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Genetically indicative features of Pt-Fe and Os-Ir-Ru alloy crystals from placers in SW Bulgaria

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Abstract. Pt-Fe and Os-Ir-Ru alloy crystals from sediments of the Kyustendil, Blagoevgrad and Gotse Delchev grabens, SW Bulgaria, were investigated. Pt-Fe alloy crystals are presented by simple cubic $a\{100\}$ or octahedron $o\{111\}$ forms, or as combinations of both forms, sometimes also with $d\{110\}$ faces. The crystals of Os-Ir-Ru alloys include osmium and ruthenium minerals, and are presented by combinations of hexagonal prism, hexagonal bipyramide and pinacoid. The primary morphological features of the crystals, the relatively homogeneous and constant composition and the character of the inclusions (Pt-Fe alloys, osmium, cuprorhodsite, bowieite, bornite, chromian spinel and clinopyroxene) in them show that they have magmatic, high-temperature origin, as Pt-Fe alloys are formed first. Some secondary morphological changes are connected only with the mechanical transportation in the placer. Dunites and peridotites from the surrounding massifs of the grabens are the most probable sources of the crystals investigated.

Key words: Pt-Fe alloys, Os-Ir-Ru alloys, placers, dunites, peridotites

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Резюме. Изследвани са кристали на Pt-Fe и Os-Ir-Ru сплави от алувиални седименти (Q) на Гоцеделчевския, Благоевградския и Кюстендилския грабен, ЮЗ България. Първите са представени от простите форми куб $a\{100\}$ и октаедър $o\{111\}$, или от техните комбинации, рядко и с $d\{110\}$ стени. Os-Ir-Ru сплави включват минералните видове осмий и рутений и са представени от комбинации на хексагонална призма, хексагонална бипирамида и пинакоид. Първичните морфоложки особености на кристалите, сравнително постоянния и равномерен състав и характера на включенията (Pt-Fe сплави, осмий, купрородсит, боуиит, борнит, хромов шпинел и клинопироксен) в тях показват, че те имат магматичен (високотемпературен) произход, като първи са образувани Pt-Fe сплави. Вторичните им морфоложки промени са свързани само с механичния транспорт в разсипите. Като най-вероятни източници на разглежданите кристали са дунити или перидотити от оградните масиви на грабените.

Ключови думи: Pt-Fe сплави, Os-Ir-Ru сплави, разсипи, дунити, перидотити

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Introduction

Investigations using original gravitational concentrators revealed the presence of platinum-group minerals (PGM) in alluvial deposits (Q) of the Kyustendil, Blagoevgrad and Gotse Delchev grabens (Tsintsov, 1994). Some samples of the individual grains of the Pt-Fe and Os-Ir-Ru alloys are everywhere presented by crystal forms. The morphology is the basis to consider these minerals as low-temperature products, formed by agglutination of the elements in exogenic conditions (Augustithis, 1965, 1967; Cousins, Kinloch, 1976; Bowles, 1986; Bowles et al., 1994, etc.). Recently, however, numerous studies have proved that they are formed in magmatic conditions and are concentrated in the placers only along their mechanical transportation (Hagen et al., 1990; Nixon et al., 1990; Weiser, Schmidt-Thomé, 1993; Krstić, Tarkian, 1997, etc.).

The aim of the present paper is to characterize the features of the crystal forms of the platinum-group elements (PGE) alloys from the above-mentioned deposits and to clarify their genesis. Such investigations are basis for various genetic reconstructions (Kostov, 1993). Crystals from placers help, in addition, to clarify the conditions of their transportation and deposition. This is a good reason to consider that the mineralogical characteristics of Pt-Fe and Os-Ir-Ru alloy crystals isolated from the sediments of SW Bulgaria provide basis for some assumptions about the processes, which led to their formation and consequent changes in exogenic conditions.

Detailed data on the geology of the region are given by Bakalov (1977), Zagorćev (1992), Bakalov and Jelev (1996), etc.

Material and methods of study

Samples from different areas of the grabens with volume >1000 m^3 each were processed with gravitational concentrators. They were further panned to obtain a superconcentrate with a predominant content (>55-60%) of placer gold. Each superconcentrate was passed through a sieve complect (BDS - 5641-75) and Pt-Fe and Os-Ir-Ru alloy crystals were isolated from the fractions between 80 and 500 μm.

The morphology of the crystals was studied by a scanning electron microscope Philips SEM-515. The chemical composition of the samples and the mineral inclusions in them were analyzed by quantitative point analyses, scanning along profile lines and total surface scanning. The analyses were performed by an energy dispersive analytical attachment (EDAX PV 9100) at 30 kV, 0.5 nA and time of 80 sec. Pure metals were used as standards for the PGE, a marcasite standard for Fe and S, and a cuprite standard for Cu X-ray diffraction data from single grains were obtained by a Gandolfi camera (57.3 mm diameter).

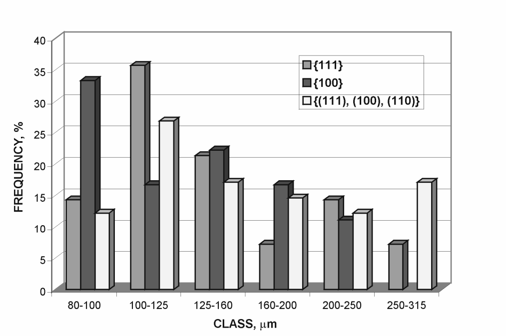

Fig. 1. Frequency distribution of Pt-Fe alloy crystals from deposits of SW Bulgaria in different grain-size fractions

Фиг. 1. Разпределение на кристали от Pt-Fe сплави от седименти на ЮЗ България по зърнометрични фракции

Mineralogy

The crystals from the Blagoevgrad graben depositions predominate because greater volumes from these sediments were processed. The samples of certain mineral and morphological species display similar features and, therefore, no subdivision in respect to deposits is made. The results of X-ray phase identification of the studied alloys was published earlier (Tsintsov, 1999). The data showed that Pt-Fe crystals (73 samples) are represented by native platinum and isoferroplatinum. This summarized notification for the two minerals is accepted following the recommendation of Cabri and Feather (1975). The crystals of Os-Ir-Ru alloys include osmium (3 in number) and ruthenium (8 in number) minerals, which display identical combination forms.

Grain size and morphological features. The distribution of Pt-Fe alloys in grain size fractions is represented in Fig. 1 and, of Os-Ir-

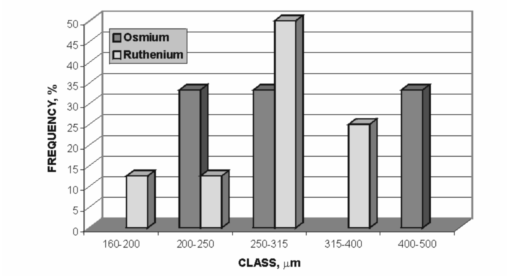

Fig. 2. Frequency distribution of Os-Ir-Ru alloy crystals from deposits of SW Bulgaria in different grain-size fractions

Фиг. 2. Разпределение на кристалите от Os-Ir-Ru сплави от седименти на ЮЗ България по зърнометрични фракции

Ru alloys – in Fig. 2. The former are distributed in the fractions from 80 to 315 μm while the latter – in the fraction from 160 to 500 μm.

The crystals of Pt-Fe alloys are represented by simple forms of cube $a\{100\}$ and octahedron $o\{111\}$, as well as by combinations of both forms, rarely complicated by rhombododecahedron $d\{110\}$ (Fig. 3, a-d). The combination forms are dominating (56%), followed by cubes (25%), and octahedrons (19%). The combinations are predominantly isometric, rarely elongated along one of the crystallographic axes. In the latter case all the faces are distorted to a certain extent. Well-developed {100} faces are most frequent. Single crystals elongated along one of the axes and attaining pseudotetragonal habit rarely occur. Best developed in the studied crystals are the octahedrons.

The natural surfaces of the crystals are coarse and with white to light-gray colour and metal luster. Very often they are eroded by singular oval caverns with sizes from 3 to 12 μm or by scratches caused by harder particles during the mechanical transport. Rarely, some negative relief forms are filled up with Fe oxides. The polished surfaces are dense, homogeneous, isotropic, and without disturbances. Only the surface of one bowieite octahedral crystal contained many elliptical caverns sized 6-8 μm.

The crystals of osmium and ruthenium display the following combinations: hexagonal prism, hexagonal bipyramide and pinacoid (Fig. 3, e, f). The hexagonal prism is often rounded and only separate parts from it are preserved. The pinacoid is well expressed but in the majority of cases it is disrupted by fissures. The natural surfaces are coarse, dense, and homogeneous. They can be perfectly polished and the obtained surfaces are homogeneous and weakly anisotropic.

Composition. The composition is presented in Table 1. The Pt-Fe crystals display insignificant variations in composition. All samples predominantly contain Pt, Fe, and Cu. The content (at.%) of Pt in the different crystals is from 69.48 to 80.21; of Fe – from 11.28 to 24.49; and of Cu – from 0.59 to 1.93. The rest of the elements in the composition of the crystals are those of PGE – Rh and Ir. Rh is detected in almost two thirds of the analyzed samples reaching in some of them up to 11.35 at.%. Ir (up to 1.75 at.%) is contained predominantly in the octahedral crystals. Correlation between composition and morphology was not found.

The Os-Ir-Ru alloys are composed entirely of PGE with the only exception of the osmium crystal which contains insignificant quantities of Fe (1.04 at.%). These compositions are disposed in the mineral regions only of Os-Ir-Ru triangular diagram (according to Harris and Cabri, 1991). About 73 % of these compositions fall in the field of ruthenium (8 compositions) and 27% (3 compositions) – in the field of osmium. Except for the three main elements in the composition of one osmium crystal, presence of additional Pt (1.51 at.%) was found. For the osmium crystals, the contents of the elements vary as follows (at.%): Os, from 51.84 to 57.03, Ir, 22.68-30.68, and Ru, 11.25-25.48. For the ruthenium crystals the variations are: Ru 58.94-65.02, Os 7.14-26.75, and Ir 14.31-27.84.

The distribution of the elements in the studied crystals is relatively uniform. Deviations from this tendency exist for the Os-

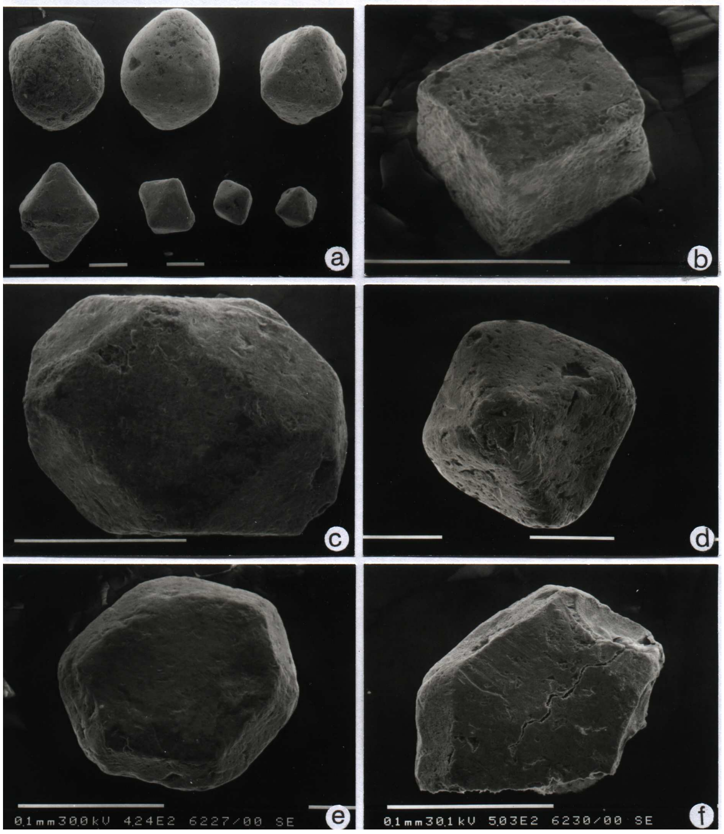

Fig. 3. PGE alloy crystals from deposits of SW Bulgaria: Pt-Fe alloys (a-d); Os-Ir-Ru alloys (e, f). Natural surfaces. SEM. Scale bar - 100 μm (a-f)

Фиг. 3. Кристали на сплави на ЕГП от седименти на ЮЗ България: Pt-Fe сплави (a-d); Os-Ir-Ru сплави (e, f). Естествени повърхности. СЕМ. Маркер - 100 μm (a-f)

Ir-Ru alloys but without definite regularities. The variance in the element distribution between rim and core in the Pt-Fe alloys is negligible. In this sense, the variation in the content of the elements in the different parts of Os-Ir-Ru alloys does not display a local character from the type “rim-core” which is an indication that these samples are not a result of exogenic processes.

Inclusions of other minerals in the samples were observed mainly in the crystals with combined forms. In Pt-Fe alloys they were presented by osmium, cuprorhodsite, bornite, chromian spinel and clinopyroxene, and in Os-Ir-Ru alloys - by Pt-Fe alloys and bornite. Bornite was found in one cubic crystal and bowieite, as many inclusions in an octahedral crystal.

The osmium inclusions have elongated, rod-like shapes and rounded ends (Fig. 4, a, b). The length of the largest inclusion reaches 70-75 μm with width up to 8-10 μm. During polishing osmium obtains a positive relief with respect to the matrix which is due to its greater hardness. Most of the inclusions are of pure Os. Admixtures of Rh (up to 7.68 at.%) and Ir (up to 3.96 at. %) are sometimes observed.

The inclusions of Pt-Fe alloys most frequently have irregular form with rounded edges. A rare finding with crystal faces and dimensions of 6-7 μm was observed in osmium (Fig. 4, c).

Spherical cuprorhodsite inclusions (with

Table 1. *Composition of Pt-Fe and Os-Ir-Ru alloy crystals from deposits of SW Bulgaria, wt.%*
Таблица 1. *Състав на кристали на Pt-Fe и Os-Ir-Ru сплави от седименти на ЮЗ България, тегл.%*

N	Pt	Rh	Ir	Ru	Os	Fe	Cu	Total
				Pt-Fe alloy				
1.	88.39	6.45	-	-	-	4.38	0.24	99.46
2.	90.65	4.61	-	-	-	4.19	0.31	99.76
3.	91.79	2.86	-	-	-	5.00	0.42	100.07
4.	86.20	7.43	-	-	-	6.48	0.38	100.49
5.	88.25	2.65	-	-	-	8.58	0.28	99.76
6.	89.48	3.87	-	-	-	5.90	0.41	99.66
7.	90.95	3.90	-	-	-	4.22	0.65	99.72
8.	91.28	1.18	1.83	-	-	4.61	0.74	99.64
9.	91.46	-	-	-	-	7.89	0.51	99.86
10.	90.74	-	-	-	-	8.53	0.42	99.69
11.	91.02	1.44	-	-	-	7.13	0.21	99.80
12.	92.59	-	-	-	-	7.21	0.24	100.04
				Ruthenium				
13.	-	-	19.43	42.59	37.85	-	-	99.87
14.	-	-	31.42	43.61	24.55	-	-	99.58
15.	-	-	29.02	47.61	23.15	-	-	99.78
16.	-	-	28.14	48.69	22.98	-	-	99.81
17.	-	-	35.41	48.84	15.36	-	-	99.61
				Osmium				
18.	-	-	27.81	15.29	56.49	-	-	99.59
19.	1.64	-	29.32	10.45	58.11	-	-	99.52
20.	-	-	32.61	6.94	59.34	0.38	-	99.27

Analyses NN 1-3, 13, 14 and 18 are of samples from the Kyustendil graben; NN 4-9, 15-17 - from the Blagoevgrad graben and NN 10-12, 19, 20 - from the Gotse Delchev graben

Анализи NN 1-3, 13, 14 и 18 са на образци от Кюстендилския грабен; NN 4-9, 15-17 - от Благоевградския грабен и NN 10-12, 19, 20 - от Гоцеделчевския грабен

sizes up to 8 μm) dominate near the rims of the samples (Fig. 4, d). They take a good polish but at the boundary with the matrix it is coarse and irregular. Under reflected light they are isotropic, dark grey with slight colour variations. Cuprorhodsite is homogeneous in composition within a given inclusion, while the Rh/Cu ratio varies between inclusions in different host grains. The S content in the samples is constant. The composition of the inclusions is from $Cu_{0.94}Rh_{2.06}S_{4.00}$ to $Cu_{1.02}Rh_{1.98}S_{4.00}$, and often includes small quantities of Fe and Ni.

The bowieite inclusions are rounded or irregular, nearly isometric in form (Fig. 4, e, f), with dimensions from 3 to 12 μm. Their surface is rough, uneven and is badly polished. They are formed only by Rh, Ir and S with a composition from $(Rh_{1.52}Ir_{0.48})_{2.00}S_{3.00}$ to $(Rh_{1.59}Ir_{0.41})_{2.00}S_{3.00}$. Single inclusions have a metal deficiency, similar to that described by Desborough and Criddle (1984).

Bornite inclusions have isometric or slightly elongated shapes with sizes from 8 to 25 μm (Fig. 5, a, b). Under reflected light their surface is smooth, well-polished and with dark brown colour. The composition of most bornite inclusions is close to the mineral stoichiometry. No other admixture elements were found in the bornite grains. The chromian spinel inclusion has a rectangular shape and size 7.5×4.8 μm (Fig. 5, c). Its surface is smooth, without defects, with dark and semi-dark areas, most probably due to its various thickness. Its composition is with high content of of Cr (43.56 wt.% Cr_2O_3) and relatively low content of Fe (19.84 wt.% Fe_2O_3) and Al (7.19 wt.% Al_2O_3).

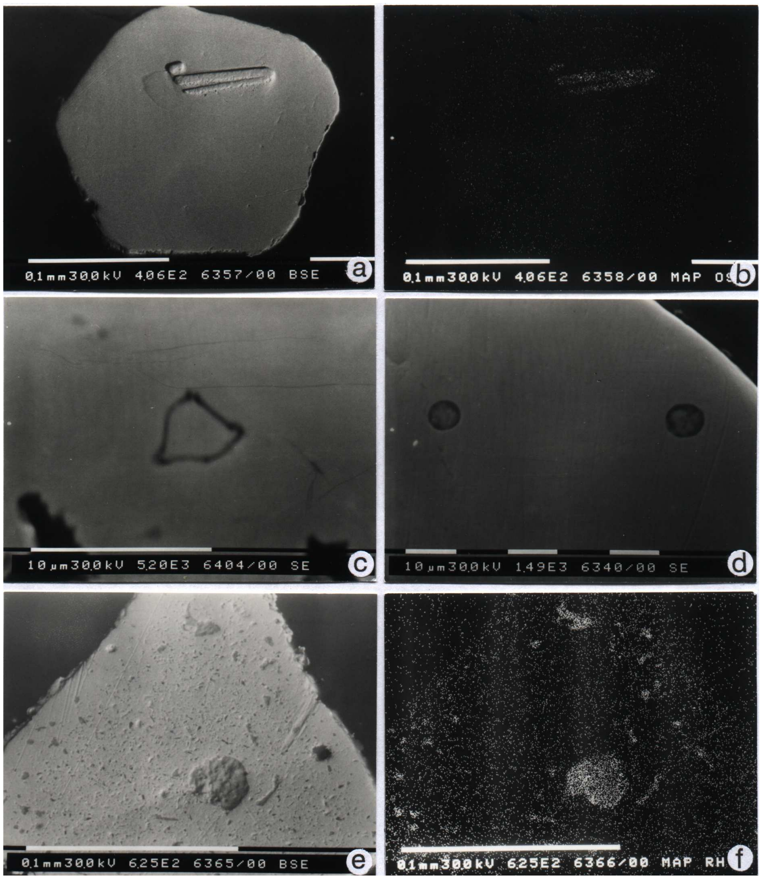

Fig. 4. Inclusions of other minerals in PGE alloy crystals from deposits of SW Bulgaria: osmium (a), cuprorhodsite (d) and bowieite (e) in Pt-Fe alloys; Pt-Fe alloy crystal in osmium (c); single element scans for Os (b) and Rh (f) in samples, respectively “a” and “e”. Polished section. Scale bar - 10 μm (c, d), and 100 μm (a, b, e, f)

Фиг. 4. Включения от други минерали в сплави на ЕГП от разсипи на ЮЗ България: осмий (a), купрородсит (d) и боуиит (e) в Pt-Fe сплави; кристал от Pt-Fe сплав в осмий (c); разпределение на Os (b) и Rh (f) в образци, съответно “a” и “e”. Полирани шлифи. Маркер - 10 μm (c, d) и 100 μm (a, b, e, f)

Clinopyroxene (probably augite) is included in the rim of crystals with combined forms (Fig. 5, d), well-shaped, with dimensions of the faces between 8 and 12 μm. Its surface is irregular, badly polished and concave. A part of it probably eroded during polishing.

Exogenic morphological changes. All crystals display common secondary marks caused by the mechanical transport. Crystals from the finer fractions are less affected by the exogenic mechanical influence than the coarser fractions. Their bounding elements (apexes, edges, and faces) are mechanically processed to a different extent. The apexes are most influenced while the faces are weakly corroded which is well demonstrated by the octahedral crystals. Among Pt-Fe crystals the combinations are most processed. Some of the combinations are rounded and even attaining the shape of spheres.

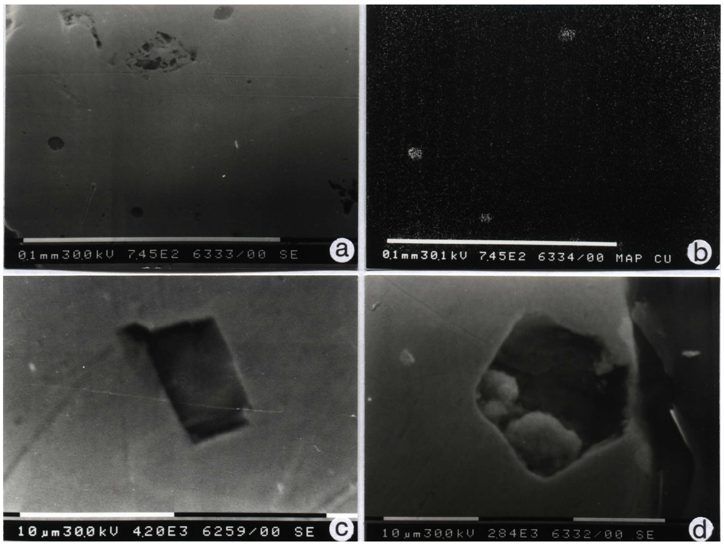

Fig. 5. Inclusions of bornite (a), chromian spinel (c) and clinopyroxene (d) in Pt-Fe alloy crystals from deposits of SW Bulgaria; single element scans for Cu in sample "a". Polished section. Scale bar - 10 μm (c, d), and 100 μm (a, b)
Фиг. 5. Включения от борнит (а), хромов шпинел (с) и клинопироксен (d) в Pt-Fe сплави от разсипи на ЮЗ България; разпределение на Cu в обр. "а". Полирани шлифи. Маркер - 10 μm (c, d) и 100 μm (a, b)

Discussion

A vigorous discussion emerged among the researchers on PGM from placer deposits concerning the conception about the formation of native platinum in laterite weathering crusts (on the example of Yubdo deposit, Ethiopia) through agglutination of the elements (Augustithis, 1965, 1967). Based on data from the study of Pt-Fe alloys, this idea has been lately accepted and further developed (Cousins, Kinloch, 1976; Bowles, 1986). Bowles et al. (1994) state that the large size (0.5-3.0 mm) and the crystal forms of PGM representatives prove that no mechanical transport of the grains had taken place. According to these authors, PGE can be transported in laterite conditions by solutions, and in case of suitable environment they form PGM "in-situ".

The studies of Evstigneeva et al. (1992) on PGM from Yubdo did not confirm such conception. These authors consider the proofs of Augustithis (1965, 1967) for the formation of these minerals in "cool" media as not enough and that the "angular" edges do not witness for "freshly-formed" crystals in laterite conditions.

There are also a lot of studies on placer PGM which prove that these minerals had been formed as a result of high-temperature (magmatic) processes (Cabri, Harris, 1975; Nixon et al., 1990; Augé, Legendre, 1992; Hagen et al., 1990, etc.). The isotopic homogeneity of Os and the low values of the $^{187}Os/^{186}Os$ ratio gave reason to Hattori and Cabri (1992) to conclude that placer alloys of PGE are a product of magma from mantle origin. According to these authors the exogenic influence is of mechanical character and their only role is to concentrate the grains in the placer.

Main arguments concerning the origin of PGM in placer deposits must be based on their grain size, habit, composition, and characteristics of PGM and silicate inclusions established in their matrix (Augé, Legendre, 1992). In the light of such considerations the studied crystals display the following peculiarities:

- The prevailing part of crystals is distributed in fractions <200 μm, forming the category of the so-called "floating" particles (Shillo, 1985). Our observations show that crystals from fractions 200-500 μm (some of them with weight >2 mg) also "float" stably. Their hydrophobic properties and the surface strain of water are the reason for this state in which the grains can be transported to a great distance. According to Hagen et al. (1990), crystals of PGE sized up to 200 μm can be transported in alluvium to a distance of hundreds of kilometers without serious disturbance of their primary forms.

- The secondary morphological *changes* of the crystals are result mainly of the abrasive action of the water stream containing floating particles. The different speed and the turbulent motion of the stream components have polished the crystal surfaces to a different extent. The more expressed the elements are, the stronger the abrasive influence upon them is. The fissures on Os-Ir-Ru alloys are formed during cooling of the grains but not as a result of the mechanical pressure on them. This is an indication for a high-temperature genesis.
- The composition of crystals of Pt-Fe alloys indicates that their sources have been enriched in Rh and Cu. The high values of Rh are indicative for a series of solid solutions between Pt and Rh, the latter lowering its content with the decrease of crystallization temperature (Slansky et al., 1991). Thus, it can be stated that the process had continued in a wide temperature range, which had probably caused the variations of Rh content in the composition of the crystals. Cu had played a significant role in the formation of the composition both of the crystals and Cu-containing inclusions. According to Rudashevskii (1984), copper concentrates in Pt-Fe alloys of the dunite-clinopyroxenite complexes. Enrichment with Rh and Cu is typical for Pt-Fe alloys of Alaska type intrusions (Johan et al., 1990).
- The absence of Ru in the composition of Pt-Fe alloys indicates that they are not related to ophiolite and stratiform chromites for which increased concentration of this element is typical (Stockman, Hlava, 1984). Regardless of the presence of Os inclusions in these crystals, this element was not detected in their composition, which indicates for a restricted solubility of Os in Pt-Fe alloys (Slansky et al., 1991). Enrichment with Rh and missing of Ru is a tendency for Pt-Fe alloys from Kamchatka and Australia (Johan et al., 1989), and the lack of Ru and Os is typical for Pt-Fe alloys from Tulameen complex, British Columbia (Nixon et al., 1990).
- The high activity of Cu during the formation of crystals of Pt-Fe alloy is reflected in the composition of a part of the inclusions in them. Cuprorhodsite and bornite indicate the presence of a complex of solid solutions of Pt, Fe, Rh, Cu, and S at high temperatures (Johan et al., 1990). Their drop-like form suggests that they had been captured from liquids (Johan et al., 1990; Augé, Legendre, 1992). According to Slansky et al. (1991), the inclusions of bowieite are early formations with high thermal stability, while the Os lamellae are a result from unmixing from solid solutions. All the above features of the studied Pt-Fe alloys are indicative for a high-temperature origin. Inclusions of osmium, cuprorhodsite and bornite have been described in Pt-Fe alloys from Duranse river, France (Johan et al., 1990), and inclusions of osmium, cuprorhodsite, bowieite and bornite – in Pt-Fe alloys from Ethiopia (Cabri et al., 1981; Weiser, Schmidt-Thomé, 1993). In these deposits the form and dimensions of a part of the inclusions are comparable with those observed in the alloys studied in the present paper.
- The crystal forms of clinopyroxene and chromian spinel are indicative for their primary origin (Nixon et al., 1990). Accordingly, the association "PGE alloys-chromian spinel" (with a high content of Cr_2O_3) is characteristic for dunites and there is no doubt about their high temperature crystallization from a primary mantle magma.
- The presence of bowieite and cuprorhodsite inclusions and the lack of laurite ones in samples of Pt-Fe alloy indicate for a crystallization process in a primary ore-forming system, characterized by not so high sulphur activity which shows that: 1) the crystallization me-

dium has been quickly depleted from S with the formation of the first two sulphides, when Rh has not been fully mobilized during this process; 2) the remaining Rh has actively participated in the formation of Pt-Fe alloys (indication for this is its high content in some of them); 3) during the formation of natural compounds S displays a greater affinity towards Rh in comparison to Ru; 4) their sources are not connected with ophiolite complexes (Stockman, Hlava, 1984; Thalhammer, Stumpfl, 1988). Obviously, these specific features of the ore-forming system had stimulated the formation of Os-Ir-Ru alloys.

- The uniform distribution of elements in the volume of the crystals of Pt-Fe alloys shows that they had been formed in a calm environment without intense physical restrictions and to a greatest extent favourable for the transport of crystallization components (Johan et al., 1989). The low compositional heterogeneity of Os-Ir-Ru alloys indicates for a lower temperature in comparison to the above case. This is also confirmed by an inclusion of Pt-Fe alloy in a crystalline form in the matrix of the Os-Ir-Ru alloy. The ore-formation system had been characterized by a higher viscosity, which had hampered the transport of crystallization components. These facts confirm the main part of the formation of the crystals under discussion, namely, Pt-Fe alloys – Os-Ir-Ru alloys.
- The exogenic processes had not caused changes in the compositions of the studied crystals compared to the described ones by Stumpfl and Tarkian (1976). This is most probably due to the non-aggressive conditions (from a chemical point of view) of the alluvial medium in which the transport and accumulation had taken place for a certain (not very prolonged) time.
- The relatively monotonous and constant composition of crystals from different sediments gives reason to propose that they had been formed in crystallization media with similar physicochemical characteristics. The Gotse Delchev graben is situated at a significant distance from the other two, the Kyustendil and Blagoevgrad grabens, and also it is located in another water collection basin not having any connection with them. It seems that no exogenic processes were able to create similar crystallization conditions in the geologically complex terrain of SW Bulgaria.

In conclusion, it is obvious to say that the features of the studied crystals are in relation mainly with the character of their sources and to a less extent depend on the peculiarities of the placers in which they had been transported and deposited. The data show that they had been formed in magmatic, high-temperature conditions at a relatively low viscosity of the crystallization medium and enough place for growth. The different degree of exogenic processing of one and the same forms in a definite grain-size fraction shows that the sources had been disposed to a certain distance one from another. In this sense, most probable are the numerous ultramafic bodies from the surrounding massifs of the three grabens built by dunites and peridotites, some of them serpentinized. This gives reason to state the prognosis that many other sediments in SW Bulgaria are carriers of such type of mineralizations but most probably the concentrations are not so high. The crystal features do not give reason to state that they had been influenced by serpentinization as this would result in zoning in their composition (Cabri, Genkin, 1991).

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