKA RIVER CONCENTRATES

No.		TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	MnO	MgO	ZnO	Σ	φ	*f*	*f′*
1	Inclusions in PGM	0.23	9.88	58.33	3.11	15.38	-	11.67	0.18	98.78	79.8	46.7	15.4
2	grains (Zolotaya	0.19	5.52	60.61	6.38	16.08	0.42	10.79	n.a.	99.99	88.1	53.1	26.3
3	and Fadeevka)	0.30	8.94	54.36	6.79	20.69	0.43	8.11	n.a.	99.62	80.3	65.0	22.8
4	Chromian	-	7.21	62.15	3.83	11.57	-	14.13	-	98.89	85.5	37.3	23.0
5	spinel	-	6.01	60.45	4.39	21.55	0.23	7.17	0.20	100.00	87.1	66.6	15.5
6	in	0.21	9.58	58.36	3.51	17.68	0.18	10.40	-	99.92	80.3	52.9	15.1
7	heavy-	-	4.61	57.84	5.83	26.30	0.43	3.38	0.46	98.85	89.4	83.9	16.6
8	mineral	0.25	6.38	57.04	7.34	22.42	0.26	6.89	0.13	100.71	85.7	70.2	22.8
9	concentrate	0.25	9.90	54.64	6.15	18.39	0.23	9.71	-	99.27	78.7	58.0	23.1
10	(Zolotaya	0.26	10.60	52.71	7.43	19.54	0.18	9.21	-	99.93	76.9	61.5	25.5
11	River)	0.24	11.62	51.63	6.79	19.11	0.20	9.32	0.14	99.05	74.9	60.3	24.2
12	Chromian spinel	0.07	3.91	59.95	6.29	23.34	0.52	5.71	n.a.	99.79	91.1	74.0	19.5
13	in heavy-mineral	0.08	8.15	58.39	3.45	21.49	0.48	7.64	n.a.	99.69	82.8	64.7	11.5
14	concentrate	0.12	6.93	58.00	5.88	20.32	0.42	8.10	n.a.	100.07	84.9	63.4	19.7
15	(Fadeevka	0.12	8.10	54.32	6.81	22.72	0.43	6.77	n.a.	99.28	81.8	71.0	20.4
16	River)	0.21	12.95	48.59	7.57	23.48	0.40	6.73	n.a.	99.93	71.6	71.6	22.5
17	Chromian	0.43	6.36	55.39	7.03	23.78	1.09	5.05	0.77	99.90	85.3	77.0	21.0
18	spinel	0.30	9.93	54.73	2.96	26.05	0.92	4.35	n.a.	99.25	78.7	78.7	9.3
19	in dunite	0.61	7.71	52.52	9.34	20.62	0.92	7.76	n.a.	99.48	81.2	67.8	28.9
20	and	0.28	6.72	57.06	4.17	26.35	0.67	3.96	n.a.	99.19	85.0	81.0	12.4
21	hornblendite	0.46	11.84	48.43	6.55	28.24	0.68	3.14	0.54	99.88	73.3	85.9	17.2

Note: φ = 100Cr/(Cr + Al); *f* = 100Fe/(Fe + Mg); *f′* = $100Fe^{3+}/(Fe^{3+} + Fe^{2+})$, all expressing atom proportions. The proportion of Fe^{3+} is calculated on the basis of mineral stoichiometry; n.a.: not analyzed; -: not detected.

hornblendite – gabbro complex within the same area. All three sample groups studied have a similar composition, suggesting a common source (Table 1). The chromian spinel has a high content of chromium, a low content of titanium, and a low oxidation state. The plot of $Fe^{3+}/(Cr^{3+} + Fe^{3+} + Al^{3+})$ *versus* $Cr^{3+}/(Cr^{3+} + Fe^{3+} + Al^{3+})$ for chromian spinel from the Zolotaya and Fadeevka areas shows a compositional field similar to Uralian–Alaskan-type occurrences and different from the ophiolitic trend (Fig. 3).

The composition of an olivine inclusion (Fo_{91}) within a PGM grain is similar to olivine in dunite and further confirms the connection of PGM mineralization from the Zolotaya River to the dunite – hornblendite – gabbro intrusions.

Associations of Platinum-Group Minerals

About 40 grains of PGM from the Zolotaya gold placer have been studied by electron-microprobe analysis. Ninety percent of the grains consist of a Pt–Fe alloy; the remaining grains consist of Os–Ir–Ru–Pt alloy. Other PGM occur as inclusions within or a rim on the main alloy phases. The grain size of the PGM seldom exceeds 2 mm (maximum is 4.4 mm across) and normally varies from 0.2 up to 1.4 mm. The grain shape is isometric or tabular, commonly irregular and angular. Usually, the PGM are poorly rounded, with euhedral outlines preserved, which indicates relatively little transport. Occasionally, the PGM are intergrown with silicates, such as forsterite, quartz, chamosite, white mica, and clay minerals.

Pt–Fe alloy

The Pt content in the Pt–Fe alloy varies from 80.0 up to 91.8 wt.% (Table 2, Fig. 4). The most common minor elements are rhodium (from 0.55 to 2.51 wt.%) and palladium (from 0.26 to 1.07 wt.%). Some grains are rich in iridium (up to 7.14 wt.%). Copper ranges from 0.26 to 1.12 wt.%, and was found in all grains analyzed.

Os–Ir–Ru–Pt alloy

The grains of Os–Ir–Ru–Pt alloy have an extremely heterogeneous texture and consist of up to four different mineral phases, reflecting various stages of exsolution of the primary solid-solution (Table 3, Fig. 5). Sample ZL22 was found to be the most interesting because it allowed us to define the composition of the primary grains and to correlate it with the composition of its products of exsolution. The grain matrix consists of a micrographic intergrowth of iridium-rich Pt-Fe alloy $(Pt_{2.47}Ir_{0.17}Rh_{0.05}Pd_{0.01}Ru_{0.01})_{\Sigma 2.71}(Fe_{0.95}Cu_{0.04}Ni_{0.01})_{\Sigma 1.00}$ and an alloy phase of composition $Ir_{0.52}Ru_{0.18}Pt_{0.16}Cu_{0.06}Rh_{0.05}Pd_{0.02}Os_{0.02}$ (Fig. 6a). Numerous inclusions of cherepanovite (RhAs) and iridarsenite ($IrAs_2$) are located in the matrix. The grain has a homogeneous rim of $Pt_{0.46}Ir_{0.25}Fe_{0.18}Ru_{0.08}Rh_{0.01}Os_{0.01}Cu_{0.01}$, with graphic inclusions of cherepanovite characterized by a high Ru content (up to 20 wt.%), in association with irarsite (Ir,Rh,Pt)AsS (Fig. 6b). We analyzed the matrix of the micrographic grain with a defocused beam (50 μm) in order to obtain its bulk composition. The

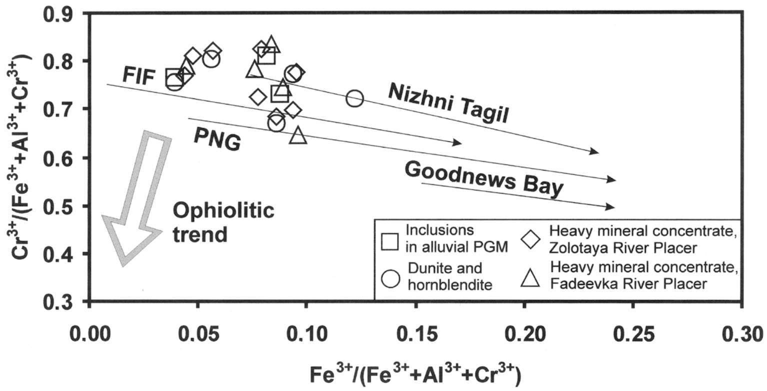


FIG. 3. Plot of $Fe^{3+}/(Cr^{3+} + Fe^{3+} + Al^{3+})$ *versus* $Cr^{3+}/(Cr^{3+} + Fe^{3+} + Al^{3+})$ for chromian spinel from the Zolotaya and Fadeevka areas. Evolution trends of chromian spinel in the Nizhni Tagil, Fifield (FIF), Goodnews Bay and Papua New Guinea (PNG) Uralian–Alaskan-type complexes, as well as for ophiolitic chromitites, according to Johan (2002).

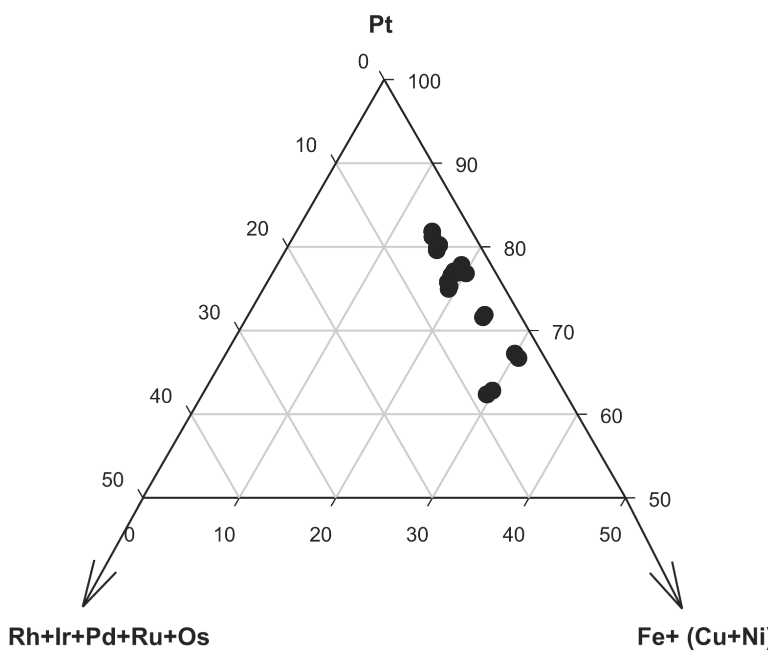


FIG. 4. Composition of Pt–Fe alloy from the Zolotaya River placer (at.%).

composition, $Pt_{0.49}Ir_{0.23}Fe_{0.17}Ru_{0.07}Rh_{0.02}Os_{0.01}Pd_{0.01}$, is nearly identical to that of the rim, suggesting a variable degree of exsolution from a homogeneous primary phase for both rim and core.

Other samples consist of aggregates of (i) zonal intergrowths of iridium, $Ir_{0.40}Ru_{0.22}Os_{0.20}Pt_{0.11}Rh_{0.04}Fe_{0.02}$, with two variants of rutheniridosmine, $Ir_{0.39}Ru_{0.30}Os_{0.28}Rh_{0.02}Pt_{0.01}$ and $Os_{0.42}Ir_{0.30}Ru_{0.23}Pt_{0.02}Rh_{0.02}$, and iridium-bearing Pt–Fe alloy $(Pt_{2.10}Ir_{0.16}Rh_{0.09}Ru_{0.01})_{\Sigma 2.36}(Fe_{0.89}Ni_{0.07}Cu_{0.04})_{\Sigma 1.00}$ (sample ZL–1/6), (ii) iridium $Ir_{0.41}Os_{0.28}Pt_{0.11}Rh_{0.09}Ru_{0.07}Pd_{0.03}$ with numerous spotted inclusions of Ir- and Rh-rich Pt–Fe alloy $(Pt_{2.66}Rh_{0.15}$

TABLE 2. SELECTED COMPOSITIONS OF Pt–Fe ALLOY OF THE ZOLOTAYA RIVER PLACER

No. Sample	1 ZL34	2 ZL1	3 ZL32	4 ZL32	5 ZL32	6 ZL1	7 ZL34	8 ZL37	9 ZL14	10 ZL25	11 ZL30
Os wt.%	1.59	1.84	0.64	0.71	0.65	0.57	2.07	0.11	-	-	0.26
Ru	0.13	0.21	0.08	-	-	0.11	0.20	-	-	-	-
Rh	1.12	1.14	2.08	2.51	2.05	1.58	0.55	1.43	1.73	1.36	2.24
Pd	0.31	-	0.46	0.57	-	1.07	-	0.94	-	0.26	0.58
Pt	90.79	91.77	89.79	88.86	89.68	89.53	88.61	88.87	83.47	80.00	80.96
Ir	-	-	-	-	-	1.26	-	-	3.72	7.14	3.90
Ni	0.09	0.18	0.06	0.07	0.05	0.09	0.07	0.03	0.06	0.28	0.29
Fe	4.05	4.66	5.71	5.62	5.64	5.48	5.76	7.96	8.95	9.20	10.22
Cu	0.37	0.30	0.56	0.67	0.61	1.12	0.77	0.77	0.37	0.26	0.57
Total	98.45	100.10	99.38	99.01	98.68	100.81	98.03	100.11	98.30	98.50	99.02
Os at.%	1.47	1.65	0.56	0.62	0.57	0.49	1.85	0.09	-	-	0.21
Ru	0.23	0.36	0.13	-	-	0.18	0.34	-	-	-	-
Rh	1.91	1.90	3.36	4.06	3.35	2.51	0.91	2.19	2.66	2.08	3.29
Pd	0.51	-	0.72	0.89	-	1.64	-	1.39	-	0.38	0.82
Pt	81.83	80.49	76.58	75.75	77.33	74.96	77.13	71.85	67.79	64.43	62.80
Ir	-	-	-	-	-	1.07	-	-	3.07	5.84	3.07
Ni	0.27	0.52	0.17	0.20	0.14	0.25	0.20	0.08	0.16	0.75	0.75
Fe	12.75	14.28	17.01	16.73	16.99	16.03	17.51	22.48	25.39	25.88	27.69
Cu	1.02	0.81	1.47	1.75	1.61	2.88	2.06	1.91	0.92	0.64	1.36
Total	100	100	100	100	100	100	100	100	100	100	100

Note: Bi, Pb, Bi, Sn, Sb, Te, As were not detected; - below detection limit.

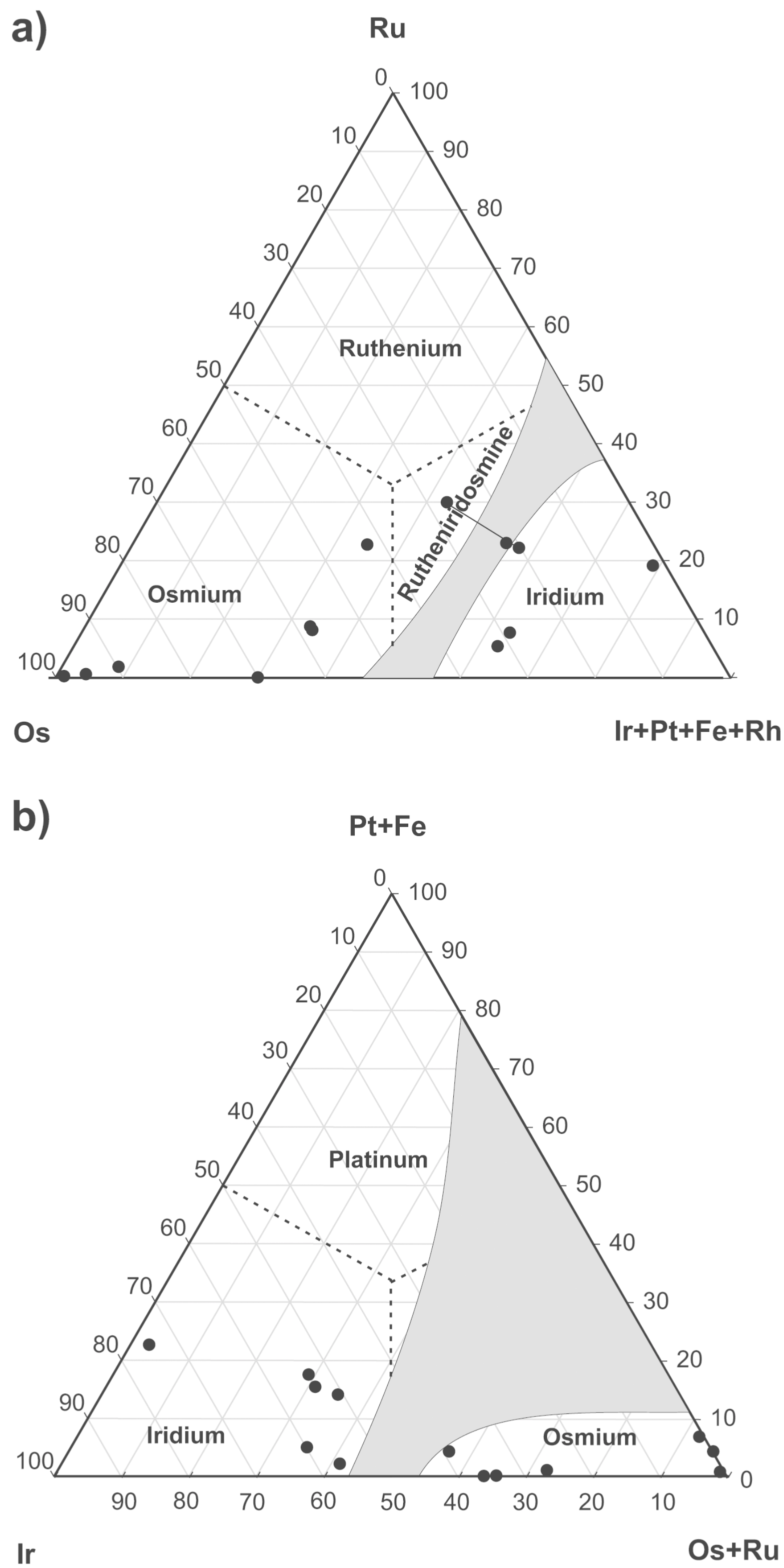
TABLE 3. SELECTED COMPOSITIONS OF Os–Ir–Ru–Pt ALLOY OF THE ZOLOTAYA RIVER PLACER

No. Sample	1 ZL34	2 ZL34	3 ZL30	4 ZL2	5 ZL1	6 ZL25	7 ZL1m	8 ZL1	9 ZL2	10 ZL1	11 ZL1	12 ZL22
Os wt.%	94.63	92.30	69.41	60.01	47.55	60.03	32.65	32.14	30.27	24.69	22.98	1.93
Ru	-	1.01	0.16	4.65	13.83	4.45	2.88	18.27	4.25	13.94	13.28	10.76
Rh	-	0.22	1.18	1.64	1.14	0.61	0.74	1.39	5.32	2.2	2.63	2.98
Pd	-	-	-	0.55	-	0.36	-	-	1.7	-	-	1.32
Pt	3.43	7.21	1.03	-	2.79	-	5.20	1.36	12.03	10.68	12.93	18.47
Ir	-	0.73	25.68	32.15	33.65	34.31	58.03	45.67	44.99	47.15	46.39	60.22
Fe	0.11	0.06	0.07	-	0.14	-	0.09	0.14	0.24	0.79	0.62	0.04
Cu	0.05	0.09	-	-	-	-	0.14	-	-	0.17	0.17	2.17
Ni	-	-	-	-	-	-	-	-	-	0.10	0.08	-
Total	98.22	101.62	97.53	99.00	99.10	99.76	99.73	98.97	98.80	99.72	99.00	97.89
Os at.%	96.07	89.75	70.43	57.37	42.38	57.65	31.80	27.69	27.97	21.35	20.12	1.69
Ru	-	1.85	0.31	8.37	23.20	8.04	5.28	29.62	7.39	22.70	21.87	17.72
Rh	-	0.40	2.21	2.90	1.88	1.08	1.33	2.21	9.09	3.52	4.26	4.82
Pd	-	-	-	0.94	-	0.62	-	-	2.81	-	-	2.06
Pt	3.40	6.84	1.02	-	2.43	-	4.94	1.14	10.84	9.01	11.04	15.76
Ir	-	0.70	25.79	30.42	29.68	32.61	55.94	38.93	41.14	40.37	40.18	52.15
Fe	0.38	0.20	0.24	-	0.43	-	0.30	0.41	0.76	2.33	1.85	0.12
Cu	0.15	0.26	-	-	-	-	0.41	-	-	0.44	0.45	5.68
Ni	-	-	-	-	-	-	-	-	-	0.28	0.23	-
Total	100	100	100	100	100	100	100	100	100	100	100	100

Note: S, Pb, Bi, Pd, Sn, Sb, Te, As were not detected; - below detection limit.

$Ir_{0.10}Pd_{0.05})_{\Sigma 2.95}(Fe_{0.94}Cu_{0.04}Ni_{0.02})_{\Sigma 1.00}$, and ribbon-like osmium $Os_{0.57}Ir_{0.30}Ru_{0.08}Rh_{0.03}$ (Fig. 6c, sample ZL2), and (iii) Ir-rich Pt–Fe alloy $(Pt_{2.57}Ir_{0.12}Rh_{0.10})_{\Sigma 2.79}(Fe_{0.96}Cu_{0.04})_{\Sigma 1.00}$ with subhedral inclusions of iridium $Ir_{0.57}Os_{0.26}Pt_{0.08}Rh_{0.06}Ru_{0.02}$ (Fig. 6d, sample ZL14). Only one homogeneous grain of iridium was found, with the composition of $Ir_{0.56}Os_{0.32}Ru_{0.06}Pt_{0.05}Rh_{0.01}$. In addition to these mineral associations, there are intergrowths of Pt–Fe alloy with plates of osmium $Os_{0.71}Ir_{0.26}Rh_{0.02}Pt_{0.01}$, and submicrometric inclusions of native osmium $Os_{0.96}Pt_{0.04}$ in Pt–Fe alloy.

On the basis of these observations, the refractory PGM of the Zolotaya placer can be subdivided into three groups: (1) heterogeneous Os–Ir–Ru–Pt grains (most common) formed as a result of breakdown of the solid


a)
Ru
Ruthenium
Rutheniridosmine
Osmium
Iridium
Os
Ir+Pt+Fe+Rh
b)
Pt+Fe
Platinum
Iridium
Osmium
Ir
Os+Ru

solution (Figs. 6a, c), (2) Pt–Fe alloy and Os–Ir alloy intergrowths, and (3) homogeneous grains.

Cooperite, PtS, and cuprorhodsite, Cu(Rh,Ir)$_2$S$_4$

Cooperite from the Zolotaya placer occurs in two different varieties. Primary cooperite intergrown with cuprorhodsite and chalcopyrite forms roundish multiphase inclusions in Pt–Fe alloy (Fig. 7). The inclusions are not more than 10–20 μm across. Cuprorhodsite from the multiphase inclusions contains up to 30.8 wt.% Pt, whereas the Ir content does not exceed 0.81% (Table 4). Chalcopyrite contains up to 5.12 wt.% Pt and 1.13% Pd. Secondary cooperite forms a rim around Pt–Fe grains (Fig. 8). The distinctive feature of primary cooperite is its palladium content, up to 1.98 wt.%, whereas secondary cooperite commonly has a Pd content below the detection limit and only rarely attains 0.66 wt.% (Table 4).

The width of the secondary rim of cooperite reaches 50 μm. One of the Pt–Fe grains studied is surrounded by a complex rim, which consists of cooperite intergrown with a Pb–Ir–Cu–Rh sulfide (Table 5, Fig. 8a). The Pb content varies from 1.60 to 7.54 wt.%. The Pb-bearing phase could be either xingzhongite, $(Ir,Pt)_2(Cu,Pb)S_4$, or konderite, $PbCu_3Rh_8S_{16}$.

In another sample, patchily intergrown aggregates of cooperite with sperrylite form a several-μm-wide rim on Pt–Fe alloy. Cooperite contains up to 3.02 wt.% Ir, and both cooperite and sperrylite contain up to 1.30 wt.% Rh.

The erlichmanite–laurite solid-solution series

Members of the erlichmanite–laurite solid-solution series, OsS_2–RuS_2, occur both in the form of idiomorphic inclusions (up to 15 μm across) in Pt–Fe alloy and as an intergrowth with Os–Ir–Ru–Pt alloy (Fig. 9). Pure laurite has been found as an intergrowth with a zoned grain of rutheniridosmine. Erlichmanite, with up to 12.1 wt.% Ru (Table 6), occurs as an intergrowth with iridium. Idiomorphic inclusions of Os-bearing laurite of hexagonal habit (up to 20.2 wt.% Os) occur within Pt–Fe alloy. The euhedral laurite is evidence of its primary formation and subsequent entrapment by Pt–Fe alloy.

The cherepanovite–ruthenarsenite solid-solution series

Minerals of the cherepanovite–ruthenarsenite solid-solution series, RhAs–(Ru,Ni)As, form irregular inclusions (up to 20 μm; Table 4) mainly close or within the rim of heterogeneous grains with a lattice-like intergrowth of Ir-bearing Pt–Fe and Ir–Ru–Pt alloy (Fig. 6a). In some cases, cherepanovite occurs as an intergrowth with iridarsenite $(Ir,Ru,Rh,Pt)As_2$. In the rim zone, cherepanovite has a high Ru content (up to 19.2 wt.%). This phase probably is an intermediate member of the cherepanovite–ruthenarsenite solid-solution series. Ru-rich cherepanovite forms a graphically intergrown aggregates with irarsite (Ir,Rh,Pt,Ru)AsS.

FIG. 5. Composition of Os–Ir–Ru–Pt alloy a) in the Os – Ru – (Ir + Pt + Fe + Rh) diagram, b) in the Ir – (Os + Ru) – (Pt + Fe) diagram (at.%). Shaded area corresponds to the miscibility gap, according to Cabri & Feather (1975).

TABLE 4. CHEMICAL COMPOSITION OF CUPRORHODSITE, CHEREPANOVITE, IRIDARSENITE, IRARSITE AND COOPERITE FROM THE ZOLOTAYA RIVER PLACER

No.	1	2	3	4	5	6	7	8
Sample	ZL-1	ZL-1	ZL22	ZL22	ZL22	ZL22	ZL33	ZL-1
	$CuRh_2S_4$		RhAs	(Rh,Ru)As	$(Ir,Ru)As_2$		PtS	
S wt.%	27.72	27.00	-	-	-	7.50	14.63	14.64
Ru	-	-	4.65	19.15	0.43	-	-	-
Rh	30.54	26.58	47.15	27.42	2.85	5.94	0.41	0.54
Pd	-	-	0.47	-	0.61	-	-	1.98
Sb	-	-	2.87	0.63	0.77	0.16	-	-
Ir	0.71	0.81	7.66	8.03	47.88	46.77	-	-
Pt	25.54	30.80	1.34	2.88	4.07	8.11	84.89	82.80
Au	-	-	-	-	-	0.68	-	-
Fe	2.55	1.77	-	0.07	0.21	0.10	-	-
Cu	11.23	11.85	-	-	-	-	0.10	0.09
As	-	-	36.78	39.6	43.03	27.8	0.09	0.11
Total	98.29	98.81	100.92	97.78	99.85	97.06	100.12	100.16
S *apfu*	3.98	3.97	0.00	0.00	0.00	0.74	1.02	1.01
Ru	0.00	0.00	0.09	0.36	0.01	0.00	0.00	0.00
Rh	1.37	1.22	0.86	0.51	0.09	0.18	0.01	0.01
Pd	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.04
Sb	0.00	0.00	0.04	0.01	0.02	0.00	0.00	0.00
Ir	0.02	0.02	0.07	0.08	0.84	0.77	0.00	0.00
Pt	0.60	0.74	0.01	0.03	0.07	0.13	0.97	0.94
Au	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Fe	0.21	0.15	0.00	0.00	0.01	0.01	0.00	0.00
Cu	0.83	0.89	0.00	0.00	0.00	0.00	0.00	0.00
As	0.00	0.00	0.92	1.01	1.93	1.17	0.00	0.00
Total	7.00	7.00	2.00	2.00	3.00	3.00	2.00	2.00

Note: 1, 2 cuprorhodsite, 3 cherepanovite, 4 cherepanovite–ruthenarsenite solid solution, 5 iridarsenite, 6 irarsite, 7 secondary cooperite, 8 primary cooperite; Bi, Os, Ni, Pb, Bi, Pd, Sn, Te, As were not detected; - below detection limit. The raw data are recast in terms of atoms per formula unit (*apfu*).

TABLE 5. COMPOSITION OF THE Pb-BEARING SOLID SOLUTION, ZOLOTAYA RIVER PLACER

No.	1	2	3		1	2	3	1	2	3
Sample	ZL30	ZL30	ZL30		ZL30	ZL30	ZL30	ZL30	ZL30	ZL30
S wt.%	18.71	16.16	15.48	S *apfu*	14.92	14.46	14.48	3.73	3.62	3.62
Pb	7.54	1.60	4.07	Pb	0.93	0.22	0.59	0.23	0.06	0.15
Rh	4.53	1.74	1.05	Rh	1.13	0.49	0.31	0.28	0.12	0.08
Pd	-	-	-	Pd	0.00	0.00	0.00	0.00	0.00	0.00
Pt	30.68	65.93	65.01	Pt	4.03	9.70	10.00	1.01	2.42	2.50
Ir	26.49	9.91	9.58	Ir	3.53	1.48	1.50	0.88	0.37	0.37
Fe	0.38	0.18	0.09	Fe	0.17	0.09	0.05	0.04	0.02	0.01
Cu	8.17	3.44	2.29	Cu	3.29	1.55	1.08	0.82	0.39	0.27
Total	96.50	98.96	97.57	Total	28.00	28.00	28.00	7.00	7.00	7.00

Note: Ru, Os, Bi, Pd, Sn, Sb, Te, As, Ni were not detected; - below detection limit. The chemical data were recast in atoms per formula unit (*apfu*) as if the mineral is konderite (28 *apfu*) and xingzhongite (7 *apfu*).

PGE arsenides and sulfarsenides

As-bearing PGM are relatively rare. They are commonly represented by sperrylite and occur as rim phases around grains of Pt–Fe alloy or fill cavities after leached magmatic Os–Ir lamellae in Pt–Fe alloy. There are also inclusions of iridarsenite and irarsite in association with minerals of the cherepanovite–ruthenarsenite solid solution (Table 4).

Discussion and Conclusions

The Zolotaya River placer contains primary (magmatic) and secondary PGM (Table 7). The primary minerals are Pt–Fe alloy, Os–Ir–Ru alloy, cooperite (in multiphase inclusions), laurite, erlichmanite, cuprorhodsite, cherepanovite and iridarsenite. The secondary minerals are distinguished by their occurrence in reaction rims around grains of Pt–Fe alloy and are represented by cooperite, irarsite, platarsite and sperrylite.

Pt–Fe alloy is the main PGM in the Zolotaya River placer. The Fe content (including Ni and Cu) varies from 14 to 30 at.%, which is characteristic of native platinum and ferroan platinum alloy (Cabri & Feather 1975). Its average composition (n = 21) is: 87.84 ± 3.25 wt.% Pt (73.35 ± 5.89 at.%), 6.88 ± 2.37 wt.% Fe (19.69 ± 5.72 at.%), 0.85 ± 0.73 wt.% Os, 0.09 ± 0.09 wt.% Ru, 1.58 ± 0.65 wt.% Rh, 0.47 ± 0.31 wt.% Pd, 0.67 ± 1.42 wt.% Ir, 0.13 wt.% ± 0.11 wt.% Ni, and 0.61 ± 0.21 wt.% Cu. The main minor PGE present is rhodium. Pt–Fe alloy of similar composition is typical of Uralian–Alaskan-type deposits (Cabri *et al.* 1996).

Ir-bearing Pt–Fe alloy forms three different morphological types: (1) lattice-like intergrowths (exsolution fabric) with Ir–Os–Ru–Pt alloy (Fig. 6a), (2) irregular patchy inclusions in Ir–Os–Ru–Pt alloy (Fig. 6c), and (3) a grain matrix with subhedral inclusions of iridium (Fig. 6d).

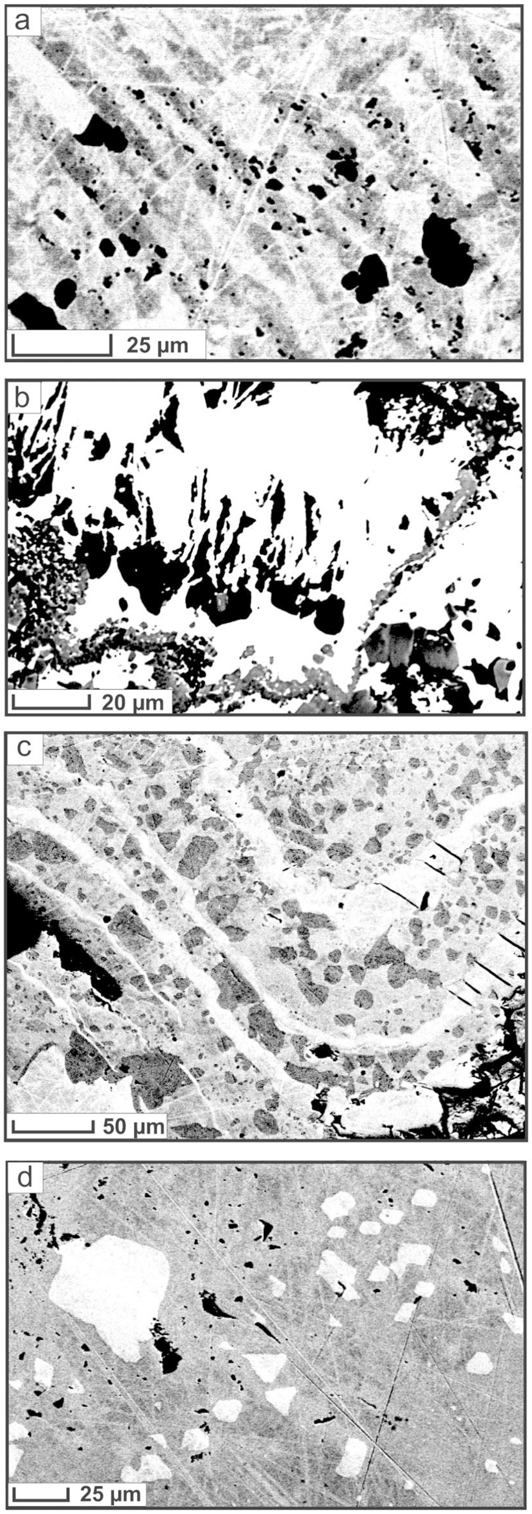


FIG. 6. Back-scattered electron (BSE) images of different exsolution-induced textures of Ir–Os–Ru–Pt alloy from Zolotaya River. a. Micrographic intergrowth of Ir-rich Pt–Fe alloy (white) with Ir–Ru–Pt alloy (grey), and cherepanovite inclusions (dark grey). Sample ZL22. b. Rim zone of Pt–Ir–Fe–Ru alloy (white) with symplectitic inclusions of Ru-rich cherepanovite (black). Irarsite (dark grey) occurs as a reaction rim and on fractures. Sample ZL22. c. Patchy inclusions of Ir-rich Pt–Fe alloy (dark grey) in iridium matrix (grey) and ribbon-like osmium (white). Sample ZL2. D. Subhedral inclusions of iridium (white) in Ir-rich Pt–Fe alloy (grey). Sample ZL14.

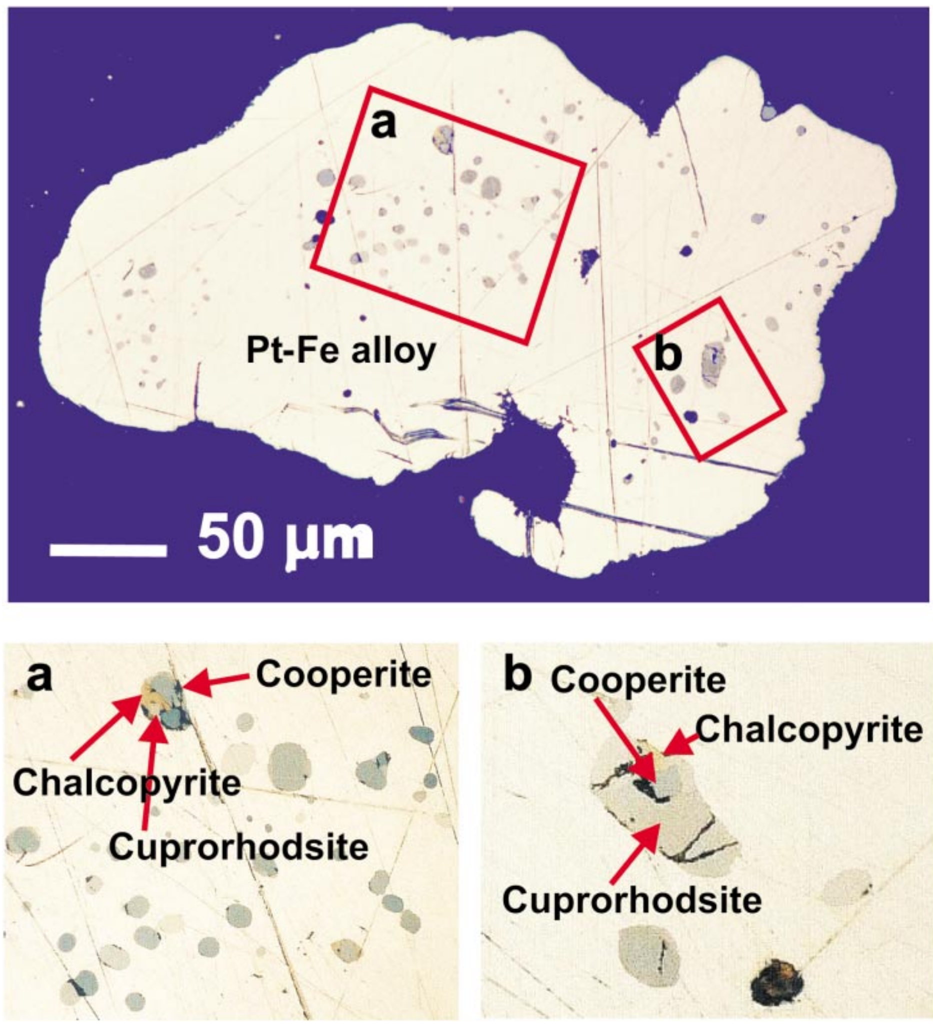


FIG. 7. Cooperite inclusions in Pt–Fe alloy. Sample ZL–1/7.

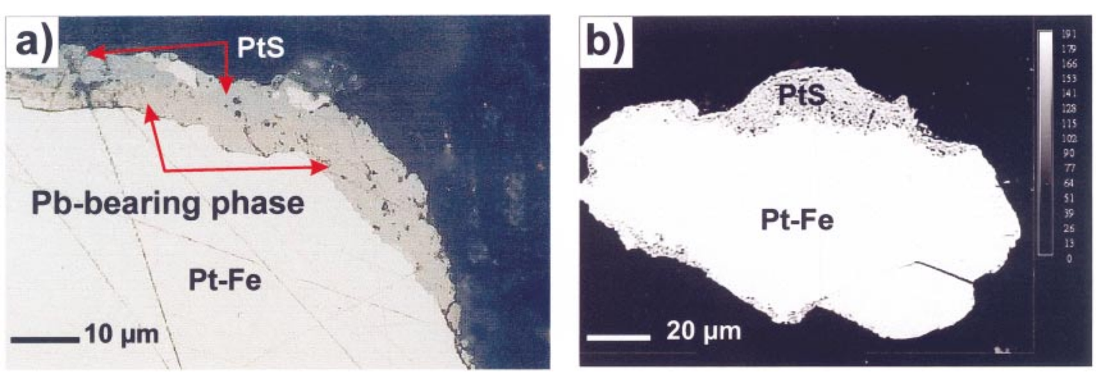


FIG. 8. Secondary rim of cooperite (a) intergrown with Pb–Ir–Cu–Rh sulfide (xingzhongite or konderite) and of cooperite (b) on Pt–Fe alloy.

The triangular diagram (Pt + Fe) – (Os + Ru) – (Ir + Rh) of Slansky *et al.* (1991) allows an estimate of the temperature of formation and was applied to the Uralian–Alaskan-type intrusions at Fifield, Nizhni Tagil and Durance River (Slansky *et al.* 1991), Inagli (Tolstykh & Krivenko 1997), Salmon River (Tolstykh *et al.* 2002), and Kondyor and Guli (Malitch & Thalhammer 2002). The composition of multiphase assemblages from the Zolotaya River is plotted in relation to temperature of formation (Fig. 10). Grain ZL22 shows the highest temperature, >850°C. Sample ZL2 shows step-like exsolution, with an Ir content corresponding to 800°C. The formation of iridium and Ir-rich Pt–Fe alloy (3.72 wt.% Ir) took place at a temperature slightly below 750°C (sample ZL14). In sample ZL-1/6, native osmium formed first, followed by phases rich in Ir (at temperatures >850°C). The textural evidence of the multiphase associations of minerals and the interpretation of the compositional data with the help of the diagram of Slansky *et al.* (1991) point to high-temperature formation of the Ir–Os–Ru–Pt alloy, similar to that for the Inagli, Kondyor and the Alaskan intrusions.

Cooperite is the most common PGE sulfide mineral, and occurs both as a primary inclusion phase enriched in Pd, and as a secondary rim. The absence of nickel in cooperite from the Zolotaya River placer is typical of Uralian–Alaskan-type deposits.

Cuprorhodsite belongs to the group of PGE-bearing thiospinels, *i.e.*, cuprorhodsite – cuproiridsite – malanite – ferrorhodsite solid solution. These minerals are most abundant in Uralian–Alaskan-type deposits (Cabri *et al.* 1981, Rudashevsky *et al.* 1985a, Nekrasov *et al.*1994, Augé *et al.* 2002, Garuti *et al.* 2002), but they occur also in ophiolitic complexes (Corrivaux & Laflamme

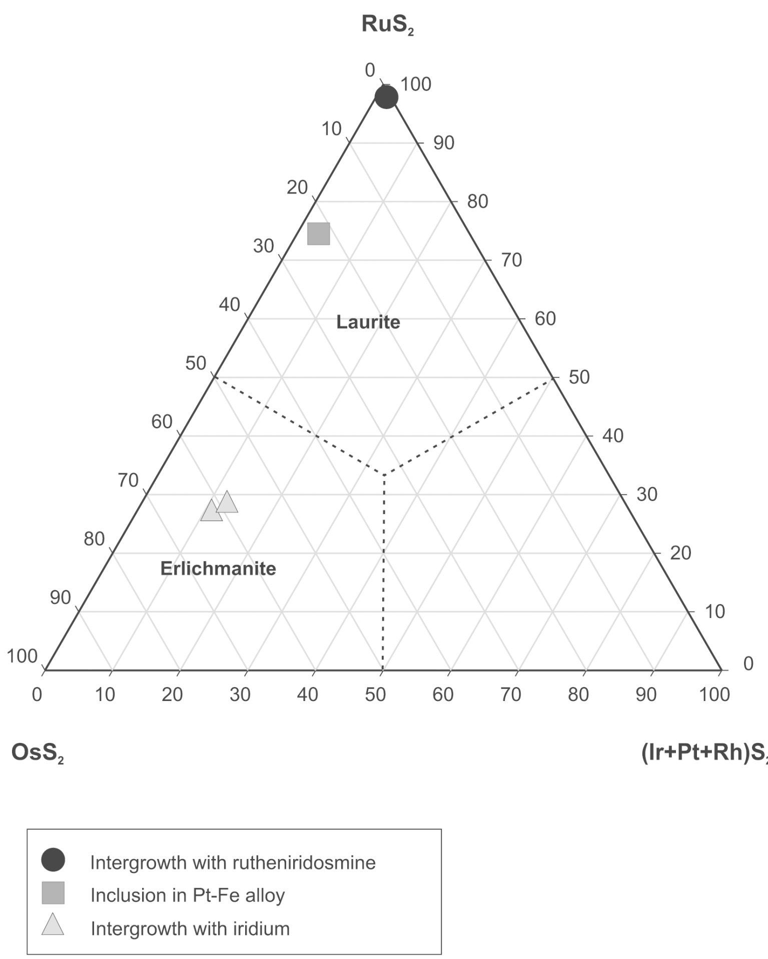


FIG. 9. Mineral composition of the laurite–erlichmanite solid-solution series (at.%).

1990, Augé & Maurizot 1995, Garuti *et al.* 1999), Alpine-type complexes (Garuti *et al.* 1995), and in layered mafic-ultramafic intrusions (Barkov *et al.* 1997, 2000). The cuprorhodsite–cuproiridsite series shows complete solid-solution, whereas pure malanite is not described in the literature. The cuprorhodsite from the Zolotaya placer is similar to occurrences in eastern Madagascar, Burma, Borneo, Ecuador, India (Baula), and Russia (Chukotka) (Fig. 11). In general, the Ir content of minerals of the cuprorhodsite–cuproiridsite solid-solution series from these occurrences is very low. Judging from the distribution of minerals at the different localities, there is no visible correlation between type of deposit and cuprorhodsite – cuproiridsite – malanite mineral composition. Rather, a compositional control is exerted by the saturation of the ore-forming system in a mineral phase containing Rh, Ir, and Pt.

Many investigators examining the PGM in Uralian–Alaskan-type deposits have given detailed descriptions of multiphase inclusions. In general, the inclusions consist of base-metal sulfides and (Pd,Pt,Rh) sulfides and tellurides. Pt–Pd mineral assemblages are characteristic of the PGM occurrences of the Durance River, France, and Pustaya River, Kamchatka, Russia (Johan *et al.* 1990, Tolstykh *et al.* 2000). Rh–Pd mineral assemblages are more common in the Santiago River, Ecuador (Weiser & Schmidt-Thomé 1993). Rh-bearing minerals are also most typical of multiphase inclusions from the Zolotaya River placer.

Such multiphase inclusions were described also in PGM from the ophiolitic complexes of northwestern Salair, Russia (Tolstykh *et al.* 1999), Troodos, Cyprus (McElduff & Stumpfl 1990), and Kraubath, Austria (Malitch *et al.* 2001), as well as in the Alpine-type complex of Ronda, southern Spain (Torres-Ruiz *et al.* 1996). The most typical paragenesis of these complexes consists of laurite + (Pt,Ir,Rh,Ni,Fe,Cu)-bearing sulfides and base-metal sulfides (including millerite, NiS). The study of multiphase inclusions leads to the assumption that complex solid-solutions of Pt, Fe, Ir, Rh, Pd, Cu, Ni, Au and S exist at high temperature (Johan *et al.* 1990). Tolstykh *et al.* (2000) suggested that these inclusions form from vapor-saturated residual melt in a closed-system situation in gas-rich miaroles.

Minerals of the erlichmanite–laurite solid-solution series vary from pure laurite (in association with ruthenarsenite), through Os-bearing laurite (in association with Pt–Fe alloy) to erlichmanite (in association with iridium). Rhodium is present up to 2.07 wt.%, which is one distinguishing feature of Uralian-Alaskan-type deposits (Johan *et al.* 1989).

Cherepanovite is a rare mineral. It was first described in the deposits of the Koryaksko–Kamchatskiy Ultrabasic Belt (Rudashevsky *et al.* 1985b). Cherepanovite has also been found in New Zealand (Railton & Watters 1990), Tasmania, Australia (Botrill 1993), and the Polar and Southern Urals of Russia (Garuti *et al.* 1999, Britvin *et al.* 1999). Cherepanovite occurs in two varieties in the Zolotaya River samples: (1) relatively poor in Ru in core zones, and (2) richer in Ru in the rim zones. The high Ru content of cherepanovite leads to the infeence that there is a wide range of solid solution between cherepanovite and ruthenarsenite at high temperature.

All mineralogical and chemical observations point to a connection of the Zolotaya and Fadeevka River placers to the Late Permian dunite – hornblendite – gabbro intrusions of Uralian–Alaskan-type. The composition of the chromite from heavy-mineral concentrates and from inclusions within PGM from the Zolotaya placer is typical of Uralian–Alaskan-type intrusions, *i.e.*, high chromium and iron content at relatively low titanium content. The primary PGM are dominated by Pt–Fe alloy (about 90%), and Os–Ir–Ru alloy is subordinate. All other PGM occur as rim or inclusion phases in the primary PGE alloys. Cooperite is impoverished in Ni. Rhodium and Cu are invariably present as minor elements of the Pt–Fe alloy, and the minerals of the laurite–erlichmanite solid-solution series have an elevated Rh content. Other Rh-bearing minerals present are cuprorhodsite and cherepanovite. The distinct rhodium-enrichment signature is one of the main features of Uralian–Alaskan type deposits.

TABLE 6. SELECTED COMPOSITIONS OF LAURITE, ZOLOTAYA RIVER PLACER

No.	1	2	3		1	2	3
Os wt.%	0.69	20.24	47.69	Os *apfu*	0.01	0.20	0.58
Ru	57.12	38.31	12.07	Ru	0.94	0.72	0.28
Ir	1.69	2.35	10.12	Ir	0.01	0.02	0.12
Rh	1.22	2.07	0.28	Rh	0.02	0.04	0.01
Pt	2.49	2.21	0.35	Pt	0.02	0.02	0.00
S	38.65	33.34	27.66	S	2.00	1.96	2.01
As	-	1.53	-	As	0.00	0.04	0.00
Total	101.86	100.05	98.17	Total	3.00	3.00	3.00

Note: 1: intergrown with zonal rutheniridosmine; 2: inclusion inside Pt–Fe grain; 3: intergrown with grain of iridium. Pb, Bi, Pd, Sn, Sb, Te, Ir, Ni, Fe, Cu were not detected; - below detection limit. The raw data are recast in terms of atoms per formula unit (*apfu*).

TABLE 7. PGM IN THE ZOLOTAYA RIVER PLACER

Mineral	Formula	Origin	Abundance
Pt–Fe alloy		magmatic	++++
Os–Ir–Ru alloy		magmatic	++
Cooperite	PtS	magmatic	+
		secondary	+++
Laurite	RuS_2	magmatic	+
Erlichmanite	$(Os,Rh,Ir)S_2$	magmatic	+
Cuprorhodsite	$CuRh_2S_4$	magmatic	+
Cherepanovite	RhAs	magmatic (?)	++
Unnamed mineral	(Rh,Ru,Ir)As	magmatic (?)	++
Iridarsenite	$(Ir,Ru)As_2$	magmatic (?)	++
Irarsite	(Ir,Ru)AsS	secondary	++
Platarsite	(Pt,Rh)AsS	secondary	+
Sperrylite	$PtAs_2$	secondary	+
Konderite or Xingzhongite (?)		secondary	+

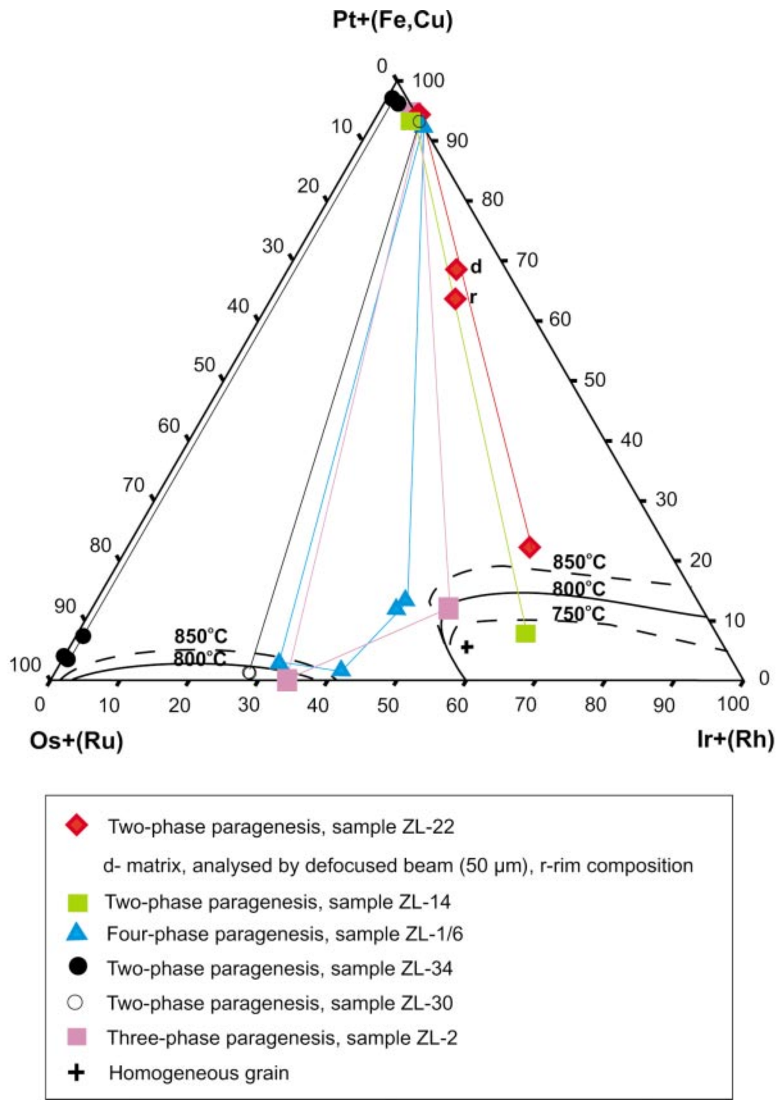


FIG. 10. Phase diagram of the Pt + (Fe,Cu) – Os + (Ru) – Ir + (Rh) system (Slansky *et al.* 1991).

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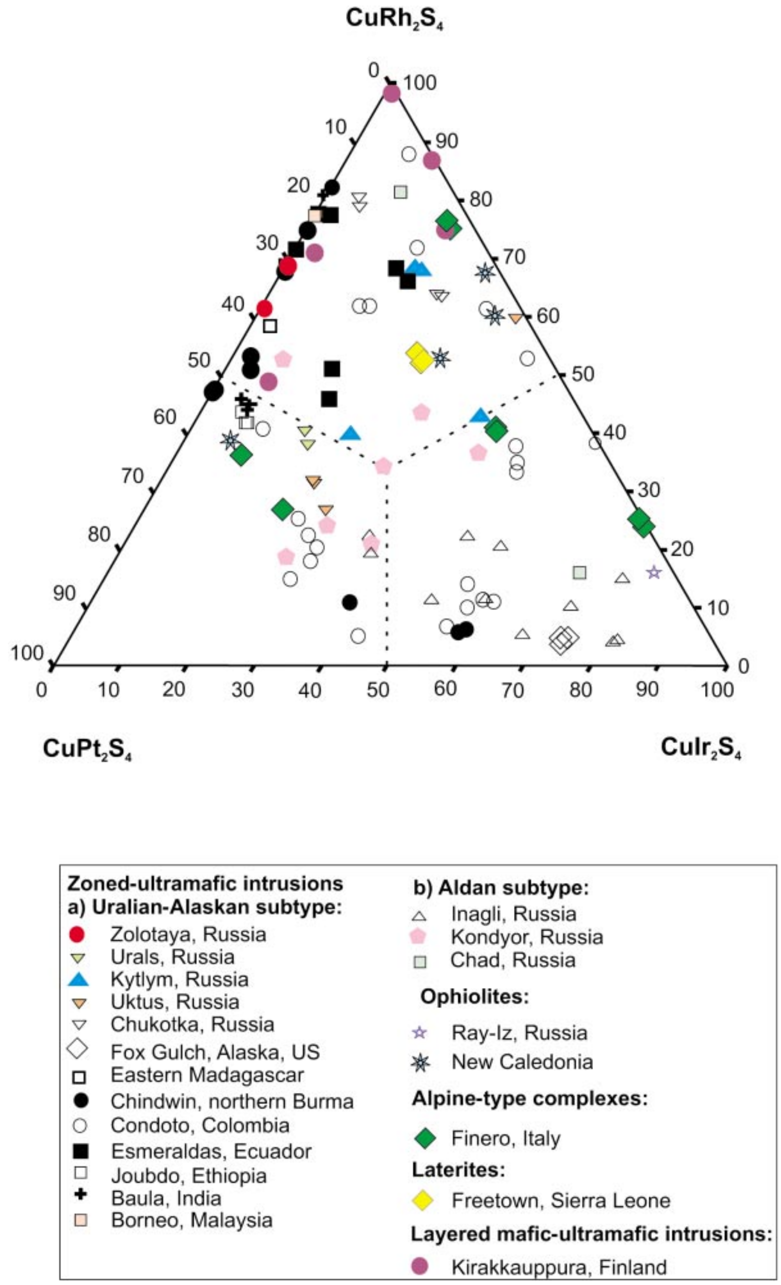

FIG. 11. Diagram showing the cuprorhodsite – cuproiridsite – malanite solid solution (at.%). Data sources: Augé & Legendre (1992), Augé & Maurizot (1995), Augé *et al.* (2002), Barkov *et al.* (2000), Cabri *et al.* (1996), Garuti *et al.* (1995, 1999, 2002), Nekrasov *et al*. (1994), Tolstykh & Krivenko (1997).

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