# PLATINUM-GROUP MINERALS FROM ONVERWACHT. II. PLATARSITE, A NEW SULFARSENIDE OF PLATINUM\*

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### Abstract

Platarsite, Pt(As,S)<sub>2</sub> with As 2S, is a new sulfarsenide found as crystals up to 1.1 mm in a sample from the former Onverwacht mine, Transvaal. Platarsite, which supersedes "rhodium sperrylite" (Stumpfl & Clark 1965), is a rhodian and ruthenian variety belonging to the PtAsS-RuAsS-RhAsS system, and contains minor Ir and Os. Under reflected light the mineral is grey, slightly darker than coexisting sperrylite, and isotropic. VHN<sub>50</sub>=1486(1379-1584), VHN<sub>100</sub> =1246 (1177-1343) for one grain, and 1402 (1288-1452) for another. Platarsite is cubic, a 5.790(1) and 5.824(6)Å for two grains (the unit cell varying with composition), space group Pa3. D(meas.) 8.0 g/cm<sup>3</sup> and, with Z=4, D(calc.) 8.375 g/cm<sup>3</sup> for the same grain whose composition was determined at Pt0.34 Rha 30 Ruo 28 Iro 05 OS0 01 AS1 03 So 98. Coexisting sperrylite contains minor elements to a maximum (in wt. %) of 1.8 Rh, 0.28 Ru, 0.63 Ir, 2.1 Sb and 0.93 S.

#### Sommaire

La platarsite, Pt(As,S)<sub>2</sub> avec As  $\simeq$  S, est un nouveau sulfarséniure qui se trouve en cristaux mesurant jusqu'à 1.1 mm, dans un échantillon provenant de l'ancienne mine d'Onverwacht, au Transvaal. La platarsite, qui supplante le "rhodium sperrylite" de Stumpfl & Clark (1965), est une varitété rhodienne et ruthénienne appartenant au système PtAsS-RuAsS-RhAsS et contenant des quantités minimes d'iridium et d'osmium. En lumière réfléchie, le minéral est gris, isotrope et légèrement plus foncé que la sperrylite coexistante. VHN<sub>50</sub>=1486 (1379-1584), VHN<sub>100</sub>=1246 (1177-1343) sur un grain et 1402 (1288-1452) sur un autre grain. La platarsite est cubique avec a 5.790(1)Å et a 5.824(6)Å, pour deux composititons différentes, et groupe spatial Pa3. D(mes.) 8.0 sur un grain de composition Pt<sub>0.34</sub>Rh<sub>0.30</sub>Ru<sub>0.28</sub>Ir<sub>0.05</sub>Os<sub>0.01</sub>As<sub>1.03</sub>S<sub>0.99</sub>; avec Z=4, D(calc.) 8.375 pour le même grain. La sperrylite coexistante contient comme éléments accessoires jusqu'à 1.8 % Rh, 0.28 % Ru, 0.63 % Ir, 2.1% Sb et 0.93% S (en poids).

### INTRODUCTION

A sample ( $\sim 15 \times 20 \times 35$  mm) from the former

Onverwacht platinum mine, Transvaal, was sent to one of us (L.J.C.) to determine whether tulameenite was present (see Cabri *et al.* 1977a for further details of the sample origin and on the Onverwacht deposit). In the course of this investigation, the new mineral platarsite was found and characterized.

### PROCEDURES

Slices 1-2 mm thick cut from the sample with a 0.3 mm diamond wafering blade were mounted in cold-setting plastic, polished on lead laps, and studied by ore microscopy. Parts of two crystals of platarsite were removed from the polished sections and exposed to X-rays in Gandolfi and precession cameras. Film-shrinkage corrections were applied and the unit-cell parameters for the indexed powder pattern were refined by a least-squares computer program (Stewart et al. 1972). Intensities were estimated on the scale  $\frac{1}{2}$  to 10. Compositions were determined with an MAC model 400 microprobe operated at 25kV, a specimen current of about 0.03 microamperes, and using as X-ray lines and (standards):  $PtL\alpha$ ,  $SK\alpha$  (synthetic  $Pt_{0.7}Pd_{0.3}S$ );  $IrL\alpha$ , RhL $\alpha$  (synthetic Ir<sub>45</sub>Rh<sub>55</sub>); AsK $\alpha$  (synthetic InAs); SbL $\alpha$ , OsL $\alpha$ , RuL $\alpha$  (metals). Corrections were applied using a slightly modified version of the EMPADR VII computer program of Rucklidge & Gasparrini (1969). Slits (0.03") were used to improve the peak/background ratio for Pt, Ir, Os, and As, and corrections were also applied for enhancement of  $PdL\alpha_1$  by  $\operatorname{Ru} L\beta_2$ ,  $\operatorname{Pd} L\alpha_1$  by  $\operatorname{Rh} L\beta_1$ ,  $\operatorname{Rh} L\alpha_1$  by  $\operatorname{Ru} L\beta_1$ , As $K\alpha_1$  by IrL $\beta_4$ , and As $K\alpha_1$  by OsL $\beta_2$ . Cu, Ni and Pd were sought, but not detected. The platarsite and sperrylite grains analyzed had HOM indices of >3 for most elements. Average values which are considered representative are reported in the Tables. Reflectance values were obtained with reference to a silicon standard, N2538.42, calibrated by the National Physical Laboratory, United Kingdom, using a 16.5:1 objective of 0.40 numerical aperture on  $20 \times 20 \ \mu m$  areas. The micro-indentation hardness measurements were made with a Leitz Durimet tester.

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- FIG. 1. Two subhedral grains of platarsite (2, grey, higher relief) with associated Pt-Fe alloy (white), sperrylite (1, lightest grey), genkinite (3, intermediate grey and rimmed by dark grey alteration product), and chromite (grey-black) in a silicate matrix. The largest platarsite grain has some microindentations, as does the genkinite adjacent to the smaller platarsite grain.
- FIG. 2. Coexisting platarsite (2) and sperrylite (1) included in a Pt-Fe alloy matrix. This assemblage is itself included in silicates.

## OPTICAL, PHYSICAL AND CHEMICAL PROPERTIES OF PLATARSITE

Platarsite is grey in polished section, isotropic, and not bireflectant in air or oil. Where adjacent to sperrylite, platarsite appears darker grey. Other associated minerals are Pt-Fe-Cu-Ni alloys, chromite, silicates, genkinite (Cabri *et al.* 1977b),

stibiopalladinite, bornite, ruthenarsenite, an unidentified Pt-Pd-Rh oxide, and mertieite II. Platarsite occurs as subhedral grains of various sizes (Fig. 1), the largest being an approximately triangular crystal with sides of 1.1 mm. Reflectance, measured in air, indicates a slight variation attributed to compositional variations. For compositions, see Table 1. The mean of 3 reflectance measurements for grain 1 is compared to the average value for grains 3 and 4. These reflectances are, respectively: 470 nm, 54.7\* and 51.3; 546nm, 50.6 and 49.7; 589nm, 49.5 and 49.4; 650nm 48.1 and 49.2. (\*This value is inexplicably considerably larger than obtained from grains 3 and 4. Three measurements on grain 1 gave 55.8, 53.0 and 55.2% at 470nm).

Platarsite is relatively hard: micro-indentation hardness values are VHN<sub>50</sub>=1486 (1379-1584) ior 5 indentations on grain 1, VHN<sub>100</sub>=1402 (1288-1452) for 5 indentations on grain 1, and VHN<sub>100</sub>=1246 (1177-1343) for 5 indentations on grain 3.

The density of a 1.7 mg fragment of grain 1 is 8.0 g/cm<sup>3</sup> using a Berman balance and hexachloro-1, 3-butadiene as immersion liquid (D= 1.6767 g/cm<sup>3</sup> at 21°C). The measurement procedure was confirmed by obtaining 2.65 g/cm<sup>3</sup> for a quartz fragment.

Electron microprobe analyses of four grains are given in Table 1. All have Pt>Rh or Ru; therefore, platarsite is part of the PtAsS-RuAsS -RhAsS system, in which the last end-member is hollingworthite. The limits of As:S have not been determined, but the observed range from 1.03:0.99 to 1.18:0.82 is typical of sulfarsenides.

The X-ray powder pattern of grain 1 was indexed as cubic with a 5.790(1)Å (Table 2). Grain 3 gave a similar powder pattern with a5.824(6)Å. Space group Pa3 was determined with a precession camera for grains 1 and 3. Using Z=4, D(calc.)=8.375 g/cm<sup>3</sup> for grain 1, and D(calc.)=9.627 g/cm<sup>3</sup> for the ideal endmember PtAsS using a 5.929Å (Hulliger 1963).

The name platarsite alludes to the composition of the ideal end-member, PtAsS, in the same manner as irarsite, IrAsS (Genkin *et al.* 1966) and osarsite, OsAsS (Snetsinger 1972).

TABLE 7. ELECTRON MICROPROBE ANALYSES OF PLATARSITE

Anal. no.	Weight percent									Atomic proportions							
	Pt	Rh	Ru	Ir	0s	As	S	Total	Pt	Rh	Ru	Ir	0s	Σ	As	s	
14	26.9	12.8	11.4	3.6	0.58	31.7	13.0	99.98	0.34	0.30	0.28	0.05	0.01	0.98	1.03	0.99	
2	30.2	13.8	8.8	0.54	1.7	33.5	11.1	99.64	0.39	0.34	0.22	0.01	0.02	0.98	1.14	0.88	
3†	31.4	10.3	8.5	6.1	0.10	33.6	10.0	100.00	0.43	0.27	0.22	0.08	<0.01	1.00	1.18	0.82	
4	30.4	10.8	9.1	5.9	0.10	33.2	10.7	100.20	0.40	0.27	0.23	0.08	<0.01	0.98	1.15	0.87	

Cu, Ni and Pd were sought for but not detected. + Grain X-rayed.

TABLE 2. X-RAY POWDER DATA FOR PLATARSITE

I	dmeas	hkl	<i>d</i> calc	I	dmeas	hkl	<i>d</i> calc
8	3.345	11.1	3.343	1	1.074	432	1.075
9	2.896	200	2.895	붋	1.057	521	1.057
5	2.590	210	2.589	5	1.022	440	1.023
5	2.364	211	2.364	4	0.9787	531	0.9788
6	2.047	220	2.047	4.	0.9650	442	0.9651
10	1.746	311	1.746	1	0.9395	532	0.9394
4	1.672	222	1.671	3	0.9153	620	0.9156
2	1.606	302	1.606	4	0.8831	533	0.8830
2	1.547	321	1.547	3	0.8732	622	0.8730
4	1.327	331	1.328	ł	0.8630	630	0.8632
4	1.294	420	1.294	1 2	0.8539	631	0.8538
٦	1.264	421	1.263	5	0.8109	551	0.8109
之	1.232	332	1.234	5	0.8030	640	0.8030
5	1.182	422	1.182	1	0.7954	641	0.7954
7	1.114	333	1.114	1	0.7880	633	0.7880

Cu/Ni radiation,  $\lambda$  = 1.5405. All reflections are broad for this sample.

The name and the mineral were approved by the Commission on New Minerals and Mineral Names, I.M.A.

### DISCUSSION

Genkin et al. (1966) discussed the crystallochemical classification of irarsite, hollingworthite, and the "rhodium sperrylite" of Stumpfl & Clark (1965). They concluded, and we concur, that it is not possible to arrive at a satisfactory classification without sufficiently detailed X-ray crystallographic research. Genkin et al. (1966) also concluded that "rhodium sperrylite", which we have recalculated on the basis of 3 atoms to be  $(Pt_{0.33}Rh_{0.31}Ir_{0.25}Pd_{0.05})_{\Sigma=0.94}As_{1.13}S_{1.92}$ , has PtAsS as the probable end-member and thus should be considered a new species. Cabri (1972) arrived at the same conclusion and listed the mineral as "unnamed mineral N". On the other hand, Tarkian & Stumpfl (1975) plotted this mineral as part of the hollingworthite-irarsite series, apparently placing little importance on the fact that Pt is greater than either Rh or Ir. The Onverwacht mineral is apparently identical, and its discovery has reopened the question of nomenclature of PtAsS minerals in which Pt predominates and As $\simeq$ S.

We have made a detailed study of platarsite grains 1 and 3 by the precession method. Using Zr-filtered Mo radiation, grain 1 was exposed for 220 hours and grain 3 for 142 hours. All precession data were consistent with Pa3 and the diffraction spots were sharp (*cf.* the broad lines in the Gandolfi pattern). A complete structural study is in progress.

Though platarsite is approximately (Pt,Rh, Ru)AsS, the increase in *a* from 5.790Å for grain 1 to 5.824Å for grain 3 is consistent with *a* 5.929Å reported for synthetic PtAsS by Hulliger (1963). It is assumed, therefore, that synthetic PtAsS is also *Pa3*. Chemically, platarsite is a sulfarsenide, but space group *Pa3* requires that the As and S atoms be statistically distributed in equivalent sites. Therefore, the mineral is, crystallochemically, either a diarsenide or a disulfide, ideally  $Pt(As,S)_2$  with  $As\simeq S$ .

Sperrylite was determined to have the pyrite structure (Pa3) by Aminoff & Parsons (1928) in a study using X-ray rotation photographs. The coexistence of platarsite with sperrylite containing a maximum 1.8 wt. % Rh and 0.93 wt. % S (Fig. 2 and Table 3) presents a problem if both are Pa3. The suggestion of a possible miscibility gap is reinforced by the small quantities of Rh and S reported in sperrylite from world-wide localities. Numerous analyses have shown that Sudbury sperrylites have a maximum of 0.5 wt. % Rh and nil S (Cabri & Laflamme 1976), Merensky Reef sperrylites have a maximum 1.2 wt. % Rh and nil S (Brynard et al. 1976), and Witwatersrand sperrylites contain up to 3.1 wt. % Rh and 3.5 wt. % S (Feather 1976). Confirmation of the sperrylite and platarsite space-group assignment by an X-ray structural investigation is required prior to explaining the problem of their coexistence.

### PRESERVATION OF TYPE MATERIAL

Polished sections containing type platarsite, which is rhodian and ruthenian, are preserved in the collections of the Royal Ontario Museum, Toronto (No. M34681), Smithsonian Institution, Washington, D.C. (No. 136485), and the Mineralogical Museum of the Academy of Sciences (No. N79000) Moscow. The remainder of the hand specimen (No. 1949) is in the Pinch Mineralogical Museum and the crystals examined by X-ray are preserved, mounted on fibres, in our Crystal Structure laboratory.

TABLE 3. ELECTRON MICROPROBE ANALYSES OF SPERRYLITE COEXISTING WITH PLATARSITE

Anal.	Weight percent								Atomic proportions								
no.	Pt	Rh	Ru	Ir	As	Sb	S	Total	Pt	Rh	Ru	Ir	Σ	As	Sb	S	Σ
1	53.3	1.8	0.28	0.40	41.5	1.2	0.93	99.41	0.92	0.06	0.01	0.01	1.00	1.87	0.03	0.10	2.00
2	53.4	1.8	0.26	0.63	41.0	2.1	0.91	100.10	0.92	0.06	0.01	0.01	1.00	1.84	0.06	0.10	2.00
3	54.8	1.5	0.05	n.d.	42.3	1.3	0.47	100.42	0.95	0.05	<0.01	0.00	1.00	1.91	0.04	0.05	2.00

Fe, Ni, Cu, Pd and Os sought for but not detected; n.d. = not detected.

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#### REFERENCES

- AMINOFF, G. & PARSONS, A. L. (1928): The crystal structure of sperrylite. Univ. Toronto Studies, Geol. Ser. 27, 5-10.
- BRYNARD, H. J., DE VILLIERS, J. P. R. & VILJOEN, E. A. (1976): A mineralogical investigation of the Merensky Reef at the Western Platinum mine, near Marikana, South Africa. Econ. Geol. 71, 1299-1307.
- CABRI, L. J. (1972): The mineralogy of the platinum-group elements. *Minerals Sci. Eng.* 4, 3-29.
- & LAFLAMME, J. H. G. (1976): The mineralogy of the platinum-group elements from some copper-nickel deposits of the Sudbury area, Ontario. *Econ. Geol.* 71, 1159-1195.
- ——, ROSENZWEIG, A. & PINCH, W. W. (1977a): Platinum-group minerals from Onverwacht. I. Pt-Fe-Cu-Ni alloys. *Can. Mineral.* 15, 380-384.
- -----, STEWART, J. M., LAFLAMME, J. H. G. & SZYMANSKI, J. T. (1977b): Platinum-group min-

erals from Onverwacht. III. Genkinite,(Pt,Pd)<sub>4</sub>-Sb<sub>3</sub>, a new mineral. Can. Mineral. 15, 389-392.

- FEATHER, C. E. (1976): Mineralogy of platinumgroup minerals in the Witwatersrand, South Africa. *Econ. Geol.* 71, 1399-1428.
- GENKIN, A. D., ZHURALEV, N. N., TRONEVA, N. V. & MURAY'EVA, I. V. (1966): Irarsite, a new sulfarsenide of iridium, rhodium, ruthenium and platinum. Zap. Vses. Mineral. Obshch. 95, 700-712 (in Russ.).
- HULLIGER, F. (1963): New compounds with cobaltite structure. *Nature* 198, 382-383.
- RUCKLIDGE, J. & GASPARRINI, E. L. (1969): Electron microprobe analytical data reduction, EMPADR VII. Dep. Geol. Univ. Toronto.
- SNETSINGER, K. G. (1972): Osarsite, a new osmiumruthenium sulfarsenide from California. Amer. Mineral. 57, 1029-1036.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972): The X-ray system of crystallographic programs. Univ. Maryland Computer Sci. Dep. TR-192.
- STUMPFL, E. F. & CLARK, A. M. (1965): Hollingworthite, a new rhodium mineral, identified by electron probe micro-analysis. *Amer. Mineral.* 50, 1068-1074.
- TARKIAN, M. & STUMPFL, E. F. (1975): Platinum mineralogy of the Driekop mine, South Africa. *Mineralium Deposita* 10, 71-85.
- Manuscript received February 1977, emended May 1977.