SPERRYLITE FROM ALLUVIAL PLACERS OF VURBITSA RIVER, SE RHODOPES

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Detailed investigations in Bulgaria during the last tens of years have shown that the platinum-group minerals (PGM) are distributed among three types of deposits: magmatic, copper porphyritic, and placer ones (Драгов и др., 1996). The magmatic deposits in Rhodopes mountain are related to the ultrabasites of the lower levels of ancient ophiolitic associations and to the chromite mineralisation in them (Найденова и др., 1984; Tarkian et al., 1991).

Placer deposits with proved presence of PGM have been established in Eocene sediments near Novoseltsi village (SE Bulgaria) and in alluvial depositions of the rivers Mesta, Struma, and Iskar (SW Bulgaria). The latter manifestations most often are in direct spatial connection with ultrabasic bodies and are rarely disposed to a greater distance (up to several tens of km). PGM in the sediments near Novoseltsi village are dominated by Pt-Fe alloy while in those from SW Bulgaria prevailing is sperrylite, i.e. in both cases Pt-containing minerals predominate (Атанасов, 1987; Tsintsov, 2000; 2003; Tsintsov & Damyanov, 1994).

Studies on the mineral composition of the heavy fraction from placers associating with closely situated ultrabasic bodies in SE Rhodopes proved the PGM presence in them also. The alluvial sediments of Vurbitsa river in the range Dobromirtsi village - Momchilgrad town (SE Rhodopes) are elsewhere "infected" with sperrylite. This mineral is additionally accompanied by single finds of alloys of the platinum-group elements (PGE) (iridium and ruthenium) only in the alluvial depositions disposed near the ultrabasites of the Dobromirtsi massif. According to recently obtained data the concentration of these minerals in the studied sediments was evaluated as <<<1 mg/m^3, which is probably related to their low content in the root sources. The establishment of such type of mineralization in placers that associate with some of the biggest ultrabasite bodies in Bulgaria (those near Dobromirtsi and Yakovitsa villages) is not a surprise. More interesting is the presence of sperrylite in these depositions, which has not been found during the large-scale prospecting of ore minerals in the ultrabasites in this region (Михайлова-Данги и др., 1986). Also of interest is the fact that laurite, which is the widely spread mineral from the group in the ultrabasites near Dobromirtsi village, has not yet been proved in the placers. These peculiarities can be explained by the very low concentration and irregular distribution of these minerals in the different parts of ultrabasites and alluvial sediments.

The purpose of the present paper is to present data for the mineralogical peculiarities of sperrylite separated from the alluvial depositions of Vurbitsa river, SE Rhodopes. This is a new manifestation for Bulgaria of such type of mineralization in these depositions.

The methods and apparatuses for terrain and laboratory investigations are published earlier (Tsintsov, 2003).

The ultrabasite rocks, which are represented by isolated bodies or groups of them with different age, petrographic composition and alteration degree, are distributed mainly in the southern part of Bulgaria. Mostly spread and biggest are the bodies in SE Rhodopes and the ultrabasites near the villages Golyamo Kamenyane, Dobromirtsi, Yakovitsa, and Brusevtsi are built by dunites and similar in composition harzburgites being strongly or fully serpentinized (Желязкова-Панайотова, 1989). PGM in magmatic deposits have been observed only as early mineralizations in the chromite ores of the ultrabasites near the villages Dobromirtsi (SE Rhodopes) and Pletena (W Rhodopes). In a quantitatively decreasing order they are represented by laurite (Ru, Os, Ir)S_2, ruarsite (Ru, Os, Ir)AsS, irarsite IrAsS, osarsite (Os, Ru, Ir)AsS, and Ir-Os alloy (Найденова и др., 1984; Tarkian et al., 1991).

The heavy mineral concentrates taken from the studied region consist mainly of magnetite, chromite, ilmenite, rutile, almandine, zircon, native gold, rarely monazite, native silver, Au-Ag amalgama, uraninite, cinnabar, very rarely PGM, etc. A characteristic feature of the alluvium concentrates taken near Dobromirtsi ultrabasite massif is the presence of phases of the Ag-Au system or/and their amalgamas, which are in much greater quantities compared to PGM. The grains of these minerals in the binocular stereomicroscope very much seem like native platinum. These data give reason to argue upon the phase composition of a big sample of placer "native platinum" taken from the region of Dobromirtsi massif and granted to Sofia University "St. Kl. Ohridski" in the middle of the last century by a native gold-digger (personal communication of Prof. D-r M. Zhelyazkova-Panayotova). Later this sample has been lost, but the geologists from the University are convinced that the grains are of "native platinum". The present data give reason for scepticism when determining the mineral composition of this sample. With a great degree of confidence it can be stated that it is practically not possible by hand washing to collect a big sample of native platinum (if it is present at all) from the sediments in the region of Dobromirtsi massif.

The grains of the studied mineral are totally concentrated in fractions <63 mm. Their form is isometric or elongated and they are tin-white to dark-gray colored and with apparent metal lustre. Sperrylite grains are subdivided in two types in respect to the degree of mechanical processing during the exogenic transport: very strongly or relatively weakly processed. The two types are regularly represented in the various parts of the studied sediments. The natural surface of the grains from the first type is dense and smooth – very well polished during their mechanical transportation in the placer (Fig. 1 a, b). They have partially preserved crystal faces but the edges and apices between them are significantly smoothed. The newly obtained surfaces are dense and well polished with color and lustre, which are similar to the natural ones. The samples from the second type are represented chiefly by relatively well preserved combinational crystals or crystal parts composed of

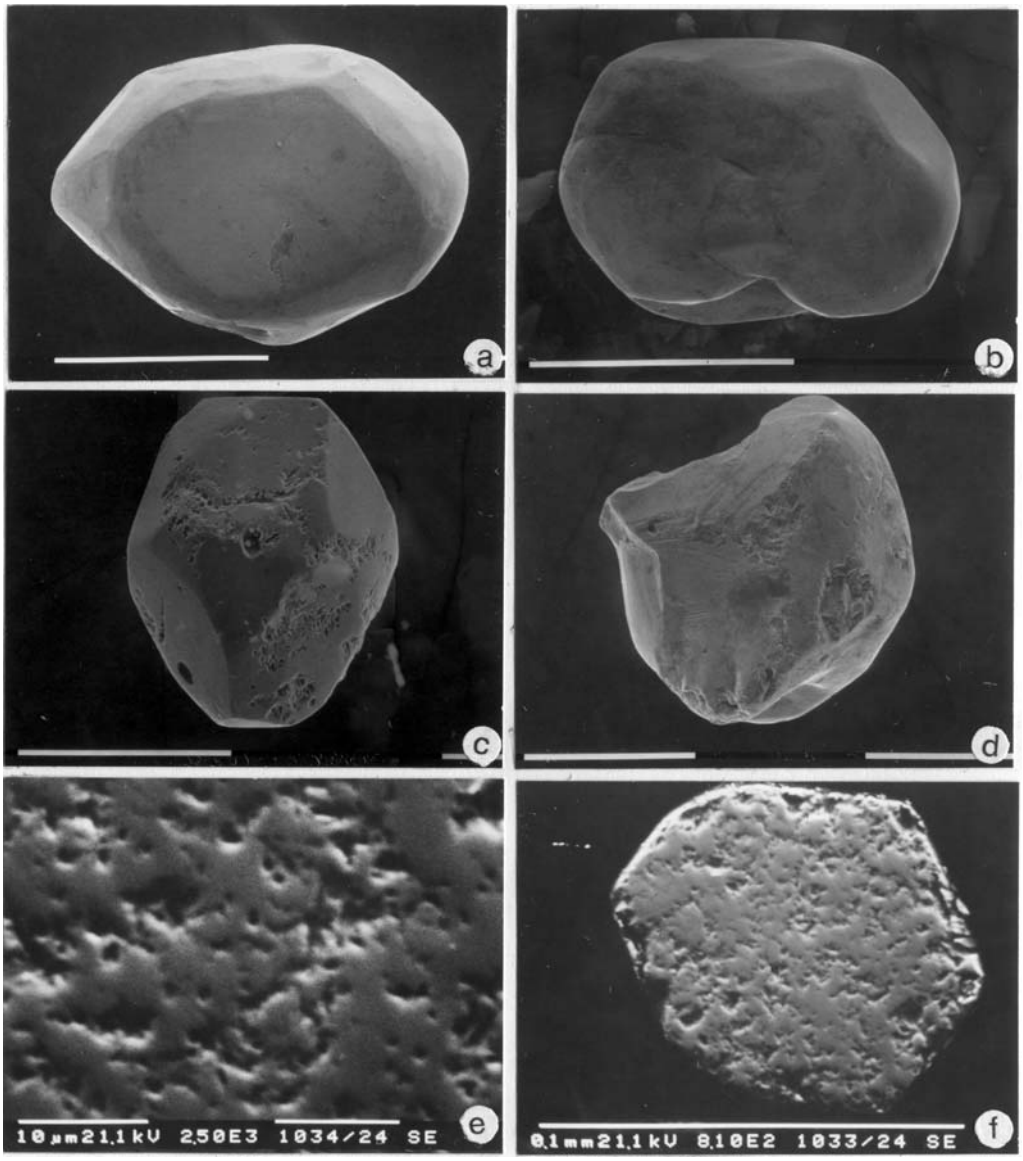

Fig. 1. Sperrylite from Vurbitsa river alluvial placers: a, b – grains with dense and well polished surfaces during mechanical transportation; c – combinational crystal; d – crystal part with surface defects; e – polished surface of a grain from the first type; f - polished surface of a grain from the second type (crystal). Natural surfaces - a-d. Polished surfaces - e, f. SEM. Scale bar - 100 mm a-d, f; 10 mm – e.

forms with indices a {100}, o {111}, rarely d {110}, etc (Fig. 1 c). Their surfaces are covered with plenty of caverns (size up to 5 mm) and/or mechanical defects (sized up to 30-35 mm) caused by exogenic factors (Fig. 1 d). This type is very rarely represented by grains with sharp, cutting edges formed during their breaking. Although hard sperrylite is fragile and when placed between hard minerals in exogenic conditions it easily obtains surface damages or is broken to smaller pieces with sharp edges and coarse surfaces. This is the main reason for presence of such specimens in the studied sediments. The polished surfaces of the grains of the two types are disturbed by plenty of caverns with irregular form and sized up to 5-6 mm (Fig. 1 e, f).

The composition of the studied sperrylite includes only the constitutionally regulated elements of the mineral (according to data of microprobe analyses). The content of Pt is in the range (wt.%) from 55.26 to 59.06, while that of As – from 41.42 to 43.22. Indications for presence of Ni were noticed in several samples but its content remained steadily under the detection limits of the analysis. Some of the grains have stoichiometry corresponding to the theoretically calculated one for this mineral – $PtAs_2$. The rest samples display some metal excess not correlated with their morphology. Inclusions of other phases in the studied grains were not observed.

The ultrabasites in SE Rhodopes have suffered multiple metamorphic alterations with part of these processes being caused by the active participation of post-magmatic solutions (Желязкова-Панайотова, 1989). The latter had played important role not only for the re-immobilization, transportation, and deposition of PGE but also for the transformation and re-crystallization of earlier formed PGM (Evstigneeva & Tarkian, 1996). According to the experimental data of these authors a product with stoichiometry $PtAs_2$ has been directly synthesized from hydrothermal solutions in the temperature range 240-500°C in the presence of graphite as a reducing agent. The obtained phase during these experiments is with

the crystallographic characteristics of sperrylite.

The hydrothermal solutions that had taken part in the metamorphic alterations of the ultrabasites in SE Rhodopes probably are the main reason for immobilization of Pt from earlier formed Pt-containing minerals. Possible indication for this is the very low content of Pt in the chromites of Dobromirtsi and Yakovitsa ultrabasite massifs (Zhelyazkova-Panayotova & Economou-Eliopoulos, 1994). At the same time these solutions have had been carriers of As, which had supported the formation of sperrylite. The later exogenic processes had caused its disintegration from the ultrabasites and deposition in the alluvial sediments of Vurbitsa river.

The very high degree of mechanical processing of part of the grains is an indication for a prolonged exogenic transport. During this transportation the crystals had probably been incorporated in bigger pieces of the root rock from which they had been liberated before their deposition in the placer where they were finally found.

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