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NEW DATA ON THE PLATINOID MINERALS IN PLACERS FROM BOURGAS REGION — SE BULGARIA

(Fig. 1, Pls. 3, Tabs. 3)

Abstract: The interesting finds of platinoids in placers from Bourgas region — SE Bulgaria showed a significant diversity of mineral species and varieties — native platinum, ferroplatinum, Pd-bearing platinum, Os-bearing platinum, Os-Ir-bearing platinum, a number of uncommonly Cu-rich Pt-Cu-Fe natural alloys, osmium, iridosmine, Cu-bearing osmium and cooperite(?). Some of the placer platinoids have regular crystal forms. There are some differences in the admixtures of Fe, Cu, Ni, Rh and Ru for the different forms.

Резюме: Интересные местонахождения платиноидов в россыпях района г. Бургас (ЮВ Болгария) показывают выразительное разнообразие минеральных видов и разновидностей — самородная платина, ферроплатина, платина содержащая Pd, платина содержащая Os, платина содержащая Os-Ir, ряд Pt-Cu-Fe естественных сплавов замечательно богатых Cu, осмий, осмистый иридий, меденосный осмий и куперит (?). Некоторые россыпные платиноиды имеют правильные кристаллические формы. У разных форм существуют некоторые различия в примесях Fe, Cu, Ni, Rh и Ru.

Introduction

After the first finds of platinoids in alluvial sands in Bourgas region (Bonev et al., 1982) many efforts were made to trace their distribution and their mineralogical peculiarities. Presence of platinoids was established in area built up mainly of Upper Cretaceous volcanic rocks and younger, dominantly coarse-grained sediments. The study of the collected materials showed a number of mineral species and varieties of the platinoid group.

Geologic setting

The area of platinoid distribution is built up of Upper Cretaceous volcanic rocks and their pyroclastites, covered by Paleogene and Pliocene sediments at some places (Fig. 1). The volcanites are presented in their great part by K-subalkalic rocks (ultrabasic, mostly basic and intermediate in composition — Stanisheva—Vassileva, 1980). They are cut trough in many places by small, polyphase Upper Cretaceous—Paleocene plutons with basic and mostly intermediate composition. In the volcanites near some of these plutons there were formed number of hydrothermal vein-type cooper, cooper-polymetal and some other sulfide deposits (Димитров—Димитрова, 1961).

The Tertiary sediments (in some places thicker than 100 m) are built up by coarse well rounded quartz pieces (up to 200 mm sometimes), rare pieces of volcanites, quartz sands and smectite type clays.

The alluvial sediments in Bourgas region are limited in the river valleys.

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Native platinoid finds

Native platinum and platinoids were established in placers of three types:
1. in recent alluvial and proluvial sediments;
2. in eluvial sediments, laying on basic und ultrabasic volcanites;
3. in coarse layers of the Pliocene sediments.

Moreover in some sands, exstracted from desintegrated volcanic rocks there are indications of platinoids.

In all finds the platinoids are in the heavy fractions of the sands in association with magnetite, chromite, garnets, rutile, apatite, cerussite, monacite, zircon, native gold etc.

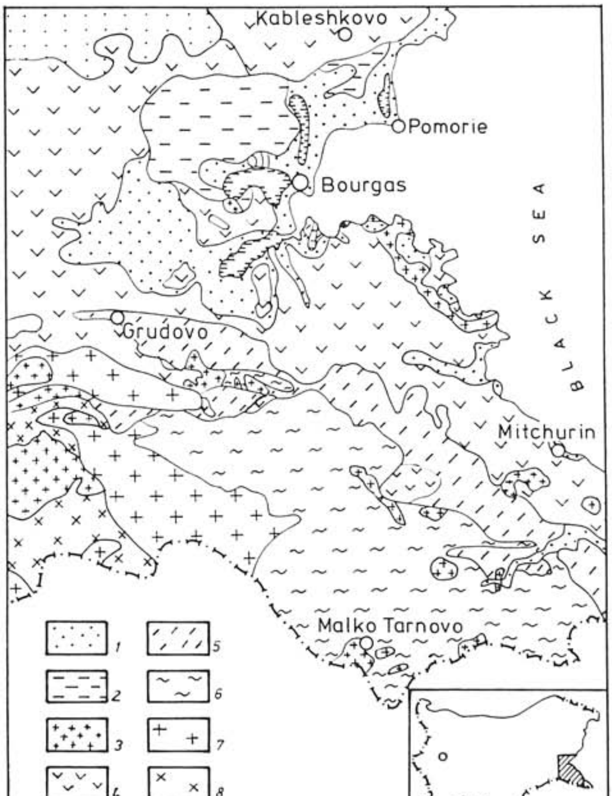

Fig. 1. Geological map of Bourgas region — SE Bulgaria.
Explanations: 1 — Pliocene coarse grain sediments; 2 — Paleogene sediments; 3 — Upper Cretaceous — Paleocene intrusions; 4 — Upper Cretaceous volcanites; 5 — Cretaceous sediments; 6 — Strandja metamorphites (Pz-Mz); 7 — old granites (Pz); 8 — old metamorphites (Az—Pz).

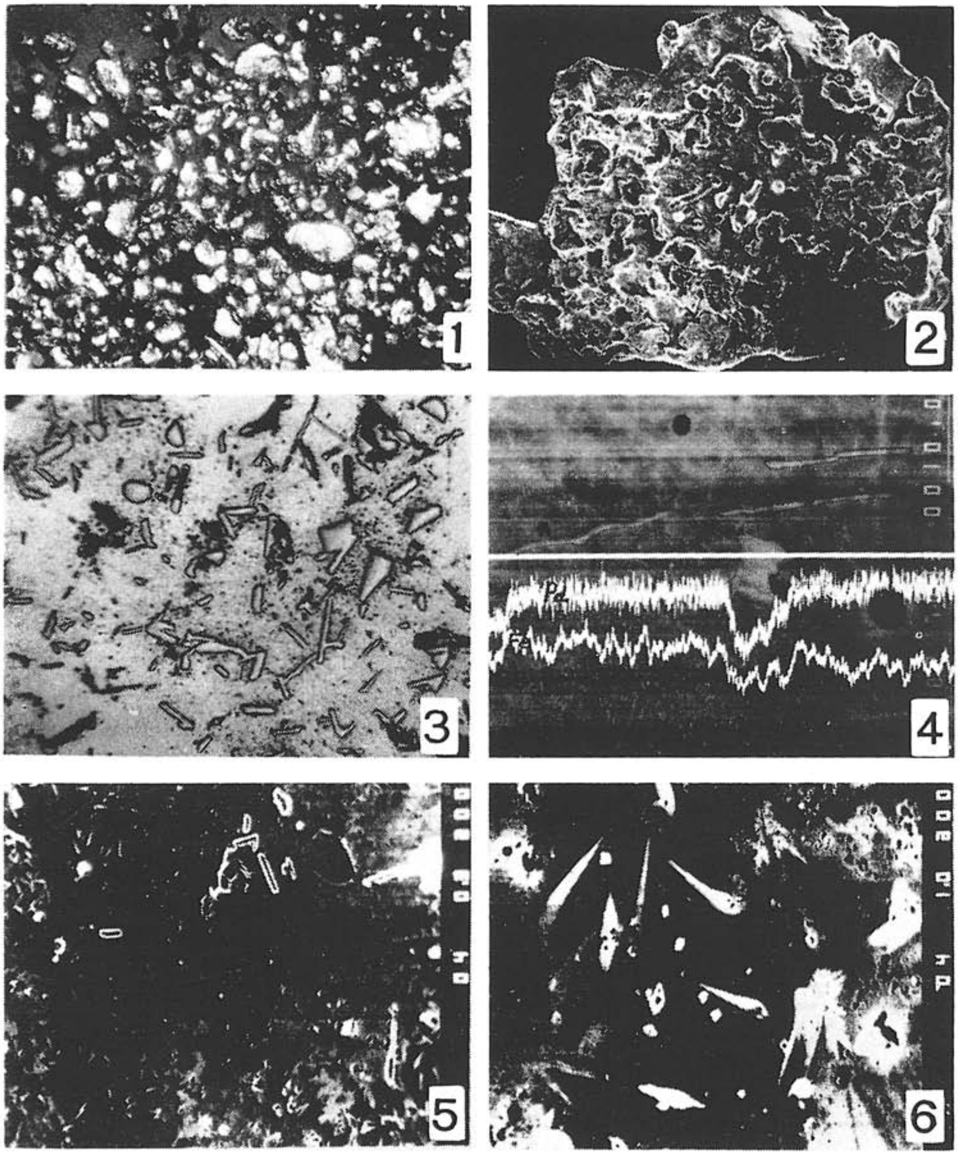

Plate 1

Fig. 1. Placer platinoids from Bourgas region, X 10.

Fig. 2. A grain with rough surface and Pt-Os composition, SEM, X 100.

Fig. 3. Oriented rodlike and isometric exsolutions of iridosmine in platinum. Polished specimen, X 150.

Fig. 4. Scanning on line for Pd and Fe trough a iridosmine inclusion in platinum, X 1200, COMPO.

Fig. 5. Platinum grain with high Cu content and admixtures of Cu-bearing osmium and Cu-rich Pt-Cu-Fe alloys X 220, COMPO.

Fig. 6. A detail of 5, showing different Cu-rich Pt-Cu-Fe alloys. X 1000, COMPO.

Methods of investigation

The field works were carried out by gravity separation of bulk placer materials as well as of desintegrated rocks. The obtained concentrates after a magnetic and electromagnetic separation and a sieve analysis were studied under a binocular microscope, the platinoid grains being separated (Pl. 1 - 1). Part of them were included in plastic matrix, polished and studied under a light microscope while the interesting grains were analysed qualitatively and quantitatively by electron microprobe (Jeol supprobe 733; Jeol T 200 CX; SEM 500 — Philips). The morphology of the platinoid grains was studied in SEI by Jeol JSMT 300 and the same time were made qualitative chemical analyses. Some of the grains were X-rayed by Gandolfi camera — 57.3 mm (aparatus TUR-61).

Description of the placer platinoids

The platinoids grains are silvery white to steely gray, 0.05—3 mm in size. In the alluvial sands the bigger grains prevail (0.2—3 mm), while in the Pliocene placers the grains are more often smaller then 0.3—0.5 mm. Their forms are mostly irregular, rounded, and their surface-polished, with concave and convex textures. In the Pliocene placers less rounded and rough grains are met, as well (Pl. 1 - 2) and sometimes regular crystal forms are present (Pl. 3 - 1—6), an evidence of comparatively limited transportation.

The X-ray diffraction patterns and the qualitative and quantitative microprobe analyses (by EDS — by standardless programme) at present give us a reason to describe the following minerals and varieties: platinum, ferroplatinum, Pd-bearing platinum, Os-bearing platinum, Os-Ir-bearing platinum, a number of uncommonly rich in Cu Pt-Fe-Cu alloys, osmium, iridosmine Cu-bearing osmium and cooperite(?). In some respects our study is a preliminary one, and may be we have some inaccuracies with respect to the names of minerals and some of the names have a descriptive character.

P l a t i n u m: The greater part of the placer platinoids from Bourgas region is represented by native platinum and its varieties. It is the main mineral in all the finds while the others are secondary and rare minerals. Earlier ferroplatinum, polyxen and platinum with admixtures of Pd, Ir, Os, Rh, Ru, Cu and Ni were described by the methods of light microscope study, X-ray study and microprobe qualitative analyses (B o n e v et al., 1982). More detailed investigations allowed us to characterise more precisely the platinum and its varieties and to enlarge their list.

In polished specimens the platinum grains are white with a weak cream hue, with a high reflectivity, isotropic. Sometimes they include in its matrix rodlike, lamelar and rarely isometric, mostly oriented exsolutions with Os—Ir composition (Pl. 1 - 3).

Native platinum with small quantity of Fe builds up the matrix of the greater part of the grains (Tab. 1 - analysis 1). In most cases it contains small admixtures of Os, Ir, Pd, Ru, Rh, Cu, Ni etc.

F e r r o p l a t i n u m: C a b r i—F e a t h e r (1975) described the ferroplatinum as a veriaty with more than 20 at. % Fe. The chemical analysis 2 in Tab. 1 shows 20.82 at. % Fe. That is why we may signify this phase as ferroplatinum with idealized formula Pt_4Fe. Some of the darker grains have higher Fe content

Table 1

Microprobe analyses* of platinum group minerals from Burgas region

№	Pt	Fe	Os	Ir	Ru	Cu	Ag	Cl	S	Total
1.	96.08	3.92	—	—	—	—	—	—	—	100
2.	93.00	7.00	—	—	—	—	—	—	—	100
3.	91.34	4.33	4.33	—	—	—	—	—	—	100
4.	77.30	2.43	8.01	12.26	—	—	—	—	—	100
5.	77.0	8.4	—	—	—	14.7	—	—	—	100
6.	76.1	8,5	—	—	—	12.8	1.5	1.2	—	100
7.	74.8	8,7	—	—	—	15.5	1.1	—	—	100
8.	73.8	7.8	—	—	—	17.2	1.3	—	—	100
9.	61.6	4.4	—	—	—	29.6	2.8	1.7	—	100
10.	—	—	93.99	6.01	—	—	—	—	—	100
11.	—	—	90.64	9.36	—	—	—	—	—	100
12.	—	—	75.29	24.71	—	—	—	—	—	100
13.	—	—	74.70	25.40	—	—	—	—	—	100
14.	6.2	1.6	82.7	—	—	8.6	0.9	—	—	100
15.	5.1	0.9	79.6	—	0.9	12.2	1.4	—	—	100
16.	3.7	0.5	81.7	—	0.9	12.7	1.3	—	—	100
17.	81.40	—	—	—	—	—	—	—	18.60	100

* All analyses were made by EDS by standartless program.

and are ferromagnetic. They are probably Fe rich ferroplatinum but are not studied completely.

P d-b e a r i n g p l a t i n u m: It was found by qualitative microprobe analyses. Besides Pd it contains small quantites of Fe, Os, Ir, and $\pm$Rh. The contents of Pd and Fe are corelative, with small variations of Fe. In the Ir-Os exsolutions their content obviously decreases (Pl. 1 - 4). The Pd-bearing platinum is rarely met in the placers from Bourgas region.

O s-b e a r i n g p l a t i n u m: Except the Fe this variety of platinum contains several per cents Os (Tab. 1 — analysis 3) and builds up some parts of the matrix of the grains with higher reflectivity. Ni and Cu are present like admixtures. Such a grain is shown on Pl. 1 - 2, where the brighter parts are higher in Os content.

I r-O s-b e a r i n g p l a t i n u m: Analysis 4 — Tab. 1 shows a mineral, rich of Os and Ir. Its idealised formula is Pt_4 (Ir, Os, Fe). This variety like the Os-bearing platinum is usually met in the grain matrix.

C u-r i c h P t-C u-F e a l l o y s: Especially interesting are the number of phases in the matrix of some platinum grains that are characteristic with his high Cu content (Pl. 1 - 5, 6). Microprobe analyses (Tab. 1 — analyses 5—8) show Pt-Cu-Fe alloys with admixtures of Ag and even Cl(!). The calculated crystalochemical formulae:

$Pt_{0.39} (Cu_{0.23} Fe_{0.15})_{0.38}$ (analysis 5)
$Pt_{0.39} (Cu_{0.20} Fe_{0.15} Ag_{0.01} Cl_{0.04})_{0.40}$ (analysis 6)
$Pt_{0.38} (Cu_{0.24} Fe_{0.16} Ag_{0.01})_{0.41}$ (analysis 7)
$Pt_{0.38} (Cu_{0.27} Fe_{0.14} Ag_{0.01})_{0.42}$ (analysis 8)

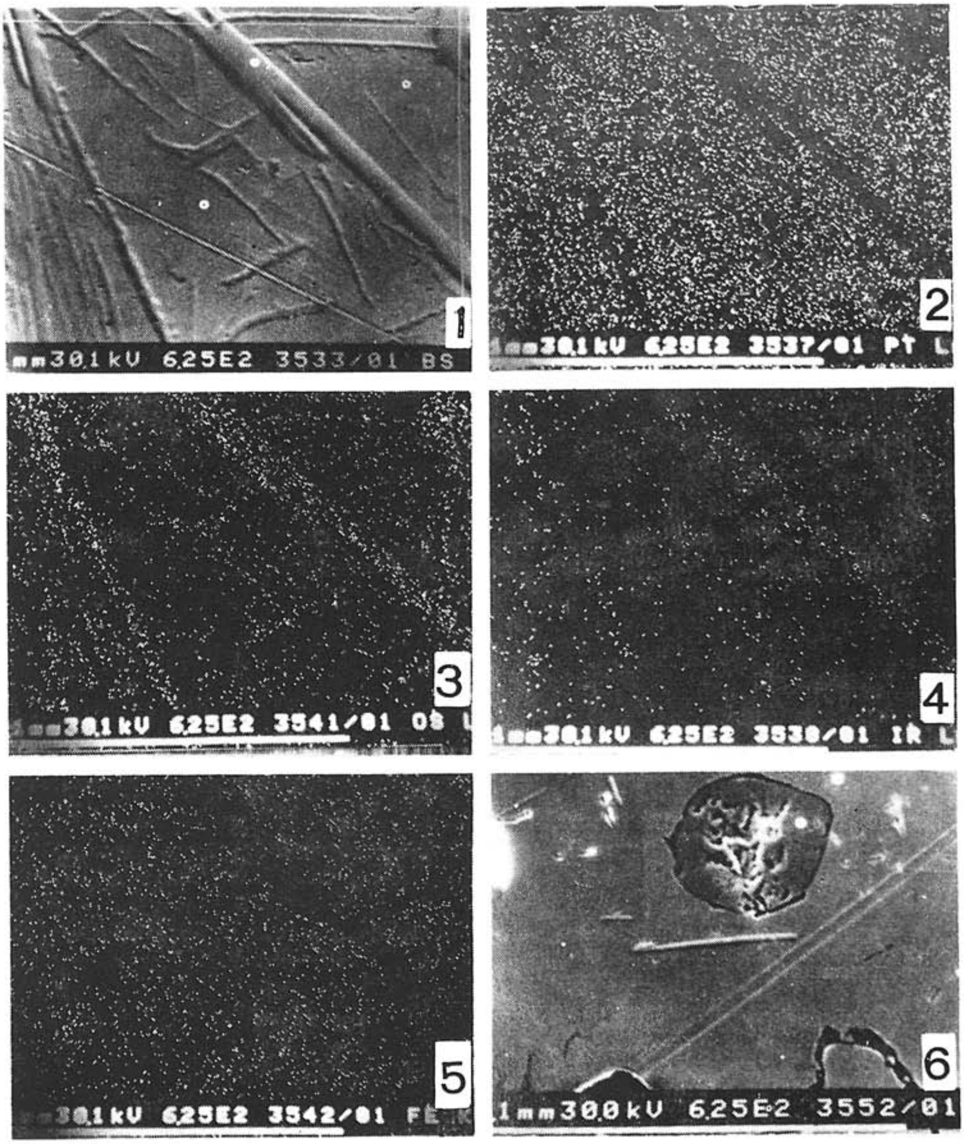

Plate 2

Fig. 1. Iridosmine exsolusion in Os-bearing platinum. X 580, COMPO.
Fig. 2. As 1, in PtL_{α}
Fig. 3. As 1, in OsL_{α}
Fig. 4. As 1, in IrL_{α}
Fig. 5. As 1, in FeK_{α}
Fig. 6. Copperite in platinum. X 650, COMPO.

are similar to that of tetraferroplatinum (C a b r i — F e a t h e r, 1975) but with more Cu than Fe, or to tulameenite (C a b r i, 1976) but with different quantities of Cu and Fe (and with Ag). Similar compositions but with significant content of Ni were described by C a b r i et al. (1977). In back scattered electrons (COMPO) in a high contrast these phases are clearly seen in the platinum matrix (Pl. 1 - 5, 6). In light microscope they are unvisible. In such grains there are dark phases near the osmium exsolutions which have an unusually high Cu content (Tab. 1 — analysis 9). The formula $Pt_{0.32}$ $(Cu_{0.47}$ $Fe_{0.08}$ $Ag_{0.03}$ $Cl_{0.15})_{0.65}$ is close like to $Pt(Cu, Fe)_2$. In the published literature up to now there are not any descriptions of platinum minerals with such high quantity of Cu (and with Cl as well).

O s m i u m: A part of the exsolutions in platinum matrix shows a composition fixing them as native osmium (Tab. 1 — analyses 10, 11). They are characteristic with their high reflectivity and hardness.

I r i d o s m i n e: When the exsolutions contain significant quantities of Ir in the base Os compositions (Tab. 1 — analyses 12, 13) the mineral is iridosmine (H a r r i s — C a b r i, 1973). The exsolutions has mostly rodlike shape and a hexagonal type orientation. On the Pl. 2 - 1—5 there are shown exsolutions of iridosmine in Os-bearing platinum and corresponding images in $PtL\alpha$, $OsL\alpha$, $IrL\alpha$ and $FeK\alpha$ characteristic rays.

C u-b e a r i n g o s m i u m: The exsolutions in the Cu-bearing platinum grains (Pl. 1 - 5) are enriched of Cu. They have some admixtures of Ag, Ru and Fe also (Tab. 1 — analyses 14—16).

C o p p e r i t e?: The bluish-gray inclusions (Pl. 2 - 6) with low reflectivity and strong anisotropic effect (earlier a similar phase was studied quantitavely by microprobe and defined as cooperite by B o n e v et al., 1982) showed a composition of a nonstoichiometric sulfide of Pt (Tab. 1 — analysis 17) in plently of S — may be a member of the row cooperite-braggite (C a b r i et al., 1978) but paladiumless. We don't except the possibility of some errors during the measurement of the elements, due to defects of the surface.

The study of the platinoid sulfides (may be arsenides and telurides also) are a work ahead of us.

Very interesting results was obtained by scaning and qualitative analyses of the grains with regular crystal forms by electron microscope. The forms that are predominant are octahedral, cube-octahedral, rarely cube and tetrahedral, but tetragonal prisms are met also (with significant admixtures of Fe, Ni and Cu; Pl. 3 - 6).

Qualitative analyses, made on the surface of the octahedral grain (Pl. 3 - 1) showed Pt, Fe, Cu and Rh presence (the darker inclusions are higher in Fe content). A similar grain was X-rayed by Gandolfi camera. The X-ray pattern (Tab. 2) showed platinum (fcc) with $a_0 = 3.893$Å (pure platinum — 3.924Å).

The cube-octahedral grain (Pl. 3 - 3) showed a presence of Pt, Fe, Cu, Ru, and Rh (the dark incorporation on the cubic face is enriched of Rh).

The matrix of the cube (Pl. 3 - 2) consist of Pt, Fe and Ru, the dark inclusions- of Pt and S with admixtures of Cu $\pm$Rh and the light parts- of nearly pure platinum.

The grains with tetrahedral shape (Pl. 3 - 4, 5) have a Pt-Fe composition with small quantity of Rh. The inclusion in the tetrahedral grain on Pl. 3 - 5 is a K-Na feldspar.

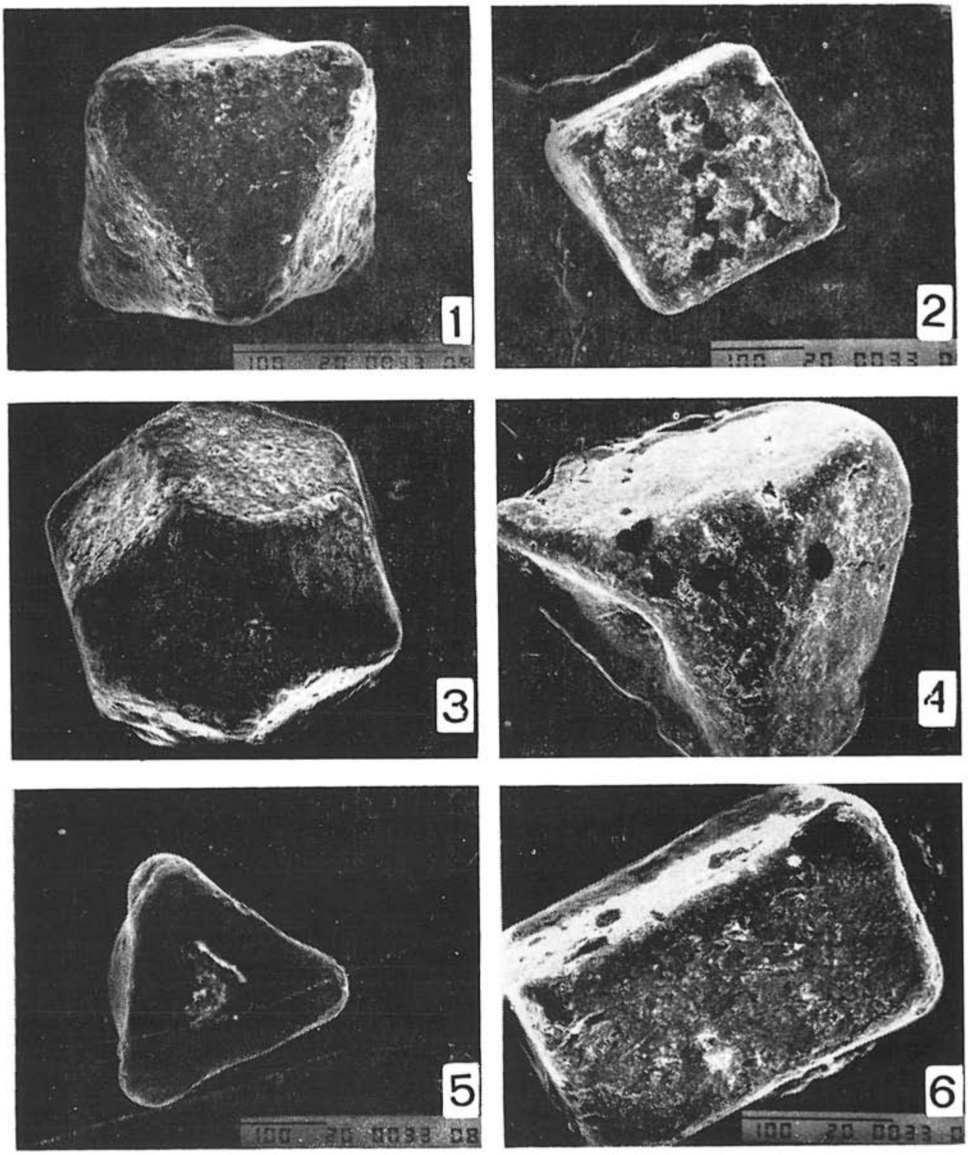

Plate 3

Fig. 1. Octahedral form of platinum, SEM, X 300.
Fig. 2. Cubic form of platinum with inclusions of Pt sulfide (cooperite?), SEM, X 140.
Fig. 3. Cube-octahedral form of platinum, SEM, X 350.
Fig. 4. Tetrahedral form of platinum, SEM, X 400.
Fig. 5. Tetrahedral form of platinum with inclusion of K-Na feldspare, SEM, X 130.
Fig. 6. Tetragonal prism (tetraferroplatinum?), SEM, X 220.

Table 2

X-ray data of platinum from Bourgas region

Platinum — Bourgas region			ASTM 4 — 0802		
№	I	d nm	I	d nm	hKl
1.	10	2.24	100	2.265	111
2.	7	1.933	53	1.962	200
3.	8	1.375	31	1.387	220
4.	9	1.182	33	1.1826	311
5.	6	1.128	12	1.1325	222
6.	3w	0.972	6	0.9808	400
7.	9	0.895	22	0.9000	331
8.	8	0.871	20	0.8773	420
9.	7w	0.794	21	0.8008	422

Analytical conditions: Gandolfi camera, 57.3 mm, CuK_{α} rays; exposition — 15.2^{h}. Analyst Bojadjieva, Durtcheva.

The study of typomorphic peculiarities of the platinoid minerals from Bourgas region is a future problem. It is necessary to collect enough samples and to aplied a wider spectrum of methods of investigation.

Conclusions

The research of the platinoid manifestations in placers from Bourgas region showed a good number of mineral species and varieties. A part of the platinoid minerals are new for Bulgaria, and may be some of them will be new for the science. We have to prospect the primary sources of the platinoids in the future. Now the main suspicions are on the basic and ultrabasic rocks of the K-subalkalic volcanic series. And a more detailed study of the mineralogy of the platinoids is ahead of us.

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